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A NOVEL DECOMPOSITION OF 3-ALKYL-1-PHENYLTRIAZENES CATALYZED BY SILICA GEL

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Treatment of 3-alkyl-1-phenyltriazene (I) with protic acid HX gives aniline and RX under evolution of nitrogen (1), while pyrolytic decomposition induces homolysis of I into anilino and alkyl radicals (2). Further type of cleavage of I has now been disclosed to occur in the presence of silica gel.

$$\underset{\text{I}}{\text{Ar-N=N-NH-R}} \rightleftharpoons \underset{\text{Ia}}{\text{Ar-NH-N=N-R}} \longrightarrow \underset{\text{II}}{\text{Ar-NH}_2} + \underset{\text{III}}{\text{Ar-NHR}} + \text{R-Ar}'\text{-NH}_2 + \text{R-OH}$$

A 10% solution of I (Ar = Ph, R = Me) (3) in benzene was added to a stirred suspension of silica gel (4) in benzene at room temperature. The decomposition was instantaneously completed under evolution of one molar equivalent of nitrogen. From the reaction mixture aniline (61%) and N-methylaniline (36%) were obtained. Other triazenes behaved similarly, and the results are given in the order of Ar and R in I, yield (%) of II and III: Ph, Et, 70, 30; Ph, n-Bu, 80, 20; Ph, i-Bu, 87, 13; *o*-tolyl, Me, 58, 42; *p*-tolyl, Me, 60, 40; Ph, cyclohexyl, 47, 32; Ph, $PhCH_2$, 21, 34; *o*-tolyl, $PhCH_2$, 25, 43; Ph, PhCH(Me), 23, 40 (5). Isomerization of the R group was observed with 3-isobutyl-1-phenyltriazene which yielded N-isobutyl- and N-*s*-butylanilines in a ratio of ca. 3:2 as determined by NMR. Migration of R group occurred when 3-cyclohexyl-1-phenyltriazene reacted to give *o*-cyclohexylaniline (7%) along with cyclohexanol (14%) and the normal products. The intramolecular nature of the reaction was established, when an equimolar mixture of 3-ethyl-1-phenyltriazene and 3-methyl-1-*p*-tolyltriazene gave no crossed products such as N-ethyl-*p*-toluidine and N-methylaniline upon the same treatment in benzene. Reaction of 3-benzyl-1-phenyltriazene afforded higher yield of benzyl alcohol (33%) along with II and III mentioned above and *o*-benzylaniline (7%)(6).

The recombination of R group with anilino group was found to occur under retention of configuration of the α-carbon of the R group. Thus, (S)-3-α-phenethyl-1-phenyltriazene ($[\alpha]_D$ -132°) gave (S)-N-(α-phenethyl)aniline (42%) ($[\alpha]_D$ +3.5°) and (S)-*o*-(α-phenethyl)aniline (15%) ($[\alpha]_D$ +13.5°), whereas the (R)-enantiomer ($[\alpha]_D$ +132°) afforded (R)-N-(α-phenethyl)aniline (36%) ($[\alpha]_D$ -3.0°) and (R)-*o*-(α-phenethyl)aniline (15%) ($[\alpha]_D$ -13.2°), respectively. (+)-α-Phenethyl alcohol (24%) ($[\alpha]_D$ +5.4°) produced from the (R)-triazene also proved to have the same configuration as the starting material (7).

The configuration of N-α-phenethylaniline was determined by preparing an authentic (S)(+)-amine ($[\alpha]_D$ +5.2°) by reaction of (S)(-)-α-phenethylamine ($[\alpha]_D$ -32.0°) with benzyne as produced by the method of Wittig (8). The recovered phenethylamine showed the unchanged activity. The (S)-configuration of (+)-*o*-(α-phenethyl)aniline was established by conversion of the amine into a phenol and the following ozonolysis to (S)(+)-hydratropic acid ($[\alpha]_D$ +26.5°) (9).

The precise function of silica gel is not known yet. However, the true mechanism should explain the additional facts:

(1) Neither biaryls nor diarylamines were detected among the products, therefore, a *free* radical path may be ruled out.

(2) No *p*-alkylated anilines have been isolated.

(3) In the strongly coordinating solvents such as alcohol and ether, the reaction was entirely suppressed.

(4) 1,3-Diphenyltriazene and 3,3-dialkyl-1-phenyltriazene did not decompose under the present reaction condition. These triazenes are probably fixed as Ph-N=N-N< type.

Based on these observations we tentatively favour a mechanism which involves an intimate ion pair of anilino and carbonium ions for the recombination.

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(2) Houben-Weyl, *Methoden der organischen Chemie*, Bd. X/3, 731 (1965).

(3) O. Dimroth, *Ber.*, **38**, 2328 (1905). In benzene I was resistant to heat up to 80° or UV irradiation at room temperature. The recorded reactions indicate that the tautomeric equilibrium favours the form Ia. Since the exact position of the equilibrium has not been determined yet, the nomenclature follows the convention adopted in the literature. Ref. 2, p. 700.

(4) Mallincrodt "Silicic Acid" AR, 100 mesh.

(5) Each component was obtained by preparative GLC or silica gel chromatography and identified by comparison of GLC retention time, IR and NMR. They also gave correct analyses for carbon and hydrogen.

(6) A trace amount of diphenylmethane was detected in this case.

(7) E. L. Eliel, *Stereochemistry of Carbon Compounds*, McGraw-Hill, New York, 1962, p. 96. The starting materials, optically active α-phenethylphenyltriazenes, were prepared from benzenediazonium chloride and respective active α-phenethylamine. The configuration of the triazene is self-evidently identical with that of the amine.

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