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PREPARATION AND REACTIONS OF THE MONO- AND DIALKALI SALTS OF DIMETHYL SULFONE, DIMETHYL SULFOXIDE, AND RELATED COMPOUNDS*

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SUMMARY

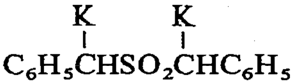
Certain sulfones and sulfoxides are rapidly and conveniently converted to their novel 1,3-dialkali salts which, in many cases, are stabilized only by the $-SO_2-$ and $-SO-$ groups, respectively. That such species are formed is demonstrated by subsequent synthetically useful double aldol-type condensations and alkylations, and, in a few cases, by deuterations. Profound metallic cation effects are observed in several of the aldol-type reactions. Finally, the anions of dibenzyl sulfoxide, though stable at low temperatures, readily decompose to *trans*-stilbene under much milder conditions than previously described.

INTRODUCTION

Sulfones and sulfoxides have routinely been singly metalated by means of a wide variety of basic reagents to afford the corresponding mono-metallo derivatives[2]. For example, dimethyl sulfone ($DMSO_2$, I) and dimethyl sulfoxide (DMSO, II) have been converted to I′ and II′, respectively, as evidenced by subsequent condensations with aldehydes, ketones, esters, and other electrophiles[2]. On the other hand, di-metalations of sulfones and sulfoxides have been unknown except for the formation of dipotassiodibenzyl sulfone (III″)[3] and the purported formation of a dimagnesium salt of I[2a]; a more recent report involving dilithiation of sulfolane appeared after our initial disclosures[2g]. The current paper describes rapid and convenient methods of converting certain sulfones and sulfoxides to their novel 1,3-dialkali salts and illustrates some of the chemistry of them. It also illustrates that the nucleophilicity of a few related monoanions may be increased by proper choice of metallic cation.

$CH_3SO_2CH_2M$
(I′)

CH_3SOCH_2M
(II′)


$C_6H_5\overset{K}{C}HSO_2\overset{K}{C}HC_6H_5$
(III″)

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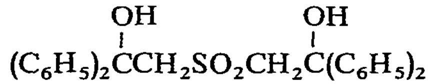
* For preliminary reports see ref. 1.
** Deceased January 6th, 1970.

RESULTS WITH SULFONES

First, attention was directed towards dimethyl sulfone (I). Thus, treatment of I with 2.2 equivalents* of lithium amide in liquid ammonia apparently gave dilithio salt I'', since subsequent condensation with two equivalents of benzophenone afforded bis-hydroxysulfone IV in 80% yield. Although similar results were obtained by employing sodium amide or potassium amide in ammonia, the use of n-butyllithium in THF–hexane was not satisfactory since subsequent reaction with benzophenone gave not only the diol IV in just 38% yield, but also the corresponding mono-alcohol V in 21% yield.

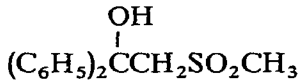
$MCH_2SO_2CH_2M$

(I'')



$(C_6H_5)_2C(OH)CH_2SO_2CH_2C(OH)(C_6H_5)_2$

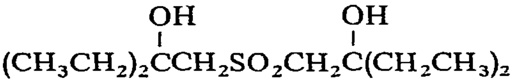
(IV)



$(C_6H_5)_2C(OH)CH_2SO_2CH_3$

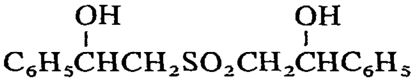
(V)

Dimethyl sulfone dianion (I'') was also condensed with certain other electrophiles including 3-pentanone and benzaldehyde to give diols VI and VII in yields of 89% and 28%, respectively. While VI was obtained free of its corresponding mono-alcohol, the reaction giving diol VII also afforded substantial amounts of mono-alcohol VIII. Dianion I'' was similarly condensed with n-butyl bromide to afford di-n-pentyl sulfone (IX), and with benzonitrile to give X (perhaps via a di-imine intermediate).



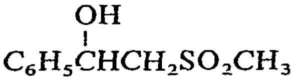
$(CH_3CH_2)_2C(OH)CH_2SO_2CH_2C(OH)(CH_2CH_3)_2$

(VI)



$C_6H_5CH(OH)CH_2SO_2CH_2CH(OH)C_6H_5$

(VII)

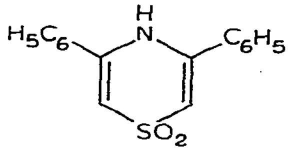


$C_6H_5CH(OH)CH_2SO_2CH_3$

(VIII)

$(n\text{-}C_5H_{11})_2SO_2$

(IX)



(X)

To test if bis-alcohols (*e.g.* IV) were indeed arising from I'' and not from stepwise ionization and condensation (Scheme 1), the following blank experiment was performed. Mono-alcohol V was first converted to the alkoxide V' by means of an equivalent of sodium amide in ammonia. This salt was then treated with an equivalent each of sodium amide and benzophenone—such a coexistence of the latter two reagents would approximate the reaction conditions if Scheme 1 were operating. Now, the sodium amide could ionize V' to give V'' or it could add to the ketone to afford XI, a reaction that is known to be rapid. The fact that little IV was obtained in the blank suggests that V'' is not formed as shown and that Scheme 1 is thus not operating.

