Kurze Mitteilungen

Bis zum 15. des Monats bei der Redaktion eingehende Kurze Mitteilungen werden in der Regel am 15. des folgenden Monats veröffentlicht. Es werden auch Manuskripte aus dem Ausland angenommen, Maximalumfang: 6 Schreibmaschinenseiten (alles inbegriffen).

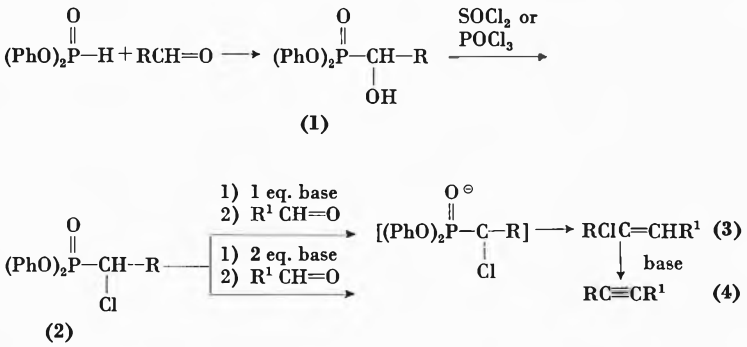
Syntheses with α-Heterosubstituted Phosphonate Carbanions (III): Diacetylenes and Substituted Vinyl Chlorides

Summary

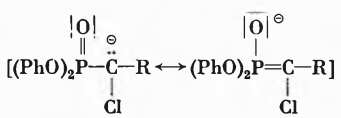
Syntheses of diacetylenes and substituted vinyl chlorides *via* α-heterosubstituted phosphonate carbanions are described. They serve as further examples for the usefulness of these species in a novel modification of the Wittig-Horner reaction.

The utility of α-heterosubstituted phosphonate carbanions in a modified Wittig-Horner[1] reaction for the preparation of chemically sensitive compounds is further demonstrated by successfully synthesizing examples of the title compounds through a simple reaction sequence from easily available starting materials. The syntheses proceeded according to Scheme (I).

Schema (I)



The α-hydroxybenzylphosphonic acid esters, **1**, were obtained by known methods[1a,2]. Their conversion into α-chlorobenzylphosphonic acid esters was achieved by treatment with thionyl chloride. In several instances phosphorus oxychloride was found to give slightly purer type **2** compounds[1c]. The substituted vinylchlorides, **3**, were obtained as a mixture of E- and Z-isomers. Though the isomers could be separated by column chromatography, so far no systematic attempt was made to investigate the stereochemistry of this reaction. The acetylenes, type **4** compounds, were obtained either from the appropriate type **2** compound by generating the corresponding carbanion



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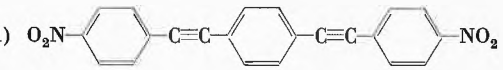
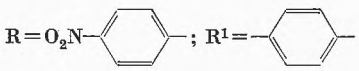
in the presence of 100 % excess base followed by addition of the appropriate aldehyde, or by first isolating a type **3** compounds and dehydrohalogenating it in a separate step. The yields of the acetylenes were generally good (> 50 %), regardless of whether they were obtained directly or *via* the vinylchlorides. The yields of type **3** compounds generally were quite satisfactory. Sometimes, however, it was difficult to prepare analytical samples freee of acetylenic impurities.

The following diacetylenes were obtained:

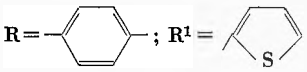
1) 

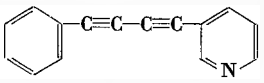
1,4-bis-[(4-nitrophenyl) ethynyl] benzene
m.p. 253 to 254°



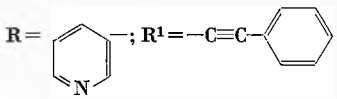
2) 

1,4-bis-[(2-thienyl) ethenyl] benzene
m.p. 197.5 to 199°



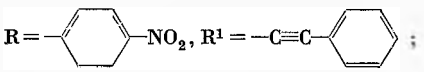
3) 

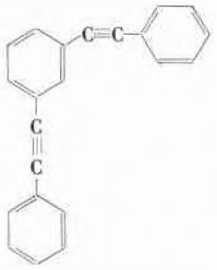
1-phenyl-4-(3-pyridyl) butadiyne
m.p. 108 to 109°

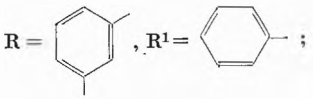


4) 

1-phenyl-4-(4-nitrophenyl) butadiyne
m.p. 213 to 214° [3]



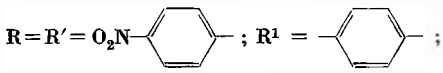
5)  1,3-bis (phenylethynyl) benzene
m. p. 111 to 113,5[4]



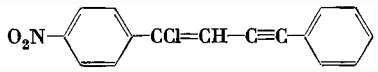
The following substituted vinyl chlorides were prepared:

1) 

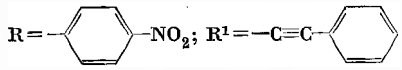
1,4-bis [2-chloro-2 (4-nitrophenyl)-ethenyl)] benzene;
m. p. 178 to 298°



C 59.88; H 3.20; N 6.35; found C 59.86; H 3.58; N 6.28; the material is apparently a mixture of (all possible) geometric isomers.

2) 

1-(4-nitrophenyl)-1-chloro-4-phenylbuta-1-ene-3-yne
m.p. 123.5 to 124°.



The analyses of all the compounds gave satisfactory: values; also all the structures were in agreement with NMR- and IR-data.

Experimental

The following procedure should serve as an example for syntheses with α-heterophosphonate carbanions to give type 3 and 4 compounds:

1-(4-Nitrophenyl)-1-chloro-4-phenylbuta-1-ene-3-yne

To a solution of 8.08 g (0.020 mole) diphenyl (α-chloro-*p*-nitrobenzyl)-phosphonate in 40 ml anhydrous dimethylsulfoxide (in a flask fitted with a drying tube and equipped with a magnetic stirrer) was added 0.915 g of 52.5% sodium hydride in mineral oil (0.020 mole), and the mixture was stirred at room temperature for one hour. To the mixture was added a solution of 2.60 g (0.020 mole) phenylpropargyl aldehyde (freshly distilled) in 20 ml anhydrous dimethyl sulfoxide. The mixture was stirred at room temperature overnight. The reaction mixture was then shaken with ice water, extracted with ether, the ether extracts were washed with water, shaken with saturated sodium chloride solution, and dried over anhydrous sodium sulfate. After filtration and evaporation of the ether, there was 3.08 (0.0109 mole) of yellow crystals which melted at 120 to 123° (54% yield). Two recrystallizations from methanol produced the desired compound, melting at 123.5–124°. Anal. calc. for $C_{16}H_{10}ClNO_2$: C, 67.73; H, 3.55; N, 4.94. Found: C, 67.67; H, 3.64; N, 5.08.

