

stituted phenols, hitherto unreported, are recorded in Table V.²⁴ Values for σ_m were calculated from the equation $pK_a = 9.919 - 2.229 \sigma$.¹

(24) Other data may be found in L. Doub and J. M. Vandenberg, *J. Am. Chem. Soc.*, **71**, 2414 (1949).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA]

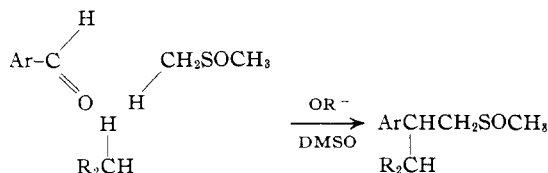
Condensation Reactions of Aromatic Aldehydes in Dimethyl Sulfoxide Solution. Asymmetric Tricarbon Condensation Involving Dimethyl Sulfoxide^{1,2}

BY GLEN A. RUSSELL³ AND HANS-DIETER BECKER

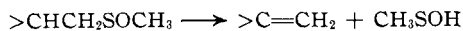
RECEIVED MARCH 1, 1963

An asymmetric tricarbon condensation involving an aromatic aldehyde, diphenylmethane, and the solvent dimethyl sulfoxide has been found to occur in the presence of potassium *t*-butoxide. The condensation product readily undergoes an elimination reaction to yield either of two isomeric triarylpropenes. The mechanism of the condensation reaction has been established by isolation of all probable intermediates.

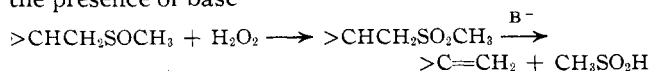
An investigation of the reaction of molecular oxygen with benzyl-type carbanions in dimethyl sulfoxide (80%) and *t*-butyl alcohol (20%) solutions led to the conclusion that the reaction products often resulted from condensation of the initially formed aldehydes with the starting toluenes.⁴ We have therefore studied, in the absence of oxygen, the reaction of aromatic aldehydes with active methylene compounds in dimethyl sulfoxide (DMSO) solution containing potassium *t*-butoxide. This study led to the discovery of a tricarbon condensation involving dimethyl sulfoxide as one of the reactants.



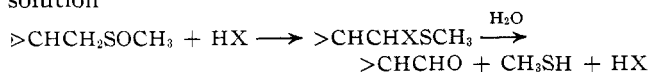
Sulfoxides are potentially valuable intermediates for the synthesis of sulfur-free compounds by virtue of their ability (a) to undergo pyrolysis or base-catalyzed elimination



(b) to form sulfones which can undergo elimination in the presence of base



(c) to undergo the Pummerer rearrangement in acid solution

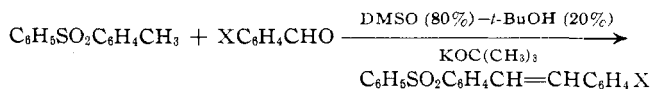


Results

Benzaldehydes and substituted benzaldehydes readily undergo condensation reactions in DMSO solution containing potassium *t*-butoxide either with DMSO itself⁴ or with added active methylene compounds. Because of the unique ability of DMSO to promote the formation of carbanions by the reaction of alkoxide ions with saturated carbon-hydrogen bonds,^{4,5} we have investi-

Acknowledgments.—We are indebted to Mr. H. K. Miller and Mrs. Anne Wright for determination of high-resolution infrared spectra, and to Dr. E. D. Becker and Mr. R. B. Bradley for measurement of n.m.r. spectra.

gated the reactivity in condensation reactions of methylene compounds that are generally considered to be unactive in alcoholic solvents. We first investigated the reaction of phenyl *p*-tolyl sulfone with aromatic aldehydes to form stilbenes. Table I summarizes the pertinent results.



No attempts were made to optimize the yields.

TABLE I

CONDENSATION OF PHENYL *p*-TOLYL SULFONE WITH BENZALDEHYDE IN DMSO (80%)-*t*-BuOH (20%)

RC ₆ H ₄ CHO (mmoles) R =	Sulfone, mmoles	KOC- (CH ₃) ₃ , g.	Sol- vent, ^b ml.	Yield of stilbene, ^c mg.	%
H (10)	2.5	0.56	16	320	40
<i>p</i> -CH ₃ O (22)	5.0	1.12	32	560	32
<i>p</i> -C ₆ H ₅ SO ₂ (1.5)	1.5	0.33	7	270	39
<i>p</i> -(CH ₃) ₂ N (3.0)	2.5	0.60	18	100	11
3,4-Methylenedioxy (5.0)	5.0	1.12	37	100	5.5

^a Sublimed. ^b DMSO (80%)-*t*-BuOH (20%). ^c Recrystallized; reaction period 40–50 min. at room temperature.

The condensation of *p*-carbomethoxybenzaldehyde and methyl *p*-toluate was thoroughly investigated due to its pertinence to the autooxidation of methyl *p*-toluate in basic solution.⁴ At room temperature yields of the dimethyl ester of *p,p'*-stilbenedicarboxylic acid in excess of 75% were achieved.

Attempts to produce a triphenylethylene derivative by the reaction of phenyl *p*-tolyl sulfone or diphenylmethane with benzophenone in DMSO always led to the benzophenone-DMSO adduct^{4,6} as the major product. When diphenylmethane was substituted for the phenyl *p*-tolyl sulfone only a small amount of a reaction product was formed from reaction with *p*-anisaldehyde at room temperature in DMSO (80%)-*t*-butyl alcohol (20%) mixtures. However, in alcohol-free DMSO at 60° either Va or VIIa, or a mixture of the two, can be formed depending upon the reaction conditions. Shorter reaction times and lower concentrations of potassium *t*-butoxide lead to the asymmetric tricarbon condensation⁷ product Va while longer reaction

(6) E. J. Corey and M. Chaykovsky, *ibid.*, **84**, 867 (1962).

