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Reaction of Methylsulfinyl Carbanion with Substituted Phthalic Esters

Yoshio Otsuji, Hideo Yabune and Eiji Imoto

Department of Applied Chemistry, Faculty of Engineering, University of Osaka Prefecture, Sakai-shi, Osaka

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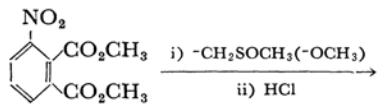
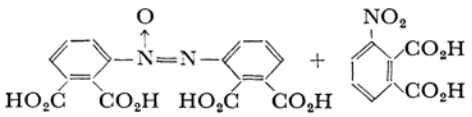
The treatment of dimethyl 3-nitrophthalate (I) with a mixture of dimethyl sulfoxide and sodium methoxide, followed by the acidification of the resulting mixture with hydrochloric acid, gave azoxybenzene-2,2',3,3'-tetracarboxylic acid (II) and 3-nitrophthalic acid (III). The similar treatment of dimethyl 4-nitrophthalate (IV) afforded 5-methoxy-2-nitroso-1,3-indanedione (V) and 4-methoxyphthalic acid (VI). The similar treatment of dimethyl 4-methoxyphthalate (XV) and dimethyl phthalate gave 2-chloro-2-methylthio-5-methoxy-1,3-indanedione (XVII) and 2-chloro-2-methylthio-1,3-indanedione (XIX) respectively. The general features of these reactions are described.

Becker and Russell[1,2] have recently found that the treatment of diethyl phthalate with methylsulfinyl carbanion and the acidification of the resulting mixture with hydrochloric acid give 2-chloro-2-methylthio-1,3-indanedione, which can then readily be converted to ninhydrin. We have extended this reaction to substituted phthalic esters in the hope of obtaining substituted ninhydrins. During the course of this investigation we have established several new features of this reaction, features which will be reported in this paper.

When dimethyl 3-nitrophthalate (I) was treated in a stream of nitrogen in dimethyl sulfoxide (DMSO) with methylsulfinyl carbanion prepared from DMSO and sodium methoxide, and when the resultant reaction mixture was acidified with hydrochloric acid, azoxybenzene-2,2',3,3'-tetracarboxylic acid (II) and the hydrolysis product, 3-nitrophthalic acid (III), were obtained in 50 and 43% yields respectively.

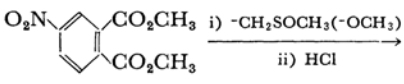


(I)

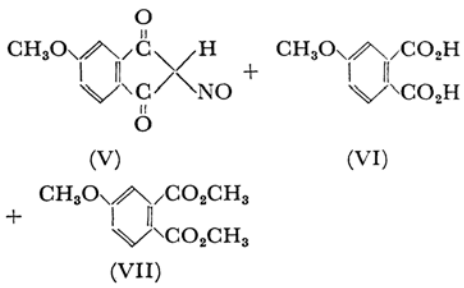


(II) (III)

The similar treatment of dimethyl 4-nitrophthalate (IV) gave 5-methoxy-2-nitroso-1,3-indanedione (V) and 4-methoxyphthalic acid (VI). The yields of V (48—14%) and VI (49—73%) varied to some extent from run to run. In some runs dimethyl 4-methoxyphthalate (VII) was also obtained.



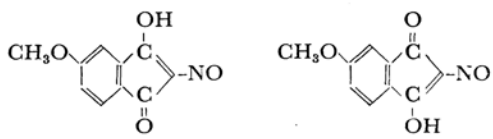
(IV)



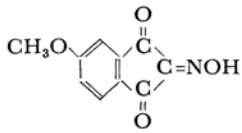
(V) (VI)

(VII)

The structure of V was established on the basis of its elemental analysis and by a study of its infrared and NMR spectra. The NMR spectrum of V in DMSO-d_6 showed the presence of an acidic proton at $-4.25\ \tau$, suggesting that V exists in the forms of Va, Vb, and Vc in polar solvents.