1-Phenyl-4-(4-Nitrophenyl) butadiyne

To a solution of 0.24 g (0.000845 mole) 1-(4-Nitrophenyl)-1-chloro-4-phenylbuta-1-ene-3-yne in 20 ml anhydrous dimethylsulfoxide (in a flask fitted with a drying tube, and equipped with a magnetic stirrer) was added 0.04 g of 50.3% sodium hydride in mineral oil (0.000845 mole). The reaction mixture was stirred overnight at room temperature. The mixture was then shaken with ice water and the aqueous mixture was extracted with ether. The ether extracts were washed with water, shaken with saturated sodium chloride solution, and dried over anhydrous sodium sulfate. After filtration and evaporation of the ether, yellow crystals of compound 4 were obtained in 96% yield (0.02 g, 0.00082 mole) which melted at 213 to 214° (MeOH). Anal. calc. for $C_{16}H_9NO_2$: C, 77.72; H, 3.67; N, 5.67. Found: C, 77.34; H, 4.03; N, 5.68.

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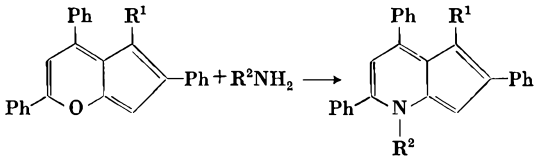
Darstellung und Elektronenspektren stabiler Pseudoazulene; neue Beispiele für Fluoreszenzanomalien*

Summary

The syntheses, ultraviolet and luminescence spectra of 1 H-pyrindines and 4 H-cyclopenta [b] chinolines, which are iso-π-electronic heteroanalogs of azulene are described and discussed.

Beim Ersatz einer C=C-Bindung in Azulenen durch ein S-Atom, ein O-Atom oder eine R–N-Gruppe erhält man die Verbindungsklasse der Pseudoazulene[1]. Zu den einfachsten Vertretern dieser aromatischen Systeme gehören die 1 H-Pyrindine und 4 H-Cyclopenta [b] chinoline. Derartige Stoffe sind bisher nur durch vielstufige Synthesen mit teilweise schlechten Ausbeuten zugänglich[1–4]. Wie wir fanden, erhält man beim kurzzeitigen Kochen der Cyclopenta [b] pyrane **1a** und **1b** oder deren Perchlorate[5, 6] mit einem Überschuß an Anilin, Benzylamin oder Butylamin in Dimethylformamid mit guten Ausbeuten die bisher unbekannten 1 H-Pyrindine **2a-f**; vgl. Tabelle 1. Offensichtlich ist die in Dimethylfor-

* Eingegangen am 23. Juli 1974.

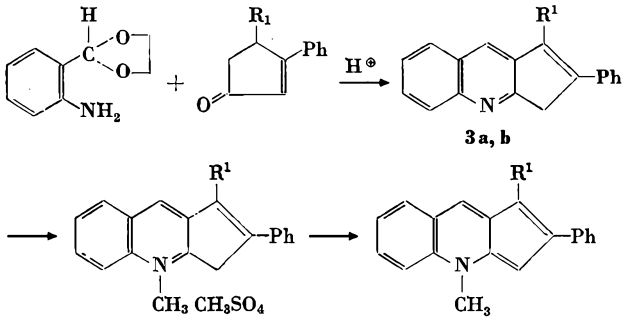


1a, b **2a-f**

1a: $R^1 = H$; **1b:** $R^1 = Ph$

mamid erreichbare Reaktionstemperatur ein entscheidender Faktor: beim Kochen in Äthanol sind **1a** und **1b** gegenüber Aminen stabil. Die so erhaltenen Verbindungen sind im Gegensatz zu zahlreichen anderen Pseudoazulenen thermisch stabil, werden beim kurzzeitigen Kochen in Säuren oder Laugen nicht zersetzt und können an neutralen Aluminiumoxidsäulen gut gereinigt werden.

Die schon bekannten 4H-Cyclopenta[b]chinoline **5a** und **5b**[2] sind von uns auf folgendem neuem Wege synthetisiert worden:



3a, b **4a, b** **5a, b**

a: R = H; **b:** R = Ph

Die Ausbeuten des Kondensationsschrittes betragen etwa 80%. Bei der Quaternierung arbeitet man zweckmäßigerweise unter Luftausschluß, da **3a** und **3b** durch Sauerstoff zur 3-Ketoverbindung oxydiert werden können. Die Pseudoazulene **5a** und **5b** sind entgegen Literaturangaben[2] thermisch recht stabil; auch nach 4wöchigem Stehen bei Zimmertemperatur ist noch kein merklicher Zerfall festzustellen.

Die Absorptionsdaten der Verbindungen **2a-f** und **5a,b** enthält Tabelle 1. Ein Vergleich der längstwelligen Absorptionsbande mit der von carbozyklischen Produkten ist nur qualitativ möglich, da die entsprechend substituierten Azulene unbekannt sind. Das 1H-Pyrindin **2a** absorbiert 60 bis 70 nm kurzwelliger als 2-Phenylazulen[7]*, während 2-Phenyl-4-methylcyclopenta[b]chinolin **5a** im gleichen Bereich wie 5,6-Benzazulen[8] absorbiert. Derartige Unterschiede im Absorptionsverhalten zwischen den Pseudoazulensystemen **2** und **5** treten beim Vergleich mit den analogen Oxopseudoazulenen ebenfalls auf: Die längstwellige Bande von **2a-f** liegt im gleichen Bereich wie bei den Cyclopenta[b]pyranen **1**; **5a** und **5b** absorbieren dagegen um etwa 50 nm längerwellig als Benzo[b]cyclopenta[e]pyrane[2]. Auch der Einfluß einer Phenylgruppe in 1- bzw. 7-Stellung ist bei **5** größer als bei **2**. N-Substituenten verändern die langwellige Absorption der 1H-Pyrindine **2** nur unbedeutend. Das langwellige Absorptionsmaximum aller acht Pseudoazulene besitzt eine negative Solvatochromie.

Die 1H-Pyrindine **2a-f** und Cyclopenta[b]chinoline **5a,b** fluoreszieren schwach. Wie an den Verbindungen **2d** und **5b** näher untersucht wurde, ist bei diesen Pseudoazulenen eine den Azulenen vergleichbare Fluoreszenzanomalie[10] vorhanden. Das Fluoreszenzmaximum (gemessen in *n*-Hexan) von **2d** liegt bei 435 nm, die Maxima von **5b** bei 405 und 426 nm (mit einer Schulter bei 450 nm). Diese Spektren sind unabhängig von der Wellenlänge des Anregungslichtes (254, 313,

* Ein solcher Vergleich ist zweckmäßig, da Phenylsubstituenten im Siebenring das Spektrum von Azulen kaum verändern[9].

