NOTES.

The Synthesis of 1 : 3-*Dihydroxyphenazine.* By G. R. CLEMO and A. F. DAGLISH.

HEGEDÜS (*Chem. Abs.*, 1947, **41**, 6252) has prepared 1 : 2-dihydroxyphenazine whose diacetoxy-derivative is different from that obtained from the pigment of *Chromobacterium iodinum* (Clemo and McIlwain, *J.*, 1938, 479).

In the course of synthetic work in this field, which will be fully reported later, we have prepared 1 : 3-dihydroxyphenazine by the hydrolysis of 1 : 3-diaminophenazine (Albert and Duewell, *J. Soc. Chem. Ind.*, 1947, **66**, 11). Although this melts at 275°, its m. p. is depressed to 250° by the dihydroxyphenazine from the pigment and its alcoholic solution gives a brown coloration with ferric chloride and no lake with alcoholic lead acetate.

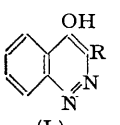
1 : 3-*Dihydroxyphenazine.*—1 : 3-Diaminophenazine (1·0 g.) and dilute sulphuric acid (60 ml.; 3N) were heated in a sealed tube at 180° for 4 hours, the product diluted with an equal volume of water, and neutralised with sodium hydrogen carbonate. The crystalline precipitate was collected, extracted with aqueous sodium hydroxide, the resulting blue solution treated with sulphur dioxide, and the brown precipitate collected, dried, and sublimed at 170°/0·1 mm. The sublimate was recrystallised from alcohol, yielding the *dihydroxy*-compound in orange-red needles (0·2 g.), m. p. 275° (Found: C, 67·6; H, 4·1; N, 13·4. $C_{12}H_8O_2N_2$ requires C, 67·9; H, 3·8; N, 13·2%).

1 : 3-*Diacetoxyphenazine.*—1 : 3-Dihydroxyphenazine (15 mg.) was refluxed for 1 hour in pyridine (1·5 ml.) and acetic anhydride (6 drops), the solvent removed under reduced pressure, and the residue crystallised from alcohol; white needles of the *diacetoxy*-derivative separated, m. p. 163° (Found: C, 65·2; H, 4·6. $C_{16}H_{12}O_4N_2$ requires C, 64·9; H, 4·1%).

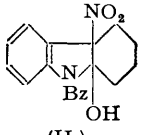
One of us (A. F. D.) is indebted to the Ministry of Education and Durham County Education Committee for maintenance grants, and our thanks are due to Mr. W. A. Campbell for making the micro-analyses.—KING'S COLLEGE, UNIVERSITY OF DURHAM, NEWCASTLE-UPON-TYNE. [*Received, January 19th*, 1948.]

Cinnolines. Part XX. 4-*Hydroxy*-3-*ethylcinnoline and* 3-4′-*Hydroxy*-3′-*cinnolyl*-n-*propane*-1-*carboxylic Acid.* By J. R. KENEFORD and J. C. E. SIMPSON.

THE synthesis of 3-substituted 4-hydroxycinnolines (as I; R = CH_2CO_2H, Me, and halogen) from the appropriate *o*-aminoacetophenones, *o*-NH_2·C_6H_4·CO·CH_2R, has already been described (Schofield and



(I.)



(II.)

Simpson, *J.*, 1945, 520; this vol., p. 1170; Keneford and Simpson, *ibid.*, p. 354). The preparation of the two compounds named in the title by the same reaction was undertaken in order to examine the scope of this method for the synthesis of analogues containing higher alkyl groups attached to C_3. *o*-Aminobutyrophenone, required for (I; R = Et), and originally prepared from butyryl chloride by Elson, Gibson, and Johnson (*J.*, 1930, 1128) in 8·6% yield, was obtained from butyric anhydride in 28% yield by suitable modifications; and 5-keto-5-2′-aminophenyl-*n*-pentane-1-carboxylic acid (δ-*o*-aminobenzoylvaleric acid), the precursor of [I; R = $[CH_2]_3$·CO_2H], is obtainable, *via* the *N*-benzoyl derivative, from (II) (Perkin and Plant, *J.*, 1923, **676**). Each amino-ketone was readily converted, by diazotisation in concentrated hydrochloric acid and cyclisation, into the corresponding 3-substituted cinnoline (I; R = Et and $[CH_2]_3$·CO_2H).

