The Nitrosation of β-Keto Sulfoxides[1]

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β-Keto sulfoxides were prepared by the reaction of the esters with the methylsulfinyl carbanion. The nitrosation of the β-keto sulfoxides, $RCOCH_2SOCH_3$ ($R=C_6H_5$, $C_6H_5CH_2CH_2$, n-C_3H_7), with sodium nitrite and hydrochloric acid gave the corresponding α-chloro-α-isonitroso ketones, RCOC(=NOH)Cl, in high yields. However, the nitrosation of α-substituted β-keto sulfoxide, $RCOCH(R')SOCH_3$, in a similar manner afforded the α-isonitroso ketones, RCOC(=NOH)R′. The mechanisms of these reactions were studied.

Aliphatic and aromatic carboxylic esters have been converted to β-keto sulfoxides by the reaction of the esters with the methylsulfinyl carbanion.[2,3] The active methylene group lying between the keto and sulfoxide groups is very reactive toward electrophilic reagents and is readily brominated or alkylated to give the corresponding substituted β-keto sulfoxides.[4,5] In a previous communication[6] we reported that ω-(methylsulfinyl)-acetophenone (IIa), which can be prepared from ethyl benzoate (Ia), afforded ω-chloro-ω-isonitrosoacetophenone (IIIa) in a high yield upon treatment with sodium nitrite and hydrochloric acid.

In this paper we will describe the results of a detailed study of this reaction and of an extension of it to other compounds; it provides a useful general method for the preparation of α-keto-α-chloro-isonitroso compounds.

Results and Discussion

Preparation of β-Keto Sulfoxides. Four carboxylic esters (Ia—Id) were treated in dimethyl sulfoxide (DMSO) with 2 equiv. of the methylsulfinyl carbanion, prepared by the reaction of DMSO with sodium hydride.[2] This treatment afforded the corresponding β-keto sulfoxides (IIa—IId) in high yields.

$$\underset{\text{I}}{RCO_2C_2H_5} + {}^{-}CH_2SOCH_3 \longrightarrow \underset{\text{II}}{RCOCH_2SOCH_3}$$

a, $R=C_6H_5$; b, $R=C_6H_5CH_2CH_2$;
c, $R=n$-C_3H_7; d, $R=n$-C_6H_{13}

Ethyl phenylacetate could not be converted to the β-keto sulfoxide by this method, but it produced phenylacetic acid in an almost quantitative yield after the treatment of the reaction mixture with dilute hydrochloric acid. These results indicate that, in the case of ethyl phenylacetate, the proton transfer from the α-carbon of the ester to the methylsulfinyl carbanion predominates over the carbonyl addition of the anion because of the high acidity of the ester relative to the carbanion.

The treatment of the sulfoxide IIa with sodium hydride in tetrahydrofuran, followed by the addition of methyl iodide to the solution, gave a mixture of diastereoisomers of ω-methyl-ω-(methylsulfinyl)-acetophenone (IIe).[5] Upon the cooling of this mixture, one of the diastereoisomers crystallized; it was used for the successive reaction.

$$\underset{\text{IIa}}{C_6H_5COCH_2SOCH_3} + CH_3I \xrightarrow{\text{NaH}} \underset{\text{IIe}}{C_6H_5COCH(CH_3)SOCH_3}$$

Nitrosation of β-Keto Sulfoxides. When an aqueous solution of the sulfoxides (IIa, IIb, and IIc) containing an equiv. of sodium nitrite was acidified with hydrochloric acid and the mixture was then stirred for 1—3 hr at room temperature, α-chloro-α-isonitroso ketones (III) were obtained in the yields indicated in Table 1. No appreciable change in the yield of III was observed by the use of 2 equiv. of sodium nitrite. The application of this reaction to the sulfoxide IId produced a brown oil which could not be purified. It was also shown that the isonitroso compounds, III, can be obtained without the isolation of the sulfoxides, II, by starting with the carboxylic esters. For example, Ia afforded IIIa in an overall yield of 80%.

$$\underset{\text{II}}{RCOCH_2SOCH_3} + NaNO_2 \xrightarrow{\text{HCl}} \underset{\text{III}}{RCOC(Cl)=NOH}$$

Table 1. Formation of α-chloro-α-isonitroso ketones (III)

Compound	R	Yield, %
IIIa	C_6H_5	80
IIIb	$C_6H_5CH_2CH_2$	84
IIIc	n-C_3H_7	82

The IR and NMR spectra of III were in accordance with the assigned structures. For example, IIIa showed an absorption due to the carbonyl group at 1660 cm^{-1} in the IR spectrum and an absorption due to an extremely acidic proton of the hydroxyl group at τ −3.68 in the NMR spectrum.

