NOTES.

335. *Acid-catalysis of Glycol Fission by Lead Tetra-acetate.*

By R. P. Bell, V. G. Rivlin, and William A. Waters.

Comprehensive studies by Criegee and his colleagues [1,2] of 1 : 2-glycol fission by lead tetra-acetate have shown that the reaction velocities depend very markedly on solvent and that *cis*- and *trans*-isomers are affected to different extents by solvent changes. Published data, though seldom extensive enough for critical review, show excellent concordance with true second-order kinetics [1-3] though this is not always the case for glycol fission by other reagents.[4]

We have measured the rates of oxidation, by lead tetra-acetate in glacial acetic acid at 25°, of pinacol and of *trans*- and *cis-cyclo*hexane-1 : 2-diol and have confirmed that each is of the second order. Moreover, all these oxidations are prone to acid-catalysis, as the tabulated results, obtained by the addition of trichloroacetic acid, show: the catalytic coefficients, $\Delta k_{bi}/[Acid]$, depend on the structure of the glycol and follow the order of the reaction velocity in the absence of added catalyst. Standard experimental procedures [3] were used for the kinetic work; the pure *cyclo*hexanediols were available from a previous investigation.[5]

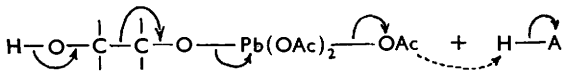
Oxidations of glycols in acetic acid at 25° in the presence of trichloroacetic acid.

Pinacol		*trans-cyclo*Hexane-1 : 2-diol		*cis-cyclo*Hexane-1 : 2-diol	
Acid added (M)	k_{bi} (min.$^{-1}$)	Acid added (M)	k_{bi} (min.$^{-1}$)	Acid added (M)	k_{bi} (min.$^{-1}$)
0·00	0·74	0·00	0·52	0·00	10·2
0·099	0·92	0·070	0·596	0·052	11·6
0·200	1·07	0·164	0·67	0·104	12·7
0·256	1·16	0·294	0·80	0·150	14·0
0·378	1·40	0·493	0·99	—	—
$\Delta k/[Acid]$	1·71 ± 0·1	—	0·95 ± 0·06	—	25·5 ± 1·6
$(\Delta k/k_0)/[Acid]$	2·3	—	1·83	—	2·5

Even more marked catalysis was observed by use of small concentrations of the stronger acids, sulphuric and methanesulphonic acid, but then the apparent second-order constants decreased with time, possibly owing to concurrent removal of pinacol by acid-catalysed rearrangement or by esterification of the glycols with acetic acid.

[1] Criegee, Höger, Huber, Kruck, Marktscheffel, and Schellenberger, *Annalen*, 1956, **599**, 81.
[2] Criegee, Buchner, and Walther, *Ber.*, 1940, **73**, 563, 571.
[3] Bell, Sturrock, and Whitehead, *J.*, 1940, 82; Cordner and Pausacker, *J.*, 1953, 102.
[4] Drummond and Waters, *J.*, 1953, 3119; Duke and Forist, *J. Amer. Chem. Soc.*, 1949, **71**, 2790; Duke and Bremer, *ibid.*, 1951, **73**, 5179.
[5] Levesley, Waters, and Wright, *J.*, 1956, 840.

This demonstration of acid-catalysis of glycol fission by lead tetra-acetate indicates that in acetic acid the process is heterolytic. If the oxidation involves a process of covalent O–Pb bond formation, *e.g.*, $R_3C{\cdot}OH + Pb(OAc)_4 \longrightarrow R_3C{\cdot}O{\cdot}Pb(OAc)_3 + HOAc$, then this, being akin to the esterification of an alcohol, may well be influenced by acid-catalysis. Again the base-catalysed process of glycol fission, recently suggested by Criegee,[1] has an obvious counterpart in the following acid-catalysed process:



THE DYSON PERRINS AND PHYSICAL CHEMISTRY LABORATORIES,
OXFORD. [*Received, November 11th*, 1957.]

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336. *The Kinetics of the Base-catalysed Decomposition of Benzyl* tert.*-Butyl Peroxide.*

By R. P. BELL and A. O. MCDOUGALL.

KORNBLUM and DELAMARE [1] showed that *tert.*-butyl 1-phenylethyl peroxide decomposes in presence of bases to acetophenone and *tert.*-butyl alcohol, and suggested the following mechanism for the base-catalysed decomposition of this type of peroxide:

$$B + R^1R^2CH{-}O{-}O{-}R^3 \longrightarrow BH^+ + [R^1R^2\dot{C}{-}O{-}O{-}R^3]^-$$

$$[R^1R^2\dot{C}{-}O{-}\dot{O}{-}R^3]^- \longrightarrow R^1R^2C{=}O + {}^-O{-}R^3;\quad R^3{-}O^- + BH^+ \longrightarrow R^3OH + B$$

The first two steps are considered to be synchronous and rate-determining, and the third rapid. Recently Kornblum and Clark [2] studied the kinetics of decomposition of benzyl *tert.*-butyl peroxide and *tert.*-butyl 1-phenylethyl peroxide in *tert.*-butyl alcohol, catalysed by piperidine, and showed that the reaction exhibits a large deuterium isotope effect; this would be expected from the above mechanism, which involves a proton-transfer in the rate-determining step. Kornblum and Clark followed the reaction by precipitating benzaldehyde 2 : 4-dinitrophenylhydrazone. We now describe an optical method, and deal mainly with catalysis by tertiary bases.

Experimental.—A sample of benzyl *tert.*-butyl peroxide was kindly provided by Professor N. Kornblum of Purdue University, U.S.A., whom we thank. Chlorobenzene and *tert.*-butyl alcohol were of " Laboratory Reagent " grade. Piperidine, triethylamine, collidine, and 2 : 6-lutidine were commercial products distilled from solid sodium hydroxide. Solvents and catalysts were examined spectrophotometrically before use.

The reaction was followed by measurements of optical density with a Unicam S.P. 500 spectrophotometer, the appearance of the carbonyl absorption band of benzaldehyde with a maximum at about 3280 Å being used. Measurements were made in the range 3000—3700 Å, where the absorption of the peroxide is negligible. The peroxide concentration was about 0·05M. At 25° and 40° the reaction took place in a thermostatically controlled cell holder in the spectrophotometer; at 60° and 80° the mixture was placed in a thermostat, and samples were removed and examined after cooling. In the absence of base the peroxide solutions showed no change of absorption under the conditions of the kinetic measurements.

A few experiments were made with piperidine in *tert.*-butyl alcohol (Kornblum and Clark's catalyst). The absorption changed with time, but the resulting spectrum did not resemble that of benzaldehyde: in particular there was little absorption in the neighbourhood of 3300 Å. This suggests that the benzaldehyde originally formed reacts rapidly with piperidine, and it was found that the carbonyl absorption of a solution of benzaldehyde disappears

[1] Kornblum and H. E. DeLaMare, *J. Amer. Chem. Soc.*, 1951, **73**, 880.
[2] Kornblum and Clark, personal communication from Professor Kornblum.

instantaneously on addition of piperidine. Possible reactions are $Ph{\cdot}CHO + C_5H_{10}NH \longrightarrow Ph{\cdot}CH(OH){\cdot}NC_5H_{10}$, or $Ph{\cdot}CHO + 2C_5H_{10}NH \longrightarrow Ph{\cdot}CH(NC_5H_{10})_2 + H_2O$. Such reactions presumably occurred in Kornblum and Clark's experiments, but the condensation products were apparently decomposed by the acid solution of 2 : 4-dinitrophenylhydrazine used as an analytical reagent.

When tertiary amines in chlorobenzene were used as catalysts, the spectrum of the peroxide was gradually replaced by that of benzaldehyde. Each reaction followed first-order kinetics, and velocity constants were obtained by plotting log $(r_\infty - r_t)$ against t, where r_t is the optical density at time t, and r_∞ that of a benzaldehyde solution of equivalent concentration. Plots for any one experiment, the optical densities at six different wavelengths being used, were parallel, showing that benzaldehyde is produced quantitatively.

The observed first-order velocity constants k_1 are given in the Table. The results for triethylamine and collidine at 80° show that k_1 is proportional to the catalyst concentration, and the last column gives the catalytic constant $k_2 = k_1/[\text{catalyst}]$.

Catalysis by tertiary amines in chlorobenzene.

[Catalyst]	Temp.	10^6k_1 (sec.$^{-1}$)	10^5k_2 (l. mole^{-1} sec.$^{-1}$)	
Triethylamine, $K_A = 1{\cdot}6 \times 10^{-11}$.				
0·512	25°	26	5·1	
0·494	40	90	22	
0·148	60	89	60	
0·011	80	12·9	117	
0·021	80	23	109	
0·050	80	65	130	Mean
0·079	80	96	121	118
0·195	80	219	112	
Collidine, $K_A = 3{\cdot}4 \times 10^{-8}$.				
0·109	80°	2·8	2·6	
0·213	80	5·1	2·4	Mean
0·322	80	6·2	1·9	2·3
0·439	80	9·9	2·2	
2 : 6-*Lutidine,* $K_A = 1{\cdot}9 \times 10^{-7}$.				
0·203	80	0·81	0·40	Mean
0·294	80	1·21	0·41	0·41

Discussion.—Although Kornblum and Clark's observations with piperidine might have been complicated by reaction between piperidine and benzaldehyde, this reaction is fast, so that the measured velocity was probably that of the decomposition of the peroxide, and their interpretation of the observed hydrogen isotope effect can be accepted.

Our other results show that solutions of tertiary amines in chlorobenzene catalyse the decomposition without complication, the velocity being proportional to the catalyst concentration. The values of the catalytic constant of triethylamine at four temperatures lead to an activation energy of about 12 kcal./mole and a collision factor of about 10^4 l. mole^{-1} sec.$^{-1}$. Similar values ($E = 14$ kcal./mole, $A = 10^5$ l. mole^{-1} sec.$^{-1}$) were found by Kornblum and Clark for catalysis by piperidine in *tert.*-butyl alcohol, again suggesting that they were measuring the rate of peroxide decomposition. Both collision factors are very much smaller than the values predicted by simple collision theory (10^{11}—10^{12} l. mole^{-1} sec.$^{-1}$) as is frequently found for reactions in which a highly polar transition state is formed from two uncharged reactants; this is consistent with the mechanism above.

The catalytic constants of the three tertiary amines studied increase with increasing basic strength, K_A in the Table being the acid dissociation constant of the amine cation at 25°. The values suggest that in the Brönsted equation $k_2 = G\ (1/K_A)^\beta$, $\beta < 1$ as is commonly the case. The reaction thus exhibits general base catalysis, in harmony with the mechanism suggested by Kornblum and DeLaMare.[1]

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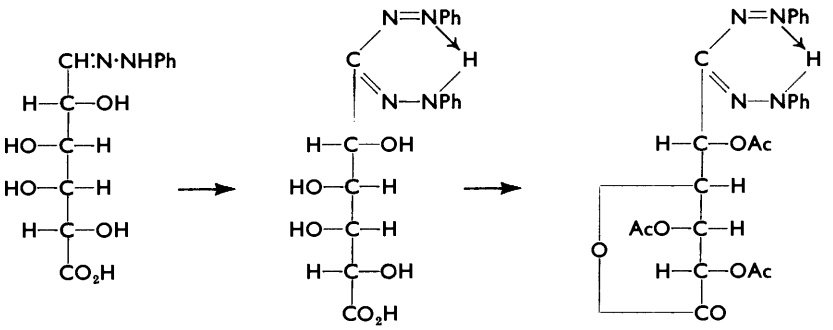
337. *Preparation of the Formazan from* D-*Galacturonic Acid.*

By L. MESTER and E. MÓCZÁR.

RECENTLY we reported the preparation of some novel types of sugar formazan.[1] It has now been found that D-galacturonic acid phenylhydrazone [2] with diazotized aniline in pyridine solution also gives a formazan; owing to the presence of the carboxyl group this dissolves more readily in water than the simple sugar formazans. Acetylation leads to the tri-*O*-acetate of the formazan of D-galacturonic acid lactone.



Experimental.—We are grateful to Miss Ilona Batta for the microanalyses.

D-*Galacturonic acid diphenylformazan.* The barium salt (1 g.) of D-galacturonic acid phenylhydrazone [2] was shaken for 30 min. with 50% ethanol (17 ml.) and 0·5N-sulphuric acid (5·34 ml.). Barium sulphate was filtered off and washed with 50% ethanol (15 ml.). After 6 hr. pyridine (5 ml.) was added and 5 min. later the product was coupled at −5° with a diazonium solution (2·6 ml.) prepared from aniline (0·26 g.). The mixture was set aside for 40 min., then ice–water (30 ml.) was added. Next day, the dark red precipitate (0·12 g.) was removed, the mother liquor evaporated *in vacuo* to one-third its volume, and the red needles which separated were removed (0·201 g.; m. p. 147—148°). Recrystallized from alcohol the *formazan* had m. p. 151—152° (0·327 g., 30%) (Found: C, 55·5; H, 5·2; N, 14·1. $C_{18}H_{20}O_6N_4$ requires C, 55·7; H, 5·2; N, 14·4%).

D-*Galacturonic lactone diphenylformazan tri*-O-*acetate.* D-Galacturonic acid diphenylformazan (0·2 g.) was set aside in pyridine (3 ml.) and acetic anhydride (3 ml.) overnight, then poured into water (20 ml.). The precipitated red *acetate* was recrystallized from alcohol and had m. p. 187° (0·16 g.) (Found: N, 11·1; OAc, 26·3. $C_{24}H_{24}O_8N_4$ requires N, 11·3; OAc, 26·0%).

INSTITUTE OF ORGANIC CHEMISTRY,
TECHNICAL UNIVERSITY OF BUDAPEST, HUNGARY.

[*Received, March 18th,* 1957.]

[1] Mester and Móczár, *J.*, 1956, 3228.
[2] Niemann, Schoeffel, and Link, *J. Biol. Chem.*, 1933, **101**, 337.

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338. *Some Constituents of the Broad Bean.*

By M. T. J. ABBOT, JOHN FREDERICK GROVE, and P. MCCLOSKEY.

DURING an investigation into the translocation of some derivatives of griseofulvin in the broad bean *Vicia faba* L.,[1] kaempferol (3 : 5 : 7 : 4′-tetrahydroxyflavone) was isolated from the shoots and fumaric acid and betulin from the roots of untreated plants. All these compounds have been obtained frequently from plant sources but have not hitherto been reported as constituents of the broad bean.

Kaempferol was isolated from the ether extract of shoot tissue which had been macerated in water; when the shoots were macerated in aqueous sodium hydrogen carbonate the

[1] Crowdy, Green, Grove, McCloskey, and Morrison, to be published.

extract contained *p*-hydroxybenzoic acid instead of kaempferol. It was subsequently established spectrophotometrically that the latter was decomposed to *p*-hydroxybenzoic acid in sodium hydrogen carbonate solution in the presence of air. In the initial (rapid) stage of the reaction the intensity of the kaempferol peak at 405 mμ decreased and there was a corresponding increase in the intensity of a new peak at 332 mμ due to the (intermediate) formation of a chromophore of *p*-hydroxyaroyl anion type. There was a sharp isosbestic point at 359 mμ. In the second (slow) stage of the reaction the intensity of the 332 mμ peak decreased and a new peak, due to the chromophore of *p*-hydroxybenzoic acid anion (present also in phloroglucinolcarboxylic acid) appeared at 280 mμ: *p*-hydroxybenzoic acid was recovered and identified.

Shaw and Simpson [2] showed that the introduction of a 5-hydroxyl group into flavone or 3-hydroxyflavone increased the carbonyl stretching frequency. Kaempferol and quercetin (C=O frequencies for both compounds: 1656 cm.$^{-1}$ in dioxan) provide additional examples of this effect.

Many flavanoids show biological activity (for review see Willaman [3]) and the parent substance, flavone, has activity [4] against several fungi at 50 μg./ml. Kaempferol might therefore be responsible for any natural resistance shown by *V. faba* towards attack by fungal pathogens: however, it failed to inhibit germination of *Botrytis allii* spores at 100 μg./ml. It had no activity against *Bacillus subtilis* at the same concentration.

A triterpene alcohol present in the root tissue was identified as betulin after the molecular weight of its diacetate had been determined by the *X*-ray method. *X*-Ray crystallographic data for betulin ethanolate and diacetate are presented below. Betulin had no activity at 100 μg./ml. against *B. allii* or against *B. subtilis*.

Experimental.—Microanalyses are by Messrs. W. Brown and A. G. Olney.

