Kurze Mitteilungen

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

Zur Interpretation von antiferromagnetischen Austauschwechselwirkungen in schwach gekoppelten Dimeren: Modellbeispiel H_2*

Summary

It is shown that the success of the one-electron interpretation of the exchange interaction of two ground state hydrogen atoms within the simple LCAO-model results from an almost perfect cancellation of two quite sizeable interelectronic repulsion terms. It is not known at the present time whether the full LCAO-treatment (with interelectronic repulsion terms included) is equally valid for other weakly coupled dimers and—if so—whether the same type of cancellation of interelectronic repulsion terms occurs in general.

1. Austauschwechselwirkungen

Von «Austausch» *(exchange)*-Wechselwirkungen zwischen paramagnetischen Atomen oder Atomgruppen innerhalb eines molekularen Gesamtsystems spricht man dann, wenn deren ungepaarte Elektronen auf eine relativ lockere Weise miteinander gekoppelt sind und so zu mehreren energetisch nur leicht verschiedenen, bei Zimmertemperatur signifikant bevölkerten Spinzuständen Anlaß geben. Obschon solche Austauschwechselwirkungen auf einem Wechselspiel zwischen kinetischer Energie und interelektronischer Repulsion beruhen, kann man sie, wie Heisenberg[1], Dirac[2] und Van Vleck[3] schon während der Entstehungszeit der Quantentheorie gezeigt haben, auf Grund des Pauli-Prinzips wie eine effektive magnetische Wechselwirkung zwischen Elektronenspins formulieren. So lautet der Heisenberg-Operator für den einfachsten Spezialfall von nur zwei gekoppelten Atomen mit totalen Elektronenspins $\vec{S}_A$ und $\vec{S}_B$

$$H_{\text{eff}} = -2\,«J»\left(\vec{S}_A \cdot \vec{S}_B\right), \tag{1}$$

wobei man im Falle von positiven Werten des Austauschparameters «J» von ferromagnetischer, im Falle von negativen Werten von antiferromagnetischer Kopplung zwischen A und B spricht.

Die Energieeigenwerte von H_{eff} befolgen die Intervallregel

$$\Delta E_S = E(S) - E(S-1) = -2\,«J»\,S. \tag{2}$$

Sowohl im Falle von unendlichen Verbänden als auch im Falle von isolierten kleinen Clustern (z. B. polynu-

* Vorläufige Mitteilung. Vorgetragen an der Herbstversammlung der Schweizerischen Chemischen Gesellschaft am 3. Oktober 1975 in Aarau. Ein ausführlicherer Text wird in *Theoretica Chimica Acta* publiziert.

klearen Übergangsmetallkomplexen) ist ein äußerst reichhaltiges Tatsachenmaterial, zumeist von magnetischen und optischen Studien stammend, vorhanden[4]. Trotz enormen Fortschritten der numerischen Quantenchemie sind jedoch quantitative *theoretische* Berechnungen von «J» selbst für die einfachsten bekannten gekoppelten Dimeren bis heute nicht durchführbar geworden; oft ist nicht einmal eine Voraussage des Vorzeichens möglich! Dieses Problem ist von den Physikern nach vieljährigen intensiven theoretischen Studien als zu komplex befunden[5] und heute weitgehend verlassen worden; um so mehr überrascht der sich in neuester Zeit plötzlich ausbreitende Optimismus der theoretischen Chemiker, welche «J» mit Hilfe von einfachen semiempirischen Einelektronenmodellen zu interpretieren und vorauszusagen versuchen[6].

Diese Einelektronennäherung geht auf die LCAO-Behandlung des einfachen Modellfalls von zwei nur schwach überlappenden, antiferromagnetisch gekoppelten H-Atomen zurück.

2. Modellbeispiel H_2

Die Singlett-Triplett-Energiedifferenz von H_2 (Abb. 1) wird durch die LCAO-Näherung[7]

$$\Delta E = E_T - E_S = -2\,«J» = -\Delta J_1 + \frac{(\Delta h + \Delta J_2)^2}{2K_{ug}} \qquad (3)$$

im relevanten Bereich ausgezeichnet wiedergegeben, wie der Vergleich mit der aufwendigen Rechnung von Kolos und Wolniewicz[8] zeigt. In Gl. (3), die den einfachsten Spezialfall ($S_A = S_B = ½$) der Intervallregel [Gl. (2)] darstellt, sind alle Größen positiv; Δh ist die Einelektronenenergiedifferenz $h(\sigma_u) - h(\sigma_g)$, ΔJ_1, ΔJ_2 und K_{ug} sind interelektronische Repulsionsterme. Die vorgeschlagene Näherung[6] besteht nun darin, die dem Chemiker seit jeher unsympathischen Zweielektronenterme (in diesem Fall ΔJ_1 und ΔJ_2) wegzulassen und auf die Dominanz des theoretisch besser zugänglichen Einelektronenterms $(\Delta h)^2/2K_{ug}$ zu hoffen. Um diese Hypothese zu prüfen, haben wir die einzelnen Terme für den relevanten Bereich (5 Bohr $< R_{H-H} <$ 10 Bohr), in welchen die Singlett-Triplett-Aufspaltung $\Delta E = E_T - E_S = -2\,«J»$ von etwa 1 cal auf etwa 1 kcal aussteigt, numerisch berechnet (siehe Tabelle).

Die Resultate zeigen, daß die Zweielektronenterme ΔJ_1 und ΔJ_2 im betrachteten R-Bereich *nicht* vernachlässigbar klein sind und daß ihre *relative* Bedeutung gegenüber dem Einelektronenterm mit wachsendem R zunimmt.

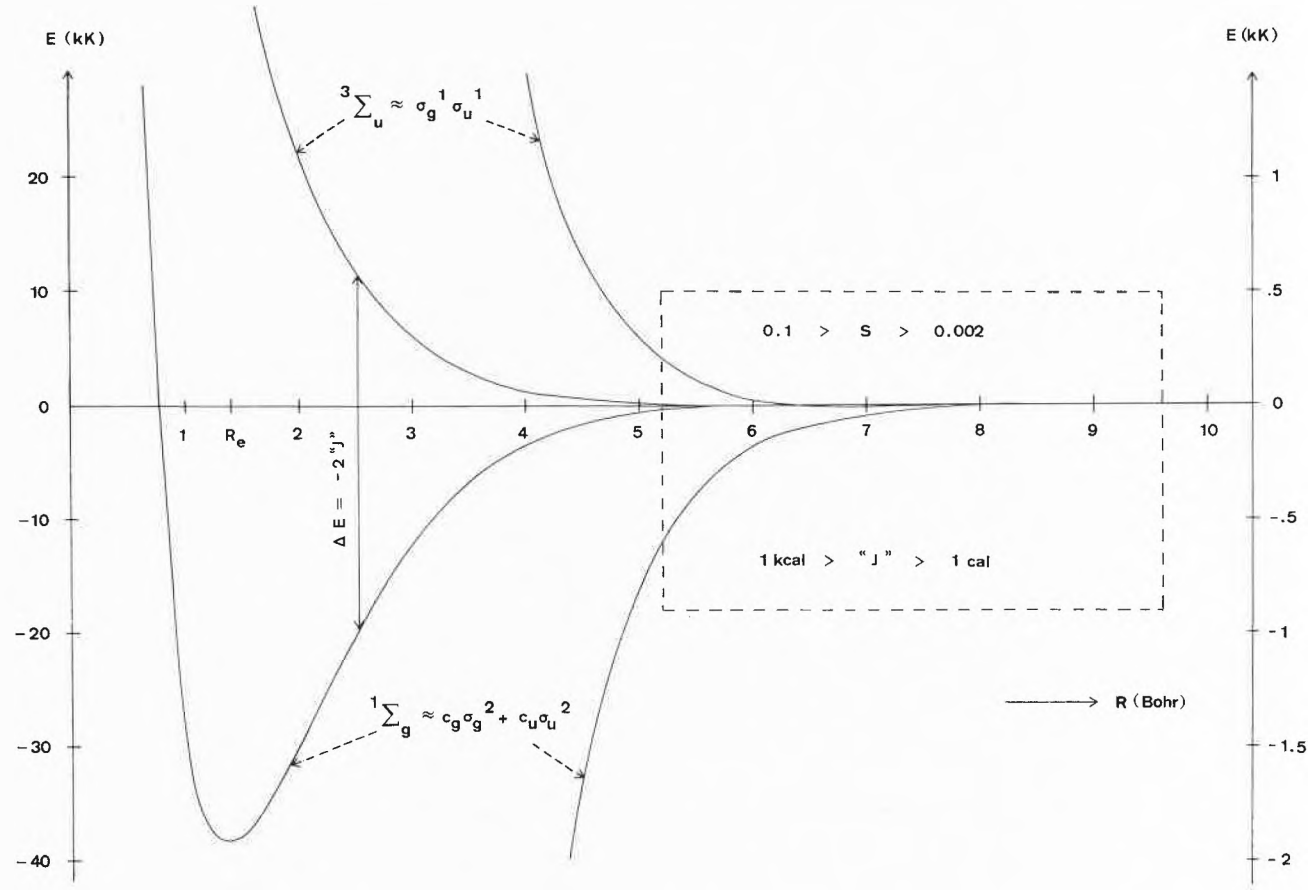

Abb. 1. Potentialkurven für die untersten $^1\sum_g$- und $^3\sum_u$-Zustände von H_2 in der nichtrelativistischen Born-Oppenheimer-Näherung nach Kolos und Wolniewicz (Ref.[8]), dargestellt mit zwei verschiedenen Energieskalen. Die halbe Singlett-Triplett-Energiedifferenz entspricht dem Heisenberg-Austauschparameter «J». Der Bereich der «schwachen Austauschkopplung» (1 kcal/Mol > «J» > 1 cal/Mol) ist eingerahmt. In der LCAO-Näherung wird σ_g durch die bindende, σ_u durch die antibindende Linearkombination der beiden Wasserstoff-1s-Orbitale beschrieben

R_{H-H} (Bohr)	S_{H-H} $<1s/1s>$	ΔJ_1 (cm^{-1})	ΔJ_2 (cm^{-1})	Δh (cm^{-1})	K_{ug} (kcm^{-1})	ΔE Gl. (3) (cm^{-1})	$\Delta h^2/2K_{ug}$ (cm^{-1})
5	0,097	362,8	2190	9356	47,1	1052	928,9
6	0,047	110,1	1470	4180	50,4	206,5	173,3
7	0,022	29,21	871	1812	52,9	38,74	31,00
8	0,010	7,019	473	767	54,9	6,99	5,360
9	0,005	1,565	242	319	56,4	1,220	0,902
10	0,002	0,330	118	131	57,6	0,207	0,149

[Das Weglassen von ΔJ_2 in Gl. (3) führt zu «J»-Überschätzungen von mehreren 100%, während die Vernachlässigung von ΔJ_1 für $R \geq 8$ gar ein falsches Vorzeichen verursacht.] Der Vergleich der beiden letzten Kolonnen zeigt jedoch, daß die Einelektronnäherung[6], $\Delta h^2/2K_{ug}$, für H_2 dennoch praktisch über den ganzen Bereich vernünftige Werte liefert (Fehler -16% bis -28%), weil sich die Effekte von ΔJ_1 und ΔJ_2 *fast exakt kompensieren.*

3. Schlußfolgerung

Ganz abgesehen von der Frage, ob das System H_2 ein adäquates Modell für Austauschwechselwirkungen in polynuklearen Metallkomplexen abgeben kann, muß man nach den hier diskutierten Resultaten bezweifeln, daß sich die interelektronischen Repulsionsterme in den experimentell untersuchten Systemen so perfekt kompensieren wie für H_2 im Rahmen der LCAO-Näherung. Weitere Modellrechnungen für zweiatomige Systeme mit ungepaarten *p*-, *d*- oder *f*-Elektronen wären in diesem Zusammenhang von einigem Interesse.

Ich möchte Herrn E. Gamp für die Durchführung der numerischen Rechnungen und Herrn Dr. H.-B. Bürgi für wertvolle Diskussionen herzlich danken.

1 W. Heisenberg. *Z. Physik 38* (1926) 411, *49* (1928) 619.
2 P. A. M. Dirac, *Proc. Roy. Soc. (London) Ser. A 112* (1926) 611, *123* (1929) 714.
3 J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities*, Oxford University Press, London 1932.
4 Siehe z. B. die neueren Übersichtsartikel von R. L. Martin in *New Pathways in Inorganic Chemistry*, Cambridge University Press, 1968, Kapitel 9, und A. P. Ginsberg, *Inorg. Chem. Acta Rev. 5* (1971) 45.
5 Siehe z. B. C. Herring, *Rev. Mod. Physics 34* (1962) 631 und in *Magnetism* (G. Rado und H. Suhl, Ed.), Academic Press, New York 1966, Vol. II B, S. 1.
6 P. J. Hay, J. C. Thibeault und R. Hoffmann, *J. Amer. Chem. Soc. 97* (1975) 4884 und dort aufgeführte Zitate.
7 J. C. Slater, *Physic. Rev. 35* (1930) 509.
8 W. Kolos und L. Wolniewicz, *J. Chem. Physics 43* (1965) 2429.

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Rearrangement of maleuric acid*

Summary

Maleuric acid I cyclises in concentrated alkali hydroxyde to 5-carboxymethylhydantoin II which is further hydrolysed to ureidosuccinic acid III.

