Forschung, Wissenschaft

Kurze Mitteilungen

Maximalumfang: 6 Schreibmaschinenseiten (alles inbegriffen). Bis zum 10. des Monats bei der Redaktion eingehende Manuskripte können günstigenfalls am 15. des folgenden Monats veröffentlicht werden.

Aminophosphonsäuren: Synthese der α-Aminophosphonsäuren aus aliphatischen Aldazinen unter Anwendung von Diisopropylphosphit *, **

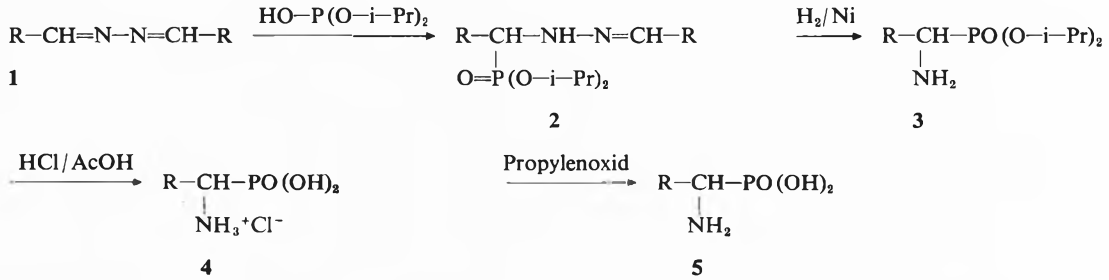
Maria Hoffmann, C. Wasielewski und J. Rachoń ***
Institut für Organische Chemie der Technischen Universität Gdańsk, Polen

Summary

A new efficient synthesis of α-aminophosphonic acids from aliphatic aldazines and diisopropyl phosphite is described.

Die Zunahme der Veröffentlichungen über synthetische Methoden für Aminophosphonsäuren belegt das wachsende Interesse an dieser Substanzklasse [2]. Die meisten der bisher bekannt gewordenen Herstellungsmethoden erfordern in einer der letzten Stufen die Hydrolyse von Phosphonsäureäthylestern. Dieser Syntheseschritt verläuft nur unter drastischen Reaktion-Bedingungen [3, 4, 5], wie mehrstündiges Erhitzen mit konzentrierten Mineralsäuren. In einer früheren Arbeit [6] beschrieben wir den Ersatz der Äthylester durch die entsprechenden Isopropylester, wodurch eine Abkürzung der Hydrolyse-Zeit in salzsäure-haltiger Essigsäure ermöglicht wurde.

Ausgehend von unsern früher beschriebenen Erfahrungen [7] haben wir auch hier an aliphatische Aldazine Isopropylphosphit angelagert, wobei die Monoadditionsprodukte **2** in hohen Ausbeuten isoliert werden konnten.



Die Hydrogenolyse von **2** mit Raney-Nickel als Katalysator in Alkohol-Wasser lieferte die Aminophosphonsäure-diisopropylester **3**. Diese wurden chromatographisch identifiziert und ohne weitere Reinigung mit Essigsäure-Salzsäure-Gemisch hydrolysiert. Die anfallenden Hydrochloride der α-Aminophosphonsäuren **5** liessen sich in guter Ausbeute mit Propylenoxid [8] in die freien Basen überführen; sie waren chromatographisch rein.

Zusammenfassend lässt sich sagen, dass die Anlagerung von Diisopropylphosphit an ein aliphatisches Aldazin mit ebensoguter Ausbeute wie mit Diäthylphosphit verläuft. Da die saure Hydrolyse der Isopropylester etwa 10–20mal schneller erfolgt als diejenige der entsprechenden Äthylester, bedeutet die hier beschriebene Synthese-Variante eine wesentliche Vereinfachung zur Herstellung von α-Aminophosphonsäuren.

1-(N-Alkyliden)-hydrazino-alkanphosphonsäure-diisopropylester **2**

0,23 g (10 mMol) Natrium wurden in 35 ml (210 mMol) Diisopropylphosphit bei 40–50 °C gelöst und mit 200 mMol aliphatischem Aldazin **1** bei Raumtemperatur versetzt. Der Kolbeninhalt soll gerührt und nach Bedarf mit laufendem Wasser auf 25 °C gekühlt werden. 30 Min. nach Abklingen der Reaktion setzte man dem Reaktionsgemisch 200 ml abs. Äther zu und kühlte während 1 Std. auf − 5 °C. Die Lösung wurde filtriert und unter vermindertem Druck destilliert. Die dargestellten Additionsprodukte sind in der Tabelle 1 zusammengestellt.

α-Aminophosphorsäuren **5**

25 mMol 1-(N-Alkyliden)-hydrazino-alkanphosphonsäure-diisopropylester **2** wurden in 100 ml Äthanol-Wasser-(1:1) Gemisch gelöst, mit 18 g Raney-Nickel versetzt und 30 Min. bei 90 bis 110 °C und 25–30 Atm. mit Wasserstoff in einen Autoklaven hydriert. Der Katalysator wurde abfiltriert und mit Alkohol und Wasser ausgewaschen, das Filtrat mit konzentrierter Salzsäure ver-

* 7. Mitteilung über Aminophosphonsäuren, 6. Mitteilung [1]

** Eingegangen am 30. Oktober 1975

*** Dr. J. Rachoń, Instytut Chemii i Technologii Organicznej oraz Żywnosciowej Politechnika Gdańska, Majakowskiego 11/12, 80 952 Gdańsk, Polen

setzt und im Vakuum zur öligen Konsistenz eingedampft. Den Rückstand versetzte man mit 100 ml Essigsäure und 100 ml konzentrierter Salzsäure und erwärmte während 30 Min. zum Sieden. Die Lösung wurde wiederholt unter Zusatz von Wasser und zum Schluss von Alkohol eingedampft. Die alkoholische Lösung versetzte man mit 2 ml Propylenoxid, saugte die ausgeschiedene α-Aminophosphonsäure ab und wusch mit abs. Alkohol aus. Die Produkte wurden durch Ausfällen aus wässriger Lösung mit Alkohol gereinigt. Die dargestellten α-Aminophosphonsäuren sind in der Tabelle 2 zusammengestellt.

Literatur

1 *M. Hoffmann* und *C. Wasielewski:* Roczniki Chem., *50* (1976) 139.
2 *K. Prajer* und *J. Rachoń:* Z. Chem. *15* (1975) 209.
3 *V. Chavane:* Bull. Soc. Chim. France *1948*, 774.
4 *E. K. Fields:* J. Am. Chem. Soc. *74* (1952) 1528.
5 *J. P. Berry, A. F. Isbell* und *G. E. Hunt:* J. Org. Chem. *37* (1972) 4396.
6 *J. Rachoń* und *C. Wasielewski:* Roczniki Chem. *49* (1975) 397.
7 *J. Rachoń* und *C. Wasielewski:* Roczniki Chem. *50* (1976) 477.
8 *J. R. Chambers* und *A. F. Isbell:* J. Org. Chem. *29* (1964) 832.

Tabelle 1:*

R—CH(O=P(O—i—Pr)$_2$)—NH—N=CH—R

R	Kp/mm Hg °C	Ausbeute % d. Th.	Summenformel Molekulargewicht	Analyse % N Ber.	Gef.
CH_3-	112/3	82	$C_{10}H_{23}N_2O_3P$ 250,28	11,20	11,04
CH_3CH_2-	112/0,8	75	$C_{12}H_{27}N_2O_3P$ 278,34	10,07	9,87
$CH_3CH_2CH_2$-	123–125/0,5	75	$C_{14}H_{31}N_2O_3P$ 306,39	9,15	9,17
$[CH_3]_2CH$-	132/3	79	$C_{14}H_{31}N_2O_3P$ 306,39	9,15	9,21

* Die gefundenen IR- und H-NMR-Spektren entsprechen der Struktur der aufgeführten Verbindungen

Tabelle 2:*

R—CH(NH$_3$)—PO(OH)$_2$

R	Ausbeute % d. Th.	Smp. °C	H-NMR-Spektra δ (ppm) in Trifluoressigsäure
CH_3-	89	272–274	1,33 (d-d, 3H, J = 7Hz, J = 18Hz, CH_3) 3,00–3,86 (m, 1H, CH) 6,25–7,00 (m, 3H, NH_3^+)
CH_3CH_2-	85	264–265	0,81 (t, 3H, J = 6Hz, CH_3) 1,25–2,00 (m, 2H, CH_2) 3,00–3,63 (m, 1H, CH) 6,25–7,00 (m, 3H, NH_3^+)
$CH_3CH_2CH_2$-	82	265–267	0,64 (t, 3H, J = 6Hz, CH_3) 0,84–2,00 (m, 4H, CH_2CH_2) 3,05–3,75 (m, 1H, CH) 6,25–7,55 (m, 3H, NH_3^+)
$[CH_3]_2CH$-	90	270–272	0,80 (d, 6H, J = 7Hz, $[CH_3]_2C$) 1,65–2,25 (m, 1H, CH) 2,90–3,50 (m, 1H, CH—P) 6,25–7,50 (m, 3H, NH_3^+)

* Die gefundenen C-, H- und N-Analysenwerte stimmen innerhalb der Fehlergrenze mit den berechneten Werten überein

Pyridines and Quinolines from 1,3-Dichloro-Trimethinecyanines Pyrimidine and Quinazoline from Azacyanine [1] *

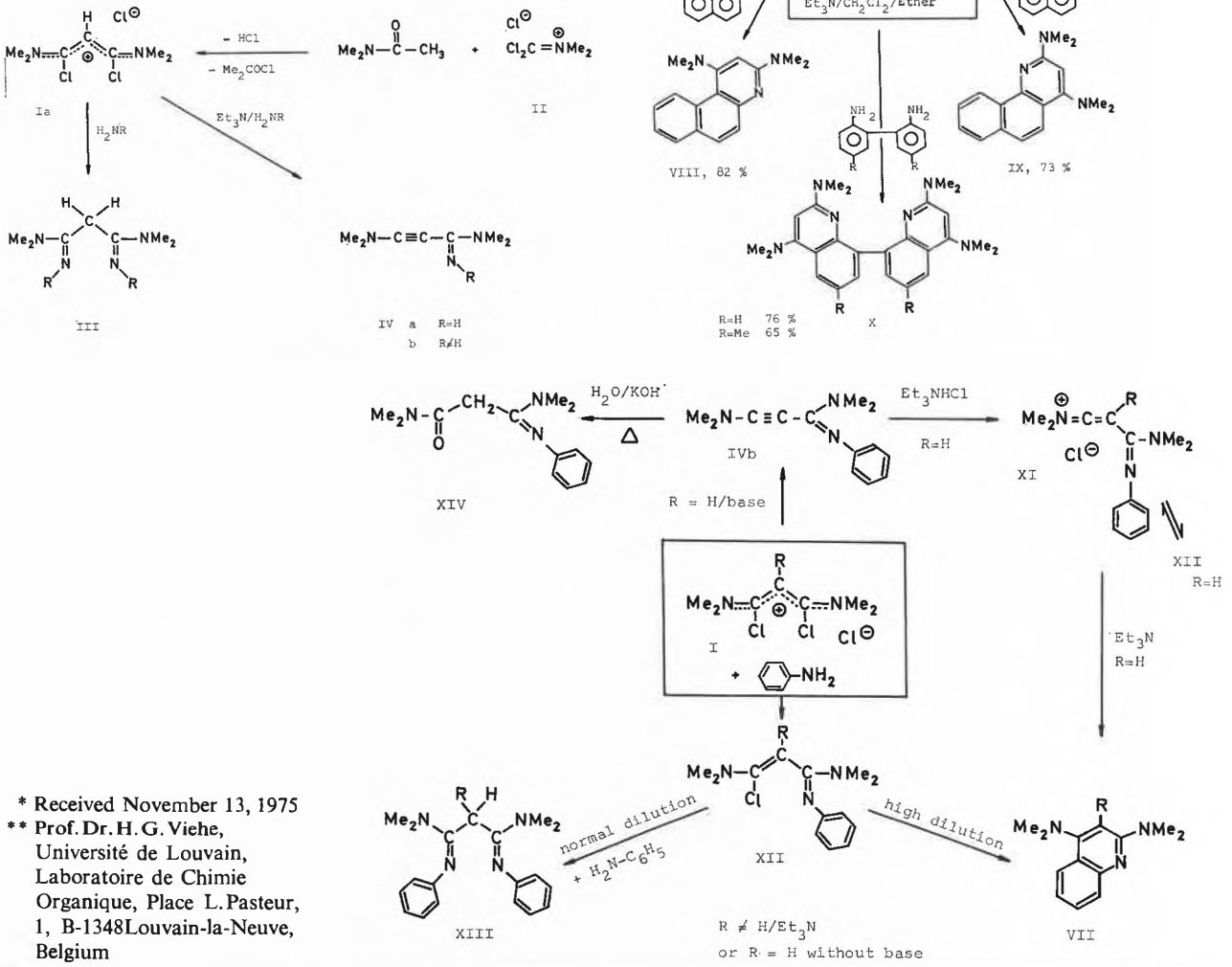
H.G.Viehe**, G.J. de Voghel and F.Smets
Laboratoire de Chimie Organique, Univeisité de Louvain, Belgium

Summary

A new synthesis of 2,4-bis(dialkylamino)-pyridines and quinolines is reported. Starting from primary aryl amines or aliphatic imines a mechanism via ynamine-amidines is followed if the cyanine Ia is used as reagent. When the cyanine is substituted, (I.R. ≠ H) it reacts well in high dilution conditions via the alternate intermediates XI and XII. In the same manner, the azacyanine XV forms the pyrimidine XVII and the quinazoline XVI.

1,3 Dichloro-trimethinecyanines I are useful reagents, readily accessible from N,N-disubstituted acetamides and phosgeniminium salts II [2]. Heterocyclizations of Ia, such as to pyrazole derivatives have been studied [3]. Aminolysis with ammonia or primary amines produces malonyl bis-amidines III or ynamine amidines IV [4,1]. as versatile intermediates.

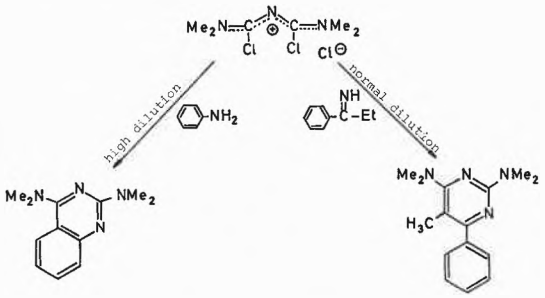
Thus, when R = H (IVa) heterocyclization occurs readily with cumulated systems such as with CO_2, CS_2 and isocyanates and with polar multiple bonds [4].
It has now been found that N-vinyl substituted ynamine-amidines IVb, obtained from imine V and in particular from aromatic amines, smoothly produce pyridines VI quinolines VII, X and annelated aromatic derivatives VIII, IX.