(Va) (Vb)



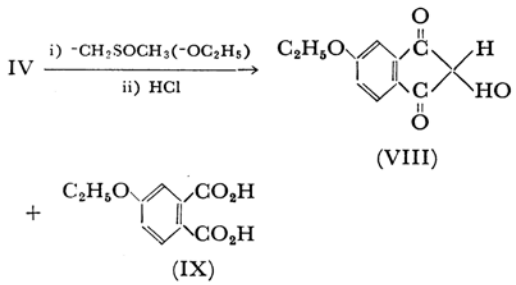
(Vc)

In accordance with this observation, the acetylation of V with acetic anhydride in pyridine gave a mono-acetylated product. The compound V

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

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

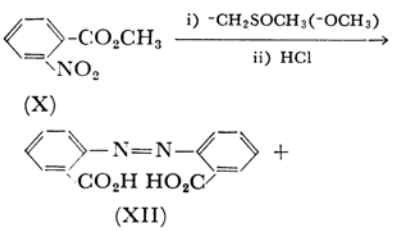
also underwent alkaline hydrolysis to give VI. All the properties of the acid VI were identical with those of the acid obtained by the alkaline hydrolysis of the ester VII.

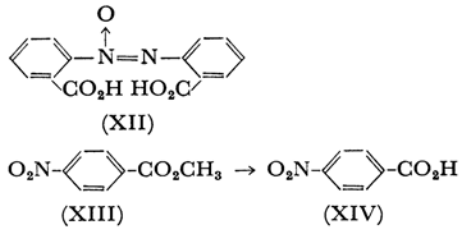


The above unexpected behavior of IV was observed even when the anion species was changed from methoxide to ethoxide. Thus, the treatment of IV with methylsulfinyl carbanion prepared from DMSO and sodium ethoxide and a similar work-up of the resultant mixture gave 5-ethoxy-2-nitroso-1,3-indanedione (VIII) and 4-ethoxyphthalic acid (IX) in 51 and 32% yields respectively.

The above reactions of IV have two noticeable features: (1) the replacement of the nitro group by the alkoxyl group, and (2) the formation of nitroso compounds.

The nucleophilic replacement of a nitro group attached to an aromatic ring by an alkoxide ion has been found to occur in the aromatic nitro compounds which are activated by an electron-withdrawing group such as nitro,[3] cyano[4] or carbonyl[5]. In the compound IV two methoxycarbonyl groups act as the activating groups. The failure of the replacement of the nitro group in I may be supposed to be due to a steric hindrance caused by the neighboring methoxycarbonyl group. The following observations are of interest in this connection. When methyl *o*-nitrobenzoate (X) was subjected to the above reaction under similar conditions, azobenzene-2,2'-dicarboxylic acid (XI) and azoxybenzene-2,2'-dicarboxylic acid (XII) were obtained in 44 and 33% yields respectively. On the other hand, methyl *p*-nitrobenzoate (XIII) afforded only the hydrolysis product, *p*-nitrobenzoic acid (XIV).

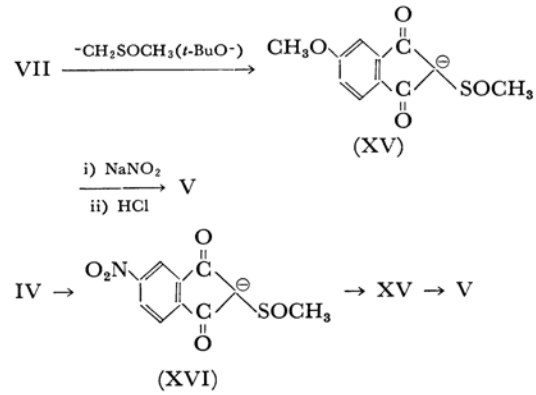




These results seem to indicate that at least two methoxycarbonyl groups are needed for the nucleophilic replacement of the nitro group by the alkoxyl group.

The nitroso compounds, V and VIII, were supposed to be formed from dimethyl 4-alkoxyphthalate, which is produced by the replacement of the nitro group in IV by the methoxyl or the ethoxyl group if the nitrite ion is present in the reaction system (the nitrite ion was, in fact, found to be liberated during the course of the reaction leading from IV to V or VIII).

This theory was partly verified by the fact that the treatment of dimethyl 4-methoxyphthalate with methylsulfinyl carbanion prepared from DMSO and potassium *t*-butoxide, the addition of sodium nitrite, and then the acidification of the resultant mixture with hydrochloric acid gave V in a 66% yield. This reaction probably proceeds through an anion of the *β*-keto sulfoxide (XV).

