Tetrahedron Letters No. 9, pp 623 - 626, 1973. Pergamon Press. Printed in Great Britain.

ON DIAZENE-HYDRAZONE REARRANGEMENT

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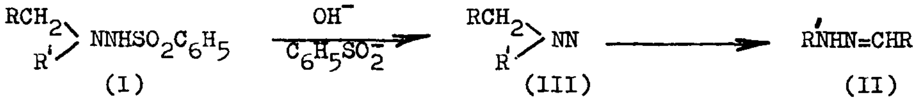
(Received in UK 16 November 1972; accepted for publication 4 January 1973)

Monosubstituted hydrazones (II) obtained by alkali **fission** of 1,1-dialkylsulphoacid hydrazides (I) have been considered products of isomeric transformation of the intermediate reactive aminonitrenes (III)[1-3]:



$$\mathrm{RCH_2(R')NNHSO_2C_6H_5} \xrightarrow[\mathrm{C_6H_5SO_2^-}]{\mathrm{OH^-}} \mathrm{RCH_2(R')NN} \longrightarrow \mathrm{R'NHN{=}CHR} \quad (1)$$

Mechanism of the so called diazene-hydrazone rearrangement attracted special attention[1,4]. Since the migration of the alkylidene fragment RCH suggested therein, has no analogy further investigation of the reaction appears necessary.

The initial assumption of the eventual **carbonium** migration leading to formation of an azo compound which later undergoes isomerization into a hydrazone, was ruled out on the ground that azo compounds isomerization was incomplete under diazene-hydrazone rearrangement conditions and azo compounds were not found among the reaction products[1].

This argumentation seems rather doubtful if previously reported data on hydrazone $\rightleftarrows$ azo equilibrium is taken account of [5]. The equilibrium concentrations of azo compounds being not negligible, they would have been found in the reaction mixtures alongside with hydrazones, if even the latter result immediately from aminonitrenes.

Liquid and gaseous products obtained by heating of 1,1-dialkylhydrazides of benzene sulphonic acid at 120° in 9% diethylene glycol solution of KOH[*], were analysed by GLC in order to get more detailed data on alkali splitting of sulphoacids hydrazides. Obtained information (see table 1) indicates the formation of disubstituted hydrazones and hydrocarbons as well as monoalkylhydrazones. The former were reported to be products of a double exchange between intermediate aminonitrenes and initial sulphonylhydrazines [6,7]. It is important to note that presence of azo compounds which were isomeric with monoalkylhydrazones, was observed. Exact determination of hydrazone : azo concentration ratio in non-equilibrium reaction mixtures might clarify the mechanism of rearrangement (1). If the aminonitrene isomerization passes through the stage of azo compounds formation, the non-equilibrium concentration of the latter is to exceed the equilibrium one. If the azo compounds are secondary products of hydrazone isomerization, their content in the reaction mixtures is not. Azo : hydrazone equilibrium constants K were precisely measured under conditions of hydrazides decomposition at 120° in diethylene glycol solution of KOH (9%) for the sets that follow: azoethane - ethanal ethylhydrazone and azopropane - propanal propylhydrazone. In each case equilibrium was established within 20-30 min from both sides, K being 0.026 and 0.074 ± 0.002, respectively.

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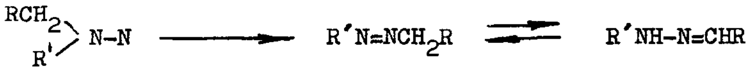
[*] Hydrazide (0.01 mole), KOH (0.03 mole) and 15 ml of diethylene glycol were heated while gas was being evolved. The total heating period averaged 1.5 h. The liquid products were analysed by JEOL-620 chromatograph equipped with a 2 m column packed with celite 545 (60-80 mesh), a 15% multicomponent stationary phase (apiezone L 73%, tripropionitrile amine 21.5 , polyethylenepropyle amine 0.5% polyethylene glycol-400 5%) in the current of nitrogen at 80°. Propanol and butanol served internal standards. The gaseous hydrocarbons were analysed in a 2 m column packed with 30% saturated solution of $AgNO_3$ in diethylene glycol upon TNDM (40-60 mesh) at room temperature (chromatograph Tswett 4).

Table 1

Yield of Hydrazide $\genfrac{}{}{0pt}{}{RCH_2}{R'}\!\!>NNHSO_2C_6H_5$ Fission Products (mol %)

Compounds	R' = RCH$_2$			
	C_2H_5	C_3H_7	i-C_4H_9	i-C_3H_7
R'NH-N=CHR	56.3	59.4	54.4	11.2
$(RCH_2)_2$N-N=CHR	11.1	16.3	15.2	5.7
R'H	8.2	12.8	10.5	5.2
RCH_2R'	traces	1.2	2.7	6.4
RCH_2N=NR'	4.7	6.2	4.9	1.2
RCH_2NN=NNR'	-	traces	1.3	25.5
RCH_2NHR'	1.2	1.8	3.3	30.7
RNH_2	1.4	1.0	0.9	6.3
RCN	1.1	1.3	-	-

Non-equilibrium concentration of azo compounds and hydrazones at hydrazide decomposition (I) were determined after heating them at 120° in the above alkali solutions for 3 min, rapid cooling with ice water, and solid carbon dioxide addition to the reaction mixture. Azo : hydrazone ratio in the decomposition products appeared to be equal to 0.056 for diethylhydrazide (I) and 0.127 for dipropylhydrazide, thus being 1.5 or 2 times greater than the corresponding K values. The discrepancies observed are beyond the limits of possible analysis errors and show azo compounds to be precursors of monoalkylhydrazones in the reaction (1), hence primary products of aminonitrenes isomerization:



$$\genfrac{}{}{0pt}{}{RCH_2}{R'}\!\!>N-N \longrightarrow R'N{=}NCH_2R \rightleftharpoons R'NH-N{=}CHR \qquad (2)$$

New evidence supporting formation of non-saturated azo compounds as primary products of sigmatropic rearrangement of allylsubstituted aminonitrenes at oxidation of allylhydrazine was recently reported [8]. Still the question whether or not simultaneous formation of hydrazone from aminonitrenes by a different reaction mechanism is possible, remains open.

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