* Received November 13, 1975
** Prof. Dr. H.G. Viehe, Université de Louvain, Laboratoire de Chimie Organique, Place L. Pasteur, 1, B-1348Louvain-la-Neuve, Belgium

The smooth reaction conditions compare favorably with related cyclisations under severe conditions [5–7] and prompted a mechanistic study. It was shown that, although derivatives IVb are isolable intermediates, the cyclization process occurs rather via the keteniminium XI arising by a proton exchange with triethylamine hydrochloride [8,9]. The formation of IVb thus prevents the intermediate α-chlorenamine amidine XII from producing the bisamidine XIII and thereby deviating from cyclization.

When the proton is removed irreversibly by using KOH as base, the formation of keteniminium XI is prohibited and IVb, detected by IR, slowly adds water to form amide amidine XIV. Furthermore, it has been found that the substituted dichloro-trimethinecyanine I (R = C_2H_5) and its azaanalogue XV lead to cyclization instead of double substitution to bis-amidines, provided that the amine is added under high dilution conditions.



The more reactive imine V did not require this care and, with I or XV, formed readily the pyridine VI or the pyrimidine XVII.

General Procedure

A mixture of 0.01 mole of amine and 0.05 mole of Et_3N in ether is added to 0.01 mole of cyanine in dry dichloromethane. The reaction mixture is stirred and kept below −10 °C. When the addition is finished the mixture is allowed to attain room temperature, the free base is liberated with aqueous KOH and extracted with small portions of dichloromethane. The organic phase is dried, evaporated and the product is purified either by bulb distillation or by crystallization. High dilution is obtained by adding the triethylamine and aromatic amine within 5 to 10 hrs through the condenser into the refluxing cyanine solution in methylenedichloride.

2,4-bis-(dimethylamino)-4-methyl-5-phenyl-pyridine VIa

Yield: 67%, mp 83 to 84 °C (hexane); NMR: $CDCl_3$/TMS: δ = 2.15(3H,s) − 2.82(6H,s) 3.08(6H,s) − 6,07(1H,s) − 7.22 to 7.77(5H,m)ppm(5H,m)ppm
IR: $CHCl_3$: ν = 2938, 1582, 1572, 1540, 1492, 1393, 1102 cm^{-1}

2,4-bis-(dimethylamino)-3-phenoxy-4-methyl-5-phenyl-pyridine VIb

Yield: 80%, mp 145 °C (MeOH − H_2O); NMR: $CDCl_3$/TMS: δ = 2.18(3H,s) − 2.72(6H,s) − 2.93(6H,s) − 6.6 to 7.95(10H, m)ppm
IR: $CHCl_3$: ν = 2902, 1600, 1590, 1582, 1568, 1490, 1400, 1065 cm^{-1}

2,4-bis-(dimethylamino)-quinoline VII

Yield: 84%, mp 80 to 81 °C (hexane); NMR: $CDCl_3$/TMS: δ = 2.91(6H,s) − 3.16(6H,s) − 6.18(1H,s) − 6.8 to 7.83(4H, m) ppm
IR: $CHCl_3$: ν = 2940, 1595, 1551, 1502, 1393 cm^{-1}

2,4-bis-(dimethylamino)-benzo-(f)-quinoline VIII

Yield: 82%, mp 97 °C (hexane). NMR: $CDCl_3$/TMS: δ = 2.77(6H,s) 3.15(6H,s) − 6.27(1H,s) − 7 to 8(5H,m) − 9.55 (1H,m) ppm
IR: $CHCl_3$ ν = 2940, 1586, 1549, 1500, 1395 cm^{-1}

2,4-bis-(dimethylamino)-benzo-(h)-quinoline IX

Yield: 73%, mp 109 to 111 °C (MeOH − H_2O); NMR: δ = 3(6H,s) − 3.3(6H,s) 6.3(1H,s) 7.4 to 8.5(6H,m) ppm
IR: $CHCl_3$: ν = 2950, 1590, 1550, 1500, 1450 cm^{-1}

2,2'-4,4'-Tetrakis-(dimethylamino)-8,8'-bisquinoline Xa

Yield: 76%, mp 224 to 226 °C (MeOH/H_2O); NMR: CD_3OD: δ = 3(12H,s) 3.2(12H,s) − 6.25(2H,s) − 7.8 to 8.3(6H,m) ppm
IR: $CHCl_3$ ν = 2950, 1590, 1550, 1580, 1450, 1390 cm^{-1}

6,6'-Dimethyl-2,2'-4,4'-tetrakis (dimethylamino)-8,8'-bisquinoline Xb

Yield: 65%, mp 180 to 182 °C (MeOH/H_2O) NMR: $CDCl_3$: δ = 2.7(6H,s) 3.05(12H,s) 3.3(12H,s) − 6.4(2H,s) − 7.8 to 8.2 (4H,m) ppm
IR: $CHCl_3$ ν = 2950, 1600, 1560, 1490, 1450, 1390 cm^{-1}

2,4-bis-(dimethylamino)-3-ethyl-quinoline VII

Yield: 74%, bp 130 °C/0.06; NMR: $CDCl_3$/TMS: δ = 1.03(3H,t) − 2.91(6H,s) − 3.01(6H,s) − 2.85(2H,q) − 7 to 7.9(4H,m) ppm
IR: $CHCl_3$ ν = 2920, 1621, 1568, 1477, 1380, 1076 cm^{-1}

2,4-bis-dimethylamino-quinazoline XVI

Yield: 50%, mp 90 °C (diisopropyl ether); NMR: $CDCl_3$/TMS: δ = 3.2/12H,s) 6.66 to 7.66(4H,m) ppm
IR: $CHCl_3$: ν = 2920, 1612, 1566, 1549, 1387 cm^{-1}

2,4-bis-(dimethylamino)-5-methyl-6-phenyl-pyrimidine XVII

Yield: 69%, mp 80 °C (MeOH/H_2O); NMR: $CDCl_3$/TMS: δ = 2.03(3H,s) − 2.97(6H,s) − 3.13(6H,s) − 7.1 to 7.7(5H,m) ppm
IR: $CHCl_3$ ν = 2940, 1581, 1552, 1387, 1374, 1.180 cm^{-1}

Dimethylcarbamoyl-N-phenyl-N,N'-dimethyl-acetamidine XIV

Yield: 54%; mp 73–4 °C* (ether/hexane) [10]NMR; $CDCl_3$/TMS: δ = 2.62(3H,s) 2.85(3H,s) − 2.98(6H,s) − 3.27(2H,s) − 6.43 to 7.23(5H,m) ppm
IR: $CHCl_3$ ν = 3000, 1650, 1617, 1592, 1400 cm^{-1}

N,N'-tetramethyl-N,N'-diphenyl-malon-bis-amidine XIII

Yield: 68% mp 139–140 °C (CH_2Cl_2/hexane) NMR: $CDCl_3$/TMS: δ = 3.04(12H,s) − 3.58(2H,s) − 6.77 to 7.83(10H,m) ppm
IR: $CHCl_3$ ν = 2940, 1607, 1587, 1478, 1390 cm^{-1}

* Lit. [10] indicates mp 75 °C.

Bibliography

1 Phosgeniminium chemistry, part 18; part 17, *G. Germain, J.P. Declercq, M. Van Meerssche, F. Hervens, H.G. Viehe* and *A. Michel.* Bull. Soc. chim. Belge *84*, (1975) 10.
2 *H.G. Viehe* and *Z. Janousek:* Angew. Chem. (Internat. Ed.) *10* (1971) 574.
H.G. Viehe and *Z. Janousek:* Angew. Chem. (Internat. Ed.) *12* (1973) 806.
3 *G.J. de Voghel, T.L. Eggerichs, Z. Janousek* and *H.G. Viehe:* J. Org. Chem. *39* (1974) 1233.
4 *B. Caillaux, P. George, F. Tataruch, Z. Janousek* and *H.G. Viehe:* to be published.

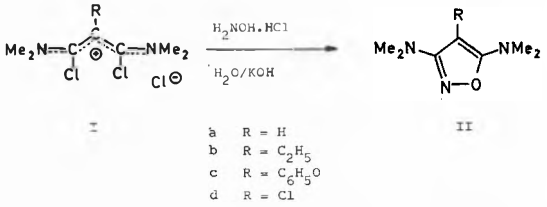
5 *W. Ried* and *P. Weideman:* Chem. Ber. *104* (1971) 3329.
6 *C. Jutz* and *R. M. Wagner:* Angew. Chem. (Internat. Ed.) *11* (1972) 315.
7 *A. H. A. Tinnemans* and *W. H. Laarhoven:* Tetr. Letters *11* (1973) 817.
8 *L. Ghosez* and *C. de Perez:* Angew. Chem. (Internat. Ed.) *10* (1971) 184.
9 *J. Marchand-Brynaert* and *L. Ghosez:* J. Am. Chem. Soc. *94* (1970) 2869.
10 *H. Bredereck* and *K. Bredereck:* Chem. Ber. *94* (1961) 2278.

Facile Synthesis of 2-Dimethylamino-Δ-1-Azirine Derivatives by Thermal or Photo-Isomerization of Isoxazoles [1] *

G. J. de Voghel, T. L. Eggerichs, Brigitte Clamot, H. G. Viehe **
Laboratoire de Chimie Organique, Université de Louvain, Belgium

Summary

3,5-Bisdimethylamino-isoxazoles II are obtained easily from 1,3-dichloro-trimethinecyanine I and a water solution of hydroxylamine. Besides precedented photo-isomerization of 4-substituted isoxazoles IIb,c to azirines III b,c near quantitative thermal isomerization of 4-unsubstituted-isoxazole IIa to amino-azirine IIIa is reported.



Azirines have become accessible by several routes including photo or thermal isomerization of isoxazoles [2,3]. We found an easy synthesis of new 3,5-bis-(dimethylamino)-isoxazoles II from the readily accessible [4] 1,3-dichloro-trimethinecyanines I and an alkaline or buffered aqueous solution of hydroxylamine.

Apparently favored by the aminosubstituents, complete isomerization of the isoxazole IIa to amino-azirine IIIa occurs during distillation at 110 °C (0.1 mmHg). Although this easy thermal rearrangement is limited to the isoxazole IIa, the new amino azirines IIIb and IIIc can be obtained by photo-isomerization.

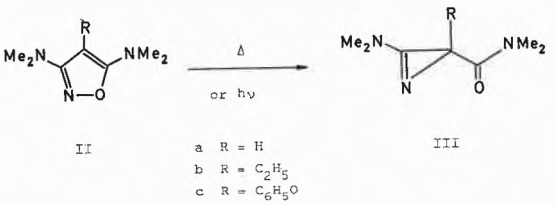
Table 1: Isoxazoles II

Compound	R	Yield %	Mp or Bp °C (mmHg)	IR ($CHCl_3$) cm^{-1} C=N	H-NMR (δ) -NMe_2	
IIa	H	90	97–8	1620	2.73 (s)	2.80 (s)
IIb	C_2H_5	79	104 (0.02)	1620	2.74 (s)	2.86 (s)
IIc	C_6H_5O	55	125	1648	2.75 (s)	2.97 (s)
IId	Cl	66	80 (0.05)	1630	2.85 (s)	3.04 (s)

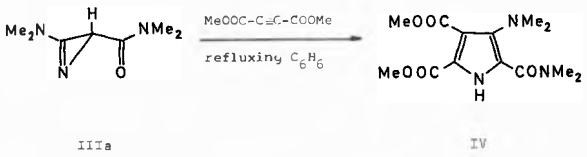
Table 2: Azirines III

Compound	R	Yield	Mp or Bp °C (mmHg)	IR ($CHCl_3$) cm^{-1} C=N	C=O	H-NMR δ (ppm) NMe_2	
IIIa	H	~100	97–8	1802	1635	3.01 (6H, s) 3.21 (3H, s)	2.91 (3H, s)
IIIb	C_2H_5	83	140 (0.15)	1783	1627	2.90 (3H, m) 3.03 (3H, s)	3.28 (3H, m) 3.13 (3H, s)
IIIc	C_6H_5O	80	86	1790	1645	3.06 (6H, s) 3.40 (3H, s)	2.93 (3H, s)

* Received November 13, 1975
** Prof. Dr. H. G. Viehe, Université de Louvain, Laboratoire de Chimie Organique, Place L. Pasteur, 1, B-1348 Louvain-la-Neuve, Belgium



To our knowledge, IIIa represents the first example of a 3-monosubstituted amino-azirine non-obtainable by the usual route [5]. III should be preparatively useful by analogy with this recently discovered reactive class of compounds [6]. Azirine IIIa was characterized by spectroscopic data (Table 2 and by its addition to dimethylacetylene dicarboxylate yielding the new pyrrole [7] IV whose structure is proven by X-ray analysis [8].



This reaction contrasts with the already known photoaddition of acetylene dicarboxylate to azirines [2].

Experimental

General procedure for the synthesis of isoxazoles II

0.01 mole of cyanine I in 50 ml of dry dichloromethane is added to an aqueous solution of 0.08 mole of KOH and 0.03 mole of hydroxylamine hydrochloride under efficient stirring and kept below 0 °C. After the addition is finished, the solution is allowed to attain room temperature. Isoxazole II is extracted with small portions of dichloromethane. After drying over $MgSO_4$ and evaporation of the solvent, the residue is purified as indicated below.

