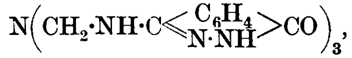
NOTES.

A Derivative of αα'α''-Triaminotrimethylamine. By FREDERIC BARRY KIPPING and FREDERICK GEORGE MANN.

IT has been shown by Ristenpart (*Ber.*, 1896, **29**, 2530) that molten phthal-β-bromoethylimide when treated with gaseous ammonia gives triphthalimidotriethylamine, $(C_6H_4{:}C_2O_2{:}N{\cdot}C_2H_4)_3N$, which on hydrolysis with hydrochloric acid furnishes ββ'β''-triaminotriethylamine trihydrochloride, $N(C_2H_4{\cdot}NH_2,HCl)_3$. This preparation has been improved by Mann and Pope (*Proc. Roy. Soc.*, 1925, [*A*], **109**, 444), who have also prepared γγ'γ''-triaminotripropylamine tetrahydrochloride similarly from phthal-γ-bromopropylimide (J., 1926, 489).

We have now investigated the stability of αα'α''-triaminotrimethylamine, $N(CH_2{\cdot}NH_2)_3$, by a similar series of reactions. Phthalbromomethylimide was prepared from phthalhydroxymethylimide by the method of Pucher and Johnson (*J. Amer. Chem. Soc.*, 1922, **44**, 817), this being a great improvement on the older method of Sachs (*Ber.*, 1898, **31**, 1225). A solution of phthalbromomethylimide (100 g.) in dry xylene (500 c.c.) was boiled under reflux for 8 hours while a stream of dry ammonia gas was passed through it. The solid product which had separated was then filtered, crushed, and extracted with water and alcohol, and the insoluble residue was recrystallised from glacial acetic acid. *Triphthalimidotrimethyl-*

amine, $(C_6H_4{:}C_2O_2{:}N\cdot CH_2)_3N,CH_3\cdot CO_2H$, separated with a molecule of acetic acid in colourless prisms, m. p. 222—223° (22 g.) (Found: C, 62·8; H, 3·8. $C_{29}H_{22}O_8N_4$ requires C, 62·8; H, 4·0%). Recrystallisation from pyridine gave the free *triphthalimidotrimethylamine* in colourless prisms, m. p. 235° (Found: C, 65·8; H, 3·5; N, 11·2. $C_{27}H_{18}O_6N_4$ requires C, 65·6; H, 3·6; N, 11·3%). The molecule of acetic acid, which is slowly lost when the compound is heated in a vacuum at 100°, may be present as acetic acid of crystallisation, or may be united to the tertiary amine group to form an unstable acetate. The formation of an acetate is most improbable, however, in view of the very feebly basic properties of the tertiary amine group in triaminotriethylamine (Mann and Pope, *loc. cit.*).

When triphthalimidotrimethylamine (10 g.) was heated gently under reflux with hydrochloric acid (1 : 1 by vol.; 300 c.c.), a complete solution was obtained after about 8 hours. This solution contained, however, only phthalic acid, formaldehyde, and ammonium chloride. Ing and Manske (J., 1926, 2348) have recently described a far less drastic method of hydrolysing phthalimido-compounds by treating them in alcoholic suspension with hydrazine hydrate. A suspension of triphthalimidotrimethylamine (3 g.) in alcohol (100 c.c.) was therefore heated on the water-bath with hydrazine hydrate (5 c.c. of 50% aqueous solution). The clear solution, which was rapidly obtained, soon deposited a white, gelatinous precipitate, which, after heating for 2 hours, was filtered off, washed, and recrystallised from alcohol. This compound, which did not melt below 330°, was probably *triphthalylhydrazidotriaminotrimethylamine*,  $N\left(CH_2\cdot NH\cdot C{<}{}^{C_6H_4}_{N\cdot NH}{>}CO\right)_3$, but was too unstable to be obtained pure (Found, after consecutive alcoholic recrystallisations: N, 25·5, 26·7. $C_{27}H_{24}O_3N_{10}$ requires N, 26·2%). When this product was treated with cold dilute hydrochloric acid, a thick suspension of phthalylhydrazide, $C_6H_4{:}C_2O_2{:}(NH)_2$ (Found: N, 17·4. Calc. for $C_8H_6O_2N_2$: 17·3%), separated with evolution of heat, whilst the solution contained formaldehyde and ammonium chloride.

It is clear from these results that $\alpha\alpha'\alpha''$-triaminotrimethylamine cannot be isolated owing to its ready hydrolysis to formaldehyde and ammonia, but is stable in the form of its triacyl derivatives. Its behaviour is thus closely akin to that of the parent methylenediamine, $CH_2(NH_2)_2$, which also hydrolyses readily into formaldehyde and ammonia, but gives stable diacetyl and dibenzoyl derivatives (Pulvermacher, *Ber.*, 1892, **25**, 310; Einhorn and Mauermayer, *Annalen*, 1905, **343**, 307) and also a stable diurethane,

$CH_2(NH\cdot CO_2Et)_2$

(Curtis, *J. pr. Chem.*, 1895, **52**, 225; Conrad and Hock, *Ber.*, 1903. **36**, 2206).