Tabelle 1. Konstanten und UV-Daten der 1H-Pyrindine **2a-f** und 4H-Cyclopenta[b]chinoline **5a,g**

Nr.	R^1	R^2	Ausbeute %	F. °C	max. (lg) a) nm				
2a	H	Ph	87	202	268 (4,39)		310 (4,09)	395 (4,32)	523 (3,37)
					269 (4,38)		310 (4,07)[b]	390 (4,28)	503 (3,23)
2b	H	$PhCH_2$	82	178	262 (4,61)		310 (3,30)[b]	388 (4,57)	510 (3,37)
					264 (4,45)		310 (3,29)[b]	385 (4,42)	494 (3,29)
2c	H	$CH_3(CH_2)_3$	64	193	260 (4,43)		310 (4,19)[b]	384 (4,41)	506 (3,26)
					264 (4,41)		310 (4,20)[b]	379 (4,38)	490 (3,17)[b]
2d	Ph	Ph	92	268	255 (4,47)	275 (4,37)	318 (4,28)	386 (4,26)	533 (3,32)
					254 (4,41)	275 (4,34)[b]	312 (4,26)	382 (4,25)	514 (3,27)
2e	Ph	$PhCH_2$	90	182	256 (4,50)	275 (4,37)[b]	313 (4,42)	382 (4,37)	520 (3,32)
					255 (4,48)		312 (4,41)	377 (4,33)	506 (3,26)
2f	Ph	$CH_3(CH_2)_3$	81	162	254 (4,43)	275 (4,36)[b]	313 (4,34)	378 (4,38)	516 (3,26)
					254 (4,42)		311 (4,31)	373 (4,33)	500 (3,20)
5a[c]	H		90	153	284 (4,56)	305 (4,33)[b]	373 (4,38)	392 (4,33)	542 (3,25)
5b	Ph		94	193	290 (4,56)	307 (4,53)[b]	373 (4,41)	385 (4,38)	562 (3,24)
					290 (4,54)	307 (4,50)[b]	372 (4,40)	384 (4,37)	557 (3,21)

a) Obere Reihe Lösungsmittel · *n*-Hexan, untere Reihe Methanol; b) Schulter; c) es treten noch Schultern bei 337 nm (4,01) und 355 nm (4,30) auf.

366, 406 nm) und werden kaum vom Lösungsmittel beeinflußt (*n*-Hexan, Äthanol, Benzol). Die Quantenausbeuten betragen für **5b**: $7{,}3 \cdot 10^{-4}$ (366 nm Anregungswellenlänge) und $7{,}0 \cdot 10^{-4}$ (313 nm Anregungswellenlänge), die für **2d** liegen bei etwa 10^{-5}*. Alle Fluoreszenzdaten sind unabhängig von der Reinigungsmethode für **2d** und **5b**; d.h. die Fluoreszenz wird tatsächlich von den Pseudoazulenen verursacht. Die Fluoreszenzbande entspricht in ihrer Lage und ihrer Symmetrie der Absorptionsbande bei etwa 390 nm, für die nach quantenchemischen Rechnungen ein $S_0 \rightarrow S_2$-Übergang anzunehmen ist[11]. Demnach wird die Fluoreszenz von **2d** und **5b** durch einen $S_2 \rightarrow S_0$-Übergang hervorgerufen.
Ein analoges Ergebnis haben wir auch bei Oxopseudoazulenen gefunden.

Experimenteller Teil

1,2,4,5,6-Pentaphenyl-1H-pyrindin **2d**. Ein Gemisch von 0,53 g (0,001 Mol) 2,4,5,6-Tetraphenylcyclopenta[b]pyryliumperchlorat[6] und 0,46 g (0,005 Mol) Anilin in 5 ml Dimethylformamid wird 3 Min. zum Sieden erhitzt. Nach dem Abkühlen setzt man 1 ml Wasser zu, saugt den Niederschlag ab, wäscht mit Wasser und kristallisiert aus Acetonitril um.
1,2-Diphenyl-4-methylcyclopenta[b]chinolin **5b**. 1,2 g (0,005 Mol) 1,2-Diphenylcyclopenten-2-on und 0,8 g (0,005 Mol) o-Aminobenzaldehydäthylenacetal werden in 10 ml 60prozentigen Äthanol unter Erwärmen gelöst, 2,5 ml konz. HCl hinzugefügt und anschließend 45 Min. gekocht. Den nach dem Abkühlen ausfallenden Niederschlag saugt man ab, löst ihn in Methanol, fügt wäßrige KOH bis zum *p*H 9 hinzu und saugt den Niederschlag ab. Ausbeute an 1,2-Diphenyl-3H-cyclopenta[b]chinolin **3b** 1,5 g (90%) F.180°C (Dimethylformamid). 1,3 g (0,004 Mol) **3b** und 0,42 g (0,0042 Mol) Dimethylsulfat werden unter N_2-Atmosphäre 2 Std. in 20 ml Benzol gekocht. Den Niederschlag saugt man ab; Ausbeute an 1,2-Diphenyl-3H-4-methylcyclopenta[b]chinoliniummethosulfat **4b** 1,55 g (90%); F.167°C (Acetonitril). 1,35 g (0,003 Mol) **4b** werden unter Erwärmen in Äthanol gelöst, 7 ml 1-n NaOAc-Lösung hinzugefügt, der blaue Niederschlag abgesaugt und mit Wasser gewaschen.

* Gemessen gegenüber Chininsulfat in 1*n* H_2SO_4.

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1-(2-Pyridylazo)-2-Phenanthrol (PAP) as an Extractive Chromogenic Reagent for Platinum (IV)*

Summary

Platinum (IV) forms a green complex with 1-(2-pyridylazo)-2-phenanthrol (ten fold excess) when heated on a boiling water bath for about 2 hours (*p*H 2.9 to 5.5). The complex is soluble in 75% ethanol, methanol and extractable in chloroform and shows maximum absorbance at 670 nm. Beer's law is obeyed upto 7.943 ppm of platinum at 670 nm. The sensitivity of the method is 0.0283 μg Pt (IV)/cm^2 for log $I_0/I = 0.001$ and the molar extinction coefficient $\epsilon_{670} = 8400$ litre mole^{-1} cm^{-1}. The composition of the complex is 1:1 as determined by Job's method. The possibility of determining platinum (IV) in the presence of various diverse ions has also been investigated.