(7) Asymmetric tricarbon condensations involving formaldehyde and two acidic methylene compounds, such as 1,3-diketones, have been extensively studied by H. Hellmann and co-workers (H. Hellmann and M. Schroder, *Ann.*, **656**, 85 (1962); H. Hellmann, *Bull. soc. chim. France*, 2197 (1961)).

(1) Reactions of Resonance Stabilized Anions. Part IX.

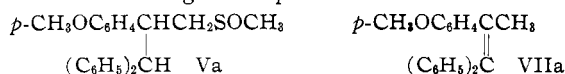
(2) This work was supported by the Air Force Office of Scientific Research.

(3) Alfred P. Sloan Foundation Fellow, 1959–1963.

(4) G. A. Russell, E. G. Janzen, H.-D. Becker, and F. J. Smentowski, *J. Am. Chem. Soc.*, **84**, 2652 (1962).

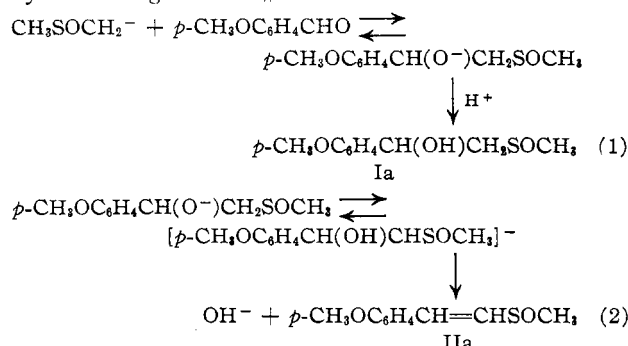
(5) (a) D. J. Cram, J. L. Matos, F. Hauck, A. Langemann, K. R. Kopecky, W. D. Nielsen, and J. Allinger, *ibid.*, **81**, 5774 (1959); D. J. Cram, B. Rickborn, and G. R. Knox, *ibid.*, **82**, 6412 (1960). (b) C. C. Price and W. H. Snyder, *ibid.*, **83**, 1773 (1961); A. Schriesheim, J. E. Hofmann, and C. A. Rowe, *ibid.*, **83**, 3731 (1961).

periods and higher concentrations of base favor the elimination-rearrangement product VIIa.

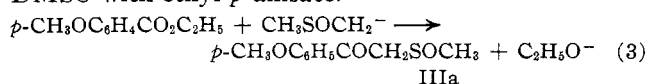


A similar reaction was observed with benzaldehyde and piperonal to give the elimination products VIIb and VIIc.

It was found that under the reaction conditions that triphenylethylene did not react with DMSO to yield the tricarbon condensation product. With this knowledge, a thorough study of the reaction of *p*-anisaldehyde with DMSO was performed. As shown in Chart I, *p*-anisaldehyde and dimethyl sulfoxide react to first form 1:1 adduct Ia which can be isolated by the proper choice of conditions. Under more drastic conditions Ia dehydrates to give the α,β -unsaturated sulfoxide IIa.

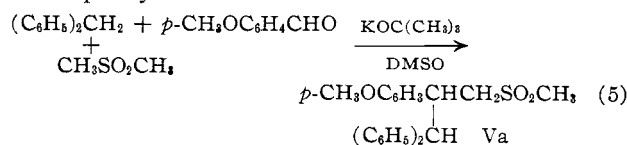


The β -hydroxysulfoxide Ia is readily oxidized by active manganese dioxide to the β -ketosulfoxide IIIa which we have also prepared by the condensation of DMSO with ethyl *p*-anisate.⁸

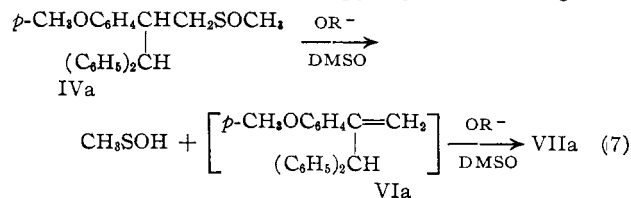


The addition of anions to α,β -unsaturated sulfoxides has been previously recognized.⁹ The mechanism of

potassium *t*-butoxide (reaction 4, Chart I). The tricarbon condensation products IV are readily oxidized by hydrogen peroxide in acetic acid to the corresponding sulfones V. We have also succeeded in preparing the same sulfones by an asymmetric tricarbon condensation between dimethyl sulfoxide, an aromatic aldehyde, and diphenylmethane in DMSO solution



