## 908. *Ionic Reactions of Fluorocarbon Iodides.*

By (Mrs.) J. Mason (Banus).

Syntheses with fluorocarbon iodides all involve homolysis (radical–atomic, sometimes anion–anionic) of the $R_F$–I bond, for weak and medium nucleophiles do not replace iodide ion, and strong ones (*e.g.*, thiophenoxide ion) abstract positive iodine [1] ($R_F^-$ being protonated by the solvent), although this will not iodinate very reactive aromatic nuclei, and Lewis acids do not promote heterolysis of either sort.

Isotopic exchange under ionising conditions can be a sensitive test of heterolysis. Trifluoroiodomethane [2] exchanges very slowly with $^{131}I^-$ in ethanol in the dark, from $-60°$ to $+80°$, and improved experiments with heptafluoroiodopropane show that the Arrhenius parameters are very low; the apparent activation energy $\Delta H^‡$ is $3{\cdot}6 \pm 1{\cdot}6$ kcal./mole, and the entropy $\Delta S^‡$ is $-85 \pm 6$ e.u., the limits expressing the variability of rate coefficients in parallel runs, and the irregularities of the Arrhenius plot. The exchange (half-time about 44 years) is homogeneous, nearly of first order in fluoroiodide, dependent also on iodide ion, and accelerated slightly by oxygen, markedly by free iodine. For trifluoroiodomethane $\Delta H^‡$ is slightly lower, and $\Delta S^‡$ a few units less negative. Above 80° the exchange has a much higher temperature coefficient, and iodine is liberated.

It is unlikely on chemical or kinetic grounds that the exchange is a nucleophilic substitution: for $S_N1$ or $S_N2$ exchanges with halide ion of the alkyl halides,[3] $\Delta H^‡$ is 15—25 kcal./mole and $\Delta S^‡$ is $-10$ to $+5$ e.u., and for aryl halides [4] (*e.g.*, iodobenzene in acetonitrile at 200°) about 30 kcal./mole and $-30$ e.u. Unimolecular heterolysis as previously suggested,[2] or the abstraction of positive iodine by $^{131}I^-$, while explaining the catalysis by iodine (and inhibition by reagents that remove it [1]), are also unlikely since the solvent would protonate the carbanion before it could form active fluoroiodide with semi-active iodine present in minute concentration.

A mechanism in which the fluorocarbanion is never free involves the rapid reversible formation of a complex $[R_FI,^{131}I^-]$ (for which there is some spectroscopic evidence) within which iodine exchanges slowly. Transition to the low-lying triplet state can lower activation energies in iodine chemistry [5] and involve low entropy factors. Free iodine may promote exchange in the complex, or exchange rapidly with $^{131}I^-$ and then more slowly with fluoroiodide, as with alkyl or aryl iodides by homolysis with " normal " Arrhenius parameters [6a] (or with acyl iodides with low parameters, *via* molecular complexes [6b]). However, a variety of organic halides show very slow exchanges with abnormally low parameters, as here (*e.g.*, iodobenzene and aqueous $^{131}I^-$, apparent $\Delta H^‡$ 3·7 kcal./mole, $\Delta S^‡$ $-80{\cdot}6$ e.u.[7]), and there may be a general explanation.

*Experimental.*—Light, oxidants, and moisture were carefully excluded, since homolysis readily occurs with polyhalogeno-compounds [8] to give the same products in hydrogen-containing solvents as does heterolysis. Ethanol was refluxed with sodium, ethyl phthalate, and quinol, and fractionated. Sodium $^{131}$iodide was dried and combined with carrier (dried at 120° for 48 hr.) to give 0·05—0·1M-solutions in ethanol, which were estimated (Volhard), and diluted

[1] Analogous reactions described by Ingold, " Structure and Mechanism in Organic Chemistry," Bell, London, 1953, 330; Hine *et al.*, *J. Amer. Chem. Soc.*, 1958, **80**, 824, 3002; 1957, **79**, 5493, 5497.
[2] Banus, Emeléus, and Haszeldine, *J.*, 1951, 60.
[3] de la Mare, *J.*, 1955, 3196; Swart and le Roux, *J.*, 1956, 2110; 1957, 406.
[4] Kristjanson and Winkler, *Canad. J. Chem.*, 1951, **29**, 154.
[5] Griffing, *J. Chem. Phys.*, 1955, **23**, 1015.
[6] Noyes *et al.*, *J. Amer. Chem. Soc.*, (*a*) 1953, **75**, 761, 763, 767; 1955, **77**, 609; 1956, **78**, 5764; 1958, **80**, 2401; (*b*) 1957, **79**, 5370.
[7] Manno and Johnston, *J. Amer. Chem. Soc.*, 1957, **79**, 807.
[8] Heberling and McCormack, *J. Amer. Chem. Soc.*, 1956, **78**, 5433; Kharasch, Alsop, and Mayo, *J. Org. Chem.*, 1937, **2**, 76; Hughes and Peeling, unpublished work.

for counting in M.R.C. type liquid β-counters. Pure heptafluoroiodopropane was shaken with mercury and made up to 0·05—0·01M in ethanol; all solutions were kept in the dark under a vacuum or dry nitrogen. Mixtures in Pyrex tubes were frozen in liquid nitrogen for sealing, and after exchange, slowly distilled *in vacuo* at low temperatures without splashing through an inverted Y-tube containing (monitored) light glass-wool plugs. Mixtures containing free iodine were treated with excess of barium oxide, and then mercury, before distillation. Different glassware was used for solutions of high and of low activity.

Measured exchanges were 0·1% or less, after 200—500 hr. (with distillate counts of at least 100 c./min.) and the back-reaction was negligible: in the equation

$$\underset{(a-x)}{R_FI} + \underset{(b-x)}{Na^{131}I} \rightleftharpoons \underset{(x)}{R_F{}^{131}I} + \underset{(x)\ \text{moles/l.}}{NaI}$$

(for a batch of $^{131}$iodide, the mixture with carrier is taken as uniformly active), $a$ and $b$ are known, and $x/b$ is the ratio of counting rates of distillate and residue (with a factor 2 if the reaction involves semi-active iodine). First-order coefficients $k_a$ and $k_b$ are $x/at$ or $x/b't$ sec.$^{-1}$, and second-order, $k_2$, $x/ab't$ l. mole$^{-1}$ sec.$^{-1}$, where $b'$ is $\gamma b$, and $\gamma$ the activity coefficient of the sodium iodide in ethanol.[9] The plot of $x$ against $t$ was roughly linear (for given $a$, $b$, and temperature) with some evidence for autocatalysis (perhaps by liberated iodine) and zero-time exchange. Rate coefficients for parallel runs agreed only within a factor of 2·5 or less, but were unchanged for tubes packed with Fenske helices; they were doubled and rather less reproducible for tubes sealed at room temperature with air in the dead space.

When $a$ and $b$ were independently varied between 0·08 and 0·008M at 25° the order was rather below 0·5 for iodide ion and between 0·5 and 1·0 for fluoroiodide. Rate coefficients in the Table, calculated on alternative assumptions as to the order, are the mean from several parallel runs. In experiments to test the effect of iodine, of increased surface, or of temperature, $a = b = 0{\cdot}04$M.

*Kinetic results.*

| | | | | | | | | | | $\Delta S^{\ddagger}$ (e.u.) | $\Delta H^{\ddagger}$ (kcal. mole$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $CF_3I$ | Temp. (°c) | −66 | −31 | | −5 | 20 | | 60 | | | |
| | $10^{10}k_a$ (sec.$^{-1}$) | 6·2 | 16·5 | | 29 | 130 | | 176 | giving | −84 ± 7 | 3·8 ± 1·9 |
| $C_3F_7{}^{131}I$ | Temp. (°c) | −10 * | 0 | 25 | 25 | 25 | 35 | 45 | | | |
| | Added iodine | — | — | — | 0·002M | 0·03M | — | — | | | |
| | $10^{10}k_a$ (sec.$^{-1}$) | 0·6 | 1·0 | 1·8 | 83 | 495 | 2·5 | 2·7 | giving | −91 ± 6 | 4·2 ± 1·6 |
| | $10^{8}k_2$ (l. mole$^{-1}$ sec.$^{-1}$) | 0·3 | 0·5 | 0·8 | 100 | 603 | 1·0 | 1·1 | giving | −85 ± 6 | 3·6 ± 1·6 |

* Less accurate determination.

The author thanks Professors Sir Christopher Ingold, E. D. Hughes, and P. B. D. de la Mare, Mr. C. A. Vernon, and Dr. A. G. Maddock, for advice.

William Ramsay and Ralph Forster Laboratories,
University College, London, W.C.1. [*Received, August 27th,* 1959.]

[9] Partington and Simpson, *Trans. Faraday Soc.*, 1930, **26**, 625.

## 909. *Acid–Base Equilibria in Acetic Acid. Effect of Increasing Methylation on the Basicity of Aliphatic Amides.*

By R. J. L. Martin and I. H. Reece.