o-Aminobutyrophenone.—Butyrophenone, b. p. 128°/30 mm. (yield, 90%), was obtained from benzene (300 c.c.), aluminium chloride (294 g.), and *n*-butyric anhydride (160 c.c., added during 1 hour with stirring); the reaction was started at room temperature, allowed to proceed without cooling, and completed by heating on the steam-bath for ½ hour. Elson, Gibson, and Johnson (*loc. cit.*) record 66%

yield using butyryl chloride. The ketone (60 c.c.) was mixed with acetic acid (8 c.c.) and added during ½ hour to stirred nitric acid (300 c.c., *d* 1·5) at 0° ±2°. After a further ½ hour the solution was poured on ice (1200 g.), and the solid collected; *m*-nitrobutyrophenone, m. p. 62—63° (all m. p.s are uncorrected), was obtained by crystallisation from alcohol, and crude *o*-nitro-ketone from the alcoholic mother liquor and also from the basified aqueous acid filtrate; 415 g. of butyrophenone gave 238·5 g. (43·5%) of *m*-nitro-ketone and 247 g. (45%) of crude *o*-nitro-ketone. The latter (25 g.), mixed with concentrated hydrochloric acid (45 c.c.), was treated with granulated tin (26 g.) during ½ hour with addition of more acid (70 c.c.), and finally heated for ½ hour on the steam-bath; the *o*-aminobutyrophenone, isolated by basification and steam-distillation, had b. p. 165—170°/26—28 mm. [161·5 g. (62%) from 310 g. of nitro-ketone]. o-*Acetamidobutyrophenone*, prepared from the amine (50 g.) and acetic anhydride (100 c.c.) at 95° for 1 hour (crude yield, 66 g.), crystallised from ligroin (b. p. 40—60°) in long, lustrous, prismatic needles, m. p. 46—47°, evidently containing a little impurity (Found: C, 70·9; H, 7·4. $C_{12}H_{15}O_2N$ requires C, 70·2; H, 7·35%).

4-*Hydroxy*-3-*ethylcinnoline*.—A solution of *o*-aminobutyrophenone (1·65 g., regenerated from the acetamido-compound by acid hydrolysis) in hydrochloric acid (10N, 200 c.c.) was diazotised (0·8 g. of sodium nitrite in 1·25 c.c. of water), the diazonium solution kept at 50—60° for 2 hours, concentrated (reduced pressure) to a small volume, and treated with aqueous sodium acetate, and the solid (1·2 g., 68%; m. p. 225°) collected. Crystallisation from acetic acid gave 4-*hydroxy*-3-*ethylcinnoline* as clumps of colourless, opaque rods, m. p. 225—226° (Found: C, 69·0; H, 5·6; N, 16·0. $C_{10}H_{10}ON_2$ requires C, 68·95; H, 5·8; N, 16·1%).

Preparation and Hydrolysis of 11-*Nitro*-10-*hydroxy*-9-*benzoylhexahydrocarbazole*.—A stirred solution of 9-benzoyl-1 : 2 : 3 : 4-tetrahydrocarbazole (20 g.; Perkin and Plant, *loc. cit.*, p. 685) in acetic acid (55 c.c.) at 30° was treated with nitric acid (6 c.c., *d* 1·42). The temperature rose to 50°, and the yellow 11-nitro-10-hydroxy-9-benzoylhexahydrocarbazole, which separated after a few seconds, was collected and washed with a little acetic acid [13·2 g. (53%), m. p. 149° (decomp.)]; this method, using a smaller volume of acetic acid than that used by Perkin and Plant, who give m. p. 150° (decomp.), gives an improved yield. Hot alkaline hydrolysis of this compound to 5-keto-5-2′-benzamidophenyl-*n*-pentane 1-carboxylic acid, using the conditions of Perkin and Plant, gave a product of inferior quality and in poorer yield than that of these authors, who give m. p. 126° and 56% yield. In the best of several variations, a solution of the nitro-compound (5 g.) in 5% potassium hydroxide (125 c.c., made up in 50% aqueous alcohol) was left at room temperature for 2 hours; dilution and acidification gave crude benzamido-acid (1·87 g., 39%; m. p. 120—122°). This acid was unchanged after ½ hour's refluxing with 5N-hydrochloric acid; hydrolysis of the acid (6 g.) in hot aqueous potassium hydroxide according to the conditions of Perkin and Plant (*loc. cit.*) gave 5-keto-5-2′-aminophenyl-*n*-pentane-1-carboxylic acid, m. p. 123—126°; yield, 2·25 g. Perkin and Plant record m. p. 129° and 3·5 g.

3-4′-*Hydroxy*-3′-*cinnolyl*-n-*propane*-1-*carboxylic Acid*.—The above amino-acid (2·25 g.) was dissolved in hydrochloric acid (10N, 450 c.c.) and treated with a solution of sodium nitrite (0·77 g.) in water (1 c.c.) at 0—5°. The solution was filtered from sodium chloride, kept for 6 hours at 50—55°, concentrated to a small volume (reduced pressure), decanted from a little oil which had separated, and treated with excess of aqueous sodium acetate. The crude solid (1·27 g., m. p. 170—185°) was crystallised from acetic acid, from which 3-4′-*hydroxy*-3′-*cinnolyl*-n-*propane*-1-*carboxylic acid* separated in fawn-coloured, lustrous blades, m. p. 201·5—202·5° [Found (two samples): C, 60·6, 60·8; H, 5·4, 5·15; N, 11·9. $C_{12}H_{12}O_3N_2,\frac{1}{3}H_2O$ requires C, 60·45; H, 5·35; N, 11·75%].