2-Pyridylazo compounds have shown immense analytical applicability[1]. 1-(2-Pyridylazo)-2-phenanthrol (PAP) is comparatively a newer ligand of this series and has been found to act as a terdentate complexing agent to give stable chelates[2-3]. Recently the use of this reagent as visual indicator in EDTA titrations of Cu (II)[4], Ni (II), Zn (II), Cd (II), Pb (II)[5] and as a spectrophotometric reagent for Co (II)[6] and UO_2 (II)[7] has been reported. Interest in the determination of platinum in the presence of several elements associated with it, has increased with the increasing use of this metal. The present communication describes 1-(2-pyridylazo)-2-phenanthrol (PAP) as an extractive chromogenic reagent for platinum (IV).

* Received August 1, 1974.

Materials and methods

A Unicam SP 600 spectrophotometer with 10 mm optically matched cells was used for absorbance and a Metrohm E 310 *p*H meter for *p*H measurements.
PAP was prepared by the method of Chiswell et al.[1] and purified by crystallization in dry benzene. A stock solution of PAP (0.025 M) was prepared in ethanol and subsequent dilutions were made from this stock solution.
A standard solution of platinum (IV) was prepared by dissolving 1 g of platinum thermocouple wire (99.99% pure) in aqua regia. The solution was evaporated to dryness, extracted with conc. HCl and again evaporated to dryness. The treatment was repeated three to four times to destroy the nitroso complexes. Finally, 5 ml of hydrochloric acid was added and the solution was filled up to 500 ml.
Sodium acetate-acetic acid buffers were used to adjust the *p*H of the solutions. Freshly distilled chloroform was used for extraction.

Recommended procedure for the determination of platinum (IV)

The *p*H of the solution containing 29.25 to 74.99 μg of platinum and 4 ml of 0.0025 M reagent solution is adjusted to 2.9 to 5.5 by sodium acetate-acetic acid buffer (3 ml) and diluted to 10 ml with water. The content is heated on a boiling water-bath for about 2 hrs to ensure complete complexation. The solution is cooled to room temperature and the resulting complex is extracted with 10 ml chloroform. The absorbance of the solution is measured against a chloroform blank. The platinum content is obtained from a precalibrated curve.

Results and Discussion

Spectral studies and effect of various factors

Complex formation between PAP and platinum(IV) is very slow at room temperature. It increases at elevated temperature and is completed after heating for about 2 hours on a boiling water bath, as evidenced by the constancy in the absorbance values.

The complex shows maximum absorbance at 670 nm, where absorbance of PAP is practically nil. In view of these facts, all the subsequent studies have been made at 670 nm using chloroform as blank.

The effect of *p*H on complexation was investigated by preparing a series of solutions containing fixed amounts of platinum and a constant excess (20 fold excess) of reagent. The results show maximum colour development in the *p*H range 2.9 to 5.5. Subsequent studies were therefore carried out at *p*H 4.2 ± 0.2.

The dependence of percentage extraction and extraction coefficient (E) on *p*H is shown below.

*p*H	Extraction %	E
1.5	35.71	0.55
2.0	58.9	1.38
2.3	71.42	2.49
2.5	83.33	5.00
2.9	100.00	∞
3.6	100.00	∞
5.0	100.00	∞
6.1	84.00	5.25
7.0	43.7	1.29

At constant metal ion concentration, the absorbance is found to increase with increase of the concentration of the reagent and becomes practically constant at about 10 fold excess of the reagent, so that, twenty fold excess of the reagent was used in further studies.

Optical constants and composition of complex

The system obeys the Beer's law upto 7.943 ppm of platinum. The accurate range for determination as evaluated from Ringbom plot is 2.925 to 7.499 ppm of platinum and the sensitivity of the method at 570 nm is 0.0283 μg/cm² for $\log I_0/I = 0.001$. The molar absorptivity is 8.4×10^3 litre mole^{-1} cm^{-1}. Job's method[8] of continuous variation indicates the formation of 1:1 (metal:ligand) complex.

Absorbance deviations

The precision of the method was tested by measuring the absorbance of eight samples each containing a final platinum concentration of 4.87 ppm. The mean absorbance was found to be 0.210 with an average relative deviation of ± 0.2 %.

Accuracy of the procedure

The absorbance measurements of a series of solutions containing different amounts of platinum in the optimum range revealed that the determination may be carried out within ± 1.05 % error.

Effect of diverse ions

A series of synthetic solutions containing known amounts of platinum (4.87 ppm) and varying amounts of diverse ions were prepared and their platinum content was determined following the recommanded procedure. The results are shown in Table 1.

Table 1. Effect of diverse ions

Diverse ion	Tolerance limit (ppm)
Chloride	500
Bromide, nitrate	400 each
Sulphate	500
Tartrate, oxalate	400 each
Citrate	200
Borate	150
Phosphate	100
Fluoride	200
Iodide	150
Thiorea	Interferes
Thiocyanate	Interferes
EDTA	Interferes
Bi(III)	20
Ba(II), Sr(II), Ca(II)	20 each
Lanthanides(III)	15 each
Os(VI)	5
Ir(III)	does not interfere

Determination of Pt (IV) in presence of Fe (III), Co (II), Ni (II), Cu (II), Pd (II) or UO_2 (II)

Since Pt(IV)-PAP complex is formed only on heating and all the above cations form complexes with PAP at room temperature, which are quantitatively extractable in chloroform at appropriate *p*H's, it is possible to avoid their interference in the determination of Pt(IV) by following the procedure described below.

To a solution containing 50 μg of Pt(IV) and 150 μg of the interfering cation, taken in a 50 ml separating funnel, is added an excess of ethanolic solution of PAP (7.5 ml, 0.0025 M). The *p*H of the content is raised to an appropriate value [Fe(III): 2.5; Co(II): 3.5; Ni(II): 4.5; Cu(II): 5.0; Pd(II): 4.0; V(V): 5.5; UO_2(II): 5.0] with acetate buffers and the volume of the aqueous phase is made up to 10 ml. The resulting mixture is extracted thrice with 10 ml of

chloroform. The foreign cation is quantitatively extracted under these conditions, while Pt(IV) remains in the aqueous phase. The aqueous solution is transferred to a spectrophotometric bottle and the volume is reduced to about 4.0 ml. To this solution is added 4.0 ml of 0.0025 M PAP solution, *p*H adjusted to 4.1 with acetate buffer and the contents heated on a water bath for about two hours. After cooling to room temperature, the platinum complex is extracted into 10.0 ml of chloroform. The absorbance of the extract is measured at 670 nm against chloroform blank and the Pt(IV) content is deduced from the calibration curve.