The raising and harvesting of the plants, *Vicia faba L.* var. Suttons Dwarf, have been described.[1] Shoots (840 g.) and roots (371 g.) were separately macerated in water and the acidified aqueous macerates extracted with ether. The recovered solutes were subjected to 50 transfers in a counter-current distribution apparatus, carbon tetrachloride–methanol–water (62 : 35 : 3) being used, and the solutions in the equilibrium tubes were examined spectrophotometrically for specific ultraviolet absorption.

Extract of shoots (3·8 g.). The contents of tubes 35—48 (particularly tube 43) showed maxima near 270 and 370 mμ. The solute from tubes 39—47 was separated into neutral, acidic, and phenolic fractions. The phenolic fraction, m. p. 230° (decomp.), was crystallised twice from ethanol–light petroleum (b. p. 60—80°) and formed lemon-yellow microcrystals of kaempferol (40 mg.), m. p. 282° (decomp.) [Found: C, 62·7; H, 3·8; OMe, nil %; *M* (Rast), 261. Calc. for $C_{15}H_{10}O_6$: C, 62·9; H, 3·5%; *M*, 286]; $\lambda_{max.}$ ~245, 267, ~295, ~325, 370 mμ, log ε 4·22, 4·32, 4·03, 4·12, 4·42 respectively (in ethanol); 3345 and 3145 cm.$^{-1}$ (OH) and 1659 cm.$^{-1}$ (C=O) ("Nujol" mull). Identity was established by comparison of m. p. and spectra with those of authentic material and by preparation of the tetra-acetate, needles (from methanol), m. p. and mixed m. p. 118—120° (loss of solvent), resetting and remelting at 182° (Found in material dried at 100° *in vacuo*: C, 60·7; H, 4·1. Calc. for $C_{23}H_{18}O_{10}$: C, 60·8; H, 4·0%). The kaempferol content of the shoot extract estimated spectrophotometrically corresponded to 180 μg./g. fresh weight of shoot tissue.

When the shoots were macerated in sodium hydrogen carbonate the ethereal extract contained only a trace of kaempferol (estimated spectrophotometrically) but the acidic fraction from tubes 35—48 showed a broad maximum near 280 mμ in 0·1N-sodium hydroxide. The acid fraction was extracted with benzene and the insoluble portion chromatographed in ether on Celite buffered at pH 7·0. The eluate yielded *p*-hydroxybenzoic acid (sublimation at 100—118°/0·5 mm. and crystallisation from ether–benzene) (5 mg.), m. p. and mixed m. p. 210—212° (Found: C, 61·2; H, 4·8. Calc. for $C_7H_6O_3$: C, 60·9; H, 4·4%).

Extract of roots (0·5 *g.*). The acidic fraction of the solute in tubes 35—44 was extracted with hot benzene and the insoluble portion treated with ether. The ethereal solution was

[2] Shaw and Simpson, *J.*, 1955, 655.
[3] Willaman, *J. Amer. Pharm. Assoc.*, 1955, **44**, 408.
[4] Weller, Redemann, Gottshall, Roberts, Lucas, and Sell, *Antibiotics and Chemotherapy*, 1953, **3**, 603.

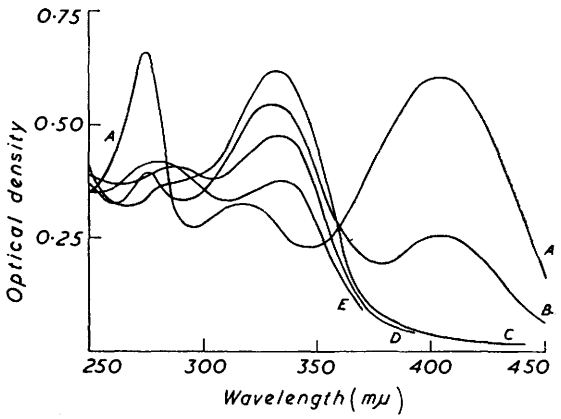
evaporated, and the pale brown residue (25 mg.) sublimed at 125°/0·1 mm. and crystallised from benzene–acetone, giving fumaric acid (5 mg.), m. p. 288° (sealed tube) (Found: C, 41·6; H, 3·8. Calc. for $C_4H_4O_4$: C, 41·4; H, 3·5%), identified by comparison of the infrared spectra.

Chromatography of the neutral fraction (53 mg.) (tubes 24—34) in benzene on alumina (12 × 1 cm.) and elution with benzene–methanol (99 : 1) gave a solid, m. p. 235—240°, which was sublimed at 200°/10^{-1} mm. and crystallised from ethanol in needles, m. p. 256° (30 mg.; 81 μg/g. fresh wt. of root tissue), identical {mixed m. p. and comparison of the infrared spectra [bands at 3370 and in 3230 cm.$^{-1}$ (OH) and 1649 and 879 cm.$^{-1}$ (>C=CH$_2$)]} with an authentic specimen of betulin (Found, in material dried at 20°: C, 78·3; H, 11·2. Calc. for $C_{30}H_{50}O_2,C_2H_5{\cdot}OH$: C, 78·6; H, 11·55%). The ultraviolet spectrum showed end absorption only. The unit cell of betulin ethanolate was orthorhombic: space group $P2_12_12_1$ or $P2_12_12$; a = 12·64, b = 33·95, c = 7·04 Å; d 1·078; M, 490.

The diacetate (prepared in acetic anhydride–pyridine at 20°) formed prisms, m. p. 218—220°, from ethanol (Found: C, 77·8; H, 10·45. Calc. for $C_{34}H_{54}O_4$: C, 77·5; H, 10·3%).

Decomposition of kaempferol by sodium hydrogen carbonate illustrated by absorption spectra.

A, initial spectrum. *B*, after 22 hr. *C*, after 46 hr. *D*, after 79 hr. *E*, after 219 hr.



The infrared spectrum showed no OH absorption and bands at 1739 (ester C=O) and 1645 and 883 cm.$^{-1}$ (>C=CH$_2$). The unit cell was orthorhombic; space group $P2_12_12_1$ or $P2_12_12$; a = 15·65, b = 15·82, c = 12·59 Å; d 1·125; M, 528. These values give $a : b : c$ = 0·9893 : 1 : 0·7958; Machatschki [5] gave 0·99165 : 1 : 0·7983.

Decomposition of kaempferol by sodium hydrogen carbonate. (*a*) Kaempferol (2·4 mg.), in ethanol (5 ml.), water (10 ml.), and saturated sodium hydrogen carbonate solution (15 ml.), was stored at 20° with occasional shaking and the absorption spectrum between 250 and 450 mμ determined (l = 0·1 cm.) at intervals up to 220 hr. Optical densities are plotted against wavelength in the Figure. (*b*) Kaempferol 25 mg.) was dissolved in ethanolic sodium hydrogen carbonate as described above; after 240 hr. at 20° ethanol was removed *in vacuo* at 25° and the solution was acidified (concentrated hydrochloric acid) and extracted with ether. Sublimation at 150°/10^{-4} mm. of the gummy extract and crystallisation from ether–benzene gave *p*-hydroxybenzoic acid (6 mg.), m. p. and mixed m. p. 208—210°.

We are indebted to Dr. E. C. Bate-Smith and Dr. T. G. Halsall for gifts of specimens, to Mr. H. G. Hemming for the biological assays, to Dr. P. G. Owston and Miss J. M. Tolliday for the *X*-ray data, and to Mr. S. C. Bishop for technical assistance.

Akers Research Laboratories, Imperial Chemical Industries Limited,
The Frythe, Welwyn, Herts. [*Received, September 10th*, 1957.]

[5] Machatschki, *Z. Krist.*, 1923, **59**, 209.

339. *Three New Coal-tar Bases.*

By P. Arnall.

A previous communication [1] reported the discovery of 2 : 3-*cyclo*pentenopyridine in vertical-retort coal-tar bases. A higher-boiling fraction has now yielded 3 : 4-*cyclo*pentenopyridine (I), 6-methyl-2 : 3-*cyclo*pentenopyridine (II), and 3 : 4 : 5-trimethyl-

(I) (II)

pyridine. Of these the first two are isolated for the first time from natural sources. 3 : 4 : 5-Trimethylpyridine has long been the elusive isomer although its preparation for comparison with a sample obtained from " coal-tar bases from low-temperature coke " is reported by Japanese workers.[2]

Experimental.—The fraction of bases boiling at 209—212° was treated by Perrin and Bailey's method [3] for removal of " non-aromatic " bases, and the primary amines were removed from the " aromatic " bases by acetylation. The aromatic bases were distilled through a fractionating column with an efficiency of about 70 plates, and selected fractions were blended and treated stepwise with picric acid, to yield, among others, picrates of m. p. 144°, 155°, and 178°.

The picrate of m. p. 144° gave on decomposition a base, which from its equivalent weight was a C_3-substituted pyridine. It had the following characteristics, those of 3 : 4-*cyclo*pentenopyridine [4] being given in parentheses: b. p. 211·8°/759 mm. (100°/10 mm.); d_{20}^{20} 1·045, d_4^{20} 1·042 (d_4^{20} 1·0385); n_D^{20} 1·5439 (1·5415); picrate, m. p. 144° (144°); picrolonate m. p. 229° (221°); styphnate, m. p. 174° (175—176°). The picrate of a sample of 3 : 4-*cyclo*pentenopyridine synthesised by Prelog and Metzler's method,[4] when mixed with our picrate, gave no m. p. depression. The infrared spectra of the " natural " and the synthetic material were identical. The retention volume relative to that of pyridine determined on Silicone M. 430 at 160° was 9·9.

The picrate of m. p. 155° gave a solid C_4-substituted pyridine. Its abnormally high density and refractive index indicated that it was not a simple pyridine homologue but contained a condensed ring system and would therefore be a homologue of 2 : 3-*cyclo*pentenopyridine (homologues of 3 : 4-*cyclo*pentenopyridine are excluded, as are also 5 : 6 : 7 : 8-tetrahydroquinoline and -*iso*quinoline, because of their higher b. p.s). The only one described is the 6-methyl derivative, the b. p. of which, given by Basu,[5] is lower than that of ours. Our base had f. p. 31·8°, b. p. 211·9°/761 mm. (Basu gave 195—196°/750 mm.), d_{20}^{33} 0·9910, $n_D^{32\cdot5}$ 1·5297, and gave a picrate, m. p. 155° (Basu gave 151—152°), picrolonate, m. p. 170° (decomp.), and styphnate, m. p. 138—139°. That the methyl group is in the 6- or 1′-position is shown by the facts that these compounds would be the lowest-boiling homologues and that a gas–liquid partition chromatogram on glycerol–kieselguhr shows the base to have a lower retention volume

Relative retention volumes (pyridine = 1).

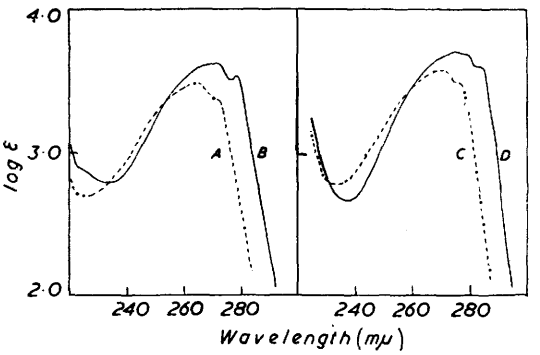
	Glycerol (90°)	Silicone M. 430 (160°)
2 : 3-*cyclo*Pentenopyridine	7·3	7·8
Base of picrate, m. p. 155°	5·5	10·8

(see Table) than 2 : 3-*cyclo*pentenopyridine, behaviour which is expected for 2- and 6-substituted pyridines [6] and expected for 6- and 1′-substituted 2 : 3-*cyclo*pentenopyridines. The 6-position of the methyl group is confirmed by reaction of the methiodide with *p*-dimethylaminobenzaldehyde in methanol,[7] which could not happen if the *cyclo*penteno-group were substituted in the

[1] Arnall, *J.*, 1954, 4040.
[2] Tsuda, Mishima, and Maruyama, *Pharm. Bull.*, 1953, **1**, 283 (*Chem. Abs.*, 1955, **49**, 8277); Ikekawa, Sato, and Maeda, *ibid.*, 1954, **2**, 205 (*Chem. Abs.*, 1956, **50**, 944).
[3] Perrin and Bailey, *J. Amer. Chem. Soc.*, 1933, **55**, 4136.
[4] Prelog and Metzler, *Helv. Chim. Acta*, 1946, **29**, 1170.
[5] Basu, *Science and Culture*, 1937, **2**, 466; *Annalen*, 1937, **530**, 140.
[6] Brooks and Collins, *Chem. and Ind.*, 1956, 1021.
[7] Phillips, *J. Org. Chem.*, 1949, **14**, 302.

1′-position. Further, the ultraviolet spectrum (in *cyclo*hexane; Unicam S.P. 500 spectrophotometer) of the base has the same similarity to the spectrum of 2 : 3 : 6-trimethylpyridine as the spectrum of 2 : 3-*cyclo*pentenopyridine has to that of 2 : 3-dimethylpyridine (see Figure).

The picrate of m. p. 178° gave a solid C_3-substituted pyridine which could not be an ethylmethylpyridine since the highest-boiling of these, 3-ethyl-4-methylpyridine, has b. p. 198°/760 mm.[8] It therefore appears to be 3 : 4 : 5-trimethylpyridine: its properties, compared with published data,[2] are f. p. 36·8° (−), b. p. 211·4—1·5°/759 mm. (205—207°), d_{20}^{40} 0·9471 (d^{15} 0·9616), n_D^{37} 1·5132 (n_D^{15} 1·5103), and it gives a picrate, m. p. 178° (174°), picrolonate, m. p. 232° (decomp.) (188°), and styphnate, m. p. 180° (−). Presence of a 2- or 4-methyl group was indicated by reaction of its methiodide with *p*-dimethylaminobenzaldehyde; [7] ability to prevent



A, 2 : 3-*Dimethylpyridine.*
B, 2 : 3-cyclo*Pentenopyridine.*
C, 2 : 3 : 6-*Trimethylpyridine.*
D, 6-*Methyl* 2 : 3-cyclo*pentenopyridine.*

the formation of a colour between trisodium pentacyanoamminoferrate and dimethyl-*p*-nitrosoaniline showed the absence of a 2-methyl group.[9] The theoretical b. p., calculated by Eguchi's method,[10] is 211°. The relative retention volumes of the base on Silicone M. 450 at 160° and glycerol at 90° are 8·3 and 9·9 respectively (pyridine = 1).

Copies of the infrared spectra of these bases, determined on a Unicam S.P. 100 spectrophotometer, have been submitted for inclusion in the Anglo-German Molecular Spectra Documentation System.[11]

The author thanks Dr. E. R. Wallsgrove for his encouragement, Mr. J. D. Earle for assistance with the experimental work, Dr. V. T. Brooks for gas–liquid partition chromatograms, Mr. D. D. Shrewsbury and Miss C. Wale for infrared and ultraviolet spectra respectively, and the Directors of The Midland Tar Distillers Ltd. for permission to publish this note.

THE MIDLAND TAR DISTILLERS LIMITED, RESEARCH DEPARTMENT,
FOUR ASHES, NR. WOLVERHAMPTON. [*Received, September 16th,* 1957.]

[8] Ruzicka and Fornasir, *Helv. Chim. Acta*, 1919, **2**, 338.
[9] Biddiscombe and Herington, *Analyst*, 1956, **81**, 711.
[10] Eguchi, *Bull. Chem. Soc. Japan*, 1928, **3**, 240.
[11] Thompson, *J.*, 1955, 4501.

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340. *The Isotope Effect of* ^{18}O *on the Infrared Spectrum of Benzophenone.*

By M. HALMANN and S. PINCHAS.

ALTHOUGH considerable experimental work has been done on the isotope effect of deuterium on the infrared spectrum of various compounds, there is almost no mention in the literature about the effect of ^{18}O. Only recently it was found by Braude and Turner [1] that the $C=^{18}O$ band of labelled cinnamyl *p*-nitrobenzoate appears at about 1700 cm.$^{-1}$, to be compared with 1730 cm.$^{-1}$ for the unlabelled ester. The highest ^{18}O concentration in the ester measured by them was however only 4·8% and no measurements in other regions

[1] Braude and Turner, *Chem. and Ind.*, 1955, 1223.

of the infrared spectrum were reported. The infrared absorption of ^{18}O-labelled compounds can be of value as a simple and direct method for the estimation of the content of ^{18}O in all carbonyl compounds: it is also interesting in connection with the assignment of vibrations in various oxygen-containing compounds. Using water containing 83 atoms % of ^{18}O, we have synthesized benzophenone containing 76% of ^{18}O and have measured its infrared spectrum in the 3700—830 cm.$^{-1}$ region (see Table).