We are indebted to the Medical Research Council for a Research Studentship (J. R. K.).—WARRINGTON YORKE DEPARTMENT OF CHEMOTHERAPY, LIVERPOOL SCHOOL OF TROPICAL MEDICINE. [*Received, February 3rd*, 1948.]

The Formation of Ketones from Semicarbazones by the Action of Nitrous Acid.

By D. H. HEY and D. S. MORRIS.

IN a recent publication (*Rec. Trav. chim.*, 1946, **65**, 796), Goldschmidt and Veer have reported that carbonyl compounds can be regenerated in good yield from semicarbazones by treatment with sodium nitrite in glacial acetic acid solution. In this manner acetophenone, *trans*-dehydroandrosterone acetate, and pregnenolone acetate were regenerated from their semicarbazones, and the method is stated to have particular advantages for the fission of semicarbazones of the *cyclo*pentanohydrophenanthrene series. Wolfrom (*ibid.*, 1947, **66**, 238) claims to have used the method previously for the regeneration of *aldehydo*-sugar acetates from the corresponding *aldehydo*-penta-acetate semicarbazones (*J. Amer. Chem. Soc.*, 1934, **56**, 1794). This work was considered as an extension of the work of Claisen and Manasse (*Ber.*, 1889, **22**, 530) on the conversion of *iso*nitrosocamphor into camphorquinone, a view which is contested by Goldschmidt and Veer (*Rev. Trav. chim.*, 1947, **66**, 238).

A similar method, used by the authors in 1943 under somewhat different experimental conditions, was suggested by the work of Harries (*Ber.*, 1901, **34**, 1494), who used nitrous acid to regenerate succindialdehyde from its oxime (cf. Robinson, *J.*, 1917, 766). The following examples illustrate the method:

(i) Nitrous fumes, generated from sodium nitrite and dilute sulphuric acid, were passed into a suspension of *cyclo*hexanone semicarbazone (10 g.) in water (200 c.c.) until a clear solution was obtained. The solution was extracted with ether and the extract washed with water and dried. Evaporation of the solvent and distillation of the residue gave *cyclo*hexanone (5·8 g.), b. p. 155°.

(ii) A suspension of cholest-4-enone semicarbazone (1·1 g., m. p. 228—230°) in water (10 c.c.) and benzene (10 c.c.) was treated with nitrous fumes, prepared as above. The benzene layer became almost clear. The aqueous layer was removed, and the benzene solution washed with dilute sodium hydrogen carbonate solution and with water, and dried. Evaporation of the benzene left a crystalline residue (1·0 g., m. p. 65—70°). Recrystallisation from methyl alcohol–ether gave pure cholest-4-enone (0·5 g.), m. p. and mixed m. p. 79—80°.

(iii) By the same procedure as in (ii) above, *trans*-dehydroandrosterone acetate semicarbazone [0·20 g., m. p. 266—267° (uncorr.)] gave *trans*-dehydroandrosterone acetate [0·15 g., m. p. 164° (uncorr.)]. —BRITISH SCHERING RESEARCH INSTITUTE, ALDERLEY EDGE, CHESHIRE. [*Received, February 16th,* 1948.]

The Preparation of Certain Urethanes and Their Conversion into N-*Nitroso-derivatives. Some Chloronitro-compounds of the Type* CRR'Cl·CCl(NO_2)R''. By A. F. CHILDS, L. J. GOLDSWORTHY, G. F. HARDING, S. G. P. PLANT, and G. A. WEEKS.

NITROSOURETHANES have long been known to possess vesicant properties, and the members of this class, and their intermediates, now described were prepared as part of an investigation designed to examine this feature more fully. A study of the properties of compounds of the type CRR'Cl·CCl(NO_2)R'' has involved the preparation of some examples not hitherto recorded.

