5-*Amino*-9-*phenylphenanthridine.*

By A. E. S. Fairfull, V. Petrow, and (the late) W. F. Short.

[Reprint Order No. 6272.]

By the action of phosphoryl chloride on 2 : 2′-dibenzamidodiphenyl Mamalis and Petrow (*J.*, 1950, 707) obtained a compound, m. p. 164° (hydrochloride, m. p. 335—338°), to which they ascribed the structure 5-amino-9-phenylphenanthridine. Fairfull, Peak, Short, and Watkins (*J.*, 1952, 4703) subsequently obtained 5-amino-9-phenylphenanthridine, m. p. 192—193° (benzoyl derivative, m. p. 214°) from 2-benzamido-2′-phthalimidodiphenyl, *via* 9-phenyl-5-phthalimidophenanthridine. We have now repeated the experiment of Petrow and Mamalis (*loc. cit.*) and find that 2 : 2′-dibenzamidodiphenyl and phosphoryl chloride yield 2-phenyl-4 : 5-6 : 7-dibenzo-1 : 3-diaza*cyclo*hepta-2 : 4 : 6-triene, m. p. 164—165° (isomeric with 5-amino-9-phenylphenanthridine), and 5-benzamido-9-phenylphenanthridine, m. p. 214° (above). The heptatriene has been obtained by Sako (*Mem. Coll. Eng. Kyushu*, 1932, **6**, 263) from 2-amino-2′-benzamidodiphenyl and phosphoryl chloride, and by Fairfull *et al.* (*loc. cit.*, p. 4708) from 2 : 2′-diaminodiphenyl, benzonitrile, and benzenesulphonic acid.

Experimental.—A mixture of 2 : 2′-dibenzamidodiphenyl (3 g.), nitrobenzene (9 c.c.), and phosphoryl chloride (6 c.c.) was boiled under reflux for 2 hr., and the solution was then cooled and repeatedly stirred with warm light petroleum (b. p. 100—120°; 6 × 100 c.c.). The tacky brown solid which separated was dissolved in ethanol (25 c.c.) and mixed with concentrated hydrochloric acid (25 c.c.) and water (15 c.c.). The precipitate solidified directly or after being triturated with ethanol (1—3 c.c.), and the yellow solid (0·6 g.) had m. p. 335—338°. Basification of this hydrochloride and crystallisation from light petroleum (b. p. 100—120°) gave pale yellow prisms of 2-phenyl-4 : 5-6 : 7-dibenzo-1 : 3-diaza*cyclo*hepta-2 : 4 : 6-triene, m. p. and mixed m. p. 164—165°. The acid–ethanol mother-liquor was diluted with water (300 c.c.), filtered through kieselguhr to remove a trace of oil, and then basified to give a white solid, which, recrystallised from toluene, had m. p. 175—185°. The white solid (1·1 g.) from three experiments was heated with ethanol (4 c.c.) and filtered hot from a residue, m. p. 208—211° (0·5 g.). Crystallisation from toluene raised the m. p. to 210—211° (Found: N, 7·6. Calc. for $C_{26}H_{18}ON_2$: N, 7·5%), and the product did not depress the m. p. of 5-benzamido-9-phenylphenanthridine.

Research Laboratories, Boots Pure Drug Co. Ltd.,
Nottingham.
The British Drug Houses Ltd., London, N.1.

[*Received, March 29th*, 1955.]

4-*Bromo- and* 4-*Chloro-cholest*-4-*en*-3-*one.*

By J. I. Shaw and Robert Stevenson.

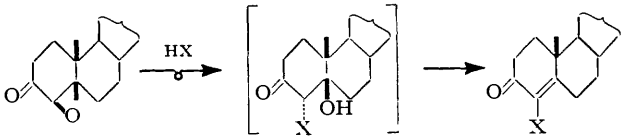
[Reprint Order No. 6346.]

This communication deals with the preparation and ultraviolet light absorption of 4-bromo- (II; X = Br) and 4-chloro-cholest-4-en-3-one (II; X = Cl). Considerable interest has been shown in the effect on the light absorption of halogen substitution on the ethylenic linkage of αβ-unsaturated ketones (Bowden, Braude, and Jones, *J.*, 1946, 948; Bowden and Braude, *J.*, 1952, 1068; Djerassi, Rosenkranz, Romo, Kaufmann, and Pataki, *J. Amer. Chem. Soc.*, 1950, **72**, 4534; Nussbaum, Mancera, Daniels, Rosenkranz, and Djerassi, *ibid.*, 1951, **73**, 3263), and the bathochromic shift observed has made it evident that many structural assignments to unsaturated bromo-ketones in the steroid field were erroneous (see, *e.g.*, Djerassi *et al.*, *loc. cit.*).

The bromo-compound (II; X = Br) was described by Barkow (Diss., Danzig, 1938), and the ultraviolet light absorption, therein reported, was quoted by Dannenberg (*Abhandl. Preuss. Akad. Wiss.*, 1939, **21**, 3) and in subsequent reviews. Because of its equivocal

method of preparation, its unsatisfactory analytical data, and its light absorption ($\lambda_{max.}$ 250 mμ, ε 15,200 in ether), Nussbaum *et al.* (*loc. cit.*) queried the assigned structure and/or purity of this compound, and since the same authors showed that the average bathochromic effect of an α-bromo-substituent in an αβ-unsaturated ketone was 23 mμ, predicted an absorption maximum *ca.* 265 mμ for 4-bromocholest-4-en-3-one (II; X = Br). Application of the standard correction factor for ether (Dannenberg, *loc. cit.*) would give $\lambda_{max.}$ 257 mμ (in EtOH) for Barkow's product.

We have discovered a simple method for the preparation of 4-bromocholest-4-en-3-one. This consists in treatment of 4β : 5-epoxycoprostan-3-one (I) (Plattner, Heusser, and Kulkarni, *Helv. Chim. Acta*, 1948, **31**, 1826) with hydrobromic acid, and involves diaxial opening of the epoxide and spontaneous dehydration of the intermediate β-hydroxy-ketone, to yield the bromide (II; X = Br), $\lambda_{max.}$ 260 mμ (ε 11,500 in EtOH) differing in properties

(I)  (II)

from Barkow's compound. In comparison with the bathochromic shift of +25 mμ observed on substitution of a bromine atom at $C_{(2)}$ in cholest-1-en-3-one (Djerassi and Scholz, *J. Amer. Chem. Soc.*, 1947, **69**, 2404), the bromide (II; X = Br) exhibits a shift of +20 mμ with respect to cholest-4-en-3-one. 4-Chlorocholest-4-en-3-one (II; X = Cl), $\lambda_{max.}$ 256 mμ (ε 11,000 in EtOH), was obtained by brief treatment of the oxide (I) with hydrogen chloride; introduction of an α-chlorine atom into cholest-4-en-3-one causes a shift of +16 mμ, in excellent agreement with the shift (+15 mμ) found for the change cholest-1-en-3-one ⟶ 2-chlorocholest-1-en-3-one (Beereboom and Djerassi, *J. Org. Chem.*, 1954, **19**, 1196; Ellis and Petrow, *J.*, 1953, 3869). Treatment of the bromide (II; X = Br) with zinc in acetic acid gave cholest-4-en-3-one; under the same conditions, the chloride was recovered unchanged.

Unlike the 2α-, 6α-, and 6β-bromo- and -chloro-derivatives of cholest-4-en-3-one, which, when boiled with 2 : 4-dinitrophenylhydrazine in acetic acid, yield cholesta-4 : 6-dien-3-one 2 : 4-dinitrophenylhydrazone (Barton and Miller, *J. Amer. Chem. Soc.*, 1950, **72**, 370, 1066; Djerassi, *ibid.*, 1949, **71**, 1003; Beereboom, Djerassi, Ginsburg, and Fieser, *ibid.*, 1953, **75**, 3500) 4-bromo- and 4-chloro-cholest-4-en-3-one give 2 : 4-dinitrophenylhydrazones with retention of the halogen atom. This parallels the behaviour of 2-bromo- and 2-chlorocholest-1-en-3-one, and provides further examples of the hypsochromic effect (−5 and −6 mμ for the bromo- and the chloro-derivative respectively) of halogen substitution on the ethylenic bond of αβ-unsaturated ketone 2 : 4-dinitrophenylhydrazones.

An attempt to prepare 4-iodocholest-4-en-3-one (II; X = I) by treatment of the oxide (I) with hydriodic acid was unsuccessful, reduction occurring and cholest-4-en-3-one being the sole product isolated.

Experimental.—Rotations were measured in $CHCl_3$ solution at room temperature.

4β : 5-*Epoxycoprostan*-3-*one*. Aqueous 30% hydrogen peroxide solution (20 c.c.) and 4N-sodium hydroxide (20 c.c.) were added simultaneously, dropwise with stirring, to a solution of cholest-4-en-3-one (5·0 g.) in methanol (500 c.c.). After the mixture had been kept at 0° for 48 hr., the solid which had separated was filtered off and crystallised from aqueous methanol, to give 4β : 5-epoxycoprostan-3-one (3·0 g.) as needles, m. p. 118—119°, $[\alpha]_D$ +128° (*c*, 2·5). Plattner *et al.* (*loc. cit.*) give m. p. 116—117°, $[\alpha]_D$ +134°, +136°. The oxide was recovered unchanged after refluxing with periodic acid in aqueous acetone.

