Electron-impact Induced Rearrangements of Dibenzylnitrosamines

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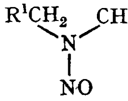
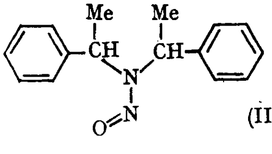
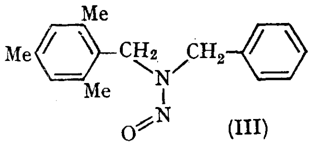
WHILST the mass spectra† of most simple dialkyl-*N*-nitrosamines are quite normal and in accord with results reported in earlier studies,[1] a series of dibenzyl-*N*-nitrosamines studied in these laboratories fragment upon electron impact with a profound skeletal rearrangement. This process results in the formation of a relatively abundant ion at *m/e* $(M-45)^+$ and is observed in the mass spectra of the dibenzyl-*N*-nitrosamines (I; $R^1 = R^2 = Ph$; $R^1 = Ph$, $R^2 = p\text{-}Me{\cdot}C_6H_4$; $R^1 = Ph$, $R^2 = 2,5\text{-}Me_2C_6H_3$; $R^1 = p\text{-}Me{\cdot}C_6H_4$, $R^2 = p\text{-}MeOC_6H_4$; $R^1 = R^2 = p\text{-}MeOC_6H_4$).



(I)

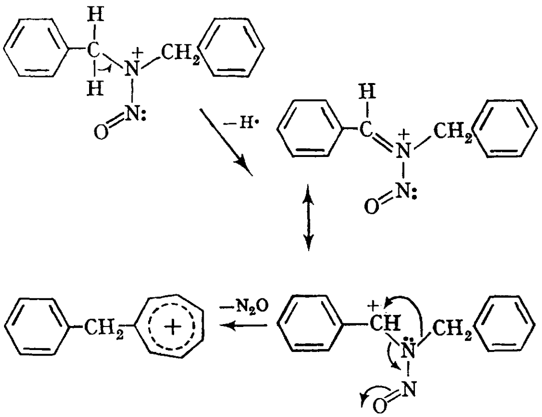


(II)



(III)

The neutral fragment lost in this rearrangement must be HN_2O, and a plausible ion-decomposition pathway leading to the loss of such a moiety may be represented by the following sequence involving a benzyl migration and the expulsion of N_2O:



The composition of this rearranged fragment ion is supported by accurate mass measurement and by labelling studies. Thus the mass spectra of $\alpha\alpha\alpha'\alpha'$-tetradeuterio-*N*-nitrosodibenzylamine and *N*-[^{15}N-nitroso]dibenzylamine exhibit ions at *m/e* 184 and 181 respectively, corresponding to $(M-46)^+$ ($D+N_2O$ and $H+{}^{15}N^{14}NO$). In addition, the presence of the appropriate metastable ions agrees with this decomposition reaction.

The structural properties that promote this rearrangement give rise to intriguing questions.

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† Mass spectra were determined with an MS-9 mass spectrometer at 70 ev, using a direct probe with a source temperature of 150—200°.

While this rearrangement is not important in simple dialkylnitrosamines,[1] its occurrence in the spectrum of *N*-nitroso-*N*-benzylaniline is suggested by the presence of an ion at *m/e* 167.

Curiously, relatively minor structural alterations in the dibenzyl series have a pronounced effect on whether or not the $M-45$ ion is observed. For example, neither (II) or (III) shows any proclivity towards the elimination of a hydrogen atom and nitrous oxide.

Finally, it may be noted that the fragmentation of dibenzylnitrosamines to give a $C_{14}H_{13}^+$ ion is similar to that of tribenzylamines, which have been found[2] also to rearrange with the formation of this ion.

(*Received, October 5th,* 1967; *Com.* 1058.)

[1] J. Collin, *Bull. Soc. Roy. Sci. Liège,* 1954, **23** 201; S. S. Dubov and A. M. Khokhlova, *Zhur. obshchei Khim.*, 1964, **34**, 1961.

[2] K. Biemann, Abstracts of 13th Annual Conference on Mass Spectrometry, ASTM Committee E-14, St. Louis, Mo., 1965, p. 427.