Tetrahedron Letters No.36, pp. 3877-3880, 1968. Pergamon Press. Printed in Great Britain.

STUDIES OF N-SULFINYL COMPOUNDS. II.(1)

REACTION OF N-SULFINYLANILINES WITH CYCLIC NITRONES

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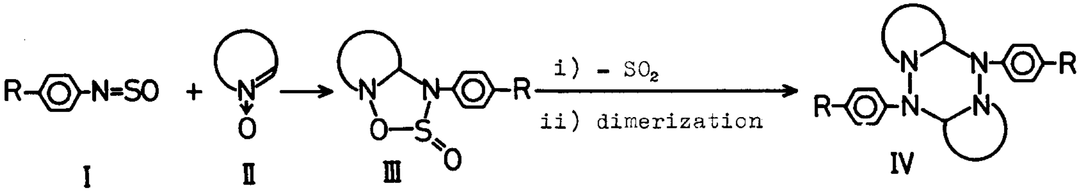
(Received in Japan 23 May 1968; received in UK for publication 7 June 1968)

It is well known that N-sulfinylaniline reacts as a 1,3-dipolarophil with benzonitril oxide(2) and with diphenylnitrilimine.(3) Stark and Ratcliffe(4) reported that N-sulfinylbenzenesulfonamide reacted with CN-diphenylnitrone to give N-benzenesulfonyl-N,N'-diphenylformamidine under the elimination of sulfur dioxide and migration of the phenyl group from carbon to nitrogen. Recently, we found that N-sulfinylanilines (I) reacted with ethylenecarbonate under the influence of lithium bromide or tetraethylammonium bromide to afford the corresponding N,N'-diarylpiperazines.(1)

Consequently, it may be expected that I reacts with cyclic nitrones (II), which can behave as 1,3-dipolar reagents,(5) to give either bicyclic 1,2,3,5-thioxadiazoline 1-oxide (III), or tricyclic tetrazine compound (IV) by the dimerization of the intermediate which is formed under the subsequent elimination of sulfur dioxide from III (Scheme 1).



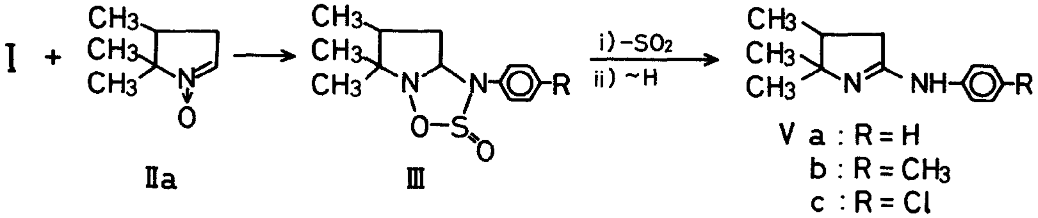
Scheme 1

After a solution of 0.01 mole of I in 30 ml of ether was added dropwise to a solution of 0.01 mole of 4,5,5-trimethyl-Δ^1-pyrroline 1-oxide (IIa) in 20 ml of ether in a dry ice-acetone bath over a period of 30 min, the reaction mixture was allowed to stand at room temperature for 1 hr: sulfur dioxide was evolved very slowly during this time. Evaporation of the mixture in vacuo and chromatography of the residue on active alumina afforded the corresponding 2-anilino-4,5,5-trimethyl-Δ^1-pyrroline as colorless prisms respectively in a fairly good yield. Va (R=H): m.p. 144-145°C, yield 74%; Vb (R=CH_3): m.p. 124°C, yield 54%; Vc (R=Cl): m.p. 157°C, yield 90%.

The structure of V was confirmed by elemental analysis and spectral evidences. For instance, spectral data of Va are as follows.

Mass spectrum: m/e M^+=202. IR: 3180 (NH), 1660 cm^{-1} (C=N). NMR in $CDCl_3$ τ : 8.95 (9H, 3 CH_3, multiplet), 7.60 (3H, CH_2 and CH, multiplet), 3.90 (1H, NH, broad peak), 2.70 (5H, aromatic protons, multiplet).

No other products were isolated, but it is evident that the probable 1:1 adduct (III) underwent ring opening under the elimination of sulfur dioxide (Scheme 2).



Scheme 2

The reaction of I with 2,5,5-trimethyl-Δ^1-pyrroline 1-oxide (IIb) was investigated under various conditions. In a typical run, a mixture of 10 ml of Ia and 0.01 mole of IIb was allowed to stand at -9∼-12°C for several days and then the reaction mixture was evaporated in vacuo. The benzene solution of the residue was chromatographed on active alumina to afford reddish orange prisms (VIa), m.p. 117-118°C, in ca. 10% yield and yellow prisms (VII), m.p. 234°C (dec), in a trace amount, together with a large amount of resinous material.