However, when the α-substituted β-keto sulfoxide IIe was nitrosated in a similar manner, a mixture of isonitrosopropiophenone (IV) and 1-phenylpropane-1,2-dione (V) was obtained. The relative yields of IV and V depended upon the reaction conditions employed.

1) A part of the results of this investigation was presented at the 19th Symposium on Organic Reaction Mechanisms, Yamagata, October, 1968.

2) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **86**, 1639 (1964); *ibid.*, **87**, 1345 (1965).

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

4) G. A. Russell and G. J. Mikol, *ibid.*, **88**, 5498 (1966).

5) G. A. Russell, E. Sabourin, and G. J. Mikol, *J. Org. Chem.*, **31**, 2854 (1966).

6) Y. Otsuji, H. Yabune, and E. Imoto, This Bulletin, **41**, 1745 (1968).

$$\text{IIe} + NaNO_2 \xrightarrow{HCl} C_6H_5COC(CH_3)(NOH) + C_6H_5COCOCH_3$$
IV V

Under conditions where the reaction was conducted at 0—5°C using an excess of sodium nitrite, IV was isolated only when the reaction time was 15 min; an extension of the reaction time to 2 hr gave only V as an isolable product.

In order to explain these observations, the hydrolysis of IV to V was studied in some detail. When IV was subjected to hydrolysis in dilute hydrochloric acid and in the presence of sodium nitrite at 0—5°C, V was obtained in a high yield. However, the treatment of IV with hydrochloric acid in the absence of sodium nitrite under identical conditions resulted in the recovery of the starting material. These results clearly indicate that the hydrolysis of IV is assisted by nitrous acid. Brooks and his co-workers[7] have previously found that steroidal ketoximes can readily be hydrolyzed to the corresponding ketones in the presence of nitrous acid, and they have proposed the following mechanism for the action of nitrous acid:

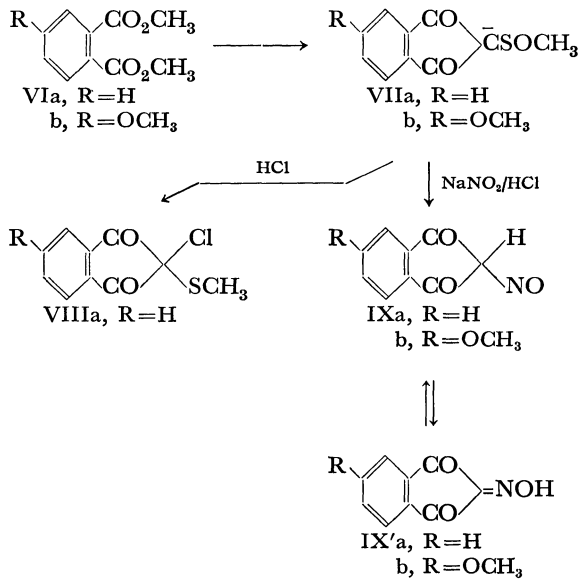
$$RR'C{=}N(\curvearrowright)\text{-}O\text{-}H \longrightarrow RR'C{=}\overset{+}{N}\text{-}O^- \longrightarrow RR'CO + N_2O$$
$$\searrow NO^+ \qquad\qquad \downarrow NO$$

The hydrolysis of IV in hydrochloric acid in the presence of nitrous acid must proceed by a mechanism similar to that shown above.

The structure of IV was confirmed by comparing it with an authentic sample prepared by the nitrosation of propiophenone.[8] The structure of V was established by converting it to its disemicarbazone.