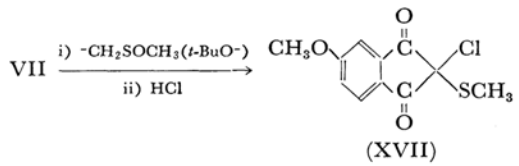


However, another possibility regarding the pathway of the reaction must also be considered. As will be mentioned later, VII did not undergo any condensation reaction leading to XV or its derivatives, but underwent hydrolysis to give the diacid VI when methylsulfinyl carbanion prepared from DMSO and sodium methoxide was used. On the other hand, the nitroso compound was produced from IV even when methylsulfinyl carbanion prepared from DMSO and sodium methoxide was used. Obviously, in the process of the formation of V from IV the condensation of the ester with methylsulfinyl carbanion, which gives an intermediate such as *β*-keto sulfoxide XVI, must be involved. These arguments, therefore, lead to a pathway in which the condensation of IV

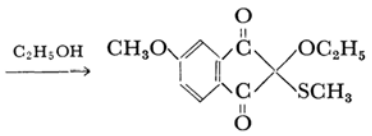
3) F. Reverdin, "Organic Syntheses," Coll. Vol. 1, p. 219 (1956).
4) V. V. Richter, *Ber.*, **4**, 21, 459, 553 (1871); **8**, 1418 (1875).
5) J. H. Gorvin, *Chem. and Ind.*, **1967**, 1525.

with methylsulfinyl carbanion may occur prior to the replacement of the nitro group by the alkoxyl group: that is, V, might be formed through 2-methylsulfinyl-5-nitro-1,3-indanedione or its anion (XVI). A detailed examination of the mechanism and a synthetic application of these reactions to afford nitroso compounds are now under way in our laboratory; our results will be published in a separate paper.

The reaction of VII with methylsulfinyl carbanion was then studied in some detail. The treatment of VII with methylsulfinyl carbanion prepared from DMSO and sodium methoxide, and the acidification of the resultant mixture with hydrochloric acid, led to the hydrolysis product, VI. However, when methylsulfinyl carbanion prepared from DMSO and potassium *t*-butoxide was used, 2-chloro-2-methylthio-5-methoxy-1,3-indanedione (XVII) was obtained; upon being refluxed in ethanol, this compound yielded 2-ethoxy-2-methylthio-5-methoxy-1,3-indanedione (XVIII).



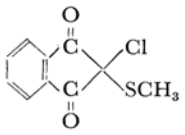
(XVII)



(XVIII)

The structure of XVIII was established on the basis of its elemental analysis, and on a study of its infrared and NMR spectra.

Since, in the above reactions, methylsulfinyl carbanion is formed in the pre-equilibrium stage, the use of a much stronger base would produce a higher concentration of the carbanion. The above results suggest, therefore, that the higher concentration of methylsulfinyl carbanion makes it possible to accomplish the condensation reaction of the carbanion with such compounds as VII, in which the reactivity of the carbonyl group toward nucleophiles is somewhat lowered by the presence of an electron-releasing group.



(XIX)

Finally, we repeated the Becker and Russell reaction on dimethyl phthalate using methylsulfinyl carbanions prepared from DMSO and sodium methoxide, and DMSO and potassium *t*-butoxide. In these cases 2-chloro-2-methylthio-1,3-indanedione (XIX) was obtained in yields of 44 and 57% respectively.

Thus, the following conclusions can be drawn from these studies: 1) for the phthalic esters having the nitro group as a substituent, the reaction leads to the reduction of the substituent or the replacement of the substituent by the nucleophiles which are present in the reaction system; 2) for the unsubstituted phthalic esters and phthalic esters with an electron-releasing substituent such as the methoxyl group, a substitution reaction with methylsulfinyl carbanion on the ester carbonyl group takes place.

Experimental

All the melting points are uncorrected. The infrared spectra were obtained with a Hitachi EPI-S_2 infrared spectrophotometer. The NMR spectra were recorded on a Hitachi H-60 high-resolution NMR spectrometer, using tetramethylsilane as the internal standard. Elemental analyses were performed with a Yanagimoto MT-1 CHN Corder.