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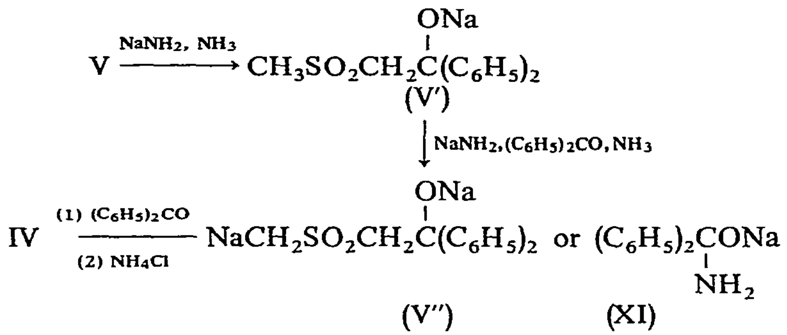
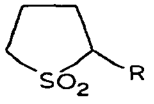
* A ten percent excess of alkali amide was used in all cases to ensure complete conversion of the active hydrogen compounds to their respective anions.

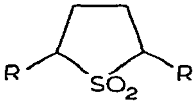
SCHEME 1



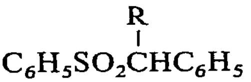
Other sulfones were similarly converted to their corresponding anions which were subsequently condensed with benzophenone to give β-hydroxysulfones. The particulars are listed in Table 1. Thus, sulfolane (XII) was converted to its monoanion XII′ by lithium amide in ammonia and to its α,α′-dicarbanion by sodium or potassium amide in this solvent since reactions with benzophenone gave XIII and XIV, respectively. In contrast, similar dialkali salts of dibenzyl sulfone (III″, M = Li, Na, or K) and monoalkali salts of benzyl phenyl sulfone (XV′, M = Li, Na, or K), prepared from III and XV and alkali amides in ammonia, respectively, failed to react with benzophenone. However, such condensations of III″ and XV′ with this ketone were realized in ethereal solvents provided magnesium cations were introduced into the reaction mixtures either as magnesium bromide complexes of the ketone or by initially metalating the sulfones with i-propylmagnesium bromide. A similar condensation of XV′ (M = Li) was also realized with an aluminum chloride complex of benzophenone.



(XII′) (R = Li)
(XIII) (R = $\underset{\displaystyle OH}{C}(C_6H_5)_2$)

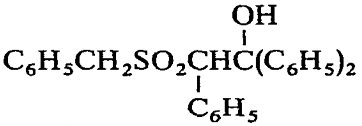


(XII″) (R = Na, K)
(XIV) (R = $\underset{\displaystyle OH}{C}(C_6H_5)_2$)



$C_6H_5SO_2\overset{R}{C}HC_6H_5$

(XV′) (R = Li, Na, K)
(XVII) (R = $\underset{\displaystyle OH}{C}(C_6H_5)_2$)
(XVII′) (R = $\underset{\displaystyle OM}{C}(C_6H_5)_2$)



$C_6H_5CH_2SO_2\underset{C_6H_5}{C}H\overset{OH}{C}(C_6H_5)_2$

(XVI)

Similarly, p-tolyl benzyl sulfone (XVIII) was converted to its monoanion XVIII′ and to its dianion XVIII″ by one and two equivalents of n-butyllithium, respectively.

