

Formation of α -Nitroso Carbonyl Compounds from Esters through β -Keto Sulfoxides

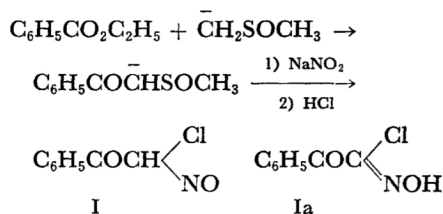
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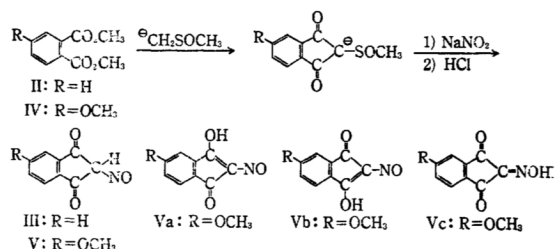
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Aliphatic and aromatic carboxylic esters have been converted to β -keto sulfoxides by the reaction of the esters with methylsulfinyl carbanion.^{1,2} Becker and Russell^{3,4} have found that the treatment of dimethyl phthalate with methylsulfinyl carbanion and the acidification of the resulting mixture with hydrochloric acid give 2-chloro-2-methylmercapto-1,3-indanedione, which can then be readily converted to ninhydrin upon hydrolysis. This reaction has been supposed to proceed through 2-methylsulfinyl-1,3-indanedione as an intermediate.^{3,4} We now wish to report a new reaction of esters, one which leads to α -nitroso carbonyl derivatives through β -keto sulfoxides.

A solution of methylsulfinyl carbanion in dimethyl sulfoxide (DMSO) was prepared by the method of Becker and Russell² from 2 g (0.05 g-atom) of potassium, 50 ml of *t*-butyl alcohol, and 40 ml of DMSO. To this mixture 3.8 g (0.025 mol) of ethyl benzoate in a stream of nitrogen were added at room temperature. The reaction mixture was agitated by a stream of nitrogen for 2 hr, and then most of the solvent was evaporated under reduced pressure. A solution of 5.2 g (0.075 mol) of sodium nitrite in 30 ml of water was added to the residue, and the mixture was extracted with 30 ml of ether. The aqueous layer was acidified with 40 ml of 6N hydrochloric acid to give a yellow oil. The oil solidified on standing overnight. The recrystallization of the solid from chloroform gave 3.6 g (80%) of ω -chloro- ω -nitroso acetophenone (I), mp 132–133°C (lit.⁵ 131–132°C).⁶ The infrared spectrum (in KBr disk) showed that I exists predominantly in the form of hydroxamoyl chloride (Ia).



In the second example, the similar treatment of dimethyl phthalate (II) afforded 2-nitroso-1,3-indanedione (III), mp 196–198°C, in a 37% yield. In this case methylsulfinyl carbanion was prepared from DMSO and sodium methoxide^{3,4}; the compound III thus obtained was identical in every respect with the authentic sample⁷ prepared by the nitrosation of 1,3-indanedione.



In the third example, when the reaction of dimethyl 4-methoxyphthalate (IV) with methylsulfinyl carbanion and sodium nitrite was carried out by a method similar to that described for ethyl benzoate, 5-methoxy-2-nitroso-1,3-indanedione (V), mp 204–206°C (decomp.), was obtained in a 66% yield. The infrared spectrum (in KBr disk) of V showed a hydroxyl absorption at 3500 cm^{-1} and carbonyl absorptions at 1730 and 1690 cm^{-1} . The hydroxyl absorption at 3500 cm^{-1} was sometimes missing, however; instead, a broad absorption appeared at 3150 cm^{-1} . The NMR spectrum (in DMSO- d_6) showed an acidic proton at τ 4.25 (1H, broad singlet), an aromatic proton at τ 2.02–2.15 (1H, broad doublet), two aromatic protons at τ 2.50–2.65 (2H, broad doublet), and a methoxy singlet at τ 6.00 (3H). These results suggest that V exists in an equilibrium among the Va, Vb, and Vc structures in polar solvents. In fact, V could be converted to the corresponding monoacetylated product, mp 185–189°C (decomp.), on acetylation with acetic anhydride in pyridine.

The scope and mechanism of these reactions are now being investigated and will be reported on in a subsequent paper.

1) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **86**, 1639; *ibid.*, **87**, 1345 (1965).

2) H-D. Becker, G. J. Mikol and G. A. Russell, *ibid.*, **85**, 3410 (1963).

3) H-D. Becker and G. A. Russell, *J. Org. Chem.*, **28**, 1896 (1963).

4) H-D. Becker, *ibid.*, **29**, 1358 (1964).

5) H. Rheinboldt and O. S. Dumont, *Ann.*, **444**, 113 (1925).

6) Satisfactory elemental analyses were obtained for all compounds reported.

7) W. Wislicenus, *Ann.*, **246**, 347 (1888).