Reagents. The dimethyl sulfoxide (DMSO) was purified by two distillations over calcium hydride at about 1 mmHg. The sodium methoxide was prepared from sodium and methanol and dried by heating at 100°C under reduced pressure. The sodium ethoxide was prepared from sodium and ethanol and dried similarly. Unless otherwise indicated, the other reagents were of commercial origin or were synthesized by known methods and purified by recrystallization or distillation.

Reaction of Dimethyl 3-Nitrophthalate (I). With DMSO-Sodium Methoxide. A suspension of 5.4 g (0.1 mol) of sodium methoxide in 45 m*l* of DMSO was stirred by introducing a stream of nitrogen into the suspension. A solution of 6.0 g (0.025 mol) of I in 30 m*l* of DMSO was added, drop by drop, to the suspension. The reaction mixture, which soon turned red-brown, was kept under nitrogen at room temperature for 4 hr, and then most of the solvent was evaporated at 1 mmHg. To the residue were added 50 m*l* of ether and 50 m*l* of ice water. The aqueous layer was added, drop by drop, to an ice-cold 100 m*l* of 4 N hydrochloric acid to obtain a precipitate. This precipitate was separated from the aqueous solution (A) by filtration to give 2.4 g (50%) of azoxybenzene-2,2',3,3'-tetracarboxylic acid (II). The analytical sample was obtained by recrystallization from water: mp 236—238°C (decomp); N. E. 93 (calcd 94). The infrared spectrum (in KBr disk) showed hydrogen-bonded multiplet hydroxyl absorptions at 3000—2500 cm^{-1}, and carbonyl absorptions at 1730 and 1680 cm^{-1}.

Found: C, 51.26; H, 2.60; N, 7.32%. Calcd for $C_{16}H_{10}O_9N_2$: C, 51.34; H, 2.69; N, 7.49%.

The acidified aqueous solution, A, was extracted with ether. The ether was evaporated to dryness to give 1.5 g (43%) of 3-nitrophthalic acid (III), which showed a mp of 214—217°C after recrystallization from water. The mixed melting point with an authentic sample prepared by the alkaline hydrolysis of the starting material showed no depression.

Reaction of Dimethyl 4-Nitrophthalate (IV) With DMSO-Sodium Methoxide. An experimental run in which dimethyl 4-methoxyphthalate was obtained will be described as a typical example. A solution of 6.0 g (0.0025 mol) of I in 30 m*l* of DMSO was added to a suspension of 5.4 g (0.1 mol) of sodium methoxide in 45 m*l* of DMSO in a stream of nitrogen. The mixture was kept at room temperature under nitrogen for 4 hr. Most of the solvent was then removed by distillation under reduced pressure. To the residue there were added 50 m*l* of ether and 50 m*l* of water, and the mixture was separated into the aqueous (A) and ether (B) layers. The ether layer, B, was dried over anhydrous sodium sulfate. The ether was removed and the residue was distilled under reduced pressure to give 1.2 g (22%) of dimethyl 4-methoxyphthalate (VII), bp 136—137°C/3 mmHg. The infrared spectrum showed carbonyl absorption at 1725 cm^{-1}. The NMR spectrum (in CCl_4) showed one aromatic proton at 2.28—2.43 τ (1H, broad doublet), two aromatic protons at 3.07—3.20 τ (2H, broad doublet), and two methoxyl singlets at 6.20 and 6.23 τ (the total of the protons due to these two singlets was 9H).

Found: C, 59.04; H, 5.35%. Calcd for $C_{11}H_{12}O_5$: C, 58.92; H, 5.45%.

The aqueous layer A was added to 100 m*l* of cold 4 N hydrochloric acid. The precipitate thus obtained was then separated from the aqueous acid solution (C) by filtration. The precipitate consisted of 0.7 g (13%) of 5-methoxy-2-nitroso-1,3-indanedione (V). The analytical sample of V was obtained by recrystallization from isopropyl alcohol, mp 204—206°C (decomp). The infrared spectrum 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, and instead a broad absorption appeared at 3150 cm^{-1}. The NMR spectrum (in DMSO-d_6) showed an acidic proton at −4.25 τ (1H, broad singlet), one aromatic proton at 2.02—2.15 τ (1H, broad doublet), two aromatic protons at 2.50—2.65 τ (2H, broad doublet), and a methoxyl singlet at 6.00 τ (3H). The molecular weight, as measured by the Rast method, was 225 (calcd 205).