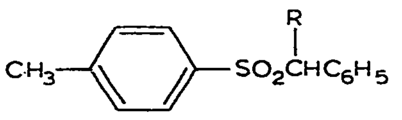
TABLE 1

INTERACTION OF ALKALI DERIVATIVES OF SULFONES WITH ELECTROPHILES

Sulfone	*Base (equiv.)*	*Solvent*	*Anion formation (min.)*	*Anion*	*Electrophile*	*Condensation time (min.)*	*Product*[a]	*M.p. (°C)*	*Yield (%)*
Dimethyl sulfone (I)	$LiNH_2$ (2.2)	NH_3	60	I″	$(C_6H_5)_2CO$	15	IV	223–223.2[b]	80
	$NaNH_2$ (2.2)	NH_3	60	I″	$(C_6H_5)_2CO$	5	IV	222–223[b]	72
	$LiNH_2$ (2.2)	NH_3	60	I″	$(C_2H_5)_2CO$	15	VI	64–67[c]	89
	$LiNH_2$ (2.2)	NH_3	60	I″	C_6H_5CHO	20	VII	147–149[d]	17[e]
	$NaNH_2$ (2.2)	NH_3	60	I″	n-C_4H_9Br	240	IX	74–75[b]	55
	$NaNH_2$ (2.2)	NH_3	60	I″	C_6H_5CN	60	X	275–276[g]	16
	$LiNH_2$ (1.1)	NH_3	60	I′	$(C_6H_5)_2CO$	15	V	139–140[b,h]	85
Sulfolane (XII)	$LiNH_2$ (2.2)	NH_3	60	XII′	$(C_6H_5)_2CO$	20	XIII	203.5–204.5[i,j]	85
	$NaNH_2$ (2.2)	NH_3	30	XII″	$(C_6H_5)_2CO$	10	XIV	279–280[k]	48
	KNH_2 (2.2)	NH_3	30	XII″	$(C_6H_5)_2CO$	10	XIV	279–280[k]	36
Dibenzyl sulfone (III)	MNH_2[l] (2.2)	NH_3	30	III″	$(C_6H_5)_2CO$	5–15	XVI	—	0
	n-C_4H_9Li (2.2)	THF–hexane	30	III″	$(C_6H_5)_2CO$	5	XVI	—	0
	n-C_4H_9Li (2.2)	THF–hexane	30	III″	$(C_6H_5)_2CO \cdot 2MgBr_2$	5	XVI	224–224.5[m]	42
	i-C_3H_7MgBr (2.0)	THF	30	III″	$(C_6H_5)_2CO$	5	XVI	224–224.5[m]	56
Benzyl phenyl sulfone (XV)	MNH_2[l] (1.1)	NH_3	30	XV′	$(C_6H_5)_2CO$	5–15	XVII	—	0
	n-C_4H_9Li (1.0)	THF–hexane	30	XV′	$(C_6H_5)_2CO$	5	XVII	—	0
	n-C_4H_9Li (1.0)	THF–hexane	30	XV′	$(C_6H_5)_2CO \cdot 2MgBr_2$	5	XVII	203–204[b]	50
	n-C_4H_9Li (1.0)	Ether	30	XV′	$(C_6H_5)_2CO \cdot 2AlCl_3$	5	XVII	203–204[b]	48
	i-C_3H_7MgBr (1.0)	THF	30	XV′	$(C_6H_5)_2CO$	5	XVII	203–204[b]	52
p-Tolyl benzyl sulfone (XVIII)	n-C_4H_9Li (1.0)	THF–hexane	30	XVIII′	$(C_6H_5)_2CO \cdot 2AlCl_3$	5	XIX	191–191.5[g]	36
	n-C_4H_9Li (2.0)	THF–hexane	30	XVIII″	$(C_6H_5)_2CO$	5	XX	210–212[g]	2
Di-*p*-tolyl sulfone (XXI)	$LiNH_2$ (2.2)	NH_3	60	XXI′	$(C_6H_5)_2CO$	5	XXII	225–226[b]	58

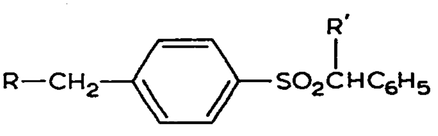
[a] All new compounds reported had correct NMR spectra and elemental analyses. [b] Recrystallized from absolute ethanol. [c] Recrystallized from carbon tetrachloride. [d] Recrystallized from chloroform. [e] The yield of VII was increased to 28% by injecting the benzaldehyde under the surface of the ammonia with a hypodermic syringe. [f] The benzonitrile was added after the ammonia was evaporated and replaced by THF. [g] Recrystallized from 95% ethanol. [h] Lit.[2e] m.p.: 137–138°. [i] Recrystallized from ethanol-acetone. [j] Lit.[2e] m.p.: 203.5–204.5°. [k] Recrystallized from acetone. [l] $LiNH_2$, $NaNH_2$ and KNH_2 were employed in three separate experiments. [m] Recrystallized from ethanol–benzene.

Also, di-*p*-tolyl sulfone (XXI) was converted to a monoanion (XXI′) by lithium amide in ammonia. These carbanions gave the expected alcohols with benzophenone (Table 1).



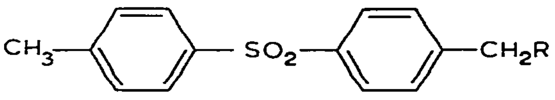
(XVIII′) ($R = Li$)

(XIX) ($R = \underset{\textstyle OH}{C}(C_6H_5)_2$)



(XVIII″) ($R = R' = Li$)

(XX) ($R = \underset{\textstyle OH}{C}(C_6H_5)_2, R' = H$)



(XXI′) ($R = Li$)

(XXII) ($R = \underset{\textstyle OH}{C}(C_6H_5)_2O$)

Three brief comments about certain of the above systems deserve mention. First, the two-fold condensations of I″ and XII″ represent the first examples in multiple anion chemistry of dianions undergoing reactions with carbonyl containing electrophiles at both anionic sites, though a few dianions have undergone two-fold alkylation reactions[3]. Second, the success of the reactions in which magnesium or aluminum cations are employed can be ascribed to the better chelating abilities of these cations in alkoxides like XVII′ thus overcoming the relatively poor nucleophilicity of the carbanions[4]. Third, the α atoms of benzyl phenyl sulfone (XV) are sufficiently acidic that this sulfone has been successfully dimetalated to give the *gem*-dilithio salt; the chemistry of this interesting species is described elsewhere[5].