The major infrared bands (cm.$^{-1}$) of [^{16}O] and [^{18}O]-benzophenone.

$Ph_2C^{16}O$	$Ph_2C^{18}O$	$Ph_2C^{16}O$	$Ph_2C^{18}O$	$Ph_2C^{16}O$	$Ph_2C^{18}O$	$Ph_2C^{16}O$	$Ph_2C^{18}O$
3070	3065	1449	1449	1178	1178	1002	1002
1664	1663 [a]	1316	1316	1152	1151	973	974
—	1635	1277	1275	1076	1075	940	940
1599	1599	1259 [b]	1259 [b]	1031	1030	919	919
1579	1575						

[a] Shoulder due to residual $C^{16}O$. [b] Shoulder.

The only significant difference between the spectra is in the C=O stretching region where normal benzophenone absorbs at 1664 cm.$^{-1}$ (Depireux [2] gives the value of 1666 cm.$^{-1}$; other values [3] are 1664, 1663, 1662, and 1665 cm.$^{-1}$), whereas ^{18}O-benzophenone absorbs at 1635 cm.$^{-1}$. This behaviour might be expected because of the relatively strong inner bond of the carbonyl group, which makes it appear as one vibrating unit with respect to external vibrations. Since the change in mass of the carbonyl group is relatively small when ^{16}O is replaced by ^{18}O, there can be no considerable difference in these frequencies.

The difference in the C=O frequency when ^{18}O is introduced into benzophenone (29 cm.$^{-1}$) is almost the same as that observed by Braude and Turner [1] (30 cm.$^{-1}$). If one looks at the C=O group and calculates the difference according to Hooke's law using the equation $\nu = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$ where ν = wave number (cm.$^{-1}$), c = velocity of light, k = force constant, and μ = reduced mass (assuming the k to be the same in both cases), the following expression is obtained for the ratio of the absorption frequencies:

$$\nu(C{=}{}^{18}O)/\nu(C{=}{}^{16}O) = \sqrt{[\mu(C{=}{}^{18}O)/\mu(C{=}{}^{16}O)]} = \sqrt{[(12 \times 16 \times 30)/(28 \times 12 \times 18)]} = 0{\cdot}9759$$

and the isotope shift $\Delta\nu = 1664(1 - 0{\cdot}9759) = 40$ cm.$^{-1}$. This value is in fair agreement with the experimental result. The molecular extinction coefficient of the 1635 cm.$^{-1}$ band of [^{18}O]benzophenone was found to be somewhat smaller than that of the 1664 cm.$^{-1}$ band of normal benzophenone.

Experimental.—The labelled benzophenone [4] was prepared by refluxing dichlorodiphenylmethane [5] [b. p. 107—113°/0·5 mm. (Found: Cl, 30·3. Calc. for $C_{13}H_{10}Cl_2$: Cl, 30·0%), made from normal benzophenone and phosphorus pentachloride (2·466 g.) with water [6] (0·493 g.) containing 83·5 atoms % of ^{18}O for 3 hr. The excess of water was then vacuum-distilled into a trap cooled with liquid air. The remaining oil crystallised, yielding [^{18}O]-benzophenone (1·81 g.). This was recrystallised [4] once from trimethylpentane and twice from *n*-hexane, yielding a ketone (1·48 g.), m. p. 47·5°. The ^{18}O content was determined by Rittenberg and Ponticorvo's method [7] by sealing 63 mg. with 59 mg. of mercuric chloride in an evacuated break-seal tube. After 4 hr. at 425°, the resulting gas was purified with 5 : 6-benzoquinoline [7] (British Drug Houses reagent) and was distilled from a trap cooled in solid

[2] Depireux, *Bull. Soc. chim. belges*, 1957, **66**, 218.
[3] Fuson, Josien, and Shelton, *J. Amer. Chem. Soc.*, 1954, **76**, 2526; Bergmann, Berthier, Ginsburg, Hirshberg, Lavie, Pinchas, Pullman, and Pullman, *Bull. Soc. chim., France*, 1951, **18**, 661; Shigorin, *Doklady Akad. Nauk S.S.S.R.*, 1954, **96**, 769; *Chem. Abs.*, 1954, **48**, 11,191; Thompson, Needham, and Jameson, *Spectrochim. Acta*, 1957, **9**, 208.
[4] Von Doering and Dorfman, *J. Amer. Chem. Soc.*, 1953, **75**, 5595.
[5] Gattermann and Schulze, *Ber.*, 1896, **29**, 2944.
[6] From the separation plant of the Weizmann Institute of Science.
[7] Rittenberg and Ponticorvo, *Internat. J. Appl. Radiation Isotopes*, 1956, **1**, 208.

carbon dioxide into a liquid-nitrogen trap. The ^{18}O content of the carbon dioxide was measured with a Consolidated Engineering Corporation Model 21—401 mass spectrometer, by scanning the masses 44—48. The atom % of ^{18}O was calculated from the peak heights p^X of the masses X:

$$^{18}O(\%) = \frac{100\,(p^{46} + p^{47} + 2p^{48})}{2(p^{44} + p^{45} + p^{46} + p^{47} + p^{48})}$$

The sample measured contained 76·4 atoms % of ^{18}O. In a duplicate sample, 76·0% was measured.

The infrared spectrum of [^{18}O]benzophenone was measured in a carbon tetrachloride solution (0·08 g. in 1 ml.) in a 0·1 mm. cell, on a Perkin-Elmer Model 12C spectrophotometer equipped with a sodium chloride prism. A carbon tetrachloride solution of normal benzophenone was measured at the same time and the calibration of the instrument was checked immediately afterwards with the aid of the water-vapour bands.

The molecular extinction coefficient of the $C=^{18}O$ band at 1635 cm.$^{-1}$ was calculated from the observed optical density of 0·42 for a solution in carbon tetrachloride (32 g./l.) in a 0·01 cm. cell. At this frequency the optical density of the remaining 24% of normal benzophenone was calculated to be 0·02. Hence $\varepsilon(C=^{18}O) = (0{\cdot}40 \times 184 \times 100)/(32 \times 0{\cdot}01 \times 76) = 300$ l. mole^{-1} cm.$^{-1}$. The optical density of a carbon tetrachloride solution (42 g./l.) of normal benzophenone at 1664 cm.$^{-1}$ in the same cell (slit-width in both cases, 0·09 mm.) is 0·84. Therefore $\varepsilon(C=^{16}O) = (0{\cdot}84 \times 182)/(42 \times 0{\cdot}01) = 360$ l. mole^{-1} cm.$^{-1}$. The difference between the values is no doubt larger than the experimental error.

The authors thank Dr. I. Dostrovsky for helpful discussions and Mrs. P. Gueron for mass-spectrometric measurements.

THE WEIZMANN INSTITUTE OF SCIENCE,
REHOVOTH, ISRAEL.

[*Received, October 28th*, 1957.]

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341. *The Effect of the Salt* Ph_3CSnCl_5 *on the Stannic Chloride-catalysed Polymerisation of Styrene.*

By T. G. BONNER, J. M. CLAYTON, and (the late) GWYN WILLIAMS.

INVESTIGATION of the polymerisation of styrene by stannic chloride in carbon tetrachloride with conditions and concentrations similar to those previously employed [1] has shown that in the presence of a trace of the (triphenylmethyl)tin pentachloride, Ph_3CSnCl_5, the polymerisation is retarded for some hours, though the reaction later occurs at approximately the same rate as for untreated reaction mixture and with formation of a similar product. The salt Ph_3CSnCl_5 is extremely sparingly soluble in carbon tetrachloride and is precipitated as golden-yellow crystals when solutions of triphenylmethyl chloride and stannic chloride in this solvent are mixed. No absorption at 4350 Å characteristic of the Ph_3C^+ ion was apparent in the carbon tetrachloride solution, although in ethylene dichloride, in which this salt is very soluble, there was a marked absorption at this wavelength corresponding to *ca.* 10% ionisation when the concentration of salt was *ca.* 10^{-4}M. In the presence of the solid salt a slow polymerisation at a constant rate is maintained throughout the reaction in carbon tetrachloride, which indicates initiation at the solid surface only, presumably by the Ph_3C^+ ions. When the amount of triphenylmethyl chloride added to the reaction mixture was in excess of that required to remove all of the stannic chloride present as Ph_3CSnCl_5 no polymerisation occurred although the solid salt precipitated was allowed to remain in contact with the styrene solution. This suggests that styrene reacts only through a monomer–catalyst complex.[2]

In a mixed solvent containing 70% of ethylene dichloride, and in pure ethylene dichloride, the pentachloride can be employed in concentrations of the same order as that of the stannic

[1] Williams, *J.*, 1938, 246, 1046; *J.*, 1940, 775.
[2] Plesch, *J. Appl. Chem.*, 1951, **1**, 269; Pepper, *Quart. Rev.*, 1954, **8**, 88.

chloride (*ca.* 0·015M). Polymerisation is much faster than in pure carbon tetrachloride and monomer begins to disappear rapidly as soon as the reactants are mixed, both when stannic chloride is present alone and when it is in excess over the pentachloride; when the latter only was added to the styrene solution, a slow reaction preceded the rapid reaction in both solvents. The weight of polymer recovered from the pure ethylene dichloride solutions by precipitation with methyl alcohol exceeded the amount of monomer consumed and indicated incorporation of the triphenylmethyl group in the polymer. In both retardations, the colour of the solution due to the Ph_3C^+ ion (orange in the mixed solvent, red in pure ethylene dichloride) faded gradually during the slow stage.

It has been shown previously [3] that triphenylmethyl chloride initiates polymerisation of alkyl vinyl ethers in strongly ionising solvents, while its retarding effect has been reported in the polymerisation of styrene by sulphuric acid in ethylene dichloride.[4] The present work confirms this dual function of triphenylmethyl chloride in the form of its stannic chloride salt but further investigation is needed particularly on the molecular-weight range of the polymeric product to establish to what extent it acts as a chain-breaker as well as a co-catalyst.[4]

ROYAL HOLLOWAY COLLEGE,
ENGLEFIELD GREEN, SURREY.

[*Received, November 6th,* 1957.]

[3] Eley and Richards, *Trans. Faraday Soc.*, 1949, **45**, 436.
[4] Jenkinson and Pepper, *Chem. and Ind.*, 1955, 741.

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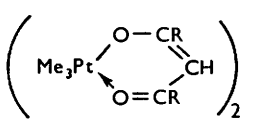
342. *Chelate Derivatives of Trimethylplatinum.*

By A. K. CHATTERJEE, R. C. MENZIES, J. R. STEEL, and F. N. YOUDALE.

TRIMETHYLPLATINUM–ACETYLACETONE was first described in 1928,[1] and trimethylplatinum–dipropionylmethane in 1932.[2] Similar stable, dimeric chelate derivatives of di-*n*- and di-*iso*-butyrylmethane, of di-*n*- and di-*iso*-valerylmethane, and of di-*n*-hexanoylmethane are now described. The double molecular weights in benzene of all these compounds confirm the stable six-covalency of quadrivalent platinum in its trimethyl derivatives already discussed.[3] The more obvious physical characteristics of compounds of the metal are changed by methylation to those of a lower group, but the less obvious, but fundamental co-ordination number remains unchanged.

In this paper attention is rather directed to the changes of properties conditioned by changing the substituents R attached to the stable chelate ring formed by the acetylacetone residue in the structural formula (I). Like trimethylplatinum–acetylacetone, these compounds can all be prepared by heating in benzene or in light petroleum equivalent weights of trimethylplatinum iodide, thallous ethoxide, and the relative β-diketone. Owing to its more sparing, but still convenient, solubility, trimethylplatinum–acetylacetone is the easiest to prepare. The derivatives of the higher diketones can then, as shown in Table 2, be made in good yield by heating it on a water-bath in an open basin with excess of the higher diketone.



(I)

These chelate derivatives of trimethylplatinum, like dimethyl- and diethyl-gold–acetylacetones [4, 5] and the chelate compounds of thallium dialkyls,[6] are white crystalline solids, soluble in organic solvents. The trimethylplatinum derivatives of acetylacetone, of dipropionylmethane, of di*iso*butyrylmethane and of di*iso*valerylmethane decompose without melting at 200°, 190°, 190°, and 156°; that of di-*n*-valerylmethane melts at 160° with

[1] Menzies, *J.*, 1928, 565.
[2] Menzies and Wiltshire, *J.*, 1933, 21.
[3] Lile and Menzies, *J.*, 1949, 1169.
[4] Brain and Gibson, *J.*, 1939, 762.
[5] Gibson and Simonsen, *J.*, 1930, 2532.
[6] Menzies, Sidgwick, Cutliffe, and Fox, *J.*, 1928, 1288.

decomposition. The di-*n*-butyrylmethane and di-*n*-hexanoylmethane derivatives alone have definite melting points at 164—166° and 68—69°. Their molecular weights, determined in boiling benzene, are given in Table 1 as are also their molecular complexities, melting points, and volatilities. Trimethylplatinum–di-*n*-butyrylmethane, –di*iso*butyrylmethane, and –di-*n*-hexanoylmethane all sublimed unchanged in a molecular still. The

TABLE 1.

R in $Me_3Pt(R{\cdot}CO{\cdot}CH{\cdot}COR)$	Volatility	*M*	Complexity
CH_3	160°/20 mm.	648·5	1·91
C_2H_5	105°/0·05 mm.	698	1·902
n-C_3H_7	110°/0·05 mm.	752·5	1·904
iso-C_3H_7	110°/0·05 mm.	732	1·853
n-C_4H_9	135°/0·01 mm.	808	1·91
iso-C_4H_9	140°/0·05 mm.	805·5	1·904
n-C_5H_{11}	120°/0·05 mm.*	862	1·91

* See below.

di*iso*valerylmethane derivative showed distinct tendency to distil at 120°/0·05 mm., but with appreciable decomposition. Table 1 shows that all the compounds were dimeric in boiling benzene, no change of complexity appearing in the range of concentration studied.

The molecular-weight determinations confirm previous results [1,2] in freezing benzene on the acetylacetone and dipropionylmethane compounds of trimethylplatinum. The corresponding thallium compounds show decrease of association with dilution.[7] The greater stability and invariable double molecular weights of the trimethylplatinum compounds are probably related to the stability of the compounds of trimethylplatinum iodide with ammonia,[10] with pyridine,[3] and with ethylenediamine,[3,12] while [13] the dialkylthallium halides can be recrystallised from these liquids and recovered on cooling without solvent of crystallisation. The dialkylgold halides also form compounds with nitrogenous bases, but the molecular weights of dimethyl- and diethyl-gold–acetylacetones have yet to be determined.

The general conditions of stability of the metallic acetylacetone derivatives were discussed by Morgan and Moss.[8,9]

Experimental.—Weighed quantities of trimethylplatinum–acetylacetone [1] were heated in an open basin on a water-bath at 100° to constant weight, with excess of each of the higher diketones, prepared by Adams and Hauser's method.[14] Yields and analyses are given in Table 2, col. 3 recording the weight (g.) of $Me_3Pt(Me{\cdot}CO{\cdot}CH{\cdot}COMe)$ taken, and col. 4 the yield (g.) of $Me_3Pt(R{\cdot}CO{\cdot}CH{\cdot}COR)$.

TABLE 2

R	$R{\cdot}CO{\cdot}CH_2{\cdot}COR$ taken (g.)			Found (%) Pt	Found (%) C	Found (%) H	Required (%) Pt	Required (%) C	Required (%) H
C_2H_5	1·20	1·65	1·71	52·8	32·8	5·55	53·1	32·7	5·5
C_3H_7	1·25	1·84	2·0	49·6	36·7	6·0	49·35	36·4	6·1
iso-C_3H_7	1·15	1·20	1·30	49·9	36·5	6·3	49·35	36·4	6·1
n-C_4H_9	3·10	2·33	2·12	46·0	39·7	6·7	46·1	39·7	6·7
iso-C_4H_9	1·24	1·12	1·26	—	39·8	6·7	—	39·7	6·7
n-C_5H_{11}	1·41	1·50	1·85	—	42·6	7·1	—	42·55	7·1

Platinum was determined by heating the compound, covered with iodine, in a crucible and after addition of a little chloroform, very slowly and finally to a red heat.[10] Some carbon and

[7] Menzies and Wiltshire, *J.*, 1932, 2734.
[8] Morgan and Moss, *J.*, 1913, **103**, 81.
[9] *Idem*, *J.*, 1914, **105**, 189.
[10] Pope and Peachey, *J.*, 1909, 571.
[11] Foss and Gibson, *J.*, 1951, 299.
[12] Truter and Cox, *J.*, 1956, 948.
[13] Lile and Menzies, *J.*, 1950, 618.
[14] Adams and Hauser, *J. Amer. Chem. Soc.*, 1944, **66**, 1220.

hydrogen estimations were by the analytical department of the Imperial College of Science and Technology.