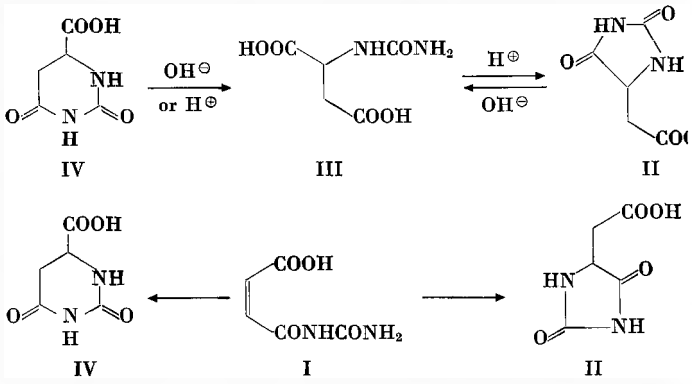
5,6-Dihydropyrimidines constitute an important class of compounds as they are intermediates in the biosynthesis and degradation of the pyrimidines[1, 2]. Orotic acid is reversibly reduced to dihydroorotic acid IV (DHOA)[3] which is reversibly hydrolysed to ureidosuccinic acid III. Ureidosuccinic acid can therefore be considered a key intermediate in the biosynthesis of pyrimidines.

Preparation of III has been accomplished from asparagine[4] as well as from aspartic acid[5, 6].

Optically active ureidosuccinic acid has been obtained from optically active aspartic acid by treatment with potassium cyanate[7]. Ureidosuccinic acid has been proposed as an intermediate in the transformation of DHOA to 5-carboxymethyl-hydantoin II with acid[8].

* Received October 6, 1975.

The facile hydrolysis of DHOA with alkali to III[9, 10] has been observed and kinetically investigated[11]. On the other hand 5-carboxymethylhydantoin is hydrolysed to ureidosuccinic acid in very good yield with base (see experimental) and also enzymatically[12].



Recently 5-carboxymethylhydantoin has been found to possess antitumor activity[13]. III is useful in the preven-

tion of ammonia poisoning[14] and its salts posess neurosedative activity[15].

With this background we attempted the preparation of II or IV from maleuric acid I.

From the literature we learned that I is hydrolysed very easily with dilute aqueous alkali[9,16] and with up to 20% KOH[17]. However 20% methanolic KOH transforms maleuric acid I to 5-carboxymethylhydantoin II in 43% yield[17] and converts fumaruric acid in 6% yield to II. Sodium ethoxide converts I and fumaruric acid to II in 50% and 12% yield respectively[17].

We have now found that in the reaction of I with sodium hydroxide the amount of hydrolysis diminishes and the amount of cyclisation to II increases with increasing concentration of NaOH in water. At 30% aqueous NaOH the formation of II is already considerable and at 50% concentration I can be transformed to II in yields up to 85%. The yield depends also on the quality of I. The mentioned yields were obtained with a recrystallised sample of I. With crude or washed material one got variable conversion of I to II.

However such drastic changes in the course of reaction was not observed with fumaruric acid. In this case hydrolysis was always the main reaction. Under the alkaline conditions employed II may be hydrolysed to ureidosuccinic acid III but reaction conditions have been worked out in order to isolate pure II from the reaction mixture. Esterification of II with alcohol and acid proceeds very smoothly in practically quantitative yield.

Experimental

The m.p. were taken on a Büchi (Dr. Totolli) apparatus and are uncorrected. IR-spectrum: Perkin Elmer 621; NMR-spectrum: Perkin Elmer R 12.

Maleuric acid I

This compound was prepared according to the method of Tawney and collaborators[18].

It was recrystallised from water at a temperature not above 60°C (to prevent partial isomerisation). m.p. 160 to 161°C.

5-Carboxymethylhydantoin II

To a cold (10 to 15°C) solution of 32 g of 50% NaOH (0,4 mole) is added with stirring a total of 15,8 g (0,1 mole) of maleuric acid after 4 hours stirring at 15°C the reaction mixture is diluted with 35 g water and is acidified to *p*H 2.0 with about 110 g of 25% H_2SO_4. After standing at least 4 hours at room temperature the precipitate is filtered, washed with a little cold water and dried at 60°C under reduced pressure to obtain 11,4 g (72,2%) of pure white crystals; m.p. 219 to 220°C. A further 15 to 17% yield of material remains in solution.

Lit. [6], m.p. 214 to 215°C.

Ureidosuccinic acid III

a) from II. A solution of 15,8 g (0,1 mole) of II in 75 g of 20% NaOH is heated 2 hours at 70°C. After cooling it is acidified to *p*H 2,0 with concentrated HCl and allowed to stand overnight. The precipitate is collected, washed with cold water and dried to obtain 16,2 g (92% yield) of pure product m.p. 188 to 190°C; Lit. [9] 171 to 172°C, [6] 178 to 180°C. The product is chromatographically pure: Cellulose F (Merck) in the system Isopropanol/pyridine/water/acetic acid (40/40/20/5), R_f 0,35, (II has R_f 0,53). IR-spectrum (KBr), 3482, 3355, 3242 cm^{-1} (NH and OH), 1730, 1700, 1635 cm^{-1} (C=O), NMR-spectrum (DMSO-d_6); 2,66 ppm, d, (J = 5,3 Hz) (CH_2—CH); 4,42 ppm, a doublet (J = 8,2 Hz) split into triplets (J = 5,3 Hz) (CH_2—CH—NH); 5,77 ppm, broad, 2H (NH_2); 6,36 ppm, d (J = 8,2) 1H (NH—CH); 10 to 14 ppm, very broad band, 2H (COOH). The NMR spectrum in NaOD shows an ABX pattern with J_{AB} = 18,5, J_{AX} = 12,2 and J_{BX} = 3,9 Hz.

b) direct from I. A total of 15,8 g (0,1 mole) I was added gradually to a solution of 32 g of 50% NaOH at 5 to 10°C. After a further 4 hours the reaction mixture was diluted with 100 g water and heated 2 hours at 80°C. After cooling (5°C) and acidifying with concentrated HCl to *p*H 1,5, the precipitate is collected, washed with cold (0 to 5°C) water and dried to obtain 15,0 g (85% yield) of ureidosuccinic acid m.p. 187 to 188°C.

About a further 0,5 g remains in solution.

5-(carbethoxymethyl)-hydantoin

A suspension of 63,5 g (0,4 mole) II in 400 ml absolute ethanol containing 3,5 g of dry HCl is heated under reflux for 2 h when all the solid passes into solution. Benzene (200 ml) is added and the solvents are slowly distilled until the head temperature reaches 78°C. The remaining solvent is evaporated under reduced pressure to obtain 5-(carbethoxymethyl)-hydantoin in practically quantitative yield. It is recrystallised from water in 75% yield. m.p. 93 to 94°C, Lit. [19] m.p. 94 to 95°C.

References

1 P. Reichard, *Advan. Enzymol. 21* (1959) 263.
2 G. W. Crosbie, *The Nucleic Acids*, Vol. III, Academic Press, New York (N.Y.) 1960, 323.
3 I. Lieberman and A. Kornberg, *Biochim. et Biophys. Acta 12* (1953) 223.
4 E. Grimeau, *Ann. Chim. Physique* (5) *11* (1887) 402.
5 S. Gabriel, *Ann. Chim. 348* (1906) 50.
6 J. F. Nyc and H. K. Mitchell, *J. Amer. Chem. Soc. 69* (1947) 1382.
7 H. Miyazaki, Y. Minaki and Y. Yoshimura, *Chem. Pharm. Bull. (Tokyo) 15* (1967) 10, 1604.
8 C. S. Miller, J. T. Gordon and E. L. Engelhardt, *J. Amer. Chem. Soc. 75* (1953) 6086.
9 R. D. Batt, J. K. Martin, J. McT. Ploeser and J. Murray, *J. Amer. Chem. Soc. 76* (1954) 3663.
10 C. Janion and D. Shugar, *Acta Biochim. Polon. 7* (1960) 309.
11 E. G. Sander, *J. Amer. Chem. Soc. 91* (1969) 3629.
12 L. H. Smith Jr., F. A. Baker, M. Sullivan and L. J. Kunz, *Nature 184* (1959) Suppl. No. 17, 1314.
13 M. Miura, M. Hirano, K. Kakizawa, A. Morita, T. Uetani and K. Yamada, Progr. Antimicrob., Anticancer Chemother., 6th Proc. Int. Congr. Chemother., (1969); 2, 170–4 = *Chem. Abstr. 74* (1971) 86202 l.
14 a) L. Chiosa, V. Niculescu, C. Bonciocat and C. Stancu, *Biochem. Pharmacol. 14* (1965) 1635. b) D. Cittadini, D. de Christofaro, C. Balestrieri and F. Cimino, *Biochem. Pharmacol. 15* (1966) 992.
15 F. Clemence, Fr. Pat. 6376 (1968); *Chem. Abstr. 74* (1971) 76655 r.
16 M. S. Dudkin, *Zhur. Obshchei Khim. 24* 1599 (1954) = *Chem. Abstr. 49* (1955) 12372 c.
17 Z. Jerzmanowska-Sienkiewiczowa, *Roczniki Chem. 15* (1935) 202.
18 P. O. Tawney, R. H. Snyder, C. E. Bryan, R. P. Conger, F. S. Dovell, R. T. Kelly and C. H. Stiteler, *J. Org. Chem. 25* (1960) 56.
19 H. K. Mitchell and J. F. Nyc, *J. Amer. Chem. Soc. 69* (1947) 674.

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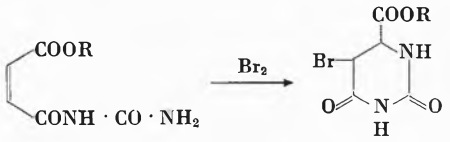
The preparation and hydrolysis of 5-bromo-5,6-dihydro-orotic acid *

Summary

The action of bromine on maleuric acid I gave 5-bromo-5,6-dihydro-orotic acid II. The structure of II was established by its various spectra, its elemental analysis and its chemical reactions. The reaction of II with sodium hydroxide was investigated.

Orotic acid III has been the subject of several investigations of both chemical and biological nature[1]. Several methods of preparation of III can be found in the literature. A reinvestigation of one of these methods[2] led us to the discovery of a very simple method for the preparation of 5-bromo-5,6-dihydro-orotic acid II. In fact simple treatment of maleuric acid with bromine in water yielded II. In methanol, I and bromine gave II as the soluble hydrobromide which could be precipitated by the addition of an equivalent of base.

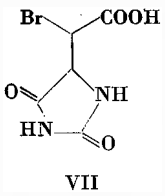
In a similar manner methylmaleurate IV reacts with bromine in aqueous suspension to give methyl 5-bromo-5,6-dihydro-orotate V.



(I, R = H; IV, R = CH_3) (II, R = H; V, R = CH_3)

It is very likely that the β-bromomaleuric acid described by Cavallito and Smith[3] is in fact II. The structure of II is deduced from its chemical and physical properties. This white powder melts with decomposition at 149 to 150 °C and elementary analysis gives an empirical formula of $C_5H_5BrN_2O_4$. The NMR spectrum of II in DMSO-d_6 shows an AB system centered at 5,12 ppm with $\Delta\nu_{AB}$ = 16,7 Hz and J_{AB} = 2,6 Hz. One also sees a small sharp singlet at 5,68 ppm but this is shown to be due to 3-hydroxy-maleuric acid VI—a reaction product of II with the water present in the DMSO (retaking the spectrum after 2 hours shows mainly the singlet at 5,68 ppm and practically no quartet at 5,12 ppm). The NMR-spectrum of the methylester V shows the AB quartet at 5,20 ppm (J_{AB} = 3,0 Hz) and is stable in DMSO. From the value of the coupling constant the AB protons should be vicinal[4, 5].

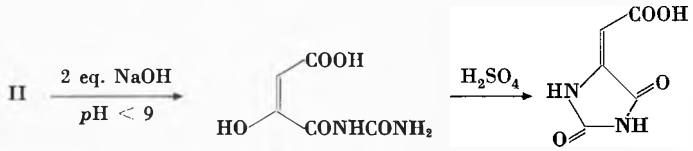
That II possesses a dihydrouracil ring and not the hydantoin ring structure VII is best shown by the IR-spectrum. The high frequency carbonyl band of hydantoins[6] absorb at about 1780 cm^{-1} whereas the highest frequency carbonyl band of dihydrouracils[7] absorb at about 1730 cm^{-1}. Since II absorbs at 1712 cm^{-1} it is clear it possesses a dihydrouracil ring.



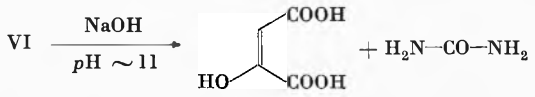
VII

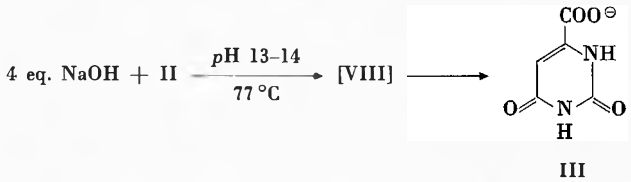
In nitric acid solution II does not precipitate AgBr from $AgNO_3$. Of course when II is first treated with excess base and then acidified, one equivalent of AgBr is precipitated. Since in addition II does not liberate iodine from hydriodic acid one can deduce that II is not a salt, does not contain a nitrogen-bromine bond but must have an easily hydrolysable C—Br bond.

The reaction of II with NaOH gives several products according to the reaction conditions. Addition of one equivalent of alkali to II gives the salt which is hydrolysed slowly even at 50 °C to give 3-hydroxymaleuric acid VI. Addition of a second equivalent of NaOH under 10 °C so that the *p*H remains below 9,0 gives VI in 70 % yield after 80 minutes at 5 to 8 °C. Treatment of VI with 50 % H_2SO_4 for 20 minutes at room temperature gives 5-(carboxymethylidene)-hydantoin VIII in very good yield.