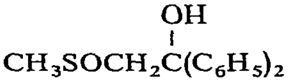
RESULTS WITH SULFOXIDES

First, interaction of an excess of DMSO (II) with alkali metal amides in liquid ammonia rapidly afforded the corresponding alkali salts II′ (M = Li, Na, K) in high yield as evidenced by subsequent condensations with benzophenone to give the known alcohol XXII in 69–89% yield. Interestingly, the above results appear to represent the first examples of the preparation of such α-sulfinyl carbanions in the very convenient liquid ammonia media.

More significantly, though, was the observation that sulfoxides like II could be just as rapidly caused to undergo dimetalation by means of two or more equivalents of bases. Thus, treatment of II with 2.2 equivalents of lithium-, sodium-, or potassium amide in ammonia presumably afforded II″ since reaction with benzophenone gave bis-hydroxy sulfoxide XXIV in yields of 32, 42, and 13%, respectively; alcohol XXIII was usually a by-product of these two-fold aldol-type condensations. The varying percentages of XXIV as a function of the metallic cation are apparently due to the lithium salts reacting more slowly with the ketone, and to the fact that the intermediate potassium alkoxides have a greater tendency to reverse to ketone and starting carbanion[6].

MCH_2SOCH_2M

(II'')



$CH_3SOCH_2\overset{\overset{OH}{|}}{C}(C_6H_5)_2$

(XXIII)

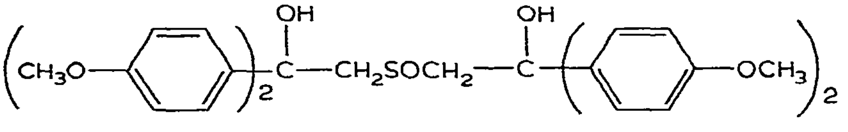
$(C_6H_5)_2\overset{\overset{OH}{|}}{C}CH_2SOCH_2\overset{\overset{OH}{|}}{C}(C_6H_5)_2$

(XXIV)

Dianion II'' was also prepared by means of lithium di-isopropylamide in ether, and by n-butyllithium in THF or triethylamine. However, II'' apparently underwent decomposition in these systems even at low temperature (see below) and only low yields of isolable products were realized. For example, treatment of II'', prepared by n-butyllithium, with benzophenone gave XXIV in maximum yields of 5–6%.

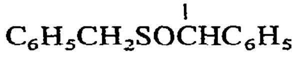
As with the dianion of $DMSO_2$, a blank experiment was run to indicate that XXIV was arising via II'', not from stepwise ionization and condensation (see Scheme 1). Thus, monohydroxy sulfoxide XXIII was converted to its alkoxide XXIII' which was then treated with an equivalent each of alkali amide and benzophenone. As above, no dialcohol XXIV was obtained thereby suggesting that it does indeed arise directly from II''.

A few other electrophiles were also caused to react with dianion II''. Thus, the use of 4,4'-dimethoxybenzophenone gave diol XXV in 75% yield. The use of acetone and 3-pentanone, though, gave inseparable mixtures of mono- and di-alcohols which could only be identified by their NMR spectra. On the other hand, II'', prepared in ammonia, has been successfully dialkylated to give long chain aliphatic sulfoxides[7].



(XXV)

Next, attention was directed towards the preparation of the 1,3-dianion of dibenzyl sulfoxide XXVI. Thus, treatment of XXVI with two equivalents of n-butyllithium at −78° in THF–hexane afforded dianion XXVI'' since addition of deuterium oxide gave XXVI containing 1.98 benzylic deuterium atoms per molecule. A blank run on XXVI with lithium deuteroxide and deuterium oxide indicated that the benzylic protiums do not substantially exchange under the conditions of the ionization reaction.



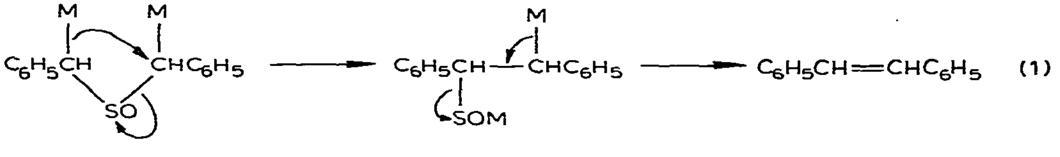
$C_6H_5CH_2SO\overset{\overset{M}{|}}{C}HC_6H_5$

(XXVI')

$C_6H_5\overset{\overset{M}{|}}{C}HSO\overset{\overset{M}{|}}{C}HC_6H_5$

(XXVI'')