Hydrochloride of 2-*Chloro*-2'-*aminodiethyl Sulphide.*—2-Chloroethylamine hydrochloride (23·2 g., prepared by the method of Ward, *J. Amer. Chem. Soc.*, 1935, **57**, 914) was added to a solution of monothioethylene glycol (15·6 g.) in aqueous potassium hydroxide (40 c.c. of 5N), and the whole treated during 10 minutes, with stirring, with more alkali (40 c.c. of 5N). After being heated for an hour at 100°, the mixture was cooled, acidified with concentrated hydrochloric acid, and evaporated under reduced pressure. The hydrochloride of 2-amino-2'-hydroxydiethyl sulphide was extracted from the residue with alcohol, and recovered as a pale brown syrup (30 g.) on evaporation of the filtered extract. A solution of thionyl chloride (34 g.) in chloroform (25 c.c.) was gradually added to a mechanically stirred suspension of this salt in chloroform (25 c.c.), and the temperature was kept at 50° until the reaction was completed. The hydrochloride of 2-chloro-2'-aminodiethyl sulphide (26 g.), isolated by evaporation of the mixture and purified by crystallisation from chloroform, was very hygroscopic and melted at 68—70° (compare Gabriel and Colman, *Ber.*, 1912, **45**, 1643).

Methyl 2-*Chloro*-n-*propylcarbamate and Other Urethanes.*—A mixture of 2-chloro-*n*-propylamine hydrochloride (32 g., prepared by the method of Abderhalden and Eichwald, *Ber.*, 1918, **51**, 1312), dissolved in water (70 c.c.), and methyl chloroformate (23·4 g.), dissolved in ether (80 c.c.), was mechanically stirred and kept below 5° while a solution of potassium hydroxide (27·6 g.) in water (200 c.c.) was gradually added. After a further 15 minutes, the ether layer and additional ether extracts were dried ($MgSO_4$), and fractionated. *Methyl* 2-*chloro*-n-*propylcarbamate* (25·5 g.) was obtained as a colourless oil, b. p. 118—119°/22 mm. (Found: C, 39·9; H, 6·9; Cl, 22·1. $C_5H_{10}O_2NCl$ requires C, 39·6; H, 6·6; Cl, 23·4%).

The following were prepared by methods which were essentially similar to the above: *Methyl allylcarbamate* (from allylamine hydrochloride), colourless oil, b. p. 179·5—183°/748 mm. (Found: C, 51·6; H, 8·0; N, 12·6. $C_5H_9O_2N$ requires C, 52·2; H, 7·8; N, 12·2%); *methyl* 3-*chloro*-n-*propylcarbamate* (from 3-chloro-*n*-propylamine hydrochloride, obtained by the action of thionyl chloride on the hydrochloride of 3-hydroxy-*n*-propylamine prepared by Putochin's method, *Ber.*, 1926, **59**, 625), colourless oil, b. p. 131°/20 mm. (Found: N, 9·3. $C_5H_{10}O_2NCl$ requires N, 9·2%); ethyl 2-chloroethylcarbamate (from 2-chloroethylamine hydrochloride and ethyl chloroformate), colourless oil, b. p. 117°/19 mm. (Found: C, 39·9; H, 6·8%), previously prepared by Wenker (*J. Amer. Chem. Soc.*, 1936, **58**, 2608) by the action of thionyl chloride on ethyl 2-hydroxyethylcarbamate; *methyl* 2-(2-*chloroethylthio*)*ethylcarbamate*, $CH_2Cl·CH_2·S·CH_2·CH_2·NH·CO_2Me$ (from the hydrochloride of 2-chloro-2'-aminodiethyl sulphide), colourless liquid, b. p. 120—130°/0·1 mm. (Found: N, 7·1. $C_6H_{12}O_2NClS$ requires N, 7·1%); NN'-*dicarbomethoxy*-2 : 2'-*diaminodiethyl sulphide* (from 2 : 2'-diaminodiethyl sulphide; Nathan and Bogert, *J. Amer. Chem. Soc.*, 1941, **63**, 2361), colourless prisms, m. p. 71—72°, from water (Found: N, 12·5. $C_8H_{16}O_4N_2S$ requires N, 11·9%) (ether extraction was here unnecessary, the crude product being collected by filtration); *methyl* s-*trichloro*-tert.-*butylcarbamate*, $(CH_2Cl)_3C·NH·CO_2Me$ (from *s*-trichloro-*tert.*-butylamine hydrochloride; Kleinfeller, *Ber.*, 1929, **62**, 1582), colourless plates, m. p. 82°, from aqueous alcohol (Found: C, 31·0; H, 4·6; Cl, 45·3. $C_6H_{10}O_2NCl_3$ requires C, 30·7; H, 4·3; Cl, 45·4%), and the corresponding *ethyl* ester, colourless plates, m. p. 79°, from aqueous alcohol (Found: C, 34·2; H, 4·8; N, 5·7; Cl, 41·9. $C_7H_{12}O_2NCl_3$ requires C, 33·8; H, 4·8; N, 5·6; Cl, 42·9%).