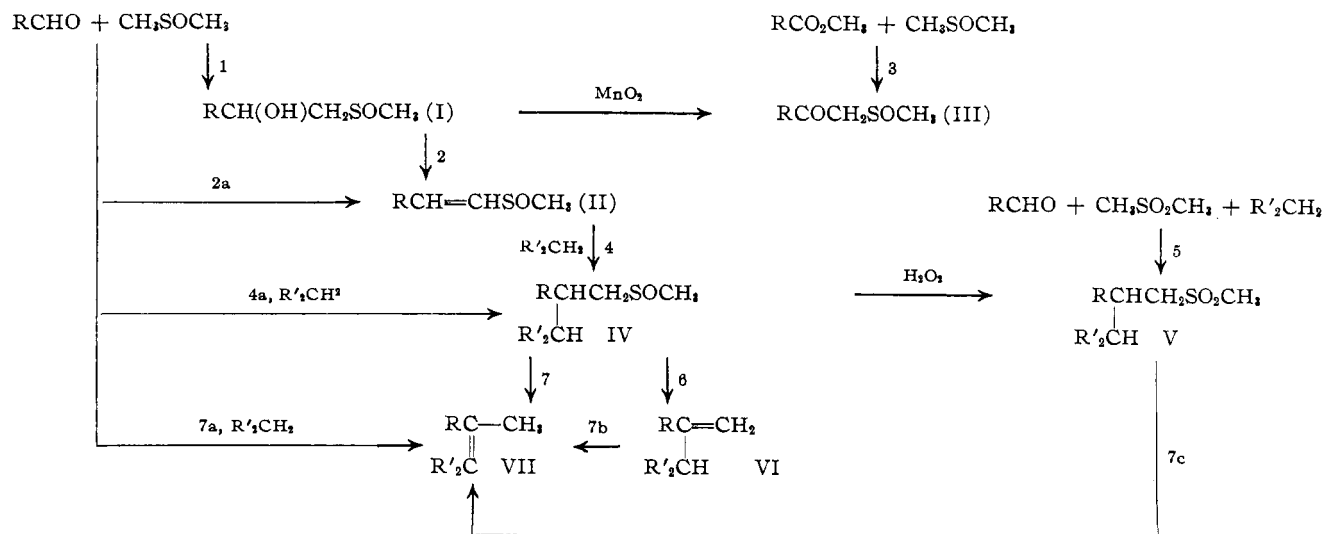
In the presence of excess potassium *t*-butoxide IVa is converted to the olefin VIIa (reaction 7). This conversion apparently involves a pyrolysis¹⁰ or an E2 β -elimination reaction followed by isomerization of the initially formed olefin.^{5b,5c,11} The corresponding sulfone Va, which was quite stable to pyrolysis (distilling under



vacuum at 275°), also underwent an elimination reaction (reaction 7c) in DMSO containing potassium *t*-butoxide to olefin VIIa in 48% yield.¹² Some evidence for the intermediary of olefin VIa in the preparation of VIIa is furnished by the observation that VIa is formed in nearly quantitative yield by the pyrolysis of IVa under vacuum at 220° (reaction 6). The olefin VIa can be isomerized to VIIa quantitatively by potassium *t*-butoxide in DMSO (80%)–*t*-butyl alcohol (20%) solution (reaction 7b).

The scope of this asymmetric tricarbon condensation has not been fully investigated. Preliminary attempts utilizing dibutyl sulfoxide in place of DMSO have given

CHART I
CONDENSATION REACTIONS IN THE PRESENCE OF BASE



formation of the tricarbon condensation product seems to be conclusively established by the observation that IVa is formed from the Michael addition of diphenylmethane to IIa in DMSO solution in the presence of

only negative results. Substitution of cyclohexanone for the Michael donor in the condensation involving

(10) C. A. Kingsbury and D. J. Cram, *J. Am. Chem. Soc.*, **82**, 1810 (1960).

(11) C. C. Price and W. H. Snyder, *Tetrahedron Letters*, 69 (1962); A. Schriesheim and C. A. Rowe, *J. Am. Chem. Soc.*, **84**, 3160 (1962).

(12) A study of eliminations in basic solution of IVa and Va prepared from α -deuterio-*p*-anisaldehyde by Mr. K. Y. Chang has shown that both eliminations are solely β -eliminations.

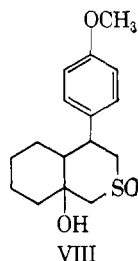
(8) H.-D. Becker, G. F. Mikol, and G. A. Russell, *J. Am. Chem. Soc.*, **85**, 3410 (1963).

(9) M. F. Shostakovskii, E. N. Prilezhaeva, L. V. Tsymbal, R. T. Tolchinskaya, and N. G. Starovca, *Zh. Obshch. Khim.*, **31**, 2326 (1961).

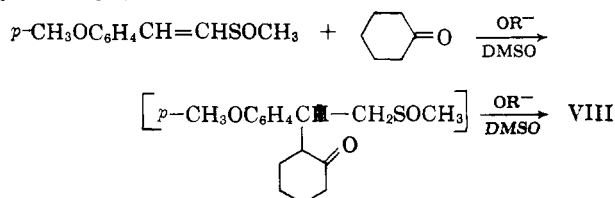
TABLE II
 MELTING POINTS AND ANALYSES OF $\text{XC}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{SO}_2\text{C}_6\text{H}_5$

X	Calculated			Found			M.p., °C.
	C	H	S	C	H	S	
H	74.99	5.03	9.99	74.82	5.01	10.01	184–185
<i>p</i> -CH ₃ O	71.99	5.18	9.13	71.77	5.02	9.36	202–203
<i>p</i> -C ₆ H ₅ SO ₂ -	67.82	4.38	13.9	67.71	4.68	13.43	315
<i>p</i> -(CH ₃) ₂ N-	72.71	5.82	3.85 (% N)	72.51	5.72	4.09 (% N)	250–251
3,4-Methylenedioxy	69.22	4.43	8.78	69.10	4.27	8.99	188

p-anisaldehyde had led to a heterocyclic product (VIII) in low yield.