3,5-bis-(dimethylamino)-isoxazole IIa

Yield: 1.40 gr (90%), mp 97–8 °C (cyclohexane). NMR: $CDCl_3$/TMS; δ = 2.73 (6H,s); 2.80 (6H,s); 4.34 (1H,s) ppm

2-Ethyl-3,5-bis-(dimethylamino)-isoxazole IIb

Yield: 1.65 gr (79%), bp 104 °C/0.02; NMR: $CDCl_3$/TMS, δ = 1.06 (3H,t); 2.34 (2H,q); 2.74 (6H,s); 2.86 (6H,s) ppm

2-Phenoxy-3,5-(dimethylamino)-isoxazole IIc

Yield: 1.38 gr (55%), mp 125 °C (methanol); NMR: $CDCl_3$/TMS; δ = 2.75 (6H,s); 2.86 (6H,s); 6.66 to 7.50 (5H,m) ppm

Isoxazole IIc was chromatographed on silica gel (cyclohexane ethyl acetate 60/40)

2-Chloro-3,5-bis-(dimethylamino)-isoxazole IId

Yield: 1.25 gr (66%); bp 80 °C (0.05 mmHg); NMR: $CDCl_3$/TMS; δ = 2.85 (6H,s); 3.04 (6H,s) ppm

2-Dimethylamino-3-dimethylcarbamoyl-Δ-azirine IIIa

Azirine IIIa is produced in quantitative yield from isoxazole IIa by simple horizontal bulb distillation at 110 °C/0.1

Mp 97–8 °C (diisopropylic ether); NMR: $CDCl_3$/TMS; δ = 2.91 (3H,s); 3.01 (6H,s); 3.07 (1H,s); 3.21 (3H,s) ppm

2-Dimethylamino-3-ethyl-3-dimethylcarbamoyl-Δ 1-azirine IIIb

Azirine IIIb is produced on irradiation of IIb with UV light λ = 3000 Å. The reaction was performed during three days in a quartz NMR tube in CD_3CN

Yield: 83%; bp 140 °C/0.15 mm; NMR: $CDCl_3$/TMS; δ = 2.90 (3H,m); 3.28 (3H,m); 3.03 (3H,m); 3.13 (3H,m); 1.83 (1H, m); 1.95 (1H,m) ppm

2-Dimethylamino-3-phenoxy-3-dimethylcarbamoyl-Δ 1-azirine IIIc

Azirine IIIc is produced upon irradiation of IIc at 2800 Å in CD_3CN for 3 hrs. Yield: 80%; mp 86 °C (methanol); NMR: $CDCl_3$/TMS; δ = 2.93 (3H,s); 3.06 (6H,s); 3.40 (3H,s); 6.80 to 7.60 (5H,m) ppm

This structure was also confirmed by X-ray analysis [8].

2,3-bis-(methoxycarbonyl)-4-dimethylamino-5-dimethylcarbamoyl-pyrrole IV

0.155 gr of azirine IIIa (1 mmole) and 0.5 gr of ethyl acetylenedicarboxylate (3 mmoles) are reacted in 20 ml of dry benzene under reflux during 4 hours. The solvent is evaporated and the pyrrole IV is distilled in Kugelrohr at ~ 180 °C/0.008. Yield: 0.198 gr (68%); mp 110 °C (diisopropylether); NMR: $CDCl_3$/TMS, δ = 2.71 (6H,s); 3.07 (6H,s); 3.80 (3H,s); 3.87 (3H,s) ppm

IR: $CHCl_3$; C = O vibrations at 1710 (ester) and 1615 (amide) cm^{-1}

The structure of IV is proved by X-ray analysis [7].

Bibliography

1 Phosgeniminium Chemistry, Part 19, Part 18: preceeding.
2 *D. Anderson, A. Hassner* and the references cited therein: Synthesis (1975) 483–95.
3 *T. Nishiwaki* and the references cited therein: Synthesis (1975) 20–37.
4 *Z. Janousek* and *H. G. Viehe:* Angew. Chem. (Internat. Ed.) *10* (1971) 574;
G. J. de Voghel, T. L. Eggerichs, Z. Janousek and *H. G. Viehe:* J. Org. Chem. *39* (1974) 1233.
5 *M. Rens* and *L. Ghosez:* Tetr. Letters *43* (1970) 3765.
6 *P. Vitorelli, H. Heimgartner, H. Schmid, P. Hoet* and *L. Ghosez:* Tetrahedron *30* (1974) 3737;
F. Schaumann, E. Kausch and *W. Walter:* Chem. Ber. *107* (1974) 3574;
A. Demoulin, H. Gorissen, A. M. Hesbain-Frisque and *L. Ghosez:* J. Am. Chem. Soc. *97* (1975) 4409;
F. Schaumann, E. Kausch and *W. Walter:* Chem. Ber. *108* (1975) 2500
7 *M. Van Meerssche* and *G. Germain:* unpublished results.
8 *J. Galloy, J. P. Putzeys, G. Germain, J. P. Declercq* and *M. Van Meerssche:* Acta Cryst. B *30* (1974) 2462.

Asymmetric Olefins Hydrocarboxylation
III. Influence of Some Reaction Variables on the Optical Yield in the Asymmetric Hydrocarboxylation Catalyzed by Chiral Palladium Complexes [1]*

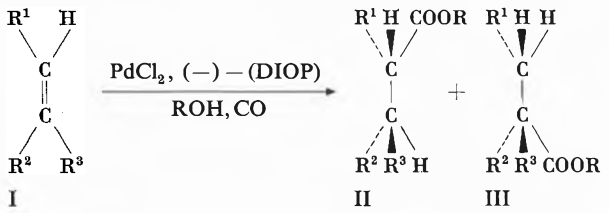
G. Consiglio** and P. Pino**
Technisch-Chemisches Laboratorium der ETH Zürich

Summary

The influence of some reaction variables on the asymmetric induction in the synthesis of esters catalyzed by palladium has been investigated; with α-methylstyrene as substrate, optical yields up to 59% have been reached.

In connection with our investigation in the field of asymmetric reactions catalysed by chiral transition metal complexes [2,3] we have briefly described the first example of asymmetric carboxylation of olefins [4] (Scheme 1), which occurs according to a cis stereochemistry [5].

Scheme 1:



The chiral catalyst was prepared "in situ" from $PdCl_2$ and (-)-2,2-dimethyl-4,5-bis(diphenylphosphinomethyl)-1,3-dioxolane (DIOP). The highest asymmetric induction (~14%) was achieved in the hydrocarboxylation of α-methylstyrene (I, R^1 = H; R^2 = C_6H_5; R^3 = CH_3) at 400 at initial pressure of carbon monoxide and 100°C, using isopropylalcohol as hydrogen donor and a molar ratio $PdCl_2$/DIOP = ½. Because of the potential synthetic interest of this reaction [6], we have attempted to improve the optical yields varying some of the reaction conditions. The substrate chosen to examine the influence of the reaction variables was α-methylstyrene, because of the lack of interfering olefin isomerisation and because it gives rise, in the presence of the catalytic system used, substantially to only one reaction product (>95%), namely the ester corresponding to the alcohol used of the 3-phenylbutanoic acid. The results obtained (Table 1) can be summarized as follows:

The alcohol used as hydrogen donor does influence the extent of the asymmetric induction; the optical yield reaches a maximum in the case of t.butanol (19,3%). No effect on the optical yield has been noticed increasing the catalyst concentration in the reaction mixture from $2.5 \cdot 10^{-3}$ to $1 \cdot 10^{-2}$ m.

The presence of a solvent in the reaction brings about a remarkable improvement of the optical yield: as a

Table 1: Asymmetric Hydrocarboxylation of α-Methylstyrene under Different Reaction Conditions [a]

Alcohol	Solvent	$PdCl_2$/DIOP molar ratio	Total pressure [d] at	Optical purity [e] of the recovered ester, %
CH_3OH [b]	–	1/2	385–360	3.0
$(CH_3)_2CHOH$ [b]	–	1/2	387–368	14.2
$C_2H_5CH(CH_3)OH$ [b]	–	1/2	386–347	8.2
$(CH_3)_3COH$ [b]	–	1/2	400–364	19.6
CH_3OH [c]	benzene	1/2	391–367	19.3
$C_2H_5CH(CH_3)OH$ [c,f]	benzene	1/2	400–364	40.6
$C_2H_5CH(CH_3)OH$ [c,f]	THF	1/2	390–365	41.1
$(CH_3)_3COH$ [c]	benzene	1/2	400	37.0
$(CH_3)_3COH$ [c]	benzene	1/2	50	3.5
$(CH_3)_3COH$	benzene	1/2	700	50.4
$(CH_3)_3COH$ [c]	benzene	1/1	400	48.3
$(CH_3)_3COH$ [c]	benzene	1/0.4	400	58.6

[a] Reaction temperature 100°C
[b] 50 ml of alcohol were used; olefin 0.1 mol; $PdCl_2$ 0.5 mmol
[c] 40 ml of solvent and 0.15 mol of alcohol were used; olefin 0.1 mol; $PdCl_2$ 0.5 mmol
[d] The experiments for which only one value is given were carried out at constant pressure
[e] The optical purity was determined either on the (+)(S)-3-phenylbutanoic acid [7] obtained through saponification or on the (+)(S)-3-phenyl-1-butanol obtained through reduction with $LiAlH_4$
Racemic 2-butanol has been used; the recovered alcohol was optically inactive

* Received December 19, 1975
** Dr. G. Consiglio and Prof. Dr. P. Pino, Technisch-Chemisches Laboratorium der ETH, Universitätsstr. 6, CH-8006Zürich

matter of fact, using benzene as solvent, the optical purity of the esters becomes much higher than without solvent, the increase being different with different alcohols. Benzene or tetrahydrofurane show about the same influence.

The extent of the asymmetric induction increases by increasing the pressure of carbon monoxide: a variation of the pressure from 50 to 700 at causes an increase of the optical yield from 3.5 to 50.4%. A similar effect is observed by decreasing the diphosphine to palladium ratios, the optical yield being higher by smaller ratios. The highest asymmetric induction has been observed for a ratio 0.4 (~ 59%). In these conditions, however, the reaction rate is much lower and some byproducts are formed: $PdCl_2$ without ligands is unable to catalyze the hydrocarboxylation of α-methylstyrene under the reaction condition used.

In all conditions examined the prevailing configuration of the ester produced is the same [(S)].

The influence of the different variables of the optical yield seems to be rather general as shown by the results obtained using aliphatic terminal or internal olefins or styrene (Table 2).

Other experiments are in progress to clarify the mechanistic implications of the reported results.

We wish to thank M. Marchetti for his skilled experimental assistance.

Literature

1 *G. Consiglio:* Part II, Helv. Chim. Acta *59* (1976) 124.
2 *P. Pino, G. Consiglio, C. Botteghi* and *C. Salomon:* Adv. Chem. Ser. *132* (1974) 295.
3 *G. Consiglio* and *C. Botteghi:* Helv. Chim. Acta *56* (1973) 460.
4 *C. Botteghi, G. Consiglio* and *P. Pino:* Chimia *27* (1973) 477.
5 *G. Consiglio* and *P. Pino:* Gazz. chim. ital. *105* (1975) 1133.
6 *K. Bittler, N. v. Kutepow, D. Neubauer* and *H. Reis*: Angew. Chem. *80* (1968) 352.
7 *D. J. Cram:* J. Amer. Chem. Soc. *74* (1952) 2137.

Table 2: Asymmetric Hydrocarboxylation of Some Olefins under Different Reaction Conditions [a]

Substrate	Alcohol [b]	Solvent [b]	$PdCl_2$/DIOP [b] molar ratio	Total pressure [c] (at)	Recovered ester, optical purity, % [d]
1-butene	C_2H_6OH	–	1/2	450–355	(+)(S)-ethyl 2-methylbutanoate 7.6
1-butene	$(CH_3)_3COH$	benzene	1/1	700	(+)(S)-t. butyl 2-methylbutanoate 20.2
cis-butene	C_2H_5OH	–	1/2	540–458	(−)(R)-ethyl 2-methylbutanoate 7.2
cis-butene	$(CH_3)_3COH$	benzene	1/1	700	(−)(R)-t. butyl 2-methylbutanoate 20.7
styrene	CH_3OH	–	1/2	463–439	(+)(S)-ethyl hydratropate 3.2
styrene	$(CH_3)_3COH$	benzene	1/1	700	(+)(S)-t. butyl hydratropate 10.0

[a] Reaction temperature 100 °C
[b] For the quantities used see table 1
[c] See table 1
[d] Determined through saponification to the corresponding acid or through reduction to the corresponding alcohol

Anion Exchange Properties of β-FeOOH *

J. Ellis **, R. Giovanoli ***, W. Stumm ****

Summary

Ion exchange processes within the hollandite structural tunnels of β-FeOOH are very slow. Chloride ion is specifically adsorbed and stabilizes the crystal lattice. Consequently, it is not possible to reduce the chloride content of synthetic β-FeOOH to less than ~ 2%; the chloride-free nature of a product described in the literature is doubtful.

* Received December 22, 1975
** Chemistry Department, University of Wollongong, Wollongong NSW 2500, Australia
*** PD Dr. R. Giovanoli, Laboratory of Electron Microscopy, Institute of Inorganic Chemistry, University of Berne, Freiestr. 3, P.O. Box 140, CH-3000 Bern 9 (Author to whom correspondence may be addressed)
**** Swiss Federal Institute for Water Resources and Water Pollution Control (EAWAG), CH-8600 Dübendorf

In the six years since the publication in Chimia of the paper by Gallagher and Phillips [1] on β-FeOOH, interest in this unusual compound has intensified. It has been examined by Mössbauer spectroscopy [2,3] and neutron diffraction [4] [1]. It has been identified as a product of the rusting of iron in marine atmospheres [5] and as an artefact in lunar rocks from the Appollo 16 mission [6]. While the adsorption behaviour of α-FeOOH (goethite) towards both anions [7, 8] and cations [9] has been examined in some detail, no simi-

[1] The H positions proposed in [4] do not seem compatible with the structure or with the IR spectrum, which shows very little hydrogen bonding.

lar studies have been reported for β-FeOOH, despite the potentially interesting ion-exchange properties predicted for this substance [10].

The vital role of chloride in β-FeOOH, which is commonly prepared by the slow hydrolysis of ferric chloride solutions (preferably at low *p*H and below 80 °C) [11], has been explained by a mechanism for nucleation where four $[Fe_2(OH)_2(H_2O)_8]^{4+}$ dimers (one of the early hydrolysis products of a Fe(III) solution) cluster around the Cl^--ion [12]. Further deprotonation and replication leads to the tubular hollandite units [13] which become themselves aligned to give the pores of ca. 30 Å diameter described by Gallagher [1, 2, 10]. It has been reported that the Cl^- content of the material so obtained may be reduced to ca. 1 ppm by prolonged washing with distilled water according to

$$FeO_{1-1/4}\,(OH)_{1+1/4} \cdot \tfrac{1}{4}\,Cl + H_2O \rightarrow FeOOH \cdot \tfrac{1}{4}\,H_2O + H^+ + Cl^-$$

We wish to report results of ion exchange studies which suggest that Cl^- ion is specifically adsorbed on β-FeOOH and cannot be fully eluted by washing with water or by exchange with inert (NO_3^-) or specifically interacting (F^-) anions. Thus, the low Cl^--content previously reported [1] for β-FeOOH may be in error.