Methyl 2 : 3-*Dichloro*-n-*propylcarbamate.*—A molecular proportion of chlorine in carbon tetrachloride solution was gradually added to methyl allylcarbamate below 15°. When the solution was washed with water, dried ($MgSO_4$), and fractionated, *methyl* 2 : 3-*dichloro*-n-*propylcarbamate* was obtained as an oil, b. p. 139—140°/12 mm., which slowly solidified. It then separated from aqueous alcohol in colourless needles, m. p. 55—56° (Found: Cl, 37·9. $C_5H_9O_2NCl_2$ requires Cl, 38·2%). The yield was 70% of the theoretical.

Methyl N-*Nitroso*-2-*chloro*-n-*propylcarbamate,* $CH_3·CHCl·CH_2·N(NO)·CO_2Me$, *and Other Nitroso-urethanes.*—Nitrous fumes, generated by the action of 56% nitric acid on arsenious oxide and freed from nitric acid by passage through a spiral condenser surrounded by ice, were passed into a solution of methyl 2-chloro-*n*-propylcarbamate (10 g.) in an equal volume of ether at 0° until the colour became blue. Most of the excess of oxides of nitrogen was removed by aspiration with air, more ether was added, and the whole shaken twice with ice-cold dilute sodium carbonate solution. After being dried ($MgSO_4$), the ether was removed under reduced pressure at 40°, and *methyl* N-*nitroso*-2-*chloro*-n-*propylcarbamate* (10·4 g.) obtained as a reddish-yellow oil (Found: C, 33·6; H, 5·2; N, 15·9; Cl, 18·9. $C_5H_9O_3N_2Cl$ requires C, 33·2; H, 5·0; N, 15·5; Cl, 19·7%).

The following were similarly prepared from the appropriate carbamates as reddish-yellow oils (except where otherwise stated) which could not be distilled: *Methyl* N-*nitroso*-3-*chloro*-n-*propylcarbamate* (Found: N, 16·1%); *ethyl* N-*nitroso*-2-*chloroethylcarbamate* (Found: C, 33·8; H, 5·1%); *methyl* N-*nitroso*-2 : 3-*dichloro*-n-*propylcarbamate* (nitrosation proceeded much more slowly in this case, and the ethereal solution containing nitrous fumes was left for two days at room temperature before the product was isolated) (Found: C, 28·4; H, 4·0; N, 13·1. $C_5H_8O_3N_2Cl_2$ requires C, 27·9; H, 3·7; N, 13·0%); *methyl* N-*nitroso*-2-(2-*chloroethylthio*)*ethylcarbamate,* $CH_2Cl·CH_2·S·CH_2·CH_2·N(NO)·CO_2Me$ (Found: N, 12·3. $C_6H_{11}O_3N_2ClS$ requires N, 12·4%); NN'-*dinitroso*-NN'-*dicarbomethoxy*-2 : 2'-*diaminodiethyl sulphide,* $S[CH_2·CH_2·N(NO)·CO_2Me]_2$, small, pale yellow plates, m. p. 104—105°, from

alcohol (Found: N, 18·7. $C_8H_{14}O_6N_4S$ requires N, 19·0%). Methyl allylcarbamate could not be made to give a pure specimen of the corresponding nitroso-compound under similar conditions, probably owing to reaction with the double link. Methyl and ethyl *s*-trichloro-*tert.*-butylcarbamate were unreactive and could not be converted into nitroso-compounds with nitrous fumes or nitrosyl chloride under various conditions.

Methyl N-*Nitroso*-2-*bromoethylcarbamate*.—An ethereal solution of methyl 2-bromoethylcarbamate was prepared from 2-bromoethylamine hydrobromide (Cortese, *J. Amer. Chem. Soc.*, 1936, **58**, 191) and methyl chloroformate by the general method described above, but an attempt to distil the urethane under reduced pressure resulted in elimination of methyl bromide and formation of 2-oxazolidone. Conversion into *methyl* N-*nitroso*-2-*bromoethylcarbamate* with nitrous fumes was effected as in analogous cases, except that the ether was removed under reduced pressure at room temperature, leaving the product as a reddish-yellow oil (Found: N, 12·9. $C_4H_7O_3N_2Br$ requires N, 13·3%).

2-*Chloroethylcyanamide*, $CH_2Cl{\cdot}CH_2{\cdot}NH{\cdot}CN$.—Potassium hydroxide (25·2 g.) in a very little water was gradually added to a vigorously stirred mixture of 2-chloroethylamine hydrochloride (29·3 g.) and a solution of cyanogen bromide (26·8 g.) in ether (150 c.c.), the whole being cooled in ice-water. After the precipitated potassium salts had been filtered off, the ethereal layer was dried ($MgSO_4$), and fractionated. 2-*Chloroethylcyanamide* was collected at 82°/0·1 mm. as a colourless oil (Found: N, 26·7. $C_3H_5N_2Cl$ requires N, 26·8%). The yield was about 60% of the theoretical. It could not be converted into an *N*-nitroso-derivative.