This product apparently involves the following sequence of reactions



The reaction product VIII represents the interested case in which the free methyl group of the first-formed tricarbon condensation product underwent further reaction with the carbonyl group of the cyclohexanone to form the cyclic β -hydroxysulfoxide. The low yield of the product is presumably determined by self-condensation reactions of cyclohexanone or by the competing reaction of cyclohexanone with the carbanion from DMSO to give as a product the unsaturated sulfoxide $\text{C}_6\text{H}_{10}=\text{CHSOCH}_3$ or products of its further reaction.

Substitution of acetophenone for the Michael donor led to the isolation of $\text{C}_6\text{H}_5\text{CH}(\text{CH}_2\text{COC}_6\text{H}_5)\text{CH}_2\text{SO}_2\text{CH}_3$, presumably from air oxidation of the corresponding sulfoxide during work-up. In the presence of piperidine the Michael olefin IIIa could be isolated from basic solutions. Substitution of *n*-butyraldehyde or crotonaldehyde for the aromatic aldehyde with diphenylmethane as the potential Michael donor gave recovered diphenylmethane as the only crystallizable product.

In dimethyl sulfoxide solution containing an active methylene compound (R_2CH_2) and potassium *t*-butoxide there are presumably three anions present, $\text{CH}_3\text{SOCH}_2^-$, R_2CH^- , and $(\text{CH}_3)_3\text{CO}^-$. The products of reaction of a carbonyl-containing compound in this solution depends on the concentrations and reactivities of the ions present as well as upon the reversibility of any addition step. For condensations involving a benzaldehyde with phenyl *p*-tolyl sulfone it seems reasonable that the concentrations of the anion from the active methylene compound predominates over the anion from DMSO, whereas in condensation reactions involving diphenylmethane the concentration of the methylsulfinyl carbanion predominates over the diphenylmethide ion. For substances of intermediate acidity, condensation involving both R_2CH^- and $\text{CH}_3\text{SOCH}_2^-$ might be expected. Possibly cyclohexanone fits into this category.

As might be expected, when the more acidic fluorene was substituted for diphenylmethane in an attempted asymmetric tricarbon condensation with benzaldehyde or *p*-anisaldehyde in DMSO solution, the reaction product was di-9-fluorenylphenylmethane, a product of a symmetrical tricarbon condensation. Di-9-fluorenylphenylmethane has been previously prepared by the addition of fluorene to 9-benzylidenefluorene in pyridine-sodium hydroxide solution.¹³

Although aldehydes preferentially react with the methylsulfinyl or methylsulfonyl carbanion rather than with the diphenylmethide ion, the reverse is true when additions to the first-formed α,β -unsaturated sulfoxide or sulfone are considered. Whether this is a kinetic or equilibrium phenomenon is unknown.

Experimental¹⁴

Condensation of Phenyl *p*-Tolyl Sulfone with Aromatic Aldehydes.—The preparation of *p*-(phenylsulfonyl)-stilbene will be used as illustrative of the procedure. Phenyl *p*-tolyl sulfone (2.5 mmoles) was dissolved 13 ml. of a mixture of DMSO (80%)–*t*-butyl alcohol (20%), 560 mg. of sublimed potassium *t*-butoxide added, and the mixture was stirred under an atmosphere of dry, prepurified nitrogen. Benzaldehyde (10 mmoles) was added as a solution in 5 ml. of the solvent mixture from a buret over a 10-min. period. Thirty minutes after the addition of the benzaldehyde was complete, 50 ml. of water was added to give a colorless, crystalline precipitate. It was washed with warm ethanol and recrystallized from chloroform to give 320 mg. (40%) of *p*-(phenylsulfonyl)-stilbene, m.p. 184–185°. The n.m.r. spectrum in chloroform-*d* at 60 Mc./sec. did not show any saturated protons. The integrated spectrum gave absorptions in the vinyl and aromatic regions having the relative intensities of 10:4:2.

A similar procedure was used to prepare the other stilbenes listed in Table I. Pertinent analytical data are summarized in Table II.

Dimethyl *p,p'*-Stilbenedicarboxylate.¹⁵—Potassium (1.2 g., 30 mg.-atoms) was dissolved in 40 ml. of *t*-butyl alcohol and the excess alcohol removed under vacuum at a temperature of 60°. The solid potassium *t*-butoxide was dissolved in 40 ml. of DMSO (80%)–*t*-butyl alcohol (20%) at 60°. Ethyl acetate (1.4 g., 16 mmoles) was added to remove hydroxide ion and after 10 min. at 60° the solution was cooled to room temperature and methyl *p*-toluate (3.0 g., 20 mmoles) was added. *p*-Carbomethoxybenzaldehyde, prepared according to the procedure of Lieberman and Connor,¹⁶ m.p. 59–60° (lit.¹⁷ 60°), dissolved in 5 ml. of the solvent mixture was added dropwise and the reaction mixture stirred for 2 hr. under dry, oxygen-free nitrogen. Upon pouring into 50 ml. of ice-water acidified with hydrochloric acid a precipitate was formed which was suspended in 50 ml. of 0.5 *M* sodium hydroxide solution, filtered, and washed with water to give 1.55 g. (77%) of *p,p'*-stilbenedicarboxylic acid. The acid was dissolved in 225 ml. of dimethylformamide-dioxane (4:5) and treated with excess diazomethane. The esterified product was isolated by the addition of water and again treated with excess diazomethane in 120 ml. of ether-dioxane (5:1). After removal of solvent the ester was recrystallized from chloroform, m.p. 236–238°, lit.¹⁸ 227–228°. The infrared spectrum and m.p. were identical with those of a sample prepared by the carboxylation of the di-Grignard reagent of *p,p'*-dibromostilbene. Upon hydrogenation of the ester over

(13) L. A. Pinck and G. E. Hilbert, *J. Am. Chem. Soc.*, **68**, 2014 (1946); E. D. Bergmann and D. Lavie, *ibid.*, **74**, 3173 (1952).