Materials and Methods

All solid reagents were analytical reagent grade. Acids were Merck Suprapur. Electron microscopy samples were dispersed in distilled water and prepared on a carbon film for direct observation or embedded in a methacrylate monomer liquid which, after polymerization, was cut by means of a Reichert Om U2 ultramicrotome. Direct preparations and thin cuts were investigated in a Hitachi HU-12A electron microscope. For XRD analysis, the substance was prepared in Bedacryl (ICI) on a Scotchtape supporting film and X-rayed in a Guinier-de Wolff mark 1 camera with focusing quartz monochromator and FeK_α radiation (exposure time ca. 3–5 h). Thermoanalysis was performed with a Mettler TA1 thermobalance in vacuo (*p* below 0.0001 Torr) at a heating rate of 2 °C/min up to 170 °C and 6 °C/min from 170 to 1000 °C. A flat Pt crucible of 16 mm dia. was used. The decomposition products were recorded with an attached Balzers QMG 311 quadrupole mass spectrometer using a Balzers QPG 101 programming unit. The range m = 35–40 was printed out with 3 sec/mass.

Washed and dried β-FeOOH was prepared as described by Gallagher [1]. Chloride rich β-FeOOH was obtained by collecting the original precipitate on a 0.45 μm membrane filter and washing it quickly three times with distilled water. The washed material was dried at 105 °C for 2 h, crushed, and dried for 1 h at 105 °C.

For the Cl^- and F^- exchange, a Cl^--rich β-FeOOH (0.9 g) was suspended in 0.1 M KF (1l) using an ultrasonic bath to facilitate dispersion. After 10 min, 100 ml of the suspension was withdrawn with a pipette and filtered (0.45 μm). A 50 ml aliquot of the filtrate was analyzed for chloride using an ion selective electrode. The precipitate was briefly washed, dried for 2 h at 105 °C, then analyzed for Cl^- and F^- as described below. The suspension was kept at 25 °C and further 100 ml aliquots analyzed at weekly intervals over 5 weeks.

For halide analysis, β-FeOOH (ca. 80 mg) was weighed in a glass ampoule and treated with 2 ml of 20% sulphuric acid. The ampoule was sealed in a flame and heated at 100 °C in a water bath until a clear solution was obtained. The ampoule was cooled and the contents immediately diluted to 50 ml with 1 M monosodium citrate. The chloride content was determined by a standard addition technique using an Orion 94-17A electrode; a correction was applied for the chloride content of the reagents. The *p*H was then adjusted to ~5.5 with solid sodium hydroxide and the fluoride concentration determined by standard addition using an Orion 94-09 electrode. A Metrohm E-500 digital voltmeter and Orion 90-02-00 double junction reference electrode with 1 M sodium sulphate outer filling solution were used in both cases (these conditions of *p*H and halide concentration conform closely to the optimum conditions established by Duff and Stuart [14] for the sequential determination of halide ions in a single sample). Alkalimetric titrations were performed as described in the literature [8], using 0.01 M HX (NaOH)/0.09 M NaX reagent solutions and suspensions of β-FeOOH which had been equilibrated for two weeks with 0.1 M NaX (X = Cl, NO_3). A Metrohm E-576 Potentiograph was modified by the addition of two time switches to control titrate and equilibration periods and permit unattended operation for periods up to 48 h. *p*H was measured with a Metrohm EA 120 glass electrode which was calibrated before and after each titration run with two buffer solutions.

Results and Discussion

Acidimetric and alkalimetric titration curves in presence of electrolytes aid characterizing the amphoteric and surface charge properties of β-FeOOH and illustrate how these are affected by ions. Fig. 1 gives acidimetric and alkalimetric titration curves for varying equilibration times (between successive additions of acid or base) for a NO_3^- and a Cl^- medium. In presence of Cl^- the slope of the titration curve is less steep than in NO_3^--medium indicating specific (surface potential determining) adsorption (i.e., including adsorption through other than coulombic forces) of Cl^- ion, thus rendering the β-FeOOH surface less acidic. While

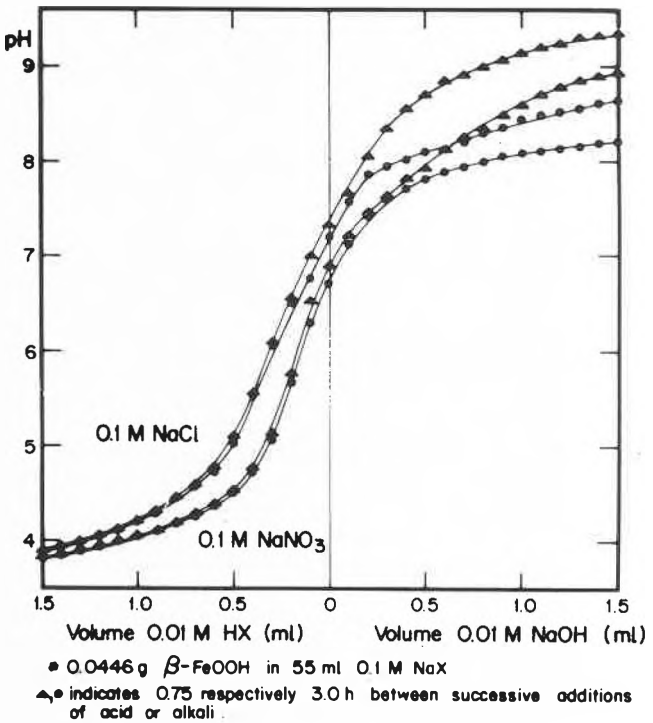


Fig. 1: Titration of β-FeOOH with H^+ and OH^-: 0,0446 g β-FeOOH in 55 ml 0,1 M NaX

little difference between fast and slow equilibration is observed in the titration curves in the acid range, equilibration time has a pronounced effect in the alkaline range. Here the curve becomes progressively flattened out by increasing equilibration time, suggesting that the reaction of OH^- with the β-FeOOH surface is a very slow process, which is presumably diffusion controlled as the incorporation of tritium reported earlier [1]. Thus, it appears that Cl^-, but not NO_3^-, may penetrate the hollandite tunnels and displace H_2O.

This is also confirmed by the fact that neither extended washing with H_2O nor anion exchange with OH^- or F^- reduced the Cl^- content to below ca. 2% (i.e., ca. 25% of the original Cl^- content cannot be removed under these conditions). In an effort to characterize the distribution of Cl^- ions in β-FeOOH crystals, materials aged for 48 h in solutions of various NO_3^- and OH^- concentrations were examined with thermal gravimetry/mass spectrometry. As Fig. 2 illustrates, crystals aged seemingly under conditions favorable for Cl^- elution, at pH = 9 (no salts added) still contain substantial Cl^-; this residual Cl^- content may reasonably be attributed to Cl^- ions remaining in the hollandite tunnels.

As shown in Table 1, suspension of a Cl^--rich β-FeOOH in 0.1 M KF leads initially to a fast elution of some Cl^- (release of ca. 50% of the Cl^- content within 1 minute) which is then followed by a progressively slower exchange of Cl^- with F^-. After 6 weeks, a residual Cl^- content of 30,000 ppm (release of ca. 65% of the original Cl^- content) remains. The rapidly displaced Cl^- is presumably associated with the external surfaces of the crystals while the slowly exchanged Cl^- comes from the hollandite tunnels and perhaps the larger structural tunnels as well. In this connection, the accessibility of the surfaces of the larger tunnels to oxalate ion has been postulated recently to account for the abnormally rapid dissolution of β-FeOOH in ammonium oxalate compared with the other iron oxide hydroxides [15].

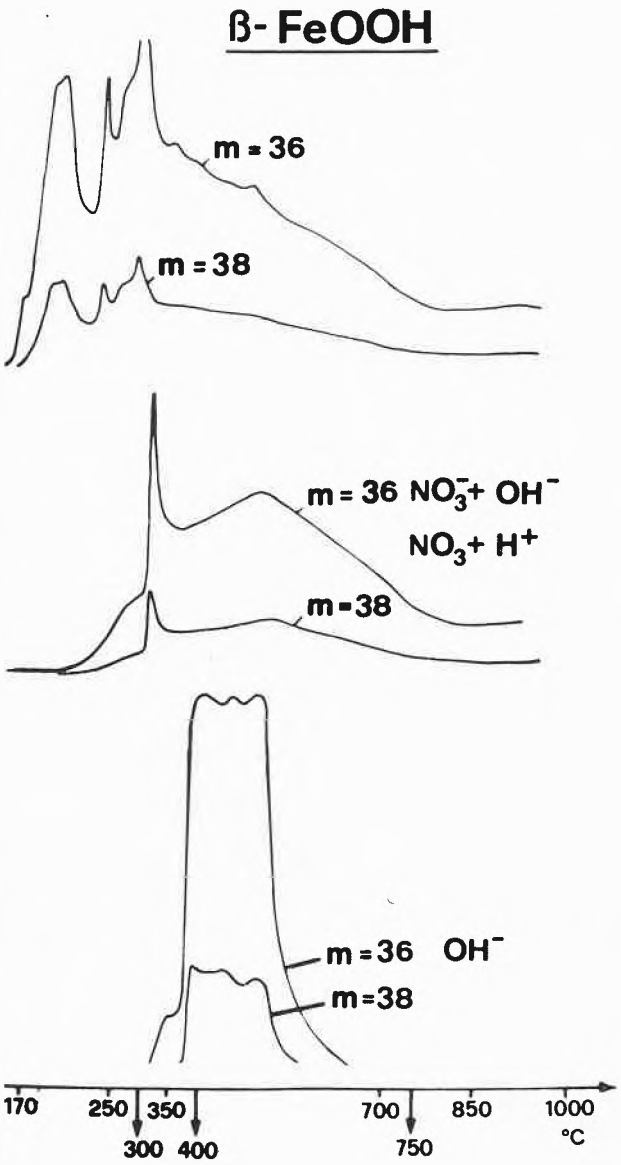


Fig. 2: Thermogravimetric/Mass Spectrometric Analysis of β-FeOOH
From top:
- *β-FeOOH washed 12 times with H_2O bidest*
- *Washed β-FeOOH after 48 hrs with H^+ or OH^- in 0,1 M $NaNO_3$*
- *Washed β-FeOOH after 48 hrs at pH 9 in NaOH*
  m = 36 is $H^{35}Cl$ and m = 38 is $H^{37}Cl$

Table 1: Replacement of Chloride in β-FeOOH by Fluoride

Time (h)	00	0.17	90	258	426	594	762
Cl Concentration *	100	53	43	36	35	37	35

* as % of original Cl concentration (8.6%); F concentration of material equilibrated for 762 h in 0.1 M KF, then washed with 1 M Na_2SO_4, was 2.5%.

It is not unreasonable that the removal of chloride from the hollandite tunnels should be such a slow process. If they run the length of the crystal as suggested [10], they are in effect long pipes in which the chloride ion is a close fit; it cannot escape through the walls of

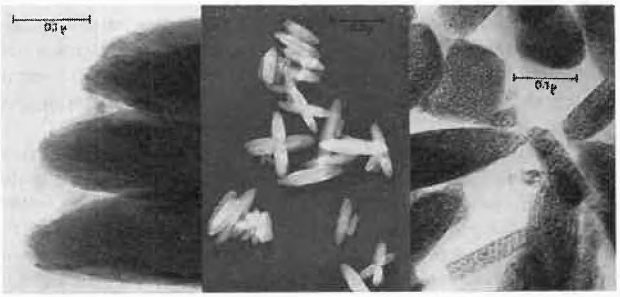


Fig. 3: Electron micrographs of exhaustively washed β-FeOOH
From left:
- *Direct picture of 30Å pore system*
- *Cr shadowed β-FeOOH crystals*
- *Thin cuts showing 30Å pores cut vertically to c axis*
  Some crystals show effects of sintering in the e beam about to begin

the pipe. Replacement of Cl^- by H_2O, OH^- or by F^- ion requires that these species enter one end of the pipe while chloride ion leaves the other end.

Cl^- ion is not only vital for the formation of β-FeOOH, but it also seems to stabilize the structure. Specimens which had been depleted in Cl^- by extensive washing were noticeably less stable in the electron beam of the microscope and tended to develop a mottled appearance (Fig. 3). Lower Cl^- content is also associated with selective line broadening in the XRD pattern (Fig. 4). However, none of the ageing or exchange experiments described above altered the overall morphology or size of the crystals (confirmed by thin section EM examination) and the XRD line positions and intensities remained virtually identical with those of the starting material (Fig. 3).

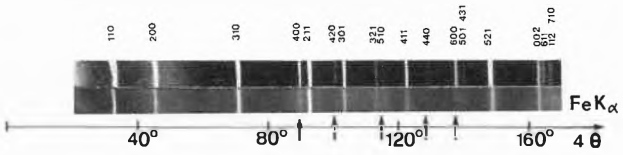


Fig. 4: Guinier powder pattern of:
- *β-FeOOH, exhaustively washed*
- *Washed β-FeOOH after 48 hrs with H^+ or OH^- in 0,1 M $NaNO_3$*

Mind the selective broadening of h00 and hk0 reflections (arrows)

The slowness of ion exchange within the crystals of β-FeOOH may impose severe restrictions on those surface-chemical studies with this compound (adsorption isotherms, determination of isoelectric point and *p*H-dependent surface potential) that require equilibrium or reversibility for proper interpretation.

These investigations corroborate that it may not be possible to prepare a Cl^--free β-FeOOH from preparations originally made by hydrolysis of Fe(III) in Cl^--media. The report of a near Cl^--free material [1] may be in error, possibly because of HCl evolution during digestion of the samples with HNO_3. We lost 99% of the original Cl^- content by warming a sample of β-FeOOH in a beaker with 30% w/v HNO_3 just long enough to dissolve the solid (in order to prevent such loss, our samples were digested in sealed ampoules). With respect to previous work it should also be noted that certain differences between the Mössbauer spectral data of Howe and Gallagher [2] and that of earlier workers [3] were ascribed to the change in Fe^{3+} coordination due to additional protons needed to balance the charge of the chloride in the small tunnels of the unwashed material used in the earlier study. These differences are perhaps more correctly attributed to a difference in chloride abundance in the respective preparations, rather than the presence of chloride in one case and its absence in the other.

We thank Dr. K.J. Gallagher for a reference specimen of β-FeOOH and for valuable discussions. Authors are indebted to Emma Ettinger for electron microscopy work and to the Swiss National Fund for financial support.

