Tetrahedron Letters No.2, pp. 263-267, 1966. Pergamon Press Ltd.
Printed in Great Britain.

REACTIONS OF SULFENES WITH DIAZOMETHANE

S.Rossi and S.Maiorana

Istituto di Chimica Industriale della Università di Milano

(Received 24 November 1965)

The existence of sulfenes as reactive intermediates has been conclusively demonstrated (1) and the synthesis of some episulfones from sulfenes and aliphatic diazo-derivatives has recently been reported (2). In the course of a research project on sulfene chemistry (3) we have investigated the reaction of p.nitro-benzyl-sulfonyl-chloride (I-a) with excess diazomethane in ethereal solution. Two products were obtained from the reaction mixture and were separated by benzene extraction at 30°C. The benzene soluble fraction furnished a solid, melting at 63°C, which underwent spontaneous decomposition at room temperature yielding sulfur dioxide and p.nitro-styrene (V-a). Owing to its instability this product could not be studied further but its chemical and spectroscopic properties (I.R. absorption bands at 3080, 1350 and 1160 cm^{-1}) were consistent with the expected structure of p.nitrophenyl-ethylene-sulfone

(IV-a). The benzene-insoluble fraction was present in the mixture in smaller quantities and it furnished a solid melting at 170°C (from acetic acid) containig sulfur and nitrogen. To this product was assigned the structure of 5-p.nitrophenyl, Δ-4 1,3,4 thiadiazoline 1,1-dioxide (VI-a) according to the following evidence :

a) - Elemental microanalysis and molecular weight determination gave results in agreement with the empirical formula: $C_8H_7N_3O_4S$.

b) - The I.R. spectrum contained absorption bands corresponding to an imino group (3250 cm^{-1}) and to a sulfone group (1300 and 1130 cm^{-1}).

c) - The N.M.R. spectrum (in deuterated dimethyl sulfoxide with tetramethylsilane as an internal standard) showed a singlet signal at 5.07 τ ($-CH_2-$), two doublets at 2.06 and 1.64 τ (aromatic protons) and an enlarget singlet at 0.39 τ (-NH-).

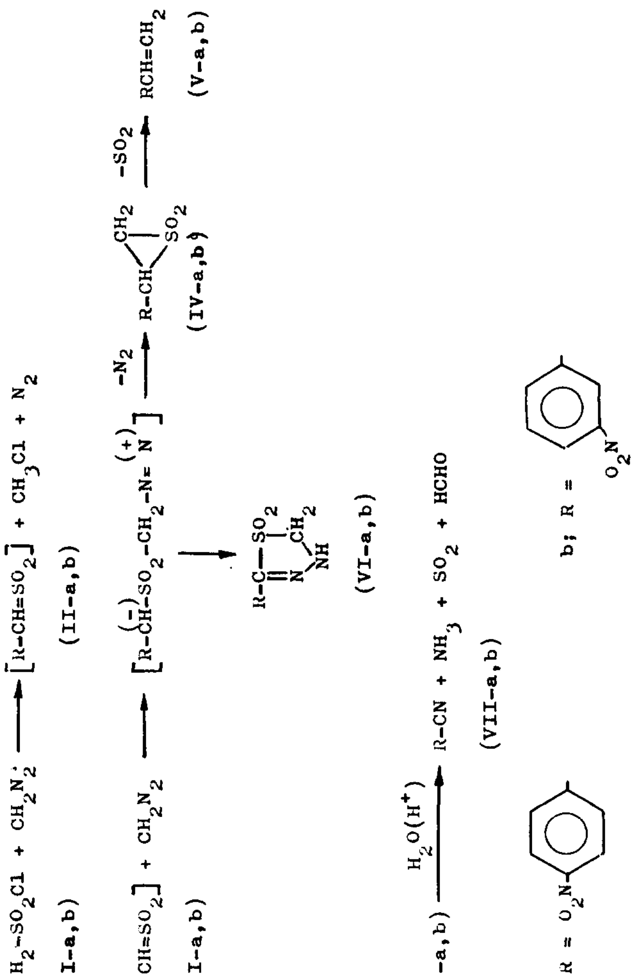
d) - On hydrolysis with hydrochloric acid in acetic acid solution ammonia, formaldehyde, sulfur dioxide and p.nitrobenzonitrile (VII-a) were produced. Sulfur dioxide and p.nitrobenzonitrile were also identified among the products of pyrolysis obtained by heating (VI-a) above its melting point.

