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

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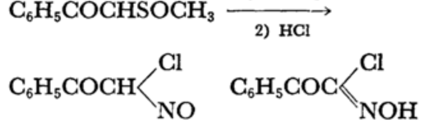
(Received May, 31, 1968)

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 Russell[2] from 2 g (0.05 g-atom) of potassium, 50 m*l* of *t*-butyl alcohol, and 40 m*l* 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 m*l* of water was added to the residue, and the mixture was extracted with 30 m*l* of ether. The aqueous layer was acidified with 40 m*l* of 6 N 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).

$$C_6H_5CO_2C_2H_5 + \bar{C}H_2SOCH_3 \rightarrow$$

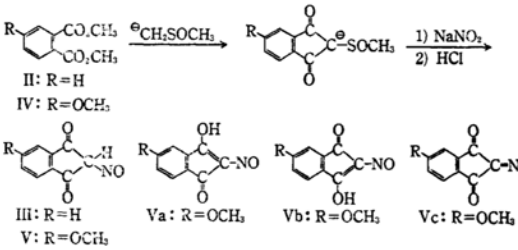
$$C_6H_5CO\bar{C}HSOCH_3 \xrightarrow[\text{2) HCl}]{\text{1) NaNO}_2}$$



$$C_6H_5COCH\begin{cases}Cl\\NO\end{cases} \qquad C_6H_5COC\begin{cases}Cl\\NOH\end{cases}$$

I 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 methylsufinyl carbanion was prepared from DMSO and sodium methoxide[3,4]; the compound III thus obtained was identical in every respect with the authentic sample[7] prepared by the nitrosation of 1,3-indanedione.



II: R=H
IV: R=OCH₃

III: R=H
V: R=OCH₃

Va: R=OCH₃ Vb: R=OCH₃ Vc: R=OCH₃

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.

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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. Rheinbodt 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).