(14) Integrated n.m.r. and infrared spectra consistent with the assigned structures were obtained for all new compounds reported. Molecular weight determinations were made using an electroosmometer. All melting points are uncorrected and were obtained using a Fisher-Johns melting point block.

(15) Experiments performed by Mr. Gerard J. Mikol.

(16) S. V. Lieberman and R. Connor, *Org. Syn.*, **18**, 61 (1938).

(17) H. Simonis, *Ber.*, **45**, 1584 (1912).

(18) G. P. Hager, A. M. VanArendonk, and H. A. Shonle, *J. Am. Chem. Soc.*, **66**, 1982 (1944).

palladium-on-carbon catalyst, dimethyl *p,p'*-dibenzylidicarboxylate, m.p. 116–117°, was obtained. The m.p. and infrared spectrum of this material were identical with those of the ester prepared by the method of Sloan and Vaughan, m.p. 117–118°.¹⁹

***p*-Anisaldehyde-Dimethyl Sulfoxide Adduct (Ia, R = *p*-CH₃OC₆H₄).**—Sublimed potassium *t*-butoxide (1.12 g.) was dissolved in 3 ml. of *t*-butyl alcohol and 12 ml. of DMSO. After the dropwise addition of 1.36 g. of *p*-anisaldehyde (10 mmoles) the mixture was kept for 3 min. at 45° and 1 hr. at room temperature. Addition of 100 ml. of water to the reaction mixture gave a slightly cloudy solution which was kept in an open beaker at room temperature. After evaporation of the solvent the solid residue was washed with water and filtered, yielding 855 mg. (40%) of Ia, m.p. 127–128°. Recrystallization from hot ethanol raised the m.p. to 129–131°.

Anal. Calcd. for C₁₀H₁₂O₄S (214.21): C, 56.07; H, 6.59; S, 14.91. Found: C, 56.09; H, 6.46; S, 15.10.

Piperonal-Dimethyl Sulfoxide Adduct (Ic, R = 3,4-CH₂O₂C₆H₃).—Sublimed potassium *t*-butoxide (112 mg.) was added to a solution of 1.7 ml. (10 mmoles) of diphenylmethane in 15 ml. of DMSO under nitrogen at 60°. Piperonal (1.5 g., 10 mmoles) in 5 ml. of DMSO was added dropwise over a period of 10 min. The temperature was kept at 60–65° for 3 more min. after which the reaction mixture was then kept at room temperature for 45 min. Water (100 ml.) and 30 ml. of ether were added to the red-brown solution. Evaporation in an open beaker yielded a solid dark brown residue that was washed with 200 ml. of water. The colorless residue (483 mg., 21%) was recrystallized from hot ethanol by the addition of chloroform to yield Ic, m.p. 160°.

Anal. Calcd. for C₁₀H₁₂O₄S (227.20): C, 52.63; H, 5.30; S, 14.0. Found: C, 52.44; H, 5.43; S, 14.21.

***ω*-(Methylsulfinyl)-*p*-methoxyacetophenone (IIIa, R = *p*-CH₃OC₆H₄).**—Compound Ia (100 mg.) was dissolved in 10 ml. of acetone and 1 g. of active manganese dioxide added. The mixture was shaken occasionally after which the manganese oxides were removed by filtration and the precipitate washed with 50 ml. of acetone. The acetone solution was evaporated to give 92 mg. (90%) of IIIa, m.p. 101°; the mixture m.p. with IIIa prepared by reaction 3 showed no depression.

***β*-(Methylsulfinyl)-*p*-methoxystyrene (IIa, R = *p*-CH₃OC₆H₄).**
Reaction 2a.—To a solution of potassium *t*-butoxide (560 mg.) in 10 ml. of DMSO at room temperature, 0.7 ml. (5 mmoles) of *p*-anisaldehyde was added dropwise under an atmosphere of dry, prepurified nitrogen at room temperature. The solution was warmed to 60–65° for 80 min. After this time 100 ml. of water was added to the brown solution to yield an emulsion. The emulsion was extracted with 500 ml. of ether, and the ether extract was dried over sodium sulfate and evaporated to yield a light yellow oily residue that crystallized upon treatment with a little ether to give 450 mg. (46%) of IIa in the form of fine, colorless needles, m.p. 65°. Recrystallization from ether raised the m.p. to 67–68°.

Anal. Calcd. for C₁₀H₁₂O₂S (196.20): C, 61.21; H, 6.17; S, 16.31. Found: C, 61.11; H, 6.33; S, 16.00.

IIa. Reaction 2.—Compound Ia (53 mg., 0.25 mmole) was added to a solution of 56 mg. of potassium *t*-butoxide in 2 ml. of DMSO. The solution was kept at 60° under nitrogen for 10 min. The deep brown solution was then diluted with 10 ml. of water to yield a yellow emulsion from which the α,β -unsaturated sulfoxide IIa was extracted by ether. The infrared spectrum was identical with IIa prepared by reaction 2a. The yield was low and was not determined.

1-(Methylsulfinyl)-2-*p*-anisyl-3,3-diphenylpropane (IVa, R = C₆H₅, R' = *p*-CH₃OC₆H₄).
Reaction 4a.—Potassium *t*-butoxide (1.24 g.) and 1.68 g. of diphenylmethane (10 mmoles) were dissolved in 15 ml. of DMSO, and *p*-anisaldehyde (1.36 g., 10 mmoles) was added dropwise. The reaction mixture was kept at 40° under dry, prepurified nitrogen for 2 hr. After that time 100 ml. of ice-water and 30 ml. of ether were added. The colorless precipitate which formed was filtered, washed with water and ether, and dried to yield 2.0 g. of IVa (50%), m.p. 175°. Recrystallization from hot ethanol raised the m.p. to 178–180°.