Methyl N-*Nitro*-2-*chloroethylcarbamate*.—Methyl 2-chloroethylcarbamate (16 g.) was added dropwise to nitric acid (37 c.c., *d* 1·5) which was mechanically stirred and cooled in ice-water. With continued stirring and cooling, the whole was made just alkaline by the gradual addition of concentrated aqueous sodium carbonate, and the oily product was extracted with ether. After the extract had been washed with water, dried, and filtered, the solvent was removed by aspiration with air under reduced pressure, and *methyl* N-*nitro*-2-*chloroethylcarbamate* obtained as a yellow oil (Found: N, 15·4. $C_4H_7O_4N_2Cl$ requires N, 15·3%). This type of compound cannot be distilled without decomposition (van Erp, *Rec. Trav. chim.*, 1895, **14**, 1).

2-*Imino-oxazolidine*.—A solution of 2-chloroethylamine hydrochloride (11·6 g.) and potassium cyanate (8·1 g.) in water (20 c.c.) was refluxed for 1½ hours, cooled, and treated with alcohol (100 c.c.) to precipitate potassium chloride. After filtration, the filtrate was evaporated under reduced pressure and the residue dissolved in a small amount of alcohol. When the whole had been again filtered and the solution evaporated, the residue was found to contain 16·6% of chloride ion. That the material contained a high proportion of 2-imino-oxazolidine hydrochloride was proved by dissolving it (0·5 g.) in hot water and adding hot aqueous sodium picrate (1 g.). After recrystallisation from water, the product which separated melted at 186—188° (Found: C, 34·6; H, 3·0. Calc. for $C_9H_9O_8N_5$: C, 34·3; H, 2·9%). This was obviously identical with the picrate of 2-imino-oxazolidine described by Gabriel (*Ber.*, 1889, **22**, 1139). Evidently 2-chloroethylurea is unstable, a fact which is not surprising in view of the similar transformations observed with the corresponding bromo- and iodo-compounds (Gabriel, *loc. cit.*; *Ber.*, 1917, **50**, 826; Birckenbach and Linhard, *ibid.*, 1931, **64**, 1076).

1 : 2 : 3-*Trichloro*-2-*nitropropane*.—When 2-chloro-2-nitro-1 : 3-dihydroxypropane (61 g., prepared as described by Schmidt and Wilkendorf, *Ber.*, 1922, **55**, 316) was intimately mixed with phosphorus pentachloride (170 g.), a vigorous reaction soon set in with evolution of hydrogen chloride. After this had subsided, the mixture was refluxed for 3½ hours and then slowly poured into warm water (500 c.c.), the temperature being kept well below 100°. The 1 : 2 : 3-*trichloro*-2-*nitropropane* was removed in steam and extracted from the distillate with ether. When distilled under reduced pressure, it was obtained as a colourless oil (15 g.), b. p. 78—80°/12 mm. (Found: Cl, 55·3. $C_3H_4O_2NCl_3$ requires Cl, 55·3%).

1 : 2-*Dichloro*-1-*nitro*cyclo*hexane*.—A mixture of 2-chloro*cyclo*hexanone (66·25 g.) and a saturated solution of hydroxylamine sulphate (41 g.) was mechanically stirred and cooled while potassium carbonate (34·5 g.), dissolved in water (150 c.c.), was gradually added at such a rate that the temperature did not exceed 0° (compare Scholl and Matthaiopoulos, *Ber.*, 1896, **29**, 1550). The whole was then allowed to reach room temperature and stirring was continued for 3 hours. The *oxime*, which separated as a thick syrup, was extracted with ether, and the extract was washed with water and dried. After removal of the ether under reduced pressure at 25°, the residue (Found: Cl, 22·6. $C_6H_{10}ONCl$ requires Cl, 24·1%) was used without further treatment for the next operation. An attempt to distil a sample under reduced pressure resulted in violent decomposition. When chlorine was passed for 2 hours through a solution of the oxime (50·3 g.) in concentrated hydrochloric acid (100 c.c.), cooled to 0° (compare Piloty and Steinbock, *Ber.*, 1902, **35**, 3101), 1 : 2-*dichloro*-1-*nitroso*cyclo*hexane* separated as a deep blue oil. Owing to the instability of this type of compound, the product was washed with cold water and the main part oxidised without delay, but a specimen was dried (Na_2SO_4) and analysed (Found: Cl, 38·8. $C_6H_9ONCl_2$ requires Cl, 39·0%). The nitroso-compound was gradually added, with shaking, to a mixture of nitric acid (43 c.c., *d* 1·42) and glacial acetic acid (105 c.c.) which was maintained at 80° (compare Rheinboldt and Dewald, *Annalen*, 1927, **455**, 300). After the whole had been poured into water (750 c.c.), the product was extracted with ether and washed with dilute aqueous sodium hydroxide. When the extract was dried and fractionated, 1 : 2-*dichloro*-1-*nitro*cyclo*hexane* was collected in good yield as a pale yellow oil, b. p. 130°/35 mm. (Found: C, 37·2; H, 4·5; Cl, 35·3. $C_6H_9O_2NCl_2$ requires C, 36·4; H, 4·5; Cl, 35·9%). This substance, which might consist of geometrically isomeric forms, almost completely solidified at room temperature, but became liquid again on being heated to 41°.