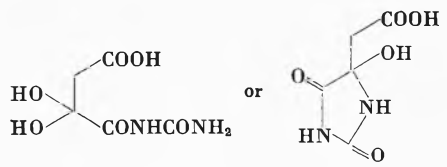
VI VIII





III

This shows that the position of the hydroxy group in VI was correctly assigned. The inverse addition i.e. adding II to two equivalents of NaOH gives only very little VI. The main product stays in solution. It is believed that IX or X is formed



IX X

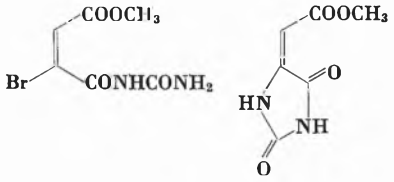
* Received October 6, 1975.

since making the solution very acidic with a large excess of concentrated H_2SO_4 gives VIII in good yield.

Addition of a third equivalent of alkali to a suspension of II in water gives oxalacetic acid and urea via hydrolysis of VI. Treatment of the reaction mixture with a arge excess of concentrated H_2SO_4 gives very little VIII. The same result is obtained by the addition of 4 equivalents of NaOH to II. However by inverse addition i.e. by adding II to 4 equivalents of NaOH one obtains water soluble products which are not oxalacetic acid and urea but are probably either IX or X. Attempts to isolate the product by evaporation of the solvent below 40°C gives 5-(carboxymethylidene)-hydantoin VIII in good yield. Finally addition of II to 4 equivalents of sodium (or potassium) hydroxide and heating 3 hours a 77°C gives orotic acid III *via* VIII in 72% yield. Addition of 4 equivalents of alkali to II and heating 3 hours at 75°C gives only low yields of orotic acid[2] on account of the rapid hydrolysis at about *p*H 11 to oxalacetic acid and urea.

Treating the methylester V with one equivalent of NaOH below 20°C gives methyl 3-bromomaleurate XI in moderate yield. Adding V to 3 equivalents NaOH at 20°C gives a mixture of XI, VIII and 5-(carbomethoxymethylidene)-hydantoin XII. However adding V to hot NaOH (75°C) and heating for 3 hours gives orotic acid in 73% yield.

II dissolves in concentrated hydrochloric acid (or 75% H_2SO_4) but it reprecipitates again within one minute as the hydrochloride (or sulfate). II can be recovered by treatment with an equivalent of base. The hydrochloride is very soluble in methanol but it does not esterify.



XI XII

Experimental part

The m.p. were taken on a Büchi (Dr.Totolli) apparatus and are uncorrected. IR-spectrum: Perkin-Elmer 621; UV-spectrum: Pye Unicam SP 1700; NMR-spectrum: Perkin-Elmer R 12.

5-bromo-5,6-dihydro-orotic acid II

To a suspension of 15,8 g of maleuric acid[8] in 100 ml H_2O was added, over a period of 20 minutes at 15 to 20°C, 16,0 g of bromine. The reaction mixture was stirred for a further 9 hours at 15 to 20°C. It was then filtered, washed with water and dried at 55°C under vacuum. Yield: 20,2 g (85%).

mp 149 to 150°C (dec.). IR-spectrum (KBr) 3390, 3260 cm^{-1} (NH and/or OH). 2940, 2955 cm^{-1} (C—H); 1712, 1660 cm^{-1} (C=O). NMR-spectrum (DMSO-d_6): 4,98 ppm doublet, J = 2,6 Hz, 1 H (CH); 5,26 ppm, doublet, J = 2,6 Hz, (CH); 8,5 to 11 ppm broad band, 3 H (COOH and NH [or OH]). UV-spectrum (H_2O); λ_{max} 217 nm (ε = 21,600). $C_5H_5BrN_2O_4$ (237,0). Calculated C 25,34, H 2,13, N 11,82, Br 33,71%; found C 25,21, H 2,34, N 10,78, Br 33,8%.

Methyl 5-bromo-5,6-dihydro-orotate V

To a suspension of 68,8 g methyl maleurate[8,9] in 600 ml water is added 64 g of bromine in 1 hour at 15°C. After stirring for a further 8 hours at this temperature the product is filtered and washed with a little water. Yield: 82,6 g (82%). mp 144 to 145°C. IR-spectrum (KBr) 3345 cm^{-1} (NH), 1733 cm^{-1} (ester —C=O), 1668 cm^{-1} (amid —C=O). NMR-spectrum (DMSO-d_6); 3,8 ppm, singlet, 3 H, (CH_3); 5,20 ppm, AB quartet ($\Delta\nu$ = 8,5 Hz, J_{AB} = 3,0 Hz), 2 H (CH—CH); 8,5 to 9,3, broad, 2 H (NH). UV-spectrum (CH_3OH): λ_{max} 219 nm (ε = 18,900), λ_{max} 248 nm (shoulder ε = 5900).

$C_6H_7BrN_2O_4$ (251) calculated Br 31,8%; found 32,0%.

3-Hydroxy-maleuric acid VI

To a suspension of 23,7 g II in 30 ml of water is added at 5 to 10°C under vigourous stirring a total of 20,0 g of 40% sodium hydroxide over a period of 2 hours. The *p*H of the reaction mixture is about 5 during the first half of the addition of alkali (10 to 15 minutes) and must be kept under *p*H 9 for the second half (105 to 110 minutes). After a further 4 hours at 5°C the reaction mixture is acidified with 10,3 g of concentrated hydrochloric acid. The white product is filtered, washed with a little water and dried at 55°C under vacuum. Yield: 12,4 g (70%). The purification consists in dissolving in a little dimethylsulfoxide, filtering and precipitating by the addition of water.

mp > 360°C (dec. darkens at 280 to 300°C). IR-spectrum (KBr): 3570 cm^{-1} (OH); 3410, 3220 cm^{-1} (NH); 3065, 3010 cm^{-1} (CH); 1750, 1710, 1690, 1638 cm^{-1} (CO). NMR-spectrum (DMSO-d_6): 5,74 ppm, sharp singlet, 1 H (C=C⁄H); 4 to 10 ppm, very broad band, 4 H (unassigned); 9,4 ppm broad peak, 1 H (unassigned). UV-spectrum (H_2O) λ_{max} 250 nm (ε = 22,800).

$C_5H_6N_2O_5$ (174,1) calculated C 34,5, H 3,47, N 16,09%; found C 34,4, H 3,44, N 15,5, Br 0,05%.

5-(Carboxymethylidene)-hydantoin VIII

As above, 20 g of 40% NaOH was added slowly (*p*H < 9) to a suspension of 23,7 g of II in 20 ml water. After 4 hours at 5°C the reaction mixture is acidified slowly (temp. 20 to 25°C) with 50 g of concentrated sulfuric acid and stirred for 30 minutes. The product is filtered, washed with water and dried under vacuum at 55°C. Yield: 11,7 g (75%). m.p. 360°C. It has properties identical to those described for VIII prepared by other methods[10–12]. IR-spectrum (KBr): 3260, 3200 cm^{-1} (NH), 3070 cm^{-1} (CH), 1787, 1742, 1729, 1696, 1682, 1655 cm^{-1} (C=O). NMR-spectrum (DMSO-d_6): 5,50 ppm, singlet, 1 H (CH); 10,4 ppm and 11,5 ppm both broad peaks superimposed on a very broad band at 9,5 to 13,5 ppm, total 3 H (2 NH and COOH).

Orotic acid

A solution of 20,0 g NaOH in 150 g water is heated to 77°C and 23,7 g of II is added over 20 minutes. After a further 3 hours at 77°C it is acidified with 63 g of concentrated HCl and stirred 1 hour. It is filtered, washed with water and dried at 125°C in vacuum to obtain 10,9 g (72,6%) of pure anhydrous orotic acid.

mp. 356 to 357°C (dec.). IR-spectrum (KBr): 1728, 1712, 1655, 1615 cm^{-1} (C=O). NMR-spectrum (DMSO-d_6): 6,10 ppm singlet 1 H (CH), 10,83 and 11,37 ppm, both broad peaks superimposed on a broad band at 10 to 13 ppm, total 3 H (2 NH and COOH). The UV-spectrum corresponds to that given in the literature[11].

References

1 D.J.Brown, *The Pyrimidines*, Vol. XVI, "The Chemistry of Heterocyclic Compounds" (A.Weissberger, Ed.), Intersience, New York (N.Y.) 1962, p. 422. Supplement I (1970), p. 320.

2 S.I.Zav'Yalov, I.A.Mikhailopulo and V.I.Gunar, *Izv. Akad. Nauk SSSR, Ser. Khim. 10* (1965) 1887 = *Chem. Abstr. 64* (1966) 2084b.

3 C.J.Cavallito and C.S.Smith, *J. Amer. Chem. Soc. 63* (1941) 995.

4 M.Chabre, D.Gagnaire and C.Nofre, *Bull. Soc. Chim. France 1966*, 108.

5 P. Rouillier, J. Delmai and C. Nofre, *Bull. Soc. Chim. France 1966*, 3515.
6 W. A. Seth Paul and P. J. A. Demoen, *Bull. Soc. Chim. Belg. 75* (1966) 524.
7 C. Nofre, M. Murat and A. Cier, *Bull. Soc. Chim. France 1965*, 1749.
8 P. O. Tawney, R. H. Snyder, C. E. Bryan, R. P. Conger, F. S. Dovell, R. T. Kelly and C. H. Stiteler, *J. Org. Chem. 25* (1960) 56.
9 P. O. Tawney; U. S. Pat. 2.794.012 (1957); *Chem. Abstr. 52* (1958) 2059 e.
10 S. Gabriel, *Liebigs Ann. 348* (1906) 50.
11 H. K. Mitchell and J. F. Nyc, *J. Amer. Chem. Soc. 69* (1947) 674.
12 J. F. Nyc and H. K. Mitchell, *J. Amer. Chem. Soc. 69* (1947) 1382.

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Beitrag zur geschichtlichen Entwicklung des Sauerstoffaufblas-Stahlerzeugungs-Verfahrens*

Summary

The present paper deals with up to now unpublished research work, which had been carried out at the "Eisenhüttenmännische Institut" of the Institute of Technology at Berlin-Charlottenburg (head of Institute: Prof. Dr. Robert Durrer) in the years 1940–43 and which had led to the basic concept of the oxygen converter process as well as its general working parameters on a laboratory scale.

Pig iron melts, which had been melted down in a laboratory type induction furnace, were oxidized with technically pure oxygen either in the furnace itself or in a small converter by using a vertically water-cooled copper lance in short times (6 to 10 kg melt in 6 to 10 minutes) below 0,1 % carbon, the decrease of alloying elements being checked constantly. Oxidation took place with a high rise in temperature but otherwise the process worked in a most simple and efficient way without causing any problems.

The further historic development of the oxygen converter process consisted in an evaluation of the results of the above mentioned research, which led to a clarification of the basic concept of the process on a laboratory scale. As a result pilot-plant size tests could be carried out in 1947 at the Von Roll'sche Eisenwerke at Gerlafingen, Switzerland, which finally led to the first big scale oxygen converter installation which was set into operation in 1952 at the VOEST plant at Linz.

In den letzten Jahrzehnten haben sich die Verfahren der Stahlerzeugung (im vorigen Jahr wurden in der Welt rund 700 Millionen t Stahl erzeugt, d.h. 20mal mehr als alle übrigen Metalle zusammen) grundsätzlich gewandelt; an die Stelle des Siemens-Martin- und vor allem des Thomas-Verfahrens ist das Sauerstoff-Aufblaseverfahren (auch Oxigen- oder LD-Verfahren benannt), ein neues europäisches Verfahren, getreten. Es wird angenommen, daß die neuen Anlagen im wesentlichen nur noch nach diesem oder nach dem Elektrolichtbogenofen-Verfahren arbeiten werden.

Aus dem Schrifttum ist die geschichtliche Entwicklung des Sauerstoff-Aufblaseverfahrens bekannt. Die ersten Pilot-Schmelzen sind bei den Von Roll'schen Eisenwerken in Gerlafingen, Schweiz, im Jahre 1947[1] durchgeführt und die erste Großbetriebsanlage im Jahre 1952 bei Voest in Linz[2] in Betrieb genommen worden.

Nicht bekannt ist dagegen. daß im Laboratorium-Maßstabe dieses Verfahren mehrere Jahre vorher in allen seinen Wesenszügen durchgeführt bzw. gelöst wurde, was hiermit nachgeholt werden soll.

Die Untersuchungen wurden im Laboratorium des Eisenhüttenmännischen Institutes der Technischen Hochschule Berlin-Charlottenburg (Institutsleiter: Prof. Dr. Robert Durrer) im Rahmen der metallurgischen Studien- und Diplomarbeiten, die in den Jahren 1940 bis 1943 angefertigt wurden, durchgeführt[3–8]; die nachfolgenden Ausführungen sind Originalen dieser Arbeiten entnommen.

Die ersten Versuche[3,4] wurden so durchgeführt, daß im Induktionsofen 5 bis 10 kg Roheisen geschmolzen und dann von oben mit reinem Sauerstoff aus Stahlflaschen durch feuerfeste Rohre das flüssige Roheisen gefrischt, d.h. oxidiert, wurde. Bei diesen ersten Versuchen konnte aber infolge der zu geringen Sauerstoffmenge kein Stahl erzeugt werden.