References

1 *K.J. Gallagher* and *D.N. Phillips:* Chimia *23* (1969) 465.
2 *A.T. Howe* and *K.J. Gallagher:* J. Chem. Soc. Faraday Trans. *1* (1975) 22.
3 *P.O. Voznyuk* and *V.N. Dubinin:* Fiz. Tverd. Tela *15* (1973) 1897 (Sov. Phys. Solid State *15* [1973] 1265).
4 *A. Szytula, M. Balanda* and *Z. Dimitrijević:* Phys. Stat. Sol. *(a) 3* (1970) 1033.
5 *T. Misawa, K. Hashimoto* and *S. Shimodaira:* Corrosion Sci. *14* (1974) 131.
6 *L.A. Taylor, H.K. Mao* and *P.M. Bell:* Geochim. Cosmochim. Acta Suppl. *4.1* (1973) 829.
7 *F.J. Hingston, R.J. Atkinson, A.M. Posner* and *J.P. Quirk:* Nature *215* (1967) 1459.
8 *D.E. Yates* and *T.W. Healy:* J. Colloid Interf. Sci. *52* (1975) 222.
9 *E.A. Forbes A.M. Posner* and *J.P. Quirk:* J. Co. Interf. Sci. *49* (1974) 403.
10 *K.J. Gallagher:* Nature *226* (1970) 1225.
11 *J.* Babčan: Geologica Carpathica *22* (1971) 11.
12 *W. Feitknecht, R. Giovanoli, W. Michaelis* and *M. Müller:* Helv. Chim. Acta *56* (1973) 2847.
13 *A.L. Mackay:* Min. Mag. *32* (1960) 545.
14 *E.J. Duff* and *J.L. Stuart:* Analyst *100* (1975) 739.
15 *K. Kauffman* and *F. Hazel:* J. Inorg. Nucl. Chem. *37* (1975) 1139.

Die Horner-Variante der Wittig-Reaktion: unter milden Bedingungen durchführbar und mit stereochemischen Optionen ausgestattet*

M. Schlosser** und Huynh Ba Tuong
Institut de chimie organique de l'Université de Lausanne

Summary

Olefin syntheses by means of metallated phosphine oxides may be carried out at room temperature. The configuration of a double-bond present in the starting material can be conserved throughout the whole reaction sequence. Moreover the new double-bond forms with extreme trans-selectivity, provided that the "PO-ylid" reagent is stabilized by an electron attracting group such as vinyl or phenyl.

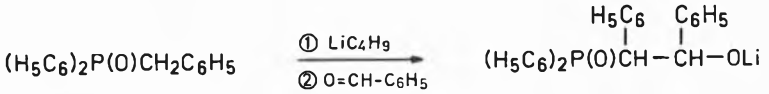
* Eingegangen am 31. Dezember 1975
** Prof. Dr. M. Schlosser, Institute de chimie organique de l'Université, Rue de la Barre 2, CH-1005 Lausanne

Soeben ist eine Mitteilung erschienen über den Einsatz metallierter Crotyldiphenylphosphinoxide zur Synthese des 3-Desoxy-Vitamin D_2 sowie einfacherer Modellverbindungen [1]. Sie enthält zwei bemerkenswerte Feststellungen:

1. Die Horner/Wittig-Methode [2] führt bereits bei Raumtemperatur rasch und mit guten Ausbeuten zu den Endprodukten, auch wenn Butyllithium zur Metallierung des Phosphinoxids diente und somit das die Olefinbildung am stärksten bremsende Alkalimetall im Spiel ist.
2. Die in der Alkenyl-Seitenkette der Ausgangsverbindung vorgegebene Konfiguration (cis- oder trans-Crotenyl) taucht unverändert im Dien, dem Zielpunkt der Reaktionsfolge, wieder auf.

Beide Befunde überraschen, wenn man sie vor dem Hintergrund anderer Erfahrungen betrachtet. Wir können sie jedoch vollauf bestätigen, sie erweitern und Widersprüche, wo sie zu bestehen scheinen, beseitigen.

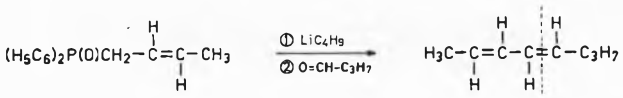
Lithium-Derivate grundsätzlich aller PO-Ylide, die in α-Stellung elektronenanziehende Liganden tragen, vermögen schon bei Raumtemperatur das Olefin zu bilden. Dies gilt nicht nur für *2-Alken-1-yl*-diphenyl-phosphinoxide, sondern unter anderem auch für das *Methoxymethyl*-diphenyl-phosphinoxid (z. B. mit Cyclohexanon nach 20 Std. 35% Methoxymethylen-cyclohexan) und insbesondere für Arylmethyl-diphenyl-phosphinoxide. So erhielten wir aus Benzyl-diphenyl-phosphinoxid, mit Butyllithium metalliert, und Benzaldehyd 78% trans-Stilben (**1**), wenn wir 20 Std. nach Vereinigung der Reaktionspartner hydrolysierten. Auf den ersten Blick erscheint dieses Ergebnis kaum vereinbar mit einem Bericht [3], wonach unter sehr ähnlichen Bedingungen nur das (1,2-Diphenyl-2-hydroxy-äthyl)-diphenyl-phosphinoxid (**2**) gewonnen wird. Indessen hatte die Reaktionsdauer damals [3] nur 3 Std. betragen. Ausserdem hatte man zur Metallierung Phenyllithium verwendet; dieses – auf übliche Weise dargestellt – enthält ein Äquivalent Lithiumbromid, dessen hemmender Salzeinfluss bekannt ist [4, 5].



Lithium-Derivate von *Methyl-* und *Alkyl*-diphenyl-phosphinoxiden lagern sich zwar rasch an Aldehyde und Ketone an; aber die so erhaltenen Addukte sind bei 25 °C beständig. Um zu den Olefinen zu gelangen, muss man sie entweder hydrolysieren, als β-Hydroxyphosphinoxide abtrennen und dann mit Natriumhydrid in Dimethylformamid behandeln [6] oder – weit einfacher – sie durch Zugabe von Kalium-t-butanolat «aktivieren» [7].

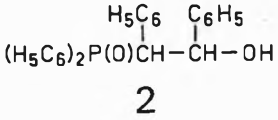
Die Konfigurationsbewahrung in der Alkenyl-Seitenkette des PO-Ylids steht in auffälligem Gegensatz zur Behendigkeit, mit welcher Organolithium-Verbindungen sonst cis/trans-isomerisieren [8]. Damit wird unsere Vermutung [9], das Metall sei in den PO-Yliden gar nicht an ein Kohlenstoff-, sondern an das Sauerstoffatom gebunden, weiter untermauert. Die konfigurative Integrität der Alkenyl-Seitenkette bleibt bei Horner/Wittig-Reaktionen auch dann gewahrt, wenn die ungesättigte Kette in 2-Stellung verzweigt ist (z. B. aus E-2-Methyl-2-buten-1-yl-diphenyl-phosphinoxid und Cyclohexanon → 10% E-2-Methyl-2-buten-1-yliden-cyclohexan). Da die benötigten Alkenyl-Bausteine neuerdings einfach zugänglich sind [10–13] lassen sich nunmehr erstmals Diene eines bestimmten Strukturtyps bequem und stereoselektiv aufbauen.

Bei dieser Sachlage war eine weitere Entdeckung höchst willkommen: auch die Konfiguration der neu zu knüpfenden Doppelbindung kann vorausgeplant werden. Denn unabhängig von der vorgegebenen räumlichen Lage der Liganden in der ungesättigten Seitenkette des PO-Ylids, entsteht bei dessen Kondensation mit einem Aldehyd die neue Olefin-Gruppierung unweigerlich mit trans-Anordnung der Kohlenstoff-Reste (z. B. aus E-2-Buten-1-yl-diphenyl-phosphinoxid und Butanal → 28% E,E-2,4-Octadien (**3**), das allenfalls spurenweise die E,Z-, Z,E- und Z,Z-Isomere enthält).

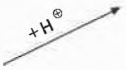


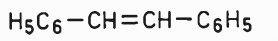
3

Man kennt bereits seit langem eine ausgeprägte trans-Selektivität der Horner/Wittig-Methode, wenn es darum geht, Alkene vom Stilben-Typ oder α,β-ungesättigte Carbonyl-Verbindungen darzustellen [3, 14]. Bislang durfte man annehmen, die ungewöhnlich grossen Unterschiede in der thermodynamischen Stabilität ($\Delta G^0 > 2$ kcal/mol) der betroffenen cis- und trans-Isomere seien dafür verantwortlich. Künftig muss man zusätzliche Faktoren zur Erklärung heranziehen, so



2





1

etwa die Gibbs-Energiedifferenzen der cis- und trans-3,4-disubstituierten Oxaphosphetane, den energiereichen Zwischenstufen [15] der Reaktionsfolge. Denn, wie sich jetzt herausstellt, liefert die Horner-Variante auch solche Alkene mit extrem hoher trans-Selektivität, deren cis-Isomer thermodynamisch nicht so wesentlich benachteiligt ist (z. B. aus Äthyl-diphenyl-phosphinoxid und Benzaldehyd in Äther bei 25° C → 67% 1-Phenyl-1-propen, Z/E = 0,5: 99,5; dagegen Gleichgewichtszusammensetzung [16] 2,2: 97,8 in Dimethylsulfoxid bei 25 °C; 5,7: 94,3 in t-Butanol bei 97 °C).

Finanzielle Unterstützung gewährte der Schweizerische Nationalfonds zur Förderung der wissenschaftlichen Forschung, Bern (Projekte 2.0530.73 und 2.293.74).

Literatur

1 *B. Lythgoe, T. A. Moran, M. E. N. Nambudiry, S. Ruston, J. Tideswell* und *P. W. Wright:* Tetrahedron Lett. (1975) 3863.
2 Übersichten: *A. W. Johnson:* Ylid Chemistry, Academic Press, New York 1966, Kap. 5;
L. Horner: Fortschritte chem. Forschung *7* (1966) 1;
M. Schlosser: Topics in Stereochemistry *5* (1970) 1.
3 *L. Horner, H. Hoffmann, H. G. Wippel* und *G. Klahre:* Chem. Ber. *92* (1959) 2499;
vgl. auch *L. Horner* und *W. Klink:* Tetrahedron Lett. (1964) 2467.
4 *G. Wittig* und *E. Benz:* Chem. Ber. *91* (1958) 874.
5 Übersicht: *M. Schlosser:* Struktur und Reaktivität polarer Organometalle, Kap. 3.3.4, Springer Verlag, Heidelberg 1973.
6 *A. J. Bridges* und *G. H. Whitham:* Chem. Commun. (1974) 142.
7 Vgl. *M. Schlosser* und *K. F. Christmann:* Angew. Chem. *76* (1964) 683; Angew. Chem. internat. Edit. *3* (1964) 636.
8 *P. West, J. I. Purmort* und *S. V. McKinley:* J. Amer. Chem. Soc. *90* (1968) 797.
9 *M. Schlosser:* in: Methodicum Chimicum, Band 7, S. 543, G. Thieme Verlag, Stuttgart 1976.
10 *M. Schlosser, J. Hartmann* und *V. David:* Helv. Chim. Acta *57* (1974) 1567.
11 *J. Hartmann, R. Muthukrishnan* und *M. Schlosser:* Helv. Chim. Acta *57* (1974) 2261.
12 *M. Schlosser* und *E. Hammer,* Helv. Chim. Acta *57* (1974) 2547.
13 *G. Rauchschwalbe* und *M. Schlosser:* Helv. Chim. Acta *58* (1975) 1094.
14 *W. S. Wadsworth* und *W. D. Emmons:* J. Amer. Chem. Soc. *83* (1961) 1733;
D. H. Wadsworth, O. E. Schupp, E. J. Seus und *J. A. Ford:* J. Org. Chem. *30* (1965) 680.
15 *M. Schlosser, A. Piskala, C. Tarchini* und *Huynh Ba Tuong:* Chimia *29* (1975) 341.
16 *S. W. Ela* und *D. J. Cram:* J. Amer. Chem. Soc. *88* (1966) 5791.

Ketoins from Primary Alkylhalides, Grignard Compounds and Carbonmonoxide in Ether-HMPT *

W. J. J. M. Sprangers, A. P. van Swieten and R. Louw **
Department of Organic Chemistry, Gorlaeus Laboratories, The University of Leiden

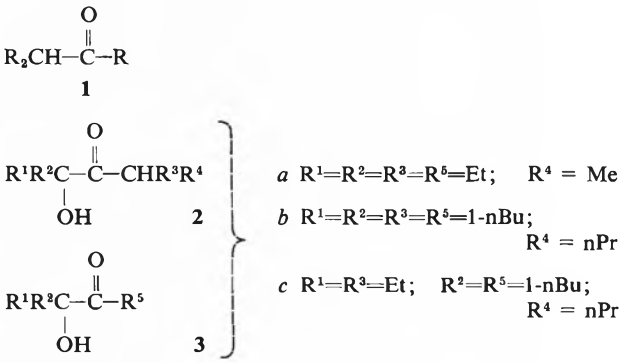
Summary

Whereas carbonylation of primary Grignard compounds in ether-HMPT leads to ketones **1**, reaction in the presence of an additional amount of alkylhalide results in the formation of hydroxyketones **2** and **3**. When using neat HMPT as solvent, **2** is the main product (up to 55% yield).

The carbonylation of a variety of organometallic compounds is known to be of great synthetic value [1]. Remarkably, the reaction of Grignard derivatives with CO has received relatively little attention. Recently we described the carbonylation of (primary) Grignard reagents in ether; addition of one mole of hexamethylphosphoric acid triamide (HMPT) led to a greatly enhanced rate of CO uptake. At room temperature and at 30 atm, the reaction is completed within 1 to 3 min [2]. Primary alkylhalides RX led to ketones **1** in an essentially one-step procedure [2]. We now wish to report that when conducting the reaction of RMgX in neat HMPT in the presence of an—additional—equivalent of RX, totally different results are obtained. Ketoins **2** are now produced, with compounds **3** as side products.

The yield of **2** (and the **2**:**3** product ratio) is much lower when ether-HMPT is used. Alternatively, carbonylation of RMgX in pure HMPT without additional RX invariably led to complex reaction mixtures of different composition, in rather low yields (30–40% by weight).

Yields of **2** are 30–55%; the simple one-step procedure, exemplified below, adds to the synthetic value of this reaction.



