

SOME DERIVATIVES OF 2-BROMOALLYLAMINE*

By J. A. LAMBERTON†

Under the conditions of the modified Gabriel reaction, in which dimethylformamide is used as solvent (Billmann and Cash 1953), 1,2,3-tribromopropane yields *N*-(2-bromoallyl)phthalimide. The constitution of the product is shown conclusively by the formation from it, on ozonolysis, of phthaloyl glycine and formaldehyde.

N-(2-Bromoallyl)phthalimide reacts with hydrazine in methanol (Ing and Manske 1926; Sheehan and Bolhofer 1950) to give 2-bromoallylamine which was converted to its benzoyl and *p*-toluene sulphonyl derivatives. The melting point of the benzoyl derivative (97–98 °C) agrees with that recorded in the literature (Galewsky 1890) but the *p*-toluene sulphonyl compound melts at 69–70 °C and not at 45–46 °C as given by Rudzick (1901).

2-Bromoallylamine was also prepared by the method given in the literature (Paal and Hermann 1889) and converted to its benzoyl and *p*-toluene sulphonyl derivatives. It gave the same benzoyl derivative melting at 97–98 °C but the *p*-toluene sulphonyl derivative was less readily purified when the amine was prepared in this way and had an indefinite m.p. of *c.* 60 °C.

2-Bromoallylamine, prepared by Paal's method, also reacts with phthalic anhydride to give *N*-(2-bromoallyl)phthalimide, identical with the product from the Gabriel reaction. 2,3-Dibromopropylamine reacts similarly to give *N*-(2,3-dibromopropyl)phthalimide, previously prepared by bromination of *N*-allylphthalimide (Neumann 1890).

Experimental

Melting points are uncorrected. Microanalyses were carried out in the C.S.I.R.O. Micro-analytical Laboratory.

(a) *N*-(2-Bromoallyl)phthalimide.—1,2,3-Tribromopropane (8.4 g), phthalimide (13.2 g), anhydrous potassium carbonate (6.2 g), and a trace of potassium iodide were heated in dimethylformamide (30 ml) at 140–145 °C for 2 hr. The mixture was poured into water and the insoluble material filtered. After washing with dilute sodium hydroxide to dissolve some unchanged phthalimide, the product was recrystallized from aqueous ethanol. It formed colourless needles, m.p. 125–126 °C. Yield, 6.5 g (Found: C, 49.7; H, 3.2; N, 4.9; Br, 30.2%. Calc. for $C_{11}H_8O_2NBr$: C, 49.6; H, 3.0; N, 5.3; Br, 30.1%).

Ozonolysis of the phthalimide compound in glacial acetic acid gave phthaloyl glycine (m.p. and mixed m.p. 189–190 °C) and formaldehyde in good yield. Formaldehyde was isolated and identified as its 2,4-dinitrophenylhydrazone and dimedone derivative. Heating with hydrazine in methanol gave phthalhydrazide and 2-bromoallylamine, which was isolated as its hydrochloride.

(b) *N*-(2-Bromoallyl)benzamide.—The benzoyl derivative, prepared from 2-bromoallylamine hydrochloride by the Schöotten-Baumann method, was obtained as needles from benzene-light

* Manuscript received November 3, 1954.

† Division of Industrial Chemistry, C.S.I.R.O., Melbourne.

petroleum, m.p. 97–98 °C (Galewsky reports 97–98 °C) (Found: C, 50.3; H, 4.1; Br, 33.3%. Calc. for $C_{10}H_{10}ONBr$: C, 50.0; H, 4.2; Br, 33.3%).

(c) *N*-(2-Bromoallyl) *p*-Toluene Sulphonamide.—Prepared from 2-bromoallylamine hydrochloride by shaking with *p*-toluene sulphonyl chloride and sodium hydroxide solution. Needles from light petroleum, m.p. 69–70 °C (Rudzick gives 45–46 °C) (Found: C, 41.6; H, 4.1; N, 4.6; S, 11.1; Br, 27.3%. Calc. for $C_{10}H_{12}O_2SNBr$: C, 41.4; H, 4.1; N, 4.8; S, 11.0; Br, 27.6%).

2-Bromoallylamine hydrochloride, prepared from 2,3-dibromopropylamine hydrobromide by the method of Paal, gave the same benzoyl derivative, m.p. 97–98 °C, but with *p*-toluene sulphonyl chloride and sodium hydroxide the product was difficult to purify and melted at c. 60 °C.

(d) *N*-(2-Bromoallyl)phthalimide.—When 2-bromoallylamine hydrochloride was heated with phthalic anhydride and sodium acetate in acetic acid, the product was *N*-(2-bromoallyl)phthalimide, m.p. 126–127 °C undepressed by admixture with the product from the Gabriel reaction.

(e) *N*-(2,3-Dibromopropyl)phthalimide.—2,3-Dibromopropylamine hydrobromide was also heated with phthalic anhydride and sodium acetate in acetic acid solution. It gave *N*-(2,3-dibromopropyl)phthalimide, m.p. 112–114 °C, after crystallization from ethanol (Found: C, 38.3; H, 2.9; Br, 46.0%. Calc. for $C_{11}H_9O_2NBr_2$: C, 38.0; H, 2.6; Br, 46.1%).

References

- BILLMANN, J. H., and CASH, R. V. (1953).—*J. Amer. Chem. Soc.* **75**: 2499.
GALEWSKY, P. (1890).—*Ber. dtsh. chem. Ges.* **23**: 1066.
ING, H. R., and MANSKE, R. H. F. (1926).—*J. Chem. Soc.* **1926**: 2348.
NEUMANN, A. (1890).—*Ber. dtsh. chem. Ges.* **23**: 1000.
PAAL, C., and HERMANN, C. (1889).—*Ber. dtsh. chem. Ges.* **22**: 3079.
RUDZICK, H. (1901).—*Ber. dtsh. chem. Ges.* **34**: 3544.
SHEEHAN, J. C., and BOLHOFFER, W. A. (1950).—*J. Amer. Chem. Soc.* **72**: 2786.