As explained above, once trimethylplatinum–acetylacetone has been obtained, the higher derivatives are most conveniently made by metathesis. The application of the thallium method will be clear from the following description.

Trimethylplatinum–di-n- *and –di*-iso-*butyrylmethane.* In two separate preparations, di-*n*-butyryl- or di-*iso*-butyryl-methane was mixed with the equivalent (0·005 mole) of thallous ethoxide and trimethylplatinum iodide in toluene, in which all are soluble, and the solution was boiled for 10 min.

The thallous iodide was filtered off, and the toluene removed by boiling with water which acts on the trimethylplatinum derivatives only slowly, and in which they do not dissolve, but which decomposes any remaining thallium compounds, and dissolves their products of decomposition. The solids then remaining in the water were filtered off, dried, and recrystallised from light petroleum; yield 50—60% before sublimation.

The reaction just described is a particular instance of a method of general application. It resembles Purdie's method for methylating sugars by the use of silver oxide and methyl iodide, and, slightly modified, has been similarly applied.[15, 16]

Supplies of trimethylplatinum iodide were obtained from Messrs. Johnson Matthey and Co., whose patient co-operation we appreciate. We also thank Dr. Evans, of the Sondes Place Research Institute, and Professor Wardlaw for their sympathetic interest.

BIRKBECK COLLEGE, MALET STREET, LONDON, W.C.1.
CHEMICAL CLUB, 2 WHITEHALL COURT, LONDON, S.W.1.
SONDES PLACE RESEARCH INSTITUTE, DORKING, SURREY. [*Received, November 8th,* 1957.]

[15] Fear and Menzies, *J.*, 1926, 937.
[16] Menzies, *J.*, 1947, 1378.

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343. *The Preparation of Tetramethylammonium Hydrogen Dichloride and the Structure of the Hydrogen Dichloride Ion,* HCl_2^-.

By T. C. WADDINGTON.

THE existence of halide salts of the organonitrogen bases containing an extra formula unit or more of the hydrogen halide has long been known[1,2] but it was realised only recently[3] that this probably points to the existence of acid halide ions, such as the hydrogen dichloride (bichloride) ion, HCl_2^-.

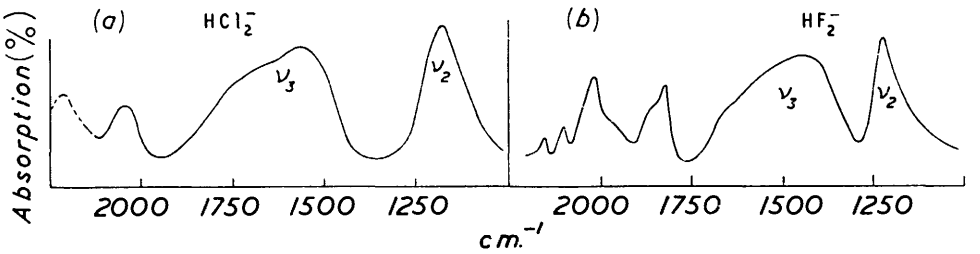
Unlike the hydrogen dichlorides of $(CH_3)_3NH^+$, $(CH_3)_2NH_2^+$, and $CH_3{\cdot}NH_3^+$ which have appreciable vapour pressures at room temperature, that of $(CH_3)_4N^+$ is stable in dry air. The *X*-ray powder photograph of the material $(CH_3)_4N^+HCl_2^-$ showed the existence of a completely new phase. The calculation of the lattice parameters was difficult because of the low crystal symmetry but an orthorhombic unit cell $a = 14{\cdot}81$ Å, $b = 11{\cdot}46$ Å, $c = 10{\cdot}38$ Å, with eight molecules to the unit cell, was assigned, giving a calculated density, $\rho_{calc.}$, of $1{\cdot}09_5$. The observed density, $\rho_{obs.}$, was 1·11.

The infrared spectrum of the solid was compared with that of $(CH_3)_4N^+Cl^-$ in order to identify the contribution of the hydrogen dichloride, HCl_2^-, ion and with that of potassium hydrogen difluoride in order to compare the absorption spectra of the ions HF_2^- and HCl_2^-. The spectrum of the HCl_2^- ion, with the $(CH_3)_4N^+$ peaks omitted, is shown in the Figure (*a*) and that of the HF_2^+ ion in the Figure (*b*).

Only the infrared spectrum of HCl_2^- from 1000 to 3000 cm.$^{-1}$ is shown, although the spectrum was recorded from 400 to 4000 cm.$^{-1}$; no other peaks were found. The spectrum has four features which lead to a tentative assignment. They are: (1) The non-occurrence

[1] McIntosh and Steel, *Proc. Roy. Soc.*, 1904, **73**, 450.
[2] McIntosh and Steel, *Proc. Roy. Soc.*, 1905, **74**, 320.
[3] Herbrandson, Dickerson (jun.), and Weinstein, *J. Amer. Chem. Soc.*, 1952, **76**, 4046.

of the HCl frequency at 2840 cm.$^{-1}$; (2) the occurrence of only two strong infrared bands (at 1180 cm.$^{-1}$ and at 1565 cm.$^{-1}$) in the region 400—4000 cm.$^{-1}$; (3) the enormous displacement of the highest frequency of the HCl_2^- ion (1565 cm.$^{-1}$) from that of the HCl molecule (2840 cm.$^{-1}$); (4) the great similarity, both in shape and position of bands, between the



infrared spectrum of the HCl_2^- ion and the HF_2^- ion,[4] which has been shown to be symmetrical by crystal-entropy [5] and neutron-diffraction [6] studies.

Although the present evidence is insufficient to establish conclusively the structure of the hydrogen dichloride ion, these four points strongly suggest that the ion is linear and that the proton is symmetrically situated, as in the hydrogen difluoride ion. On this basis a tentative assignment of the band at 1180 cm.$^{-1}$ as ν_2 and of the band at 1565 cm.$^{-1}$ as ν_3 is made. Further work is in progress to confirm this assignment and the presence of a symmetric proton.

Experimental.—Tetramethylammonium hydrogen dichloride, $(CH_3)_4N^+HCl_2^-$. Carefully dried hydrogen chloride (1) was passed over pure, dry tetramethylammonium chloride at room temperature, or (2) was condensed on it. The chloride dissolves in liquid hydrogen chloride and when the solution warms much hydrogen chloride is retained above the b. p. of the liquid and comes off at a higher temperature. The compound left at room temperature is the *hydrogen dichloride* [Found, from method (1): C, 33·0; H, 9·0; Cl, 48·1%. Found, from method (2): C, 32·2; H, 9·3; Cl, 48·0. $(CH_3)_4N^+HCl_2^-$ requires C, 32·9; H, 9·0; Cl, 48·5%]. Carbon and hydrogen were determined by combustion and chlorine gravimetrically as AgCl.

X-*Ray powder photograph.* Cu-$K\alpha$ radiation was used. A sample was inserted into a Pyrex capillary by using the " dry box " technique and the capillary was at once sealed with warm picein wax. All the lines on the powder photograph could be indexed on the basis of the assigned orthorhombic cell.

Infrared spectra. Those of $(CH_3)_4N^+HCl_2^-$, $(CH_3)_4N^+Cl^-$, and KHF_2 were taken on a Perkin-Elmer recording infrared, double-beam, spectrophotometer, Model 21, the solids being mulled with Nujol or hexachlorobutadiene in a dry box and smeared between rock-salt plates.

Grateful acknowledgment is made to Dr. N. Sheppard for discussion of the infrared spectra.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, November 12th,* 1957.]

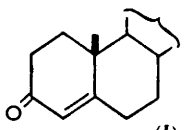
[4] Coté and Thompson, *Proc. Roy. Soc.*, 1952, *A*, **210**, 206.
[5] Westrum and Pitzer, *J. Amer. Chem. Soc.*, 1949, **71**, 1940.
[6] Patterson and Levy, *J. Chem. Phys.*, 1952, **20**, 704.

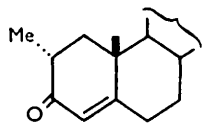
344. *Synthesis of 2α-Methylcholest-4-en-3-one.*

By J. A. K. Quartey.

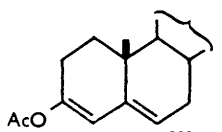
The synthesis of 2-methylcholest-4-en-3-one was studied as a model for that of 2-methyltestosterone. Certain 2-substituted analogues of steroid hormones have been shown to possess enhanced activity,[1] and 4-substituted analogues of testosterone to possess anabolic activity.[2]

Cholest-4-en-3-one (I) with ethyl formate in the presence of sodium methoxide gives the formyl derivative, which on treatment with methyl iodide and potassium carbonate yields 2-methylcholest-4-en-3-one. The product, which is obtained crystalline only after chromatography on alkaline alumina, must have the more stable (*i.e.*, equatorial) 2α-configuration (II).


(I)



(II)



(III)

An attempt to prepare the 4-methyl compound from the enol acetate (III) by the same method resulted in the 2-substituted derivative. It appears, therefore, that $C_{(2)}$ is the preferred position for reaction,[3] though the heteroannular dienol anion should be formed initially.

By the same general procedure, testosterone has been converted into the 2-formyl derivative and thence 2-methyltestosterone whose properties agree with those reported by Ringold and Rosenkranz.[4] Biological assays carried out by Dr. L. Golberg, of Benger's Ltd., England, show 2-α-methyltestosterone to possess an androgenic : anabolic activity ratio of 0·12 : 0·35 relatively to testosterone.

Since this work was completed, Sondheimer and Mazur [3] have described the preparation of 4-methylcholest-4-en-3-one both *via* the enol lactone and by direct methylation of (I), and Ringold and Rosenkranz [4] have described the preparation of 2α-methyltestosterone *via* the ethoxide.

Experimental.—Formylation of cholest-4-en-3-one. Cholest-4-en-3-one (2·56 g.) was briefly boiled in dry benzene to ensure that it was completely anhydrous, then cooled, and ethyl formate (3·3 c.c.) was added. The mixture was added to sodium methoxide (from 0·92 g. of the metal) suspended in benzene, and the total volume made up with benzene to *ca.* 100 c.c. The mixture was kept at room temperature for 3 days, after which the insoluble sodium salt was filtered off, washed with ether, and decomposed with dilute hydrochloric acid. The formyl compound was then extracted with ether, and the ether extract was washed with saturated aqueous sodium chloride, dried (Na_2SO_4), and evaporated. 2-Hydroxymethylenecholest-4-en-3-one (2·76 g.) was obtained; crystallised from aqueous acetone it had m. p. 109—110°.

2α-Methylcholest-4-en-3-one. The crude formyl compound (620 mg.) was treated in dry acetone (5 c.c.) with methyl iodide (0·60 c.c.). To the mixture was added freshly ignited potassium carbonate (400 mg.), and after refluxing gently for 24 hr. the mixture was cooled, poured into ether, and washed once with a little water. The ether layer was washed with N-sodium hydroxide until free from acid, then with water and evaporated. The product was dissolved in acetone, and the solution made 0·5N with dilute hydrochloric acid and kept for 24 hr. at room temperature, after which it was poured into ether. The ether layer was washed with water, with dilute aqueous sodium hydroxide (to extract unchanged formyl compound), again with water, dried (Na_2SO_4), and evaporated. The crude product (290 mg.) was chromatographed on alkaline alumina (30 g.; grade 0) and, after a preliminary fraction in benzene,

[1] Hogg, Lincoln, Jackson, and Schneider, *J. Amer. Chem. Soc.*, 1955, **77**, 6401.
[2] Camerino, Patelli, and Vercellone, *ibid.*, 1956, **78**, 3540.
[3] Sondheimer and Mazur, *ibid.*, 1957, **79**, 2906.
[4] Ringold and Rosenkranz, *J. Org. Chem.*, 1956, **21**, 1333.

2α-methylcholest-4-en-3-one was eluted with benzene–ethyl acetate (2 : 1) and crystallised from methanol; it had m. p. 120—122° (Found: C, 84·3; H, 11·6. Calc. for $C_{28}H_{46}O$: C, 84·4; H, 11·6%), $\lambda_{max.}$ 241 mμ (ε 14,000 in ethanol).

MANCHESTER UNIVERSITY.
UNIVERSITY COLLEGE, GHANA.

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345. *5-Alkyl-1 : 2-benzacridines. Synthesis of 5-Methyl-1 : 2-benzacridine.*

By A. CAMPBELL and E. N. MORGAN.

EARLIER syntheses of 5-methyl-1 : 2-benzacridine,[1] like those of 5-methylacridine,[2] possessed drawbacks for large-scale preparations. In attempts to adapt the later synthesis of 5-methylacridine,[3] we found that 5-chloro-1 : 2-benzacridine did not react with diethyl malonate or ethyl cyanoacetate under the usual conditions.

More stringent conditions enabled 5-chloro-1 : 2-benzacridine to react with malononitrile in the presence of sodium butoxide to give 5-dicyanomethyl-1 : 2-benzacridine. Hydrolysis with concentrated sulphuric acid then furnished 5-methyl-1 : 2-benzacridine in good yield. As in the acridine series, 5-methyl-1 : 2-benzacridine was converted by *N*-bromosuccinimide into 5-bromomethyl-1 : 2-benzacridine which with potassium acetate gave 5-acetoxymethyl- and thence 5-hydroxymethyl-1 : 2-benzacridine, and with diethylaminopropylamine gave 5-(3-diethylaminopropylamino)methyl-1 : 2-benzacridine. Ethyl 1 : 2-benzacridine-5-carboxylate [4] was reduced with lithium aluminium hydride to 5-hydroxymethyl-1 : 2-benzacridan. The latter on oxidation with manganese dioxide in benzene at room temperature [5] furnished 5-formyl-1 : 2-benzacridine. This oxidation procedure was also found to be applicable in the acridine series: ethyl acridine-5-carboxylate [6] was reduced to 5-hydroxymethylacridan which, likewise, on treatment with manganese dioxide in benzene furnished 5-formylacridine.

Experimental.—*5-Dicyanomethyl-1 : 2-benzacridine.* 5-Chloro-1 : 2-benzacridine (26 g.) in xylene (200 c.c.) was added to a solution of sodium butoxide (29·1 g.) and malononitrile (20 g.) in butan-1-ol (750 c.c.), and the mixture refluxed for 16 hr. The butanol and xylene were removed by steam and the residue washed with dilute acetic acid before crystallisation from aqueous dimethylformamide, to give *5-dicyanomethyl-1 : 2-benzacridine* (23 g., 78·5%) in orange platelets, m. p. 310° (Found: C, 81·6; H, 4·1; N, 14·0. $C_{20}H_{11}N_3$ requires C, 81·9; H, 3·8; N, 14·3%).

5-Methyl-1 : 2-benzacridine. 5-Dicyanomethyl-1 : 2-benzacridine (23 g.) was heated in boiling 20N-sulphuric acid (250 c.c.) for 3 hr., the colour of the solution changing from deep orange to yellow-green. After cooling, the mixture was poured into excess of iced aqueous ammonia, and the product filtered off, dried, dissolved in light petroleum (b. p. 60—80°), and passed down a column of activated alumina. Evaporation of the eluate gave 5-methyl-1 : 2-benzacridine (19·4 g., 75·5%), m. p. 125—126°, in very pale yellow prisms.

5-Bromomethyl-1 : 2-benzacridine. 5-Methyl-1 : 2-benzacridine (3·6 g.), *N*-bromosuccinimide (3·6 g.), and benzoyl peroxide (0·5 g.) in carbon tetrachloride (250 c.c.) were refluxed for 4 hr. When cold, the succinimide was filtered off and the filtrate evaporated to small volume under reduced pressure to give *5-bromomethyl-1 : 2-benzacridine* (3·3 g., 69·2%) which recrystallised from carbon tetrachloride in orange prisms, m. p. 194—195° (decomp.) (Found: C, 66·9; H, 3·8; N, 4·3; Br, 24·7. $C_{18}H_{12}NBr$ requires C, 67·0; H, 3·8; N, 4·4; Br, 24·8%).