Found: C, 58.72; H, 3.38; N, 6.65%. Calcd for $C_{10}H_7O_4N$: C, 58.54; H, 3.44; N, 6.83%.

The aqueous acid solution C was extracted with ether. The ether was then evaporated, and the residue was washed with benzene to give 2.8 g (51%) of 4-methoxyphthalic acid (VI). The analytical sample was obtained by recrystallization from water: mp 157—160°C, (lit.[6] mp 168—170°C); N. E. 97 (calcd 98). The acid VI was identical in every respect with the acid obtained by an alkaline hydrolysis of the ester VII.

Found: C, 54.92; H, 4.20%. Calcd for $C_9H_8O_5$: C, 55.10; H, 4.11%.

In a separate experiment, the compounds V and VI were obtained respectively, in 49 and 48% yields while none of the ester VII was isolated.

Acetylation of 5-Methoxy-2-nitroso-1,3-indanedione V. A mixture of 500 mg (0.0024 mol) of V, 5 m*l* of acetic anhydride, and 5 m*l* of pyridine was heated at reflux for 10 min. After cooling, the reaction mixture was subjected to distillation under reduced pressure to remove the unreacted reagents at room temperature. The residue was then washed with cold methanol and recrystallized from benzene to give 280 mg (47%) of a yellow monoacetylated product, mp 185—189°C (decomp). The infrared spectrum showed carbonyl absorptions at 1802, 1747, and 1708 cm^{-1} and absorptions at 1626 (w), 1590 (s), 1492 (s), 1470 (w), and 1436 (w) cm^{-1}. The NMR spectrum showed an aromatic proton at 1.97—2.13τ (1H, broad doublet), two aromatic protons at 2.41—2.57 τ (2H, broad doublet), a signal due to methoxyl at 6.03 τ (3H, singlet), and a signal due to acetyl at 7.72 τ (3H, singlet). The molecular weight, as measured with a Hitachi-Perkin Elmer 115 molecular-weight apparatus, using benzene as the solvent, was 254 (calcd 248).

Found: C, 58.33; H, 3.84; N, 5.68%. Calcd for $C_{12}H_9O_5N$: C, 58.30; H, 3.67; N, 5.67%.

Alkaline Hydrolysis of V. A mixture of 500 mg (2.4 mmol) of V and 4 g of potassium hydroxide in 13 m*l* of methanol and 8 m*l* of water was refluxed for 48 hr, and then most of the solvent was removed by distillation under reduced pressure. The residue was neutralized with hydrochloric acid, extracted with ether, and dried over anhydrous sodium sulfate. The ether was evaporated to give a precipitate. The recrystallization of the precipitate from water gave 400 mg (83%) of 4-methoxyphthalic acid VI, mp 158—160°C, which was identical in every respect with the acid VI obtained above.

Detection of Nitrite Ion Liberated During the Course of the Reaction of IV with DMSO-Sodium Methoxide. The reaction of IV with DMSO-sodium methoxide was carried out in a nitrogen stream as above. The Griess-Romijn reagent[7] was then added to a small portion of the aqueous acid solution C (see above) obtained in this experiment. The ultraviolet spectrum of the resultant solution showed an absorption maximum at 514 mμ, indicating the presence of the nitrite ion.

Reaction of IV with DMSO-Sodium Ethoxide. This experiment was carried out by a method similar to that employed for the reaction of IV with DMSO-sodium methoxide. However, in this case the DMSO-sodium ethoxide system was used for the preparation of methylsulfinyl carbanion. This experiment gave 5-ethoxy-2-nitroso-1,3-indanedione (VIII), mp 174—181°C, and 4-ethoxyphthalic acid (IX), mp 151—154°C, in yields of 51 and 32% respectively. The infrared spectrum of VIII showed a hydroxyl band at 3510 cm^{-1} and carbonyl bands at 1742 and 1694 cm^{-1}. The NMR spectrum (in DMSO) showed an acidic proton at −4.10τ (1H, broad singlet), one aromatic proton at 2.16—2.27 τ (1H, broad doublet), two aromatic protons at 2.59—2.75 τ (2H, broad doublet), two methylene protons in the ethoxyl group at 5.66—6.01 τ (2H, quartet), and three methyl protons in the ethoxyl group at 8.56—8.84 τ (3H, triplet). However, since the analytical data showed that the VIII obtained here was slightly contaminated even after repeated recrystallizations from ethanol - water, the VIII was converted to the *O*-acetyl derivative and the structure was confirmed (see below).

