

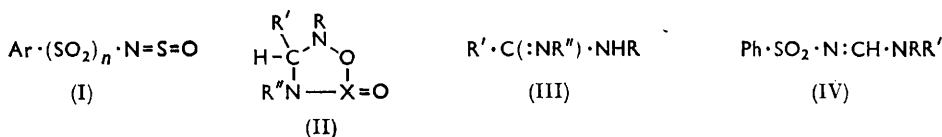
2640 Reactions of Nitrones with *N*-Sulphonylbenzenesulphonamide.505. Reactions of Nitrones with *N*-Sulphonylbenzenesulphonamide.

By B. P. STARK and M. H. G. RATCLIFFE.

Nitrones react with *N*-sulphonylbenzenesulphonamide under mild conditions, sulphur dioxide being eliminated. *CN*-Diphenylnitronone yields *N*-benzenesulphonyl-*N'**N'*-diphenylformamidine; other *N*-phenylnitrones appear to react in a similar manner, whereas the reaction of *N*-methyl-*C*-phenylnitronone follows a different course.

N-SULPHINYL COMPOUNDS (I; $n = 0$ or 1) behave as dienophils in the Diels–Alder reaction,¹ and undergo 1,2-addition to certain carbonyl compounds;^{2,3} *N*-sulphonylaniline (I; Ar = Ph, $n = 0$) reacts as a 1,3-dipolarophil with diphenylnitrilimine⁴ and with benzonitrile oxide.⁵ The adduct which is formed by benzonitrile oxide decomposes at 100° to form sulphur dioxide and diphenyl carbodi-imide.⁵ Nitrones, which can behave as 1,3-dipolar reagents,⁶ react with phenyl isocyanate to give adducts (II; R'' = Ph, X = C) which decompose when they are treated with sodium alkoxide, forming amidines (III; R'' = Ph) and carbon dioxide.⁷

We have studied the reaction of various nitrones with *N*-sulphonylbenzenesulphonamide (I; Ar = Ph, $n = 1$), and have found that *CN*-diphenylnitronone reacts (in ether, at 20–35°) to form sulphur dioxide and *N*-benzenesulphonyl-*N'**N'*-diphenylformamidine (IV; R = R' = Ph). The last compound can also be formed⁸ by reaction of benzenesulphonamide with diphenylformamide in the presence of thionyl chloride; it is possible that in this reaction *N*-sulphonylbenzenesulphonamide is first formed¹ and then reacts² with the formamide. The infrared and nuclear magnetic resonance spectra of the product



formed from *CN*-diphenylnitronone support the acyclic structure (IV; R = R' = Ph). Certain other diarylnitrones (the *C*-9-anthryl-*N*-phenyl, *C*-*p*-methoxyphenyl-*N*-phenyl, and *C*-2-furyl-*N*-phenyl compounds) react with *N*-sulphonylbenzenesulphonamide to form sulphur dioxide and products whose infrared spectra are similar to that of the formamidine (IV; R = R' = Ph). In contrast, *N*-methyl-*C*-nitronone gives, besides sulphur dioxide, a product (C₁₄H₁₄N₂O₂S) which has m. p. 130–132°, and which is therefore not the known formamidine (IV; R = Me, R' = Ph; m. p. 105–106°).⁸ It is believed, on the basis of the elementary analysis and infrared spectrum of this compound, that the product is a benzamidine (III; R' = Ph, R and R'' = Me and SO₂·Ph). Since the compound dissolves in concentrated hydrochloric acid and can be recovered unchanged by treatment of the solution with alkali, the alternative possible diaziridine structure appears unlikely.