Becker and Russell[9,10] have recently found that the treatment of dimethyl phthalate (VIa) with 2 equiv. of the methylsulfinyl carbanian, followed by the acidification of the reaction mixture with hydrochloric acid, yields 2-chloro-2-methylthio-1,3-indanedione (VIIIa) through the intermediate (VIIa), which is analogous in structural type to IIe, *i.e.*, α-substituted β-keto sulfoxide. In the light of their investigations, VIa was treated with 2 equiv. of the methylsulfinyl carbanion, and the resulting mixture was nitrosated with sodium nitrite and hydrochloric acid. As expected, the reaction took place in a manner similar to that for IIe to give 2-nitroso-1,3-indanedion (IXa) in a 37% yield.[6] In a similar manner, dimethyl 4-methoxyphthalate (VIb) was converted to 5-methoxy-2-nitroso-1,3-indanedione (IXb) in a 66% yield.[6]

The structure of IXa was confirmed by comparing it with an authentic sample prepared by the nitrosation of 1,3-indanedione,[11] its IR and NMR spectra (see Experimental section) showed that IXa exists predominantly in the form of IX'a. The structure of IXb was established by comparing it with an authentic sample obtained by a method previously reported.[12] However, the predominant form among the possible isomeric structures for IXb remains unestablished.



Mechanistic Studies. Inspection of the structures of the products obtained above suggests that two reactions, the Pummerer rearrangement of the sulfoxide group and the nitrosation of the active methylene group, may somehow be involved in the nitrosation of the β-keto sulfoxide. Which reaction takes place first? In order to solve this question, the following experiments were undertaken.

Compound VIIIa, prepared by the method of Becker and Russell,[9] was subjected to nitrosation under conditions similar to those employed for the nitrosation of β-keto sulfoxides. This experiment resulted in the recovery of the starting material, implying that the nitrosation takes place in advance of the Pummerer rearrangement. Futher evidence was obtained by the isolation of a plausible intermediate of the reaction.

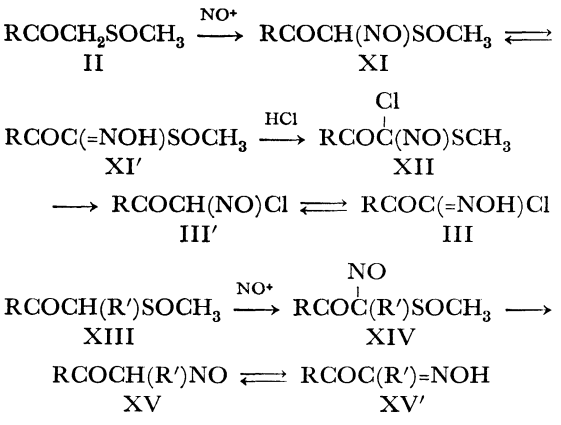
The treatment of IIa with isoamyl nitrite in ethanol, using sodium ethoxide, gave ω-nitroso-ω-(methylsulfinyl) acetophenone (X). The IR and NMR spectra (see Experimental section) showed again that X exists predominantly in the form of X'. Upon refluxing X' in hydrochloric acid for 5 hr, IIIa was isolated from the reaction mixture.

$$\text{IIa} + i\text{-AmONO} \xrightarrow{C_2H_5ONa} C_6H_5COCH(NO)SOCH_3$$
X

$$\rightleftharpoons C_6H_5COC(=NOH)SOCH_3 \xrightarrow{HCl} \text{IIIa}$$
X'

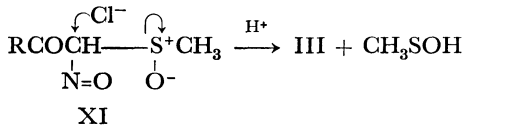
These results suggest that the reaction proceeds through the pathways represented in Scheme 1:

7) S. G. Brooks, R. M. Evans, G. F. H. Green, J. S. Junt, A. G. Long, B. Mooney, and L. J. Wyman, *J. Chem. Soc.*, **1958**, 4614.
8) W. H. Hartung and F. Crossley, "Organic Syntheses," Coll. Vol. II, p. 363 (1948).
9) H.-D. Becker and G. A. Russell, *J. Org. Chem.*, **28**, 1896 (1963).
10) H.-D. Becker, *ibid.*, **29**, 1358 (1964).
11) W. Wislicenus, *Ann. Chem.*, **246**, 347 (1888).
12) Y. Otsuji, H. Yabune, and E. Imoto, This Bulletin, **42**, 732 (1969).