Erst das Arbeiten mit mehr Sauerstoff und besonders durch eine senkrecht von oben angeordnete wassergekühlte Sauerstoff-Kupferdüse brachte es fertig, in 5 bis 15 Minuten eine Menge von 5 bis 10 kg Roheisen weitgehend (unter 0,1 % C) zu frischen[5]. Diese Versuchsanordnung zeigt Abb. 1. Bei verschiedenen auf saurer (Klebsand) und basischer (Dolomit) Ofenausstampfung durchgeführten Schmelzen wurde die Oxidation durch die laufende Probenahme (was allerdings die Versuchsdauer verlängerte und die Wärmeverluste erhöhte) der Schmel-

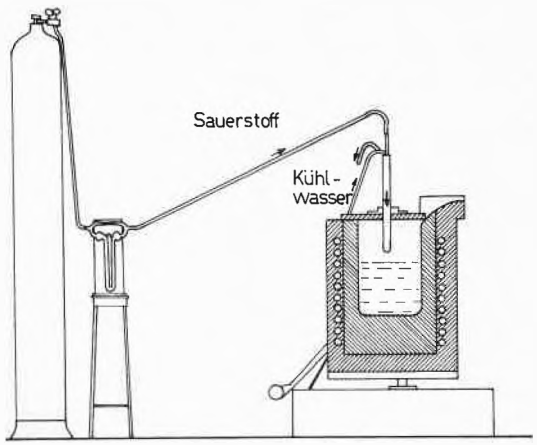

Abb. 1. Aufblase-Versuchseinrichtung

* Eingegangen am 9. Oktober 1975.

zen, die anschließend chemisch untersucht wurden, und durch die optische Temperaturmessung verfolgt (s. Abb. 2). Es zeigte sich, daß durch die gewählte Versuchsanordnung problemlos das Frischen der Roheisenschmelze bis zum Stahl vor sich geht. Wurde das Frischen mit Sauerstoff ohne die Probenahme-Unterbrüche durchgeführt, dann erreichten die Schmelzen bereits nach 6 Minuten Werte unter 0,1 % C.

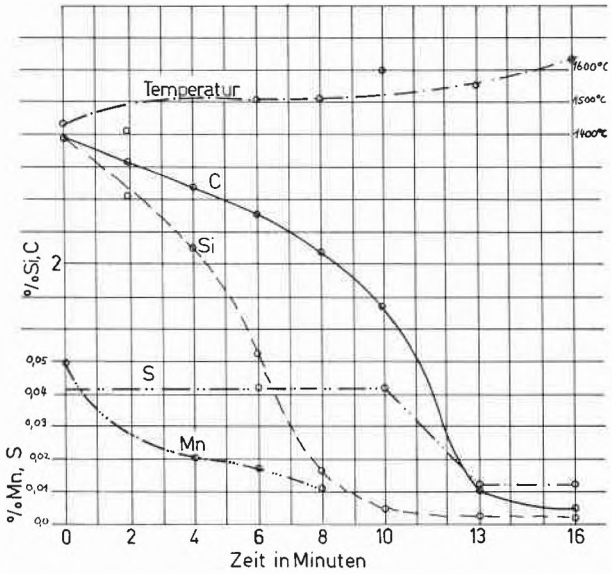

Abb. 2. Ablauf des Frischvorganges

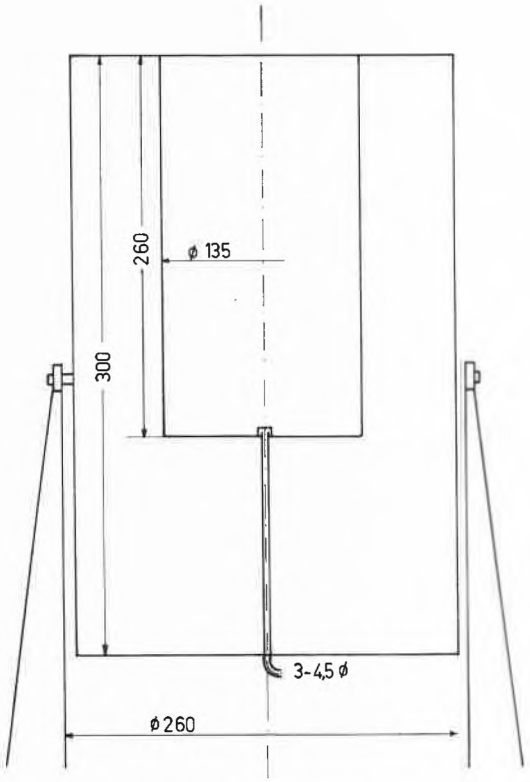

Abb. 3. Durchblase-Versuchsanordnung

In weiteren Arbeiten[6,7] wurde festgestellt, daß Schwefel um gegen 50 % gesenkt und daß Chrom bei Ausgangswerten gegen 2 %, besonders bei tiefen Temperaturen des Frischvorganges, weitgehend entfernt werden kann. Auch diese Schmelzen wurden in 6 bis 10 Minuten bei gleicher Versuchsanordnung auf die Stahlzusammensetzung oxydiert.

In einer weiteren Arbeit[8] wurde untersucht, wieweit Vanadin mit reinem Sauerstoff in die basische Schlacke übergeführt werden kann. Die Versuchsanordnung war zuerst gleich der Abb. 1; später wurde das im Induktionsofen erschmolzene Roheisen in einer Menge von etwa 10 kg in einen kippbaren Konverter (s. Abb. 3) gebracht und von unten mit Sauerstoff verblasen. Die Oxydation bis unter 0,1 % C erfolgte in einer Zeit unter 5 Minuten. Die Temperatur konnte optisch nicht gemessen werden. Es wurde deshalb aufgrund der Oxydationswärme der entfernten Legierungselemente die Temperatur der Schmelze berechnet und in das Chargen-(Frisch-) Diagramm eingezeichnet. Ein Beispiel der Konzentrationsänderung dieser Versuche (es wurden 16 Schmelzen verblasen) zeigt Abb. 4.

Diesen Schmelzen[3–8] sind alle wesentlichen Merkmale des später entwickelten Sauerstoff-Aufblaseverfahrens eigen. Sie wurden in den Studienarbeiten beschrieben; die wesentlichsten Punkte sind:

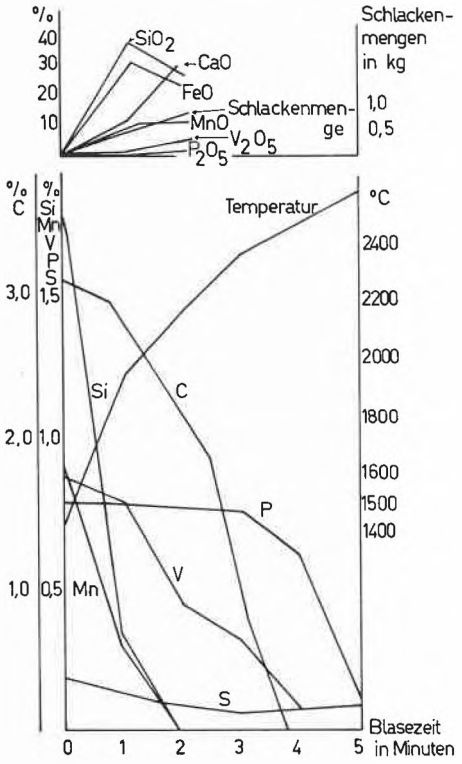

Abb. 4. Ablauf der vanadiumhaltigen Charge

- problemlose und sehr schnelle Oxydation der Legierungselemente (C, Si, P, S, V) des flüssigen Roheisens mit reinem Sauerstoff, d.h. Zufuhr großer Sauerstoffmengen und somit Abkürzung der Chargenzeit oder wesentliche Vergrößerung des Chargengewichtes; das Verblasen erfolgte praktisch ohne Auswurf[5] und lieferte Schmelzen unter 0,1 % C;
- einwandfreies Einbringen des Sauerstoffs mit einer von oben senkrecht auf die Schmelze gerichteten Kupferdüse; Sauerstoff dringt in die Roheisenschmelze ein und wird praktisch aufgenommen, dabei kommt es infolge der CO-Bildung (Kohlenstoff-Oxydation) zu zusätzlicher Bewegung der Schmelze (Kochreaktion) und somit zur weiteren Beschleunigung des Vorganges, weil es dadurch zu einer inneren Vermischung zwischen Schlacke- und Metallschmelze kommt;
- sehr starke Temperaturzunahme der gefrischten Eisenschmelze, was die Zugabe von Kühlschrott (und somit Erhöhung des Ausbringens) bedingt[5,8];
- festgestellte Oxydationsfolge der Legierungselemente zeigt, daß diese etwa der des Thomas-Verfahrens entspricht; dabei muß allerdings der Temperatur der Schmelze, die ohne Kühlschrott sehr hoch sein kann, und dadurch besonders der Veränderung der Reihenfolge der Oxydation der Legierungselemente (besonders des Kohlenstoffs) Rechnung getragen werden;
- die Untersuchung des Verhaltens einiger spezieller Legierungselemente zeigte, daß keine besonders umfangreiche Entschwefelung auftritt, daß Chrom (z.B. des Roheisens) besonders bei tiefen Temperaturen weitgehend oxydiert wird, und wie sich vanadinhaltiges Roheisen auf vanadinreiche Schlacke verarbeiten läßt.

Somit haben diese Versuche im Laboratoriumsumfange wichtige Merkmale des späteren Sauerstoff-Aufblase-Verfahrens festgestellt und dessen Arbeitsweise vorausbestimmt.

Der Verfasser war bis Ende 1943 als Assistent bei Professor R. Durrer im Eisenhüttenmännischen Institut der Technischen Hochschule in Berlin-Charlottenburg tätig und betreute die hier beschriebenen Arbeiten.

Schrifttum

1 R. Durrer, H. Hellbrügge und H. R. Richter-Brohm, *Stahl Eisen 85* (1965) 1751–4.
2 H. Weltzer, *Ein Jahr LD-Sauerstoff-Frischverfahren*, Linz (Donau) 1954.
3 M. Ibing und T. Schmid, *Untersuchung der Abbrandverhältnisse beim Einblasen von reinem Sauerstoff in flüssiges Roheisen*, 2. Hüttenmännische Arbeit, 4.10.1940, 25 S.
4 M. Ibing und T. Schmid, *Erweiterte Untersuchungen beim Einblasen von reinem Sauerstoff in flüssiges Roheisen*, 3. Hüttenmännische Arbeit, 28.1.1941, 15 S.
5 J. Bohun, *Untersuchung der Möglichkeit, flüssiges Roheisen mit reinem Sauerstoff zu frischen*, Diplomaufgabe, 4.12.1942, 30 S.
6 C. Evren, *Entschwefelung von Roheisen beim Frischen mit reinem Sauerstoff*, 2. Hüttenmännische Arbeit, 6.1.1943, 24 S.
7 M. Abbas, *Oxydation des Chroms im flüssigen Roheisen mit hochhaltigem Sauerstoff*, 2. Hüttenmännische Arbeit, 6.9.1943, 26 S.
8 B. Weiland, *Oxydation des Vanadins in der Roheisenschmelze mit hochhaltigem Sauerstoff auf basischem Futter*, Diplomaufgabe 6.9.1943, 63 S.

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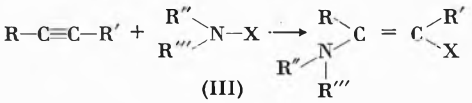
N-Haloamine and N-Haloimine Additions to Electron Poor Acetylenes*

Summary

The addition of N-haloamines and their "Iminologs", N-haloimines to electron poor acetylenes opens a simple way to the functionalisation of triple bonds.

Additions of amines to electron poor multiple bonds are well known[1] in contrast to additions of N-halo compounds which have been restricted to nonactivated acetylenes[2] or olefines[2]. Normally, amine additions are of nucleophilic, whereas N-haloamine additions are of radical or radicalcation nature[3]. We have found now, that electron poor acetylenes add tertiary N-chloro- and bromoamines in methanol but not in benzene, which hints at a polar addition.

* Received October 14, 1975.



[IV a–h]

[I] R = H, R′ = $COOCH_3$
[II] R = R′ = $COOCH_3$

Thus methylpropiolate [I] produces stereospecifically adducts which result from cis-addition of N-halodialkylamines to the triple bond as evidenced by NMR comparison with known compounds[4]. With acetylene dicarboxylate [II] again only one geometric isomer is obtained (Table I). The question of competitive N–H or N-halo addition was raised by the reaction of N-bromo-*n*-butylamine to acetylene dicarboxylate. Although this bromoamine could be obtained only in mixture with unreacted *n*-butylamine, the mass spectrum

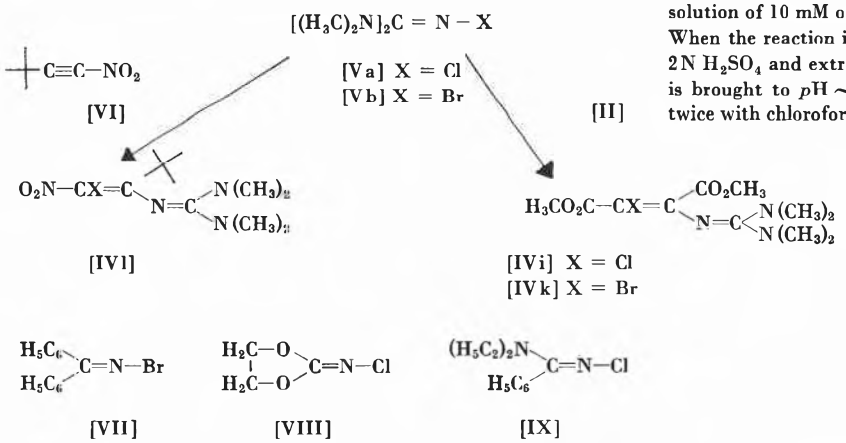
Table I. N-haloamine Addition to Electron-poor Acetylenes

Compound IV	R	R′	R″	R‴	X	Yield %	Reaction Conditions	M.p. (B.p.) °C/Torr
a	CH_3COO	CH_3COO	C_2H_5	C_2H_5	Cl	60	20°, 24 h	110°/0.02
b	CH_3COO	CH_3COO	n-C_4H_9	n-C_4H_9	Br	73	20°, 12 h	145°/0.03
c	CH_3COO	CH_3COO	n-C_4H_9	n-C_4H_9	Cl	85	20°, 48 h	140°/0.05
d	CH_3COO	CH_3COO	$(C_6H_5)CH$	CH_3	Cl	85	5°, 4 h	170°/0.05
e	H	CH_3COO	C_2H_5	C_2H_5	Cl	42	reflux, 8 h[c]	80°/0.02
f	H	CH_3COO	n-C_4H_9	n-C_4H_9	Cl	65	reflux, 8 h[c]	120°/0.03
g	H	CH_3COO	C_2H_5	C_2H_5	Br	57	20°, 12 h	90°/0.03
h		CH_3COO	n-C_4H_9	n-C_4H_9	Br	65	20°, 12 h	dec.[a]
i	CH_3COO	CH_3COO	$[(CH_3)_2N]_2C=$		Cl	35	reflux, 8 h[a]	104 to 106°
k	CH_3COO	CH_3COO	$[(CH_3)_2N]C=$		Br	15	20°, 18 h[b]	98 to 100°
l	$(CH_3)_3C$	NO_2	$[(CH_2)_4N]C=$		Cl	37	20°, 8 h	45 to 48°

a Purified by chromatography (Silicagel/$CHCl_3$) b Recrystallised from n-hexane c Methanol

of the resulting mixture showed substantial amounts of the N-bromo-adduct.