Surprisingly, XXVI'' had to be prepared at −78° or substantial amounts of *trans*-stilbene were obtained from the reaction mixtures. Thus, treatment of XXVI with two equivalents of n-butyllithium at −25°, 0°, or 25° gave stilbene in yields of 33, 61, and 61 % respectively. Likewise, preparation of XXVI" at −78° followed by warming to 0° and then recooling to −78° also afforded stilbene in 50% yield. In contrast, interaction of XXVI with one equivalent of n-butyllithium at 25° gave stilbene in only 11% yield. Such base-promoted transformations of XXVI to stilbene can thus be affected under much milder conditions than previously supposed[8]. Indeed, trace amounts of stilbene were obtained from such current reactions even at −50°. Though earlier base-catalyzed decompositions of XXVI were pictured as proceeding via monoanions, it is attractive to postulate that the current ones proceed via dianions (Eq. 1), though this has not been proven.

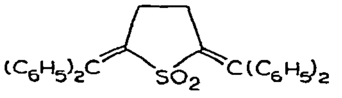


(XXVI")

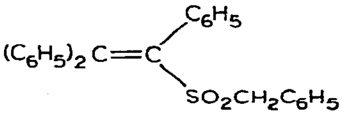
It should be mentioned that the structures of the new products described above were confirmed by elemental analyses, by NMR and IR spectroscopy, and in the case of the alcohols, by conversion to olefins. The following dehydrations were thus effected by concentrated phosphoric acid: IV to XXVII, XIV to XXVIII, XVI to XXIX, XVII to XXX, and XXIV to XXVII. Attempts to dehydrate XXIV with sulfuric acid, though, led to divinyl sulfone XXVII, divinyl sulfide XXXI, and a polymer of 1,1-diphenylallene XXXII. Also, dihydroxysulfoxide XXIV was oxidized to dihydroxysulfone IV by 30% hydrogen peroxide.

$\left[(C_6H_5)_2C{=}CH\right]_2SO_2$

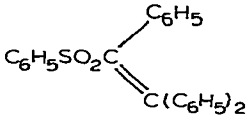
(XXVII)



(XXVIII)



(XXIX)



(XXX)

$\left[(C_6H_5)_2C{=}CH\right]_2S$

(XXXI)

$\left[(C_6H_5)_2C{=}C{=}CH_2\right]_x$

(XXXII)

The above work should be capable of extension not only to a wide variety of other sulfones and sulfoxides, but to many other electrophiles as well.

EXPERIMENTAL

General

All starting sulfones and sulfoxides were purchased from Aldrich Chemical

Company or prepared by standard oxidations of the corresponding sulfides. Melting points were taken on a Thomas–Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were determined on Perkin–Elmer Model 137 or 237 Spectrophotometers as nujol mulls. NMR spectra were obtained with a Varian Associates A-60 Spectrometer using tetramethylsilane as internal standard. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

The results obtained by condensing various sulfones with certain electrophiles are listed in Table 1. Since the reactions effected by the respective bases seem to be general, only certain specific examples which typify the chemistry will be presented.

Condensation of dialkali derivatives of dimethyl sulfone

Benzophenone. To a suspension of 0.11 mole of lithium amide in 300 ml of anhydrous liquid ammonia[9] was added 4.7 g (0.05 mole) of solid dimethyl sulfone. After 1 hour, the resulting blue-green suspension of I″ was treated during 5 minutes with a solution of 18.2 g (0.1 mole) of benzophenone in 50 ml of ethyl ether to afford a voluminous white suspension. After 15 minutes, the mixture was poured with stirring into 200 ml of ammonia containing 15 g of ammonium chloride (inverse neutralization). The ammonia was allowed to evaporate and the residue was hydrolyzed by 100 ml of 3 *N* hydrochloric acid. The resulting crude, solid product was collected under suction, washed thoroughly with water and ether, and recrystallized from ethanol to afford 18.25 g (80%) of bis(2,2-diphenyl-2-hydroxyethyl) sulfone (IV), m.p. 223–223.2°; IR 3600 (OH), 1352 (OH), 1310 (SO_2), 1170 (OH) and 1130 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 7.3 (s, 20 ArH), 4.8 (s, 2, OH) and 3.63 (s, 4, CH_2SO_2). (Found: C, 73.09; H, 5.66; S, 7.20. $C_{28}H_{26}SO_4$ calcd.: C, 73.36; H, 5.68; S, 6.99%.)