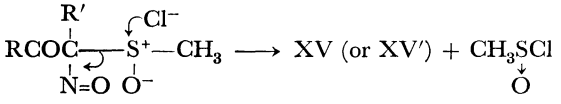
Scheme 1

For the β-keto sulfoxides (II), the nitrosation takes place first to produce XI, which would be in equilibrium with XI'. The Pummerer rearrangement of XI[13] gives XII, which then affords the final product, III, by an unusual cleavage of the C–S bond. The driving force of this cleavage might be an accumulation of the electronegative groups on the α-carbon which stabilizes the carbanion. Thus, upon the hydrolysis of XII, the sulfur bore a positive charge and was removed as methylsulfenic acid. The other plausible mechanism of the cleavage of XI would be a direct nucleophilic attack of the chloride ion on the α-carbon of XI to form III:



However, the above both mechanisms remained undiscriminated in this investigation.

For the α-substituted β-keto sulfoxides, XIII, the nitrosation gives XIV, which then produces the final product, XV or XV'. A possible mechanism of this final conversion would be:



Although this kind of nucleophilic substitution on the sulfoxide sulfur is very rare, the electronegative groups at the α-position may force it to take place.

Experimental

The melting points are uncorrected. The IR spectra were recorded on a Hitachi EPI-S2 infrared spectrophotometer. The NMR spectra were obtained on a Hitachi H-60 high-resolution NMR spectrometer, with TMS as the internal standard. The elemental analyses were performed with a Yanagimoto MT-1 CHN Corder.

13) It is necessary, if the Pummerer rearrangement is to take place, that β-keto sulfoxides have an acidic hydrogen at the α-position. Thus, the rearrangement of the β-keto sulfoxides must occur from the form of XI (not from the form of XI'). In the rearrangement of the isolated X, relatively vigorous conditions were required for the reaction; this supports the idea that the favorable form of the compound is X (not X').

Reagents. DMSO was purified by two distillations over calcium hydride under reduced pressure. A commercial sodium nitrite (97% purity) was used without further purification. Unless otherwise noted, the methylsulfinyl carbanion in DMSO was prepared by the method of Corey and Chaykovsky[2] from sodium hydride and DMSO.

Preparation of β-Keto Sulfoxides. General Procedure: A 1.5 to 2 M solution of the methylsulfinyl carbanion in DMSO was prepared and diluted with an equal volume of dry tetrahydrofuran (THF). A solution of the carboxylic ester (0.5 equiv. based on 1 equiv. of the carbanion) in THF was stirred, over a period of 30 min, into the solution of the carbanion under cooling in an ice bath. The ice bath was then removed, and stirring was continued for 1 hr; the reaction mixture was then poured into three times its volume of water, acidified with hydrochloric acid to a pH of 3—4, and thoroughly extracted with chloroform. The combined chloroform extracts were washed four times with water, dried over anhydrous sodium sulfate, and evaporated to dryness to yield the crude β-keto sulfoxide. The crude product, if solid, was triturated with cold ether or isopropyl ether and collected by filtration to give the product, which was generally in a good state of purity and which could be used for the successive reactions without further purification. The crude product, if liquid, was distilled under reduced pressure to give the pure product.

The reaction of the methylsulfinyl carbanion with ethyl phenylacetate under similar conditions did not afford the corresponding β-keto sulfoxide, but it did give the hydrolysis product, phenylacetic acid, in an almost quantitative yield.

ω-(Methysulfinyl)acetophenone (IIa).[2] The treatment of 15 g (0.1 mol) of ethyl benzoate (Ia) with 0.2 mol of the methylsulfinyl carbanion yielded 14.4 g (79%) of IIa as a white crystalline solid after the trituration of the crude product with ether; mp 86—87°C (lit,[2] mp 86—86.5°C).

Methylsulfinylmethyl β-Phenethyl Ketone (IIb). The treatment of 8.9 g (0.05 mol) of ethyl dihydrocinnamate with 0.1 mol of the methylsulfinyl carbanion yielded 8.7 g (88%) of IIb as a white crystalline solid after recrystallization from isopropyl ether; mp 64—65°C.

Found: C, 62.74; H, 6.81%. Calcd for $C_{11}H_{11}O_2S$: C, 62.86; H, 6.67%.

IR (KBr): 1700 (C=O), 1360, 1020 cm^{-1} (SO). NMR ($CDCl_3$): τ 6.30 (2H, *s*, $COCH_2SO$), 7.10(4H, *s*, CH_2CH_3), 7.44 (3H, *s*, $SOCH_3$).

