21. *Influence of Poles and Polar Linkings on the Course pursued by Elimination Reactions. Part X. Formation and Decomposition of Dibenzyldiallylammonium Hydroxide.*

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ALLYL and benzyl groups behave similarly to each other in many reactions and the present experiments were designed to determine whether allyl alcohol or benzyl alcohol would be preferentially eliminated from an ammonium hydroxide containing two radicals of each kind.

The preparation of dibenzyldiallylammonium hydroxide involved certain unexpected observations. Von Braun and Schwarz (*Ber.*, 1902, **35**, 1279) have described the preparation of dibenzylallylamine from dibenzylamine and allyl iodide. Reaction between these substances proceeded easily, but the saline product was the hydriodide not of dibenzylallylamine but of dibenzylamine, and this result could not be altered by wide variations in conditions. Other results of a similar character are described in the experimental section, and, no matter in what order we attempted to introduce the radicals, we found it impossible to prepare dibenzylallylamine.

The other possible tertiary basic intermediate, benzyldiallylamine, was, however, readily obtained by the action of benzyl bromide on diallylamine in nitromethane, and further benzylation in the same solvent produced dibenzyldiallylammonium bromide.

Thermal degradation of the hydroxide yielded a singular result. The allyl group was preferentially eliminated, though it appeared in part as acraldehyde (compare Collie and Schryver, J., 1899, **75**, 776), and no benzyl alcohol could be detected. The basic product, however, was not the expected, but still elusive, dibenzylallylamine: it was dibenzylamine, two allyl groups having been lost in the reaction. Comment is deferred, as other examples of this unique decomposition are being sought.

EXPERIMENTAL.

Action of Allyl Iodide and Allyl Bromide on Dibenzylamine.—The reaction with allyl iodide was carried out as described by von Braun and Schwarz (*loc. cit.*). We conducted it also in the absence of a solvent, in Et_2O solution, and in $MeNO_2$, at temp. varying in each case from 0° to near the b. p. The halogen-content of the salt, which was pptd. completely by the addition of dry Et_2O, was const. throughout this range of conditions (Found: I, 39·2 ± 0·2, extreme range. Calc. for $C_{17}H_{20}NI$: I, 34·8; and for $C_{14}H_{16}NI$: I, 39·1%) and in many expts. the yield was almost quantitative. The salt on basification gave substantially pure dibenzylamine (comparison), b. p. 170°/10 mm., and on treatment with sodium picrate yielded dibenzylamine picrate (comparison), m. p. 141—142°. A similar and equally extensive series of expts. with allyl bromide gave parallel results. The remaining product was amorphous.

Action of Allyl Iodide and Allyl Bromide on Benzylamine.—These expts. were in all respects similar to the foregoing, the hydrohalide formed being converted into picrate, m. p. 199—200°, for identification (comparison) as benzylamine picrate (Found: C, 46·2; H, 3·6. Calc.: C, 46·6; H, 3·6%).

Action of Benzyl Bromide on Benzylallylamine.—Gabriel and Eschenbach's method of prepn. of allylamine (*Ber.*, 1897, **30**, 1124) was found the most convenient. The base was converted into benzylallylamine by interaction with *N*-nitroso-*N*-benzylacetamide and subsequent hydrolysis (Paal and Apitzsch, *Ber.*, 1899, **32**, 79). The action of benzyl bromide on this base in $MeNO_2$ solution at 30° yielded only benzylallylamine hydrobromide (Found: Br, 35·1. Calc.: Br, 35·1%) and a product which could not be crystallised. The identity of the salt was further confirmed by conversion into the picrate (comparison), m. p. 185°.

Benzyldiallylamine.—Diallylamine was prepared *via* diallylcyanamide by Vliet's method (" Organic Syntheses," V, 44). The reaction with benzyl bromide in Et_2O yielded diallylamine hydrobromide (Found: Br, 44·9. Calc.: Br, 44·9%), but with $MeNO_2$ as solvent combination readily occurred and on addition of Et_2O the tertiary salt was pptd. as a gum. This was collected and basified with 50% KOH aq., and the benzyldiallylamine, b. p. 121—124°/20 mm., characterised as *picrate*, m. p. 114° after crystn. from MeOH (Found: C, 54·5; H, 5·0. $C_{19}H_{20}O_7N_4$ requires C, 54·8; H, 4·8%).

Dibenzyldiallylammonium Salts.—Benzyldiallylamine (1 part) and benzyl bromide (1 part) were mixed in $MeNO_2$ (2 parts). After a short time EtO_2 was added and the gummy ppt. was dissolved in EtOAc and repptd. in a cryst. form by the slow addition of light petroleum. ***Dibenzyldiallylammonium bromide*** (yield, about theo.) is moderately sol. in cold H_2O and readily sol. in hot H_2O and EtOH (Found : Br, 22·8. $C_{20}H_{24}NBr$ requires Br, 22·3%). The *picrate*, pptd. by the addition of aq. sodium picrate to a solution of the bromide, separated from the EtOAc–ligroin in needles, m. p. 143° (Found : C, 61·6; H, 5·2. $C_{26}H_{26}O_7N_4$ requires C, 61·6; H, 5·1%).

Decomposition of Dibenzyldiallylammonium Hydroxide.—The solution prepared from aq. dibenzyldiallylammonium bromide and a suspension in H_2O of Ag_2O (10% excess) was distilled to 170° (bath temp.) at atmos. press. and then under reduced press. The products were as stated in the introduction. The acraldehyde was identified as its *p*-nitrophenylhydrazone (m. p. and mixed m. p.) and resinous materials were also present. The dibenzylamine was identified as its picrate (m. p. and mixed m. p.) (Found : C, 56·1; H, 4·3. Calc. : C, 56·3; H, 4·2%).

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