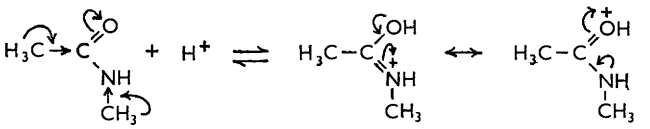
Although the acid–base equilibrium constants have been determined for a number of bases in acetic acid [1-3] none has been reported for a series of aliphatic amides successively methylated at the carbon atoms adjacent to the carbonyl group or the nitrogen atom. The equilibrium constants in the annexed Table, where $K = [B][H^+ClO_4^-]/[BH^+ClO_4^-]$ for the reaction $B + H^+ClO_4^- \rightleftharpoons BH^+ClO_4^-$, have been determined spectrophotometrically for such a series in acetic acid at 25°. In the calculations it was assumed that the ion pairs were weakly dissociated into ions so that the ionic concentrations could be neglected.

| Series A | $10^{-5}K$ (mole l.$^{-1}$) | Series B | $10^{-5}K$ (mole l.$^{-1}$) |
|---|---|---|---|
| $CH_3{\cdot}CO{\cdot}NH_2$ | 22 | $Me{\cdot}CO{\cdot}NH_2$ | 22 |
| $CH_3{\cdot}CO{\cdot}NHMe$ | 4·3 | $Et{\cdot}CO{\cdot}NH_2$ | 30 |
| $CH_3{\cdot}CO{\cdot}NHEt$ | 3·8 | $Pr^i{\cdot}CO{\cdot}NH_2$ | 43 |
| $CH_3{\cdot}CO{\cdot}NHPr^i$ | 3·2 | $Bu^t{\cdot}CO{\cdot}NH_2$ | 59 |
| $CH_3{\cdot}CO{\cdot}NHBu^t$ | 2·5 | | |

It is generally agreed that the ideal way to assess the effect of structural changes on acidity is by comparison of the heat changes at absolute zero.[4,5] This requires a thermodynamical analysis which is difficult partly because of lack of precise experimental data and partly because of the doubtful validity of the extrapolations to absolute zero.[4,6] It appears that the free-energy change at a definite temperature which is related to the equilibrium constant is more useful than heat change for structure comparisons.[4,6] In this discussion the effect of structural changes on basicity will be related to the equilibrium constant at 25° c.[4,6] This is a reasonable assumption because substituents are some distance from the oxygen atom at which protons are added, the solvation shell will be little affected, and the entropy changes will be small. The validity of our method appears to be justified because the equilibrium constant changes in a regular manner with the inductive or hyperconjugative effect of the alkyl groups.

In series A, introduction of one *N*-methyl group produces a large decrease in the equilibrium constant. Further methyl groups in the *N*-methyl group produce a very small progressive decrease in the equilibrium constants.

The carbonyl-oxygen is more basic than the amide-nitrogen atom, so that protons are added to the carbonyl oxygen to produce a conjugate acid which is a resonance hybrid.[7]



The inductive effect of the *N*-methyl group increases the electron accession to the carbonyl-oxygen atom and increases its basicity. Successive replacement of the hydrogen atoms in the *N*-methyl group by additional methyl groups will produce small increases in

[1] Lemaire and Lucas, *J. Amer. Chem. Soc.*, 1951, **73**, 5198.
[2] Smith and Elliott, *J. Amer. Chem. Soc.*, 1953, **75**, 3566; Kolthoff and Bruckenstein, *ibid.*, 1956, **78**, 1; Bruckenstein and Kolthoff, *ibid.*, pp. 10, 2974.
[3] Martin and Reece, *Austral. J. Chem.*, 1959, **12**, 524.
[4] Ingold, "Mechanism and Structure in Organic Chemistry," G. Bell and Son, London, 1953, p. 727.
[5] Everett and Wynne-Jones, *Trans. Faraday Soc.*, 1941, **37**, 373.
[6] Dippy and Jenkins, *Trans. Faraday Soc.*, 1941, **37**, 366.
[7] Pauling, "Nature of the Chemical Bond," Cornell Univ. Press, 1940, p. 207.

the inductive effect because this cannot be relayed with any intensity through a saturated carbon atom. Mesomeric effects do not operate in this case because the *N*-alkyl groups cannot hyperconjugate with the carbonyl group so as to increase the polarisation of the molecule and facilitate the addition of a proton. This is supported by the experimental evidence for which there is no simple relation between the equilibrium constant and the number of hydrogen atoms available at the *N*-carbon atom. However the *N*-alkyl groups can hyperconjugate with the charged centres in the conjugate acid and contribute towards its stability. The net result is that *N*-alkyl groups increase the basicity by means of a predominating inductive effect.

In series B, successive methylation produces a regular increase in the equilibrium constants, by combined operation of the inductive and the mesomeric effects. With increasing methylation there is a very small increase in the inductive effect which increases the basicity of the amide. However, increasing methylation regularly decreases the number of hydrogen atoms capable of hyperconjugating with the carbonyl group, thus reducing the basicity of the amide. Of the two effects the mesomeric is the larger, and increasing methylation decreases the basicity.

In acetic acid, salts exist in solution as weakly dissociated ion pairs [8] and it is impossible for the solution to maintain a high concentration of ions. In certain circumstances it should be possible for the structure of the base to hinder ion-pair formation and affect its basicity. Although the perchlorate ion is large, Catalin models indicate that there is no steric inhibition of ion-pair formation.

*Experimental.*—Acetic acid was purified, and the stock solution of perchloric acid was prepared, as previously described.[9]

Purification and preparation of the stock solution of acetamide has been described elsewhere.[3]

*N*-Methyl-, b. p. 141·5—141·8°/98·3 mm., and *N*-ethyl-acetamide, b. p. 144·0—144·2°/96·4 mm., were prepared from the corresponding alkylamine hydrochloride and acetamide [10] and were purified by distillation.

*N*-Isopropyl-, b. p. 142·2°/98·0 mm., and *N*-t-butyl-acetamide were prepared from the corresponding amines, acetic acid, and acetic anhydride.[11] *N*-t-Butylacetamide, crystallised from light petroleum (b. p. 70—80°), had m. p. 98·0—99·0°.

Propionamide, m. p. 79·8—80·5°, was a commercial sample, crystallised from benzene and then from chloroform.

Isobutyramide, prepared by distillation of ammonium isobutyrate [12] and crystallised from chloroform, had m. p. 128·0—128·5°.

Pivalamide, prepared from pivaloyl chloride [13] and ammonia, and crystallised from chloroform and then from ethyl acetate, had m. p. 153·7—154·3°.

*Methods.* *NN*-Diethyl-2,4-dinitroaniline was used as the indicator.[1,3] Spectra were recorded at 25° with a Cary spectrophotometer model 12. Concentrations used were: $HClO_4$, 0·0010—0·0075M; amide, 0·0022—0·032M; indicator $10^{-4}$M.

*Results.* At 25° *NN*-diethyl-2,4-dinitroaniline had an extinction coefficient of 16,300 at 373 mμ and an indicator constant of $5{\cdot}46 \times 10^{-5}$ (Lemaire and Lucas [1] report 15,700 and $6{\cdot}55 \times 10^{-5}$ respectively).

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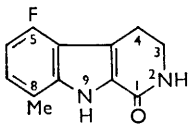
Broadway, Sydney, N.S.W., Australia. [*Received, March 7th*, 1960.]

[8] Harned and Owen, "Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, 3rd edn., 1958, Chapter 7.
[9] Martin, *Austral. J. Chem.*, 1957, **10**, 268.
[10] Galat and Elion, *J. Amer. Chem. Soc.*, 1943, **65**, 1566.
[11] Heyns and Bebenburg, *Chem. Ber.*, 1953, **86**, 278.
[12] Mitchell and Reid, *J. Amer. Chem. Soc.*, 1931, **53**, 1881.
[13] *Org. Synth.* Coll. Vol. III, p. 490.

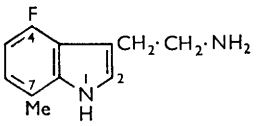
## 910. *Substituted Tryptamines and Their Derivatives.*

By Zvi Pelchowicz and Ernst D. Bergmann.

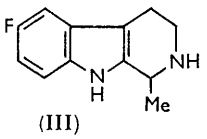
The method applied recently [1] to the preparation of 5-fluorotryptamine has now been used for the synthesis of the known 5- and 7-methyl analogues [2,3] and of 4-fluoro-7-methyltryptamine (II). A 4-substituted derivative appeared of interest in view of the biological activity of the 4-hydroxytryptamine derivatives psilocin and psilocybin.[4] Therefore the diazonium salt from 5-fluoro-2-methylaniline was condensed with ethyl 2-oxopiperidine-3-carboxylate, to give in two steps the carboline (I), whence hydrolysis and decarboxylation afforded the desired tryptamine derivative (II).



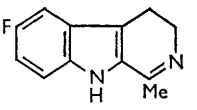
(I)



(II)



(III)



(IV)

The final objective of these studies was the synthesis of methyl- and/or fluorine-substitution products of the indole alkaloids. In view of the recent description of 10-fluorodeserpidine,[5] the preparation of 6-fluoro-1,2,3,4-tetrahydroharmaline (III) and 6-fluoro-3,4-dihydroharmaline (IV) by classical methods [6,7] is recorded below.

*Experimental.*—3-o-*Tolylhydrazone of* 2,3-*dioxopiperidine.* *o*-Toluidine (21·3 g.) in 36% hydrochloric acid (54 ml.) and water (236 ml.) was diazotised at $\gtrless 5°$ with sodium nitrite (15 g.). Any excess of nitrous acid was destroyed by addition of urea, and the solution brought at 0° to pH 5—6 by addition of 10% sodium carbonate solution (160 ml.). The solution (filtered, if necessary) was added with stirring to an ice-cold solution of ethyl 2-oxopiperidine-3-carboxylate (34 g.) in water (400 ml.) containing potassium hydroxide (12 g.), which had been kept at room temperature for 24 hr. before use. When the reaction was complete (5 min. of additional stirring), the solution was brought to pH 3—4 by acetic acid and kept at 0° for 48 hr. The product (35 g., 81%) was filtered off, washed with water, and dried; the yellow-reddish *hydrazone* so obtained was used directly in the next step; it crystallised from aqueous alcohol as yellowish crystals, m. p. 140—140·5° (Found: C, 66·4; H, 7·0; N, 19·4. $C_{12}H_{15}N_3O$ requires C, 66·3; H, 7·0; N, 19·3%).