Phthalbromomethylimide unites vigorously with pyridine to give *phthalimidomethylpyridinium bromide*, $C_6H_4{:}C_2O_2{:}N{\cdot}CH_2{\cdot}NC_5H_5Br$, which, after recrystallisation from alcohol, is obtained in large, colourless prisms, m. p. (on rapid heating) 244° (Found: Br, 25·2. $C_{14}H_{11}O_2N_2Br$ requires Br, 25·1%). This quaternary ammonium bromide, when boiled with dilute hydrochloric acid (1 : 1 by vol.), gave pyridine, ammonia, phthalic acid, and formaldehyde.

Phthalbromomethylimide reacts violently with anhydrous diethylamine, and, even when the reaction occurs in dilute xylene solution, phthalimide is the chief product. Pucher and Johnson (*loc. cit.*) have shown that phthalimide is also produced by the action of potassium cyanide, ethyl sodioacetoacetate, or ethyl sodio-γ-diethoxyacetoacetate on phthalbromomethylimide, and the latter, they suggest, often acts as if it were a methyleneammonium bromide of constitution $C_6H_4{:}C_2O_2{:}N(Br){:}CH_2$. Its reactions with ammonia and pyridine described above are, however, those of the true phthalbromomethylimide, $C_6H_4{:}C_2O_2{:}N{\cdot}CH_2Br$.—UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, November 25th*, 1926.]

The Action of Nitrous Acid on ar-*Tetrahydro-α-naphthol and on* 5 : 8- *and* 5 : 6(*or* 7 : 8)-*Dihydro-α-naphthols.*

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SCHROETER'S statement (*Annalen*, 1922, **426**, 104, 152) that nitrous acid converts *ar*-tetrahydro-α-naphthol into 4-nitroso-*ar*-tetrahydro-α-naphthol, greenish-yellow needles, m. p. 161—163° (decomp.), led the authors to re-examine the product of this reaction, yellow needles, m. p. 163° (decomp.), obtained by Green and Rowe (J., 1918, **113**, 965) and described as 4-nitro-*ar*-tetrahydro-α-naphthol. That this product was really the 4-nitroso-compound has now been proved as follows: An aqueous suspension of *ar*-tetrahydro-α-naphthaquinone was mixed with an aqueous solution of hydroxylamine hydrochloride, the mixture was kept for 24 hours and then rendered alkaline and filtered, and the filtrate was acidified. The precipitated *ar*-tetrahydro-α-naphthaquinoneoxime (4-nitroso-*ar*-tetrahydro-α-naphthol) crystallised from dilute alcohol in yellow needles, m. p. 163° (decomp.) (Found:* C, 68·1; H, 6·3; N, 7·8. Calc.: C, 67·8; H, 6·2; N, 7·9%) and was identical in all respects with Green and Rowe's "4-nitro"-compound. Further, the finely powdered compound, prepared in either way, was oxidised

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* To obtain accurate results, it was essential to carry out the combustions extremely slowly.

to the corresponding nitro-derivative by adding 2 g. in small portions at a time to a mixture of 3 c.c. of nitric acid (*d* 1·4) and 9 c.c. of water at 40°. *4-Nitro-*ar*-tetrahydro-α-naphthol* crystallises from toluene in faintly coloured needles, m. p. 123°; it is not volatile with steam and forms yellowish-brown salts (Found: C, 62·2; H, 5·9; N, 7·3. $C_{10}H_{11}O_3N$ requires C, 62·2; H, 5·7; N, 7·2%).

Finally, the products of the interaction of an aqueous solution of phenylhydrazine hydrochloride and a glacial acetic acid suspension of *ar*-tetrahydro-α-naphthaquinone, and of a mixture of 4-nitroso-*ar*-tetrahydro-α-naphthol and aniline acetate at the temperature of a boiling water-bath, were identical with benzeneazo-*ar*-tetrahydro-α-naphthol, prepared by coupling benzenediazonium chloride with *ar*-tetrahydro-α-naphthol (Jacobson and Turnbull, *Ber.*, 1898, **31**, 898).

Also the compounds described as 4-nitro-5 : 8-dihydro-α-naphthol and 4-nitro-5 : 6(or 7 : 8)-dihydro-α-naphthol (J., 1921, **119**, 2024) gave, on very slow combustion, results which show that they are really the 4-nitroso-compounds: *4-Nitroso-5 : 8-dihydro-α-naphthol*, brownish-yellow needles, m. p. 161° (decomp.) (Found: C, 68·6; H, 5·2; N, 7·9. $C_{10}H_9O_2N$ requires C, 68·6; H, 5·1; N, 8·0%); *4-nitroso-5 : 6(or 7 : 8)-dihydro-α-naphthol*, yellow needles, m. p. 162° (decomp.) (Found: C, 68·7; H, 5·3; N, 7·8. $C_{10}H_9O_2N$ requires C, 68·6; H, 5·1; N, 8·0%). These compounds are too sensitive to oxidation to permit their conversion into the corresponding nitro-derivatives with nitric acid; moreover, the dihydro-α-naphthylamines cannot be oxidised to dihydro-α-naphthaquinones (J., 1922, **121**, 1001).—THE UNIVERSITY, LEEDS. [*Received, December 8th*, 1926.]