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THE EXO-METHYLENE INTERMEDIATE IN THE REARRANGEMENT OF N,N,N-TRIMETHYLBENZYLAMMONIUM SALTS[a]

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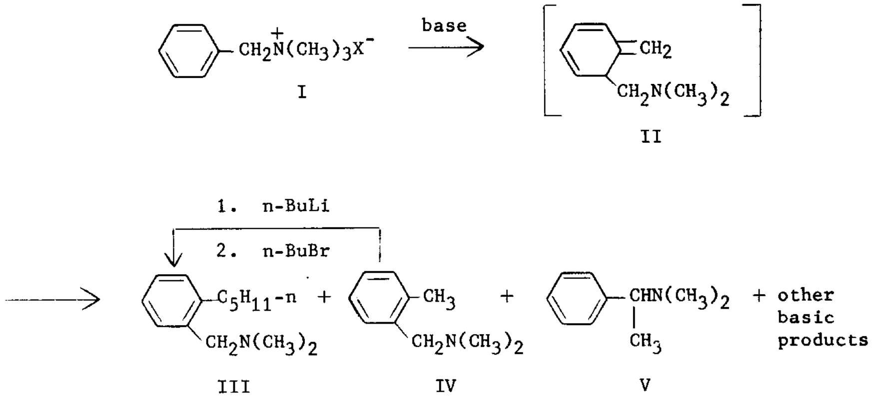
As a result of their extensive investigations into the ortho rearrangement of benzyltrimethylammonium salts (I), Hauser and co-workers proposed that the reaction proceeds through an exo-methylene intermediate II (1). These workers were able to isolate model exo-methylene



intermediates in 2,4 and 2,4,6-trisubstituted benzylamines in which simple rearomatization to rearranged product is not possible (2), but did not obtain evidence for the exo-methylene intermediate II in the parent system I. We now wish to report the isolation of N,N-dimethyl-2-n-pentylbenzylamine III from the reaction of I with n-butyl lithium in hexane. We believe that this provides strong support for the presence of the exo-methylene intermediate II in this rearrangement.

When I (18 mmoles) was allowed to react with n-butyl lithium (38 mmoles) in hexane at 25°C for 48 hours, III was isolated from the basic products in 10% yield along with

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Sommelet-Hauser rearrangement product IV (45%), Stevens rearrangement product V (32%), and other basic materials (13%) (3). When the amount of base was increased to 90 mmoles, III and IV increased similarly (to 23% and 58% respectively) while V decreased. This suggests that both III and IV arise through the common intermediate II. A control run with IV demonstrates that III is not formed from IV during the reaction. Similarly, the presence or absence of air during the reaction appears to have little effect on the product ratios.

Examples of the nucleophilic addition of the *n*-butyl carbanion to analogous exo-methylene triene systems has been demonstrated by Hauser et. al. (2). The presummed formation of lithium hydride during the rearomatization would not be expected to significantly affect the reaction (4).

Product III was isolated from the reaction mixture through preparative gas chromatography on a carbowax 20M column. The isolated material was identical to material synthesized by the reaction of IV with *n*-butyl lithium (5) followed by the addition of *n*-butyl bromide. Bp 235^o, nmr (CCl_4-internal TMS) 0.7 - 1.7 (m, 9), 2.17 (s, 6), 2.67 (t, 2), 3.34 (s, 2), 7.0 - 7.3, (m, 4).

Anal. Calcd for $C_{14}H_{23}N$: C, 51.88; H, 7.55; N, 4.03. Found: C, 51.78; H, 7.61; N, 4.14.

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