*The* 3-p-*tolylhydrazone of* 2,3-*dioxopiperidine*, obtained analogously in 81% yield, crystallised from alcohol in elongated yellow crystals, m. p. 209—209·5° (Found: C, 66·3; H, 6·9; N, 19·1%).

1,2,3,4-*Tetrahydro*-8-*methyl*-1-*oxo*-β-*carboline.* The former hydrazone (crude; 45 g.) in acetic acid (200 ml.) and concentrated hydrochloric acid (100 ml.) was refluxed for 1 hr., cooled, and diluted with water. The precipitated *carboline* (28·8 g., 72%), recrystallised from aqueous alcohol, had m. p. 228·5—229° (Found: C, 72·0; H, 6·3. $C_{12}H_{12}N_2O$ requires C, 72·0; H, 6·0%).

1,2,3,4-*Tetrahydro*-6-*methyl*-1-*oxo*-β-*carboline*, obtained analogously in 83% yield, had m. p. 187·5—188·5° (from aqueous alcohol) (Found: C, 71·9; H, 5·9%).

7-*Methyltryptamine*-2-*carboxylic acid.* A solution of the 8-methylcarboline (28 g.) in ethyl

[1] Pelchowicz and Bergmann, *J.*, 1959, 847; cf. Protiva, Adlerová, Vejdělek, Novak, Rajšner, and Ernest, *Naturwiss.*, 1959, **46**, 263.
[2] Eiter and Nezval, *Monatsh.*, 1950, **81**, 404.
[3] Gaddum, Hameed, Hathway, and Stephens, *Quart. J. Expt. Physiol.*, 1955, **40**, 49.
[4] Hofmann, Heim, Brack, Kobel, Frey, Ott, Petrzilka, and Troxler, *Helv. Chim. Acta*, 1959, **42**, 1557; Hofmann, Heim, Brack, and Kobel, *Experientia*, 1958, **14**, 107; Hofmann and Troxler, *Experientia*, 1959, **15**, 101.
[5] Novak and Protiva, *Naturwiss.*, 1959, **46**, 579.
[6] Akabori and Saito, *Ber.*, 1930, **63**, 2245.
[7] Späth and Lederer, *Ber.*, 1930, **63**, 120.

alcohol (260 ml.) and 4N-aqueous potassium hydroxide (260 ml.) was refluxed for 1 hr., concentrated to half its volume, diluted with water (250 ml.), shaken with charcoal (2 g.), filtered, and neutralised with acetic acid. The precipitate was redissolved in aqueous sodium hydroxide (charcoal), filtered, and reprecipitated with acetic acid. The *product* (24·1 g., 79%), m. p. 278—281° (decomp.), was filtered off, washed with water and acetone, and dried (Found: C, 66·2; H, 6·4; N, 12·8%)..

*5-Methyltryptamine-2-carboxylic acid*, obtained in 83% yield, decomposed at 267—267·5° (Found: C, 65·9; H, 6·7; N, 12·7%).

*7-Methyltryptamine*. The 7-methyl-acid (10·5 g.) was heated with 5% hydrochloric acid (400 ml.) until the evolution of carbon dioxide had ceased. Neutralisation with sodium hydroxide solution precipitated part of the amine; the rest was isolated by extraction with ether, drying (NaOH), and evaporation. The product (7·2 g., 83%) was best purified by sublimation, forming needles, m. p. 130—131° (lit., 122—123°,[2] 120—122° [3]) (Found: C, 75·7; H, 7·9; N, 16·1. Calc. for $C_{11}H_{14}N_2$: C, 75·9; H, 8·1; N, 16·0%).

*5-Methyltryptamine*. Decarboxylation was carried out as in the preceding example. All the product (76%) was isolated by extraction with ether and distilled *in vacuo*. Recrystallised from ether–light petroleum, it had m. p. 99—99·5° (lit.,[3] 93—95°) (Found: C, 75·8; H, 8·2; N, 16·0%).

*3-(5-Fluoro-2-methylphenylhydrazono)-2-oxopiperidine*. To ethyl 2-oxopiperidine-3-carboxylate (47 g.) in water (500 ml.), potassium hydroxide (16·5 g.) was added, followed after 12 hr. by a solution prepared from 5-fluoro-2-methylaniline hydrochloride [8] (44·5 g.), water (350 ml.), 30% hydrochloric acid (50 ml.), and sodium nitrite (21 g.) at 0°. The mixture was neutralised with 10% sodium carbonate solution (230 ml.), brought to pH 3—4 by acetic acid, and stirred for 5 hr. at 5°. The precipitated *product* (47 g., 72%), when recrystallised from ethanol and sublimed had m. p. 183·5—184·5° (38 g., 58%) (Found: C, 61·2; H, 6·1; N, 17·6; F, 8·0. $C_{12}H_{14}FN_3O$ requires C, 61·3; H, 6·0; N, 17·9; F, 8·1%).

*5-Fluoro-1,2,3,4-tetrahydro-8-methyl-2-oxo-β-carboline* (I). A mixture of the foregoing compound (28 g.), acetic acid (180 ml.) and concentrated hydrochloric acid (90 ml.) was refluxed for 3 hr., and then cooled. The crystals were filtered off, and a second crop obtained by dilution of the mother-liquor with water. The *product* (17 g., 73%) recrystallised from aqueous alcohol as plates, m. p. 204·5—205° (with sublimation) (Found: C, 66·0; H, 5·0; N, 12·8; F, 8·7. $C_{12}H_{11}FN_2O$ requires C, 66·1; H, 5·0; N, 12·8; F, 8·7%).

*4-Fluoro-7-methyltryptamine-2-carboxylic acid* (II). The compound (I) (15 g.) and potassium hydroxide (40 g.) were refluxed in alcohol (150 ml.) and water (150 ml.) for 20 min., and concentrated to half-volume. Water (150 ml.) was added and the solution treated with charcoal, filtered, cooled, and acidified with acetic acid. The *acid* (13 g., 80%) formed needles, m. p. 273° (decomp.), from water (Found: C, 61·2; H, 5·9; N, 11·8; F, 7·9. $C_{12}H_{13}FN_2O_2$ requires C, 61·0; H, 5·6; N, 11·8; F, 8·0%).

*4-Fluoro-7-methyltryptamine*. The acid (II) (11 g.) was refluxed in 7% hydrochloric acid (250 ml.) until evolution of carbon dioxide ceased (12 hr.); the solution was decolorised with charcoal, filtered, made alkaline, and extracted with ether. This extract afforded the *tryptamine* (7 g., 79%) which had m. p. 141—142° after sublimation (Found: C, 68·5; H, 6·7; N, 14·5; F, 10·0. $C_{11}H_{13}FN_2$ requires C, 68·7; H, 6·7; N, 14·6; F, 9·9%).

*6-Fluoro-1,2,3,4-tetrahydroharmaline* (III). 10% aqueous acetaldehyde (100 ml.) and 5-fluorotryptamine (5 g.) were heated in 2N-sulphuric acid (16 ml.) and water (100 ml.) at 110° for 20 min.; the product was cooled and made alkaline with sodium carbonate solution. The crystals so obtained were dissolved in dilute sulphuric acid, and the solution treated with charcoal, filtered, and made alkaline again. The *product* (4·9 g., 80%), best purified by sublimation, melted at 201—202° (Found: C, 70·3; H, 6·2; N, 13·7; F, 9·1. $C_{12}H_{13}FN_2$ requires C, 70·6; H, 6·4; N, 13·7; F, 9·3%). It is almost non-toxic to white mice ($LD_{50}$ 600 mg./kg.).

*$N^{\alpha}$-Acetyl-5-fluorotryptamine*. 5-Fluorotryptamine hydrochloride (5·74 g.), sodium hydrogen carbonate (1 g.), and acetic anhydride (25 ml.) were refluxed for 15 min., then poured into water (200 ml.); the mixture was made alkaline with sodium carbonate. Ether extracted the acetyl derivative which, recrystallised from ether–light petroleum (b. p. 60—80°), had m. p. 127·5—128° (5·5 g.) (Found: C, 65·8; H, 5·8; F, 9·1; N, 12·7. $C_{12}H_{13}FN_2O$ requires C, 65·5; H, 5·9; F, 8·7; N, 12·7%).

[8] Steck and Fletcher, *J. Amer. Chem. Soc.*, 1948, **70**, 439.

6-*Fluoro*-3,4-*dihydroharmaline* (IV). To a solution of the preceding acetyl derivative (5 g.) in hot xylene (200 ml.), phosphorus pentoxide (50 g.) was added in small portions and the mixture was refluxed for 2 hr. The solid product was filtered off, washed with ether, and added in small portions to 5% hydrochloric acid (500 ml.). The solution obtained was heated at 80°, filtered, cooled, made strongly alkaline, and extracted three times with ether (100 ml.). This extract yielded the *product*, which after sublimation recrystallised from aqueous alcohol as slightly yellow needles, m. p. 206—207° (3·5 g., 75%) (Found: C, 70·8; H, 5·3; F, 10·1; N, 14·2. $C_{12}H_{11}FN_2$ requires C, 71·3; H, 5·4; F, 9·4; N, 13·9%).

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## 911. *Interaction between Boron Trichloride and Alkoxysilanes.*

By M. J. FRAZER, W. GERRARD, and J. A. STRICKSON.