4-*Bromocholest*-4-*en*-3-*one*. Aqueous 40% hydrobromic acid (2 c.c.) was added to a solution of the oxide (200 mg.) in chloroform (20 c.c.) and glacial acetic acid (2 c.c.). After 16 hr. at room temperature, the mixture was diluted with water and extracted with chloroform. Removal of the solvent from the washed and dried extract gave an oil which crystallised from aqueous methanol or aqueous acetone to furnish 4-*bromocholest*-4-*en*-3-*one* as long needles (120 mg.), m. p. 114—115°, $[\alpha]_D$ +107° (*c*, 1·4) (Found: C, 70·2; H, 9·7. $C_{27}H_{43}OBr$ requires C, 69·9; H, 9·35%).

Zinc dust (250 mg.) was added portionwise to a solution of the unsaturated bromo-ketone (50 mg.) in acetic acid (30 c.c.) and the mixture refluxed for 4 hr. The product was worked up in the usual way, to give cholest-4-en-3-one, m. p. and mixed m. p. 81—82°. The bromo-ketone was recovered unchanged after treatment under reflux for 1 hr. with collidine.

The bromo-ketone (500 mg.) and 2 : 4-dinitrophenylhydrazine (250 mg.) in acetic acid were heated at 100° for 15 min., and the product was collected and recrystallised from chloroform–ethanol, to yield 4-*bromocholest*-4-*en*-3-*one* 2 : 4-*dinitrophenylhydrazone* as red blades, m. p. 217° (decomp.), $\lambda_{max.}$ 262 and 385 mμ (ε 17,000 and 26,800 in $CHCl_3$) (Found : C, 61·9; H, 7·4. $C_{33}H_{47}O_4N_4Br$ requires C, 61·6; H, 7·4%).

4-*Chlorocholest*-4-*en*-3-*one*. A stream of hydrogen chloride was passed through a solution of 4β : 5-epoxycoprostan-3-one (500 mg.) in chloroform (20 c.c.) for 2 min., and the solution then washed with water, dried (Na_2SO_4), and evaporated, to yield an oil which crystallised from aqueous methanol, giving 4-*chlorocholest*-4-*en*-3-*one* as long needles (450 mg.), m. p. 124·5—125°, $[\alpha]_D$ +106° (*c*, 1·5) (Found : C, 77·65; H, 10·6. $C_{27}H_{43}OCl$ requires C, 77·4; H, 10·3%).

4-*Chlorocholest*-4-*en*-3-*one* 2 : 4-*dinitrophenylhydrazone* crystallised from ethanol–chloroform as red plates, m. p. 255° (decomp.), $\lambda_{max.}$ 263 and 384 mμ (ε 16,800 and 27,300 in $CHCl_3$) (Found : C, 66·5; H, 7·8. $C_{33}H_{47}O_4N_4Cl$ requires C, 66·2; H, 7·9%). 4-*Chlorocholest*-4-*en*-3-*one semicarbazone* separated from methanol–chloroform as needles, m. p. 165° (decomp.), $\lambda_{max.}$ 270 mμ (ε 21,000 in EtOH) (Found : C, 70·9; H, 9·3. $C_{28}H_{46}ON_3Cl$ requires C, 70·7; H, 9·7%).

Action of hydriodic acid on 4β : 5-*epoxycoprostan*-3-*one*. The epoxy-ketone (500 mg.) was refluxed in freshly distilled 48% hydriodic acid (6 c.c.) and chloroform (25 c.c.) for 1 hr. The solution was washed with water, 10% aqueous sodium thiosulphate, and water, dried (Na_2SO_4), and evaporated. Crystallisation of the residue from methanol gave cholest-4-en-3-one (420 mg.), m. p. and mixed m. p. 81—82°, $[\alpha]_D$ +91° (*c*, 1·4), $\lambda_{max.}$ 240 mμ (ε 17,100 in EtOH).

We thank Professor F. S. Spring, F.R.S., for his encouragement and interest and acknowledge the award of a D.S.I.R. Maintenance Grant (to J. I. S.).

THE ROYAL TECHNICAL COLLEGE, GLASGOW. [*Received, April 20th*, 1955.]

O-*Alkylation of Urea.*

By J. W. JANUS.

[Reprint Order No. 6371.]

IN the direct *O*-methylation of urea with methyl sulphate (Werner, *J.*, 1914, **105**, 927), the isolation of a pure solid derivative from the syrup obtained is difficult and is usually done *via* the picrate (Hughes, Saroff, and Carney, *J. Amer. Chem. Soc.*, 1949, **71**, 2476; Brown and Hoerger, *J. Appl. Chem.*, 1954, **4**, 284). *O*-Methyl*iso*urea hydrochloride has been prepared, however, by addition of methanol to cyanamide in the presence of hydrogen chloride (Stieglitz and McKee, *Ber.*, 1900, **33**, 1517; see also *Org. Synth.*, **34**, 67). It has hitherto been considered necessary to perform the methylation of urea with methyl sulphate at temperatures above 100°, where the reaction may be too violent if large batches are prepared (Werner, *loc. cit.*). It is here shown that urea reacts quietly with methyl sulphate even at room temperature, and the yield is slightly higher. It is, however, no easier to isolate a crystalline derivative from the resulting syrup. For preparative purposes an intermediate temperature is preferred, since the reaction takes some days at room temperature.

It has now been found that urea can also be smoothly methylated with methyl toluene-*p*-sulphonate and the resulting *O*-methyl*iso*urea toluene-*p*-sulphonate can be readily isolated pure and in good yield. The homologue, *O*-ethyl*iso*urea toluene-*p*-sulphonate can be prepared by the analogous reaction.

Experimental.—Methylation with methyl sulphate. Urea (60 g.) and methyl sulphate (126 g.) were stirred together on a water-bath at 40° for 7 hr. Stirring must be such that the urea is completely suspended, for most rapid reaction, and must be continued until after the mixture has become clear. The *iso*urea picrate was precipitated by adding 2M-lithium picrate (350—400 ml.) and alcohol (300 ml.). The mixture was then boiled on the steam-bath for 5 min., the greater part of the picrate dissolving. The mixture was left overnight at 0°, and then

filtered, and the salt washed with ethanol. The air-dried yield was 182 g. (60%), and the m. p. 177°.

The picrate can be converted into the hydrogen sulphate (Hughes *et al.*, *loc. cit.*) or the hydrochloride (Brown *et al.*, *loc. cit.*).

The syrup from the methylation may be used direct for many purposes, but it is advisable to estimate the methyl*iso*urea content by precipitation of the picrate from a small portion (yield 60—64%).

A similar methylation at about 18° required 5 days for completion (3 days to clear). At 60° about 1 hr. is required.

O-*Methyl*iso*urea toluene*-p-*sulphonate*. Urea (60 g.) and methyl toluene-*p*-sulphonate (186 g.) were heated together on the steam-bath with mechanical stirring for 3 hr. After ½—1 hr. the temperature rose by 30° and fell again soon after; after 1½ hr. crystals appeared. After the mixture had cooled somewhat, but before complete solidification (50—60°), acetone (200 ml.) was added and the mixture was stirred for 1 hr., left at 0° overnight, and filtered. The O-*methyl*iso-*urea toluene*-p-*sulphonate* was washed with ice-cold acetone (4 × 50 c.c.) and dried (yield 164—167 g., 67%; m. p. 124—126°). Recrystallization may be from acetone (40 ml./g.) or dioxan (15 ml./g.). The compound was discoloured on prolonged boiling with dioxan. Dioxan was heated to 90° and the compound added with vigorous stirring and heating continued for 5 min. The solution was filtered out from 5—12 g. of insoluble matter and an 80% recovery of pure material, m. p. 134°, was obtained on cooling. Recrystallization once from acetone and once from dioxan gives white needles, m. p. 134° (Found: C, 43·7; H, 6·1; N, 11·3; S, 13·1. $C_2H_6ON_2,C_7H_8O_3S$ requires C, 43·9; H, 5·75; N, 11·4; S, 13·05%).

The residue insoluble in hot dioxan was recrystallized from alcohol (6 ml./g.). More than half was recovered as ammonium toluene-*p*-sulphonate. A second recrystallization (10 ml./g.) yielded colourless needles, m. p. 324—326° (decomp.) (Clemo and Walton *J.*, 1928, 726, give 325—330°) (Found: C, 44·15; H, 6·0; N, 7·45. Calc. for $C_7H_{11}O_3NS$: C, 44·4; H, 5·9; N, 7·4%). Analysis (Nessler) of an aqueous solution showed that all the nitrogen was combined as ammonia.

O-*Ethyl*iso*urea toluene*-p-*sulphonate*. Urea (6 g.) and ethyl toluene-*p*-sulphonate (20 g.) were heated as above for 7 hr. The waxy solid, obtained on cooling, was dissolved in warm ethyl methyl ketone (50 ml.) and the solution filtered from a small white residue (1·7 g.), m. p. 314—316° (decomp.). The residue was washed with ethyl methyl ketone (5 × 5 ml.), and the filtrate and washings were left in a refrigerator for 3 days with occasional shaking, giving O-*ethyl*iso*urea toluene*-p-*sulphonate* (14·75 g.), m. p. 91—93°. Addition of ether to the mother liquors provided a further 1·4 g. (m. p. 90—92°) (total yield 62%). Recrystallization from ethyl methyl ketone (10 ml./g.) at 50—55° removed a further 0·17 g. of insoluble matter and gave a 90% recovery. Recrystallization from ethyl methyl ketone and from *iso*butyl methyl ketone (50 ml./g.) gave m. p. 94° (Found: C, 46·5; H, 6·25; N, 10·65; S, 12·6. $C_{10}H_{16}O_4N_2S$ requires C, 46·15; H, 6·2; N, 10·75; S, 12·3%).

Analyses were by Mr. C. B. Dennis and Miss D. Williams.

RESEARCH LABORATORIES, KODAK LTD.,
WEALDSTONE, HARROW, MIDDX.