Methylsulfinylmethyl n-*Propyl Ketone (IIc).* The treatment of 5.8 g (0.05 mol) of ethyl butyrate (Ic) with the methylsulfinyl carbanion yielded a brown liquid. The distillation of the liquid gave 4.0 g (54%) of IIc as a yellow liquid; bp 114—115°C/2 mmHg.

Found: C, 48.38; H, 8.24%. Calcd for $C_6H_{12}O_2S$: C, 48.64; H, 8.16%.

IR ($CHCl_3$): 1720 (C=O), 1310, 1030 cm^{-1} (SO). NMR (CCl_4): τ 6.22 (2H, *s*, $COCH_2SO$), 7.4 (3H, *s*, $SOCH_3$), 8.22—9.20 (7H, *m*, $CH_3CH_2CH_2$).

Methylsulfinylmethyl n-*Pentyl Ketone (IId).*[2] The treatment of 7.2 g (0.05 mol) of ethyl caproate (Id) with 0.1 mol of the methylsulfinyl carbanion yielded 6.8 g (72%) of IId after the recrystallization of the crude product from 1 : 1 isopropyl ether-petroleum ether; mp 44—45°C (lit,[2] mp 45—46.5°C).

ω-Methyl-ω-(methylsulfinyl)acetophenone (IIe).[5] This compound was prepared by the method of Russell, Sabourin, and Mikol[5] from IIa and methyl iodide. The crude product, obtained as a yellow oil, was cooled in an ice bath to give a solid which was a diasteroisomer. The crude solid was then washed with ether to afford a white solid which melted

at 74—75°C and which was used for the successive reactions without further purification.

Nitrosation of β-Keto Sulfoxides with Sodium Nitrite in Hydrochloric Acid. General Procedure. Into a mixture of the β-keto sulfoxide (0.01 mol) and sodium nitrite (0.02 mol) in water (25 m*l*), we stirred, drop by drop, an equal volume of a concentrated hydrochloric acid with cooling in an ice bath. After the ice bath had then been removed, stirring was continued for 2 hr at room temperature. The solid thus obtained was separated by filtration and recrystallized to yield the nitroso compound.

The nitrosation of methylsulfinylmethyl *n*-pentyl ketone (IId) by this procedure gave a brown oil which could not be solidified and which was decomposed upon distillation under reduced pressure.

ω-Chloro-ω-isonitrosoacetophenone (IIIa). **A.** The treatment of 1.5 g (0.008 mol) of IIa with 1.2 g (0.016 mol) of sodium nitrite and hydrochloric acid immediately gave the crude product as a white precipitate. Recrystallization from chloroform afforded 1.23 g (84%) of IIIa as white needles; mp 132—133°C (lit,[14] 131—132°C).

Found: C, 52.40; H, 3.29; N, 7.76%. Calcd for $C_8H_6O_2NCl$: C, 52.33; H, 3.29; N, 7.63%.

IR (KBr): 3350 (OH), 1660 cm^{-1} (C=O). NMR (DMSO-d_6): τ −3.68 (1H, *s*, OH), 1.95—2.46 (5H, *m*, aromatic).

This compound was identical in every respect with the authentic sample prepared by the method of Rheinbodt and Dumont.[14]

B. A similar treatment of 3.8 g (0.025 mol) of IIa and 1.8 g (0.025 mol) of sodium nitrite and hydrochloric acid gave 3.4 g (80%) of IIIa. Thus, no appreciable change in the yield of IIIa was observed upon using equal molar quantities of IIa and sodium nitrite.

1-Chloro-1-isonitroso-4-phenylbutanone-2 (IIIb). The treatment of a mixture of 3 g (0.014 mol) of IIb and 2 g of sodium nitrite in 50 m*l* of water with 50 m*l* of hydrochloric acid for 2.5 hr yielded a yellow solid which was collected by filtration and washed with water. The recrystallization of the solid from carbon tetrachloride gave 2.5 g (84%) of IIIb as white needles; mp 98°C.

Found: C, 56.74; H, 4.67; N, 6.69%. Calcd for $C_{10}H_{10}O_2NCl$: C, 56.73; H, 4.73; N, 6.62%.