EVIDENCE is accumulating that the mode of fission of the Si–O–C linkage in alkoxy-silicon compounds caused by interaction with certain inorganic non-metal halides depends upon the groups attached to silicon and those attached to carbon. Thus tetra-alkoxy- and alkoxychloro-silanes with thionyl chloride [1] and boron tribromide,[2] and alkoxytrimethylsilanes with boron tribromide,[2] silicon tetrachloride,[3] thionyl chloride,[4] phosphorus trichloride,[5] phosphorus oxychloride (when R = Bu$^n$, Bu$^i$, and Bu$^s$),[5] or phosphorus oxybromide [5] undergo mutual replacement of alkoxyl and halogen. On the other hand, 1-phenylethoxytrimethylsilane ($SiMe_3$·O·CHPh·$CH_3$) or diphenylmethoxytrimethylsilane ($SiMe_3$·O·$CHPh_2$), in which the alkoxyalkyl group is very reactive, and phosphorus oxychloride gave alkyl chloride and trimethylsilyl phosphorodichloridate ($SiMe_3$·O·$POCl_2$), by fission of the alkyl–oxygen bond.[5]

It has been shown [6] that boron trichloride and n-butoxysilanes undergo stepwise replacement of alkoxyl by chlorine, with a noticeable fall in rate for each successive step. Tributoxychlorosilane and butyl dichloroborinate were obtained at room temperature from a mixture of the tetra-ester and boron trichloride:

$$(Bu^nO)_4Si + BCl_3 \longrightarrow (Bu^nO)_3SiCl + Bu^nO{\cdot}BCl_2$$

whereas 80% of the trichlorosilane could be recovered after being heated with boron trichloride at 50° for 3 hr., although there was some evidence for the formation of silicon tetrachloride.

With tetra-s-butoxysilane and tetra-1-phenylethoxysilane it was obvious that another mode of fission was occurring but, owing to the complexity of the overall reaction sequences, a clear indication of this mode came only from the extreme example of s-butoxytrichlorosilane which gave the novel tristrichlorosilyl borate:

$$Cl_3Si{\cdot}OBu^s + BCl_3 \longrightarrow (Cl_3Si{\cdot}O)_3B + Bu^sCl$$

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[1] Currell, Frazer, Gerrard, Haine, and Leader, *J. Inorg. Nuclear Chem.*, 1959, **12**, 45.
[2] Wiberg and Kruerke, *Z. Naturforsch.*, 1953, **8***b*, 608.
[3] Gerrard and Kilburn, *J.*, 1956, 1536.
[4] Currell, Frazer, and Gerrard, *J.*, 1960, 2776; Gerrard and Tolcher, *J.*, 1954, **734**.
[5] Fertig, Gerrard, and Herbst, *J.*, 1957, 1488.
[6] Gerrard and Strickson, *Chem. and Ind.*, 1958, 860.

Isopropoxytrichlorosilane gave a similar result. That s-butoxytrimethylsilane underwent the usual mutual replacement but, on the other hand, s-butoxychlorodimethylsilane gave trischlorodimethylsilyl borates show that a second factor favouring alkyl–oxygen fission is the electronegativity of the silicon atom. Electron-attracting groups attached to silicon weaken the carbon–oxygen bond (R–O–Si–).

*Experimental.—Tetra-alkoxysilanes.* Tetraisobutoxysilane (15·00 g., 1 mol.) and boron trichloride (1 mol.), mixed at −80° and warmed to 20°, gave on distillation five fractions (15·15 g.), b. p. <60°/0·5 mm., containing boron and chlorine, and finally tri-isobutoxychlorosilane (39·0%), b. p. 81—83°/0·3 mm. (Found: Cl, 12·4; Si, 10·1. Calc. for $C_{12}H_{27}ClO_3Si$: Cl, 12·6; Si, 9·9%). Similarly, tetra-n-propoxysilane gave several fractions, b. p. 56—88°/15 mm., containing boron, chlorine, and silicon, and finally tri-n-propoxychlorosilane, b. p. 92°/15 mm. (Found: Cl, 14·8; Si, 12·2. Calc. for $C_9H_{21}ClO_3Si$: Cl, 14·8; Si, 11·7%).

Tetra-s-butoxysilane (21·70 g., 1 mol.) and boron trichloride (1 mol.) were mixed at −80°. At room temperature hydrogen chloride (0·8 g.) and butene (4·80 g.) (characterised by treatment with bromine) were evolved. Distillation gave several fractions including s-butyl chloride (3·70 g.), b. p. 62°, $n_D^{20}$ 1·3949, and s-butyl borate (1·40 g.), b. p. 114°/40 mm., $n_D^{20}$ 1·3962 (Found: B, 4·7. Calc. for $C_{12}H_{27}BO_3$: B, 4·7%). There was a non-volatile brown solid residue (8·40 g.) (Found: B, 6·7; Cl, 2·7; Si, 22·6%).

Tetra-1-phenylethoxysilane (8·00 g., 3·0 mol.) and boron trichloride (3·5 mol.), mixed at −80°, gave on warming to room temperature a brown solid from which was distilled 1-chloro-1-phenylethane (5·50 g., 63%) (Found: Cl, 24·5. Calc. for $C_8H_9Cl$: Cl, 25·3%) [redistilled, it (4·00 g.) had b. p. 26°/0·05 mm. (Found: Cl, 24·9%)], leaving a black solid (2·35 g.) which was fused at 900° (1·80 g.) (Found: B, 8·3; Si, 23·2%).

*Trialkoxychlorosilanes.* Tri-n-butoxychlorosilane (30·20 g., 1 mol.) and boron trichloride (1 mol.) gave n-butyl dichloroborinate (12·35 g., 75%), b. p. 42°/12 mm. (Found: B, 6·6; Cl, 44·5. Calc. for $C_4H_9BCl_2O$: B, 7·0; Cl, 45·9%), and di-n-butoxydichlorosilane (21·5 g., 84%). Similarly tri-isobutoxychlorosilane gave the dichloroborinate (86%) and the dichlorosilane (84%), b. p. 28°/0·1 mm. (Found: Cl, 28·2; Si, 11·2. Calc. for $C_8H_{18}Cl_2O_2Si$: Cl, 29·0; Si, 11·4%).

*Dialkoxydichlorosilanes.* A mixture of boron trichloride (1 mol.) and di-n-butoxydichlorosilane (26·80 g., 1 mol.) was heated at 140° under a −80° reflux condenser for 6 hr. Distillation gave n-butoxytrichlorosilane (14·20 g., 62·5%), b. p. 40°/15 mm. (Found: Cl, 50·5; Si, 13·2. Calc. for $C_4H_9Cl_3OSi$: Cl, 51·3; Si, 13·3%). Di-n-propoxydichlorosilane (1 mol.) and boron trichloride (1 mol.), heated at 150° for 2 hr., gave several fractions including n-propoxytrichlorosilane (31·0%), b. p. 64—66°/100 mm. (Found: Cl, 54·9; Si, 12·3. Calc. for $C_3H_7Cl_3OSi$: Cl, 55·0; Si, 14·5%) (confirmed as the trichlorosilane by gas chromatography).

*Alkoxytrichlorosilanes.* Isobutoxytrichlorosilane (7·85 g., 1 mol.) and boron trichloride (1 mol.) were heated under a −80° reflux condenser for 27 hr. at 120°. Distillation gave silicon tetrachloride (5·00 g., 78%), b. p. 48—54° (Found: Cl, 83·1. Calc. for $Cl_4Si$: Cl, 83·5%), and higher-boiling fractions containing boron and chloride. Similarly, n-propoxytrichlorosilane (15·95 g., 1 mol.) and boron trichloride (1 mol.), heated for 2 hr. at 180°, gave silicon tetrachloride (35%), b. p. 52—54° (Found: Cl, 82·5%), and the unchanged silane (49·9%), b. p. 110—112° (Found: Cl, 54·8%).

s-Butoxytrichlorosilane (14·70 g., 2 mol.) and boron trichloride (1 mol.) gave several fractions (6·05 g.), b. p. <68°, and *tristrichlorosilyl borate* (5·40 g., 49·5%), b. p. 124—128°/35 mm., $d_4^{20}$ 1·586 (Found: *M*, 484; B, 2·4; Cl, 68·9; Si, 17·9%. $BCl_9O_3Si_3$ requires *M*, 462; B, 2·3; Cl, 69·1; Si, 18·2%), a fuming, colourless, viscous liquid, soluble in benzene and violently hydrolysed by water. Isopropoxytrichlorosilane (25·95 g., 3 mol.) and boron trichloride (1 mol.) gave isopropyl chloride (6·30 g., 58·0%), b. p. 35°, $n_D^{20}$ 1·3815, and tristrichlorosilyl borate (10·05 g., 48·5%), b. p. 108—112°/28 mm. [redistilled (5·65 g.), b. p. 98—102°/12 mm. (Found: B, 2·5; Cl, 69·0; Si, 16·7%)].

*Alkoxytrimethylsilanes.* Boron trichloride vapour (5·30 g., 1 mol.) was passed into n-butoxytrimethylsilane (3 mol.) which was heated under reflux during the addition. Distillation gave chlorotrimethylsilane (9·10 g., 62·0%), b. p. 62—70° (Found: Cl, 31·2. Calc. for $C_3H_9ClSi$: Cl, 32·7%), and n-butyl borate (9·55 g., 92·0%), b. p. 116°/15 mm. (Found: B, 4·5. Calc. for

$C_{12}H_{27}BO_3$: B, 4·7%). Similarly, s-butoxytrimethylsilane (3 mol.) gave impure chlorotrimethylsilane (61·2%), b. p. 58—60° (Found: Cl, 30·2%), and s-butyl borate (75·0%), b. p. 92—96°/26 mm., $n_D^{21}$ 1·3983 (Found: B, 4·8%).

s-Butoxychlorodimethylsilane (19·80 g., 3 mol.) and boron trichloride (1 mol.) gave several fractions (13·1 g.), b. p. <72°, and *tris(chlorodimethylsilyl) borate* (1·85 g.), b. p. 60°/0·1 mm. (Found: B, 3·2; Cl, 31·3. $C_6H_{18}BCl_3O_3Si_3$ requires B, 3·2; Cl 31·4%).