A Grignard reagent was prepared from 0.2 mole of EtBr in 250 ml of dry ether; 0.6 mole of HMPT was slowly added and the ether stripped off in vacuo. The resulting solution was transferred to a 1 l autoclave and 0.2 mole of EtBr added. The autoclave was pressurized with CO (35 atm). Upon stirring, the temperature rapidly rose to 35 °C and the pressure fell to ca. 24 atm within 5 minutes. After 4 h the pressure was reduced to 20 atm at 20 °C, corresponding to an uptake of 0.18 mole of CO. After work-up (addition of 200 ml 1 N aq. hydrochloric acid, extraction with ether (4 × 200 ml), drying over $CaCl_2$ and evaporation in vacuo) 15.8 g of oil was obtained. By comparison with standard mixtures[1], VPC analysis showed **2a** (54%)[2]. Side products were **3a**

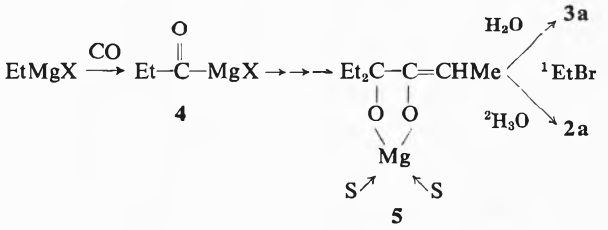
* Received January 7, 1976. Preliminary communication
** Dr. Robert Louw, Gorlaeus Laboratories, University of Leiden, P. O. Box 75, Leiden, The Netherlands

[1] Reference compounds were isolated from crude reaction mixtures via preparative VPC.
[2] Yields are based on starting alkylhalide and are not corrected for e. g. Wurtz coupling, occurring after addition of HMPT and RX.

(10%), Et_2CO (3%), Et_2CHOH (3%), EtCOCOEt (5%) and EtCH(OH)COEt (7%). Pure **2a** could readily be isolated via distillation (or via preparative VPC); bp. 76°C/50 mm Hg, n_D^{20} = 1.4414.

Analogously, **2b** was obtained in 33% yield from 0.2 mole of n-butylbromide. When employing ether-HMPT (1:1 v/v) rather than neat HMPT as solvent, the yield dropped to ca. 10%, that of **3b** amounting to 35%.

The mixed products **2c** (20%) and **3c** (50%) were formed upon reacting nBuMgBr with one equivalent of EtBr in HMPT—ether (1:1 v/v), HMPT: RMgX = 3. In neat HMPT, a **2c**/**3c** ratio of 1.0 was attained. The novel compounds **2** (and **3**) showed spectral properties (NMR, including lanthanide-induced shifts; IR, MS[3]) in full accord with the proposed structures. As formation of especially **2** must involve a considerable number of steps, this reaction may be considered as rather selective. Starting with carbonylation to give **4**[4], it can be rationalized on the basis of **5**—or (an) equivalent(s) thereof—as the "last" intermediate. As depicted for the ethyl derivative, hydrolysis gives **3a**, but C-alkylation [4] leads to **2a**.



[3] Mass spectra were as expected for ketoins, showing primary fragmentation between the $R_2C(OH)$ and C(O)R functions [3]. For example, **3c** gave M^+ = 200, m/e = 115 ($C_7H_{15}O$), 85 (C_5H_9O) as the main components.

[4] Such an acylmagnesiumhalide has been shown to occur as an intermediate for R = phenyl (hydrolysis leading to benzaldehyde as a side product) and for R = 1-n-butyl (in situ reduction with $NaBH_4$ resulting in 1-n-pentanol as one of the products) [2a].

Literature

1a *J. Falbe:* Carbon Monoxide in Organic Synthesis, Springer Verlag, Berlin 1970;
b *C. W. Bird:* Transition metal Intermediates in Organic Synthesis, Acad. Press, 1966;
c *H. C. Brown:* Accounts Chem. Res. *2* (1969) 65;
d *G. P. Chiusoli:* Accounts Chem. Res. *6* (1973) 422
2a *W. J. J. M. Sprangers:* Thesis, Leiden 1975;
b *W. J. J. M. Sprangers, A. P. van Swieten* and *R. Louw:* Tetrah. Letters (1974) 3377.
3 *K. Biemann:* Mass Spectrometry, Organic Chemical Applications, McGraw-Hill, New York 1962.
4a *J. Fauvarque* and *J-F Fauvarque:* C. R. Acad. Sci; Sér. C., *263* (1966) 488;
b *J. Fauvarque* and *J-F Fauvarque:* Bull. Soc. Chim. France (1969) 160.

The Isotherms of Ethane on Ni-Surfaces *

V. Almaşan and T. Gäumann **

Departement of Physical Chemistry, Swiss Federal Institute of Technology, Lausanne

Summary

The isotherms of ethane were determined at 20°C, 65°C and 105°C in a flow system with He or H_2 as carrier gas. The latter reduces the plateau value of the Langmuir isotherm by a factor of 0.7, but increases the heat of adsorbtion of ethane from 19 to 27 kJ/mol.

Hydrogen and paraffins can both be chemisorbed on Ni-surfaces. This effect can be used to deuteriate substances in a continuous process using deuterium as carrier gas [1]. It has been shown that the reactivity depends on the fraction of the surface covered [2]. In order to gain a better understanding of the isotopic exchange between hydrogen and the paraffin [3], we measured the isotherm of ethane on a Ni-surface in a flow system. Two carrier gases were used: He, which does not chemisorbe on the catalytic surface [4] and H_2 which competes with ethane. The isotherms are shown in Fig. 1. They are reversible and correspond nearly, but not completely, to Langmuir isotherms with a plateau value of 5.5 mg ethane/g catalyst and 3.9 mg/g for He and H_2 as carrier gas resp. This shows that ethane competes favorably with hydrogen. It might also be mentioned that the plateau value is the same below and above the critical temperature of ethane (32.3°C). The specific surface of our Ni-catalyst has been measured by BET-measurements to be about 60 m^2/g [5]. Assuming a surface of 6.8 A^2 for a Ni-atom, we can estimate that 8–12 Ni-atoms of a "BET-surface" are needed to adsorb one ethane molecule.

A closer inspection of the isotherms showed that they deviate slightly but systematically from the form of a Langmuir isotherm. Other types of isotherms were tried, but without better success. Assuming a Langmuir isotherm, we can estimate the isosteric heat of adsorption q_{st} of ethane from the following equation [6]:

$$q_{st} = -RT^2 (\delta \ln P/\delta T)_x$$

where P is the partial pressure of ethane at a constant surface coverage x and the temperature T. The values thus obtained vary slightly with the surface coverage, but since we find it difficult to estimate the influence of systematic errors, we limit ourselves to an average value of 19 kJ/mol for He and 26 kJ/mol for H_2 as carrier gas. However, we consider the difference between these two values to be real.

* Received January 11, 1976

** Prof. Dr. T. Gäumann, Institute de Chimie Physique de l'EPF, Avenue des Bains 31, CH-1007 Lausanne

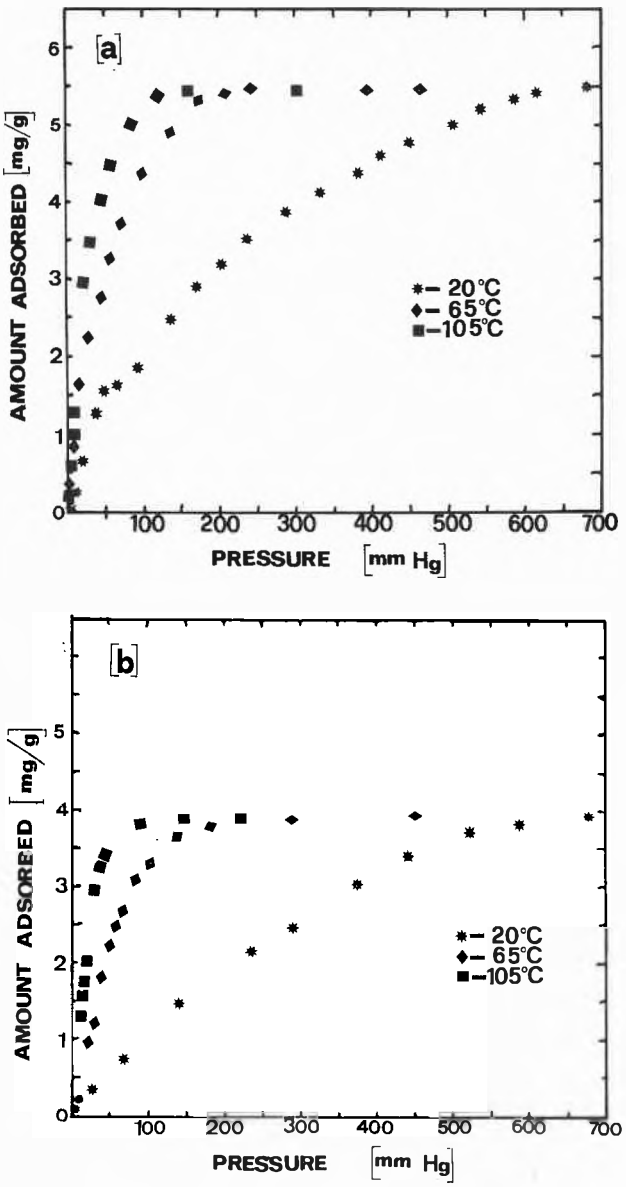


Fig. 1: Isotherms of ethane on Ni as a function of the partial pressure of ethane. Carrier gas used: a) He; b) H_2

It is generally assumed that ethane adsorbs on Ni-films according to a dissociative mechanism [7]. According to Kemball the following reaction takes place [7b]:

$$CH_3 - CH_3 + Ni \rightleftarrows H_2C - CH_2 + H + H \qquad (1)$$
$$\qquad\qquad\quad \downarrow \quad \downarrow \quad \downarrow \quad \downarrow$$
$$\qquad\qquad\quad * \quad * \quad * \quad *$$

where * stands for the Ni-surface with sites which probably have a wide variety of activity. For the sake of simplicity, we distinguish only two kinds of sites: about one third adsorbes ethane relatively weakly; hydrogen competes favorably for these sites. Two thirds tend to adsorb ethane more strongly than hydrogen allowing reaction (1) to take place even in the presence of hydrogen or deuterium. In order to explain the exchange properties of our catalyst we have to assume however that the adsorbed hydrogen atoms of reaction (1) either exchange with hydrogen in the gas phase or with hydrogen adsorbed on sites of the first kind. The existence of two different kinds of surfaces (however in the approximate ratio of 1 : 1) on Ni has also been postulated by Taylor and Creasey [9a] and Martin et al. [8c].

Experimental

The catalyst (85 weight % Ni) was prepared from Ni $(NO_3)_2$ and Al $(NO_3)_3$ with a final granulation of 0.2 to 0.3 mm [5]. It was activated by passing hydrogen during 12 h at 200 °C. Hydrogen is desorbed by letting pass He during 24 h over the catalyst. It is not probable that this procedure eliminates all the hydrogen adsorbed [9]. Ethane was of Philips Research Grade quality; the purity of hydrogen and helium was > 99.9 %. The apparatus

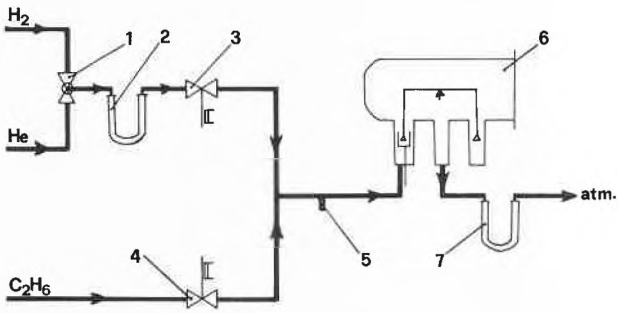


Fig. 2: Apparatus used

used is shown in Fig. 2. The carrier gas passed through column "2" filled with active catalyst in order to remove any nocive trace impurities. The electromagnetic regulation valves "3" and "4" maintained a chosen flow rate to better than 1 % over long periods of time. Samples for gas chromatographic analysis were taken through septum "5". About 0.1 g of catalyst was placed on the thermobalance "6" (Cahn, long time stability of $\pm 2\,\mu g$). This stability was not sufficient for measuring the isotherms of H_2 in helium, however these have been obtained by Morgan and King [8b]. A column "7" filled with catalyst was added to avoid any backdiffusion of air from the gas outlet.

We thank the Swiss National Science Foundation for a grant.

References

1 *C. Bosshard, G. Dessauges, H. Öz, O. Piringer* and *T. Gäumann:* to be published.
2 *K. Tamaru:* Adv. in Catalysis *15* (1964) 67.
3 *G. Dessauges* and *T. Gäumann:* Helv. Chim. Acta, in press.
4 *A. J. Halley:* J. Appl. Chem. *13* (1963) 392.
5 *Al. Olariu* and *P. Märgineau:* Rev. Roum. Physique *13* (1968) 823.
6 *C. Létoquart, F. Rouquerol* and *J. R. Rouquerol:* J. chim. phys. *70* (1970) 559.
7a *P. Q. Wright, P. Q. Ashmore* and *C. Kemball:* trans. Farad. Soc. *54* (1958) 1692;
b *K. Galway* and *C. Kemball:* ibid. *55* (1959) 1959
c *G. C. Bond* and *P. B. Wells:* Adv. in Catalysis *15* (1964) 91.
8a *N. Taylor* and *R. Creasey:* p. 297 in Adsorption-Desorption Phenomena, ed. by F. Ricca, Academic Press, 1972;
b *A. M. Morgan* and *D. A. King:* ibid. p. 329;
c *G.-A. Martin, Q. Dalmai-Imelik* and *B. Imelik:* ibid p. 433.
9 *J.-P. Candy, J.-A. Dalmon, P. Fouilloux* and *Q. A. Martin:* J. chim. phys. *72* (1975) 1075.

Photo-electron Spectra of Germanate, Tellurite and Tungstate Glasses Especially Apt to Show Lanthanide Luminescence *

Renata Reisfeld **, C. K. Jørgensen *** and H. Berthou
Département de Chimie minérale, analytique et appliquée, Université de Genève

Summary

The photo-electron spectra of vitreous samples are essentially similar to comparable crystalline compounds, and the local ordering of neighbour oxygen atoms inferred from europium (III) emission spectra of certain glasses containing both tungstate and phosphate has no perceptible effect. The chemical shifts and semi-quantitative analysis are interesting.

