SHORT COMMUNICATION

Synthesis and Thermal Decomposition of 2,2′-Diazido-2,2′-azoadamantane

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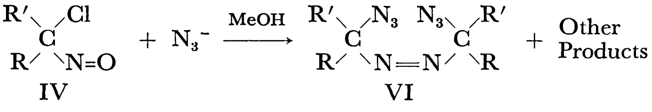
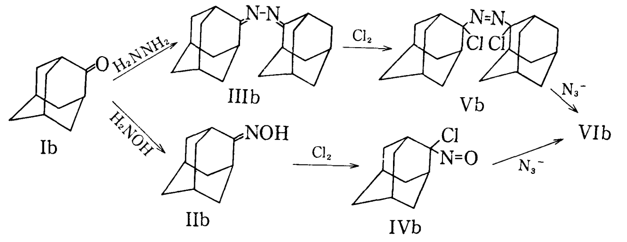
During the couse of our investigation of the reaction of 1,1-chloronitrosocyclohexane (IVa) with azide ion,[3] we have identified 1,1′-diazido-1,1′-azocyclohexane (VIa) as one product of a very complex reaction mixture. The reported explosive nature of the corresponding isopropyl analogue (VIc)[4] and our hope to reduce the number of products formed led us to utilize 2-chloro-2-nitrosoadamantane (IVb)[5] as a substrate with azide ion. As expected, the number of products decreased drastically[6] and 2,2′-diazido-2,2′-azoadamantane (VIb), mp 164°C (decomp.), was isolated as yellow crystals. It exhibited a strong azide absorption at 2080 cm^{-1} and was conclusively identified by its elemental analysis and by comparison with an authentic sample prepared from 2,2′-dichloro-2,2′-azoadamantane (Vb).[7]

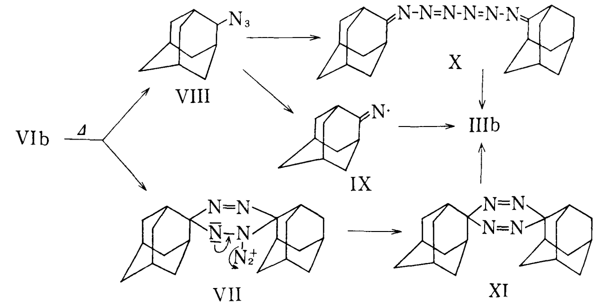


$$R'(R)C(Cl)N{=}O + N_3^- \xrightarrow{MeOH} R'(R)C(N_3){-}N{=}N{-}C(N_3)R'(R) + \text{Other Products}$$

a) R, R′ = $-(CH_2)_5-$
b) R, R′ = 2-adamantyl
c) R, R′ = CH_3



The presence of two functional groups capable of eliminating nitrogen prompted us to investigate the behavior of VIb on pyrolysis.[4] A solution of VIb in 1,2-dichlorobenzene at reflux smoothly evolved nitrogen as it gradually changed from yellow to colorless. Evaporation of the solution gave an 88% yield of a colorless solid, mp >300°C, which was identified as adamantanone azine (IIIb). Since α,α'-diazidoazoalkanes (VI) can be regarded as "formal" dimerization products of α-azidonitrenes, it is interesting to contrast our results with the fact that in all the decompositions of *gem*-diazides studied so far,[8] only in one case was azine reported as a minor product; an α,α'-diazidoazoalkane (VI) was suggested as a possible precursor to the azine.[9] Although mechanistic studies have yet to be carried out, one may speculate that rupture of the azo linkage would yield radical VIII which can eliminate to the ketimino radical (IX) or couple to give the hexazatetraene (X), both of which could lead to the azine by coupling or further loss of nitrogen respectively. Alternatively, internal "displacement" a nitrene intermediate (VII) on the neighbouring azide could lead to the cyclic bis azo compound XI, thence to IIIb.



We are presently investigating the scope and the mechanism of the decomposition of α,α'-diazidoazoalkanes.

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[3] The origin of the α,α'-diazidoazoalkanes is still not completely clear. One possible reaction path might involve the *dimeric* nitroso compounds; this will be discussed as part of the report of our investigation of *gem*-chloronitroso compounds with azide ion.

[4] Authentic VIa was prepared by the reaction of azobis(1-chlorocyclohexane) with azido ion; E. Benzing, *Ann.*, **631**, 1 (1960).

[5] Mp 161—163°, prepared in 95% yield as shown in the equation. Since the completion of this work, the preparation and photolysis of IVb has been reported by A. H. M. Kayen, L. R. Subramanian and Th, J. DeBoer, *Rec. Trav. Chim. Pays-Bas*, **90**, 866 (1971). We wish to thank Prof. DeBoer and Dr. Kayen for informative correspondence.

[6] Glc examination of the product mixture of the reaction of *gem*-chloronitrosocyclohexane with azide ion revealed the presence of at least thirteen components. The presumption was that the presence of α-hydrogens was in large part responsible for the complexity of the reaction. This presumption was confirmed by the fact that in addition to nitrous oxide (formed as a major product), only five solid products were formed. They were identified as 2,2′-diazidoadamantane, 2,2′-dichloroadamantane, 2-chloro-2-nitroadamantane, adamantanone and VIb.

[7] 2,2′-Diazido-2,2′-azoadamantane (VIb) was obtained in 70% yield (from ethanol). So far as we have been able to determine, it dose not display the explosive properties reported for VIc; a correct elemental analysis was obtained routinely. However, we *urge all due caution* because no detailed study of its properties has been performed.

[8] F. D. Lewis and W. H. Saunders in "Nitrens", ed. by W. Lwowski, Interscience Publisher, New York, N. Y. (1970), p. 47.

[9] G. Ege and G. Joos, *Chem. Zeitung*, **94**, 215 (1970). These investigators have isolated benzophenone azine in 4% yield from the photolysis of diphenylazidomethane in acetone.