Anal. Calcd. for C₂₃H₂₄O₂S (364.42): C, 75.80; H, 6.64; S, 8.78. Found: C, 75.78; H, 6.94; S, 8.94. mol. wt. (dioxane), 380.

IVa. Reaction 4.—Compound IIa (196 mg., 1 mmole) was dissolved in 5 ml. of DMSO at room temperature under nitrogen and 168 mg. (1 mmole) of diphenylmethane and 112 mg. of potassium *t*-butoxide added. After 60 min. the brown solution was added to 50 mg. of ice to yield an emulsion which was extracted with 200 ml. of ether. Evaporation of the ether gave a yellow oil which crystallized upon treatment with ether to yield (after recrystallization from ether) 85 mg. (23%) of IVa, m.p. 178°. The infrared spectrum was identical with that of IVa obtained in direct condensation (reaction 4a).

1-(Methylsulfonyl)-2-*p*-anisyl-3,3-diphenylpropane (Va, R' = C₆H₅, R = *p*-CH₃OC₆H₄).—Compound IVa (500 mg., 1.37 mmoles) was dissolved in 5 ml. of acetic acid. Addition of 2.7 ml. of 30% hydrogen peroxide at 50° (2 min.) gave a clear solution from which colorless crystals started to precipitate after 2 hr. at room temperature. After 12 hr., the crystals were removed by filtration to give 510 mg. (97.5%) of Va, m.p. 202–204°. Recrystallization from hot ethanol raised the m.p. to 205–207°.

Anal. Calcd. for C₂₃H₂₄O₄S (380.42): C, 72.61; H, 6.36; S, 8.41. Found: C, 72.43; H, 6.38; S, 8.49.

Va. Reaction 5.—Dimethyl sulfone (471 mg., 5 mmoles), 560 mg. of sublimed potassium *t*-butoxide, and 0.84 g. of diphenylmethane (5 mmoles) were dissolved in 8 ml. of DMSO. To this solution at 55° 0.69 g. of *p*-anisaldehyde (5 mmoles) was added dropwise and the reaction mixture held at 55° for 3 min. followed by 1 hr. at room temperature. Addition of 50 ml. of ice-water and 50 ml. of ether yielded colorless crystals which were filtered off to yield 650 mg. (34%) of Va, m.p. 205–207°. The mixture m.p. with Va prepared by the oxidation of the corresponding sulfoxide with hydrogen peroxide showed no depression. When the above experiment was repeated by first dissolving the dimethyl sulfone (5 mmoles) and potassium *t*-butoxide (560 mg.) in 8 ml. of DMSO at 55° followed by the addition of diphenylmethane (5 mmoles), only 117 mg. (6.2%) of Va could be isolated. It thus appears that reaction 5 gives a reasonable yield of V only when the diphenylmethide ion is present to trap the Michael olefin (ArCH=CHSO₂CH₃) as it is formed.

1-(Methylsulfonyl)-2,3,3-triphenylpropane (Vb, R = R' = C₆H₅).—Compound IVb (50 mg.) was dissolved in 0.6 ml. of acetic acid on a steam bath. After addition of 0.6 ml. of 30% hydrogen peroxide the solution was kept on a steam bath for 5 min. and at room temperature for 1 hr. The colorless needle-shaped crystals which separated from the reaction mixture were isolated by filtration to yield 50 mg. (96%) of Vb, m.p. 229°.

Anal. Calcd. for C₂₂H₂₂O₂S (350.40): C, 75.41; H, 6.33; S, 9.13. Found: C, 75.61; H, 6.46; S, 9.16.

3,3-Diphenyl-2-*p*-methoxyphenyl-1-propene (VIa, R' = C₆H₅, R = *p*-CH₃OC₆H₄).—Compound IVa (400 mg.) was heated in an oil bath under aspirator vacuum at 200–220° for 17 min. After this period the evolution of gas had ceased. The colorless oily residue was dissolved in 8 ml. of a chloroform-ethanol mixture and filtered. After standing overnight, 300 mg. (91%) of VIa was isolated as precipitated crystals, m.p. 71°. Compound VIa reacts readily with bromine in chloroform. The n.m.r. spectrum supports the structure assigned to the reaction product since the terminal methylene group is readily apparent.

Anal. Calcd. for C₂₂H₂₀O (300.38): C, 88.03; H, 6.63; -OCH₃, 10.03. Found: C, 87.96; H, 6.71; -OCH₃, 10.33.

2,3,3-Triphenyl-1-propene (Vib, R' = R = C₆H₅).—Compound IVb (200 mg.) was heated under vacuum in an oil bath at 220–225° for 10 min. Gas evolution ceased after 5 min. The almost colorless oil which remained was dissolved in 2 ml. of warm ethanol to yield 96 mg. (61%) of colorless Vib, m.p. 49–50°, after evaporation of solvent.

Anal. Calcd. for C₂₁H₁₈ (270.35): C, 93.29; H, 6.71. Found: C, 93.10; H, 6.76.