As a part of our study of iminologous systems[5], sym-tetramethyl-N-halo-guanidines [V][6], which can be considered as iminologs of N-halodimethylamines, did also react with II and even with tertbutylnitroacetylene VI[7]. On the other hand the less electron rich chloroimines [VII][8] and [VIII][9] and even N, N-diethyl-N-chlorobenzamidine [IX][10] gave no addition products.



[VII] [VIII] [IX]

(+ = tert. butyl)

Experimental

N-bromamines have been prepared by a modification of the method used for N-chloramines[2].

General procedure for addition of N-haloamines [V a to h]

10 mM of the freshly distilled N-haloamine[2] *(Caution!* bromamines explode at temperatures higher than 70°; handling under N_2 is important) are added to 10 mM of the acetylene dissolved in 10 ml of dry methanol. The solution is heated if necessary (Table I) and then methanol is evaporated, ether is added and the insoluble salts are filtered. Ether is evaporated and the residue is distilled under high vacuum, or purified by chromatography (Table I).

Sym-tetramethyl-N-chloro-guanidine[8] Adducts [IV i, l]

A solution of 10 mM of [V a][6] in 5 ml dry methanol is added to a solution of 10 mM of the acetylenic compound in 5 ml dry methanol. When the reaction is finished (Table I) the solution is acidified with 2N H_2SO_4 and extracted twice with chloroform. The acidic solution is brought to pH ~ 12 with 6N NaOH in the cold and extracted twice with chloroform. The chloroform layer is dried and evaporated.

Preparation of the sym-tetramethyl-N-bromo-guanidine adduct [IV k]

To a solution of 10 mM of [II] in 20 ml dry ether, a solution of 10 mM sym-tetramethyl-N-bromoguanidine[6] in dry ether is addde at 0°. The solution is stirred at room temperature for 18h, the precipitate is filtered and extracted with warm n-hexane.

The warm solution is filtered and partly evaporated. [IV k] crystallises on cooling (Table II).

Acknowledgement

The authors gratefully acknowledge support of this research by BASF, le Fonds National de la Recherche Scientifique Belge and Professor E. Dubois of the Université de Paris.

Table II. NMR and Mass Spectra of Compounds IV

Compound IV	^{1}H-NMR (δ) ($CDCl_3$)	MS
a	1.18 (t, 6H); 3.35 (q, 4H); 3.67 (s, 3H); 3.80 (s, 3H)	249 (M^+), 234, 219, 190
b	0.76 to 1.78 (m, 14H); 3.30 (t, 4H); 3.71 (s, 3H); 3.80 (s, 3H)	349 (M^+), 318, 306, 290
c	0.80 to 1.76 (m, 14H); 3.39 (m, 4H); 3.77 (s, 3H); 3.94 (s, 3H)	305 (M^+), 270, 262, 246
d	2.91 (s, 3H); 3.78 (d, 6H); 4.45 (s, 2H); 7.36 (s, 5H)	297 (M^+), 266, 262, 238
e	1.22 (t, 6H); 3.42 (q, 4H); 3.70 (s, 3H); 7.49 (s, 1H)	191 (M^+), 176, 156, 148
f	0.74 to 1.80 (m, 14H); 3.32 (t, 4H); 3.71 (s, 3H); 7.48 (s, 1H)	247 (M^+), 232, 216, 212
g	1.28 (T, 6H); 3.50 (q, 4H); 3.71 (s, 3H); 7.77 (s, 1H)	235 (M^+), 220, 204, 192
h	0.75 to 1.76 (m, 14H); 3.38 (t, 4H); 3.63 (s, 3H); 7.72 (s, 1H)	291 (M^+), 260, 248, 212
i	2.88 (s, 12H); 3.72 (s, 3H); 3.80 (s, 3H)	291 (M^+), 260, 232, 200
k	2.92 (s, 12H); 3.81 (d, 6H)	335 (M^+), 304, 276, 256
l	1.42 (s, 9H); 2.87 (s, 12H)	276 (M^+), 187, 142, 131

Bibliography

1 E. Winterfeldt in *Chemistry of Acetylenes* (H. G. Viehe, Editor), Dekker, New York 1969, p. 267.
2 R. S. Neale, *Synthesis 1971*, 1. P. Kovacic, M. K. Lowery and K. W. Field, *Chem. Rev. 66* (1970) 639.
3 O. E. Edwards, G. Bernath, J. Dixon, J. M. Paton and D. Vocelle, *Canad. J. Chem. 52* (1974) 2123.
4 K. Hafner and N. Neuenschwander, *Angew. Chem. 80* (1968) 443; R. Gompper and G. Seybold, *Angew. Chem. 80* (1968) 804.
5 H. G. Viehe, J. Baum, F. Tataruch and D. Scholz, following paper, p. 514.
6 A. J. Papa, *J. Org. Chem. 31* (1966) 1426.
7 V. Jäger and H. G. Viehe, *Angew. Chem. 81* (1969) 259.
8 P. L. Pickard and T. L. Tolbert, *J. Org. Chem. 26* (1961) 4887. L. Spialter and D. H. O'Brien, *J. Org. Chem. 32* (1967) 223.
9 T. Fulisawa, Y. Tamura and T. Mukaiyama, *Bull. Chem. Soc. Jap. 1964*, 793.
10 Prepared in analogy to ref.[6]; white crystalls M.p. 54 to 55,5°; b.p. 100°/0.05.

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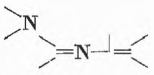
New Syntheses of Amino-Substituted 2-Azabutadienes*

Summary

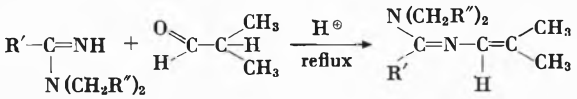
N,N-Disubstituted benzamidine and sym-tetramethylguanidine react with isobutyric aldehyde or acetylene dicarboxylate to give amino-substituted 2-azabutadienes. Tetramethylureadichloride condenses with suitable ketimines to produce similar compounds in high yields.

Enimines (2-azabutadienes) and their salts are polar dienes of high synthetic potential[1–4]. Several new ways have been elaborated for the synthesis of the mono- or bis-dialkylaminoenimines [I].



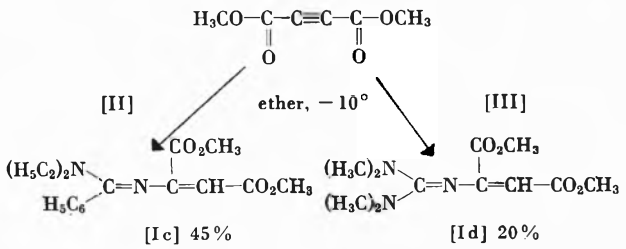
[I]

Thus either substituted amidines [II] or guanidines [III] react with isobutyric aldehyde to produce [I] in good yields.



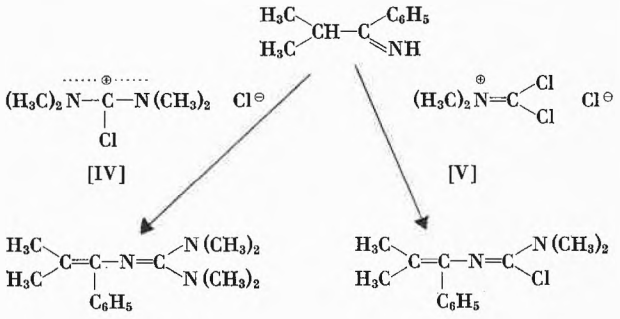
[II] R′ = C_6H_5; R″ = CH_3; 86% [I a, b]
[III] R′ = $N(CH_3)_2$; R″ = H; 62%

This reaction fails with aldehydes bearing only one or no α-substituent. In this case only aldol condensation products are obtained. In analogy to the preceeding report on the addition of N-haloimines to electron poor acetylenes producing also derivatives of [I], now the imine [II] and guanidine [III] were added to dimethyl acetylene dicarboxylate.

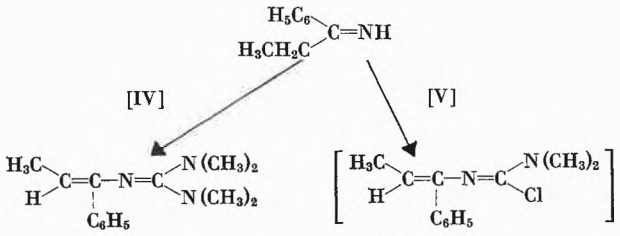


[Ic] 45% [Id] 20%

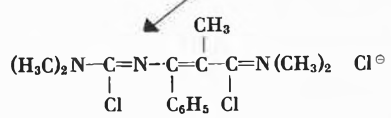
The yields vary from fair to low which is caused by the fact that acetylene dicarboxylate is base-sensitive. Further, it was found that the reaction of ketimines with tetramethylurea dichloride leads also to [I]. An analogous condensation takes place with phosgeniminium chloride[5] which forms [I] in a fast reaction.[7]



[Ie] 52% [If] 78%



[Ig] 55% [Ih]



[VI]

Phosgeniminium chloride being a stronger electrophile than [IV][6], reacts further with the intermediate enimine Ih to 1,5-dichloro-2-aza-pentamethinecyanine [VI][7].

* Received October 14, 1975.

The condensations of [V] with different imines will be published separately.

Experimental

General Procedure for preparation of [Ia,b]

0.1 Mole of imine is refluxed in an excess of isobutyraldehyde with a trace of *p*-toluolsulfonic acid until the separation of water stops. Then the excess of the aldehyde is evaporated and the residue is distilled in vacuum.

1-Diethylamino-4,4-dimethyl-1-phenyl-2-azabutadiene [Ia]

B.p.: 96°/0.02; yield: 86%
^{1}H-NMR ($CDCl_3$) δ: 1.12 (t, 6H); 1.50 (s, 3H); 1.92 (s, 3H); 3.32 (q, 4H); 5.98 (s, 1H); 7.00–7.46 (m, 5H).
IR (film): 2970, 1570, 1420, 1096 cm^{-1}.

1,1-Bis-dimethylamino-4,4-dimethyl-2-azabutadiene [Ib]

B.p.: 102°/10; yield: 62%.
^{1}H-NMR ($CDCl_3$) δ: 1.72 to 1.86 (m, 6H); 2.81 (s. 12H); 6.37 (m, 1H);
IR (film): 2880, 1590, 1500, 1370, 1190, 1008 cm^{-1}.
General procedure for addition of imines [II], [III] to methyl-acetylenedicarboxylate.
10 mmoles of imine are added to 20 mmoles of methyl acetylendicarboxylate in 20 ml dry ether at − 10°. The solution is first allowed to reach room temperature then it is acidified with 2N H_2SO_4 under cooling and the acidic solution is extracted with ether. The aqueous phase is made alkaline with 6N NaOH (*p*H ~12 to 14) and extracted with CH_2Cl_2. The organic layer is dried and evaporated.

1-diethylamino-3,4-bis-methoxycarbonyl-1-phenyl-2-azabutadiene [Ic]

Yield: 45%; mp 114 to 115° (cyclohexane).
^{1}H-NMR ($CDCl_3$) δ: 0.92 to 1.12 (m, 6H); 3.04 to 3.59 (m, 4H); 3.46 (s, 3H); 3.54 (s, 3H); 4.61 (s, 1H); 7.19 to 7.43 (m, 5H).
IR ($CHCl_3$) 2950, 1740, 1700, 1580, 1040 cm^{-1}.

1,1-Bis-dimethylamino-3,4-bis-methoxycarbonyl-2-azabutadiene [Id]

Yield: 20%, mp 58 to 61° (hexane), bp 150°/0.02.
^{1}H-NMR ($CDCl_3$): δ: 2.83 (s, 12H); 3.71 (d, 6H); 5.84 (s, 1H).
MS: M^+ 257, 266, 198, 185, 166.
IR ($CHCl_3$) 2940, 1730, 1695, 1530, 1395, 1020 cm^{-1}.

General procedure for the condensation of imines with [IV]
Equimolar amounts of tetramethylurea dichloride and imine are refluxed in dry CH_2Cl_2 with double excess of triethylamine for 4h. The reaction mixture is evaporated and the residue is treated with a saturated solution of KOH at 0°. Then the mixture is extracted several times with ether, the organic layer is dried, evaporated and the residue distilled under high vacuum.

1,1-Bis-dimethylamino-4,4-dimethyl-3-phenyl-2-azabutadiene [Ie]

Yield 52%, b.p. 140°/0.03.
^{1}H-NMR ($CDCl_3$) δ: 1.81 (s, 3H); 1.83 (s, 3H); 2.57 (s, 12H); 7.00 to 7.40 (m, 5H).
MS: M^+ 245, 244, 230, 201, 131.