e) - Benzoylation with benzoyl chloride in pyridine afforded the corresponding N-benzoyl-derivative (M.P. 182°C - acetic acid) whose analytical and spectroscopical features were in accord with theory.

From the reactions of m.nitro-benzyl-sulfonyl chloride (I-b) with excess diazomethane in ethereal solution two products were also obtained: the first of them (IV-b) (soluble in chloroform - M.P. 60°C) decomposed quickly at room temperature yielding sulfur dioxide and m.nitro-styrene (V-b). The second one (M.P. 140°C from ethanol) was assigned the structure of 5-m.nitrophenyl, Δ-4 1,3,4-thiadiazoline 1,1-dioxide (VI-b) on the strength of chemical and physico-chemical evidence similar to that reported for the p.nitro-isomer (VI-a).

The above illustrated results can be rationalized considering the transformations outlined in CHART 1. Sulfenes (II) are originally formed by reaction of sulfonyl-chlorides (I) with one molecule of diazomethane. Subsequently sulfenes add to a second mole of diazomethane and the addition intermediates (III) may further evolve to epi-sulfones (IV), by loss of nitrogen, or to thiadiazoline-dioxide (VI) by cyclization. The above illustrated experiments confirm that the reaction of sulfenes with diazomethane may simultaneously develop along two independent pathways only one of which (epi-sulfones formation) has already been described (2-4); and that thiadiazoline

CHART 1


R-CH2-SO2Cl + CH2N2 → [R-CH=SO2] + CH3Cl + N2
(I-a,b)
(II-a,b)
[R-CH=SO2] + CH2N2 → [R-CH(-)-SO2-CH2-N≡N(+)]
(II-a,b)
-N2
R-CH CH2 SO2
(IV-a,b)
-SO2
RCH=CH2
(V-a,b)
R-C—SO2 N NH CH2
(VI-a,b)
(VI-a,b)
H2O(H+)
R-CN + NH3 + SO2 + HCHO
(VII-a,b)
a; R = O2N
b; R = O2N

derivatives (°) are not to be considered as intermediates in this reaction .

Work on this subject is still in progress and full details will be published elsewhere.

Aknowledgment - This work was supported in part by the Italian Research Council (Consiglio Nazionale delle Ricerche).

R E F E R E N C E S

(1) - J.F.King and T.Durst - J.Am.Chem.Soc. 86-287-(1964).
W.E.Truce,R.W.Campbell and J.R.Norell -
- J.Am.Chem.Soc. 86-288-(1964).

(2) - G.Opitz and K.Fischer- Angew.Chem. 77-40-(1965).

(3) - R.Fusco, S.Rossi, S.Maiorana and G.Pagani -
- Gazz.Chim.Ital. 95-774-(1965).

(4) - G.Hesse, E.Reichold and S.Majmudar -
- Ber. 90-2106-(1957).
H.Staudinger and F.Pfenninger -Ber.49-1941-(1916).
L.V.Vargha and E.Kovács - Ber. 75-794-(1942).

(5) - G.Hesse and G.Reichold - Ber. 90-2101-(1957).

(°) - From the reaction of ethyl-cyclohexyl-diazomethane with sulfur dioxide Hesse and Reichold (5) obtained 2,5-diethyl,2,5 dicyclohexyl 1,3,4 thiadiazoline 1,1-dioxide which, however, could be pyrolyzed only at 240°C producing diethyl, dodecahydro stilbene in very low yields.