[*Received, April 29th*, 1955.]

5-*Formyl*-8-*hydroxyquinoline.*

By G. R. CLEMO and R. HOWE.

[Reprint Order No. 6374.]

IN connection with another problem we have repeated the synthesis (Sen and Ray, *J. Indian Chem. Soc.*, 1932, **9**, 178) of 5- and 7-formyl-8-hydroxyquinoline. Only 5-formyl-8-hydroxyquinoline has now been obtained, as shown by conversion *via* the oxime and nitrile into 8-hydroxyquinoline-5-carboxylic acid (Matsumura and Sone, *J. Amer. Chem. Soc.*, 1931, **53**, 1494). Our aldehyde differs from that reported by Sen and Ray. 5-Formyl-8-hydroxyquinoline has been condensed with dimethylaniline in the presence of hydrochloric acid, and the product obtained was identical with that prepared by Ray (*J. Indian Chem. Soc.*, 1937, **14**, 414) from the alleged 7-formyl-8-hydroxyquinoline. The ultraviolet spectrum of our aldehyde has the characteristics of *p*-hydroxybenzaldehyde and not of salicylaldehyde in accordance with its being the 5-isomer.

Experimental.—Ultraviolet light absorptions were measured in ethanol by using a Hilger Uvispectrometer.

5-Formyl-8-hydroxyquinoline. 8-Hydroxyquinoline (20 g.), ethanol (80 c.c.), and aqueous sodium hydroxide (40 g. in 50 c.c. of water) were refluxed while chloroform (27 g.) was added dropwise during 1 hr. After refluxing for 12 hr., ethanol and excess chloroform were distilled off, the residue was dissolved in water (600 c.c.), and the solution acidified with hydrochloric acid. The solid which separated was dried, and then continuously extracted with light petroleum (b. p. 100—120°). The extract furnished *5-formyl-8-hydroxyquinoline* as straw-coloured needles (2·5 g.), m. p. 173° (from ethanol), giving an emerald colour with aqueous ferric chloride and having $\lambda_{max.}$ 241, 262, and 329 mμ (log ε 4·48, 4·01, 4·03) (Found : C, 69·45; H, 4·1; N, 8·3. $C_{10}H_7O_2N$ requires C, 69·4; H, 4·05; N, 8·1%). The *oxime* formed pale yellow plates, m. p. 196°, from ethanol (Found : C, 63·6; H, 4·4; N, 14·55. $C_{10}H_8O_2N_2$ requires C, 63·8; H, 4·25; N, 14·9%). The *phenylhydrazone* formed brown plates, m. p. 132°, from benzene (Found : C, 72·95; H, 5·3; N, 16·05. $C_{16}H_{13}ON_3$ requires C, 73·0; H, 4·9; N, 16·0%). *8-Acetoxy-5-formylquinoline* gave colourless needles, m. p. 118°, from ethanol (Found : C, 67·2; H, 4·55; N, 6·8. $C_{12}H_9O_3N$ requires C, 67·0; H, 4·2; N, 6·5%).

5-Cyano-8-hydroxyquinoline. Phosphoric oxide (2 g.) was added to the oxime (0·5 g.), dissolved in xylene, and the mixture refluxed for 3 hr. The xylene layer furnished *5-cyano-8-hydroxyquinoline* which formed colourless needles, m. p. 174° (0·2 g.), from light petroleum (Found : C, 70·6; H, 3·95; N, 16·1. $C_{10}H_6ON_2$ requires C, 70·6; H, 3·5; N, 16·5%). The oxime (1 g.), refluxed with acetic anhydride (5 c.c.) for 1 hr., gave *8-acetoxy-5-cyanoquinoline*, colourless needles (0·9 g.), m. p. 150° (from light petroleum) (Found : C, 67·7; H, 3·8; N, 13·0. $C_{12}H_8O_2N_2$ requires C, 67·9; H, 3·8; N, 13·2%). Hydrolysis with aqueous sodium hydroxide gave 5-cyano-8-hydroxyquinoline.

8-Hydroxyquinoline-5-carboxylic acid. 5-Cyano-8-hydroxyquinoline (0·5 g.) was heated on a steam-bath with 80% sulphuric acid (2 c.c.) for 5 hr. The pale yellow needles which separated were collected and washed with water, the filtrate being retained. The needles, after being boiled with water, gave the acid as egg-yellow needles, m. p. and mixed m. p. 272—273° (decomp.) (from ethanol) (cf. Lippmann and Fleissner, *Ber.*, 1886, **19**, 2467), formed a green colour with aqueous ferric chloride, and had $\lambda_{max.}$ 243 and 321 mμ (log ε 4·50 and 3·90) (Found : C, 63·5; H, 3·9; N, 7·3. Calc. for $C_{10}H_7O_3N$: C, 63·5; H, 3·7; N, 7·4%). The hydrochloride separated in colourless columns, m. p. and mixed m. p. 239° (decomp.), from 10% hydrochloric acid (Found : Cl, 16·0. Calc. for $C_{10}H_8O_3NCl$: Cl, 15·7%).

The retained filtrate was neutralised with aqueous ammonia, and the solid collected and washed with water. It was purified by dissolution in dilute aqueous ammonia and reprecipitation with acetic acid. *5-Carbamoyl-8-hydroxyquinoline* was obtained as pale yellow plates, m. p. 264—265° (decomp.), from ethanol (Found : C, 63·8; H, 4·6; N, 14·6. $C_{10}H_8O_2N_2$ requires C, 63·8; H, 4·3; N, 14·9%).

Condensation of 5-formyl-8-hydroxyquinoline with dimethylaniline. The aldehyde (1 g.) and dimethylaniline (2·5 c.c.) were heated on a steam-bath for 30 hr., hydrochloric acid (3 c.c.) being added gradually. The solution was made alkaline and then steam-distilled. The residual blue-green solid was purified by dissolution in hydrochloric acid and reprecipitation with aqueous ammonia, and gave a blue-green powder, m. p. 175—177°, from chloroform–ethanol (Found : N, 10·3. Calc. for $C_{26}H_{27}O_3N$: N, 10·6%). Ray (*loc. cit.*) reports a blue-green powder, m. p. 177° (from chloroform), prepared from the alleged 7-formyl-8-hydroxyquinoline.

2-(8-Hydroxy-5-quinolyl)vinyl phenyl ketone. Acetophenone (2·75 g.) was added with shaking to the aldehyde (4 g.) in warm hydrochloric acid (50 c.c.). The yellow needles which separated on standing were washed with ether, and treatment with aqueous sodium acetate liberated the free *ketone* which forms yellow prisms, m. p. 172° (from ethanol), $\lambda_{max.}$ 249 and 328·5 mμ (log ε 4·52 and 4·32) (Found : C, 78·5; H, 4·8; N, 5·15. $C_{18}H_{13}O_2N$ requires C, 78·55; H, 4·7; N, 5·1%). The *hydrochloride* forms yellow needles, m. p. 247—249° from hydrochloric acid (Found : C, 69·45; H, 4·4; N, 4·6; Cl, 11·65. $C_{18}H_{14}O_2NCl$ requires C, 69·3; H, 4·5; N, 4·5; Cl, 11·4%).

One of us (R. H.) is indebted to the Department of Scientific and Industrial Research and Durham Education Committee for maintenance grants.

KING'S COLLEGE, UNIVERSITY OF DURHAM,
NEWCASTLE-ON-TYNE, 1.

[*Received, April 30th*, 1955.]

Paper Chromatography of Uronic Acids.

By R. A. Edington and Elizabeth Percival.

[Reprint Order No. 6400.]

Although paper chromatography of uronic acids has been mentioned in the literature on a number of occasions (Lederer and Lederer, "Chromatography," Elsevier, London, 1953, p. 158—171) there are remarkably few reliable records of the R_G values of the uronic acids and their methyl ethers. This is probably owing, first, to the scarcity of authentic specimens of the uronic acids, and, secondly, to the practical difficulties of "trailing" and poorly defined spots. A number of methylated uronic acids synthesised in this laboratory (Edington, Hirst, and Percival, *J.*, 1955, 2281) were, therefore, examined on the paper chromatogram, various solvent systems and spray reagents being used. Most of the chromatograms were run in a room thermostatically controlled at 21°, although comparable chromatograms run at temperatures between 18° and 21° gave the same R_G values. From preliminary experiments it appeared that for most purposes the two types of solvent system available were, on the one hand, those containing acetic acid, typified by butanol–acetic acid–water, and on the other the butanol–formic acid–water system proposed by Smith *et al.* (*J.*, 1952, 2637). The properties of both of these solvent mixtures slowly change owing to esterification of the acid by the butanol. While Smith and Spriesterbach (*Nature*, 1954, **174**, 467) have recently overcome this difficulty by coating the paper with alginic acid before elution, we have obtained consistent results by the use of an aged or otherwise equilibrated mixture. Although rhamnose has been proposed as a control substance for the paper chromatography of uronic acids, we found that it gave very variable $R_{rhamnose}$ values for the various uronic acids, whereas tetramethylglucose gave reasonably consistent results, the derived R_G values of the uronic acids being generally within 3% of one another on different papers and at different times, butanol–aqueous–formic acid being used. In the case of butanol–acetic acid–water, however, results were less consistent, the maximum variation in the R_G value of the uronic acid being about 6%. The formic acid system has certain other advantages over those containing acetic acid: it is faster, gives better separation, and is much less liable to cause badly shaped spots or trails through incomplete de-ionisation. It is noteworthy that the "heart-shaped spot" which is occasionally mentioned in the literature (Partridge, *Biochem. J.*, 1948, **42**, 238; Reid, *J. Sci. Food Agric.*, 1950, **1**, 234; Chanda, Hirst, and Percival, *J.*, 1951, 1240) as being characteristic of uronic acids has, in the present work, been observed only with solvents containing acetic acid in the presence of inorganic cations. As a rule, the spots are discrete and spherical or elliptical in outline. Aqueous aniline oxalate and butanolic *p*-anisidine hydrochloride were the most generally useful spray reagents. With uronic acids having a free hydroxyl group at $C_{(2)}$, these spray reagents give a brown or reddish-brown colour, whereas with acids substituted at $C_{(2)}$ a brilliant red or purple colour is produced.