1,1-Bis-dimethylamino-4-methyl-3-phenyl-2-azabutadiene [Ig]

Yield: 55%, b.p. 130°/0.05.
^{1}H-NMR ($CDCl_3$) δ: 1.70 (d, 3H); 2.64 (s, 12H); 5.29 (m, 1H); 7.00 to 7.50 (m, 5H);
MS: M^+ 231, 216, 202, 187, 117.

Bibliography

1 A. Demoulin, H. Gorissen, A. Hesbain-Frisque and L. Ghosez, *J. Amer. Chem. Soc. 97* (1975) 4409.
2 E. Goffin, Dissertation, Louvain-la-Neuve 1974.
3 Z. Janousek, J. Collard and H. G. Viehe, *Angew. Chem. 84* (1972) 993; *(Internat. Ed.) 11* (1972) 917.
4 T. van Vyve and H. G. Viehe, *Angew. Chem. 86* (1974) 45; *(Internat. Ed.) 13* (1974) 79.
5 H. G. Viehe and Z. Janousek, *Angew. Chem. 85* (1973) 837; *(Internat. Ed.) 12* (1973) 806.
6 R. L. N. Harris, *Austr. J. Chem. 27* (1974) 2635 and the references cited therein.
7 Th. van Vyve, Dissertation, Louvain-la-Neuve 1976.

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Oxidation and Reduction of *tert*-Butylnitrosoacetylene[1]*

Summary

Tert-butylnitrosoacetylene [I] can be oxidized to the corresponding nitroacetylene [II] in spite of the low temperature rearrangement of [I] to the isomeric pivaloylcyanide [III]. [I] is reduced with triethylphosphite to an intermediate which reacts with tetramethylethylene formally as the cyanocarbene [VI] rather than as the ethinylnitrene [V].

Tert-butylnitrosoacetylene [I] was detected earlier in the reaction of bis-(*tert*-butylethinyl) mercury with nitrosyl chloride at low temperature[2].

$$[(CH_3)_3C{-}C{\equiv}C]_2Hg + 2NOCl \xrightarrow[-60\,^\circ C]{CHCl_3} 2(CH_3)_3C{-}C{\equiv}C{-}NO + HgCl_2 \qquad [I]$$

Analogously [I] is also obtained from the corresponding stannylacetylene and dinitrogen tetroxide.

$$(CH_3)_3C{-}C{\equiv}C{-}Sn(CH_3)_3 + N_2O_4 \xrightarrow[-60\,^\circ C]{ether} (CH_3)_3C{-}C{\equiv}C{-}NO + (CH_3)_3SnONO_2 \qquad [I]$$

[I] is formed in at least 40% yield based on further reactions[3]. Thus [I] is oxidized at − 60°C by peracids or better by hydrogen peroxide to *tert*-butylnitroacetylene [II].

$$[I] + CH_3{-}\overset{O}{\overset{\|}{C}}OOH \xrightarrow[-60\,^\circ C]{ether} (CH_3)_3C{-}C{\equiv}C{-}NO_2 \quad 15\%\ \text{yield}$$

$$[I] + H_2O_2 \xrightarrow[-60\,^\circ C]{ether} (CH_3)_3C{-}C{\equiv}C{-}NO_2 \quad 40\%\ \text{yield}$$

* Received October 14, 1975.

[II] was identified spectroscopically and by its ready cycloaddition to cyclopentadiene[4].
The low temperature is necessary because [I] rearranges easily to pivaloyl cyanide[2] [III].

$$[I] \xrightarrow[-30\,^\circ C]{\text{4 hours}} (CH_3)_3C{-}\underset{\underset{O}{\|}}{C}{-}CN \qquad 30\,\%$$

[III]

This rearrangement occurs together with other undefined reactions. Dimerisation to furoxanes was observed only with sterically less hindered nitroso-acetylenes like *n*-butyl or *i*-propyl derivatives[2]. Attempts to trap [I] by condensation of the nitrosogroup with nitromethane or carbomethoxy-triphenylphosphorylene[3] failed and led to derivatives of the acylcyanide [III].
Reduction of [I] with triethylphosphite in the presence of tetramethylethylene produces adduct [IV]: [III] is inert under these conditions.

$$[I] + P(OC_2H_5)_3 \xrightarrow[-40\,^\circ C]{(CH_3)_2C{=}C(CH_3)_2} (CH_3)_3C{-}\underset{N\equiv C}{\overset{}{C}}(C(CH_3)_2)_2$$

[IV]

Thus [IV] is derived formally from cyanocarbene mesomers [VI] rather than from ethinyl nitrene mesomer [V].

$$[I] + P(OC_2H_5)_3 \rightarrow$$
$$[(CH_3)_3C{-}C{\equiv}C{-}\overline{N} \longleftrightarrow (CH_3)_3C{-}\overline{C}{-}C{\equiv}N] \rightarrow [IV]$$

[V] [VI]

This finding is in agreement with results reported for other ethinylnitrenes obtained by different routes[5].

Experimental

Tert-butylnitrosoacetylene (I): Trimethylstannyl acetylene (2.24 g, 0.01 mole) in 20 cm³ cooled ether at −60 °C is added rapidly to an ethereal (30 cm³) solution of dinitrogentetroxide (0.92 g, 0.01 mole). During the addition efficient stirring is required to have the solution as homogenous as possible. Simultaneously the solution turns green and a white solid precipitates. U.V. and I.R. data of [I] in ether confirm previous reports[2].

Reaction of (I) with hydrogen peroxide: 0.03 m of 40 % H_2O_2 are added to a vigorously stirred solution of 0.01 m of [I] in 50 cm³ ether at −60 °. After one hour at −60 ° the color changes from green to orange and the mixture is filtered at −40 °.
The solution is dried over sodium sulfate and evaporated. Kugelrohr distillation affords [II] in up to 40 % yield[3].

Bibliography

1 Nitroacetylenes Part 7; Part 6, H.G. Viehe and R. Verbruggen, *Chimia 29* (1975) 352.
2 E. Robson and J.M. Tedder, *J. Chem. Soc. 1968*, 321.
3 J.C. Motte, Dissertation, Louvain-la-Neuve 1974, Belgium.
4 V. Jäger and H.G. Viehe, *Angew. Chem. 81* (1969) 257; *Angew. Chem. (Internat. Ed.) 8* (1969), 273; b) *Angew. Chem. 82* (1970), 836; *Angew. Chem. (Internat. Ed.) 9* (1970) 795.
5 a) J.H. Boyer, W.E. Krueger and G.J. Micol, *J. Amer. Chem. Soc. 89* (1967) 5504; b) J.H. Boyer and R. Selvarajan, *J. Amer. Chem. Soc. 91* (1969) 6122.

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Synthesis of Nitroacetylenes by Electrophilic Substitution on Trialkylstannylacetylenes[1]*

Summary

By electrophilic substitution, nitronium ion transforms trialkylstannylacetylenes into the corresponding nitroacetylenes. Two different routes are described.

Nitroacetylenes[2] are very reactive dienophiles, dipolarophiles and electrophiles[3]. Syntheses reported to date result from elimination reactions of β-iodo or β-chloroolefines[3] and from the oxidation of the alkylnitrosoacetylenes[4]. It is reported now that trimethylstannylacetylenes [I] and nitronium ion also produce nitroacetylenes [II]. Thus in ether at −60 °, dinitrogenpentoxide reacts with [I] to produce [II] in up to 40 % yield.

$$(R^2_3)Sn{-}C{\equiv}C{-}R^1 + N_2O_5 \xrightarrow[-60\,^\circ]{\text{ether}} R^1{-}C{\equiv}C{-}NO_2 + (R^2_3)SnONO_2$$

[I] [II]

With nitronium tetrafluoroborate, at −20 ° in dichloromethane, even 70 % yield are obtained.

$$(R^2_3)Sn{-}C{\equiv}C{-}R^1 + NO_2BF_4 \xrightarrow[20\,^\circ]{CH_2Cl_2} R^1{-}C{\equiv}C{-}NO_2 + (R^2_3)SnBF_4$$

[I] [II]

Similar to the above reaction with unstable dinitrogen pentoxide, the reaction of commercial dinitrogentetroxide with [I] at −60 ° in ether leads to the already known nitrosoacetylenes. These at −60 ° form the corresponding nitroacetylenes on treatment with organic peracids, or better, with hydrogen peroxide[4].

$$[I] + \xrightarrow[2.\ [O]]{1.\ N_2O_4\ -60\,^\circ} [II]$$

* Received October 14, 1975.

The yields of the three methods are compared in the following table.

	$(R^2_3)Sn-C\equiv C-R^1$ [I]		$R^1-C\equiv C-NO_2$ [II]		
	R^1	R^2	N_2O_5	NO_2BF_4	from nitroso-acetylene
a	$(CH_3)_3C$	CH_3	40%	70%	40%
b	$(CH_3)_3C$	n-C_4H_9	35%	40%	30%
c	$(CH_3)_2CH$	CH_3	30%	50%	20% (G.C.)
d	$(CH_3)_2CH$	n-C_4H_9	–	10% (G.C.)	–
e	n-C_4H_9	CH_3	10% (G.C.)	–	–

Experimental: Attention because of potential explosives!

Nitration of I a with dinitrogenpentoxide

An ethereal colution cooled to $-60°$ (10 cm³) of [I a] (2.24 g, 0.01 mole) is added rapidly to an ethereal solution (40 cm³) of dinitrogenpentoxide (1.08 g, 0.01 mole). The initial colorless solution turns deep yellow.

After 15 min. the mixture is allowed to attain room temperature. Evaporation and Kugelrohr distillation of the residual oil affords II a (0.5 g, 40%).

Nitration of I a with nitronium tetrafluoroborate

A solution of [I a] (2.24 g, 0.01 mole) in 10 cm³ dichloromethane is added slowly with vigorous stirring to a nitronium tetrafluoroborate suspension in dichloromethane (40 cm³) cooled at 0°. After the addition is complete, the ice-bath is removed and the solution stirred until the suspension has reacted (2 hours). The mixture is evaporated and the residual yellow oil is distilled under reduced pressure (Kugelrohr) affording II a (0.88 g, 70%).

Bibliography

1 Nitroacetylenes, Part 8. Part 7 preceeding. Heterosubstituted Acetylenes, Part 33; Part 32, C. Derycke, V. Jäger, J. P. Putzeys, M. Van Meerssche and H. G. Viehe, *Angew. Chem. 85* (1973) 447.

2 a) V. Jäger and H. G. Viehe, *Angew. Chem. 81* (1969) 257; *Angew. Chem. (Internat. Ed.) 8* (1969) 273. b) *Angew. Chem. 82* (1970) 836; *Angew. Chem. (Internat. Ed.) 9* (1970) 795.

3 V. Jäger, Dissertation, Erlangen-Nürnberg 1970, Germany.

4 a) J. C. Motte and H. G. Viehe, Preceeding. b) J. C. Motte, Dissertation, Louvain-la-Neuve 1974, Belgium.

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Layer Structured Manganese Oxide Hydroxides. IV: The Buserite Group; Structure Stabilization by Transition Elements*

Summary

As colloidal manganese oxide hydroxides in natural waters occur in an infinity of finely divided varieties of an apparently limited number of (unknown) phases, an attempt has been made to prepare standard samples of the so-called "10 Å phase" which we propose to call buserite. As evidenced by X-ray powder patterns, bivalent metal ions may become incorporated into the lattice of buserite. While Na^+-, Ca^{2+}-, and Mg^{2+}-buserite become unstable in slightly acid suspensions and dehydrate at low vapour pressure, transition metal ions which are more tightly built into the structure of buserite stabilize this structure. Fe^{3+} cannot be incorporated into the lattice, presumably due to its insolubility characteristics.

Introduction

There is great interest in the "sorption" of transition metal ions on manganese oxide hydroxides[1]; this is treated by most authors as an ion exchange or surface complex formation reaction.

We shall demonstrate in this paper that suitable transition metal cations—subsequent to their adsorption onto the oxide hydroxide surface—may become built into the lattice of manganese oxide hydroxides of a particular lattice type, thereby stabilizing this structure. Our experiments were carried out with buserite*, a material originally called "10 Å Manganite" by Feitknecht et al.[2] Our evidence is based on studying the effects of transition metal ions on X-ray diffraction, on dehydration, thermal stability and H^+ ion induced decomposition reactions.

Experimental

Na-buserite was prepared by rapid oxidation of an aqueous $Mn(OH)_2$ suspension: 250 ml of a 5.2 M NaOH are added to 200 ml 0.5 M $Mn(NO_3)_2$. O_2 is then passed through the suspension (in a narrow 1 litre cylinder), using a glass frit G-1 (flow at least 2.5 L. min^{-1}). It is essential that full saturation with O_2 is attained immediately. After 4 to 5 hours the black precipitate is collected and washed thoroughly; it must not be dried. Na-buserite is stable for many years if kept under water.

Cu-, Zn-, Ni-, Co-, Ca-, and Mg-buserite were prepared by transferring thoroughly washed Na-buserite into 0.1 M solutions of the respective metal nitrate. After standing for 1 day, the solid phase is separated and washed until the supernatant is free of NO_3^- (diphenylamine test); then it is formed into a sphere of 1 to 2 cm diameter and dried—without using any desiccant—at room temperature in air (usual H_2O vapour pressure) until weight constance.

* Received November 10, 1975.

* In remembrance of the late W. Buser, who found this compound in marine manganese nodules[3]. The initial designation "manganite" must be reserved for the mineral γ-MnOOH.

(Drying at higher temperature[4] or at lower vapour pressure or even in finely divided form in a differential pressure filter decomposes the Me-buserite.)