1 : 2-*Dichloro*-2-*nitropropane*.—(a) Chlorine was passed through a suspension of the sodium salt of 2-nitro-*n*-propyl alcohol (67 g., Earl, Ellsworth, Jones, and Kenner, *J.*, 1928, 2697) in dry ether (300 c.c.), the whole being cooled in ice and mechanically stirred. The course of the reaction was followed by stopping the stream of chlorine from time to time and testing the solution with starch–potassium iodide paper after a few minutes of continued stirring. When the chlorination was completed, the sodium chloride was filtered off and washed with a little ether. After the solvent had been removed from the united ethereal solutions, the residue was distilled, and 2-chloro-2-nitro-*n*-propyl alcohol (60 g.) collected at 82—89°/10 mm. (Found: Cl, 25·6. Calc. for $C_3H_6O_3NCl$: Cl, 25·4%). It solidified

at room temperature but was liquid again at 27° (compare Henry, *Rec. Trav. chim.*, 1897, **16**, 193; also Wilkendorf and Trénel, *Ber.*, 1924, **57**, 306). When treated with phosphorus pentachloride under conditions similar to those described for 1 : 2 : 3-trichloro-2-nitropropane, the hydroxy-compound gave 1 : 2-*dichloro*-2-*nitropropane* as a colourless oil, b. p. 76—78°/33 mm. (Found : Cl, 44·3. $C_3H_5O_2NCl_2$ requires Cl, 44·9%).

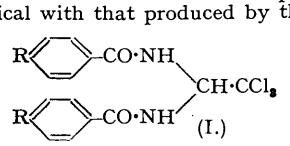
(b) The blue oil which separated when chlorine was passed through a solution of the oxime of chloroacetone in concentrated hydrochloric acid, cooled in ice, was immediately oxidised under conditions similar to those used for 1 : 2-dichloro-1-nitroso*cyclo*hexane. 1 : 2-Dichloro-2-nitropropane was obtained as an almost colourless oil, b. p. 77—78°/34 mm. (Found : C, 22·3; H, 3·2; N, 9·1; Cl, 44·2. $C_3H_5O_2NCl_2$ requires C, 22·8; H, 3·2; N, 8·9; Cl, 44·9%). The yield was 46% of the theoretical.

We are indebted to Sir Robert Robinson for his interest in these investigations, and to the Chief Scientist, Ministry of Supply, for permission to publish the work.—Dyson Perrins Laboratory, Oxford University. [*Received, February 20th*, 1948.]

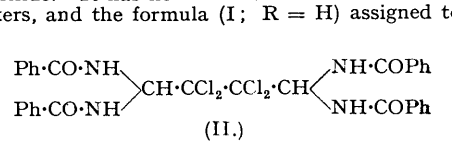
The Condensation of Chloral with Aryl Cyanides. By R. F. Batt and D. Woodcock.

The reaction between phenyl cyanide and chloral has been investigated by several workers. Thus Hepp and Spiess (*Ber.*, 1876, **9**, 1424) obtained a compound, m. p. 257°, from the exothermic reaction which took place in the presence of sulphuric acid. Pinner and Klein (*Ber.*, 1878, **11**, 10) obtained an impure product by using gaseous hydrogen chloride, whilst Béhal and Choay's product, m. p. 267° (*Ann. Chim.*, 1892, **26**, 33), was prepared from chloralimide and benzoyl chloride.

During the preparation of D.D.T. analogues by Wain (*Ann. Rept. Res. Sta. Long Ashton*, 1944, 126) attempts to prepare the *pp'*-dicyano-derivative by the Baeyer condensation (*Ber.*, 1872, **5**, 25, 280, 1094) with phenyl cyanide led to a product, m. p. 272—273° (decomp.), which decomposed on attempted dehydrochlorination with alcoholic potassium hydroxide. It has now been shown that this compound is identical with that produced by the earlier workers, and the formula (I; R = H) assigned to it by



(I.)



(II.)