6) S. N. Chakravarti and W. H. Perkin, Jr., *J. Chem. Soc.*, **131**, 196 (1929).

7) F. H. Welcher, "Organic Analytical Reagents," Vol. 11, D. van Nostrand, New York, N. Y. (1948), p. 406.

The structure of IX was established on the basis of the following data. The neutralization equivalent was 101 (calcd 105). The infrared spectrum was consistent with the structure of IX in every respect.

Found: C, 56.92; H, 4.85%. Calcd for $C_{10}H_{10}O_5$: C, 57.14; H, 4.80%.

Acetylation of 5-Ethoxy-2-nitroso-1,3-indanedione (VIII). A mixture of 300 mg of the crude VIII, 3 m*l* of acetic anhydride, and 3 m*l* of dry pyridine was refluxed for 10 min. The unreacted reagents were evaporated at room temperature under reduced pressure. The residue was washed to give 290 mg (96%) of the acetylated product. The analytical sample was obtained by recrystallization from ligroin, mp 137—141°C (decomp). The infrared spectrum showed carbonyl absorptions at 1798, 1748 (w), and 1713 cm^{-1}.

Found: C, 60.00; H, 4.80; N, 5.44%. Calcd for $C_{13}H_{11}O_5N$: C, 59.77; H, 4.24; N, 5.36%.

Reaction of Methyl *o*-Nitrobenzoate (X) with DMSO - Sodium Methoxide. To a suspension of 5.4 g (0.1 mol) of sodium methoxide in 75 m*l* of DMSO, there was added, drop by drop, 4.5 g (0.25 mol) of X in a stream of nitrogen at room temperature. The reaction mixture was kept under the same conditions for 4 hr, and then most of the solvent was evaporated under reduced pressure. The addition of 50 m*l* of ether and 50 m*l* of ice water to the residue, and the subsequent acidification of the aqueous layer with 100 m*l* of 4 N hydrochloric acid, gave a red precipitate. This precipitate was separated from the aqueous acid solution (A) to afford 1.5 g (44%) of azobenzene-2,2'-dicarboxylic acid (XI). The analytical sample of XI was obtained by recrystallization from acetic acid, mp 230—232°C (decomp) (lit.[8] mp 238—239°C (decomp)).

The neutralization equivalent was 135 (calcd 135).

Found: C, 62.60; H, 3.81; N, 10.10%. Calcd for $C_{14}H_{10}O_4N_2$: C, 62.22; H, 3.73; N, 10.37%.

The extraction of the aqueous acid solution A with ether and the evaporation of the ether gave 1.2 g (33%) of azoxybenzene-2,2'-dicarboxylic acid (XII), which, after recrystallization from acetic acid, showed a mp 230°C (decomp) (lit.[9] 253—255°C (decomp)). The neutralization equivalent was 147 (calcd 143).

Found: C, 59.04; H, 3.46; N, 9.32%. Calcd for $C_{14}H_{10}O_5N_2$: C, 58.74; H, 3.52; N, 9.79%.

Reaction of Methyl *p*-Nitrobenzoate (XIII) with DMSO - Sodium Methoxide. The compound XIII was allowed to react with DMSO-sodium methoxide in a manner similar to that described above. By this reaction *p*-nitrobenzoic acid, mp 238—240°C, was obtained in an almost quantitative yield.