Analytical methods. X-ray diffraction, electron diffraction, electron microscopy, and the method for determining the oxidation degree O/Mn have been described before[5,6]. Mn, Co, Cu, Ni, and Zn were determined by AAS. A Mettler thermoanalyzer TA1 with a Pt crucible T-DT-3 was used at 1 atm. N_2 pressure and 4 L.h^{-1} gas flow. The sample weight was of the order of 10 to 15 mg and the heating rate was 4 or 8 °C. min^{-1}. The total water (H_2O and OH^-) was determined in a Bell & Howell Moisture Analyzer 26-321-MA, by integration of the electrolysis current in a P_2O_5 coated cell which collects the H_2O produced by thermal decomposition.

Ion exchange with H^+ ions. In order to get an impression as to how fast Me^{2+} ions exchange against H^+, about 2 mMoles of each Me-buserite [calculated as Mn from the initially used $Mn(NO_3)_2$ solution and assuming a preparative yield of 100%] were added to 50 ml 0.05 M HNO_3. *p*H was followed as a function of time. With the help of an automatic titrator a few exchange experiments were carried out at constant *p*H.

Results

Me-buserites, prepared by exposing Na-buserite to solutions of Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Ca^{2+}, and Mg^{2+} (table 2), give for each type specific X-ray powder patterns which are distinctly different from that of Na-buserite (Fig. 1). Each of these Me-buserites, hence, represents a defined phase; these phases may be considered end members of a large number of possible varieties. The 10 Å layer separation and the almost hexagonal symmetry in the platelet zone are common to all types. Some superstructure reflections indicate a distortion as in the case of synthetic Na-birnessite[6]. In terms of pseudo-hexagonal symmetry the unit cells (as far as determined) are very similar to each other (Table 1).

Table 1

	Co	Cu	Ni	Zn
a_0 (Å)	2,88	2,85	2,88	2,88
c_0 (Å)	9,67	9,62	9,67	9,72

The lattice contraction in Cu-buserite is significant.

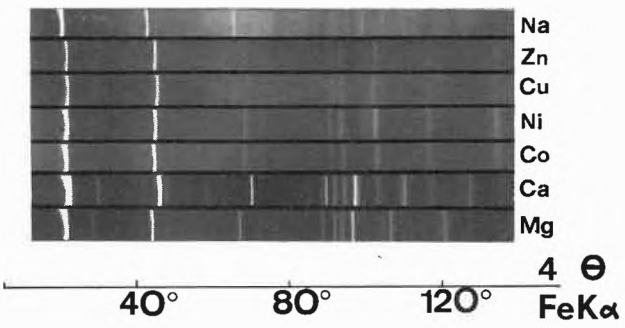

Fig. 1. X-ray powder patterns of seven varieties of Me-buserite (Guinier-de Wolff camera, FeK_α radiation). Mind the distinctive lattice contraction in Cu-buserite

The drying behaviour is given for a representative set of samples in Fig. 2. Independent from investigator, season, building, and laboratory each sample looses weight at a linear rate (the slope and the intersect depending on the particular batch) until weight constance it attained within 1 day. This state of the various samples has been reproducible and we define it as "air dried sample" to be used for analysis. All along this procedure samples were X-rayed daily.

The thermogravimetric curves and its first derivatives (Differential Thermal Gravimetry; DTG) shown in Fig. 3 for Cu- and Zn-buserite, indicate that the weight loss from Me-buserite to the respective Me-birnessite overlaps with the subsequent dehydration of Me-birnessite; no plateau is attained. The Differential Thermal Analysis curve (DTA) confirms this.

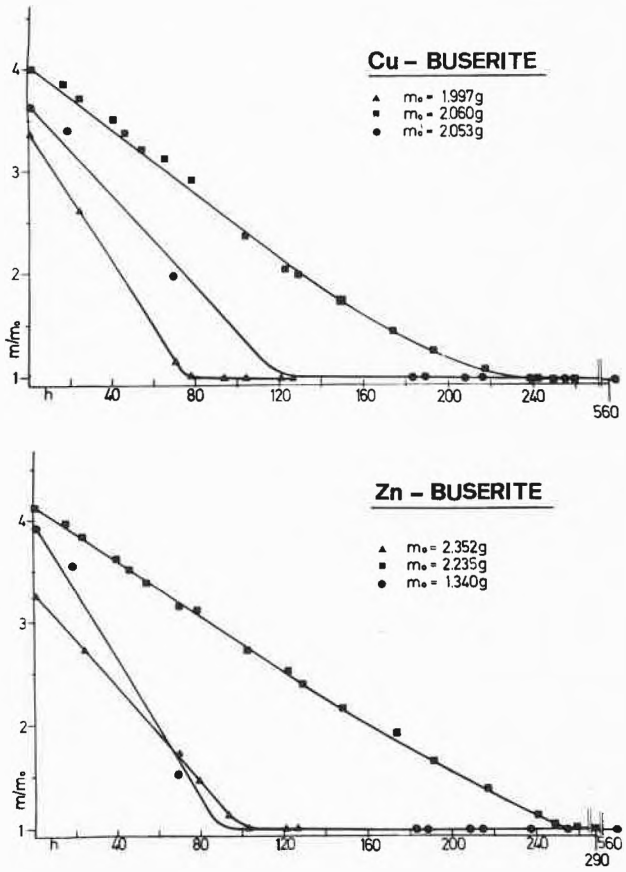

Fig. 2. Drying behaviour of two buserite varieties (three batches of each) in room air and room temperature, as a function of time

Analytical results are shown in Table 2.

Table 2

Me incorporated:	Mg	Ca	Zn	Co	Cu	Ni
Total Mn (%)	–	47,0	47,6	43,0	46,2	46,6
Oxidation degree O/Mn	–	1,79	1,88	1,88	1,89	1,88
Total Me (%)	2,77	4,88	7,83	8,54	11,77	8,77
Total H_2O (%)	23,7	23,6	16,3	16,9	14,3	17,7

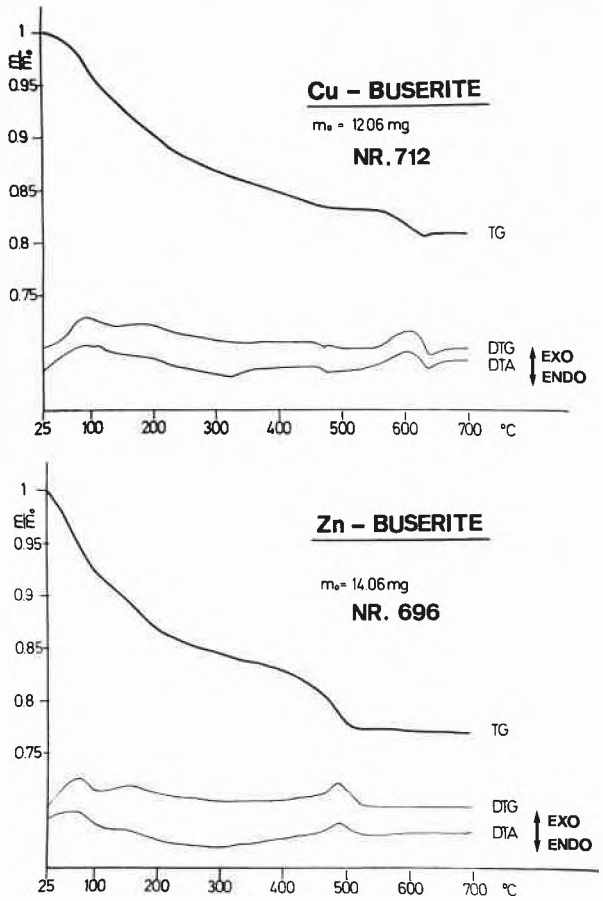

Fig. 3. Thermoanalysis curves for two varieties of Me-buserite. TG = Thermogravimetric trace; DTG = First derivative of TG; DTA = Differential Thermal Analysis; EXO = Direction of exothermal peaks; ENDO = Direction of endothermal peaks

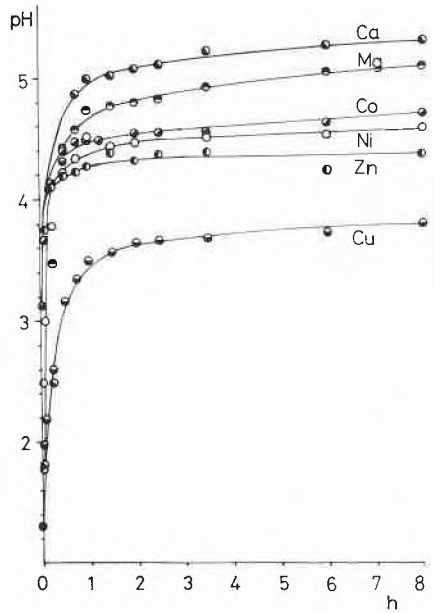

Fig. 4. *p*H change in a acid suspension of various Me-buserites. Cu-buserite is the most stable variety. Ca^{2+} is released (and H^+ ions are consumed in exchange) much faster than Cu^{2+}

Na-buserite could not be dried without decomposition. The Me contents listed are saturation values and it may be assumed that the members of the buserite group are stable also with lower Me contents.

Na-buserite, very significantly, can only undergo ion exchange with H^+ ions within a narrow, near neutral *p*H range without desintegrating. Already at *p*H 6.2, as a consequence of the partial leaching of Na^+, the lattice collapses from the 10 Å separation to the 7 Å separation, eventually forming Mn-birnessite $Mn_7O_{13} \cdot 5H_2O$. Below *p*H 6, γ-MnO_2 prisms nucleate as demonstrated previously for leaching of Na-birnessite in acid media[6]. Ca-buserite, if introduced into 0.05 M HNO_3, disappears entirely on account of a new phase presenting bipyramids. This is under way within hours while transition metal stabilized buserites are, in term of X-rays, still intact (Fig. 4). The electron micrograph of an intermediate stage with Ca-buserite (platelet shaped) and the new bipyramids is depicted in Fig. 5. The X-ray pattern of the new phase is of the hausmannite type.

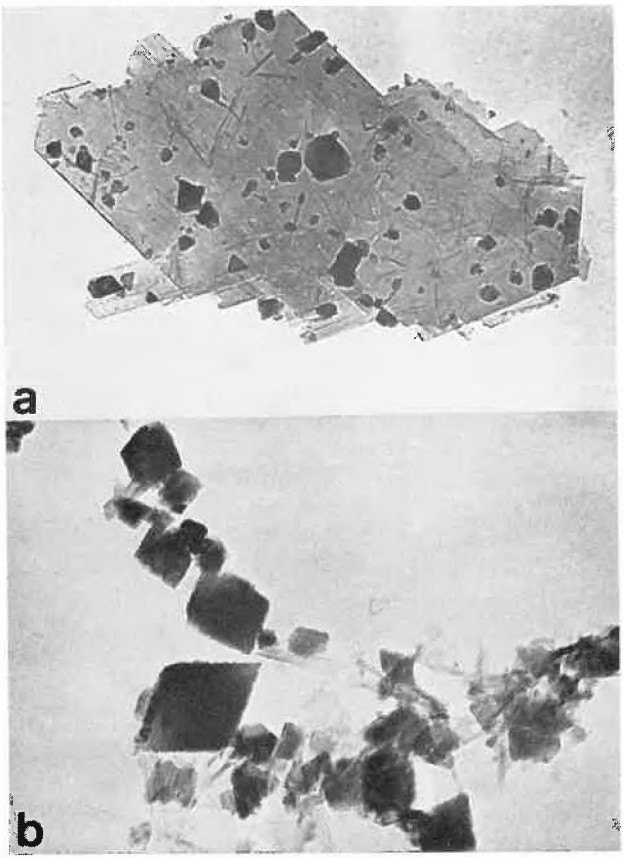

Fig. 5. Ca-buserite, partly decomposed, from experiment shown in Fig. 4. The initial platelets (a) disappear on account of a new phase in the habit of bipyramids (b) with hausmannite-type lattice. (a) = 42 000 ×, (b) = 82 000 ×

As Fig. 4 illustrates, the transition metal ions investigated appear to be more tightly built into the lattice than Ca; these latter ions are released faster and more complete upon acidification.

Conclusions

Among the transition metals, Fe ions cannot enter the buserite lattice, because Fe^{2+} would be oxidized by Mn^{4+} to insoluble Fe^{3+} to form "amorphous" $FeOOH \cdot xH_2O$[7]. The buserite lattice, although its structure remains unknown, may be interpreted in terms of Feitknecht et al.[1] and is stable under given conditions provided transition metal ions are built into the structure. Na^+, Ca^{2+} etc. may also be forced into the lattice but are released under nucleation of a hausmannite type phase or of γ-MnO_2 already at *p*H slightly below 7. It thus appears plausible that buserite varieties can only form in the presence of suitable transition metal ions *which then are incorporated selectively*. This is what Buser et al.[2] had already pointed out qualitatively.
A full account on this subject will be submitted elsewhere.

Acknowledgments

Authors are grateful to Dieter Diem (Zürich) for equilibration experiments, to Chantal Coullery (Berne) for preparations and analyses, to Emma Ettinger (Berne) for electron microscopy and other assistance, and to the Swiss National Foundation for the Promotion of Scientific Work for financial support.

Literature

1 J.W.Murray, *Geochim. Cosmochim. Acta 39* (1975) 505. See here for further references.
2 W.Marti, PhD Thesis, Berne 1944; W.Feitknecht and W.Marti, *Helv. Chim. Acta 28* (1945) 129, 149.
3 A.Grütter and W.Buser, *Chimia 11* (1952) 132; W.Buser and A.Grütter, *Schweiz. Mineral. Petrogr. Mitt. 36* (1956) 49.
4 R.M.McKenzie, *Min. Mag. 38* (1971) 493.
5 R.Giovanoli and P.Bürki, *Chimia 29* (1975) 266.
6 R.Giovanoli, E.Stähli and W.Feitknecht, *Helv. Chim. Acta 53* (1970) 209, 453; R.Giovanoli, W.Feitknecht and F.Fischer. *Helv. Chim. Acta 54* (1971) 1112; R.Giovanoli and E.Stähli, *Chimia 24* (1970) 49.
7 W.Feitknecht, R.Giovanoli, W.Michaelis and M.Müller, *Helv. Chim. Acta 56* (1973) 2847.