IR (KBr): 3230 (OH), 1695 cm^{-1} (C=O). NMR ($CDCl_3$): τ 0.73 (1H, *s*, OH), 2.30—3.25 (5H, *m*, aromatic), 6.64—7.16 (4H, *m*, CH_2CH_2).

1-Chloro-1-isonitrosopentanone-2 (IIIc). The treatment of a mixture of 3 g (0.02 mol) of IIc and 3 g of sodium nitirte in 50 m*l* of water with 50 m*l* of hydrochloric acid for 2 hr, after which the mixture was allowed to stand overnight, yeilded a brown solid. The recrystallization of the solid from carbon tetrachloride gave 2.5 g (82%) of IIIc as white crystals; mp 65—67°C.

Found: C, 39.98; H, 5.42; N, 9.31%. Calcd for $C_5H_8O_2NCl$: C, 40.14; H, 5.39; N, 9.37%.

IR (KBr): 3250 (OH), 1680 cm^{-1} (C=O). NMR ($CDCl_3$): τ 2.65 (1H, *s*, OH), 7.1 (2H, *t*, J=7.0 Hz, $CH_3CH_2\mathbf{CH_2}CO$), 7.98—8.73 (2H, *m*, $CH_3\mathbf{CH_2}CH_2CO$), 9.05 (3H, *t*, J=7.0 Hz, $CH_3\mathbf{CH_2}CH_2CO$).

Formation of Isonitroso Compounds from Esters. ω-Chloro-ω-isonitrosoacetophenone (IIIa). A solution of the methylsulfinyl carbanion in DMSO was prepared by the method of Becker and Russell[9] 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 were added in a stream of nitrogen at room temperature. We continued to agitate the reaction mixture by a stream of nitrogen for 2 hr, then most of the solvent was evaporated under reduced pressure on a water bath, with the temperature kept bellow 60°C. A solution of 5.2 g (0.075 mol) of sodium nitrite in 30 m*l* of water was then 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 6N hydrochloric acid to give yellow oil, which solidified on standing overnight. The recrystallization of the solid from chloroform gave 3.6 g (80%) of IIIa.

Nitrosation of ω-Methyl-ω-(methylsulfinyl)acetophenone (IIe). **A.** Into a solution of 1.0 g (0.005 mol) of IIe and 0.6 g (0.0065 mol) of sodium nitrite in 30 m*l* of 50% aqueous dioxane, 20 m*l* of concentrated hydrochloric acid were stirred at 0—5°C. Stirring was continued for 15 min, and then the reaction mixture was extracted with ether. The ether layer was washed with 10% sodium carbonate and then with water. The ether was dried over sodium sulfate and then evaporated. The brown residue was chromatographed on a column packed with silica gel. The development was carried out by using two different solvents. Methylene chloride was used first, and then 95% ethanol. The evaporation of the first solvent, methylene chloride, and the subsequent distillation of the residue afforded 1-phenylpropane-1,2-dione (V); bp 101—102°C/7 mmHg (lit,[15] 123°C/22 mmHg). IR ($CHCl_3$): 1700, 1660 cm^{-1} (C=O).

The disemicarbazone formed from the above residue by the usual manner melted at 230°C (lit,[15] mp 229—230°C) and was identical in every respect with the disemicarbazone prepared from the authentic sample of V.

The evaporation of ethanol and the recrystallization of the residue from toluene gave 400 mg (48%) of isonitrosopropiophenone (IV); mp 111—113°C (lit,[8] 112—113°C).

B. The same reaction was carried out under similar conditions, but stirring was continued for 2 hr instead of for 15 min. A similar work-up of the reaction mixture gave 0.53 g (70%) of V. In this case, IV was not obtained.

Hydrolysis of Isonitrosopropiophenone (IV) in the Presence of Sodium Nitrite in Hydrochloric Acid. Into a stirred mixture of 1 g (0.006 mol) of IV and 0.42 g (0.006 mol) of sodium nitrite in 30 m*l* of 50% aqueous dioxane, we added 20 m*l* of concentrated hydrochloric acid over a period of 30 min at 0—5°C. The reaction mixture was then extracted with ether. The ether layer was washed with water, dried over sodium sulfate, and then evaporated. The IR spectrum of the residue was identical with that of V. Furthermore, the treatment of the residue with an excess of semicarbazide gave the disemicarbazone of V; mp 231—232°C.

The treatment of IV with hydrochloric acid under the same conditions in the absence of sodium nitrite resulted in the recovery of the starting material in a 90% yield.