	Colour with		R_G in	
Uronic acid	aniline oxalate	*p*-anisidine hydrochloride	BuOH–H·CO_2H–H_2O	BuOH–AcOH–H_2O
D-Galacturonic acid	Brown	Brown	0·03	0·15
D-Mannuronic acid	Brown	Brown	0·05	0·16
D-Mannuronolactone	Brown	Brown	0·13	0·29
2-*O*-Methyl-D-galacturonic acid	Orange-red	Red-purple	0·20	0·22
D-Glucuronolactone	Brown	Brown	0·21	0·37
4-*O*-Methyl-D-mannuronic acid	Red-brown	Red-brown	0·25	0·29
3 : 4-Di-*O*-methyl-D-galacturonic acid	Red-brown	Red-brown	0·43	0·46
2 : 3-Di-*O*-methyl-D-glucuronic acid	Orange-red	Red-purple	0·47	0·56
2 : 3 : 4-Tri-*O*-methyl-D-galacturonic acid	Orange-red	Red-purple	0·63	0·61
2 : 3 : 4-Tri-*O*-methyl-D-mannuronic acid	Orange-red	Red-purple	0·79	0·80
2 : 3 : 4-Tri-*O*-methyl-D-glucuronic acid	Orange-red	Red-purple	0·84	0·84

Methyl glycosiduronic acids were generally hydrolysed, before chromatography, with N-sulphuric acid at 100° for 24 hr., followed by neutralisation with barium carbonate, filtration, and de-ionisation with Amberlite IR-100-H cation-exchange resin. Butanol–acetic acid–water (40 : 10 : 50) and butanol–formic acid–water (500 : 115 : 385) were either kept at room temperature for 14 days or boiled under reflux for 1 hr. before use.

The Table summarises the results obtained.

CHEMISTRY DEPARTMENT, UNIVERSITY OF EDINBURGH. [*Received, May 7th*, 1955.]

The Infrared Spectra of Some Compounds containing the Pentacyanoferrate Group.

By E. F. G. HERINGTON and W. KYNASTON.

[Reprint Order No. 6412.]

MILLER and WILKINS (*Analyt. Chem.*, 1952, **24**, 1253) have recorded the spectra of solid sodium and potassium ferro- and ferri-cyanide, and Emschwiller (*Compt. rend.*, 1954, **238**, 1414) has reported that the CN group gives rise to a more intense band in the ferro- than in the ferri-cyanides and that these bands appear at wave-numbers 2040 and 2115 cm.$^{-1}$ for the respective potassium salts. The present note records the spectra of the following compounds :

$Na_3[Fe(CN)_5NH_3],6H_2O$; $Na_2[Fe(CN)_5NH_3]H_2O$; $Na_3[Fe(CN)_5H_2O],H_2O$; $Na_2[Fe(CN)_5H_2O]$; $Na_2[Fe(CN)_5NO],2H_2O$ (sodium nitroprusside).

These salts all have sodium as the common cation and contain the group $Fe(CN)_5$ although in some the iron is in the bivalent state and in others in the tervalent state. It has been found that the CN bands occur at the following wave-numbers (cm.$^{-1}$) for the first four of these compounds :

$[Fe^{II}(CN)_5NH_3]^{3-}$	2036,	$[Fe^{III}(CN)_5NH_3]^{2-}$	2126
$[Fe^{II}(CN)_5H_2O]^{3-}$	2043,	$[Fe^{III}(CN)_5H_2O]^{2-}$	2120

The bands in the compounds containing Fe^{II} are broad with half band-widths of about 70 cm.$^{-1}$, while those containing Fe^{III} are narrow with half band-widths of approximately 35 cm.$^{-1}$. Moreover, the intensity of the CN band in these Fe^{II} compounds is approximately twice that in the Fe^{III} compounds; a similar relationship was found for the bands in $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$. Thus it appears that the position, shape, and intensity of the CN band in the neighbourhood of 2000 cm.$^{-1}$ are determined by the formal charge on the iron atom and do not depend on the formal charge on the whole anion, since the band appears at the same wave-number in $[Fe^{II}(CN)_5NH_3]^{3-}$ and $[Fe^{II}(CN)_5H_2O]^{3-}$ as in $[Fe^{II}(CN)_6]^{4-}$ and at the same wave-number in $[Fe^{III}(CN)_5NH_3]^{2-}$ and $[Fe^{III}(CN)_5H_2O]^{2-}$ as in $[Fe^{III}(CN)_6]^{3-}$. Alternatively, it may be considered that the CN frequency in $[Fe^{II}(CN)_5X]$ is the same whether X be a neutral group (*e.g.*, NH_3 or H_2O) or a negatively charged ion (*i.e.*, CN^-). A similar relationship exists for the series $[Fe^{III}(CN)_5X]$.

The result for the sodium nitroprusside was unexpected. Formula (I) is the normally accepted structure for the nitroprusside ion (Sidgwick, " Chemical Elements and Their Compounds," Oxford, 1950, p. 1344) although structure (II) is also permissible.

(I) $[(CN)_5Fe:N:::O:]^{2-}$, *i.e.*, $[(CN)_5Fe{-}N{\equiv}O]^{2-}$

(II) $[(CN)_5Fe::N::\ddot{O}]^{2-}$, *i.e.*, $[(CN)_5Fe{=}N{=}O]^{2-}$

Either structure explains the diamagnetism of the compound. It is known experimentally that the presence of a negative CN group or a neutral NH_3 group or a neutral H_2O

group in the complex $[Fe(CN)_5X]$ (where X = CN, NH_3, or H_2O) has in each case the same effect on the position and intensity of the CN band. Therefore it is reasonable to assume that if the structure of nitroprusside corresponded to formula (I) then the CN band in this compound would probably resemble that in the complexes $[Fe(CN)_6]^{4-}$, $[Fe(CN)_5NH_3]^{3-}$, and $[Fe(CN)_5H_2O]^{3-}$. In fact, the spectrum of the nitroprusside exhibits a narrow band at 2152 cm.$^{-1}$ which is even higher than the frequency of the CN band in the compounds $[Fe(CN)_6]^{3-}$, $[Fe(CN)_5NH_3]^{2-}$, and $[Fe(CN)_5H_2O]^{2-}$ but resembles the band in the latter compounds in shape and intensity. The true nitroprusside structure would appear to be intermediate between that of (I) and (II), *i.e.*, it might be called a resonance mixture. Such an admixture of structures (I) and (II) is likely to have the effect of draining electrons from the Fe atom (to make it resemble Fe^{III} or even Fe^{IV} if formal valency has much meaning) and thus accounts for the high CN frequency.

Moreover, this resonance mixture will give rise to a N–O bond which is intermediate between a double and triple bond and therefore such an admixture of structures (I) and (II) would probably account for the strong band observed at 1938 cm.$^{-1}$ in nitroprusside.*

The spectra of all these compounds in the range 2—15 μ are simple and contain but few bands which are listed in the Table.

Frequencies (cm.$^{-1}$) of main absorption bands.

$Na_3[Fe(CN)_5NH_3]$, $6H_2O$	$Na_2[Fe(CN)_5NH_3]$, H_2O	$Na_3[Fe(CN)_5H_2O]$, H_2O	$Na_2[Fe(CN)_5H_2O]$	$Na_2[Fe(CN)_5NO]$, $2H_2O$
3530 sh.	3550 s.	3390 m.	3400 s.	3580 s.
3360 s.	3360 s.	2043 s.	2152 sh.	3440 sh.
3290 sh.	3290 sh.	1617 m.	2120 s.	2152 s.
2036 s.	2126 s.		2060 w.	1938 s.
1685 sh.	2050 w.		1617 m.	1618 s.
1629 m.	1614 s.			663 m.
1266 m.	1410 w.			
714 w.	1252 s.			
	708 m.			

(s = strong; m = medium; w = weak; sh = shoulder.)

The spectra of the compounds containing co-ordinated H_2O show broad OH bands around 3400 and 1617 cm.$^{-1}$ in addition to the CN bands at 2043 or 2120 cm.$^{-1}$. The compounds containing NH_3 show, in addition to OH bands, extra bands at 3360, 3290, and around 1614—1630 assigned to NH vibrations, together with a fairly strong band in the range 1250—1260 cm.$^{-1}$.

Experimental.—The sample of sodium nitroprusside was used as purchased; specimens of the other salts were prepared according to the directions given by Hofmann (*Annalen*, 1900, **312**, 1). Ground samples of the salts were prepared as pressed KCl discs (Hales and Kynaston, *Analyst*, 1954, **79**, 702), and the spectra were recorded on a double-beam spectrometer (Hales, (*J. Sci. Instr.*, 1953, **30**, 52). The uncertainties in the measurement of the wave-number are believed to be approximately ±10 cm.$^{-1}$ at 2000 cm.$^{-1}$.

The work described formed part of the research programme of the Chemical Research Laboratory and this paper is published by permission of the Director.

CHEMICAL RESEARCH LABORATORY,
TEDDINGTON, MIDDLESEX.

[*Received, May 10th*, 1955.]

* We wish to thank a referee of this paper for valuable comments on the structure and spectra of the nitroprusside ion.