5-Hydroxymethyl-1 : 2-benzacridine. 5-Bromomethyl-1 : 2-benzacridine (0·5 g.) and potassium acetate (0·5 g.) were refluxed in absolute ethanol (20 c.c.) for 1 hr., then poured into water (100 c.c.). The precipitated product was extracted with ether. Crystallisation of the ether

[1] Postowski and Lundin, *J. Gen. Chem. U.S.S.R.*, 1940, **10**, 71; Buu-Hoï, *J.*, 1949, 670.
[2] Albert, " The Acridines," Edward Arnold, London, 1951, p. 128.
[3] Campbell, Franklin, Morgan, and Tivey, *J.*, 1958, 1145; Morgan and Tivey, B.P. 789,696.
[4] Braun and Wolff, *Ber.*, 1922, **55**, 3675.
[5] Turner, *J. Amer. Chem. Soc.*, 1954, **76**, 5175.
[6] Jensen and Rethwisch, *ibid.*, 1928, **50**, 1144.

residue from benzene–light petroleum (b. p. 40—60°) gave *5-acetoxymethyl-1 : 2-benzacridine* (0·2 g.) in platelets, m. p. 123—124° (Found: C, 80·0; H, 5·0; N, 4·7. $C_{20}H_{15}O_2N$ requires C, 80·2; H, 5·1; N, 4·9%). This acetate (0·1 g.) was kept in absolute ethanol (10 c.c.), containing N-sodium hydroxide (0·5 c.c.) overnight at room temperature, then poured into water, and the precipitate was collected, dried, and recrystallised from aqueous ethanol, giving pale yellow needles of *5-hydroxymethyl-1 : 2-benzacridine* (50 mg.), m. p. 165—166° (decomp.) (preheated to 160°) (Found: C, 83·0; H, 5·1; N, 5·4. $C_{18}H_{13}ON$ requires C, 83·3; H, 5·0; N, 5·4%).

5-Formyl-1 : 2-benzacridine. A solution of ethyl 1 : 2-benzacridine-5-carboxylate [4] (25 g.) in tetrahydrofuran (200 c.c.) was added dropwise with stirring to ethereal lithium aluminium hydride solution (100 c.c.; 5%) and subsequently refluxed for 2 hr. The cooled mixture was worked up by Micovic and Mihailovic's procedure,[7] to give *5-hydroxymethyl-1 : 2-benzacridan* (18 g.) which recrystallised in pale cream-coloured aggregates, m. p. 148—149° (17 g., 78·4%) (Found: C, 82·4; H, 5·7; N, 5·2. $C_{18}H_{15}ON$ requires C, 82·7; H, 5·8; N, 5·4%). The acridan (16 g.) was shaken in benzene (500 c.c.) with manganese dioxide [5] (40 g.) for 18 hr. After filtration, the benzene residue crystallised from benzene–light petroleum (b. p. 40—60°), to give long needles of *5-formyl-1 : 2-benzacridine* (11 g., 69·8%), m. p. 146—147° (Found: C, 83·9; H, 4·2; N, 5·2. $C_{18}H_{11}ON$ requires C, 84·0; H, 4·3; N, 5·4%).

5-(3-Diethylaminopropylamino)methyl-1 : 2-benzacridine trihydrochloride. 5-Bromomethyl-1 : 2-benzacridine (3·3 g.) and 3-diethylaminopropylamine (10 c.c.) in benzene (100 c.c.) were refluxed for 2 hr. The cooled solution was washed with water, and the benzene evaporated. To the residue in 2N-hydrochloric acid, acetone was added, giving *5-(3-diethylaminopropylamino)-methyl-1 : 2-benzacridine trihydrochloride* in yellow needles (3 g., 62·5%), m. p. 220° (decomp.) (Found: C, 55·9; H, 7·2; N, 8·0. $C_{25}H_{29}N_3,3HCl,3H_2O$ requires C, 56·1; H, 7·2; N, 8·0%).

5-Formylacridine.—Ethyl acridine-5-carboxylate [6] (13 g.) in dry ether (200 c.c.) was added dropwise to a stirred solution of lithium aluminium hydride (10%) in ether (30 c.c.), and the mixture refluxed for 2 hr. Working up [7] gave *5-hydroxymethylacridan* (9 g.), needles [from benzene–light petroleum (b. p. 60—80°)], m. p. 130—131° (decomp.) (Found: C, 79·4; H, 6·3; N, 6·4. $C_{14}H_{13}ON$ requires C, 79·6; H, 6·2; N, 6·6%). Shaking this alcohol (9 g.) in benzene (100 c.c.) overnight at room temperature with manganese dioxide (50 g.), gave 5-formylacridine (7 g.), golden-yellow needles (from aqueous methanol) (6·5 g.), m. p. and mixed m. p. 146—147°.

The authors thank Dr. R. E. Bowman for many helpful discussions.

RESEARCH DEPARTMENT, MESSRS. PARKE, DAVIS & CO. LTD.,
STAINES ROAD, HOUNSLOW, MIDDX. [*Received, November 15th*, 1957.]

[7] Micovic and Mihailovic, *J. Org. Chem.*, 1953, **18**, 1192.

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346. *Dodecylquinolinium Bromide.*

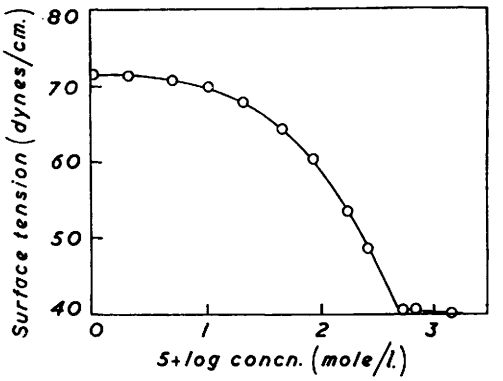
By A. V. FEW, A. R. GILBY, R. H. OTTEWILL, and H. C. PARREIRA.

OUR physical [1] and biological [2] work on cationic detergents required dodecyl-trimethyl-ammonium, -pyridinium, and -quinolinium bromide. Reaction of dodecyl bromide with the tertiary base gave the first two bromides directly in a pure state, but the quinoline derivative required wasteful purification. This is a new compound [3] and we record its preparation and some of its properties.

Experimental.—Synthetic quinoline (5 g.) and 1-bromododecane (10 g.) were heated for 5 hr. at 115° in a stream of oxygen-free nitrogen. The reddish solid obtained on cooling was dissolved in 9 : 1 v/v dioxan–acetone at 60°: cooling to 4° gave orange crystals. Fractional recrystallization from dioxan–acetone gave pale yellow crystals of the *salt* (10·6 g.), m. p. 100° (Found: C, 67·0; H, 8·4; N, 4·0; Br, 21·2. $C_{21}H_{32}NBr$ requires C, 66·7; H, 8·2; N, 3·7; Br, 21·2%). This had $\lambda_{max.}$ 2370 and 3160 Å (ε 35,300 and 7450 respectively) in H_2O. A plot

[1] Ottewill and Parreira, unpublished work.
[2] Few and Gilby, unpublished work.
[3] Cf. Schwartz and Perry, "Surface Active Agents," Interscience Publ. Inc., 1949, p. 159.

of surface tension against log concentration in water at 25° (drop volume method [4]) is shown in the Figure. Freedom from surface-active impurities was indicated by the absence of a



minimum in the curve at the onset of micelle formation. The critical micelle concentration was $4{\cdot}80 \times 10^{-3}$M.

DEPARTMENT OF COLLOID SCIENCE,
CAMBRIDGE UNIVERSITY.

[*Received, November 19th*, 1957.]

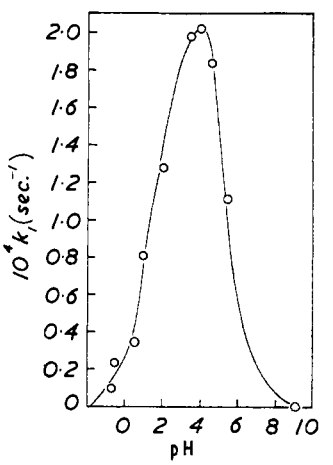
[4] Harkins and Brown, *J. Amer. Chem. Soc.*, 1919, **41**, 499.

347. N-*Phosphourethane: Synthesis and Hydrolytic Studies.*

By A. LAPIDOT and M. HALMANN.

ALTHOUGH many amino-derivatives of phosphorus have been synthesized,[1] the only acyl derivative of phosphoramidic acid which has been described [2] is *N*-benzoylphosphoramidic acid, $C_6H_5{\cdot}CO{\cdot}NH{\cdot}PO(OH)_2$. In connexion with studies of the mechanism of carcinogenesis,[3] we prepared *N*-phosphourethane (*N*-ethoxycarbonylphosphoramidic acid; urethane phosphate), $CO_2Et{\cdot}NH{\cdot}PO(OH)_2$, and studied its hydrolysis. It was synthesised by way of an *iso*cyanato-derivative of phosphorus. Recently, Kirsanov [4] described the convenient preparation of phospho*iso*cyanatidic dichloride, from which he prepared the acid dichloride of phosphourethane by addition of ethanol to the *iso*cyanate.

In the present work, hydrolysis of this dichloride, $CO_2Et{\cdot}NH{\cdot}POCl_2 + 2H_2O = CO_2Et{\cdot}NH{\cdot}PO(OH)_2 + 2HCl$, was tried under a variety of conditions. (*a*) Hydrolysis in water at room temperature was very slow. (*b*) Hydrolysis in N-sodium hydroxide solution was very rapid and complete; however, difficulties were encountered in removing the inorganic reagents and the water without partially decomposing the phosphourethane. (*c*) Hydrolysis in aqueous dioxan in the presence of silver carbonate was rapid and was the method of choice. Pure phosphourethane is a very hygroscopic, white, crystalline solid. Its acid dissociation constants at 29° are pK_1 2·4 and pK_2 6·3.



Dependence of rate of hydrolysis on pH.

The rate of hydrolysis of phosphourethane in water and in buffer solutions at various ranges of pH was studied. It proceeded with first-order kinetics and was followed by

[1] Kosolapoff, " Organophosphorus Compounds," John Wiley & Sons, Inc., London, 1950.
[2] Titherley and Worral, *J.*, 1909, **95**, 1143.
[3] Haran and Berenblum, *Brit. J. Cancer*, 1956, **10**, 57, giving previous references.
[4] Kirsanov, *Zhur. obshchei Khim.*, 1954, **24**, 1033; *Chem. Abs.*, 1955, **49**, 8787b.

determination of the phosphoric acid produced. No carbon dioxide was released under the conditions of kinetic experiments, as was shown by a separate experiment in aqueous solution. Thus the only products must be urethane and phosphoric acid. Results for the dependence of the rate of hydrolysis on the pH of the solution are given in Table 1 and in the Figure; they indicate a maximum rate of hydrolysis at about pH 4, at which practically all the phosphourethane is in the monoionised form. A similarly high reactivity had been observed for the monoanion of monoesters of phosphoric acid.[5]

It has been suggested [5] that the pH-dependence of rate of hydrolysis of monoalkyl and monoaryl phosphates, outside the highly acid range, can be explained as a unimolecular

TABLE 1. *Dependence of rate of hydrolysis of phosphourethane on* pH.

Temp.	36·3°	37·0°								40·1°	40·1°
Solvent *	$HClO_4$ 5·5N	$HClO_4$ 3·5N	$HClO_4$ 0·35N	HCl 0·11N	HCl 0·01N	KHT 0·03M	KHP 0·05M	A.B. 0·1M	A.B. 0·1M	H_2O	$Na_2B_4O_7$ 0·5M	NaOH 0·1M
pH	—	—	0·45	0·96	1·96	3·58	4·02	4·65	5·4	—	9·07	13
10^4k_1 (sec.$^{-1}$)	0·094	0·23	0·34	0·81	1·28	1·98	2·02	1·83	1·11	0·86	0·0024	0·001

* KHT = potassium hydrogen tartrate; KHP = potassium hydrogen phthalate; A.B. = acetate buffer.

decomposition of the monoanion in the rate-determining step. It seems possible that a similar mechanism occurs in the hydrolysis of phosphourethane:

$$CO_2Et{\cdot}NH{\cdot}PO(OH){\cdot}O^- \xrightarrow{\text{Slow}} CO_2Et{\cdot}NH^- + PO_2{\cdot}OH \xrightarrow[H_2O]{\text{Fast}} CO_2Et{\cdot}NH_2 + PO(OH)_2{\cdot}O^-$$

In a slow stage of heterolysis of the N–P bond, unstable intermediates are formed, which are rapidly hydrated to the products. It is here assumed that metaphosphoric acid is the unstable phosphorus derivative.

Experimental.—Phospho*oiso*cyanatidic dichloride, prepared according to Kirsanov,[4] had b. p. 20°/5 mm. (Found: Cl, 44·5. Calc. for CO_2NCl_2P: Cl, 44·5%).

The dichloride [4] of phosphourethane was obtained by gradually adding dry ethanol (20 ml., 0·34 mole) to phospho*oiso*cyanatidic dichloride (58 g., 0·36 mole) with cooling in an ice-bath. The resulting oil crystallized in salt–ice. The crystals, filtered off in the cold, washed with light petroleum, and dried *in vacuo*, had m. p. 20—25° (61·5 g., 82%). Their chlorine content was determined by dissolving a sample in a 10-fold excess of N-sodium hydroxide, neutralization with nitric acid, and titration with standard mercuric nitrate, diphenylcarbazide being used as indicator (Found: Cl, 34·3. Calc. for $C_3H_6O_3NCl_2P$: Cl, 34·5%).

Hydrolysis of the dichloride. This dichloride (6·5 g., 0·027 mole) was added to a suspension of silver carbonate (9 g., 0·033 mole) in aqueous dioxan (1 : 1., 50 ml.) cooled in ice. The reaction was exothermic. Silver chloride was precipitated instantly and was separated by centrifugation. The supernatant liquid was still cloudy; after ordinary filtration it was evaporated and dried in high vacuum, yielding 4·9 g. (91%) of *phosphourethane* (*N-ethoxycarbonylphosphoramidic acid*), a white, powdery, hygroscopic material, which was stored in a desiccator over P_2O_5 at −30°. When heated in a sealed capillary, it melted at about 125° (decomp.) (Found: C, 21·7; H, 5·1; N, 7·8; P, 17·9. $C_3H_8O_5NP$ requires C, 21·3; H, 4·7; N, 8·3; P, 18·3%). The equivalent weight was determined by potentiometric titration with 0·1N-sodium hydroxide. Sharp inflection curves were observed at pH 4·5 and 8·7, corresponding to equivalent weights of 170 and 85 ($C_3H_8O_5NP$ requires 169 and 84·5).

The dissociation constants of phosphourethane were calculated from results of a titration (carried out with a Metrohm AG, Type El48c, pH meter), according to Henderson's formula $pK = -\log (H^+)(B + H^+)/[C - (B + H^+)]$, where H^+ is the hydrogen-ion activity, B is the concentration of sodium hydroxide added, and C is the total concentration of phosphourethane. The average of four determinations gave pK_1 2·4, and the average of three measurements gave pK_2 6·3, both at 29°.

[5] Bailly, *Bull. Soc. chim. France*, 1942, **9**, 421; Desjobert, *ibid.*, 1947, **14**, 809; *Compt. rend.*, 1947, **224**, 575; Vernon, *Proc. Chem. Soc.*, 1957, 136; Butcher and Westheimer, *J. Amer. Chem. Soc.*, 1955, **77**, 2423; Kumamoto and Westheimer, *ibid.*, p. 2515; Chanley and Feageson, *ibid.*, p. 4002; Bernard, Bunton, Llewellyn, Oldham, Silver, and Vernon, *Chem. and Ind.*, 1955, 760.

Kinetics of hydrolysis. Samples of 10—20 mg. of phosphourethane were weighed into 25-ml. volumetric flasks. The appropriate solvent was added, and the flask placed in a thermostat. At intervals, 0·5—2 ml. portions were withdrawn and analyzed for free phosphoric acid by Fiske and Subbarow's method,[6] a Coleman Junior Model 6B Spectrophotometer being used. The low starting values prove that the phosphate itself does not react with the molybdate reagent.

Example of kinetic run: Phosphourethane (initially 3·40 mmoles) in acetate buffer (0·1M; pH 4·65) at 37·0°:

Time (sec.)	0	600	1200	1800	2460	3180	4080	4620	Infinity
H_3PO_4 (mmole) ...	0·32	0·56	0·70	0·86	1·02	1·14	1·36	1·40	2·25
10^4k_1 (sec.$^{-1}$)	—	2·04	1·75	1·75	1·76	1·76	1·83	1·71	—

Average: $k_1 = (1{\cdot}80 \pm 0{\cdot}01) \times 10^{-4}$ sec.$^{-1}$.