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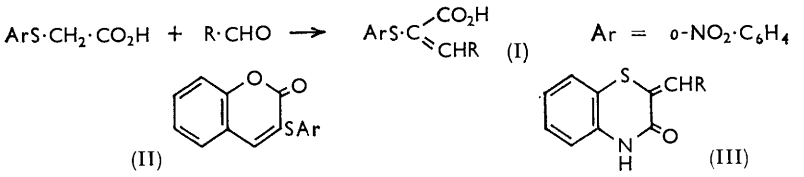
## 912. *Preparation of Some 2-Arylidene-3,4-dihydro-3-oxobenzo-1,4-thiazines.*

By V. BALIAH and T. RANGARAJAN.

*o*-(NITROPHENYLTHIO)ACETIC ACID has been found to condense with aromatic aldehydes to give α-(*o*-nitrophenylthio)cinnamic acids (I). The conditions were essentially those used




by Baliah and Varadachari [1] for condensation of phenylthioacetic acid with aldehydes. When salicylaldehyde was used the product was 3-(*o*-nitrophenylthio)coumarin (II).

The α-(*o*-nitrophenylthio)cinnamic acids underwent reduction with zinc dust and acetic acid but gave 2-arylidene-3,4-dihydro-3-oxobenzo-1,4-thiazines (III).

*Experimental.—Condensation of o-nitrophenylthioacetic acid with aldehydes.* A mixture of (*o*-nitrophenylthio)acetic acid [2] (4·26 g.), ammonium acetate (1·5 g.), piperidine (0·5 g.), and the aldehyde (0·02 mole) in acetic acid (4 ml.) was refluxed for 20 hr., then cooled and extracted with ether (50 ml.). Evaporation of the ether gave a yellow solid that was dissolved in a solution of sodium hydrogen carbonate. The solution was filtered and extracted with ether, and the aqueous layer was neutralised with 50% sulphuric acid. The precipitated acid was recrystallised from ethanol or acetic acid. Details regarding the compounds are given in Table 1.

*3-(o-Nitrophenylthio)coumarin.* *o*-(Nitrophenylthio)acetic acid (4·26 g.), ammonium acetate (1·5 g.), salicylaldehyde (2·44 g.), and piperidine (0·5 g.) were refluxed in acetic acid (4 ml.) for 4 hr. The solution was cooled and ether (50 ml.) was added. The yellow solid that separated was filtered off and washed with water. Recrystallisation from glacial acetic acid gave the *coumarin* as yellow needles (1·2 g., 20%), m. p. 223—225° (decomp.) (Found: C, 60·3; H, 3·0. $C_{15}H_9NO_4S$ requires C, 60·2; H, 3·0%).

*Preparation of 2-arylidene-3,4-dihydro-3-oxobenzo-1,4-thiazines.* To a boiling solution of α-(*o*-nitrophenylthio)cinnamic acid (0·0015 mole) in acetic acid (15 ml.) zinc dust (2 g.) was added in small portions. Then the mixture was filtered hot and diluted with water, and the

[1] Baliah and Varadachari, *J. Indian Chem. Soc.*, 1954, **31**, 666.
[2] Claasz, *Ber.*, 1912, **45**, 750.

*oxothiazine* that separated on cooling was filtered off. It was suspended in a saturated solution of sodium hydrogen carbonate and warmed on a water-bath to remove any unchanged acid.

TABLE 1. *Substituted* α-(o-*nitrophenylthio*)*cinnamic acids* (I).

| R | Yield (%) | M. p. | Found (%) C | Found (%) H | Formula | Required (%) C | Required (%) H |
|---|---|---|---|---|---|---|---|
| Ph | 48 | 184—186° | 60·15 | 3·9 | $C_{15}H_{11}NO_4S$ | 59·8 | 3·7 |
| *p*-$C_6H_4Me$ | 24 | 194—197 | 60·9 | 4·2 | $C_{16}H_{13}NO_4S$ | 60·95 | 4·2 |
| *o*-$C_6H_4Cl$ † | 54 | 215—217 | 53·2 | 3·1 | $C_{15}H_{10}ClNO_4S$ | 53·7 | 3·0 |
| *p*-$C_6H_4Cl$ | 62 | 212—214 | 53·3 | 3·2 | $C_{15}H_{10}ClNO_4S$ | 53·7 | 3·0 |
| 3,4-$C_6H_3Cl_2$ | 49 | 194—196 | 48·6 | 2·8 | $C_{15}H_9Cl_2NO_4S$ | 48·7 | 2·45 |
| *o*-$C_6H_4$·OMe | 50 | 202—204 | 58·45 | 4·1 | $C_{16}H_{13}NO_5S$ | 58·0 | 4·0 |
| *p*-$C_6H_4$OMe | 33 | 198—200 * | 57·6 | 4·1 | $C_{16}H_{13}NO_5S$ | 58·0 | 4·0 |
| 3,4-$C_6H_3(OMe)_2$ | 22 | 188—190 | 56·8 | 4·0 | $C_{17}H_{15}NO_6S$ | 56·5 | 4·2 |
| 3,4-$CH_2O_2$·$C_6H_3$ † | 25 | 232—235 * | 55·25 | 3·4 | $C_{16}H_{11}NO_6S$ | 55·65 | 3·2 |
| *o*-$C_6H_4$·$NO_2$ | 14 | 236—239 * | 51·8 | 3·2 | $C_{15}H_{10}N_2O_6S$ | 52·0 | 2·9 |
| *m*-$C_6H_4$·$NO_2$ | 30 | 194—196 | 51·9 | 2·8 | | | |
| *p*-$C_6H_4$·$NO_2$ | 32 | 206—208 | 51·8 | 2·9 | | | |
| α-Naphthyl | 24 | 220—225 * | 64·9 | 3·85 | $C_{19}H_{13}NO_4S$ | 64·9 | 3·7 |
| 2-Thienyl | 38 | 232—235 * | 50·8 | 3·3 | $C_{13}H_9NO_4S_2$ | 50·8 | 3·0 |

* With decomp. † Recrystallised from acetic acid; the others from ethanol.

After filtration the residue was recrystallised from a suitable solvent. The yields were almost quantitative. Details are in Table 2.

TABLE 2. 2-*Arylidene*-3,4-*dihydro*-3-*oxobenzo*-1,4-*thiazines* (III).

| R | M. p. | Found (%) C | Found (%) H | Formula | Required (%) C | Required (%) H |
|---|---|---|---|---|---|---|
| Ph | 200—202° | 71·45 | 4·15 | $C_{15}H_{11}NOS$ | 71·15 | 4·40 |
| *p*-$C_6H_4Me$ * | 232—235 | 71·6 | 4·8 | $C_{16}H_{13}NOS$ | 71·9 | 4·9 |
| *o*-$C_6H_4Cl$ | 225—227 | 63·0 | 3·4 | $C_{15}H_{10}ClNOS$ | 62·6 | 3·5 |
| *p*-$C_6H_4Cl$ * | 245—247 | 63·0 | 3·9 | $C_{15}H_{10}ClNOS$ | 62·6 | 3·5 |
| 3,4-$C_6H_3Cl_2$ † | 245—247 | 56·1 | 2·9 | $C_{15}H_9Cl_2NOS$ | 55·9 | 2·8 |
| *o*-$C_6H_4$·OMe | 214—216 | 67·8 | 4·7 | $C_{16}H_{13}NO_2S$ | 67·8 | 4·6 |
| *p*-$C_6H_4$·OMe * | 207—208 | 67·7 | 4·5 | $C_{16}H_{13}NO_2S$ | 67·8 | 4·6 |
| 3,4-$C_6H_3(OMe)_2$ | 232—234 | 64·9 | 5·2 | $C_{17}H_{15}NO_3S$ | 65·15 | 4·8 |
| 3,4-$CH_2O_2$·$C_6H_3$ | 212—214 | 64·7 | 4·0 | $C_{16}H_{11}NO_3S$ | 64·65 | 3·7 |
| α-Naphthyl | 223—225 | 75·4 | 4·5 | $C_{19}H_{13}NOS$ | 75·2 | 4·3 |
| 2-Thienyl * | 233—235 | 60·6 | 3·8 | $C_{13}H_9NOS_2$ | 60·2 | 3·5 |

* Recrystallised from acetic acid. † Recrystallised from dioxan; the others from ethanol.

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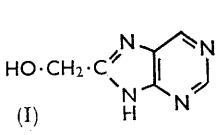
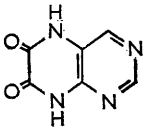
## 913. *Purine-8-carboxylic Acid.*

By Adrien Albert.

Although 4,5-diaminopyrimidines usually give pteridines with 2-hydroxycarbonyl compounds,[1] 8-hydroxymethylpurine (I) was the sole product obtained from 4,5-diaminopyrimidine and glycollic acid or its ethyl ester.[2] The assignment of this constitution rested on the non-identity of the substance (as measured by spectra and ionization constants) with its isomers, 6-hydroxy-7,8- and 7-hydroxy-5,6-dihydropteridine. This constitution has now been confirmed by degradation. The purine (I) was oxidized to purine-8-carboxylic acid which rapidly decarboxylated to purine below the melting point, or when boiled with water for 5 min. Whereas it is decarboxylated much more readily than purine-6-carboxylic acid,[3] it is quite stable as the potassium salt.