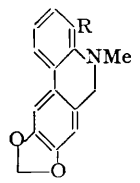
Lycorineanhydromethine.

By T. SHINGU, S. UYEO, and H. YAJIMA.

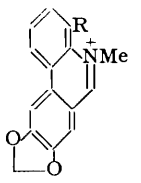
[Reprint Order No. 6433.]

BOTH lycorineanhydromethine (I) and its dihydro-compound (II) gave crystalline hydriodides which were readily hydrolysed in water. Attempted preparation, however, of their methiodides afforded the corresponding phenanthridinium compounds (III) and (IV), which on treatment with a base yielded as expected the dimeric ethers derived from the pseudo-bases. The phenanthridinium compound (IV) was also prepared by the oxidation of dihydrolycorineanhydromethine (II) with a limited amount of potassium permanganate or with cyanogen bromide; further oxidation of this salt with potassium ferricyanide gave the phenanthridone. Dihydrolycorineanhydromethine was regenerated on treatment of the phenanthridone or the phenanthridinium salt with lithium aluminium hydride.

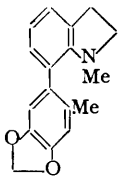
Kondo and Katsura (*Ber.*, 1940, **73**, 1424) claimed to have prepared lycorineanhydromethine methiodide, which they stated had m. p. 226° and on Emde degradation gave lycorineanhydrohydromethine (V). Although we methylated lycorineanhydromethine under conditions similar to those used by the above authors we obtained only the phenanthridinium iodide (III), m. p. 226°, which on Emde degradation did not yield the Emde base (V). We consider it likely that Kondo and Katsura may have made, without recognising it, anhydrolycorine methiodide (VI), m. p. 226° from its corresponding carbonate which we have recently shown (Humber, Kondo, Kotera, Takagi, Takeda, Taylor, Thomas, Tsuda, Tsukamoto, Uyeo, Yajima, and Yanaihara, *J.*, 1954, 4622) accompanies lycorineanhydromethine in the Hofmann degradation of lycorine, and the Emde degradation of the former compound is known (*idem, ibid.*) to give the Emde base (V).



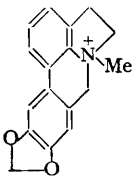
(I; R = $CH{:}CH_2$)
(II; R = Et)



(III; R = $CH{:}CH_2$)
(IV; R = Et)



(V)



(VI)

Experimental.—Ultraviolet spectra were measured for ethanol solutions.

Lycorineanhydromethine hydriodide. The *salt* was prepared by dissolving lycorineanhydromethine in 5% hydriodic acid; it hydrolysed on attempted crystallisation from water but was obtained from ethanol with m. p. 186° (decomp.) (Found: C, 51·9, 52·0; H, 4·2, 4·1. $C_{17}H_{15}O_2N,HI$ requires C, 51·9; H, 4·1%).

Dihydrolycorineanhydromethine hydriodide. This *hydriodide* was obtained similarly and had m. p. 210° (from ethanol) (Found: C, 51·3; H, 4·6. $C_{17}H_{17}O_2N,HI$ requires C, 51·7; H, 4·6%).

10-*Methyl*-6 : 7-*methylenedioxy*-1-*vinylphenanthridinium iodide* (III). Lycorineanhydromethine (0·3 g.) and methyl iodide (1 ml.) were refluxed for 10 hr. in methanol, then evaporated to dryness. Extraction of the residue with a small quantity of hot water gave, after cooling, the *iodide* (0·12 g.), m. p. 226° (decomp.). For analysis it was dried at 105° for 10 hr. *in vacuo*, the m. p. then being 216° (decomp.) (Found: C, 52·5; H, 3·5. $C_{17}H_{14}O_2NI$ requires C, 52·2; H, 3·6%). The ultraviolet absorption spectrum had $\lambda_{max.}$ 262, 272, 280, and 348 mμ (log ε 4·46, 4·49, 4·51, and 4·10 respectively). The water-insoluble residue from the above extraction yielded unchanged starting material (0·17 g.) from light petroleum.

The iodide (50 mg.) was shaken with lithium aluminium hydride (50 mg.) in absolute ether for 20 min., to afford lycorineanhydromethine (30 mg.), m. p. and mixed m. p. 94—96°. The iodide (III) was dissolved in hot water, aqueous alkali added, and the precipitate taken up in chloroform. Concentration, and recrystallisation of the crystals from ethyl methyl ketone gave the *pseudo-base ether*, m. p. 196° (decomp.) (Found: C, 74·6; H, 5·4. $C_{34}H_{28}O_5N_2$ requires

C, 74·9; H, 5·2%). The product was only slightly soluble in ether, methanol, or ethanol and was converted back into the iodide by hydriodic acid.

1-*Ethyl*-10-*methyl*-6 : 7-*methylenedioxyphenanthridinium iodide* (IV). Dihydrolycorineanhydromethine (0·3 g.) and methyl iodide (2 ml.) in ethanol (6 ml.) were heated in a sealed tube at 100° for 5 hr., then concentrated to dryness. The aqueous extract gave, after chilling and recrystallisation of the product from ethanol, the *iodide* (0·22 g.), m. p. 214°, raised to 236° after drying *in vacuo* at 105° (Found : C, 52·3; H, 4·4. $C_{17}H_{16}O_2NI$ requires C, 52·0; H, 4·1%). The ultraviolet spectrum had $\lambda_{max.}$ 260, 270, 280, and 347 mμ (log ε 4·41, 4·47, 4·48, and 4·01 respectively).

Refluxing dihydrolycorineanhydromethine (0·5 g.) with cyanogen bromide (1·5 g.) in benzene for 6 hr. gave the corresponding *phenanthridinium bromide*, m. p. 228° (decomp.) (from water), which when dried at 100° *in vacuo* or left in the air for a week had m. p. 217° (decomp.) (Found, on a dried sample : C, 57·4, 57·6, 57·4; H, 4·8, 4·9, 4·9; N, 4·0; Br, 22·9. $C_{17}H_{16}O_2NBr,0·5H_2O$ requires C, 57·5; H, 4·7; N, 3·9; Br, 22·5%). This bromide was indistinguishable from that obtained by treatment of the iodide (IV) with silver bromide. Reduction of the bromide with lithium aluminium hydride regenerated dihydrolycorineanhydromethine, m. p. and mixed m. p. 84—86°. Basification of an aqueous solution of the bromide gave the corresponding *pseudo-base ether*, m. p. 213° (decomp.) (from benzene), which after drying had m. p. 218° (decomp.) (Found, on a dried sample : C, 74·4, 74·4; H, 5·8, 5·7; N, 5·6, 5·5. $C_{34}H_{32}O_5N_2$ requires C, 74·4; H, 5·9; N, 5·1%). This compound was only slightly soluble in ether, ethanol, methanol, acetone, or ethyl acetate, but was soluble in chloroform.

0·1% Potassium permanganate solution (11 ml.) was added dropwise to dihydrolycorineanhydromethine (0·2 g.) in acetone (8 ml.), then after 1 hr. the whole was filtered, the filtrate evaporated to dryness, and the residue taken up into chloroform. A hydrochloric acid extract from the chloroform solution, on basification, gave a precipitate, from which ether removed starting material (70 mg.); then crystallisation from benzene yielded the pseudo-base ether (90 mg.), m. p. and mixed m. p. 213° (Found : C, 74·5; H, 5·6; N, 5·3%).

1-*Ethyl*-10-*methyl*-6 : 7-*methylenedioxyphenanthridone*. 1-Ethyl-10-methyl-6 : 7-methylenedioxyphenanthridinium bromide (85 mg.), potassium hydroxide (70 mg.), and potassium ferricyanide (500 mg.) were heated under reflux for 5 hr. in 50% aqueous ethanol (10 ml.). A chloroform extract of the cooled mixture was washed with hydrochloric acid, then water, and concentrated, to yield the *phenanthridone* (53 mg.), m. p. 106° or 114° (from ether) according to the rate of crystallisation (Found : C, 72·5, 72·9; H, 5·5, 5·5; N, 5·2. $C_{17}H_{15}O_3N$ requires C, 72·6; H, 5·4; N, 5·0%). The ultraviolet absorption spectrum had $\lambda_{max.}$ 241, 251, 274, 305, and 340 mμ (log ε 4·58, 4·60, 4·17, 4·03, and 3·65 respectively). Reduction of the phenanthridone with lithium aluminium hydride afforded dihydrolycorine anhydromethine, m. p. and mixed m. p. 85—86°.

The authors thank Dr. W. I. Taylor, University of New Brunswick, Canada, for help in preparing the manuscript.

School of Pharmacy, University of Osaka, Japan. [*Received, May 16th*, 1955.]

Protection of the Ethynyl Group during Reduction.

By N. A. Dobson and R. A. Raphael.

[Reprint Order No. 6442.]

All the geometrical isomers of undeca-1 : 7-diene-1-carboxylic acid are now known The 1(*cis*) : 7(*cis*)- and the 1(*trans*) : 7(*cis*)-isomer were prepared from the readily available undeca-1 : 7-diyne (Raphael and Sondheimer, *J.*, 1950, 115; 1951, 2693) while the starting materials for the 1(*trans*) : 7(*trans*)- and the 1(*cis*) : 7(*trans*)-isomers were *trans*-1-bromonon-5-ene and *trans*-undec-7-en-1-yne, the preparation of the latter necessitating eight stages from dihydropyran (Crombie, *J.*, 1952, 2997). A procedure is now described for the direct stereospecific conversion of undeca-1 : 7-diyne into *trans*-undec-7-en-1-yne, the 1-ethynyl group of the diyne being protected as the sodium salt by reaction with sodamide in liquid ammonia; reduction of the sodium salt with sodium then reduced only the bilaterally

substituted triple bond with the formation, after hydrolysis, of the *trans*-enyne. At first, preformed sodamide was used but it was later found that sodamide prepared *in situ* from sodium by the usual catalytic procedure was more convenient and gave higher yields. Although the catalyst remained present during the ensuing sodium reduction, it seems that, of the two competing processes, *viz.*, the catalytic conversion of sodium into sodamide and the reduction of a triple bond by sodium, the latter is the more rapid.

