The O/C product ratios were calculated directly from peak areas. Thermal response values relative to acetophenone were determined for a number of the products, but their use was not warranted.

Conductivity Measurements.—Resistances were measured in a 25-ml conductivity cell surmounted on the kinetic apparatus in place of the automatic sampling buret. Solvents and solutions were forced into the cell by increasing the nitrogen pressure in the reaction vessel. The cell was drained under a nitrogen atmosphere and flushed thoroughly with dry solvent before and after measurements were made. Resistances were measured with a Wheatstone bridge, 5000-cps audiofrequency oscillator, and earphones to detect the null point.

Cleavage of Sodiodiphenylacetophenone by Oxygen.—Immediate formation of solid, evolution of heat, and fading of yellow color occurred when oxygen gas was bubbled through a solution of 11.1 mmol of enolate in 150 ml of diglyme. After 12 hr of oxygen treatment, the semisolid mixture was dissolved in 100 ml of water to give a clear solution which required only 0.4 mmol of standard acid for titration to phenolphthalein. The solution was steam distilled to give 1.84 g (92%) of benzophenone, mp 43–46°. The infrared spectrum was superimposable on that of an authentic sample of benzophenone. The steam distilland was made alkaline with potassium carbonate solution and extracted with three 100-ml portions of ether. Evaporation of these extracts yielded no more than a trace of oily substance. The alkaline layer was acidified with concentrated hydrochloric acid and extracted with three 100-ml portions of ether. Evaporation of these extracts left 1.32 g (99%) of white solid, mp 120–122.5°. This substance did not depress the melting point of pure benzoic acid.

Registry No.—Sodiodiphenylacetophenone, 16282-12-5; sodiobutyrophenone, 16310-84-2; α-methylbutyrophenone, 938-87-4; α,α-diphenylacetophenone, 1733-63-7; α,α-dimethylbutyrophenone, 829-10-7; 1-ethoxy-1-phenyl-2-methylpropene, 16282-15-8; α-ethyldeoxybenzoin, 16282-16-9; α-mesityldeoxybenzoin, 16282-17-0.

Condensations at Methyl Groups of Phenyl *o*- and *p*-Tolyl Sulfones with Electrophilic Compounds by Sodium Amide. Truce–Smiles Rearrangement[1]

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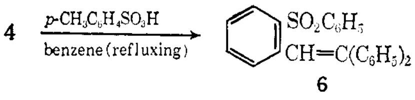
Ionizations of methyl hydrogens of phenyl *o*- and *p*-tolyl sulfones were effected by sodium amide in liquid ammonia to form sodio salts, which were condensed with benzyl chloride, 1,4-dibromobutane, benzophenone, and methyl benzoate to give corresponding derivatives. Ionization of the phenyl *o*-tolyl sulfone occurred more slowly than that of the *para* isomer. The addition reactions of the sodio salts with benzophenone were kinetically controlled. The condensations of the sodio *o*-tolyl sulfone with the electrophilic compounds represent trapping of the intermediate carbanion in the Truce–Smiles rearrangement of the sulfone to form a sulfinic acid, which was observed in low yield through the sodio salt in liquid ammonia and in good yield in refluxing tetrahydrofuran. The benzyl derivative of the *o*-tolyl sulfone underwent this type of rearrangement with *n*-butyllithium. Di-*p*-tolyl sulfone was benzylated at one of its methyl groups by means of sodium amide. The method appears to be quite general.

Although base-catalyzed condensations at the α carbon of dimethyl sulfone and other sulfones with electrophilic compounds are well known,[2] related reactions at the methyl groups of *o*- and *p*-tolyl sulfones have rarely been reported. The present investigation was concerned with such a study of phenyl *o*- and *p*-tolyl sulfones; the former sulfone promised to be of particular interest because it can undergo the base induced Truce–Smiles type of rearrangement.

Results with Phenyl *o*-Tolyl Sulfone.—This compound (**1**) was converted by sodium amide in liquid ammonia into sodio salt **1′**, which was condensed with benzyl chloride, 1,4-dibromobutane (0.5 mol equiv), benzophenone, and methyl benzoate to form **2**, **3**, **4**, and **5**, respectively (Scheme I).

The yields of the benzyl derivative **2**, the bis derivative **3**, and the addition product **4** were dependent on the conditions employed (see Discussion); the best yields obtained were 61, 58, and 76%, respectively. The yield of the benzoyl derivative **5** was dependent on the proportions of the reactants since, similar to other Claisen-type acylations and aroylations,[3] the product **5** was converted in the reaction mixture into its sodio salt; this last step was effected by either sodio sulfone **1′** or sodium amide. When 2 mol equiv of sodio sulfone **1′**/1 mol equiv of methyl benzoate was used (last step effected by **1′**), the yield of **5** based on the ester was 50%;[4] when 1 extra equiv of sodium amide was used to effect the last step, the yield of **5** based on sulfone **1** was 34%.

The structures of the condensation products were supported by analyses and absorption spectra. The structure of adduct **4** was confirmed by dehydration to form unsaturated sulfone **6** in 86% yield (eq 1).