The compound VIa was in agreement with the formula $C_{13}H_{16}ON_2S$ (m/e M^+=248), which was equivalent to the compound derived from an 1:1 adduct of Ia and IIb by dehydration. As is illustrated in Fig. 1, the NMR spectrum in $CDCl_3$ shows signals at τ 8.52 (6H, 2 CH_3), 8.04 (2H, CH_2), 6.78 (2H, CH_2), 2.8-2.0 (5H, aromatic protons) and -4.75 (1H, NH).

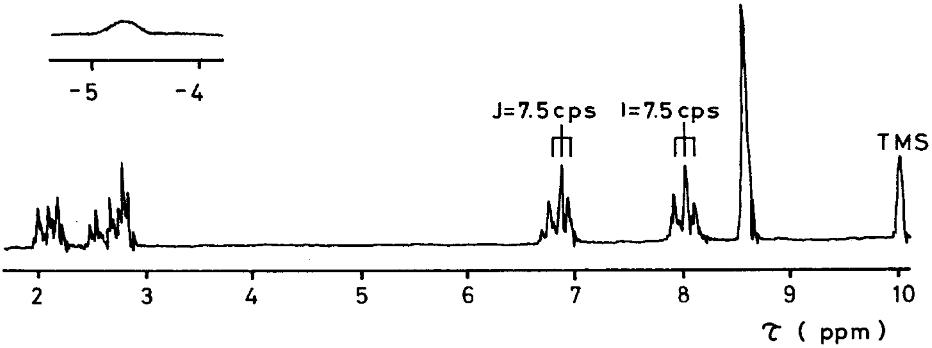


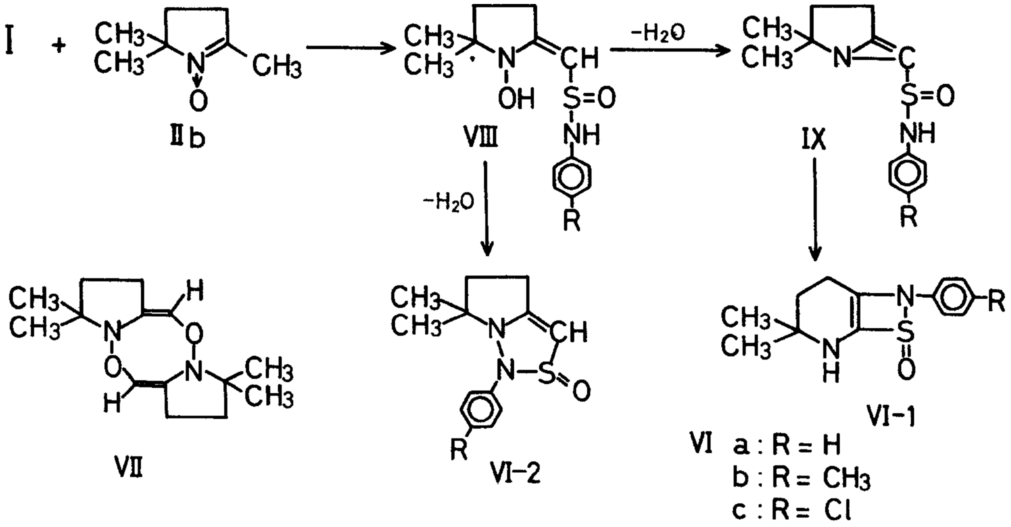
Fig. 1 The NMR spectrum of VIa in $CDCl_3$

The above observations suggest that Ia attacks on the methyl group at 2-position in IIb, giving the intermediate 1:1 adduct (VIIIa) followed by dehydration. Although two courses for the dehydration are possible, the structure of VIa is consistent with VIa-1 formed through 1H-azirine intermediate (IX) rather than VIa-2. The probable formation course is shown in Scheme 3.

The compound VII was assumed to be the oxocine compound from the following evidences. Molecular formula: $C_{14}H_{22}O_2N_2$ (m/e M^+=250). NMR in $CDCl_3$ τ : 8.56 (12H, 4 CH_3, singlet), 7.90 (4H, 2 CH_2, triplet, J=6.8 cps), 7.18 (4H, 2 CH_2, triplet, J=6.8 cps), 2.99 (2H, 2 >C=CH, singlet). IR: 955 cm^{-1} (-C-O-).

In similar reactions of Ib and IC the corresponding 2H-2-aryl-1,2-thiazete 1-oxide compounds, VIb (R=CH_3) and VIc (R=Cl), were obtained, accompanied with a trace amount of VII respectively.

VIb: m.p. 128-129°C, reddish orange leaves. VIc: m.p. 130-130.5°C, reddish orange leaves.



Scheme 3

Further studies are in progress and the results will be reported shortly.

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