A simple, though possibly naïve, explanation of the protective influence of sodium salt formation on an ethynyl group is the consequent development of a negative charge on the terminal carbon atom, a barrier thus being formed against attack by the nucleophilic sodium. The structure of the *trans*-enyne was confirmed by its infrared spectrum and its hydration and hydrogenation to methyl nonyl ketone. The *trans*-enyne was converted into the 1(*trans*) : 7(*trans*)- and the 1(*cis*) : 7(*trans*)-isomer of undecadienecarboxylic acid by the techniques already developed (Raphael and Sondheimer, *loc. cit.*). Thus all four geometrical isomers of the acid can now be made from undeca-1 : 7-diyne.

Experimental.—trans-*Undec-7-en-1-yne.* To a stirred suspension of sodamide (made from sodium, 5·3 g., by the use of ferric nitrate catalyst) in liquid ammonia (450 c.c.) cooled to −40° was added during 30 min. a solution of undeca-1 : 7-diyne (22·2 g.) in ether (23 c.c.), and stirring was continued for a further hour. Sodium (10·5 g.; 50% excess) was then introduced in small pieces during 45 min. Stirring was continued for a further hour and ammonium chloride (9 g.) added. The ammonia was allowed to evaporate overnight through a water-cooled condenser, water and ether were added to the residue, and working up was in the usual fashion. Drying ($MgSO_4$), evaporation, and distillation gave *trans*-undec-7-en-1-yne (17 g., 75%), b. p. 77—78°/19 mm., n_D^{18} 1·4480 (Crombie, *loc. cit.*, gives 82—84°/18 mm., n_D^{20} 1·4462) [Found : C, 87·85; H, 11·9; ·C:CH, 16·0; microhydrogenation (Pd–AcOH) : 3·0 H_2. Calc. for $C_{11}H_{18}$: C, 87·9; H, 12·1; ·C:CH, 16·6%]. The infrared spectrum showed the expected maxima at 970 (C–H deformation associated with *trans*-CH:CH–) and 3300 cm.$^{-1}$ (≡C–H stretching). The *mercury salt* made according to Elsner and Paul's directions (*J.*, 1951, 893) was difficult to purify owing to its extreme solubility in all organic solvents. It was finally obtained as a microcrystalline solid, m. p. 34°, by setting aside a concentrated solution in ethyl acetate (Found : Hg, 41·3. $C_{22}H_{34}Hg$ requires Hg, 40·2%). The *mercury salt* of undeca-1 : 7-diyne crystallised from *n*-propanol in needles, m. p. 38·5° (Found : Hg, 40·5. $C_{22}H_{30}Hg$ requires Hg, 40·5%). A mixture of these two salts liquefied at room temperature.

trans-*Undec-7-en-2-one.* A solution of *trans*-undec-7-en-1-yne (4·4 g.) in ethanol (20 c.c.) was added to a warm mixture of mercuric oxide (1 g.), boron trifluoride–ether complex (0·5 c.c.), trichloroacetic acid (10 mg.), and ethanol (2 c.c.). After 20 hours' shaking at room temperature the mixture was poured into 2N-sulphuric acid, and the product isolated with ether. Drying, evaporation, and distillation gave trans-*undec-7-en-2-one* (3·2 g.), b. p. 100—102°/10 mm., n_D^{16} 1·4491 (Found : C, 78·6; H, 12·0. $C_{11}H_{20}O$ requires C, 78·5; H, 12·0%). The *semicarbazone* crystallised from ethanol in plates, m. p. 99·5—100° (Found : N, 18·9. $C_{12}H_{23}ON_3$ requires N, 18·7%). Catalytic hydrogenation (10% palladium–charcoal in methanol) of the ketone resulted in the uptake of 1 mol. of hydrogen to give methyl nonyl ketone [semicarbazone needles, m. p. 122—123°, from ethanol (Schmalfuss and Treu, *Biochem. Z.*, 1927, **189**, 49, give m. p. 122°)].

Undeca-1(cis) : 7(trans)-*diene*-1-*carboxylic acid.* Treatment of the Grignard derivative of *trans*-undec-7-en-1-yne with carbon dioxide and partial catalytic hydrogenation of the resulting *trans*-undec-7-en-1-yne-1-carboxylic acid according to Crombie's directions (*loc. cit.*) gave undeca-1-(*trans*) : 7(*trans*)-diene-1-carboxylic acid. The physical constants of the two acids and their *S*-benzylthiuronium salts tallied closely with the values reported by Crombie (*loc. cit.*).

trans-1 : 1-*Diethoxydodec*-8-*en*-2-*yne.* To a solution of ethylmagnesium bromide [from magnesium (3 g.), ethyl bromide (20 g.), and ether (200 c.c.)] was added one of *trans*-undec-7-en-1-yne (17 g.) in ether (20 c.c.), and the mixture refluxed for 45 min. Ethyl orthoformate (18 g.) in ether (20 c.c.) was run in rapidly, and refluxing continued for a further 6 hr. To the cooled mixture was added ice-cold aqueous acetic acid (50%), and the ethereal layer was washed with sodium hydrogen carbonate solution and water. Drying (Na_2SO_4), evaporation, and distillation gave the *enyne acetal* (19·5 g., 75%), b. p. 112—114°/0·05 mm., n_D^{20} 1·4552 (Found : C, 75·8; H, 11·1. $C_{16}H_{28}O_2$ requires C, 76·15 ; H, 11·2%).

1 : 1-*Diethoxydodeca*-2(cis) : 8(trans)-*diene.* A solution of the above acetal (10·1 g.) in ethyl acetate (100 c.c.) was stirred under hydrogen with 10% palladium–charcoal (1 g.) until 1 mol. of hydrogen had been absorbed (975 c.c. at 21°/752 mm.). Removal of catalyst and solvent

gave the *diene acetal*, b. p. 94—98°/0·1 mm., n_D^{18} 1·4496 (Found : C, 75·5; H, 11·8. $C_{16}H_{30}O_2$ requires C, 75·5; H, 11·9%).

Undeca-1(trans) : 7(trans)-*diene*-1-*carboxylic acid*. A suspension of the preceding diene acetal (5 g.) in water (50 c.c.) and oxalic acid (5 g.) was distilled in steam until no more oil appeared in the condensate. Isolation by means of ether gave *dodeca*-2(trans) : 8(trans)-*dienal*, which, purified by distillation, had b. p. 78—80°/0·04 mm., n_D^{17} 1·4709 (Found : C, 79·3; H, 11·2. $C_{12}H_{20}O$ requires C, 79·9; H, 11·2%). The *semicarbazone* crystallised from ethanol in plates, m. p. 151° (Found : N, 17·6. $C_{13}H_{23}ON_3$ requires N, 17·7%).

The crude aldehyde (2·2 g.) in ethanol (45 c.c.) was mixed with silver nitrate (2 g.) in water (4 c.c.), and N-sodium hydroxide (19 c.c.) was added slowly. After 18 hr. the solid was filtered off and washed with water. Ethanol was removed from the combined filtrates under reduced pressure and the resulting aqueous solution washed with ether. Acidification of the solution with 2N-sulphuric acid and isolation by means of ether gave undeca-1(*trans*) : 7(*trans*)-diene-1-carboxylic acid, b. p. 128—130°/0·1 mm., n_D^{20} 1·4731, crystallising from light petroleum (b. p. 40—60°) in plates, m. p. 35° (Found : C, 73·3; H, 10·3. Calc. for $C_{12}H_{20}O_2$: C, 73·45; H, 10·3%). The *S*-benzylthiuronium salt crystallised from ethyl acetate in plates, m. p. 158—159°. All these properties tally closely with those obtained by Crombie (*loc. cit.*) for the acid prepared by a different route.

We thank the Colonial Products Council (N. A. D.) and the Chemical Society for research grants.

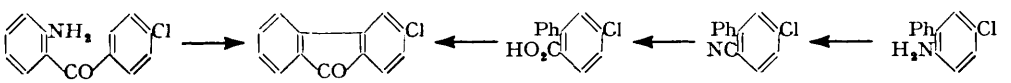
THE QUEEN'S UNIVERSITY, BELFAST. [*Received, May 18th*, 1955.]

The Chlorination of 2-Acetamidofluorene.

By F. BELL and J. A. GIBSON.

[Reprint Order No. 6444.]

ALTHOUGH 2-acetamidofluorene is known to undergo nitration at position 3, the position taken by other entering groups has been assigned only by analogy. In view of the structure of fluorene (Burns and Iball, *Nature*, 1954, **173**, 635) the possibility of substitution in position 1 cannot be excluded. It is now shown that chlorination of 2-acetamidofluorene occurs mainly, or even exclusively, in position 3. The chloro-derivative was oxidised to the chloro-2-acetamidofluorenone, which was hydrolysed and de-aminated to 3-chlorofluorenone. 3-Chlorofluorenone (I) was prepared (*a*) from 2-amino-4′-chlorobenzophenone (II) and (*b*) from 5-chloro-2-aminodiphenyl (III). The product agreed with that obtained



(II) (I) (III)

by Heilbron, Hey, and Wilkinson (*J.*, 1938, 113) by a Gomberg synthesis. 1-Chlorofluorenone was prepared for comparison from 1-aminofluorenone, obtained in turn from fluorenone-1-carboxylic acid by the Curtius reaction.