When the reaction was repeated employing 0.11 mole of sodium amide allowing the benzophenone to react for 5 minutes, 16.3 g (72%) of IV was obtained, m.p., mixed m.p. 222–223°. Similar results were obtained by using potassium amide.

n-Butyl bromide. To 0.05 mole of disodio salt I″ in 300 ml of ammonia was added during 10 minutes a solution of 15.07 g (0.11 mole) of n-butyl bromide in 50 ml of ether. After stirring for 4 hours, the suspension was directly neutralized by the slow addition of 15.0 g of solid ammonium chloride. The reaction mixture was then worked-up to give, after recrystallization from ethanol, 5.69 g (55%) of di-n-pentyl sulfone (IX), m.p. 74–75°. (Found: C, 58.48; H, 10.71; S, 15.61. $C_{10}H_{22}SO_2$ calcd.: C, 58.20; H, 10.67; S, 15.53%.)

Benzonitrile. Disodio salt I″ was prepared as usual in 300 ml of ammonia, then the ammonia was allowed to evaporate while it was replaced by anhydrous THF. The resulting dark gray suspension was treated during 5 minutes with a solution of 10.3 g (0.1 mole) of benzonitrile in 50 ml of THF. The mixture was refluxed for 1 hour, cooled, and poured into iced hydrochloric acid. The layers were separated and the mixture was worked-up as usual to afford, upon recyrstallization from 95% ethanol, 4.47 g (16%) of 3,5-diphenyl-*p*-isothiazine-1,1-dioxide (X), m.p. 275–276°; NMR ($CDCl_3$) δ 8.48 (s, 10, ArH), 7.30 (s, 1, NH), 6.40 (d, 2, vinyl). (Found: C, 67.64; H, 4.57; N, 5.09; S, 11.20. $C_{16}H_{13}NSO_2$ calcd.: C, 67.84; H, 4.59; N, 4.95; S, 11.31%.)

Blank experiment to demonstrate the intermediacy of dianions of dimethyl sulfone. To 0.05 mole of sodium amide in 250 ml of ammonia was added in portions 13.8 g (0.05 mole) of monohydroxysulfone V. After 5 minutes, the resulting black solution was treated with 9.1 g (0.05 mole) of benzophenone dissolved in 50 ml of ether followed immediately by a suspension of 0.05 mole of sodium amide in 200 ml of ammonia. After 5 minutes, the intense blue mixture (probably due to $(C_6H_5)_2C(NH_2)$-ONa) was inversely neutralized. The usual work-up gave 1.0 g (4.4%) of dihydroxysulfone IV, m.p., mixed m.p. 220–222°; 9.05 (66%) of monohydroxysulfone V, m.p., mixed m.p. 134–136°; and 10.3 g (113%) of benzophenone, m.p., mixed m.p. 45–47°. Obviously, a portion of V underwent reversion to sodiodimethyl sulfone and benzophenone.

Condensations of dibenzyl sulfone with benzophenone

By means of i-propylmagnesium bromide. i-Propylmagnesium bromide (0.1 mole), prepared in the usual fashion from 2.4 g (0.1 g-atom) of magnesium and 12.3 g (0.1 mole) of i-propyl bromide in a total of 100 ml of THF, was treated at 0° with 12.3 g (0.05 mole) of solid dibenzyl sulfone added in portions. After 30 minutes, the resulting green solution was treated during 12 minutes with a solution of 9.1 g (0.05 mole) of benzophenone in 50 ml of THF to give a brown solution which, after 5 minutes, was poured into iced hydrochloric acid. The crude solid product was collected and recrystallized from ethanol–benzene to afford 11.92 g (56%) of 1,2,2-triphenyl-2-hydroxyethyl benzyl sulfone (XVI), m.p. 224–224.5°; NMR (CF_3CO_2H) δ 7.29 (m, 20, ArH) and 4.33 (s, 2, CH_2). (Found: C, 75.56; H, 5.57; S, 7.42. $C_{27}H_{24}SO_3$ calcd.: C, 75.68; H, 5.65; S, 7.50%.)

By means of n-butyllithium–magnesium bromide. To a solution of 12.3 g (0.05 mole) of the sulfone in 70.3 ml of THF was added during 8 minutes 70.3 ml (0.1125 mole) of 1.6 *M* n-butyllithium in hexane. After 30 minutes, the solution was treated during 10 min. with a solution of 9.1 g (0.05 mole) of benzophenone and 0.1 mole of magnesium bromide (prepared from 2.4 g (0.1 g-atom) of magnesium and 18.8 g (0.1 mole) of ethylene bromide) in 250 ml of THF. After 5 minutes, the mixture was poured into iced hydrochloric acid and worked-up to give 8.85 g (42%) of XVI, m.p., mixed m.p. 224–224.5°.

Condensation of benzyl phenyl sulfone with benzophenone using n-butyllithium–aluminum chloride

To a suspension of 11.6 g (0.05 mole) of the sulfone in 90 ml of THF was added 39.0 ml (0.063 mole) of 1.6 *M* n-butyllithium in hexane. After 30 minutes, the mixture containing XV′ was cooled to 0° and treated during 15 minutes with a solution of 9.1 g (0.05 mole) of benzophenone and 13.3 g (0.1 mole) of aluminum chloride in 50 ml of ether. After 5 minutes, the tacky suspension was poured into iced hydrochloric acid and worked-up to give 9.9 g (48%) of XVII, m.p., mixed m.p. 203–204°, and 3.3 g (29%) of recovered sulfone, m.p., mixed m.p. 148–149°. No reaction was realized in the absence of aluminum chloride.