1,1-Diphenyl-2-*p*-methoxyphenylpropene (VIIa). Reaction 7a.—Sublimed potassium *t*-butoxide (2.24 g.) and 1.68 g. of diphenylmethane (10 mmoles) were dissolved in 30 ml. of DMSO. *p*-Anisaldehyde (1.36 g., 10 mmoles) was added dropwise under an atmosphere of dry, prepurified nitrogen. The reaction mixture was kept at 65° for 2.5 hr. after which time 100 ml. of ice water and 50 ml. of ether were added. A precipitate of 185 mg. of IVa was removed by filtration. The aqueous layer was extracted with 700 ml. of the ether. After drying over sodium sulfate, evaporation of the ether yielded an oil which crystallized upon treatment with ethanol to yield 2.09 g. (70%) of VIIa, m.p. 103–104°.

Anal. Calcd. for C₂₂H₂₀O (300.38): C, 87.96; H, 6.71. Found: C, 88.07; H, 6.86; mol. wt. (dioxane), 313.

VIIa. Reaction 7b.—Compound VIa (50 mg.) was dissolved in 0.4 ml. of DMSO and 0.1 ml. of *t*-butyl alcohol. Potassium *t*-butoxide (5 mg.) was added and the solution kept under nitrogen for 5.5 hr. Crystals precipitated after 1.5 hr. Water (10 ml.) was added and after 12 hr. crystals were separated by filtration to yield 48 mg. of VIIa, m.p. 102–103°, with an infrared spectrum identical with VIIa, obtained from reactions 7, 7a, and 7c.

VIIa. Reaction 7.—Compound IVa (300 mg., 8 mmoles) was dissolved in 4 ml. of DMSO and 1 ml. of *t*-butyl alcohol at 60° under nitrogen. Potassium *t*-butoxide (112 mg.) was added and the solution kept at 60–65° for 1 hr. and then at room temperature for 3.5 hr. and again at 60° for 0.5 hr. Water (50 ml.) was added together with 50 ml. of ether. The mixture was shaken and filtered, leaving the unreacted starting material

as an ether-insoluble residue. From the ether solution 118 mg. (48%) of VIIa crystallized after evaporation of the solvent.

VIIa. Reaction 7c.—Compound Va (50 mg., 0.13 mmole) and 100 mg. of potassium *t*-butoxide were dissolved in 0.4 ml. of *t*-butyl alcohol and 1.6 ml. of DMSO. The reaction mixture was kept under nitrogen at 75° for 2 hr. Addition of 10 ml. of water yielded an emulsion which was shaken with 3 ml. of ether. The crystalline product which separated from the ether-water mixture was separated after 2 days. Recrystallization from hot ethanol gave 19 mg. (48%) of VIIa, m.p. 103°. The infrared spectrum was identical with that of compounds prepared in reactions 7, 7a, and 7b.

VIIb and IVb (R' = R = C₆H₅). **Reactions 4a and 7a.**—Diphenylmethane (1.68 g., 10 mmoles) and 1.12 g. of potassium *t*-butoxide were dissolved under nitrogen at 60° in 15 ml. of DMSO. Benzaldehyde (1.0 g., 10 mmoles) in 5 ml. of DMSO was added over a period of 15 min. The color of the solution changed from red to green during the addition. The mixture was kept at room temperature for 30 min. after which time 100 ml. of ice-water was added. The mixture was extracted with 300 ml. of ether. Separation and evaporation of the ether layer yielded a yellow oil which contained colorless crystals. The oily residue was treated with few cc. of ether and filtered, yielding 155 mg. of IVb (5%). The m.p. after recrystallization from a chloroform-methanol mixture was 195–196°.

Anal. Calcd. for C₂₂H₂₂OS (334.40): C, 79.01; H, 6.63; S, 9.52. Found: C, 78.98; H, 6.72; S, 9.21.

The oil obtained after evaporation of the filtrate was heated with ethanol, yielding 430 mg. of VIIb (15.8%), m.p. 88–90°; lit.²⁰ m.p. 87–89°; 92–93°.

Anal. Calcd. for C₂₁H₁₈ (270.35): C, 93.29; H, 6.71. Found: C, 93.39; H, 6.94; mol. wt. (dioxane), 294.

VIIc (R' = C₆H₅, R = 3,4-CH₂O₂C₆H₃). **Reaction 7a.**—Diphenylmethane (1.68 g., 10 mmoles) and 1.12 g. of potassium *t*-butoxide were dissolved in 15 ml. of DMSO and 60°. From a buret 1.5 g. of piperonal (10 mmoles) in 5 ml. of DMSO was added over a period of 13 min. The reaction mixture, which turned red and finally green-brown, was kept at room temperature for 30 min. After addition of 100 ml. of ice-water the mixture was extracted with 600 ml. of ether. Evaporation of the ether layer yielded an oil which upon treatment with ethanol gave 600 mg. of crude VIIc (19%). The substance was recrystallized from a hot ethanol-chloroform mixture to give VIIc, m.p. 123–125°.

Anal. Calcd. for C₂₂H₁₈O₂ (314.6): C, 84.05; H, 5.77. Found: C, 83.87; H, 5.89.

Condensation between *p*-Anisaldehyde, DMSO, and Cyclohexanone. (VIII).—*p*-Anisaldehyde (2.8 ml., 20 mmoles) was added to a solution of 2.75 g. of potassium *t*-butoxide in 15 ml. of DMSO at 60° under nitrogen. After 5 min. at 60°, 2 ml. of cyclohexanone (20 mmoles) was added to the brown solution. After 30 min. at 60°, 100 g. of ice was added to the reaction mixture and the mixture extracted with 200 ml. of ether. From the ether solution 380 mg. of VIII separated (6.5%), m.p. 275°.

(20) W. Schlenk and E. Bergmann, *Ann.*, **463**, 1 (1928); K. Ziegler, H. Grabbe, and F. Ulrich, *Ber.*, **57**, 1983 (1924).