Hepp and Spiess (*loc. cit.*) has been confirmed by its synthesis from benzamide and chloral.

Analogous compounds (I; R = Cl and R = Me) have been prepared from *p*-chlorophenyl cyanide and *p*-tolyl cyanide.

Reduction of (I; R = H) with zinc dust in alcoholic solution gave a product which probably possesses the bimolecular structure (II).

1 : 1 : 1-*Trichloro*-2 : 2-*dibenzamidoethane* (I; R = H).—(*a*) (cf. Wain, *loc. cit.*). Phenyl cyanide (10·2 g.) and freshly distilled chloral (7·4 g. ≡ 0·5 mol.) were stirred during the addition of concentrated sulphuric acid (5 c.c.) and oleum (1—2 c.c.). The colour became a deep yellow, and the whole set to a vitreous mass which crystallised from a large amount of glacial acetic acid in a mass of felted needles (6·9 g.), m. p. 265—266° (decomp.).

(*b*) Benzamide (2·4 g.) and chloral (1 c.c. ≡ 0·5 mol.) were heated in an oil-bath at 150—160° for 3 hours. The solid obtained on cooling crystallised from acetone–benzene (1 : 1) in colourless needles (2·5 g.), m. p. 264° (decomp.) undepressed by admixture with the product from (*a*) above or with Wain's product (Found : C, 51·6; H, 3·5; N, 7·3; Cl, 28·5. Calc. for $C_{16}H_{13}O_2N_2Cl_3$: C, 51·7; H, 3·5; N, 7·5; Cl, 28·6%).

Hydrolysis with 70% sulphuric acid gave benzoic acid, chloral, and ammonia, but no benzamide could be obtained by using 2N-acid (cf. Hepp and Spiess, *loc. cit.*).

2 : 2 : 3 : 3-*Tetrachloro*-1 : 1 : 4 : 4-*tetrabenzamidobutane* (II).—The compound (I; R = H) (2·0 g.) was refluxed with ethyl alcohol (30 c.c.), zinc dust (4 g.) and concentrated hydrochloric acid (5 c.c.) for 0·5 hour, the excess alcohol distilled off, and the residual syrup extracted with chloroform. The extract was washed with sodium hydrogen carbonate solution, dried (Na_2SO_4), and the solvent removed. The residue crystallised from ethyl alcohol in rosettes of tiny prisms (0·9 g.), m. p. 200—201° (decomp.) [Found : C, 56·4; H, 4·4; N, 8·5; Cl, 20·3; *M* (Rast), 622, 645. $C_{32}H_{26}O_4N_4Cl_4$ requires C, 57·2; H, 3·9; N, 8·3; Cl, 21·1%; *M*, 672]. The m. p. of this product was undepressed by admixture with a substance, m. p. 196—197°, isolated by Wain (unpub.) from the product of a phenyl cyanide–chloral condensation which was left for several weeks before being examined.

1 : 1 : 1-*Trichloro*-2 : 2-*di*-p-*toluamidoethane* (I; R = Me).—*p*-Tolyl cyanide (11·7 g.) and freshly distilled chloral (7·3 g. ≡ 0·5 mol.) were warmed together until homogeneous and then stirred during the dropwise addition of oleum (2 c.c.). The ensuing exothermic reaction gave a viscous dark brown liquid which crystallised from glacial acetic acid in rosettes of prisms (7·9 g.), m. p. 237—238°, raised to 248° by recrystallisation from the same solvent [Found : C, 53·7; H, 4·4; N, 6·7; Cl, 26·0; *M* (Rast), 376, 390. $C_{18}H_{17}O_2N_2Cl_3$ requires C, 54·1; H, 4·3; N, 7·0; Cl, 26·6%; *M*, 399·4]. Hydrolysis with 70% sulphuric acid yielded *p*-toluic acid as well as chloral and ammonia.

1 : 1 : 1-*Trichloro*-2 : 2-*di*-p-*chlorobenzamidoethane* (I; R = Cl).—*p*-Chlorophenyl cyanide (13·7 g.) and chloral (7·3 g. ≡ 0·5 mol.) were treated as in the previous experiment. Crystallisation of the product from glacial acetic acid gave rosettes of prisms, m. p. 274—275° (decomp.) [Found : C, 44·0; H, 2·7; N, 5·7; Cl, 38·0; *M* (Rast), 410, 421. $C_{16}H_{11}O_2N_2Cl_5$ requires C, 43·6; H, 2·5; N, 6·3; Cl, 40·3%; *M*, 440·3]. Ammonia, chloral, and *p*-chlorobenzoic acid were obtained on hydrolysis.—University of Bristol, Department of Agriculture and Horticulture, Research Station, Long Ashton, Bristol. [*Received, February 27th*, 1948.]