Formation of 5-Methoxy-2-nitroso-1,3-indanedione (V) from Dimethyl 4-Methoxyphthalate (VII). Potassium (0.8 g, 0.02 g-atom) was dissolved in 20 m*l* of refluxing *t*-butyl alcohol. After cooling to room temperature, 15 m*l* of DMSO was added and the solution was distilled under a reduced pressure of about 2 mmHg, using a Vigreux column, until the DMSO started to distill out (bp 45°C), and then the solution was cooled. To the partially-solidified residue there was added, drop by drop, 1.0 g (4.5 mmol) of VII in 5 m*l* of DMSO in a stream of nitrogen at room temperature. The reaction mixture was kept for 2.5 hr under nitrogen, and then most of the solvent was evaporated under reduced pressure. Ether (10 m*l*) and ice water (10 m*l*) were added to the residue, and the aqueous layer was separated. To this aqueous solution there was added, drop by drop, a solution of 800 mg of 97% sodium nitrite in 40 m*l* of 4 N-hydrochloric acid under ice-cooling. A yellow precipitate soon appeared; it was separated by filtration to give 630 mg (66%) of V. Recrystallization from isopropyl alcohol showed a mp of 203—206°C (decomp). This material was identical in every respect with that obtained in the reaction of IV with DMSO - sodium methoxide.

Reaction of Dimethyl 4-Methoxyphthalate (VII) with DMSO - Potassium *t*-Butoxide. A mixture of potassium *t*-butoxide in DMSO was prepared from 2.8 g (0.072 g-atom) of potassium, 70 m*l* of *t*-butyl alcohol and 70 m*l* of DMSO as has been described above. To this mixture there was added, drop by drop, 3.5 g (0.016 mol) of VII in 10 m*l* of DMSO in a stream of nitrogen at room temperature. The reaction mixture, which first turned green and then brown, was kept for 3 hr under nitrogen. Most of the solvent was evaporated under reduced pressure, and 36 m*l* of ether and 36 m*l* of ice water were added to the residue. The aqueous layer was separated and acidified with 75 m*l* of 4N-hydrochloric acid. The precipitate thus obtained was separated by filtration to give 3.7 g (92%) of a material which contained sulfur and chlorine atoms. This material, mp 110—115°C, showed absorption bands at 1752, 1713, 1600, 1493 cm^{-1} in its infrared spectrum and the positive Beilstein test. Therefore, the compound was presumed to be 5-methoxy-2-chloro-2-methylthio-1,3-indanedione (XVII). However, no pure sample of this material was obtained because of the difficulty of purification.

Therefore, XVII was converted to 2-ethoxy-5-methoxy-2-methylthio-1,3-indanedione (XVIII). A mixture of 500 mg (2 mmol) of the crude XVII in 5 m*l* of ethanol was refluxed for 3 hr. The solvent was then evaporated under reduced pressure to give an oil which solidified upon standing for 2 days. The recrystallization of the solid from petroleum ether gave 400 mg (80%) of XVIII, mp 73—74.5°C. This compound contained sulfur atoms. The infrared spectrum showed carbonyl absorptions at 1742 and 1707 cm^{-1}. The NMR spectrum (in CCl_4) showed an aromatic proton at 2.10—2.26 τ (1H, broad doublet), two aromatic protons at 2.61—2.76τ (2H, broad doublet), two methylene protons of the ethoxyl group at 5.81—6.16τ (2H, quartet), three methyl protons of the methoxyl group at 6.05τ (3H, singlet), three methyl protons of the methylthio group at 7.84 τ (3H, singlet), and three methyl protons of the ethoxyl group at 8.67—8.91 τ (3H, triplet).

Found: C, 58.90; H, 5.39%. Calcd for $C_{13}H_{14}O_4S$: C, 58.64; H, 5.30%.

Reaction of Dimethyl 4-Methoxyphthalate (VII) with DMSO-Sodium Methoxide. This reaction was carried out in a manner similar to that employed for the reaction of I with DMSO - sodium methoxide, using VII as a substrate. By this reaction 4-methoxyphthalic acid was obtained in an almost quantitative yield.

Reaction of Dimethyl Phthalate with DMSO-Sodium Methoxide and DMSO - Potassium *t*-Butoxide. The reaction of dimethyl phthalate with

8) H. D. K. Drew and J. K. Landquist, *J. Chem. Soc.*, **1938**, 292.

9) J. S. Morley, *ibid.*, **1959**, 2280.

DMSO-sodium methoxide was carried out in a manner similar to that described for the reaction of I with DMSO-sodium methoxide to give 2-chloro-2-methylthio-1,3-indanedione (XIX) in a 44% yield, mp 63—64°C (lit.[1] 63—64°C).

The reaction of dimethyl phthalate with DMSO-potassium *t*-butoxide was carried out in a manner similar to that described for the reaction of VII with DMSO-*t*-butoxide to give XIX in a 62% yield.