(I)




(II)

Purine-8-carboxylic acid differed markedly in spectra and ionization constants from the isomeric 6,7-dihydroxypteridine (II) obtained by heating 4,5-diaminopyrimidine and oxalic acid.[4]

*Experimental.*—8-Hydroxymethylpurine (0·3 g.) and kieselguhr (0·1 g.; " Filter-cel ") were stirred in 0·1N-potassium hydroxide (20 ml.) at 20° while 0·1M-potassium permanganate (27 ml., 1 equiv.) was added during 20 min. The suspension was filtered at the b. p., and the precipitate was extracted with water (4 ml.). The filtrates were adjusted to pH 7 by phosphoric acid, concentrated at 100° to 7 ml., refrigerated, and acidified to pH 2 by sulphuric acid, giving 80% of colourless *purine-8-carboxylic acid*, m. p. 210—212° which gave no depression of m. p. with purine (m. p. 212—213°) (paper-chromatography in butanol–acetic acid showed the absence of purine before, and its presence after, melting) (Found, for material dried at 20°: C, 43·7; H, 2·7; N, 33·8. $C_6H_4N_4O_2$ requires C, 43·9; H, 2·5; N, 34·1%). It is soluble in cold 3N(but not in N)-hydrochloric acid. Apart from this evidence of a basic p$K$ at about 0, two acidic p$K$'s were found, by titration, at 2·91 and 9·37 in water at 20°. The monoanion has $\lambda_{max.}$ 275 mμ (log ε 4·09) at pH 6·5.

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[1] Forrest and Walker, *J.*, 1949, 2077.
[2] Albert, *J.*, 1955, 2690.
[3] Mackay and Hitchings, *J. Amer. Chem. Soc.*, 1956, **78**, 3511.
[4] Albert, Brown, and Cheeseman, *J.*, 1952, 1620.

## 914. *The Paper Chromatography of Triphenylmethyl Ethers of Carbohydrate Derivatives.*

By D. A. Applegarth and J. G. Buchanan.

Triphenylmethyl ethers are frequently used as intermediates in the synthesis of partially substituted sugars,[1] and methods for examining reaction mixtures containing such compounds would clearly be of value.

We had noticed that the Hanes–Isherwood phosphate reagent [2] gave a transient yellow spot on chromatograms containing triphenylmethanol. This reagent contains perchloric acid, and we have now found that a perchloric acid spray is a sensitive method for the detection of triphenylmethyl ethers. The yellow colour, which appears when the sprayed paper is heated to 75°, is certainly due to the formation of the triphenylmethyl cation.[3] The colour fades rapidly in a moist atmosphere, but reappears when the paper is heated. Dilute sulphuric or nitric acid behaves in similar fashion, but both are inferior to perchloric acid. Triphenylmethyl ethers can also be detected on chromatograms by conventional reagents for sugars or sugar alcohols. The sensitivity can often be increased by prior hydrolysis on the paper with formic acid.

The solvent systems developed by Wickberg [4] for the chromatography of sugar acetates have proved useful for triphenylmethyl ethers. $R_F$ values are variable, but rates of movement relative to triphenylmethanol are fairly constant. Some typical values are given in the Table.

*Rates of movement of ethers in relation to triphenylmethanol.*

| | |
|---|---|
| 2,3,4-Tri-*O*-acetyl-1,5-di-*O*-triphenylmethylribitol [7] | 1·7 |
| Me 3,4-anhydro-6-*O*-triphenylmethyl-α-D-galactoside [8] | 0·50 |
| Me 2,3-anhydro-6-*O*-triphenylmethyl-α-D-guloside [8] | 0·31 |
| 1,5-Di-*O*-triphenylmethylribitol [7] | 0·28 |
| 1-*O*-Triphenylmethylribitol [7] | 0·00 |

The $R_F$ value of triphenylmethanol varied from 0·50 to 0·75.

*Experimental.*—Paper chromatography, on Whatman No. 1 paper, was carried out by the descending technique. The paper was impregnated by dipping it twice in a 20% v/v solution of dimethyl sulphoxide in benzene and drying it at 60° for 90 sec. after each treatment.[4] Samples were introduced to the chromatogram as solutions in acetone or chloroform. Irrigation was with di-isopropyl ether, without pre-equilibration, in a well-sealed tank. Solvents were not specially purified. The dimethyl sulphoxide was removed by heating the paper for 25 min. at 75°.

*Detection of the compounds.* (*a*) The triphenylmethyl grouping was detected by spraying the paper with aqueous ~N-perchloric acid and heating it at 75° for 5 min. The yellow spots fade when the paper is taken from the oven, but can be readily restored by reheating. A good spot is given by $10^{-5}$ g. of triphenylmethanol.

(*b*) Removal of triphenylmethyl groups. The paper is dipped in ethereal formic acid solution (25% v/v of 98% formic acid) and heated at 100° for 10 min. After an hour at room temperature, in a forced draught to remove residual formic acid, alkaline silver nitrate [5] or periodate and Schiff's reagent [6] may be used to detect polyols and similar compounds.


[1] Helferich, *Adv. Carbohydrate Chem.*, 1948, **3**, 79.
[2] Hanes and Isherwood, *Nature*, 1949, **164**, 1107.
[3] Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, 1940, p. 54.
[4] Wickberg, *Acta Chem. Scand.*, 1958, **12**, 615.
[5] Trevelyan, Proctor, and Harrison, *Nature*, 1950, **166**, 444.
[6] Baddiley, Buchanan, and Carss, *J.*, 1957, 4138.
[7] Bien and Ginsburg, *J.*, 1958, 3189.
[8] Buchanan, *J.*, 1958, 995, 2511.

We thank Professor David Ginsburg for reference samples of mono- and di-*O*-triphenylmethylribitol, Mr. F. E. Hardy for helpful discussions, and Professor J. Baddiley for his interest and encouragement. One of us (D. A. A.) thanks the Department of Scientific and Industrial Research for a maintenance grant.

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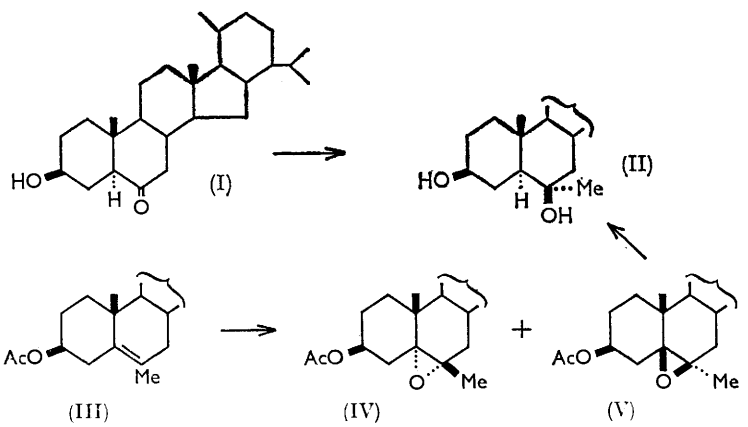
## 915. *The Reaction of Methylmagnesium Iodide with 3β-Hydroxy-5α-cholestan-6-one.*

By M. DAVIS and G. H. R. SUMMERS.

THE reaction of 5α-cholestan-6-one and its 3β-substituted derivatives with methylmagnesium iodide has been stated by Fieser and Rigaudy,[1] and later by Shiota,[2] to afford the 6β-tertiary alcohol, whereas recently the alternative 6α-orientation was preferred by Sneen.[3] These assignments were reached by differing interpretations of dehydration and molecular-rotation data.

It has been shown [4] from optical rotatory dispersion data that methylmagnesium iodide and 3β-hydroxy-5α-cholestan-6-one (I) give a *trans*-A/B-product, and this excludes a possibility suggested by Sneen [3] that a chair–boat conformational change occurs in ring B so as to




minimise the strong 1,3-interaction that would exist between a 6-alkyl group (assigned by him to the β-configuration) and the 10-methyl group. Since also such a change would be most unlikely because of the double locking of ring B by rings A and C, it is clear that only the stereochemistry of the 6-substituents has to be settled to prove the correctness of either Fieser and Rigaudy's [1] or Sneen's [3] views.

[1] Fieser and Rigaudy, *J. Amer. Chem. Soc.*, 1951, **73**, 4660.
[2] Shiota, *Nippon Kagaku Zasshi*, 1954, **75**, 1217; 1956, **76**, 1272; 1956, **77**, 778. *Chem. Abs.*, 1957, **51**, 17969; 1958, **52**, 416, 417.
[3] Sneen, *J. Amer. Chem. Soc.*, 1958, **80**, 3971, 3977, 3982.
[4] Davis, Julia, and Summers, *Bull. Soc. chim. France*, 1960, 742.

We find that oxidation of 6-methylcholesteryl acetate (III) with monoperphthalic acid gives the known [2] 3β-acetoxy-5,6α-epoxy-6β-methyl-5α-cholestane (IV) (73%) and the previously unknown 3β-acetoxy-5,6β-epoxy-6α-methyl-5β-cholestane (V) (14%). Reduction of the β-epoxide (V) with lithium aluminium hydride gave 6α-methyl-5α-cholestane-3β,6β-diol (II) identical with diol obtained by treatment of 3β-hydroxy-5α-cholestan-6-one (I) with methylmagnesium iodide. This result confirms the conclusions of Fieser and Rigaudy [1] and also shows that the Grignard reaction of a 6-oxo-5α-steroid involves least hindered α-attack by the reagent.

*Experimental.*—$[\alpha]_D$ are for $CHCl_3$ solutions, unless stated otherwise. Light petroleum refers to the fraction of b. p. 40—60°.