Test for formation of carbon dioxide during hydrolysis: Nitrogen was bubbled through a solution of phosphourethane (33 mg.) in water (10 ml.) while the temperature was gradually raised from 35° to 80°. No carbon dioxide was detected by barium hydroxide solution in the issuing gas.

The authors are indebted to Professor I. Berenblum for suggesting this problem, and to Dr. D. Rosenthal for valuable comments on the manuscript.

ISOTOPE DEPARTMENT and DEPARTMENT OF EXPERIMENTAL BIOLOGY,
WEIZMANN INSTITUTE OF SCIENCE, REHOVOTH, ISRAEL. [*Received, November 25th*, 1957.]

[6] Fiske and Subbarow, *J. Biol. Chem.*, 1925, **66**, 375.

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348. *Application of the Bruckner Method to the Synthesis of Phenanthridine Derivatives. Part II.*[1]

By T. R. GOVINDACHARI, B. R. PAI, and V. N. SUNDARARAJAN.

THE synthesis of several 1 : 2 : 3 : 4 : 4a : 10a-hexahydro-9-phenylphenanthridines by a modified extension of the Bruckner method [2] was described earlier.[1] In the present work acetyl and phenylacetyl derivatives of the *cis*-2-aryl*cyclo*hexylamines there reported have been prepared and cyclised by phosphorus oxychloride in refluxing toluene to the 9-methyl and the 9-benzyl derivative of 1 : 2 : 3 : 4 : 4a : 10a-hexahydrophenanthridines and then dehydrogenated to the fully aromatic phenanthridines, whose structures in two cases were confirmed by comparison with authentic samples. The ultraviolet absorption maxima of the phenanthridines obtained in this study are tabulated.

Ultraviolet absorption spectra of phenanthridine hydrochlorides in 95% *ethanol.*

Derivative	$\lambda_{max.}$ (mμ)	log ε
9-Methyl-	250, 330, 345	4·64, 3·37, 3·35
9-Benzyl-	250, 330, 345	4·62, 3·41, 3·28
5 : 9-Dimethyl-	245, 295, 350	4·80, 3·81, 3·35
6(8) : 9-Dimethyl-	250, 295, 330, 345	4·60, 3·66, 3·31, 3·22
7 : 9-Dimethyl-	250, 335, 340, 370	4·64, 3·40, 3·40, 3·01
6-Methoxy-	255, 305, 330	4·68, 4·03, 3·79
6-Methoxy-9-methyl-	230, 255, 308, 325	4·19, 4·57, 3·75, 3·66
9-Benzyl-6-methoxy-	230, 255, 303, 330	4·51, 4·77, 4·02, 3·76
5-Methyl-9-phenyl- (base)	250, 300, 338. 355	4·66, 3·94, 3·43, 3·39

Experimental.—cis-1-*Acetamido*-2-*phenyl*cyclo*hexane*. *cis*-2-Phenyl*cyclo*hexylamine [1] (3 g.), acetic anhydride (9 ml.), and dry pyridine (0·5 ml.) were heated at 100° for 4 hr., then poured into water, and the product (2·4 g.) crystallised from alcohol, giving cis-1-*acetamido*-2-*phenyl*-cyclo*hexane*, m. p. 118—119° (Found: C, 77·0; H, 8·6; N, 6·7. $C_{14}H_{19}ON$ requires C, 77·3; H, 8·8; N, 6·5%).

[1] Part I, Govindachari, Nagarajan, Pai, and Arumugam, *J.*, 1956, 4280.
[2] Bruckner, *Annalen*, 1935, **518**, 227; Bruckner and Kramli, *J. prakt. Chem.*, 1936, **145**, 291; Bruckner, Kiss, and Kovacs, *J.*, 1948, 885; Bruckner and Fodor, *Ber.*, 1943, **76**, 466.

1 : 2 : 3 : 4 : 4*a* : 10*a*-*Hexahydro*-9-*methylphenanthridine*. A mixture of the acetyl derivative (3 g.) in toluene (75 ml.) and phosphorus oxychloride (15 ml.) was refluxed for 3 hr., cooled, and decomposed with ice. The aqueous layer was made alkaline and extracted with ether. The base in the ethereal layer was purified by one more passage through acid, to give the phenanthridine as an oil (0·4 g.). The *hydrochloride* crystallised from alcohol–ether (m. p. 218—220°) (Found: C, 71·0; H, 8·0; N, 5·6. $C_{14}H_{17}N$,HCl requires C, 71·3; H, 7·7; N, 5·9%); it had $\lambda_{max.}$ 278, 355—375 mμ (log ε 4·01, 2·91).

9-*Methylphenanthridine*. The hexahydrophenanthridine (0·35 g.) was dehydrogenated in *p*-cymene (25 ml.) by 30% palladised charcoal (0·2 g.) during 5 hr. The solution was filtered and extracted with dilute hydrochloric acid. Basification of the acid extract and extraction with ether gave the oily phenanthridine (0·2 g.) whose *hydrochloride*, crystallised from alcohol, had m. p. 282—284° (Found: C, 73·2; H, 5·1. $C_{14}H_{11}N$,HCl requires C, 73·2; H, 5·2%), alone or mixed with the hydrochloride of 9-methylphenanthridine.[3]

9-*Benzylphenanthridine*. *cis*-2-Phenyl*cyclo*hexylamine (3 g.) and phenylacetyl chloride (6 ml.) gave by the Schotten–Baumann method the *phenylacetamide* (2 g.), plates (from methanol), m. p. 149—150° (Found: C, 82·0; H, 7·7; N, 4·5. $C_{20}H_{23}ON$ requires C, 81·9; H, 7·9; N, 4·8%), and thence, by the usual procedure, 9-benzyl-1 : 2 : 3 : 4 : 4*a* : 10*a*-hexahydrophenanthridine (0·35 g. from 3·1 g.) whose yellow *picrate*, m. p. 160—162°, crystallised from alcohol (Found: C, 61·6; H, 4·5. $C_{20}H_{21}N,C_6H_3O_7N_3$ requires C, 61·9; H, 4·8%). Dehydrogenation yielded 9-benzylphenanthridine (0·15 g. from 0·45 g.) whose *hydrochloride* crystallised from alcohol–ether as plates, m. p. 250—252° (Found: C, 78·9; H, 5·3. $C_{20}H_{15}N$,HCl requires C, 78·6; H, 5·2%) alone or mixed with the hydrochloride of 9-benzylphenanthridine.[4]

Similarly were prepared: *N*-*Acetyl*-cis-2-o-*tolyl*cyclo*hexylamine*, plates (from benzene–light petroleum), m. p. 121—122° (Found: C, 77·6; H, 9·3; N, 6·4. $C_{15}H_{21}ON$ requires C, 77·9; H, 9·2; N, 6·1%); 1 : 2 : 3 : 4 : 4*a* : 10*a*-*hexahydro*-5 : 9-*dimethylphenanthridine hydrochloride* (from alcohol–ether), m. p. 224—226° (Found: C, 71·9; H, 8·0. $C_{15}H_{19}N$,HCl requires C, 72·1; H, 8·1%), $\lambda_{max.}$ 285, 370—380 mμ (log ε 3·98, 2·68); and 5 : 9-*dimethylphenanthridine hydrochloride* (from alcohol–ether), m. p. 256—258° (Found: C, 73·8; H, 6·0. $C_{15}H_{13}N$,HCl requires C, 73·9; H, 5·8%).

5-*Methyl*-9-*phenylphenanthridine* (0·25 g. from 0·35 g. of 1 : 2 : 3 : 4 : 4a : 10a-hexahydro-5-methyl-9-phenylphenanthridine [1]), needles (from light petroleum), m. p. 133—134° (Found: C, 89·2; H, 5·7. $C_{20}H_{15}N$ requires C, 89·2; H, 5·6%).

N-Acetyl-*cis*-2-*m*-tolyl*cyclo*hexylamine, an oil; 1 : 2 : 3 : 4 : 4a : 10a-*hexahydro*-6(8) : 9-*dimethylphenanthridine hydrochloride* (from alcohol–ether), m. p. 210—212° (Found, after drying at 138° for 6 hr.: C, 67·1; H, 8·5. $C_{15}H_{19}N$,HCl,H_2O requires C, 67·3; H, 8·3%), $\lambda_{max.}$ 270, 285 mμ (log ε 3·80, 3·78); and 6(8) : 9-*dimethylphenanthridine hydrochloride* (from alcohol–ether), m. p. 276—278° (Found: C, 74·1; H, 6·1%).

N-*Acetyl*-cis-2-p-*tolyl*cyclo*hexylamine* (from benzene–light petroleum), m. p. 160° (Found: C, 77·7; H, 9·3%); 1 : 2 : 3 : 4 : 4*a* : 10*a*-*hexahydro*-7 : 9-*dimethylphenanthridine hydrochloride* (from alcohol–ether), m. p. 228—230° (Found, after drying at 138° for 6 hr.: C, 66·9; H, 8·0%), $\lambda_{max.}$ 280, 375 mμ (log ε 3·99, 3·30); and 7 : 9-*dimethylphenanthridine hydrochloride*, yellow needles (from alcohol–ether), m. p. 296—298° (Found: C, 73·8; H, 6·0%).

cis-2-(*m*-Methoxyphenyl)*cyclo*hexylamine [1] (2 g.) and 95% formic acid (8 ml.) gave the gummy *N*-formyl derivative and thence 1 : 2 : 3 : 4 : 4*a* : 10*a*-*hexahydro*-6-*methoxyphenanthridine picrate* (from alcohol), m. p. 204° (Found: C, 54·4; H, 4·8; N, 12·8. $C_{14}H_{17}ON,C_6H_3O_7N_3$ requires C, 54·1; H, 4·5; N, 12·6%), and 6-*methoxyphenanthridine hydrochloride*, needles (from alcohol), m. p. 236—238° (Found: C, 68·4; H, 5·2; N, 5·5. $C_{14}H_{11}ON$,HCl requires C, 68·4; H, 4·9; N, 5·7%).

N-*Acetyl* cis-2-(m-*methoxyphenyl*)cyclo*hexylamine*, leaflets (from benzene–light petroleum), m. p. 114—115° (Found: C, 72·9; H, 8·2; N, 6·0. $C_{15}H_{21}O_2N$ requires C, 72·9; H, 8·5; N, 5·7%); 1 : 2 : 3 : 4 : 4a : 10a-*hexahydro*-6-*methoxy*-9-*methylphenanthridine picrate* (from alcohol), m. p. 168° (Found: C, 54·9; H, 4·8; N, 11·7. $C_{15}H_{19}ON,C_6H_3O_7N_3$ requires C, 55·0; H, 4·8; N, 12·2%), and 6-*methoxy*-9-*methylphenanthridine hydrochloride* (from alcohol), m. p. 245° (Found: C, 69·7; H, 5·4; N, 5·7. $C_{15}H_{13}ON$,HCl requires C, 69·4; H, 5·4; N, 5·4%).

cis-2-(*m*-Methoxyphenyl)*cyclo*hexylamine gave the *phenylacetyl derivative* (from benzene–light petroleum), m. p. 114—116° (Found: C, 77·8; H, 7·4; N, 4·4. $C_{21}H_{25}O_2N$ requires C, 78·0; H, 7·7; N, 4·3%), and thence 9-*benzyl*-6-*methoxyphenanthridine hydrochloride*, needles

[3] Morgan and Walls, *J.*, 1931, 2447.
[4] Ritchie, *J. Proc. Roy. Soc., New South Wales*, 1945, **78**, 147; *Chem. Abs.*, 1946, **40**, 877.

(from alcohol), m. p. 262—264° (Found: C, 74·8; H, 5·4. $C_{21}H_{17}ON,HCl$ requires C, 75·1; H, 5·4%).

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PRESIDENCY COLLEGE, MADRAS, INDIA. [*Received, November 26th*, 1957.]

349. *Florisil as an Adsorbent for Basic Substances.*

By A. ASATOOR and C. E. DALGLIESH.

THE advantages of adsorption for preliminary separation of groups of compounds from complex mixtures have been outlined.[1,2,3] The synthetic adsorbent Florisil (a magnesia–silica gel: Floridin Company, Tallahassee, Florida) has been used to isolate certain polycyclic molecules, *e.g.*, riboflavin,[4] alkaloids such as morphine, codeine, and heroin,[5] and flavins.[6] We have now found that Florisil is a good general adsorbent for bases, which can subsequently be eluted with high recoveries with pyridine–acetic acid.

Adsorption behaviour on Florisil.

The figures under "filtrate" and "eluate" represent percentage recoveries under the standard experimental conditions. The concentration of adsorbate solution was 0·0005M except where otherwise stated.

Substance	Filtrate	Eluate	Substance	Filtrate	Eluate
		Bases			
Adenine	0	94	Adrenaline	0	96
2-Phenylethylamine	0	98	Tryptamine	0	94
Tyramine	0	95	5-Hydroxytryptamine	0	96
3 : 4-Dihydroxyphenylethylamine	0	92	Histamine	0	94
Noradrenaline	6	92	Codeine	0	100
		Amino-acids			
Glycine	100	0	Thyroxine	95	6
Cystine (0·00025M)	100	0	Tryptophan	97	2
Glutamic acid	100	0	5-Hydroxytryptophan	96	0
Glutamine	100	0	Citrulline	91	6
Asparagine	100	0	Histidine	97	4
Phenylalanine	97	0	Lysine	5	95
Tyrosine	100	0	Arginine	5	96
3 : 4-Dihydroxyphenylalanine	96	1	Ornithine	0	100
		Miscellaneous			
Urea	100	0	Guanine	73	22
Creatinine	100	0	Cytosine	86	15
Uric acid	100	0	Riboflavin (2 mg./l.)	0	80
Anthranilic acid	100	0	Riboflavin (2 mg./l.)	0	95[a]
5-Hydroxyindolylacetic acid	100	0	Xanthopterin	12	81
Glucosamine	93	7	Xanthopterin	0	92[b]
Xanthine	85	15			
		Inorganic ions			
Cl^- [as 0·9% (w/v) NaCl]	100	0	K^+ [as 0·4% (w/v) KCl]	2	95
PO_4^{2-} (as 0·037M-KH_2PO_4)	91	5	Ca^{2+} (as 0·005M-$CaCl_2$)	0	96
Na^+ [as 0·9% (w/v) NaCl]	63	40			

[a] Increased recovery of riboflavin by using 75 ml. of eluant instead of standard 50 ml. [b] Increased adsorption and recovery of xanthopterin by using twice the standard amount of adsorbent.

The results in the Table were obtained by using a standard set of conditions (see Experimental) and are largely self-explanatory. It is noteworthy that basic amino-acids are

[1] Dalgliesh, *J. Clin. Path.*, 1955, **8**, 73.
[2] Asatoor and Dalgliesh, *J.*, 1956, 2291.
[3] *Idem, ibid.*, *J.*, 1958, 1498.
[4] Ferrebee, *J. Clin. Invest.*, 1940, **19**, 251.
[5] Stolman and Stewart, *Analyst*, 1949, **74**, 536.
[6] Dimant, Sanadi, and Huennekens, *J. Amer. Chem. Soc.*, 1952, **74**, 5440.

readily separated from other amino-acids. Histidine behaves like a non-basic amino-acid, which is compatible with its low isoelectric point (*ca.* 7·6) relative to, say, that of lysine (*ca.* 9·7). The biogenic amines can also be separated from their precursor amino-acids, or non-basic metabolites (cf. 5-hydroxyindolylacetic acid). Glucosamine behaves like a non-basic substance, which is compatible with its unusually low pK_a (7·8; cf. isoelectric point of histidine, 7·6) relative to that of other monoamines (*e.g.*, methylamine, pK_a 10·7). Inorganic cations are also adsorbed and recovered to varying extents. Xanthine, guanine, and cytosine are only partially adsorbed under the standard conditions.