The present method, involving PAP as colorimetric extractive reagent for platinum(IV), has a sensitivity comparable with other known spectrophotometric methods for platinum(IV). The *p*H range for colour development is not too narrow to work with and only a ten fold excess of reagent is required for complete complexation. Moreover, use of the reagent blank is also avoided, since the reagent does not absorb at the maximum of the complex (670 nm).

Acknowledgement

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3-Nitroso-4-hydroxy-5,6-benzocoumarin (NHBC) as a reagent for the spectrophotometric determination of copper(II) in alloys*

Summary

Copper(II) forms in the *p*H range 6.3 to 7.8 a yellowish brown complex with 3-nitroso-4-hydroxy-5,6-benzocoumarin which is soluble in a 60% dioxan medium giving a deep yellow coloured solution. Beer's law is obeyed up to 2.80 ppm of copper(II) at 420 nm. The sensitivity of the colour reaction is 0.0032 μg Cu(II)/cm^2, for log I_0/I = 0.001 and the molar absorptivity is 1.98×10^4 litre mole^{-1} cm^{-1}. The composition of the complex is 1:2 as determined by Job's and mole ratio methods. The colour reaction of copper(II) with NHBC has been made the basis for spectrophotometric determination of copper in alloys containing iron, zinc, nickel and copper.

3-Nitroso-4-hydroxy-5,6-benzocoumarin (NHBC) is a chelating agent which forms coloured complexes with most of the transition metals, including platinum metals. It has already been used as a reagent for the determination of nickel[1], ruthenium[2] and for the detection of iron[3] and cobalt[4]. In the present communication the use of NHBC as a spectrophotometric reagent for the determination of copper is reported.

NHBC forms yellowish brown complex with copper(II) which is soluble in 60% dioxan medium, giving deeply coloured solution. This reaction can be used for a sensitive spectrophotometric determination of copper. The Interference of other cations can be easily avoided using suitable masking agents.

Experimental

All the absorbance measurements were made with a Unicam SP-600 spectrophotometer, with matched 10 mm cells. A Metrohm *p*H meter, type E350, was used for *p*H measurements.

A stock solution (1×10^{-2} M) of 3-nitroso-4-hydroxy-5,6-benzocoumarin* (NHBC) was prepared with pure freshly distilled 1,4-dioxan as solvent. For the copper (II) stock solution (1×10^{-2} M) reagent grade copper sulphate pentahydrate and doubly distilled water were used; it was standardized gravimetrically.

Results

The absorption spectra of the reagent NHBC alone and the copper complex against the reagent are recorded in Fig. 1. The copper complex shows an absorption maximum at 420 nm. Since the absorbance of the reagent at this wave length is significant, reagent blanks were employed in subsequent studies.

Complete complexation takes place instantaneously on mixing the reactants. The absorbance was found to remain constant for at least 3 hrs in a 60% dioxan medium, than the copper complex gradually precipitates.

The effect of *p*H on the colour development was studied by preparing a series of solutions varying in *p*H from 3.0 to 9.0. Absorbance measurements were made at 420 nm. *p*H adjustments were made with sodium acetate (0.2M) – acetic acid (0.2M) buffers. For lower and higher *p*H's dilute solutions of hydrochloric acid and

* Received August 9, 1974.

* *Method of preparation of NHBC:* Starting material for the preparation of NHBC is β-naphthol which was first acetylated with acetic anhydride to give β-naphthyl acetate which on Fries migration in presence of anhydrous $AlCl_3$ yielded 1-acetyl-2-naphthol. 1-Acetyl-2-naphthol, on condensation with diethyl carbonate in presence of sodium metal gave 4-hydroxy-5,6-benzocoumarin. Finally, 3-nitroso-4-hydroxy-5,6-benzocoumarin was obtained by the nitrosation of 4-hydroxy-5,6-benzocoumarin with $NaNO_2$/HCl at 0°C; m.p. 178 to 180°(d).

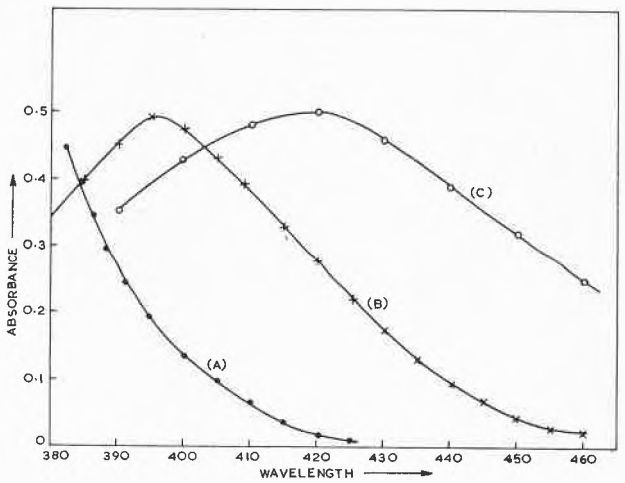

Fig. 1. Absorption spectra of reagent, Ni-NHBC complex and Cu-NHBC complex. A. Reagent alone against water, B. Ni-NHBC complex against reagent, C. Cu-NHBC complex against reagent. Reagent = 2.5×10^{-3} M; Nickel = 2.0×10^{-5}; Copper = 2.5×10^{-5} M

sodium hydroxide were employed. No change in absorbance was observed over the *p*H range 6.3 to 7.8. At higher or lower *p*H values, absorbance of the solutions decreases. Subsequent studies were therefore carried out at *p*H 7.0.

It has been found that 5 moles of the reagent per mole of cobalt are adequate for full colour development, beyond which ratio a constancy in absorbance was observed. However, a 10 times molar excess of the reagent was maintained in subsequent studies.

The system was found to obey Beer's law up to 2.80 ppm of copper. The optimum concentration range for an accurate determination of copper, as deduced from Ringbom's method[5], was found to be between 0.63 and 2.14 ppm. The sensitivity of the colour reaction, as calculated from Beer's law plot, is 0.0032 μg of copper/cm^2 for log I_0/I = 0.001. The molar absorptivity is 1.98×10^4 litre mole^{-1}cm^{-1}.

The ratio of copper to NHBC in the complex was determined by Job's method of continuous variations[6]. The curve indicated the formation of a 1:2 complex. The conclusion reached by the mole ratio method is in agreement with it.

The apparent instability constant calculated by using the conventional relationships $\alpha = E_m - E_s/E_m$ and $K = \frac{C(n\alpha C)^n}{C(1-\alpha)}$, was found to be 2.5×10^{-11}, at room temperature at *p*H 7.0 (where C is the concentration of the complex in moles/litre and $n = 2$). At *p*H 7.0 and 25 °C the values of E_m and E_s were found to be 0.500 and 0.400 respectively, where E_s is the absorbance at the mole ratio 1:2 and E_m is the maximum absorbance. The value of degree of dissociation α was found to be 0.200.