3β-*Acetoxy*-6-*methylcholestane epoxides.* A solution of 6-methylcholesteryl acetate (3 g.) in ether (60 ml.) was mixed with a 0·88N-solution of monoperphthalic acid in ether (60 ml.) and kept for 5 days at 0°. The solution was washed with 2N-aqueous sodium hydroxide and water, dried, and evaporated. Two recrystallisations of the residue from methanol gave 3β-acetoxy-5,6α-epoxy-6β-methyl-5α-cholestane (2·14 g., 69%), double m. p. 138—140°, 149—150°, $[\alpha]_D$ −29·5° (*c*, 1·39) (lit.,[2] m. p. 140—141° and 149—149·5°). The mother-liquors were evaporated and the residue chromatographed in light petroleum on activated aluminium oxide (20 g.; May and Baker Ltd.). Elution with light petroleum and recrystallisation of the product from methanol gave 3β-*acetoxy*-5,6β-*epoxy*-6α-*methyl*-5β-*cholestane* (0·44 g., 14%), m. p. 95—95·5°, $[\alpha]_D$ −2° (*c*, 0·94) (Found: C, 78·6, 78·25; H, 10·9, 11·1. $C_{30}H_{50}O_3$ requires C, 78·5; H, 11·0%). Elution with 1 : 4 ether–light petroleum gave some more α-epoxide acetate (0·13 g., 4%).

The β-epoxide acetate was hydrolysed with excess of 4% ethanolic potassium hydroxide for 2 hr. 5,6β-*Epoxy*-6α-*methyl*-5β-*cholestan*-3β-*ol* separated from aqueous methanol as needles, m. p. 133—135°, $[\alpha]_D$ +2° (*c*, 1·28) (Found: C, 80·8; H, 11·5. $C_{28}H_{48}O_2$ requires C, 80·7; H, 11·6%). Similar treatment of the α-epoxide acetate gave 5,6α-epoxy-6β-methyl-5α-cholestan-3β-ol, m. p. 168—169°, $[\alpha]_D$ −31° (*c*, 1·76) (lit.,[2] m. p. 160—162°), as needles from ether–light petroleum.

6α-*Methyl*-5α-*cholestane*-6β,3β-*diol.* The β-epoxide acetate (100 mg.) in dry ether (10 ml.) was added to a suspension of lithium aluminium hydride (100 mg.) in dry ether (20 ml.), and the mixture was refluxed for 2 hr. The product, isolated in the usual way, recrystallised from aqueous ethanol, giving 6α-methyl-5α-cholestane-3β,6β-diol (32 mg.), m. p. 196—196·5°, $[\alpha]_D$ +21° (*c*, 0·51 or 1·1 in dioxan) {lit.,[1,3] m. p. 193—194°, 192·5—194°, $[\alpha]_D$ +20° (in dioxan), +17·5°}, identical (mixed m. p. and infrared spectrum) with an authentic sample. Evaporation of the mother-liquors and crystallisation from ether–light petroleum gave a further 19 mg. of material having m. p. 196—198° (total yield, 51 mg., 56%).

One of us (M. D.) thanks Professor M. Julia and Dr. S. Julia for laboratory facilities and advice, Mr. A. F. Ivens for the infrared spectra, and the Directors of May and Baker, Ltd., for the award of a Stickings Memorial Fellowship.

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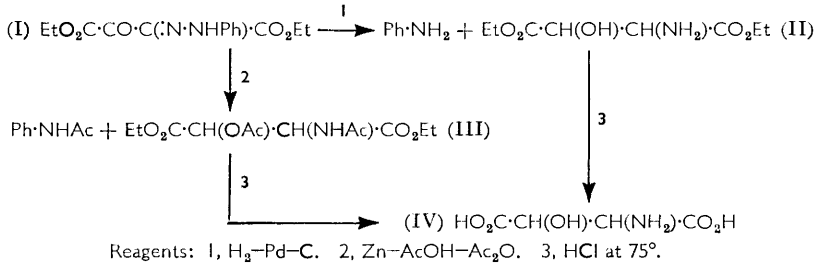
## 916. *A New Synthesis of β-Hydroxyaspartic Acid.*

By C. S. Franklin.

β-Hydroxyaspartic acid (IV) has been prepared previously by Dakin [1] in poor yield by heating chloromalic acid with ammonia. Recently it has been isolated from pancreatic digests of casein [2] while its formation *in vitro* by a transamination between oxaloglycollate and glutamate has been established.[3,4]

Catalytic hydrogenation of ethyl α-oxo-β-phenylhydrazonosuccinate [5] (I) in acid solution over palladised charcoal followed by hydrolysis of the resulting amino-ester (II) gave a mixture of the diastereoisomeric acids (IV) in excellent yield. The isomers were separated by fractional crystallisation from water.[1]

The phenylhydrazone was also reduced by zinc in acetic acid and acetic anhydride to the ester (III). The formation of this compound is of interest as there appears to be no previous example of the reductive acetylation of the carbonyl group in α-phenylhydrazono-




ketones although α-keto-acids are easily converted into the corresponding α-hydroxy-acids by zinc and acetic acid.[6]

*Experimental.*—*β-Hydroxyaspartic acid.* (i) By reductive acetylation. A stirred solution of the phenylhydrazone (I) (29·3 g., 0·1 mole) in acetic acid (100 ml.) and acetic anhydride (50 ml.) was treated with zinc dust (45 g.) in 5 g. portions, the temperature being kept at 35—45° by cooling. After 40 g. of zinc had been added the supernatant liquid became colourless and further addition of the metal produced no rise in temperature. The mixture was then heated at 45° for 2 hr., cooled, and filtered, and the residue washed with cold acetic acid (25 ml.). The filtrate was evaporated to dryness at 100°/15 mm. and the residual oil (33·5 g.) shaken with carbon tetrachloride (50 ml.). A solid separated which was filtered off and identified as acetanilide (6·9 g., 51%) (m. p. and mixed m. p.). The filtrate was distilled to afford *diethyl α-acetamido-β-acetoxysuccinate* (III) (5·5 g., 19%), b. p. 148—160°/0·7 mm. (bath 180—200°) (Found: C, 49·7; H, 6·6. $C_{12}H_{19}O_7N$ requires C, 49·8; H, 6·6%). This ester (5 g., 0·017 mole) was heated at 75° with N-hydrochloric acid (40 ml.) in a sealed tube for 4 days, and the mixture then evaporated at 40°/20 mm. The glass-like residue (4·2 g.) was dissolved in absolute ethanol (50 ml.) and neutralised to Congo Red by aniline. The resulting gelatinous mass was centrifuged, the supernatant liquid decanted, and the residue washed with absolute ethanol (3 × 10 ml.), then acetone (3 × 10 ml.) and finally dried *in vacuo* to give a mixture of the

[1] Dakin, *J. Biol. Chem.*, 1921, **48**, 273.
[2] Sallach and Kornguth, *Biochim. Biophys. Acta*, 1959, **34**, 582.
[3] Garcia-Hernandez and Kun, *Biochim. Biophys. Acta*, 1957, **24**, 78.
[4] Sallach and Peterson, *J. Biol. Chem.*, 1956, **223**, 629.
[5] Rabischong, *Bull. Soc. chim. France*, 1904, **31**, 78.
[6] Debus, *Annalen*, 1863, **127**, 332.

β-hydroxyaspartic acids (2·1 g., 84%), p$K_a'$ 2·18, 3·31, and 9·04 in water (glass electrode–saturated calomel half-cell system at 20°). Chibnall and Cannan,[7] using a hydrogen electrode–saturated calomel half-cell system at 25°, obtained p$K_a'$ 1·95, 3·47, and 9·03) (Found: C, 32·4; H, 4·9; N, 9·0. Calc. for $C_4H_7NO_5$: C, 32·2; H, 4·7; N, 9·4%). Fractional crystallisation of the mixture (2·0 g.) from water yielded the *erythro*- (0·6 g.) and the *threo*-isomer (0·8 g.) as cubes and prisms respectively, the former being the less soluble.

(ii) By hydrogenation. The phenylhydrazone (I) (11·7 g., 0·04 mole) in absolute ethanol (150 ml.) containing 12N-hydrochloric acid (8 ml.) was hydrogenated at room temperature and pressure with 10% palladised charcoal (2 g.), 2·85 l. of hydrogen (required 2·69 l. at N.T.P.; 0·12 mole) being rapidly absorbed. After removal of the catalyst the filtrate was evaporated to dryness at 40°/15 mm. and the residue heated at 75° for 10 hr. with N-hydrochloric acid (100 ml.) in a sealed tube. The resulting solution was then treated as above and yielded a mixture of the isomeric acids (3·5 g., 58%).

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[*Received, June 15th,* 1960.]

[7] Chibnall and Cannan, *Biochem. J.*, 1930, **24**, 945.

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## 917. *An Improvement in the Preparation of Benzotrifuroxan; Further Examples of Complex-formation by this Reagent.*

By A. S. BAILEY.

TREATMENT of 1,3,5-trichloro-2,4-dinitrobenzene with sodium azide in boiling acetone–methanol gave a moderate yield of the corresponding tri-azide, this compound decomposing in the hot solution.[1] This reaction is markedly affected by the solvent used and occurs very smoothly in dimethyl sulphoxide; this solvent has been used previously [2] for the reaction between alkyl halides and sodium nitrite and may prove to be useful for nucleophilic reactions of this type.[3] This modification gives benzotrifuroxan in 63% yield, based on trichlorobenzene.

Some new complexes between aromatic compounds and benzotrifuroxan are listed in the Table.

Dr. W. D. Phillips [4] has found a lower association constant ($K = 24$) for benzotrifuroxan and durene than for tetracyanoethylene and durene [5] ($K = 54$), both in dichloromethane; but, although tetracyanoethylene is an apparently better complexing agent than benzotrifuroxan, few solid complexes from it have been described.[6]

It was of interest to examine a compound containing features of both tetracyanoethylene and benzotrifuroxan. Therefore dicyanofuroxan has been prepared; [6] but it appears to have very little complex-forming ability, as it yields only an ill-defined complex with pyrene and fails to form one with naphthalene.

