SOME DERIVATIVES OF 2-BROMOALLYLAMINE*

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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. Microanalytical 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_{12}O_{2}NBr: 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 dimesone derivative. Heating with hydrazine in methanol gave phthalaldehydrazide and 2-bromoallylamine, which was isolated as its hydrochloride.

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

* Manuscript received November 3, 1954.
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petroleum, m.p. 97-98 °C (Galewsky reports 97-98 °C) (Found: C, 50·3; H, 4·1; Br, 33·3%).
Calc. for C₁₉H₂₀ONBr: 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. 97-98 °C (Galewsky reports 97-98 °C) (Found: C, 30·3; H, 4·1; Br, 33·3%).
Calc. for C₁₉H₂₀O₂SNBr: C, 50·0; H, 4·2; Br, 33·3%).

2-Bromoallylamine hydrochloride, prepared from 2,3-dibromopropylamine hydrobromide by the method of Paal, gave the same benzoyle 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 C₁₉H₂₀O₂NBr₃: C, 38·0; H, 2·6; Br, 46·1%).

References

THE ISOLATION OF CHRYSOPHANIC ACID AND PHYSCI On FROM RUMEX HYMENOSEPALUS TORR.*

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The tubers of Rumex hymenosepalus Torr. (known as canaigre) contain about 25 per cent. of tannin and they have been considered as a commercial source of this material (Rogers and Russell 1944). Recently, investigations were made to ascertain whether they could be grown as an economic crop in certain Australian localities. The roots were analysed for tannin by leaching with acetone : water (1 : 1) at 60 °C by the method of Luvisi and Rogers (1948). In the initial stages of the leaching, the liquor from some samples deposited a bright yellow substance. This was identified as a mixture of chrysophanic acid (1,8-dihydroxy-3-methylanthaquinone) and physcion (6-methoxy-1,8-dihydroxy-3-methylanthaquinone). Chrysophanic acid has been isolated from

* Manuscript received December 8, 1954.
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