Synthetic samples containing known amounts of copper (II) and varying amounts of diverse ions were prepared and copper was determined in their presence. Using 1.59 ppm of copper (at *p*H 7.0), it was found that the following ions, present in amounts in ppm shown in parentheses, did not cause a deviation of more than ± 2% in absorbance: chloride (3000), bromide (2500) iodide (2500), sulphate (5000), nitrite (2000), nitrate (3000), thiocyanate (250), sulphite (200), fluoride (250), persulphate (500), iodate (500), Ba(II) (150), Ca(II) (150), Sr(II) (150), Mn(II) (75), U(VI) (150), Pb(II) (100), Cd(II) (150), Sn(IV) (150), Sc(III) (20), Bi(III) (100), Zn(II) (20), Mo(VI) (100), Hg(II) (50), Ag(I) (20), Mg(II) (200), Th(IV) (20), In(III) (50), Al(III) (20), La(III) (100), As(III) (50) and Sb(III) (50). Thiosulphate, thiourea, citrate, tartrate, oxalate, phosphate, cyanide, EDTA, borate, vanadium(V), iron(III), palladium(II), nickel(II) and cobalt(II) interfere in the determination.

Interference due to 10 ppm of iron(II) and vanadium (V) was removed using fluoride (200 ppm) as masking agent. Palladium(II) (15 ppm) was eliminated by using nitrite. Attempts to mask nickel(II) and cobalt(II) were unsucessful.

Simultaneous determination of nickel and copper

The spectral curves for nickel(II) and copper (II) complexes with NHBC (Fig. 1) indicate a difference of 25 nm in the λ_{max} of the complexes of the two metals. In view of this, the following equations derived by Sandell[8] for simultaneous determination of the two components were employed for the determination of nickel (A) and copper (B).

$K_1^A C_A + K_1^B C_B = A_1$ (total absorbance at 395 nm)

$K_2^A C_A + K_2^B C_B = A_2$ (total absorbance at 420 nm)

where K_1^A, K_2^A and K_1^B and K_2^B the molar extinction coefficients for nickel and copper complexes at 395 nm and 420 nm respectively are 2.48×10^4 (K_1^A), 1.40×10^4 (K_2^A), 1.60×10^4 (K_1^B) and 1.98×10^4 litre mole^{-1} cm^{-1} (K_2^B). The results for the determination of nickel and copper in synthetic mixtures of the two are tabulated below.

Table 1. Simultaneous determination of nickel and copper in synthetic mixtures

Nickel taken ppm	Copper taken ppm	Nickel found ppm	Copper found ppm
0.58	1.59	0.60	1.58
1.17	0.80	1.15	0.82
0.58	0.80	0.58	0.82
0.98	1.90	1.00	1.89
0.75	0.80	0.76	0.79

Determination of nickel and cooper in alloys

Solutions of a few alloys containing nickel, copper, iron and zinc were prepared and suitable aliquots of the solution were taken. Ammonium fluoride was added in

order to mask iron. Determinations were then done as described above by measuring the absorbances of the solutions at 395 and 420 nm against the corresponding reagent blanks. The results for a few such determinations are recorded in Table 2.

Table 2. Determination of nickel and copper in alloys

Alloy	Nickel reported, %	Copper reported, %	Nickel found, %	Copper found, %
Monel Metal	64.0	30.0	63.6	29.8
Nickel silver	12.0	58.0	11.7	57.5
Brass	–	65.0	–	64.8

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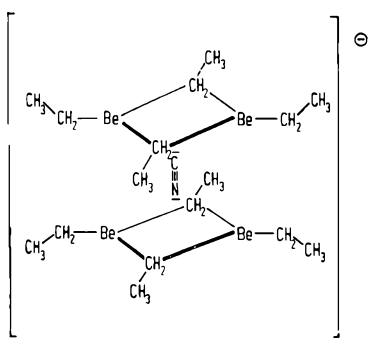
Das Schwingungsspektrum von Tetramethylammonium(tetrakis)-Diäthylberylliumcyanid, $[NMe_4]\,[(Ät_2Be)_2CN(BeÄt_2)_2]$*

Summary

The vibrational spectrum of the title compound is assigned on the basis of a sandwich like complex, bridging of dimeric diethylberyllium by the cyanide ion.

Frischdestilliertes Diäthylberyllium bildet nach kryoskopischen Molekulargewichtsbestimmungen dimere Moleküle[1], in denen ein planarer Be_2C_2-Vierring vorliegt, der wegen der in flüssiger Phase möglichen freien Rotation der Äthylgruppen um die Bindungsachsen für das Molekül $[(C_2H_5)_2Be]_2$ zu einer hohen Pseudosymmetrie (Punktgruppe D'_{2h}) führt[2]. Als typische Elektronenmangelverbindung bildet Diäthylberyllium mit Fluorid-,[3] Chlorid-,[3] Cyanid-[3] und Thiocyanationen[2] stabile Donator-Akzeptorkomplexe, darunter das erstmalig von Strohmeier *et al.* beschriebene Addukt mit KCN, das die ungewöhnliche Zusammensetzung $KCN \cdot 4\,Be(C_2H_5)_2$ aufweist[3]. Wir fanden, daß auch Tetramethylammoniumcyanid mit Diäthylberyllium zu einem Addukt der Zusammensetzung $NMe_4CN \cdot 4\,Be(C_2H_5)_2$ reagiert, dessen gegenüber K^+ größereres Kation wir aus Gründen einer günstigeren Größenrelation bevorzugten. Die Verbindung stellt bei Zimmertemperatur eine farblose, viskose, sauerstoff- und hydrolyseempfindliche Flüssigkeit dar, die Raman-spektroskopisch gegenüber polykristallinem Material den Vorteil der Meßbarkeit des Polarisationsverhaltens bietet.



* Eingegangen am 17.September 1974.