6 (1)

The infrared spectra of the products were similar to those of the starting sulfone **1** with certain significant differences (Table I).[5] The spectrum of carbinol sulfone **4** showed a strong hydroxyl peak, which was absent in that of the dehydration product **6**. The spectrum of the keto sulfone **5** exhibited a strong carbonyl peak.

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(1) Supported by U. S. Public Health Service Research Grant No. CA 04455 from the National Cancer Institute and by the Army Research Office (Durham).

(2) See especially L. Field and E. T. Boyd, *J. Org. Chem.*, **26**, 1787 (1961), and D. F. Tavares and P. F. Vogt, *Can. J. Chem.*, **45**, 1519 (1967), and references cited therein.

(3) For related aroylations of ketones with esters by sodium amide, see *Org. Reactions*, **8**, Chapter 3 (1954).

(4) Theoretically one-half of sulfone **1** would be regenerated; actually the yield of **5** based on starting sulfone **1** used minus that recovered was 38%.

(5) See R. T. Conley, "Infrared Spectroscopy," Allyn and Bacon, Inc., Boston, Mass., 1966.

SCHEME I

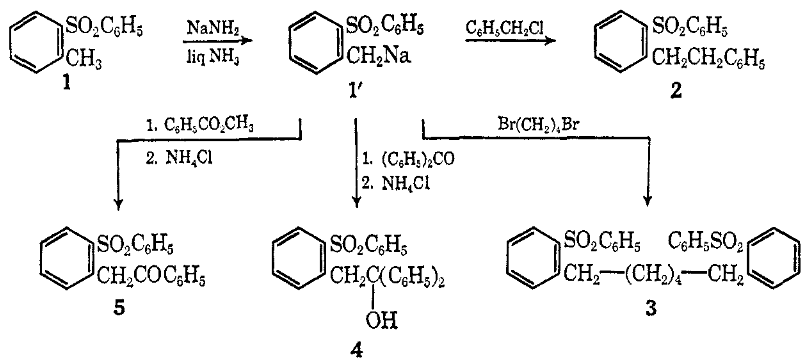


TABLE I

ASSIGNED INFRARED PEAKS OF PHENYL o-TOLYL SULFONE AND CONDENSATION PRODUCTS

(cm^{-1})

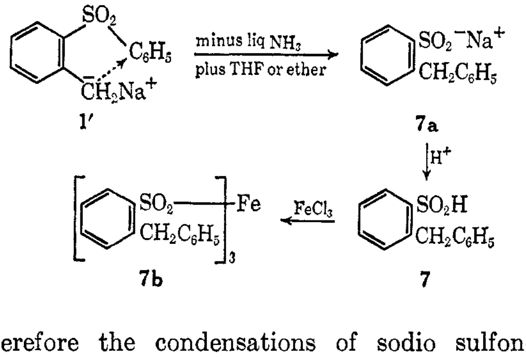
Sulfone	SO_2 stretching Asymm	Symm	*ortho* disubstitution	Monoaromatic substitution[a]	Other
1	1305, 1280	1145	763	752, 704	1380[b]
2	1290, 1285	1155	764	755, 698	*c*
3	1310, 1285	1150	760	*d*, 692	*c*
4	1300, 1285	1140	767	754, 706	3450[e]
5	1310, 1295, 1285	1140	762	750, 713	1675[f]
6	1290, 1280	1140	762	754, 695	

[a] The spectra of all these compounds except **3** had two other strong peaks in this region at 730–724 and at 687–682 cm^{-1}, possibly from C–S vibration. The spectrum of **3** had only the one peak at 727 cm^{-1}. [b] Symmetrical methyl bending. [c] No peaks in the 1380 region. [d] Absent or perhaps underneath the broad *ortho* peak at 760 cm^{-1}. [e] Hydroxyl. [f] Carbonyl.

The nmr spectrum[6] of the benzyl derivative **2** showed a sixteen-peak multiplet centered at 2.40 ppm (4.0 H) for the methylene protons and a complex aromatic multiplet from 6.7 to 7.9 ppm (14.0 H).

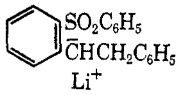
Interestingly, sodio sulfone **1′**, which was condensed in good yields with electrophilic compounds in liquid ammonia (see Scheme I), underwent the Truce–Smiles rearrangement on replacing the ammonia with tetrahydrofuran (THF) and refluxing to form 2-benzylbenzenesulfinic acid (**7**) in good yield; even in liquid ammonia, **7** was obtained in about 1% yield in connection with the benzylation of sodio sulfone **1′** (see Experimental Section). Sulfinic acid **7** was isolated as its sodio salt **7a** or, preferably, as its ferric derivative **7b** (Scheme II).