Since the major non-radiative decay of excited $4f^q$ states of trivalent lanthanides, competing with the luminescence, is a multi-phonon de-excitation [1, 2] it is a great advantage to use crystalline chlorides or bromides with as heavy atoms and weak force constants as possible, producing a low wave-number of the highest normal mode phonon. Interestingly enough, the phonon spectra of vitreous materials do not enhance the multi-phonon de-excitation if the conventional silicon oxide glasses are replaced by germanium (IV) and tellurium (IV) with distinctly lower phonon energies [2]. Thus, the Einstein coefficients of spontaneous emission and rate constants for energy transfer and other non-radiative processes have recently been determined [3] for $4f^{11}$ erbium (III) and $4f^{12}$ thulium (III) in tellurite glasses, incorporating parameters of the Judd-Ofelt theory of absorption band intensities [4]. We are convinced that the Judd-Ofelt parameters, and in particular the hypersensitive pseudoquadrupolar transitions [5] are determined by chemical bonding much more than by local symmetry, as elaborated in our book [6]. Since vitreous materials do not allow several techniques available to the study of crystals, it is of interest to obtain as much information as possible about the chemical bonding with accessible data.

One applicable technique [7] is the photo-electron spectra induced by soft X-rays (in our case 1253.6 eV photons from a high-intensity magnesium anti-cathode in a Varian IEE-15 spectrometer) where two of us [8] previously measured above 600 compounds containing 77 elements, to which xenon (VIII) recently has been added [9]. Though the chemical shifts of the ionization energies I of inner shells are not exclusively determined by the combined Hartree + Madelung potential [10] but contain strong relaxation effects [9, 11] in the electronic density of the adjacent atoms, and though the semi-quantitative analysis [12, 13] of the relative concentration of the elements in the outermost 20 Å of the sample encounters well establishedd iffi-culties [10, 14] the results for the glasses are of some interest, already because very few solids containing germanium [8, 15], tellurium [8, 16] and tungsten [8, 17] have been studied. Table 1 gives the two carbon signals [18] indicating the quasi-stationary positive potential (C_{st}–C'_{st}) where C_{st} is the difference between 290 eV and the I* recorded by the photo-electron spectrometer for the unperturbed hydrocarbon on the scotch tape and C'_{st} the difference between 290 eV and I* recorded for the tiny amount of hydrocarbon in electric contact with the isolating sample. If the surface of the sample contains carbonate, a third C1s signal is observed with I* close to 291.5 eV, and the negative quantity given in parenthesis is the difference between 290 eV and the latter I*. The other elements in Table 1 have I′ values (corrected for charging effects) being each time the sum of I* of the signal and C'_{st}. The chemical compositions known of the glasses are compared with the semi-quantitative results [13] expressed as ratios between atomic concentrations in the superficial layer. Sometimes, two kinds of oxygen atoms are distinguished.

The borate glass has I′ (B1s) considerably below 200.8 eV known [8] for KBF_4. This shift 4.8 eV can be compared with the variation of I′ (P2p) between 143.6 eV for KPF_6 and 138.7 eV for $CePO_4$ and 138.6 eV for Li_3PO_4 which are comparable to the phosphorus content in our tungstate glasses, and slightly below the straightforward phosphate glass. Our I′ (Na1s) close to 1076.5 eV are similar (within experimental uncertainty) to NaF and Na_2WO_4 but slightly below NaCl, NaBr and NaI (1077.2 eV). I′ ($Ge3p_{3/2}$) = 130.8 eV for K_2GeF_6 and 130.3 eV for GeO_2, whereas these two substances have I′ (Ge3d) = 38.9 and 38.4 eV, both slightly above our germanate glass. There is a specific problem with our nominal admixture of 1 percent Sm (III) and 1 percent Bi (III). Though the strong Bi4f signals [13] could not be perceived, signals at I* = 138 and 134 eV suggested the presence of several percent samarium, which may be enhanced in the surface layer by atmospheric attack. The samples arrived as molten, coin-shaped disks, and were crushed to a fine powder in the last moment before the measurement. Nevertheless, carbonate was frequently detected. For comparison, tellurium (IV) oxide and sodium tellurite are included in Table 1, the chemical shift from the tellurite glasses and the oxides to Na_2TeO_3 can be compared to the decrease [15] of I′ 1.2 eV from GeO_2 to Na_2GeO_3. If 5 eV are added to I* ($Te3d_{5/2}$) reported [16], 581.7 eV for $(NH_4)_2TeO_4$, 581.8 eV for TeO_3, 580.7 eV for

* Received January 15, 1976
** Department of Inorganic and Analytical Chemistry, Hebrew University, Jerusalem, Israel
*** Prof. Dr. Ch. K. Jørgensen, Département de Chimie minérale, analytique et appliquée de l'université, 30, quai E. Ansermet, CH-1211 Genève 4

K_2TeO_3 and 577.9 eV for the element show a regular dependence on the oxidation state, which is not always the case when the surrounding ligands are varied [10]. For comparison with the barium (II) in glasses, it may be noted that a sample of $BaCO_3$ shows the two I′ (Ba3d) = 800.5 and 785.2 eV, and previously [8] measured BaF_2 800.3 and 785.0 eV.

In tungstate glasses made from mixtures of WO_3 and Na_2HPO_4 the emission spectrum [19] of europium (III) show interesting details of relative intensity of the magnetic dipole transition $^5D_0 \rightarrow {}^7F_1$ and of the pseudo-quadrupolar [4, 5] transition $^5D_0 \rightarrow {}^7F_2$ as previously discussed in terms of radiative and non-radiative transition probabilities in phosphate glasses [20]. Another striking effect is that phosphotungstate glasses [19] containing 75 weight percent WO_3 show distinct sub-levels, two for $^7F_1$ and three for $^7F_2$ suggesting micro-crystallites suspended in the truly amorphous matrix, whereas 68 weight percent WO_3 show broad features compatible with a rather random distribution of neighbour oxygen atoms from tetrahedral tungstate and phosphate groups. Among the samples in Table 1, the first with 37 molar percent WO_3 is genuinely vitreous, whereas the three subsequent samples show luminescence of microcrystallites, but the photo-electron spectra are virtually identical, showing the negative result that formation of microcrystallites and other instances of local ordering has very small influence on ionization energies. Quite generally, the optical spectra are more sensitive to local distortions than crystallographic evidence based on diffraction of X-rays. Thus, Faucher and Caro [21] report increasing sub-level separations of $^7F_1$ in $Eu_xLa_{1-x}AlO_3$ decreasing the temperature from 500 to 77 °K in spite of the fact that this crystal goes through a phase transition at 700 °K from a low-temperature rhombohedric form to a cubic perovskite, where the tetrakaidecahedral Eu (III) O_{12} is not expected to separate the three states belonging to $^7F_1$. The Auger signals of sodium perturb our $W4d_{3/2}$ signals; the positions of $W4d_{5/2}$ and W4f are marginally higher than I′ = 252.4, 42.5 and 40.7 eV observed [8] for Na_2WO_4. (I* + 5 eV) [17] for $W4d_{5/2}$ and $W4f_{7/2}$ are 253.4 and 41.8 eV for WO_3 and 252.8 and 41.2 eV for Li_2WO_4 to be compared with 249.2 and 36.8 eV for the element.

Acknowledgments

We would like to thank L. Boehm (phosphate), Y. Eckstein (germanate), J. Hormodaly and E. Muranevich (tellurite) and H. Mack (tungstate) for assistance in preparing the glass samples. The photo-electron spectrometer was provided with the grant (2323 – 70) from the Swiss National Science Foundation.

Literature

1 *R. Reisfeld:* Structure and Bonding *13* (1973) 53.
2 *R. Reisfeld:* Structure and Bonding *22* (1975) 123, and in press.
3 *R. Reisfeld* and *Y. Eckstein:* J. Chem. Phys. *63* (1975) 4001.

Table 1: Photo-electron spectra of glasses with ionization energies I′ corrected for charging effects [8,18] relative to vacuo. Values connected with "&" correspond to two j-values of the same nl-shell; values separated by a comma refer to non-equivalent atoms of the same element

Chemical composition Semi-quantitative ESCA analysis	C_{st}	C'_{st}	I′ (M*nl*) values in eV
$0.35\,Na_2O:0.65\,B_2O_3$ 3 B:1 CO_3^{-2}:7 O:1 Na	4.5 (−1.5)	2.3	B 1s:196.0; O 1s:535.8; O 2s:28.5; Na 1s:1075.8; Na 2s:67.4; Na 2p:34.5
$0.5\,Na_2O:0.5\,P_2O_5$ 1 CO_3^{-2}:7 (+3.5) O:1 Na:2 P	4.9 (−2)	3.5	O 1s:(538.3), 536.6; O 2s:29.7; Na 1s:1076.8; Na 2s:68.4; Na 2p:35.4; P 2p:139.2
$0.17\,K_2O:0.17\,BaO:0.66\,GeO_2$ 5 (+1) O:1 K:1 Ge:0.5 Ba	4.5	2.6	O 1s:(538), 536.0; K 2p:300.4 & 297.7; Ge 3p:129; Ge 3d:37.1; Ba 3d:799.7 & 784.4; Ba 4d:96.85 & 94.2
$0.2\,Na_2O:0.8\,TeO_2$ 0.4 CO_3^{-2}:2 O:0.5 Na:0.8 Te	4.7 (−1.5)	2.2	O 1s:535.9; Na 1s:1076.7; Te 3d:591.8 & 581.5; Te 4d:49.3
$0.35\,ZnO:0.65\,TeO_2$ 5 O:1 Zn:2 Te	4.45	2.0	O 1s:535.8; Zn 2p:1049.8 & 1026.8; Zn 3p:96.5 & 93.7; Te 3d:591.7 & 581.4
$0.15\,BaO:0.85\,TeO_2$ 11 O:5 Te:1 Ba	4.7	2.7	O 1s:535.7; Te 3d:591.7 & 581.3; Te 4d:49.35; Ba 3d:800.3 & 784.7; Ba 4d:97.1 & 94.65
Solid TeO_2	4.4	2.5	Te 3d:592.0 & 581.55; Te 4d:49.2
Na_2TeO_3 (+ CO_3^{-2})	4.7 (−1.4)	3.1	Te 3d:591.4 & 580.95; Te 4d:48.35
$0.37\,WO_3:0.42\,Na_2O:$ $0.21\,P_2O_5:0.01\,EuO_{1.5}$ 7 O:1.3 Na:1 P:1 W	4.7	3.3	O 1s:536.2; Na 1s:1076.5; P 2p:138.6; W 4d:265 & 252.8; W 4f:43.0 & 40.9
$0.48\,WO_3:0.34\,Na_2O:$ $0.17\,P_2O_5:0.01\,EuO_{1.5}$ 0.8 CO_3^{-2}:5 O:0.9 Na:0.7 P:1 W	4.6 (−1.4)	3.1	O 1s:536.1; Na 1s:1076.4; P 2p:138.6; W 4d:265 & 252.7; W 4f:42.9 & 40.9
$0.46\,WO_3:0.32\,Na_2O:$ $0.16\,P_2O_5:0.06\,EuO_{1.5}$ 0.7 CO_3^{-2}:4 O:0.7 Na:0.5 P:1 W	4.4 (−1.4)	3.1	O 1s:535.9; Na 1s:1076.4; P 2p:138.5; W 4d:265 & 252.6; W 4f:42.8 & 40.7
$0.44\,WO_3:0.30\,Na_2O:$ $0.15\,P_2O_5:0.10\,EuO_{1.5}$ 0.7 CO_3^{-2}:4 O:0.6 Na:0.3 P:1 W	4.5 (−1.2)	3.1	O 1s:535.9; Na 1s:1076.6; P 2p:138.7; W 4d:265 & 252.8; W 4f:42.8 & 40.7

4 *R.D.Peacock:* Structure and Bonding *22* (1975) 83.
5 *C.K.Jørgensen* and *B.R.Judd:* Mol.Phys. *8* (1964) 281.
6 *R.Reisfeld* and *C.K.Jørgensen:* Lasers and Excited States of Rare Earths, Springer-Verlag, Berlin, in preparation.
7 *C.K.Jørgensen:* Structure and Bonding *24* (1975) 1.
8 *C.K.Jørgensen* and *H.Berthou:* Mat. Fys. Medd. Dan.Vid. Selskab *38* (1972) No.15.
9 *C.K.Jørgensen* and *H.Berthou:* Chem.Phys.Letters *36* (1975) 432.
10 *C.K.Jørgensen:* Chimia *29* (1975) 53.
11 *C.K.Jørgensen:* Adv.Quantum Chem. *8* (1974) 137.
12 *C.K.Jørgensen* and *H.Berthou:* Disc. Faraday Soc. *54* (1973) 269.
13 *H.Berthou* and *C.K.Jørgensen:* Analyt.Chem. *47* (1975) 482.
14 *K.T.Ng* and *D.M.Hercules:* J.Electron Spectr. *7* (1975) 257.
15 *W.E.Morgan* and *J.R.Van Wazer:* J.Phys.Chem. *77* (1973) 964.
16 *W.E.Swartz, K.J.Wayne* and *D.M.Hercules:* Analyt.Chem. *43* (1971) 1884.
17 *G.E.McGuire, G.K.Schweitzer* and *T.A.Carlson:* Inorg. Chem. *12* (1973) 2450.
18 *C.K.Jørgensen* and *H.Berthou:* Chem.Phys.Letters *31* (1975) 416.
19 *R.Reisfeld, H.Mack, A.Eisenberg* and *Y.Eckstein:* J.Electrochem.Soc. *122* (1975) 273.
20 *R.Reisfeld, R.A.Velapoldi* and *L.Boehm:* J.Phys.Chem. *76* (1972) 1293.
21 *M.Faucher* and *P.Caro:* J.Chem.Phys. *63* (1975) 446.

Neutral Carrier Ca^{2+}-Microelectrode *

M.Oehme, M.Kessler** and W.Simon***
Departement of Organic Chemistry, Swiss Federal Institute of Technology, Zürich

Summary

The use of a synthetic electrically neutral ion carrier in Ca^{2+}-selective microelectrodes is described. High ion-selectivities especially in respect to Na^+ and Mg^{2+} as well as a long lifetime of the electrodes open new possibilities for a wide range of intracellular measurements of ion activities.

Certain natural as well as synthetic, neutral, lipophilic organic complexing agents, which selectively complex cations, open new possibilities for the local potentiometric measurement of ion activities [1–3]. Such ion carriers have been used as ion selective components in macroelectrodes for the measurement of Ba^{2+} [2, 4, 5], Ca^{2+} [3, 6], K^+ [3, 7, 8, 9], Na^+ [10], Li^+ [11], and NH_4^+ [12, 13] (see also [2, 3]).