Die Ergebnisse des Schwingungsspektrums (IR, Raman), das in Tabelle 1 und Abb.1 wiedergegeben ist, lassen für die Struktur des $NMe_4CN \cdot 4\,Be(C_2H_5)_2$ bezüglich des

Tabelle 1. IR- und Raman-Spektren von $[NMe_4]\{[C_2H_5)_2Be]_2CN[Be(C_2H_5)_2]_2\}$

IR cm^{-1}	Int.[a]	Raman cm^{-1}	Int.[a]	Polarisationszustand[a]	Zuordnung
3035	s	3035	s	dp	$\nu CH_3\,[N(CH_3)_4]^+$
		2978	s	p	
2935	st				
		2922	s	p	νCH_2, CH_3
2860	st	2850	m	p*	
2840	st				
2780	st	2780	s	p	
2710	ss				Ober- und
2620	ss				Kombinations-
2475	ss				schwingungen
2195	st	2200	st	p*	νCN
1483	st				δCH_3
1465	Sch	1460	st	dp	
1408	st	1415	m	dp	δCH_2
1372	m				δCH_2
1281	ss				
1225	s				
1185	st	1185	m	p*	τCH_2
990	sst	995	m	p*	$\nu C{-}C$
945	st	952	m	dp	$\nu_{as} NC_4[N(CH_3)_4]^+$
910	Sch	905	s	p	νBeC
790	st	795	m	p*	ϱCH_3
		752	st	p	$\nu_s NC_4[N(CH_3)_4]^+$
740	st			p	$\nu Be_2(CN)Be_2$
680	st				ϱCH_2
575	st				Ring ν (B_{1u}, B_{3u})
		505	st	p	Ring ν (A_g)
		475	st	p*	δ, γ CC (B_{1g})
448	s				
375	s	375	s	dp	$\delta NC_4[N(CH_3)_4]^+$
		250	s	dp	δ BeCC (B_{3g})
220	s				δ BeCC

a) sst = sehr stark, st = stark, m = mittel, s = schwach, ss = sehr schwach, Sch = Schulter, p = polarisiert, p* = teilweise polarisiert, dp = depolarisiert.

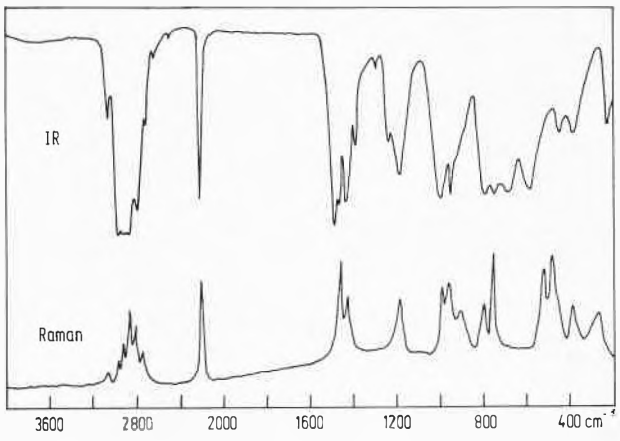


Abb. 1. Schwingungsspektrum von $[NMe_4][(Ät_2Be)_2CN(BeÄt_2)_2]$

komplexen Anions die von sandwichartig über eine Cyanidbrücke verbundenen dimeren Diäthylberylliummolekeln zu. (Siehe Tabelle 1).

Für diesen Strukturvorschlag lassen sich folgende Argumente erbringen:

1. Die CN-Valenzschwingungsfrequenz weist dieser Gruppe wegen der sehr kurzwelligen Lage (2200 cm^{-1}) eindeutig Brückenfunktion zu. Gegenüber NMe_4CN (2050 cm^{-1}) wird diese Schwingung somit um 150 cm^{-1} kurzwellig verschoben, was MO-theoretisch mit dem antibindenden Charakter der beiden freien Elektronenpaare an N und C zusammenhängt.

2. Die Frequenzlagen sowie die Intensitäten der für das vorliegende Strukturproblem besonders aufschlußreichen Gerüstschwingungen der Diäthylberylliumkomponente weisen mit dem Spektrum[2] des nichtkomplexen $[(C_2H_5)_2Be]_2$ sehr große Ähnlichkeit auf. Eine im IR-Spektrum neu auftretende starke Absorption bei 740 cm^{-1} kann der $Be_2(CN)Be_2$-Gerüstschwingung zugeordnet werden. Sie liegt zwar in der Nähe der symmetrischen NC_4-Valenzschwingung des Tetramethylammoniumkations (752 cm^{-1}), doch ist diese Schwingung nach den Auswahlregeln im IR-Spektrum nicht aktiv und in allen bisher untersuchten Komplexen auch nicht beobachtet worden. Das Nichtauftreten der $Be_2(CN)Be_2$-Gerüstschwingung im Raman-Effekt ist ein Hinweis auf eine polare Bindungsbeziehung zwischen CN^- und den Diäthylberylliumgruppen.

3. Das im Schwingungsspektrum des $[(C_2H_5)_2Be]_2$ beobachtete Alternativverbot[2] bleibt auch im komplex gebundenen Diäthylberyllium des Cyanidkomplexes erhalten. Auch die Polarisationsverhältnisse des Raman-Spektrums entsprechen diesen Bedingungen und stehen mit unserem Strukturvorschlag im Einklang. Das Schwingungsspektrum erbringt keine Anzeichen einer Schwingungskopplung der beiden $[(C_2H_5)Be]_2$-Ringe über die CN-Brücke hinweg, was mit dem unter 2. genannten polaren Bindungsverhalten korreliert. Ein Ausbleiben von Schwingungskopplung über die Al—CN—Al-Brücken konnte kürzlich auch bei $[(CH_3)_2AlCN]_4$ beobachtet werden[4].

4. Das Protonenresonanzspektrum des $[NMe_4][(Ät_2Be)_2CN(BeÄt_2)_2]$ läßt wegen des raschen Alkylgruppenaustausches bei Zimmertemperatur ebenso wenig wie im Diäthylberyllium[2] selbst eine Unterscheidung zwischen brücken- und terminalgebundenen Äthylgruppen zu. Nach der Bildung des Cyanidkomplexes erfahren die CH_2-Protonen eine deutliche Verschiebung nach höherem Feld (+ 19 Hz), während die CH_3-Protonen der Äthylgruppen nur unwesentlich beeinflußt werden (+ 4 Hz). Dies entspricht einer gegenüber $[Be(C_2H_5)_2]_2$ von J_{CH_2/CH_3} = 45 Hz nach 59 Hz vergrößerten Kopplungskonstanten. Der deutlichen *Hoch*feldverschiebung der CH_2-Protonen des Komplexes entspricht die Ladungsübertragung vom Cyanidion auf die Be-Atome, was für die Methylenprotonen zu einer erhöhten Abschirmung führt. Für das vorliegende Problem erhalten diese Befunde jedoch erst Gewicht durch den Vergleich mit den spektroskopischen Verhältnissen des Komplexes $[(C_2H_5)_2BeSCN]^-$, bei dem keine äthylgruppenverbrückten Berylliumspezies mehr vorliegen.[2] Hier führt nämlich die Ladungsübertragung vom SCN^--Ion auf Diäthylberyllium zu einer *Tief*feldverschiebung der CH_2- und der CH_3-Protonen, was eine Folge der Überlagerung der beiden Effekte darstellt: Ladungsübertragung/Lösung der Mehrzentrenbindungen.