Experimental.—1-*Aminofluorenone*. Fluorenone-1-carboxylic acid (7 g.; prepared from fluoranthene by Fieser's method, *J. Amer. Chem. Soc.*, 1935, **57**, 2174) was converted by thionyl chloride into the acid chloride and this was dissolved in benzene (50 c.c.). Sodium azide (5 g.) was added and the mixture boiled for 8 hr. Sodium hydroxide solution (25 c.c.; 3N) was then added and heating continued for another 2 hr. After evaporation of benzene, the base was extracted with hydrochloric acid, and the extract precipitated with ammonia solution, giving the base (1·1 g.; m. p. 109°) (Goldschmiedt, *Monatsh.*, 1902, **23**, 886, gives m. p. 110° for the base prepared by the Hofmann reaction).

1-*Chlorofluorenone*. 1-Aminofluorenone (1·1 g.) was diazotised in hydrochloric acid, the diazonium solution introduced into cuprous chloride solution, and the mixture distilled in steam.

The resultant **1-*chlorofluorenone*** crystallised from ethanol in yellow, prismatic needles (0·7 g.), m. p. 140° (Found : C, 72·9; H, 3·4. $C_{13}H_7OCl$ requires C, 72·7; H, 3·3%).

2-*Amino*-4'-*chlorobenzophenone*. 2-Toluene-*p*-sulphonamidobenzoic acid (13·6 g.), chlorobenzene (140 c.c.), and phosphorus pentachloride (11 g.) were stirred at 50° for ½ hr. The solution was cooled to 25° and aluminium chloride (27 g.) added; the temperature was then gradually raised to 110° and maintained thereat for 6 hr. After cooling, the mixture was poured on ice, and the chlorobenzene removed in steam. The residue was washed first with dilute hydrochloric acid and then with sodium carbonate solution. The yellowish-brown residue was warmed on a steam-bath for 3 hr. with sulphuric acid (100 c.c.) and then poured on ice and neutralised with ammonia solution. After being kept overnight the product was filtered off and recrystallised from aqueous ethanol. **2-*Amino*-4'-*chlorobenzophenone*** was obtained in bright yellow needles, m. p. 102° (Found : C, 67·4; H, 4·4. $C_{13}H_{10}ONCl$ requires C, 67·4; H, 4·3%).

3-*Chlorofluorenone*. The method was based on that employed by Miller and Bachmann (*J. Amer. Chem. Soc.*, 1935, **57**, 2443) for 3-bromofluorenone. A solution of the diazonium sulphate of 2-amino-4'-chlorobenzophenone was allowed to warm to room temperature and was finally heated on a steam-bath for 20 min. The orange-yellow precipitate was crystallised from ethanol giving 3-chlorofluorenone as yellow platelets, m. p. **159°** (Heilbron, Hey, and Wilkinson, *loc. cit.*, give 157°).

2-*Acetamido*-5-*chlorodiphenyl*. Chlorine (1 mol.) was passed into 2-acetamidodiphenyl (13 g.) in chloroform (100 c.c.), the filtered solution was evaporated, and the residue was crystallised from chloroform–light petroleum and then from aqueous ethanol giving material (11·7 g.), m. p. 120—121° (Scarborough and Waters, *J.*, 1927, **93**, give 123° as the m. p. of pure 2-acetamido-5-chlorodiphenyl).

2-*Amino*-5-*chlorodiphenyl*. The acetyl derivative (11·5 g.), ethanol (130 c.c.), and concentrated hydrochloric acid (15 c.c.) were boiled for 3 hr. The concentrated solution deposited the hydrochloride, which was filtered off and decomposed with ammonia solution. The resulting oil soon solidified and the solid was recrystallised from methanol. **2-*Amino*-5-*chlorodiphenyl*** formed fawn needles (7·2 g.), m. p. 51° (Found : C, 70·8; H, 4·7. $C_{12}H_{10}NCl$ requires C, 70·8; H, 4·9%).

5-*Chloro*-2-*cyanodiphenyl*. 2-Amino-5-chlorodiphenyl (7 g.) in hydrochloric acid (20 c.c.) and water (20 c.c.) was diazotised, and excess of nitrous acid removed by urea. The cold filtered solution was introduced beneath the surface of a solution containing copper sulphate (13 g.), potassium cyanide (13 g.), and sodium carbonate (10 g.) in water at 25°. The brown, granular precipitate was extracted with ethanol, and the extract precipitated by water. The product, after several recrystallisations from ethanol, formed dark red prisms (3·8 g.), m. p. 100° (Found : C, 73·4; H, 3·9. $C_{13}H_8NCl$ requires C, 73·1; H, 3·7%).

5-*Chlorodiphenyl*-2-*carboxylic acid*. The ***nitrile*** (3·5 g.) in 10% potassium hydroxide–glycol (40 c.c.) was gently boiled for 7 hr. The cooled solution was filtered, diluted with water, and acidified. The product was reprecipitated from ammonia solution and finally recrystallised from aqueous ethanol. 5-Chlorodiphenyl-2-carboxylic acid formed needles (2 g.), m. p. 152° (Found : C, 67·0; H, 3·7. Calc. for $C_{13}H_9O_2Cl$: C, 67·1; H, 3·9%). Cyclisation by sulphuric acid gave 3-chlorofluorenone, m. p. 159° (cf. Heilbron, Hey, and Wilkinson, *loc. cit.*).

Chlorination of* 2-*acetamidofluorene*.** Chlorine (1 mol.), considerably diluted by carbon dioxide, was passed into the amide (5 g.) dissolved in cold chloroform (150 c.c.). The precipitate was essentially unchanged material (1·5 g.) but on concentration of the solution material was obtained which, after recrystallisation from acetic acid, gave slightly impure **2-*acetamido*-3-*chlorofluorene as fine needles (2·5 g.), m. p. 204° (Found : C, 68·7; H, 4·1. $C_{15}H_{12}ONCl$ requires C, 69·9; H, 4·7%). No further purification was brought about by repeated recrystallisation or use of adsorbents, and the small amount of dichloro-derivative persisted in the following experiments. Hydrolysis by boiling with ethanol–hydrochloric acid gave **2-*amino*-3-*chlorofluorene***, needles (from aqueous ethanol), m. p. 131° (Found : C, 71·5; H, 4·3. $C_{13}H_{10}NCl$ requires C, 72·4; H, 4·7%). This base was readily deaminated by the ethanol–sulphuric acid–sodium nitrite method to **3-*chlorofluorene***, which, after distillation in steam and crystallisation from methanol, formed glistening plates, m. p. 95° (Found : Cl, 18·2. $C_{13}H_9Cl$ requires Cl, 17·7%). Sodium dichromate (5 g.) in the minimum of water was added to 2-acetamido-3-chlorofluorene (1 g.) in acetic acid (10 c.c.), and the mixture boiled for 2 hr. The filtered solution on cooling deposited **2-*acetamido*-3-*chlorofluorenone***, golden-yellow needles (from acetic acid) (0·5 g.), m. p. 260° (Found : C, 66·1; H, 3·8. $C_{15}H_{10}O_2NCl$ requires C, 66·3; H, 3·7%).

2-*Amino*-3-*chlorofluorenone*. A mixture of 2-acetamido-3-chlorofluorenone (1 g.), ethanol

(25 c.c.), amd hydrochloric acid (5 c.c.) was boiled for 2½ hr. and then filtered from the yellow hydrochlorides, which separated on cooling. The bases, liberated by ammonia solution, were dissolved in boiling ethanol. On cooling, purple needles (0·2 g.), m. p. 238—239°, separated; this is probably an impure dichloro-derivative (Found : C, 59·7; H, 2·6. Calc. for $C_{13}H_8ONCl_2$: C, 58·8; H, 3·0%). The filtrate gave red needles (0·3 g.) of *2-amino-3-chlorofluorenone*, m. p. 189° (from ethanol) (Found : C, 68·1; H, 3·6. $C_{13}H_9ONCl$ requires C, 67·7; H, 3·9%). This base was deaminated by the sodium nitrite–ethanol procedure, and the product distilled in steam. The product (m. p. 148—150°) was repeatedly recrystallised from acetic acid, giving 3-chlorofluorenone, m. p. 157—158° (m. p. 158° when mixed with the synthetic sample).

Chlorination of 2-acetamidofluorenone. Chlorine (1 mol.) was passed into 2-acetamidofluorenone (Diels, *Ber.*, 1901, **34**, 1758) in warm acetic acid, and the mixture allowed to cool. The product was 2-acetamido-3-chlorofluorenone (see above).

The authors are indebted to the Carnegie Trust for the Universities of Scotland for a grant.

HERIOT-WATT COLLEGE, EDINBURGH. [*Received, May 18th*, 1955.]

Reaction of Potassium Bromide–Bromate Solution with Some Sulphur Compounds.

By F. W. SHIPLEY.

[Reprint Order No. 6496.]

ESTIMATION of unsaturation by bromination with potassium bromide–bromate in acid solution has been shown to give reasonably accurate results for many simple alkenes (Francis, *Ind. Eng. Chem.*, 1926, **18**, 821; Mulliken and Wakeman, *Ind. Eng. Chem. Anal.*, 1935, **7**, 59). When, however, the method is applied to certain *cyclo*alkenes and alkadienes (*idem, loc. cit.*; Cortese, *Rec. Trav. chim.*, 1929, **48**, 564) inaccuracies arise which are not substantially reduced by modification of the procedure. Lewis and Bradstreet (*Ind. Eng. Chem. Anal.*, 1940, **12**, 387) report serious inaccuracies introduced by the presence of sulphur compounds.