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Olefinbildende Elimination von Wasser aus Alkoholen mit Carbodiimidium-Verbindungen*

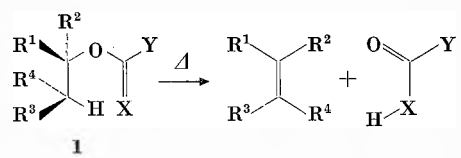
Summary

N-Methyl- N,N'-dicyclohexylcarbodiimidium-tetrafluoroborate **2a** and the corresponding fluorosulfonate **2b** are formed by alkylation of DCC. Both compounds crystallise as their DCC-adducts. **2a** and **2b** dehydrate alcohols on boiling in dioxane, toluene or heptane or by pyrolysis at 100 to 150°. From the configuration of the olefins which are formed from *threo*-1,2-diphenyl propanol and from *threo*- and *erythro*-3-deutero-2-butanol it is deduced, that *syn*-elimination is preferred over *anti*-elimination by a factor of 1,7.

Einleitung

Unter den olefinbildenden Eliminationen von Wasser aus Alkoholen sind für den Synthetiker stereospezifisch verlaufende Reaktionen von besonderem Interesse. Es sind dies vor allem die pyrolytischen *syn*-Eliminationen[1] von Estern **1a** bei 300 bis 600°, von S-Methyl-Xanthaten[2] **1b** bei 120 bis 250° (Tschugaejew-Reaktionen) und von O-Aryl-thiocarbonaten[3] **1c** bei 120 bis 200°.
Aus der Literatur[1] geht hervor, daß die für die Elimination erforderliche Pyrolyse-Temperatur sinkt, wenn bei Variation von X der Bindungsenergiegewinn beim Übergang von $O-\underset{|}{C}=X$ in $O=\underset{|}{C}-X^-$ ansteigt oder wenn bei Variation von Y die Brønsted-Basizität von X in $-O-\underset{|}{C}=X$ erhöht wird.

	X	Y
1a	O	R
1b	S	SCH_3
1c	S	O-Aryl
1d	NR	NRR'



1

Für den Praktiker ist die Senkung der Pyrolysetemperatur wohl erstrebenswert; ebenso wichtig ist ihm aber auch eine einfache Synthese des Esterderivats **1** aus dem Alkohol. Wir untersuchten deshalb Synthese und pyrolytischen Zerfall von Isoharnstoff-Derivaten **1d***. Diese lassen sich durch Cu-II-katalysierte[6] Addition von Al-

* Eingegangen am 21. November 1975.

* Ein nur auf der Differenz der Summen von mittleren Bindungsenergien[4] beruhender Vergleich der Reaktionsenthalpien der Pyrolyse von Esterderivaten **1** läßt erwarten, daß die Xanthat- bzw. Thiocarbonatpyrolyse (X = S) um etwa 8 kcal/Mol exothermer, die Iminoester- bzw. Isoharnstoffpyrolyse (X = NR) jedoch um etwa 5 kcal/mol weniger exotherm als die Esterpyrolyse (X = O) sein sollte. Ein Vergleich der relevanten Basizität der intramolekularen Base X = O, S oder N ist schwierig, da in der zyklischen *syn*-Elimination möglicherweise nicht ein unbesetztes Elektronenpaar von X, sondern die π-Elektronen der C = X-Bindung in die Reaktion einbezogen sind. Mit guten Gründen kann jedoch angenommen werden, daß die relevante Basizität im Falle von X = N größer sein dürfte.
Das unseres Wissens erste und einzige Beispiel der olefinbildenden Dehydratisierung von Alkoholen mit Carbodiimiden wurde von Corey und Mitarbeitern[5] beschrieben. Es handelt sich um den speziellen Fall der Wasserabspaltung aus einem β-Hydroxy-keton mit DCC in Gegenwart von Cu-II-Chlorid in Äther.

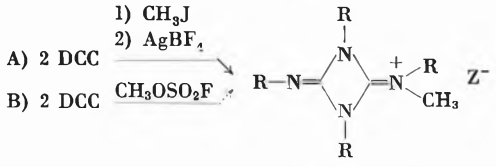
koholen an Carbodiimide oder – noch einfacher und rascher – durch Addition an N,N,N'-Trialkylcarbodiimidium-Verbindungen[7,8] darstellen.

Synthese von Eliminierungs-Reagentien

N,N,N'-Trialkyl-carbodiimidium-Verbindungen werden durch Alkylierung von N,N'-Dialkyl-carbodiimiden gebildet. Als Alkylierungsmittel wurden Dimethylsulfat[9], Trialkyloxonium-tetrafluoroborate[10] und Alkylhalogenide[7] eingesetzt. Sind die Alkylgruppen im Carbodiimid nicht extrem raumbeanspruchend, wie etwa im Di-tert.butyl-carbodiimid[10], so bilden sich in der Regel nicht die «freien» Trialkyl-carbodiimidium-Salze, sondern deren Carbodiimid-Addukte **2** (Diazetidinium-Salze). Diese verhalten sich bei Umsetzungen mit Alkoholen wie 1:1-Gemische der Addenden.

Sind Carbodiimidium- bzw. Diazetidinium-Salze **2** als Eliminierungsreagentien vorgesehen, so muß das Anion Z^- möglichst stabil und von geringer Nukleophilie sein. Eine einfache Synthese soll zudem von leicht erhältlichen Edukten ausgehen. Als Carbodiimid-Komponente kommt deshalb praktisch nur Dicyclohexylcarbodiimid (DCC) in Frage.

Es bieten sich somit zwei einfache Syntheseverfahren an:



	R	Z
2a	Cyclohexyl	BF_4
2b	Cyclohexyl	SO_3F
2c	Cyclohexyl	J

A) Methylierung von DCC mit Methyljodid[7] und anschließend Austausch des Anions J^- gegen BF_4^- mit Silberfluoroborat in CH_2Cl_2. Nach Kristallisation aus Benzol-Hexan wird **2a** (Smp. 140 bis 145°) in 68% erhalten.

B) Direkte Methylierung von DCC mit Methylfluorosulfonat in CH_2Cl_2 bei 0 bis 25°, 1 Std. und Kristallisation aus Benzol, wobei **2b** (Smp. 135 bis 140°) in 65% erhalten wird.

Sowohl **2a** wie **2b** sind kristallin und in verschlossenen Gefäßen beliebig lange haltbar.

Anwendung der Carbodiimidium-Salze als Eliminationsreagentien

Carbodiimidium-Salze der Struktur **2a** und **2b** reagieren mit Alkoholen bei 30 bis 40° unter Bildung von Isoharnstoff-Derivaten und DCC. Wird die Temperatur weiter auf 100° und mehr gesteigert, so tritt Elimination zum Olefin ein. Für die praktische Durchführung der Dehydratisierung von Alkoholen stehen zwei Verfahren offen.

A) Ein äquimolares Gemisch des Alkohols und **2a** bzw. **2b** wird langsam auf 100° und darüber erwärmt und das Olefin (allenfalls im Vakuum) abdestilliert. Das Olefin kann durch DCC verunreinigt sein.

B) Ein äquimolares Gemisch des Alkohols und **2a** bzw. **2b** wird in einem Lösungsmittel vom Sdp. etwa 100° (Dioxan, Toluol, Heptan) am Rückfluß während etwa 10 bis 20 Std. gekocht, das Lösungsmittel abdestilliert und der Rückstand an wenig Silicagel chromatographiert.

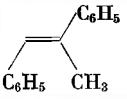
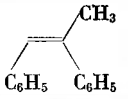
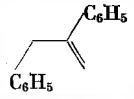
Gemäß Verfahren B wurde zum Beispiel aus 5α-Cholestan-3β-ol und dem Reagenz **2b** (16 Std. Rückfluß in Dioxan) 5α-Cholest-2-en in 97% Ausbeute gebildet.

Untersuchungen zur Stereochemie der Elimination wurden an offenkettigen Alkoholen durchgeführt. Die folgende Tabelle orientiert über die Resultate vergleichender Dehydratisierungen von *threo*-1,2-Diphenylpropanol[12] mit:

a) Reagens **2a**, 16 Std., 100° in Dioxan (Ausbeute an Olefinen 78%).

b) Chlorthionameisensäure-4-methylphenyl-ester nach Gerlach[3].

c) Über das Methylxanthat[12].

Verfahren	Reaktionstemperatur	Produkte		
				
a	100°	29%	53%	18%
b	100–200°	17%	83%	Spuren
c[12]	145–195°		65% c)	

Es ist auffallend, daß die Dehydratisierung von *threo*-1,2-Diphenylpropanol mit **2a** als Hauptprodukt das thermodynamisch instabilere[13] *cis*-α-Methylstilben, also das Produkt einer *syn*-Elimination, liefert.

Weitere Studien zur Stereochemie der Dehydratisierung wurden an *threo*- und *erythro*-3-Deuterio-2-butanol[14] durchgeführt. Die Elimination erfolgte mit **2a** in Dioxan bei 90 bis 100°. Die praktisch quantitativ gebildeten Butene wurden gaschromatographisch getrennt[15].

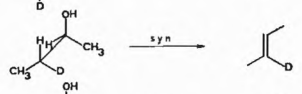
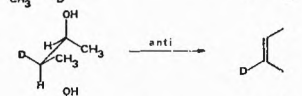
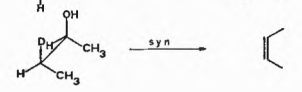
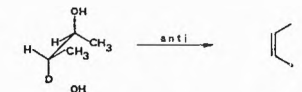
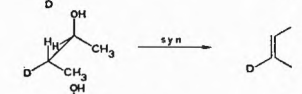
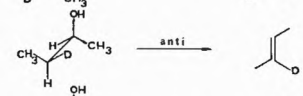
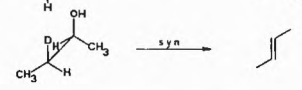
Olefin	aus *erythro*-Alkohol	aus *threo*-Alkohol
1-Buten	20%	20%
trans-2-Buten	47%	43%
cis-2-Buten	33%	37%

Die reinen *cis*- bzw. *trans*-Butene wurden anschließend massenspektroskopisch auf ihren Gehalt an Deuterium untersucht.

In der folgenden Tabelle ist die Produktverteilung der deuterierten bzw. nichtdeuterierten *cis*- und *trans*-2-Butene mit den korrespondierenden Konformationen der Edukte korreliert.

Die Produktverteilung erlaubt folgende Schlüsse:

a) Aus dem Vergleich der Ausbeuten an strukturell gleichen Olefinen bei der Eliminierung von Wasser aus dem *erythro*- und *threo*-Alkohol (paarweiser Vergleich von A und H, B und G, C und F, D und E) geht hervor, daß die *syn*-Elimination gegenüber der *anti*-Elimination im Mittel um den Faktor 1,7 bevorzugt ist.

Elimination von Wasser aus *erythro*-3-Deuterio-2-butanol		Produktverteilung [a]
A		15 %
B		45 %
C		20 %
D		20 %
Elimination von Wasser aus *threo*-3-Deuterio-2-butanol		
E		10 %
F		35 %
G		30 %
H		25 %

[a] Bezogen auf die Summe der 2-Butene = 100%.

b) Aus dem Vergleich der Ausbeuten von deuteriertem und nichtdeuteriertem Olefin gleicher Konfiguration und gleicher Bildungsweise (*syn* bzw. *anti*) (paarweiser Vergleich von A und G, B und H, C und E, D und F) geht hervor, daß der Isotopeneffekt im Mittel 2,0 beträgt.

Die Arbeit wurde durch den Schweizerischen Nationalfonds zur Förderung der wissenschaftlichen Forschung, Projekt 2.0410.73, unterstützt.

Literaturverzeichnis

1 C. H. De Puy und R. W. King, *Chem. Rev. 60* (1960) 431.
2 H. R. Nace, *Org. Reactions 12* (1962) 57.
3 H. Gerlach, T. T. Huong und W. Müller, *J. Chem. Soc. Chem. Commun.* (1972) 1215; W. Müller, Diss. ETH Nr. 4807 (1972).
4 J. D. Cox und A. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, London/New York 1970, S. 525 ff.
5 E. J. Corey, N. H. Anderson, R. M. Carlson, J. Paust, E. Vedejs, I. Vlattas und R. E. Winter, *J. Amer. Chem. Soc. 90* (1968) 3245.
6 E. Schmidt und F. Moosmüller, *Liebigs Ann. Chem. 597* (1956) 235.
7 R. Scheffold und E. Saladin, *Angew. Chem.* 84 (1972) 158.
8 E. E. von Tamelen und R. C. Schnur, *J. Amer. Chem. Soc. 97* (1975) 464.
9 K. Hartke und F. Roßbach, *Angew. Chem.* 80 (1968) 83; K. Hartke und H. Radau, *Arch. Pharmaz.* 305 (1972) 654.
10 K. Hartke, F. Roßbach und M. Radau, *Liebigs Ann. Chem. 762* (1972) 167.
11 E. Saladin, Diss. Nr. 693 Universität Freiburg (Schweiz), 1974; U. Mareis, Diss. Universität Bern, 1975.
12 D. J. Cram und F. A. Elhafez, *J. Amer. Chem. Soc. 74* (1952) 5828.
13 D. J. Cram, F. D. Greene und C. H. De Puy, *J. Amer. Chem. Soc. 78* (1956) 790.
14 P. S. Skell, R. G. Allen und G. K. Helmkamp, *J. Amer. Chem. Soc. 82* (1960) 410.
15 S. M. Csicsery und H. Pines, *J. Chromatogr. 9* (1962) 34.

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