*Experimental.*—*1,3,5-Triazido-2,4-dinitrobenzene.* To a solution of 1,3,5-trichloro-2,4-dinitrobenzene (5 g.) in dimethyl sulphoxide (30 c.c.) (at 38—40°), water (4 c.c.) was added dropwise; the solution became cloudy. Very finely powdered sodium azide (4·5 g.) was added

[1] Bailey and Case, *Tetrahedron*, 1958, **3**, 113.
[2] Kornblum and Powers, *J. Org. Chem.*, 1957, **22**, 455; Kornblum, Blackwood, and Powers, *J. Amer. Chem. Soc.*, 1957, **79**, 2507; Kornblum and Weaver, *ibid.*, 1958, **78**, 4333.
[3] Smith and Winstein, *Tetrahedron*, 1958, **3**, 317; Smiley and Arnold, *J. Org. Chem.*, 1960, **25**, 257.
[4] Phillips, personal communication.
[5] Merrifield and Phillips, *J. Amer. Chem. Soc.*, 1958, **80**, 2778.
[6] Cram and Bauer, *J. Amer. Chem. Soc.*, 1959, **81**, 5971.

| Compound | Complex | M. p. | Found (%) C | H | N | Br | Formula | Required (%) C | H | N | Br |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Iodomesitylene | Pale yellow needles | 135—140° [i] | 38·3 | 3·0 | 10·9 | | $2C_9H_{11}I,C_6N_6O_6$ | 38·7 | 3·0 | 11·3 | |
| Bromodurene | Cream needles | 186—190 | 43·6 | 3·7 | 14·9 | 20·8 | $3C_{10}H_{13}Br,2C_6N_6O_6$ | 44·0 | 3·4 | 14·7 | 21·0 |
| Bromopentamethylbenzene | Cream needles | 212—215 | 47·3 | 4·4 | 11·6 | 22·2 | $2C_{11}H_{15}Br,C_6N_6O_6$ | 47·6 | 4·3 | 11·9 | 22·7 |
| *m*-Terphenyl | Lemon-yellow needles | 159—161 | 59·6 | 2·8 | 17·4 | | $C_{18}H_{14},C_6N_6O_6$ | 59·8 | 2·9 | 17·4 | |
| 5,6-Dibenzocyclooctadiene | Yellow prisms | 208—210 | 47·8 | 2·5 | 23·3 | | $C_{16}H_{16},2C_6N_6O_6$ | 47·2 | 2·3 | 23·6 | |
| *m*-Xylylene | Cream needles [d] | 223—225° * | 57·8 | 3·4 | 18·2 | | $C_{16}H_{16},C_6N_6O_6$ | 57·4 | 3·5 | 18·2 | |
| 13,14-Dioxatricyclo-[8,2,1,1 $^{7,14}$]tetradecane [e] | Yellow laths [b] | 150 [f] | 49·2 | 2·6 | 18·5 | | $C_{12}H_{12}O_2,C_6N_6O_6$ | 49·1 | 2·7 | 19·1 | |
| 13,14-Dithiatricyclo-[8,2,1,1 $^{7,14}$]tetradecane [e] | Yellow rods | 150 | 15·8 | 2·5 | 17·6 | | $C_{12}H_{12}S_2,C_6N_6O_6$ | 45·8 | 2·5 | 17·8 | |
| 1-Bromonaphthalene | Cream rods | 236—238 * | 42·4 | 1·8 | 18·1 | 17·0 | $C_{10}H_7Br,C_6N_6O_6$ | 41·9 | 1·5 | 18·3 | 17·4 |
| 2-*o*-Tolylnaphthalene | Yellow rods | 183—184 | 49·4 | 1·6 | 22·3 | | $C_{17}H_{14},2C_6N_6O_6$ | 48·2 | 1·9 | 23·2 | |
| Azulene | Black needles | 140—145 [f] | 50·8 | 2·9 | 20·9 | | $(C_{10}H_8,C_6N_6O_6)_2C_3H_8O$ | 51·2 | 2·9 | 20·5 | |
| 1-Bromo-2,3-dimethylnaphthalene | Yellow rods [a] | 235—238 | 44·4 | 2·2 | 17·0 | 16·7 | $C_{12}H_{11}Br,C_6N_6O_6$ | 44·4 | 2·3 | 17·2 | 16·4 |
| 5-Bromoacenaphthene | Yellow needles | 198—201 | 44·7 | 2·2 | 17·1 | | $C_{12}H_9Br,C_6N_6O_6$ | 44·6 | 1·9 | 17·4 | |
| Fluorenone | Yellow rods [b] | 137—139 | 53·1 | 1·9 | 19·6 | | $C_{13}H_8O,C_6N_6O_6$ | 52·8 | 1·9 | 19·4 | |
| 9-Bromophenanthrene | Cream plates [a] | 235—237 | 47·5 | 1·9 | 16·7 | 16·2 | $C_{14}H_9Br,C_6N_6O_6$ | 47·2 | 1·8 | 16·5 | 15·7 |
| Pyrene | Yellow needles [c] | 280—282 | 58·3 | 2·0 | 18·6 | | $C_{16}H_{10},C_6N_6O_6$ | 58·2 | 2·2 | 18·5 | |
| Chrysene | Orange needles [d] | 256—258 | 59·8 | 2·3 | 18·0 | | $C_{18}H_{12},C_6N_6O_6$ | 60·0 | 2·5 | 17·5 | |
| Diphenylacetylene | Orange laths | 170—185 [j] | 55·7 | 2·4 | 19·4 | | $C_{14}H_{10},C_6N_6O_6$ | 55·8 | 2·3 | 19·5 | |
| Diphenylacetylene | Orange prisms [h] | 190—192 | 45·7 | 1·6 | 24·9 | | $C_{14}H_{10},2C_6N_6O_6$ | 45·8 | 1·5 | 24·7 | |
| 1,4-Diphenylbutadiene | Golden-yellow plates | 198—200 * | 47·8 | 2·1 | 23·2 | | $C_{16}H_{14},2C_6N_6O_6$ | 47·3 | 2·0 | 23·6 | |
| 1,6-Diphenylhexatriene | Orange needles [d] | 160—163 * | 49·1 | 2·3 | 22·9 | | $C_{18}H_{16},2C_6N_6O_6$ | 48·9 | 2·2 | 22·8 | |
| Azobenzene | Orange rods | 162—164 | 49·3 | 2·4 | 25·8 | | $C_{12}H_{10}N_2,C_6N_6O_6$ | 49·8 | 2·3 | 25·8 | |
| Azoxybenzene | Cream plates | 137—139 | 48·1 | 2·3 | 24·5 | | $C_{12}H_{10}N_2O,C_6N_6O_6$ | 48·0 | 2·2 | 24·9 | |
| Aniline | Orange rods [b] | 133—134 * [k] | 42·0 | 2·2 | 28·3 | | $C_6H_7N,C_6N_6O_6$ | 41·8 | 2·0 | 28·4 | |
| *p*-Bromoaniline | Orange needles [b] | 126—129° * [l] | 34·1 | 1·7 | 23·2 | 18·5 | $C_6H_6BrN,C_6N_6O_6$ | 34·0 | 1·4 | 23·1 | 18·9 |
| *NN*-Dimethylaniline | Crimson rods [b] | 118—120 * [m] | 45·3 | 3·0 | 25·9 | | $C_8H_{11}N,C_6N_6O_6$ | 45·0 | 2·9 | 26·3 | |
| *p*-Bromo-*NN*-dimethylaniline | Crimson rods [b] | 122—124 * | 37·3 | 2·3 | 21·6 | 17·7 | $C_8H_{10}BrN,C_6N_6O_6$ | 37·2 | 2·2 | 21·7 | 17·7 |

Solvents: (*a*) 1 : 1 ethanol–acetic acid; (*b*) propan-1-ol; (*c*) toluene; (*d*) 2-methoxyethanol; (*e*) Winberg, Fawcett, Mochel, and Theobald, *J. Amer. Chem. Soc.*, 1960, **82**, 1428; (*f*) exploded; (*g*) prepared by using 3 mol. of benzotrifuroxan; (*h*) the 1 : 1 complex changed into the 1 : 2 complex during 12 hr. storage in the mother liquors; (*i*) softens at 100°; (*j*) softens at 145°; (*k*) darkens at 130°; (*l*) darkens at 120°; (*m*) darkens at 106°.

1,2-Diphenylbenzene, 1,4,5,8-tetrahydronaphthalene, and [2,2]paracyclophane did not give solid complexes. * With decomp.

during 15 min. and the mixture stirred for 3 hr. at 30—35°. Solid began to separate after 1 hr. The mixture was then kept at 0° overnight and next day diluted with water (50 c.c.). The product that separated was washed with water and dried *in vacuo* (yield 5·3 g.). It (m. p. 100—105°) was suitable for nitration.[1]

*Complexes.* The *complexes* (see Table) were prepared as previously described,[1] with 1 : 4 acetic acid–ethanol as solvent unless otherwise indicated. They were dried *in vacuo* at room temperature.

*Dicyanofuroxan.* This compound had m. p. 40—42° (Wieland [7] reports m. p. 42°) and $\lambda_{max.}$ 275 mμ (ε 4400 in EtOH).

Solutions of dicyanofuroxan in benzene or mesitylene were colourless. Addition of dicyanofuroxan to a solution of naphthalene in hot ethanol gave a colourless solution from which naphthalene crystallised on cooling. Dicyanofuroxan (80 mg.) was added to a boiling solution of pyrene (100 mg.) in propan-1-ol; when the bright yellow solution was cooled, the hydrocarbon separated and so the solution was re-heated, more dicyanofuroxan (60 mg.) was added, and the solution allowed to cool slowly; bright yellow plates of the *complex* separated; when washed with ethanol and dried, they (120 mg.) softened at 110° and melted at 120—123° (Found: N, 15·6. $C_{16}H_{10},C_4N_4O_2$ requires N, 16·6%).

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[7] Wieland, *Annalen*, 1925, **444**, 30; 1929, **475**, 54.