Application of the method in these laboratories to αβ-unsaturated sulphides, sulphoxides, and related compounds has in many cases led to an unexpectedly high bromine uptake, part of which is associated with scission of the allylic carbon–sulphur bond.

From the compounds studied, the following generalisations appear to hold. (1) Unconjugated carbon–carbon double bonds take up the expected two atoms of bromine. (2) The sulphur atom (in saturated and unsaturated compounds) takes up two atoms (followed by hydrolysis to the sulphoxide; oxidation to the sulphone is negligible). (3) Carbon–sulphur scission does not take place in saturatedc ompounds or in those sulphides in which the allylic carbon atom adjacent to the sulphur atom is primary, but usually occurs when this carbon atom is substituted. (4) Carbon–sulphur scission itself accounts for the uptake of four bromine atoms involving the oxidation of the sulphur-containing moiety to the sulphonic acid, a process analogous to the brominative cleavage of the sulphur–sulphur bond in disulphides reported by Siggia and Edsburg (*Analyt. Chem.*, 1948, **20**, 938). In compounds containing two allylic substituents attached to the sulphur atom, no more than one carbon–sulphur bond is broken. (5) Simple saturated ketones appear to be unattacked. The keto-sulphides examined therefore take up two atoms only (*i.e.* to give sulphoxides).

Exceptions to (3) are methyl 1-methylprop-2-enyl sulphide, where no scission occurs, and 1-dimethylbut-2-enyl phenyl sulphide, where only partial scission appears to take place.

Representative examples are listed in the experimental section. The bromine values quoted are the result of fairly rapid absorption but in certain examples, indicated with an asterisk, further very slow absorption takes place, probably owing to continued scission or substitution.

The absorption of eight atoms of bromine by an alkyl (R') or aryl (R')-alkenyl (R) sulphide can be expressed as follows :

$$R(OH)_2Br \xleftarrow{3Br,2H_2O} R\text{-}\overset{|}{\underset{|}{C}}\text{-}S\text{-}R' \xrightarrow{3Br,2H_2O} R'\cdot SO_2H \xrightarrow{2Br,H_2O} R'\cdot SO_3H$$

The unsaturated thio-ester (18) would be expected to follow a similar scheme giving methanesulphonic acid and a substituted *cyclo*pentanecarboxylic acid.

From the bromination of *cyclo*hex-2-enyl phenyl sulphide on a somewhat larger scale, the expected benzenesulphonic acid was identified. From the reaction with ethyl *cyclo*hex-2-enyl sulphide ethanesulphonic acid has not been isolated, but from the non-sulphur fragment, a bromodihydroxy*cyclo*hexane was obtained. That the bromodihydroxy-compound should be produced instead of the expected tribromo-compound strongly suggests the intermediacy of hypobromous acid.

Experimental.—Bromination procedure. The compound to be brominated (0·005—0·01 mole) was dissolved in glacial acetic acid (40 ml.). Water (6 ml.) and concentrated hydrochloric acid (3 ml.) were added and the solution was titrated at room temperature with potassium bromide–bromate solution (0·1N) until a permanent faint yellow coloration was obtained. As a rule, bromine uptake was fairly rapid up to within approximately half an atom of the value shown. The last half atom was usually absorbed rather more slowly, *i.e.*, in a few seconds. Beyond this there was either no uptake or a limited and extremely slow absorption.

	Br absorbed, atoms/mole		Br absorbed, atoms/mole
1. *cyclo*Hexyl methyl sulphide	2	11. *cyclo*Hex-2-enyl methyl sulphide	8
2. *cyclo*Hexyl methyl sulphoxide	0	12. Ethyl *cyclo*hex-2-enyl sulphide	8
3. *cyclo*Hexanone	0 *	13. Di*cyclo*hex-2-enyl sulphide	10
4. 2-Methylthio*cyclo*hexanone	2	14. Di*cyclo*hex-2-enyl ether	4
5. 3-Methylthio*cyclo*hexanone	2	15. *n*-Butyl 1-methylbut-2-enyl sulphide	8
6. *n*-Butyl 2-methylprop-2-enyl sulphide	4 *	16. *cyclo*Hex-2-enyl phenyl sulphide	8
7. *n*-Butyl crotyl sulphide	4	17. *cyclo*Hex-2-enyl methyl sulphoxide	6
8. Diallyl sulphide	6 †	18. Methyl *cyclo*pentene-1-carbothiolate	7·5—8·0
9. Allyl phenyl sulphoxide	2 *	19. *cyclo*Pentene-1-carboxylic acid	2
10. Methyl 1-methylprop-2-enyl sulphoxide	2 *		

† 2 rapidly, 4 in few minutes.

Bromination of cyclo*hex-2-enyl phenyl sulphide.* To the sulphide (0·22 g.) in glacial acetic acid (75 ml.), water (12 ml.), and concentrated hydrochloric acid (6 ml.), there was added, with shaking, the equivalent of eight atoms of bromine as bromide–bromate solution (0·1N). The solution was carefully evaporated to dryness at as little above room temperature as possible and the residue dissolved in hydrochloric acid (4 ml.; 0·5N). After this had been boiled with a solution of *S*-benzylthiuronium chloride (0·2 g.), crystals of *S*-benzylthiuronium benzenesulphonate appeared; these formed plates (from hydrochloric acid), m. p. 148° (literature value 148°) (Found : C, 51·5; H, 5·0; S, 19·7; N, 8·6. Calc. for $C_{14}H_{16}O_3S_2N_2$: C, 51·8; H, 5·0; S, 19·8; N, 8·6%).

The corresponding salt of ethanesulphonic acid could not be isolated (possibly owing to the very high solubility of the latter) from a similar oxidation of ethyl *cyclo*hex-2-enyl sulphide. Part of the oxidation mixture was neutralised (NaOH) and evaporated to dryness, and the residue extracted with chloroform. Removal of the chloroform and distillation [at $100°/10^{-2}$ mm. (bath temp.)] of the residue gave a few drops of somewhat impure bromodihydroxy*cyclo*hexane (Found : C, 37·7; H, 5·7; Br, 40·7. Calc. for $C_6H_{11}O_2Br$: C, 36·9; H, 5·6; Br, 41·0%).

Thanks are expressed to Dr. L. Bateman for valuable advice and to Dr. J. I. Cunneen for helpful criticism and for supplying samples of some of the sulphides. The work forms part of the programme of research of the British Rubber Producers' Research Association.

THE BRITISH RUBBER PRODUCERS' RESEARCH ASSOCIATION,
48, TEWIN RD., WELWYN GARDEN CITY.

[*Received, June 10th*, 1955.]

Esters Containing Phosphorus. Part XIII. Dialkyl Phosphorobromidates.*

By H. GOLDWHITE and B. C. SAUNDERS.

[Reprint Order No. 6507.]

DIALKYL PHOSPHOROBROMIDATES, $(RO)_2P(:O)\cdot Br$, have been prepared by the action of bromine on trialkyl phosphites (Gerrard and Jeacock, *J.*, 1954, **3647**). We have recently found that the reaction between *N*-bromosuccinimide and dialkyl hydrogen phosphites, $(RO)_2P\cdot OH$, proceeds very smoothly, and gives pure phosphorobromidates in good yield (cf. the use of *N*-chlorosuccinimide in the preparation of phosphorochloridates, Kenner, Todd, and Weymouth, *J.*, 1952, 3675). The lower members of the series are liquids which can be distilled under reduced pressure. They are readily hydrolysed, and react instantly with aniline to yield the corresponding *N*-phenylphosphoroamidates, $(RO)_2P(:O)\cdot NHPh$. They also undergo ready thermal decomposition; for example, after 20 min. at 100°, or 72 hr. at 17°, diethyl phosphorobromidate gives a quantitative yield of ethyl bromide, together with a polymeric, bromine-free, residue. The compound can, however, be stored for long periods without change at −40°.

Experimental.—General procedure. To a solution of the dialkyl hydrogen phosphite (0·05 mol.) in dry carbon tetrachloride (20 ml.), *N*-bromosuccinimide (8·9 g., 0·05 mol.) was added in portions (0·5 g.) with shaking and cooling. The solution was cooled to 0° and the succinimide filtered off. Carbon tetrachloride was removed by drawing dry air under reduced pressure through the filtrate at, or a little below, room temperature. The residue was distilled under reduced pressure, with a dry air leak, to yield the pure phosphorobromidate.

Phosphorobromidates, $(RO)_2P(:O)\cdot Br$

			Analysis						
			Found (%)			Reqd. (%)			M. p. and mixed m. p. of *N*-phenylphosphoroamidate *
R	Yield	B. p.°/mm.	C	H	Br	C	H	Br	
Me	67	45—47/0·8	13·05	3·2	42·7	12·7	3·2	42·3	88—89° [1]
Et	65	75/1·5	22·0	4·4	37·4	22·1	4·6	36·9	95—96 [2]
Pr^n	45	88—90/0·4	29·3	5·8	32·5	29·4	5·7	32·6	54—55 [3]
Pr^i	65	77—78/0·4	29·9	5·7	32·5	29·4	5·7	32·6	120·5—121 [2]

* Authentic samples were prepared by method of: [1] McCombie, Saunders, and Stacey, *J.*, 1945, 921; [2] *Idem*, *J.*, 1945, 380; [3] Ramaswami and Kirch, *J. Amer. Chem. Soc.*, 1953, **75**, 1763.

One of us (H. G.) is indebted to the Department of Scientific and Industrial Research for a maintenance allowance.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, June 13th*, 1955.]

* Part XII, *J.*, 1955, 2040.