Experimental.—Standard adsorption and elution procedure. Florisil (100—200 mesh; it resembles alumina in its handling properties) was first freed from dust and adsorbed gases by suspending it in 2% (v/v) acetic acid and stirring at intervals for ½ hr.[4] The supernatant liquid was decanted and the granular mass repeatedly washed with water and then poured as a slurry into a glass chromatography tube plugged with glass wool. The column of adsorbent (1½ × 8 cm.) was washed with water and finally a pad of glass wool placed on top. The solution of adsorbate [25 ml. of a solution (usually 0·0005M) previously adjusted to pH 4 with acetic acid] was poured on the column and after adsorption the column was washed with 50 ml. of water. The combined effluent and washings (" Filtrate ") was kept for analysis. The column was then eluted with 50 ml. of a solution of 20% (v/v) pyridine in 2% (v/v) acetic acid, followed by 50 ml. of water. The combined effluent and washings (" Eluate ") was evaporated to dryness under reduced pressure in a water-bath kept below 80°. The dried residue was again taken up in water and re-evaporated to ensure removal of pyridine, and the residue finally dissolved and made up to a known volume. The " filtrate " was similarly evaporated.

Estimation of adsorbates. Riboflavin was estimated fluorimetrically at pH 7 with Laurence's fluorimeter [7]; a Chance blue OB 10 filter was used on the primary (activation) side and an Ilford orange-yellow filter on the secondary (emission) side. Codeine was estimated by measuring its absorption at 284 mμ in 0·1N-hydrochloric acid. Other substances were estimated as previously described.[2,3]

POSTGRADUATE MEDICAL SCHOOL,
DUCANE ROAD, LONDON, W.12.

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[7] Laurence, *Biochem. J.*, 1957, **65**, 27P.

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350. *The Dimer of* o-*Benzoquinone.*

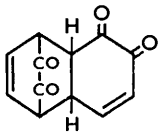
By JOHN HARLEY-MASON and A. H. LAIRD.

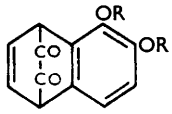
OXIDATION of catechol in ethereal solution with silver oxide has long been known to give *o*-benzoquinone. We have now found that on similar oxidation in acetone solution, *o*-benzoquinone is first formed (and can be isolated by rapid evaporation of the solvent) but that, if the solution is kept, a yellow crystalline dimer soon separates. The dimer, in contrast to *o*-benzoquinone, is stable indefinitely in the solid state.

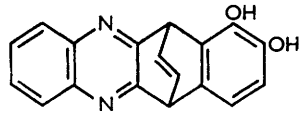
The structure (I), similar to that proposed by Horner and Sturm [1] for the dimer of 4 : 5-dimethyl-*o*-benzoquinone and formed by a Diels–Alder addition of one molecule of the quinone to another, is proposed for our product on the following grounds. The infrared spectrum showed no hydroxyl peak and no peaks characteristic of a benzene ring. Four carbonyl peaks were present, at 5·69, 5·75, 5·80, and 5·93 μ, the first three corresponding to unconjugated carbonyl groups and the last to a conjugated carbonyl group. In addition a peak at 6·19 μ corresponded to the double bond of the system $-CO\cdot CH{=}CH-$. The ultraviolet spectrum showed a single maximum, at 233 mμ, a wavelength which is too low for any benzenoid compound. When boiled in aqueous solution the dimer was rapidly converted into a more soluble phenolic isomer (II; R = H) which gave an intense green ferric chloride reaction, indicating a catechol nucleus. The infrared spectrum showed sharp peaks at 2·97 (OH) and 6·23 and 6·67 μ (benzene ring), and there was a single ultraviolet maximum at 270 mμ.

[1] Horner and Sturm, *Annalen*, 1955, **597**, 1.

With acetic anhydride, the new isomer gave a diacetyl derivative (II; R = Ac); and with *o*-phenylenediamine a quinoxaline derivative (III), which gave an intense green ferric chloride reaction.


(I)


(II)


(III)

This Diels–Alder type of dimerisation appears to take place only in polar but non-hydroxylic organic solvents; *o*-benzoquinone rapidly decomposes in hydroxylic solvents and in water, but in such cases no dimer can be isolated.

Experimental.—o-*Benzoquinone dimer.* To a solution of catechol (2 g.) in acetone (100 ml.) freshly precipitated silver oxide (8 g.) was added, and the mixture was shaken for 10 min. and then filtered. Overnight the filtrate deposited the *dimer* (0·6—1 g.) as bright yellow plates, which melted partially at 125—130°, then resolidified, and finally melted at 194—195°, probably indicating thermal conversion into the phenolic isomer [Found: C, 66·5; H, 3·8%; *M* (Rast), 189. $C_{12}H_8O_4$ requires C, 66·7; H, 3·7%; *M*, 216].

Boiling the dimer (1 g.) with water (50 ml.) for 5 min. produced an orange solution. This was extracted with ethyl acetate (3 × 30 ml.), the extracts were separated and evaporated to dryness, and the residue was recrystallised from ethyl acetate–light petroleum, giving the phenolic *isomer* (II; R = H) as orange-yellow plates, m. p. 195—196° (Found: C, 66·4; H, 3·8%). The compound was acetylated by boiling acetic anhydride for an hour. The excess of anhydride was removed under reduced pressure and the residue recrystallised from ethyl acetate–light petroleum, giving yellow prisms of the *diacetate* (II; R = Ac), m. p. 144° (Found: C, 63·4; H, 4·0. $C_{16}H_{12}O_6$ requires C, 64·0; H, 4·0%).

To a solution of *o*-benzoquinone dimer (keto-isomer; 0·359 g.) in boiling ethanol (50 ml.) a solution of *o*-phenylenediamine (0·375 g.) in ethanol (20 ml.) was added. On concentration and cooling, colourless needles of the *quinoxaline derivative* (III) separated; they had m. p. 333° after recrystallisation from ethanol (Found: C, 74·8; H, 3·8; N, 9·6. $C_{18}H_{12}O_2N_2$ requires C, 75·0; H, 4·2; N, 9·7%).

The authors thank Dr. N. Sheppard for valuable discussions of the spectroscopic data.

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351. *The Synthesis of* 1-*Arylarsindolines.*

By EMRYS R. H. JONES, and FREDERICK G. MANN.

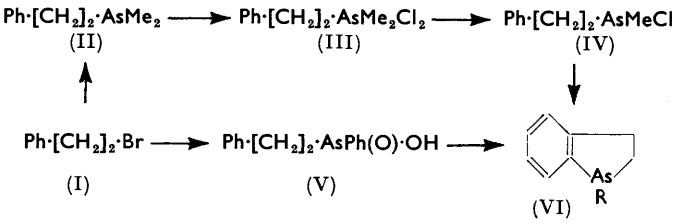
THE first member of the arsindoline series, 1-methylarsindoline (VI; R = Me), was prepared by Turner and Bury,[1] who converted phenethyl bromide (I) into a Grignard reagent, which with iododimethylarsine gave dimethylphenethylarsine (II). This arsine combined directly with chlorine to give the arsine dichloride (III), which when heated afforded methyl chloride and the chloroarsine (IV): cyclisation by using aluminium chloride in carbon disulphide finally gave the methylarsindoline.

We have prepared 1-phenylarsindoline (VI; R = Ph) by a much shorter route, wherein phenethyl bromide (I) is added to dichlorophenylarsine in boiling aqueous sodium hydroxide (the Meyer reaction) to furnish the purified phenethylphenylarsinic acid (V) in 33% yield. This acid is readily cyclised by sulphuric acid to 1-phenylarsindoline oxide, which without isolation is reduced by sulphur dioxide to the arsindoline (VI; R = Ph) in 76% overall yield from the acid (V).

The acid (V) can be reduced by sulphur dioxide and hydrochloric acid to *As*-chloro-*As*-phenethyl-*As*-phenylarsine, $Ph{\cdot}[CH_2]_2{\cdot}AsPhCl$, in 67% yield, but cyclisation of this chloroarsine using aluminium chloride gives the arsindoline (VI; R = Ph) in only 17% yield.

[1] Turner and Bury, *J.*, 1923, **123**, 2489.

It is not known whether this ready cyclisation of arsinic acids of type (V) is limited to those having an aryl group directly linked to the arsenic atom.



Attempted dehydrogenation of the arsindoline (VI; R = Ph) to 1-phenylarsindole, by boiling its xylene solution with tetrachloro-*o*-benzoquinone or its ethylene glycol solution with palladised charcoal, failed; the arsindoline was also largely unaffected when its solution in carbon tetrachloride containing *N*-bromosuccinimide and benzoyl peroxide was boiled for 4 hr. Attempted oxidation of the arsindoline to a 2- or 3-oxo-derivative, by hot aqueous potassium permanganate (cf. Jones and Mann [2]) or by selenium dioxide in hot ethanol, gave mainly the arsine oxide, identified by reduction with sulphur dioxide and then conversion into 1-phenylarsindoline methiodide.

Experimental.—Phenethylphenylarsinic acid (V). Dichlorophenylarsine (90 c.c., 147 g.) was added dropwise to a warm solution of sodium hydroxide (118 g., 4·5 mol.) in water (500 c.c.), to which phenethyl bromide (100 c.c., 135 g., 1 mol.) was then added, and the mixture was boiled for 6 hr. The cold solution was extracted with ether to remove unchanged bromide and was then made just acid (Congo-red) with hydrochloric acid. The *acid* (V) was deposited as an oil which solidified when washed with much cold water and recrystallised from acetone as colourless crystals (63 g., 33%), m. p. 142—143° (Found: C, 58·2; H, 5·3. $C_{14}H_{15}O_2As$ requires C, 57·9; H, 5·2%). Repetition of the experiment on one-tenth of the above scale gave a yield of 47%.

1-*Phenylarsindoline* (VI; R = Ph). A mixture of the acid (V) (20 g.) and concentrated sulphuric acid (100 c.c.) was heated at 100° for 15 min., cooled, poured into water (500 c.c.), and neutralised with 30% aqueous sodium hydroxide. The precipitated oily arsindoline oxide was extracted with chloroform (2 × 75 c.c.), and the united extracts were added to a mixture of concentrated hydrochloric acid (100 c.c.) and water (100 c.c.) containing potassium iodide (0·1 g.), through which sulphur dioxide was then passed for 2 hr. The mixture was set aside overnight, and the chloroform layer, when collected, dried (Na_2SO_4) and distilled, afforded the *arsindoline* (VI; R = Ph) (13·5 g., 76%) as a colourless odourless liquid, b. p. 126—128°/0·6 mm. (Found: C, 65·8; H, 5·4. $C_{14}H_{13}As$ requires C, 65·6; H, 5·1%).

The arsine readily combined with cold methyl iodide, and the product when crystallised from ethanol afforded the colourless *methiodide monohydrate*, m. p. 174—175° (effervescence) (Found: C, 43·3; H, 4·1. $C_{15}H_{16}IAs,H_2O$ requires C, 43·2; H, 4·3%). The oxide and the metho- and etho-bromide were obtained only as gums.

A hot aqueous-ethanolic solution of potassium palladobromide, when treated with the arsindoline (2 mols.), rapidly deposited orange *dibromobis-1-phenylarsindolinepalladium*, m. p. 229—230° (decomp.) (Found: C, 43·1; H, 3·4. $C_{28}H_{26}Br_2As_2Pd$ requires C, 43·1; H, 3·4%). This compound is insoluble in most solvents, but could be recrystallised (without change of m. p.) by adding dioxan dropwise to a boiling ethanolic suspension until a clear solution was obtained.

As-*Chloro*-As-*phenethyl*-As-*phenylarsine*. Sulphur dioxide was passed for 6 hr. through a suspension of the acid (V) (28 g.) in a mixture of concentrated hydrochloric acid (250 c.c.) and water (250 c.c.) containing potassium iodide (0·2 g.). The oily layer, when collected, dried (Na_2SO_4), and distilled gave: (*a*) dichlorophenylarsine (b. p. *ca.* 60°/0·3 mm.); and (*b*) the yellow liquid *chloro-arsine*, b. p. 137—140°/0·3 mm. (18·9 g., 67%) (Found: C, 57·85; H, 4·9. $C_{14}H_{14}ClAs$ requires C, 57·4; H, 4·8%).

A mixture of the chloro-arsine (15·0 g.), powdered aluminium chloride (7 g.), and benzene (50 c.c.) was heated at 100° for 3 hr., although evolution of hydrogen chloride ceased after 15 min. The mixture was poured into dilute hydrochloric acid, warmed gently with stirring,

[2] Emrys R. H. Jones and Mann, *J.*, 1958, 294.

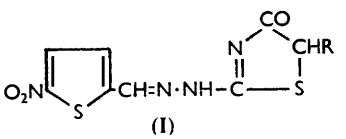
and filtered. The benzene layer, when dried and distilled, gave the fractions: (*a*) b. p. 90—95°/0·5 mm., 2·5 g.; (*b*) the crude arsindoline (VI; R = Ph), b. p. 115—140°/0·5 mm., 2·3 g., 17%. The latter gave the above methiodide, m. p. and mixed m. p. 174° (from ethanol).

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, December 5th*, 1957.]

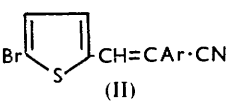
352. *Thiophen Derivatives. Part XI.* Substitution in 2-Thenaldehyde.*

By NG. PH. BUU-HOÏ and DENISE LAVIT.

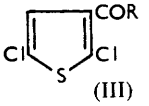
ALTHOUGH nitration of 2-thenaldehyde and its derivatives has often been investigated, the records are confused and at times contradictory. Foye, Hefferen, and Feldmann,[1] treating 2-thenaldehyde with fuming nitric acid in sulphuric acid at low temperature, obtained as sole substitution product 4-nitro-2-thenaldehyde; Gever [2] nitrated 2-thenaldehyde diacetate in acetic anhydride and obtained a eutectic, inseparable mixture of 4- and 5-nitro-2-thenaldehyde, a result similar to that of Rinkes [3] in the nitration of 2-acetylthiophen. Patrick and Emerson,[4] however, using a similar procedure, reported the successful preparation of 5-nitro-2-thenaldehyde, m. p. 75—76°. Campaigne *et al.*[5] prepared the latter aldehyde anew, and recorded m. p. 252—255° for its thiosemicarbazone. It has now been found that nitration of 2-thenaldehyde with fuming nitric acid in acetic anhydride gives mainly 5-nitro-2-thenaldehyde (m. p. 77°), along with some of the 4-isomer, which is eliminated by crystallisation from ethanol. 5-Nitro-2-thenaldehyde thiosemicarbazone was obtained as a yellow product, m. p. 185° (decomp.); its condensation with chloroacetic acid and with higher α-brominated fatty acids yielded the corresponding 5-nitro-2-thenaldehyde 4-oxo-Δ^2-thiazolin-2-ylhydrazones (I). A remarkable feature of the chemistry of 5-nitro-2-thenaldehyde is its failure to react with arylaceto-



(I)



(II)



(III)

nitriles in the presence of alkaline catalysts (*e.g.*, piperidine), a reaction which can be effected with a number of thenaldehydes to give the corresponding α-aryl-β-thienylacrylonitriles; [6] attempts to condense 5-nitro-2-thenaldehyde with ethyl malonate and with 2 : 4 : 6-trinitrotoluene in the presence of piperidine were likewise unsuccessful.

2-Thenaldehyde readily underwent monobromination, mainly to 5-bromo-2-thenaldehyde, a liquid (thiosemicarbazone, m. p. 182°), which had previously been prepared by formylation of 2-bromothiophen in the presence of phosphorus oxybromide [7] and by the Sommelet method.[5] Unlike the nitro-aldehyde, 5-bromo-2-thenaldehyde readily condensed with arylacetonitriles to the corresponding α-aryl-β-bromothienylacrylonitriles (II).

These results underline the outstanding reactivity of position 5 in 2-substituted thiophens, even when the substituent is *meta*-directing. The considerably less pronounced reactivity of the 3- and the 4-position is further demonstrated by the relative inertia of 2 : 5-dichlorothiophen in Friedel–Crafts acylations; only poor yields of 3-acyl-2 : 5-dichlorothiophens (III) were recorded when acid chlorides were used, and no normal keto-acid was formed with phthalic anhydride in the presence of aluminium chloride.

* Part X, Buu-Hoï. Lavit, and Xuong, *J.*, 1955, 1581.

[1] Foye, Hefferen, and Feldmann, *J. Amer. Chem. Soc.*, 1954, **76**, 1378.
[2] Gever, *ibid.*, 1955, **77**, 577.
[3] Rinkes, *Rec. Trav. chim.*, 1933, **52**, 538.
[4] Patrick and Emerson, *J. Amer. Chem. Soc.*, 1952, **74**, 1356.
[5] Campaigne, Monroe, Arnwine, and Archer, *ibid.*, 1953, **75**, 988.
[6] Buu-Hoï, Hoán, and Lavit, *J.*, 1950, 2130; 1951, 251; 1952, 4590; Cagniant, *Bull. Soc. chim. France*, 1949, **16**, 850.
[7] Cf. King and Nord, *J. Org. Chem.*, 1948, **13**, 635.

