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THE REACTION OF 1-ARYL-3-ALKYLTRIAZENES WITH POSITIVE HALOGEN COMPOUNDS

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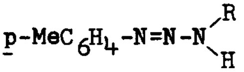
Abstract: The title reaction forming arylnitrenes is described; these intermediates react in triplet state only.

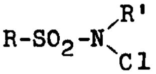
In this paper we report the reaction of 1-aryl-3-alkyltriazenes with positive halogen compounds which has not been described hitherto. However, 1,3-diphenyltriazene was used[1] as radical source in reactions with 3 and other halogenating agents; besides, 1,3-diaryltriazenes react[2] with lead tetraacetate generating arylnitrenes and aryl radicals as intermediates.



$p\text{-MeC}_6\text{H}_4\text{-N=N-N}\begin{smallmatrix}\diagup R\\ \diagdown H\end{smallmatrix}$

1

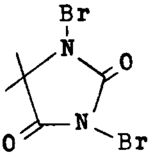
a, R= Me; b, R= Et
c, R= Pr; d, R= i-Pr



$\text{R-SO}_2\text{-N}\begin{smallmatrix}\diagup R'\\ \diagdown Cl\end{smallmatrix}$

2

a, R= Me; R'= PhCH$_2$
b, R= p-MeC$_6$H$_4$; R'= Me



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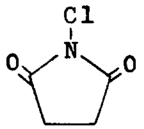

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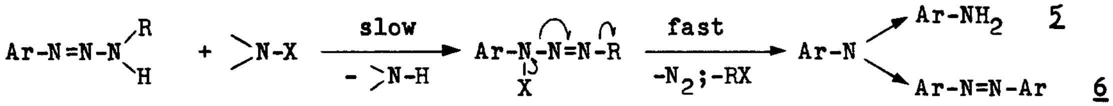
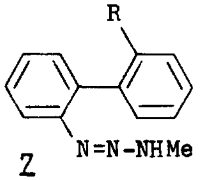
A solution of 1d and 2a (1 mmole each) in anhydrous dioxane (2 ml) was heated at 50º for 6 hr; gas evolution occurred. Iodometric analysis of positive chlorine showed that the reaction was complete. After removal of the solvent the residue (in C$_6$H$_6$) was successively extracted with aqueous NaOH and HCl to give fractions of acidic, basic and neutral products; usual work-up and crystallisation afforded, respectively, N-benzylmethanesulphonamide (72%), p-toluidine (as picrate, 25%) and p-azotoluene (35%) which were identified with authentic samples by m.p., mixed m.p. and IR spectra.

Similar results were obtained with the triazenes 1a-c and the positive halogen compounds 2b, 3 and 4 in the same or other non-protic solvents(CCl$_4$, CHCl$_3$, C$_6$H$_6$). As compound 3 reacts vigorously at 50º it is recommendable to operate at 0º; N-chloro-N-methylacetamide, with a "less positive" halogen, reacts very slowly even at 80º. In a reaction of 1a and 3 in CCl$_4$ (stream of N$_2$), a volatile fraction was collected in CCl$_4$. NMR spectra of this solution showed the presence of CH$_3$Br and CH$_3$Cl (4:1); treatment with sodium 4-nitrophenoxide in DMF gave 4-nitroanisole, m.p. and mixed m.p. 54-55º. Experiments with 1a and 2a in $CDCl_3$ were monitored in a NMR probe over two half-lives; reactants and products (N-benzylmethanesulphonamide taken as 100%; CH_3Cl 67%; p-toluidine 36%; p-azotoluene 62%) were observed but no intermediates could be detected.

The above results are reasonably explained in the following scheme which includes two very common reactions of arylnitrenes[3] (Ar-N).

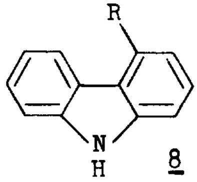


The new triazenes 7a (m.p. 69-70°) and 7b (m.p. 72-73°), prepared by a known method,[4] were characterised by analytical, IR and NMR data. Both triazenes were treated under argon with 2b at 40° in benzene solution (0.67 M) and at 180° in 1,2-dichlorobenzene solution (0.014 M) giving similar results; no significant changes occurred by irradiation with a Hg lamp. The products were fractionated as above; the N-methyl-p-toluenesulphonamide was isolated in 65-82% yield. TLC examination of the basic and neutral fractions from 7a and 7b showed the corresponding compounds 5 and 6; in addition, phenanthridine was formed with 7b. Carbazoles 8 were not detected.



7

a, R= H
b, R= Me



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The formation of the amines 5 and phenanthridine, and the absence of carbazoles 8 support the triplet state for the reacting nitrenes. It is noteworthy that the same nitrenes when generated from azides, afford carbazoles (singlet products) even under conditions favouring the formation of triplets.[3]

References:

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