Condensations of dimethyl sulfoxide with benzophenone

By means of a deficiency of lithium amide. To 0.05 mole of lithium amide in 300 ml of ammonia was added 15.6 g (0.2 mole) of DMSO. After 1 hour, the mixture was treated with 4.55 g (0.025 mole) of solid benzophenone. After stirring for 20 minutes, the mixture was inversely neutralized and worked-up as with the condensations of dimethyl sulfone. The crude product was chromatographed on an alumina column to give: (1) with benzene, 0.4 g (9%) of benzophenone, isolated as its 2,4-dinitrophenylhydrazone; and (2) with ethanol, 5.8 g (89 %) of 2,2-diphenyl-2-hydroxyethyl methyl sulfoxide (XXIII), m.p. 144–146°, lit[2e] m.p. 144–146°; NMR ($CDCl_3$) δ 7.07–7.57 (m, 10, ArH), 5.43 (s, 1, OH), 3.53 (d, 2, J 1.5 cps, CH_2SO), and 2.47 (s, 3, CH_3SO).

By means of two equivalents of sodium amide. To 0.11 mole of sodium amide in 300 ml of ammonia was added 3.9 g (0.05 mole) of DMSO. After 25 minutes, the mixture was treated with a solution of 18.2 g (0.1 mole) of benzophenone in 50 ml of ether. After another 5 minutes, the mixture was inversely neutralized and worked-up. Extraction of the aqueous phase with ether gave a white solid which was combined with the residue obtained by concentrating the organic extracts. Recrystallization of this solid from acetone–water gave 9.3 g (42 %) of bis(2,2-diphenyl-2-hydroxyethyl) sulfoxide (XXIV), m.p. 151–157°; IR 3210 (OH), 1055 (SO) and 705 cm^{-1} (aromatic); NMR ($CDCl_3$) δ 7.28 (s, 20, ArH), 4.82 (s, 2, OH), and 3.63 (s, 4, CH_2SO). (Found: C, 76.13; H, 5.93; S, 7.12. $C_{28}H_{26}SO_3$ calcd.: C, 76.09; H, 5.89; S, 7.24 %.)

Blank experiment to demonstrate the intermediacy of dianions of dimethyl sulfoxide. To 0.055 mole of sodium amide in 150 ml of ammonia was added 13.0 g (0.05 mole) of hydroxysulfoxide XXIII. After 30 minutes, the solution of the corresponding alkoxide was poured into a second solution of 0.055 mole of sodium amide in 150 ml of ammonia; the combined mixture was immediately treated with a solution of 9.1 g (0.05 mole) of benzophenone in 50 ml of ether. After 5 minutes, the mixture was inversely neutralized and worked-up to afford only recovered starting materials in quantitative yield.

Condensation of dilithiodimethyl sulfoxide with 4,4′-dimethoxybenzophenone

This reaction was accomplished essentially as described above for DMSO and benzophenone using 0.03 mole of lithium amide, 1.0 g (0.013 mole) of DMSO, and 6.05 g (0.025 mole) of 4,4′-dimethoxybenzophenone. After a 20 minute condensation period, the reaction mixture was inversely neutralized, worked-up, and chromatographed on alumina to afford, upon elution with ethanol, 5.5 g (75 %) of bis[2,2-di-(*p*-methoxyphenyl)-2-hydroxyethyl]sulfoxide (XXV), m.p. 104° (dec.); IR 3115 (OH), 1600 (arom.), and 1250, 1090 and 1045 cm^{-1} (SO); NMR ($CDCl_3$) δ 6.67–7.33 (m, 16, ArH), 4.73 (s, 2, OH), 3.73 (d, 12, J 1.5 cps, OCH_3), and 3.57 (s, 4, CH_2SO). (Found: C, 68.48; H, 6.14; S, 5.62. $C_{32}H_{34}SO_7$ calcd.: C, 68.33; H, 6.05; S, 5.70 %.)

Preparation and deuteration of dilithiodibenzyl sulfoxide.

To 2.3 g (0.01 mole) of dibenzyl sulfoxide in 100 ml of THF at −78° was added 13 ml (0.02 mole) of 1.6 *M* n-butyllithium in hexane. After 30 minutes, the resulting greenish-brown solution was treated with 2.0 ml of deuterium oxide; the now light yellow mixture was allowed to warm to 25° and dried with magnesium sulfate. After filtering, the solution was concentrated to give, upon recrystallization from carbon tetrachloride, deuterated dibenzyl sulfoxide, m.p. 130–132°; NMR ($CDCl_3$) δ 7.3 (s, 10, ArH) and 3.85 (s, 1.59, CHDSO). In a blank experiment, 2.3 g (0.01 mole) of the parent sulfoxide was added to a mixture of 2.0 ml of deuterium oxide and 13.0 ml (0.02 mole) of n-butyllithium in 100 ml of THF at −78°. Work-up of the mixture as above gave dibenzyl sulfoxide, m.p. 133–134°; NMR ($CDCl_3$) δ 7.3 (s, 10, ArH) and 3.85 (s, 3.57, CH_2SO).