Experimental.—Nitration of 2-thenaldehyde. An ice-cooled solution of 2-thenaldehyde (13 g.; prepared by formylation of thiophen with dimethylformamide and phosphorus oxychloride) in acetic anhydride was treated dropwise with fuming nitric acid (9·9 g.; *d* 1·49) in acetic acid, with stirring. As soon as the first crystals appeared, water was added, and the solid precipitate (14·5 g.) was collected, washed with water, and recrystallised twice from ethanol, giving 5-nitro-2-thenaldehyde as needles, m. p. 77°. Small amounts of 4-nitro-2-thenaldehyde (m. p. 35°) were isolated from the mother-liquors. The semicarbazone formed pale yellow needles, m. p. 269° (decomp.), from acetic acid; Patrick and Emerson [4] gave m. p. 242—243°. The thiosemicarbazone, prepared from the thenaldehyde (9·5 g.) and thiosemicarbazide (5·5 g.) in acetic acid, formed yellow flakes, m. p. 185° (decomp.), from acetic acid.

5-Nitro-2-thenaldehyde 4-oxo-Δ²-thiazolin-2-ylhydrazone (I; R = H) was formed when the thiosemicarbazone (2·4 g.), chloroacetic acid (0·3 g.), and methanol (30 c.c.) were refluxed for 8 hr. with sodium acetate (0·3 g.), and the precipitate was recrystallised from ethanol, giving yellow needles (0·4 g.), m. p. 289—290° (Found: C, 35·3; H, 2·0. $C_8H_6O_3N_4S_2$ requires C, 35·6; H, 2·2%). The *5-ethyl-4-oxo-Δ²-thiazolin-2-ylhydrazone* (I; R = Et), similarly prepared from α-bromobutyric acid, formed yellow needles, m. p. 265° (Found: C, 40·0; H, 3·3. $C_{10}H_{10}O_3N_4S_2$ requires C, 40·3; H, 3·4%); the *5-butyl* (I; R = Bu), yellow needles, m. p. 238° (Found: C, 44·0; H, 4·2. $C_{12}H_{14}O_3N_4S_2$ requires C, 44·2; H, 4·3%), *5-pentyl* (I; R = C_5H_{11}), needles, m. p. 228° (Found: C, 45·6; H, 4·5. $C_{13}H_{16}O_3N_4S_2$ requires C, 45·9; H, 4·7%), and *5-tetradecyl analogue* (I; R = $C_{14}H_{29}$), pale yellow needles, m. p. 161° (Found: C, 56·3; H, 7·1. $C_{22}H_{34}O_3N_3S_2$ requires C, 56·6; H, 7·4%), were also prepared.

Bromination of 2-thenaldehyde. To an ice-cooled solution of 2-thenaldehyde (16 g.) in dry chloroform, bromine (22·7 g.) was added dropwise with stirring, and the mixture left at room temperature for 2 hr., then poured into water ; the product was then taken up in chloroform, washed with aqueous sodium carbonate, then with water, and dried (Na_2SO_4), the solvent distilled off, and the residue fractionated *in vacuo*. The bromo-aldehyde (18 g.), b. p. 148—150°/40 mm., gave 5-bromo-2-thenaldehyde thiosemicarbazone, which melted at 182° after several recrystallisations from ethanol (Found: C, 27·0; H, 2·1. Calc. for $C_6H_6N_3S_2Br$: C, 27·3; H, 2·3%). The fact that the crude thiosemicarbazone did not melt sharply is taken to indicate the presence of isomeric bromo-2-thenaldehydes.

5-Bromo-2-thenaldehyde-4-oxo-Δ²-thiazolin-2-ylhydrazone crystallised as colourless needles, m. p. 292°, from ethyl acetate (Found: C, 31·8; H, 2·3. $C_8H_6ON_3S_2Br$ requires C, 31·5; H, 2·0%); the *5-butyl*, needles, m. p. 196°, from ethanol (Found: C, 39·7; H, 3·7. $C_{12}H_{14}ON_3S_2Br$ requires C, 40·0; H, 3·9%), and the *5-hexadecyl analogue*, needles, m. p. 140° (ethanol) (Found: C, 54·1; H, 7·0. $C_{24}H_{38}ON_3S_2Br$ requires C, 54·5; H, 7·2%), were prepared.

The *nitriles* shown in the Table were prepared, with the exception of the *p*-nitrophenyl derivative, by shaking an ethanolic solution of equimolar amounts of the bromo-aldehyde and the appropriate arylacrylonitrile with a few drops of 20% aqueous sodium hydroxide, and recrystallisation of the precipitate from ethanol.

α-Aryl-β-(5-bromo-2-thienyl)acrylonitriles (II).

Aryl subst.	M. p.	Formula	Found (%) C	Found (%) H	Required (%) C	Required (%) H
Phenyl	146°	$C_{13}H_8NSBr$	54·0	3·0	53·8	2·8
p-Tolyl	150	$C_{14}H_{10}NSBr$	55·2	3·2	55·3	3·3
p-Chlorophenyl	179	$C_{13}H_7NSBrCl$	47·8	2·2	48·1	2·2
p-Bromophenyl	183	$C_{13}H_7NSBr_2$	42·5	1·8	42·3	1·9
p-Methoxyphenyl	151	$C_{14}H_{10}ONSBr$	52·6	3·4	52·5	3·1
p-Nitrophenyl *	230	$C_{13}H_7O_2N_2SBr$	46·5	2·0	46·6	2·1
2-Thienyl	120	$C_{11}H_6NS_2Br$	44·5	2·3	44·6	2·0
2-Naphthyl	194	$C_{17}H_{10}NSBr$	60·1	3·2	60·0	2·9

* Prepared with piperidine as catalyst.

2 : 5-Dichloro-3-propionylthiophen (III; R = Et). To a solution of 2 : 5-dichlorothiophen (7 g.) and propionyl chloride (4·6 g.) in dry carbon disulphide (50 c.c.), aluminium chloride (7 g.) was added in small portions at room temperature, and the mixture left for 12 hr. with frequent shaking. After decomposition with water, the organic layer was washed with aqueous sodium hydroxide, then with water, dried (Na_2SO_4), and evaporated, and the residue distilled *in vacuo*; recrystallisation from ethanol gave colourless needles (6 g.), m. p. 60°, of the *ketone* (Found: C, 39·9; H, 2·8. $C_7H_6OSCl_2$ requires C, 40·2; H, 2·9%). When reaction was limited to 15 min. (which in the case of thiophen gave a yield above 90%), only negligible amounts of the

ketone were isolated. 2 : 5-*Dichloro*-3-*butyroylthiophen* (III; R = Pr), prepared similarly, formed a pale yellow oil, b. p. 143—144°/17 mm., n_D^{21} 1·5720 (Found: C, 43·3; H, 3·9. $C_8H_8OSCl_2$ requires C, 43·0; H, 3·6%). 2 : 5-*Dichloro*-3-*phenylacetylthiophen* was obtained as prisms (from ethanol), m. p. 67° (Found: C, 52·9; H, 3·3. $C_{12}H_8OSCl_2$ requires C, 53·1; H, 3·0%). The yield was particularly poor when the Friedel–Crafts reaction was performed with aromatic acid chlorides; from 2 : 5-dichlorothiophen (22 g.), benzoyl chloride (22 g.), and aluminium chloride (22 g.) in carbon disulphide (180 c.c.), 3-*benzoyl*-2 : 5-*dichlorothiophen* (5 g.) was obtained as a pale yellow oil, b. p. 192—194°/17 mm., n_D^{20} 1·6649 (Found: C, 51·5; H, 2·6. $C_{11}H_6OSCl_2$ requires C, 51·4; H, 2·3%). 2 : 5-*Dichloro*-3-2′-*thenoylthiophen* was a yellow oil, b. p. 210—212°/20 mm., n_D^{22} 1·6860 (Found: C, 41·4; H, 1·8. $C_9H_4OS_2Cl_2$ requires C, 41·1; H, 1·5%).

THE RADIUM INSTITUTE, UNIVERSITY OF PARIS. [*Received, December 10th*, 1957.]

353. *Reactions of Ammonia with Nickel(II) Cyanide.*

By E. E. AYNSLEY and W. A. CAMPBELL.

NICKEL cyanide in concentrated aqueous ammonia solution deposits dark blue crystals [1] of $Ni(CN)_2,4NH_3,2H_2O$ which, on exposure to air, quickly crumble to a pale blue powder and lose ammonia and water leaving stable $Ni(CN)_2,NH_3,H_2O$. Also, the material $Ni(CN)_2,NH_3$ obtained by the (almost complete) dehydration of the monoammine monohydrate, is only superficially like [2] that obtained by the almost complete removal of benzene from the clathrate compound $Ni(CN)_2,NH_3,C_6H_6$, a striking difference being that the dehydrated hydrate re-absorbs atmospheric moisture very rapidly but the decomposed clathrate compound does not.

We examined the reactions of anhydrous ammonia (gas and liquid) with nickel cyanide. When dry ammonia gas is passed over anhydrous nickel cyanide a strongly exothermic reaction occurs and a grey-violet diammine, $Ni(CN)_2,2NH_3$, is produced. When this is exposed to the atmosphere for a few hours one molecule of ammonia is replaced by one of water and stable $Ni(CN)_2,NH_3,H_2O$ is obtained. The same change, with effervescence, is rapidly brought about by adding the diammine to water. When kept in dry air in a desiccator ($CaCl_2$) for 12 hr., the diammine loses ammonia and leaves the monoammine, $Ni(CN)_2,NH_3$, which does *not* absorb moisture from the atmosphere. This points to some structural difference in the lattices of the two forms of $Ni(CN)_2,NH_3$.

When nickel cyanide is shaken with anhydrous liquid ammonia an unstable dark blue product is obtained which rapidly loses ammonia. The maximum increase in weight of the nickel cyanide suggests the formation of a tetrammine $Ni(CN)_2,4NH_3$ which after a few hours' standing in dry air leaves the stable monoammine, $Ni(CN)_2,NH_3$.

Experimental.—Preparation of nickel cyanide. Aqueous solutions containing " AnalaR " nickel sulphate (28 g. in 100 ml.) and potassium cyanide (13 g. in 100 ml.) were mixed and the precipitated hydrated nickel cyanide was recovered by centrifugation. The gelatinous product was washed and centrifuged four times to remove occluded potassium salts, and when dried at 140° gave yellow-brown anhydrous nickel cyanide.

Nickel was determined (*a*) by ignition to oxide and (*b*) as nickel dimethylglyoxime, total nitrogen by Kjeldahl digestion in a sealed tube, and ammonia by distillation from 0·1N-sodium hydroxide.

Preparation of $Ni(CN)_2,2NH_3$. Dry ammonia gas was passed over a few g. of nickel cyanide contained in a porcelain boat at laboratory temperature. The cyanide swelled considerably, much heat was evolved, and the *diammine* was left as a grey-violet powder [Found: Ni, 40·8; N, 38·1; NH_3, 22·9. $Ni(CN)_2,2NH_3$ requires Ni, 40·5; N, 38·7; NH_3, 23·5%].

Effect of water on $Ni(CN)_2,2NH_3$. (*a*) On exposure to the atmosphere the compound gradually lost ammonia and left odourless, pale blue $Ni(CN)_2,NH_3,H_2O$. (*b*) When the diammine was added to water it effervesced, forming the *monohydrate* [Found: Product from (*a*); Ni, 40·1; N, 28·2; NH_3, 11·4. Product from (*b*); Ni, 40·0; N, 28·4; NH_3, 11·3. $Ni(CN)_2,NH_3,H_2O$ requires Ni 40·1; N, 28·8; NH_3, 11·6%].

[1] Aynsley and Campbell, *J.*, 1957, 4137.
[2] Aynsley, Campbell, and Dodd, *Proc. Chem. Soc.*, 1957, 210.

Decomposition of $Ni(CN)_2,2NH_3$ *in dry air.* A weighed amount of the diammine was exposed overnight to dry air in a desiccator ($CaCl_2$). No colour change was observed but the *product* was $Ni(CN)_2,NH_3$ [Found: Ni, 45·8; N, 33·0; NH_3, 13·4. $Ni(CN)_2,NH_3$ requires Ni, 45·9; N, 32·9; NH_3, 13·3%. The loss in weight was 11·8% corresponding to 100% conversion].

Action of liquid ammonia on $Ni(CN)_2$. Excess of liquid ammonia was condensed on a weighed quantity of nickel cyanide and left for a few hours. The excess was allowed to boil off and the product, which was greater in bulk than the original cyanide and darker in colour than the diammine, was rapidly weighed. The weight increased, corresponding to the formation of a tetrammine $Ni(CN)_2,4NH_3$, but a complete analysis of the product was impossible because it rapidly lost ammonia. On exposure to dry air for a few hours, the monoammine was left.

KING'S COLLEGE, NEWCASTLE UPON TYNE, 1. [*Received, December 20th*, 1957.]

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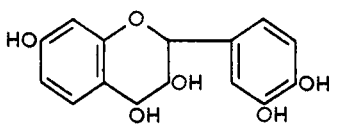
354. *The Identity of Gleditsin and Mollisacacidin.*

By J. W. CLARK-LEWIS and M. MITSUNO.

HEARTWOOD of the Japanese tree *Gleditsia* (or *Gleditschia*) *japonica* Miquel, also known as *G. horrida* Schneider, yields a crystalline substance (*ca.* 0·3%) termed gleditsin.[1] Typical leucoanthocyanidin properties indicated that gleditsin is the flavan-3 : 4-diol [2] (I) and not the corresponding flavan-3-ol or catechin as was originally supposed. Gleditsin is now shown to be identical with mollisacacidin [3] (I) by comparison of physical constants, by mixed melting point determinations and, more convincingly, by the close similarity of the infrared absorption curves determined with mulls. Each curve shows thirty-eight absorption bands in the range 2—15 μ, with minor differences appearing in only three of them, and this close correspondence suggests strongly that gleditsin is stereochemically as well as structurally identical with mollisacacidin. Stereochemical features of mollisacacidin (gleditsin) have yet to be determined, although it is tentatively regarded as a *cis*-glycol [3] like the related melacacidin.[4]



(I)

Experimental.—Gleditsin [1] crystallises as a dihydrate, $C_{15}H_{14}O_6,2H_2O$, m. p. 124—125° (decomp.), $[\alpha]_D^{12}$ +33·6° (in 50% acetone), and yields a trimethyl ether, m. p. 99—100·5° (sesquihydrate), 129·5—131° (anhydrous). Mollisacacidin dihydrate,[3] m. p. 125—130° (decomp.), $[\alpha]_D^{18}$ +12·6° (1% in MeOH), forms a trimethyl ether, m. p. 129° after sintering at 76—77°. A sample of mollisacacidin supplied by Dr. H. H. Keppler became red and decomposed gradually in the range 125—170° when heated in capillary tubes, and this behaviour was unchanged when mollisacacidin was mixed with gleditsin, which melted sharply at 125—126° (decomp.) under the same conditions. With a hot-stage microscope, thread-like filaments of both mollisacacidin and gleditsin were seen to soften and coalesce in the range 125—130° without obviously melting, and behaved similarly when mixed.

Gleditsin and mollisacacidin had the same R_F value (0·62) in butanol–acetic acid–water (5 : 1 : 4) and behaved similarly when sprayed with ammoniacal silver nitrate or with toluene-*p*-sulphonic acid (3% in ethanol).

Infrared absorption curves of Nujol mulls of gleditsin and mollisacacidin were determined with a Grubb-Parsons double beam spectrometer S4 (NaCl prism) and were closely similar throughout the recorded range (2—15 μ).

The authors thank Dr. H. H. Keppler for a sample of mollisacacidin and Dr. H. J. Rodda for determining the infrared spectra.

UNIVERSITY OF ADELAIDE, SOUTH AUSTRALIA.
UNIVERSITY OF TOYAMA, JAPAN. [*Received, December 27th*, 1957.]

[1] Mitsuno and Yoshizaki, *J. Pharm. Soc. Japan*, 1957, **77**, 557, 1280.
[2] Clark-Lewis, "Stereochemistry of Catechins and Related Flavan Derivatives," presented at a Symposium on Heterocyclic Chemistry, Canberra, September 2—4th, 1957 (*Chem. Soc. Special Publ.*, in the press).
[3] Keppler, *J.*, 1957, 2721.
[4] King and Bottomley, *J.*, 1954, 1399; King and Clark-Lewis, *J.*, 1955, 3384.