It is suggested that adducts (II; R'' = SO₂·Ph, X = S) are first formed and then lose sulphur dioxide, either to form the final products directly, or to form diaziridines which

¹ Wichterle and Roček, *Chem. Listy*, 1953, **47**, 1768; Kresze, Maschke, Albrecht, Bederke, Patzschke, Smalla, and Trede, *Angew. Chem., Internat. Edn.*, 1962, **1**, 89; Houben-Weyl, "Methoden der organischen Chemie," Georg Thieme, Stuttgart, 1958, Vol. 11/2, p. 738; Kataev and Plemenkov, *Zhur. obshchei Khim.*, 1962, **32**, 3817; Levchenko, Bal'on, and Kirsanov, *ibid.*, 1963, **33**, 1579.

² Kresze and Albrecht, *Angew. Chem., Internat. Edn.*, 1962, **1**, 595.

³ Beeken and Korte, *Tetrahedron*, 1962, **18**, 1527.

⁴ Huisgen, Grashey, Seidel, Knupfer, and Schmidt, *Annalen*, 1962, **658**, 169.

⁵ Rajagopalan and Daeniker, *Angew. Chem., Internat. Edn.*, 1963, **2**, 46.

⁶ Huisgen, *Proc. Chem. Soc.*, 1961, 357; *Chem. Weekblad*, 1963, **59**, 89; *Angew. Chem., Internat. Edn.*, 1963, **2**, 565, 633.

⁷ Grashey, Huisgen, and Leitermann, *Tetrahedron Letters*, 1960, No. 12, 9; Beckmann, *Ber.*, 1894, **27**, 1957.

⁸ Tosolini, *Chem. Ber.*, 1961, **94**, 2731.

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may then yield acyclic products. A formamidine (IV; R = Ph) would result by migration of an organic group (R') from carbon to nitrogen, whereas migration of a hydrogen atom would lead to the formation of a benzamidine.

The bisnitronone $\text{PhN(O):CH}\cdot\text{CH:N(O)Ph}$ (obtained from phenylhydroxylamine and glyoxal) reacted with two molar equivalents of *N*-sulphonylbenzenesulphonamide, two moles of sulphur dioxide being eliminated.

EXPERIMENTAL

A solution of *N*-sulphonylbenzenesulphonamide (10.15 g., 0.05 mole) in ether (150 ml.) was added dropwise to a suspension of *CN*-diphenylnitronone (9.85 g., 0.05 mole) in ether (200 ml.); the mixture was stirred for 30 min. at room temperature, then heated under reflux for a further 30 min., and cooled. The solid filtered off was recrystallised from ethanol. The reactions with other nitronones were carried out similarly, two molar equivalents of $\text{PhSO}_2\cdot\text{NSO}$ being used with the bisnitronone $\text{PhN(O):CH}\cdot\text{CH:N(O)Ph}$; the results are in the Table.

Reaction of nitronones with $\text{PhSO}_2\cdot\text{NSO}$.

Nitronone	Product		Analysis (%)				
	(yield)	(m. p.)	C	H	N	O	S
<i>CN</i> -diphenyl	50%	187—189°	Found: 67.66 Calc.: * 67.70	4.97 5.08	8.17 8.31	9.64 9.45	9.72 9.52
<i>C</i> -9-anthryl- <i>N</i> -phenyl	60%	238—240	Found: 74.50 Calc.: * 74.29	4.80 4.62	6.42 6.42	7.33 7.32	7.42 7.35
<i>C</i> - <i>p</i> -methoxyphenyl- <i>N</i> -phenyl	55%	112—113.5 †					
<i>C</i> -2-furyl- <i>N</i> -phenyl	20%	140—141.5 †					
<i>N</i> -methyl- <i>C</i> -phenyl	70%	130—132	Found: 61.05 Calc.: * 61.28	5.23 5.14	10.18 10.21		11.42 11.69
PhN(O):CH	5%	185—186	Found: 60.01 Calc.: * 60.24	3.93 3.38	10.50 10.80	12.49 12.35	12.15 12.37

* Values calculated by assuming that one molecule of SO_2 is lost per molecule of $\text{PhSO}_2\cdot\text{NSO}$ used.

† These compounds were very sensitive to air and could not be obtained analytically pure.

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