Recrystallization from ethanol by the addition of a little chloroform gave a compound, m.p. 275–276°. The infrared and n.m.r. spectra were consistent with structure VIII. The n.m.r. spectrum failed to show a methyl group other than that of the *p*-methoxy group.

Anal. Calcd. C₁₅H₂₂O₃S (294.34): C, 65.29; H, 7.53; S, 10.82. Found: C, 65.31; H, 7.69; S, 11.00.

Di-9-fluorenylphenylmethane.—Benzaldehyde (0.3 ml., 3 mmoles) was added to a solution of 499 mg. of fluorene (3 mmoles) in 7.5 ml. of DMSO containing 0.37 g. of sublimed potassium *t*-butoxide under a nitrogen atmosphere. The red solution turned blue after 6 min. at room temperature. At this time 100 ml. of water was added and the resulting solution extracted with 600 ml. of ether. Evaporation of the ether solution gave crystals which after recrystallization from a mixture of ethanol and chloroform yielded 74 mg. (9%) of di-9-fluorenylphenylmethane, m.p. 230°, lit.¹³ 239°. The n.m.r. shows an A₂B pattern of methine protons with the benzylic proton absorbing as a triplet (*J*_{AB} = 7.6 c.p.s. at 60 Mc./sec.) at τ = 6.8 and the 9-fluorenyl protons absorbing as a doublet at τ = 5.0.

Di-9-fluorenyl-*p*-methoxyphenylmethane.—*p*-Anisaldehyde (0.4 ml., 3 mmoles) was added to 499 mg. (3 mmoles) of fluorene dissolved in 7.5 ml. of DMSO under nitrogen. The addition of 366 mg. of potassium *t*-butoxide resulting in warming and the development of a red color which turned to a blue (reminiscent of fluorenyl ketyl) after 15 min. When the blue color developed, 100 ml. of water was added to give a yellow emulsion which was extracted with 200 ml. of ether. Evaporation of the ether extract to 30 ml. yielded 400 mg. (70%) of di-9-fluorenyl-*p*-methoxyphenylmethane, m.p. 230–232°. The n.m.r. spectrum appears unequivocal for this structure since it shows an A₂B pattern for the three methine hydrogens. The *p*-methoxybenzyl-hydrogen appeared as a triplet at τ = 6.8, *J*_{AB} = 6.9 c.p.s. at 60 Mc./sec., area = 1.0; the 9-fluorenyl hydrogens absorbed as a doublet at τ = 5.05, area = 2.0; methoxy protons at τ = 6.4, area = 3.0; *p*-methoxyphenyl protons (A₂B₂) at τ = 3.6, area = 4.0; and fluorenyl ring protons as a complex absorption between 420 and 480 c.p.s. relative to tetramethylsilane, area = 16.

1-Benzoyl-2-phenyl-3-(methylsulfonyl)-propane.—To 0.53 g. of benzaldehyde (5 mmoles) in 15 ml. of DMSO, 1.12 g. of potassium *t*-butoxide and 0.54 g. (5 mmoles) of acetophenone were added. After 1 hr. at 30–35°, 100 ml. of water was added and the resulting emulsions extracted with 300 ml. of ether. The ether was evaporated to yield an oil which did not readily crystallize. After 10 days in an open vessel, the oil crystallized to give 70 mg. (15%) of 1-benzoyl-2-phenyl-3-(methylsulfonyl)-propane, m.p. 125–126°, recrystallized from ethanol. The infrared showed sulfone and carbonyl absorptions. The n.m.r. (60 Mc./sec.) showed one methyl group (τ = 7.5), area 3.0 units; aromatic protons 438 to 480 c.p.s. relative to tetramethylsilane, area 10.1 units; and a complicated 5-proton absorption (area = 5.1 units) between 155 and 266 c.p.s. relative to tetramethylsilane. The complexity of the 5-proton area is undoubtedly due to the presence of two methylene groups attached to an asymmetric methine group.

Anal. Calcd. C₁₇H₁₈O₃S (302.37): C, 67.54; H, 6.00; S, 10.60. Found: C, 67.78; H, 5.94; S, 10.30.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA]

Preparation and Pummerer Rearrangement of β -Ketosulfoxides^{1,2}

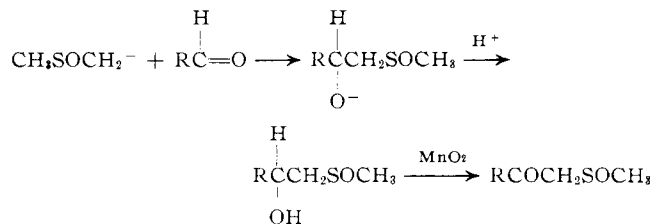
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The preparation of β -ketosulfoxides from aromatic esters and dimethyl sulfoxide is described. Acid-catalyzed rearrangement of these β -ketosulfoxides leads to the formation of methyl hemimercaptals of α -ketoaldehydes. The mechanism of this rearrangement is discussed.

Introduction

The carbanion formed in solutions of dimethyl sulfoxide (DMSO) containing bases such as sodium hydride or alkali metal alkoxides, undergoes reaction with carbonyl compounds such as aldehydes or ketones.⁴ β -Hydroxysulfoxides formed in this manner can be



oxidized to β -ketosulfoxides by active manganese dioxide.⁵ We have found that β -ketosulfoxides can

(1) Reactions of Resonance Stabilized Anions. X.

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(3) Alfred P. Sloan Foundation Fellow, 1959–1963.

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