Microelectrodes with tip diameters of about 1 μm may be used for the intracellular measurement of ion activities in living cells [14–16]. Using glass micropipets filled with solutions of classical, electrically charged ion exchangers, the intracellular study of Cl^- [17, 19], K^+ [18, 19] and Ca^{2+} [17, 19] became possible. By incorporating solutions of neutral carriers into such micropipets, the rather poor selectivity of these electrodes may be improved and microelectrodes with ion selectivities suitable for a wide range of intracellular studies may be obtained.

In this paper the use of the neutral carrier N,N′− di (11-ethoxycarbonyl) undecyl-N,N′,4,5-tetramethyl-3,6-dioxaoctane diacid diamide [6, 20] as ion selective component in microelectrodes of high Ca^{2+} selectivity will be discussed.

* Reseived January 21, 1976
** Max-Planck-Institut für Systemphysiologie, Rheinlanddamm 201, D-46 Dortmund
*** Prof.Dr.W.Simon, Laboratorium für Organische Chemie der ETH, Universitätsstr. 16, CH-8006 Zürich

Experimental

Electrode system

Cells of the type
Ag/AgCl, KCl (std.)/1 M CH_3COOLi/sample solution/membrane/0.1 M $CaCl_2$, AgCl; Ag
have been used. The external reference electrode was a double junction half cell Philips Type R 44/2/SD 1.

Microelectrodes

Micropipets were drawn from double barreled (see [21]) pyrex glass tubing (W.Krannich KG, D-34 Göttingen, Germany). The tip diameter of these micropipets was about 2 μm. The two channels of these micropipets were filled with 0.1 M $CaCl_2$ and 0.1 M KCl solutions respectively. The large bore ends were closed by introducing Teflon (Du Pont) tubes (outer diameter 0.5 mm) and sealing them with dental wax (Deiberit 502, L.Böhme KG, D-3423 Bad Sachsa/Harz, Germany). After placing the tip into a solution of 5% w/w dichloro-dimethyl-silane in CCl_4 and simultaneously applying air pressure on the KCl channel as well as intermittant air pressure and vacuum on the $CaCl_2$ channel the inner walls of the latter are hydrophobised.

A solution of 10% w/w of the neutral carrier and 1% w/w of sodium tetraphenylborate (NaTPB) in o-nitro-phenyl-octyl-ether (o-NPOE) was introduced by applying vacuum on the $CaCl_2$ channel up to a height of about 200 μm.

After remowing the Teflon (Du Pont) tubes, chlorinated silver wires were introduced into both channels and the upper ends sealed with dental wax. In the experiments described below the reference channel (KCl) was not used.

EMF-measurements

The EMF measurements were performed at 20 °C using a varactor bridge operational amplifier (Burr Brown 3431 J) having an input impedance of $10^{14}\ \Omega$ and an input capacitance of 2 pF in common mode operation (see also [18]). With a source resistance of $10^{10}\Omega$ the response time (10 to 90%) amounts to 0.6 sec. The amplifier output is connected to a digital voltmeter. The electrode assembly as well as the other high impedance components were located in a faraday cage.

Results and Discussion

The response of the electrode assembly is linear in the range of $1 \cdot 10^{-1}$ to at least $1 \cdot 10^{-5}$M $CaCl_2$ (see fig. 1) giving a slope of 31.0 ± 0.4 mV (theoretical: 29.1 mV) for the linear regression of the calcium ion activity. In

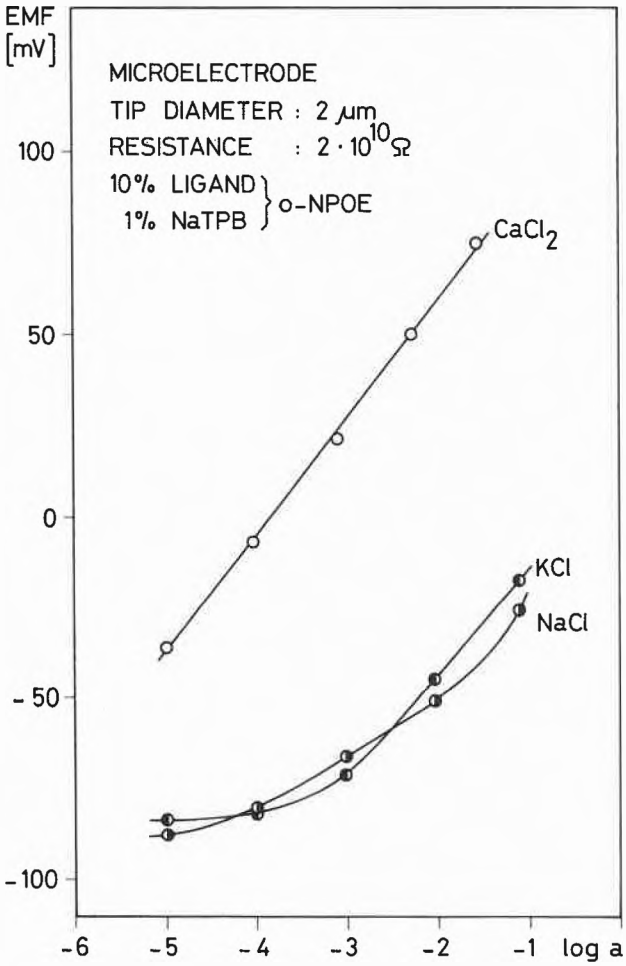


Fig. 1: EMF Response of the Ca^{2+} Microelectrode Cell Assembly to Aqueous Solutions of the Chlorides of Ca^{2+}, Na^+ and K^+. Activities a were calculated by using the activity coefficients suggested by Bates [22] (see [6])

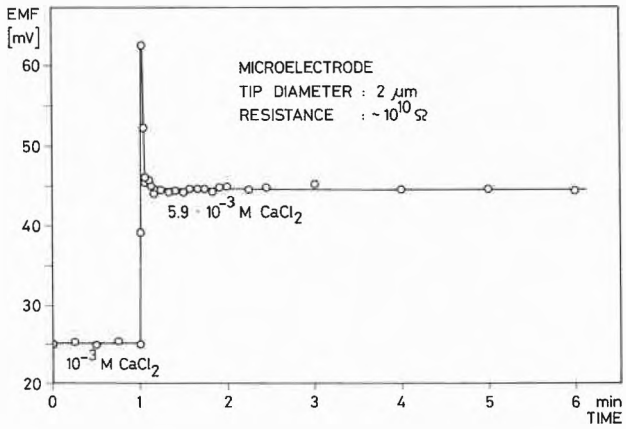


Fig. 2: Response Time of a Ca^{2+} Microelectrode Obtained by Changing the Concentration through Injecting a $CaCl_2$ Solution

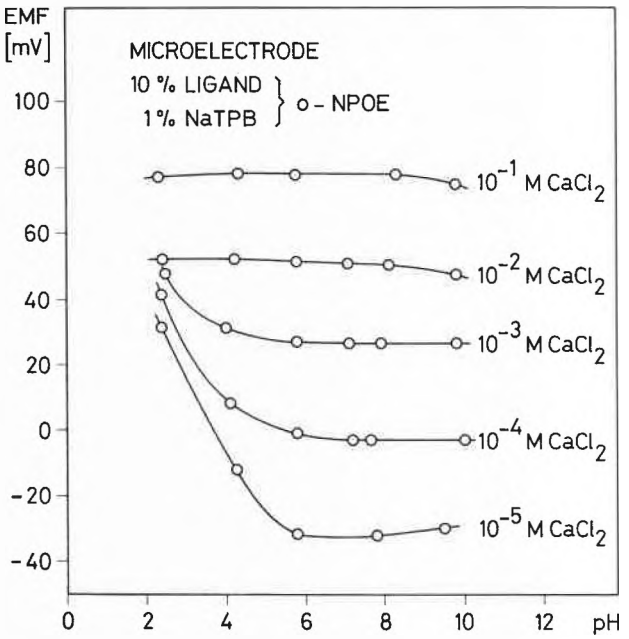


Fig. 3: Dependence of the EMF of a Ca^{2+} Microelectrode Cell Assembly on the pH of the Sample Solution for Different $CaCl_2$ concentrations. The pH was adjusted by adding 0.1 M HCl and 0.1 M NaOH solutions respectively

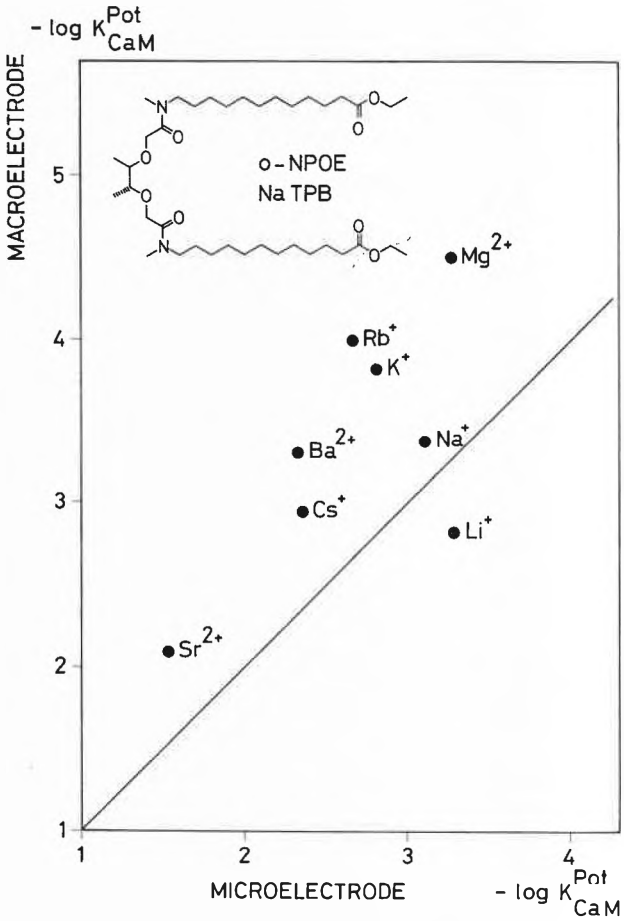


Fig. 4: Comparison of the Selectivity Coefficients Obtained by the Separate Solution Technique for a Ca^{2+}-Macro- and Microelectrode Using 0.1 M Solutions of the Chlorides (see also [6])

10^{-1}M solutions of $CaCl_2$ the EMF is constant within ± 0.3 mV (standard deviation) over periods of 12 hours. This corresponds to the noise of the electronic system. Comparable EMF stabilities were obtained by using undiluted blood serum as sample. An example of the dynamic response of the electrode is given in fig. 2.

In comparison to the rather classical Ca^{2+} selective liquid-membrane electrodes [17, 23, 24] the selectivities of Ca^{2+} relative to Mg^{2+}, H_3O^+, Na^+ and Zn^{2+} [6] are very high (see fig. 1, 3 and 4). A loss in selectivity of the microelectrode was observed when compared with a corresponding macroelectrode using the same ligand in a PVC matrix [6] (see fig. 4).

The neutral carrier microelectrodes have life times of at least one month. In some cases life times of 4 months have been obtained.

Acknowledgment

This work was partly supported by the Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung.

Literature

1 *J. Koryta:* Ion-selective Electrodes, Cambridge University Press, Cambridge, London, New York 1975.
2 *E. Pretsch, D. Ammann* and *W. Simon:* Research/Development *25* (3) (1974) 20.
3 *D. Ammann, R. Bissig, Z. Cimerman, U. Fiedler, M. Güggi, W. E. Morf, M. Oehme, H. Osswald, E. Pretsch* and *W. Simon:* Proceedings of the International Workshop on Ion Selective Electrodes and on Enzyme Electrodes in Biology and in Medicine, Urban & Schwarzenberg, München, Berlin, Wien 1975, in press.
4 *R. J. Levins:* Anal. Chem. *43* (1971) 1045.
5 *R. J. Levins:* Anal. Chem. *44* (1972) 1544.
6 *D. Ammann, M. Güggi, E. Pretsch* and *W. Simon:* Anal. Letters *8* (1975) 709.
7 *L. A. R. Pioda, V. Stanková* and *W. Simon:* Anal. Letters *2* (1969) 665.
8 *J. Petránek* and *O. Ryba:* Anal. Chim. Acta *72*(1974) 375.
9 *M. S. Frant* and *J. W. Ross:* Science *167* (1970) 987.
10 *D. Ammann, E. Pretsch* and *W. Simon:* Anal. Letters *7* (1974) 23.
11 *M. Güggi, U. Fiedler, E. Pretsch* and *W. Simon:* Anal. Letters, *8* (1975) 857.
12 *R. E. Cosgrove, I. H. Krull* and *C. A. Mask,* Anal. Letters *3* (1970) 457.
13 *R. D. Scholer* and *W. Simon:* Chimia *24* (1970) 372.
14 *M. Lavallée, O. F. Schanne* and *N. C. Hebert* (Ed.): Glass Microelectrodes, Wiley, New York, London 1969.
15 *N. C. Hebert* and *R. N. Khuri* (Ed.): Ion Selective Microelectrodes, Dekker, New York, in press.
16 *H. J. Berman* and *N. C. Hebert* (Ed.): Ion Selective Microelectrodes, Plenum Press, New York, London 1974.
17 *F. W. Orme:* in M. Lavallée, O. F. Schanne and N. C. Hebert (Ed.), Glass Microelectrodes, Wiley, New York, London 1969.
18 *J. L. Walker,* Jr.: Anal. Chem. *43* (1971) 89A.
19 *J. L. Walker,* Jr.: in N. C. Hebert and R. N. Khuri [Ed.), Ion Specific Microelectrodes, Dekker, New York, London, in press.
20 *D. Ammann, R. Bissig, M. Güggi, E. Pretsch, W. Simon, I. J. Borowitz* and *L. Weiss:* Helv. Chim. Acta *58* (1975) 1535.
21 *J. S. Coombs, J. C. Eccles* and *P. Fatt:* J. Physiol. *130* (1955) 291.
22 *R. G. Bates:* in R. A. Durst (Ed.) Ion-Selective Electrodes, National Bureau of Standards, Spec. Publ. 314, Washington 1969.
23 *J. W. Ross:* Science *156* (1967) 1378.
24 *J. Ružička, E. H. Hansen* and *J. Ch. Tjell:* Anal. Chim. Acta *67* (1973) 155.