Beispiele für das Festhalten von Metallalkylen an der Ausbildung von Mehrzentrenbindungen der α-C-Atome der Alkylgruppen, selbst bei einem für die Sättigung des Elektronenmangels ausreichenden Donatorangebot, konnten wir kürzlich auch bei Methyllithium[5] und Dimethylmagnesium[6] erbringen.

Die Frage, ob das CN^--Ion zwischen den beiden möglichen Diagonalstellungen des komplexen Anions oszilliert, kann mit der Abschätzung des Zeitbedarfs für diesen Vorgang geklärt werden. Hierfür ist etwa ¼ einer Rotationsschwingung des Cyanidions erforderlich, somit $\sim 1 \times 10^{-13}$ sec. Damit wäre für diesen Zeitraum das Alternativverbot aufgehoben, das wir im Bereich der Gerüstschwingungen (200 bis 800 cm^{-1} $\sim$ $1{,}7 \times 10^{-13}$ bis $\sim 4{,}2 \times 10^{-14}$ sec) allerdings beobachten. Es ist folglich ein mögliches Oszillieren der CN-Brücke sehr unwahrscheinlich.

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Stereochemistry of the Carbon-Nitrogen Bond Cleavage by Chloroformate Esters*

Summary

Nicotine reacts with chloroformic esters to give the chloro-carbamates resulting from the cleavage of the $C_{2'}-N_{1'}$ bond. The reaction is shown to proceed with at least 96 to 98% inversion of configuration. In the same way, (R)-(+)-N,N-dimethyl-α-phenethylamine gave (S)-(−)-α-phenethyl chloride with inversion.

The chloroformate ester cleavage of tertiary aliphatic and alicyclic amines to a carbamate and an alkyl chloride[1] often provides a convenient method for promoting dealkylation. It was found to be an interesting alternative reaction to the von Braun cyanogen bromide cleavage in the alkaloid field[2,3] and for synthetic purposes[4] but the stereochemistry of the process has not been previously investigated.

We now wish to report that this cleavage reaction, when applied to nicotine, is highly stereoselective—if not stereospecific—and proceeds with inversion.

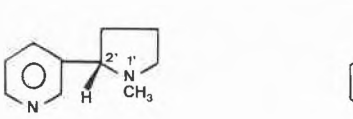
Based on the relative lability of the groups attached to the nitrogen atom[5] (and on the related cleavage by benzoyl chloride[6]), it was anticipated that nicotine (I) would react with chloroformate esters to open specifically the pyrrolidine ring at the $C_{2'}-N_{1'}$ bond.

Indeed, reaction of (−)-nicotine (I) with methyl-, ethyl-, phenyl- and *p*-nitrophenyl chloroformate (1 equivalent) in dichloromethane solution at 25° gave, after purification, a 60 to 80% yield[7] of the expected δ-chlorocarbamates as optically active[8] colorless oils. The complete analysis of mass spectra and n.m.r. spectra was only consistent with (plane) structures (II), (III), (IV) and (V) respectively. Furthermore, the structure of the urethane (III) was corroborated by dehydrochlorination (pyrolysis at 200°) to the corresponding 3-vinylpyridine derivative (VI) (λ_{max}^{EtOH}: 248 nm (ε 16,000) and 282 nm (4,300); acidified EtOH: 228 nm (12,300), 258 nm (12,300) and 298 nm (4,550); hydrochloride, m.p. 119–121°).

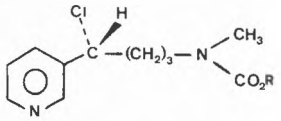
Compound	$[\alpha]_D^{20}$ ($CHCl_3$)	$\nu_{C=O}$ (film)	δ ($CDCl_3$; TMS = 0) CHCl	N−CH_3
(II)	+ 72° (c 1.5)	1695 cm^{-1}	4.99 (t)	2.90 (s)
(III)	+ 66° (c 3.1)	1695 cm^{-1}	4.99 (t)	2.87 (s)
(IV)	+ 54° (c 2.4)	1715 cm^{-1}	4.99 (t)	3.00*
(V)	+ 44° (c 3.6)	1730 cm^{-1}	4.99 (t)	3.08*

* Broad signals were observed, attributable to hindered rotation about the carbonyl carbon-nitrogen bond (see e.g. reference 9)

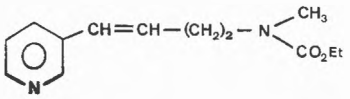
By treatment with 2.5% sodium hydroxide in aqueous ethanol, the carbamates (II), (III), (IV) and (V) were reconverted into levorotatory nicotine (yield ca. 50%) of 96 to 98% optical purity. This result indicates that the cleavage reaction of nicotine by the chloroformate esters, as well as the subsequent ring-closure reaction, had a minimum stereoselectivity of 96 to 98%. As it is reasonable to assume an inversion of configuration during ring-closure of the intermediary chloroamine, the cleavage reaction must also proceed with inversion. Compounds (II), (III), (IV) and (V) are therefore assigned the (R) configuration as depicted. This stereochemical attribution is also in agreement (on the basis of Brewster's treatment[10] of compounds for which both atomic and conformational asymmetry come into play) with the dextrorotatory rotation of the carbamates (as pure liquids) at the *D* line. In this connection, it may be noted that the molecular rotations of (II), (III), (IV) (λ: 589 to 313 nm; $CHCl_3$) and (V) (λ: 589 to 404 nm; $CHCl_3$) were found to be of the same sign and order of magnitude as those of (+)-α-phenethyl chloride (VII) of established (R) configuration[11].



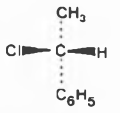
(I)



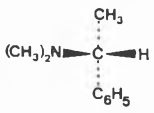
(II) R = CH_3
(III) R = CH_2-CH_3
(IV) R = C_6H_5
(V) R = p-$NO_2C_6H_4$



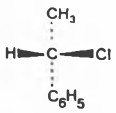
(VI)



(VII)



(VIII)



(IX)

That the chloroformate ester cleavage unambiguously proceeds with inversion in the case of benzylic rupture also rests on the observation that treatment of (+)-N,N-dimethyl-α-phenethylamine (VIII) (59% optical purity) of established (R) configuration[12] with methyl chloroformate (CH_2Cl_2 solution at −10°) gave (−)-α-phenethyl chloride (IX) [(S) configuration; 44% optical purity] with 75% inversion (using the value of $[\alpha]_D^{25} = -109°$ for the rotation of $C_6H_5CHClCH_3$[13]). Optimum conditions for effecting this reaction have not been systematically investigated as yet.

Full details of this work will be reported elsewhere.

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