Conversion of dibenzyl sulfoxide to trans-stilbene by means of n-butyllithium

To a solution of 2.3 g (0.01 mole) of dibenzyl sulfoxide in 200 ml of THF at 25°

was added 13.0 ml (0.02 mole) of 1.6 *M* n-butyllithium in hexane. After 30 minutes, the solution was treated with 2 ml of 48 % hydrochloric acid. The ethereal layer was dried ($MgSO_4$), filtered, and concentrated to give 1.45 g (61 %) of *trans*-stilbene, m.p., mixed m.p. 122–124°. The reaction was repeated at various temperatures to give *trans*-stilbene in the following yields: 0°, 61 %; −25°, 33 %; −50°, trace; −78°, 0%. An experiment in which the temperature was raised from −78° to above 0°, then lowered back to −78° after 30 minutes gave stilbene in 50 % yield.

Dehydrations of hydroxysulfones by means of concentrated phosphoric acid

Certain of the hydroxysulfones described above were dehydrated by 85% phosphoric acid; the general procedure is illustrated by the following conversion of IV to XXVII. To 40 ml of 85 % phosphoric acid was added 3.0 g of solid dihydroxysulfone IV. With stirring, the suspension was heated to reflux for 15 minutes. The resulting solution was allowed to cool to 25°, then it was poured into 40 g of ice. The resulting precipitate was collected and recrystallized from ethanol to give 1.24 g (44 %) of bis(2,2-diphenylvinyl) sulfone XXVII, m.p. 162–164°; NMR ($CDCl_3$) δ 7.2–7.55 (m, 20, ArH) and 6.48 (s, 2, vinyl). (Found: C, 79.44; H, 5.23; S, 7.90. $C_{28}H_{22}SO_2$ calcd.: C, 79.60; H, 5.25; S, 7.58 %.) Other dehydrations were as follows: XIV gave XXVIII in 100 % yield, m.p. 224–225.5° (found: C, 80.53; H, 5.39; $C_{30}H_{24}SO_2$ calcd.: C, 80.35; H, 5.35 %.) XVI gave XXIX in 88 % yield, m.p. 171–173°. (Found: C, 78.84; H, 5.50. $C_{27}H_{22}SO_2$ calcd.: C, 79.02; H, 5.36 %.) XVII gave XXX in 80 % yield, m.p. 164–165°. (Found: C, 78.43; H, 5.08. $C_{26}H_{20}SO_2$ calcd.: C, 78.78; H, 5.05 %.) XXIV gave XXVII in low yield, m.p., mixed m.p. 162–164°.

Dehydration of XXIV with sulfuric acid

To a solution of 11.05 g (0.025 mole) of XXIV in 250 ml of benzene was added 3 drops of concentrated sulfuric acid. After refluxing for 5 hours, the solvent was removed on the rotary evaporator and the residue was chromatographed on alumina. The use of 60–70° petroleum ether caused the elution of a yellow oil which gradually crystallized to afford a small amount of a polymer of 1,1-diphenylallene XXXII m.p. 192–193°; NMR ($CDCl_3$) δ 7.05 (s, 5, ArH), 6.87 (s, 5, ArH), and 6.50 (s, 2, vinyl). (Found: C, 93.72; H, 6.25. $(C_{15}H_{12})_x$ calcd.: C, 93.76; H, 6.24 %.) Further treatment of the column with ethyl ether gave an additional oil which, upon crystallization from acetone–water, gave bis(2,2-diphenylvinyl) sulfide (XXXI), m.p. 105–107°; NMR ($CDCl_3$) δ 7.25 (d, 20, *J* 3 cps, ArH) and 6.81 (s, 2, vinyl). (Found: C, 86.45; H, 5.82. $C_{28}H_{22}S$ calcd.: C, 86.15; H, 5.64 %.) Finally, methanol caused the elution of crude XXVII which was recrystallized from acetone–water, m.p. 158.5–165.5; the NMR was identical to that of an authentic sample.

Oxidation of XXIV to IV

A mixture of 50 ml each of glacial acetic acid and acetic anhydride along with 4.42 g (0.01 mole) of XXIV was treated with 3.0 g (0.03 mole) of 30 % hydrogen peroxide. After 72 hours at 25°, the mixture was filtered and poured into iced water. The resulting precipitate was recrystallized from acetone–water, then several times from benzene to give 1.7 g (37 %) of IV, m.p. 208–212°. The IR and NMR spectra of this compound were identical to those of authentic samples.

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