2-Nitroso-1,3-indanedione (IXa). A suspension of 2.7 g (0.05 mol) of sodium methoxide in 30 m*l* of DMSO was stirred for 15 min at room temperature in a stream of nitrogen. To this suspension we then added, drop by drop, a solution of 2.5 g (0.0125 mol) of dimethyl phthalate (VIa) in 10 m*l* of DMSO. We continued to stir the reaction mixture, which soon turned yellow, for 3 hr in a stream of nitrogen, and then most of the solvent was evaporated at 1 mmHg on a water bath at 60°C. The residue was mixed with a solution of 1.8 g (0.025 mol) of sodium nitrite in 25 m*l* of ice water, and the mixture was extracted with ether. The aqueous layer was acidified by striring in 50 m*l* of 6N hydrochloric acid with cooling in an ice bath. The precipitated solid was collected by filtration and recrystallized from acetic acid to

14) H. Rheinbodt and O. S. Dumont, *Ann. Chem.*, **444**, 113 (1925).

15) D. Vom Dorp, *Ber.*, **36**, 3187 (1906); *ibid.*, **50**, 1612 (1917).

give 800 mg (37%) of IXa; mp 196—198°C (decomp) (lit,[11] 197—198°C).

Found: C, 61.56; H, 2.73; N, 7.98%. Calcd for $C_9H_5O_3N$: C, 61.72; H, 2.88; N, 8.00%.

IR (KBr): 3500 (OH), 1738, 1705 cm^{-1} (C=O).

This compound was identical in every respect with the authentic sample prepared by the nitrosation of 1,3-indanedione by the method of Wislicenus.[11]

5-Methoxy-2-nitroso-1,3-indanedione (IXb). A solution of the methylsulfinyl carbanion in DMSO was prepared from 0.8 g (0.02 g-atom) of potassium, 20 m*l* of *t*-butyl alcohol, and 15 m*l* of DMSO. Into this solution we then stirred a solution of 1.0 g (0.0045 mol) of dimethyl 4-methoxyphthalate (VIb) in 5 m*l* of DMSO in a stream of nitrogen at room temperature. Stirring was continued for 2.5 hr, and then most of the solvent was evaporated under reduced pressure. To the residue 10 m*l* of ice water were added, and the mixture was extracted with 10 m*l* of ether. The aqueous layer was separated, poured into an aqueous saturated solution containing 0.8 g of sodium nitrite, and then acidified with 40 m*l* of 6N hydrochloric acid. The solid thus precipitated was recrystallized from ispropyl alcohol to yield 0.65 g (70%) of IXb; mp 204—206°C (decomp).

This compound was identical in every respect with the sample prepared by the method previously reported.[12]

Nitrosation of ω-(Methylsulfinyl)acetophenone (IIa) with Isoamyl Nitrite. To a solution of 0.25 g (0.011 mol) of sodium in 50 m*l* of absolute ethanol, we added 2 g (0.011 mol) of IIa. Isoamyl nitrite (2 g, 0.017 mol) was then stirred in at room temperature. Stirring was continued for 2 hr, and the solvent was evaporated. The residue was poured into 50 m*l* of ice water, and subsequently extracted with 50 m*l* of ether. The aqueous layer was acidified with hydrochloric acid to pH 4—5 to yield a yellow solid. Recrystallization from ethanol gave 1.2 g (40%) of ω-nitroso-ω-(methylsulfinyl)acetophenone (X) as a white solid; mp 124°C.

Found: C, 51.85; H, 4.49; N, 6.66%. Calcd for $C_9H_9O_3NS$: C, 51.28; H, 4.30; N, 6.63%.

IR (KBr): 1640 (C=O), 1040 cm^{-1} (SO). NMR (DMSO-d_6): τ −3.96 (1H, *s*, OH), 1.87—2.41 (5H, *m*, aromatic), 6.92 (3H, *s*, $SOCH_3$).

Pummerer Rearrangement of ω-Nitroso-ω-(methylsulfinyl)acetophenone (X). A suspension of 1 g of X in 30 m*l* of concentrated hydrochloric acid was refluxed for 5 hr and then cooled to room temperature. The solid separated was collected by filtration and recrystallized from chloroform to yield 0.3 g of IIIa; mp 131—133°C.