SCHEME II

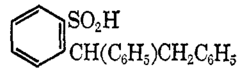


Therefore the condensations of sodio sulfone **1′** with the electrophilic compounds (Scheme I) represent trapping of the intermediate carbanion in the Truce–Smiles rearrangement. Although *n*-butyllithium effects the rearrangement of sulfone **1** in refluxing ether–hexane to form sulfinic acid **7** in good yield,[7] this reagent appears not very satisfactory for trapping the intermediate carbanion. Thus the intermediate lithio sulfone formed with *n*-butyllithium has been trapped as its carbonation product by Truce and Norman[8] in only 12% yield, and as its benzophenone adduct **4** by us in only 13% yield, which is much less than that realized by us with sodio sulfone **1′** prepared with sodium amide (see Experimental Section).

Moreover, certain of the condensation products prepared by means of sodium amide in liquid ammonia (see Scheme I) were found to undergo the Truce–Smiles rearrangement. For example, the benzyl derivative **2** underwent rearrangement with *n*-butyllithium, presumably through lithio sulfone **2′**, to form sulfinic acid **8** in good yield; **8** was isolated as its ferric derivative and characterized as its *p*-toluidine salt.



2′



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At least certain of the other derivatives of sodio sulfone **1′** could probably also be rearranged under appropriate conditions.

Results with Phenyl *p*-Tolyl Sulfone and Di-*p*-tolyl Sulfone.—The former compound (**9**) was converted by sodium amide in liquid ammonia into sodio salt **9′**, which was condensed with four types of electrophilic compounds (Scheme III).

The yields of derivatives **10**, **11**, and **12** were dependent on the conditions employed (see Discussion); the best yields obtained were 92, 82, 51%, respectively. The yield of the benzoyl derivative **13** was 70% when the ratio of sodio sulfone **9′** to ester was 2:1,[9] and 53% when 1 extra equiv of sodium amide was used.[3]

Similarly, di-*p*-tolyl sulfone (**14**) was converted by a molecular equivalent of sodium amide in liquid ammonia into the corresponding monosodio salt, which was

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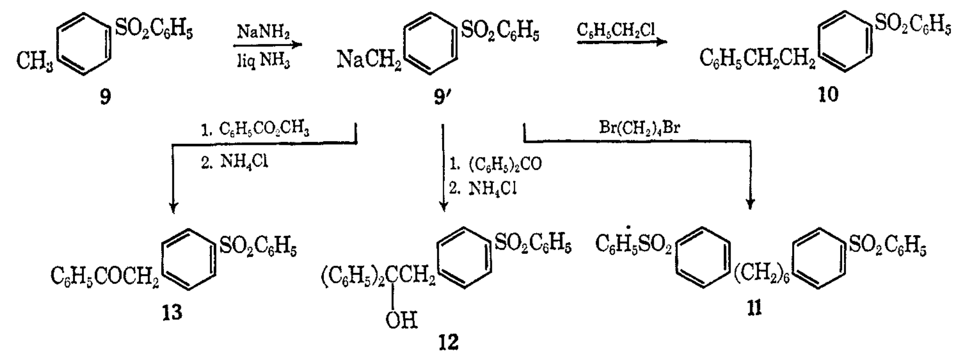
[6] All chemical shifts are reported as parts per million (δ) downfield from tetramethylsilane. Samples were determined in deuteriochloroform unless otherwise noted.

[7] (a) W. E. Truce and W. J. Ray, Jr., *J. Amer. Chem. Soc.*, **81**, 481 (1959); (b) for other interesting papers on the mechanism of this rearrangement of carbanions, see W. E. Truce, C. R. Robbins, and E. M. Kreider, *ibid.*, **88**, 4027 (1966), and references therein.

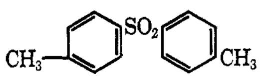
[8] O. L. Norman, Ph.D. Dissertation, Purdue University, 1953.

[9] The yield of **13** was 51% when based on starting sulfone **9**; see ref 4.

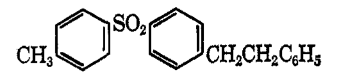
Scheme III



alkylated with benzyl chloride to form benzyl derivative **15** in 67% yield.



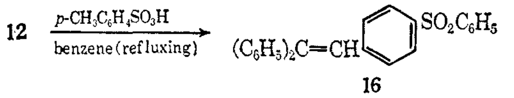
14



15

However, treatment of sulfone **14** with 2 mol equiv of sodium amide in liquid ammonia followed by 2 mol equiv of benzyl chloride failed to yield satisfactorily the corresponding dibenzyl derivative; instead there was obtained a mixture of the monobenzyl derivative **15**, starting sulfone **14**, and stilbene which arose through self-condensation of the halide, a type of reaction known to be effected by sodium amide.[10] The dibenzyl derivative possibly might be prepared by further benzylation of **15** through its monosodio salt.

The structures of the condensation products (Scheme III and **15**) were supported by analyses and absorption spectra. The structure of adduct **12** was confirmed by dehydration to form unsaturated sulfone **16** in 80% yield (eq 2).



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(2)

Infrared data (Table II) show that the spectra of the products were similar to those of the starting sulfones with the expected differences for carbinol sulfone **12** and keto sulfone **13** which exhibited strong hydroxyl and carbonyl peaks, respectively. Surprisingly, the spectrum of the benzyl derivative **10** was practically identical with that of the starting sulfone **9**, both showing a peak at 1390 cm^{-1} which, in the case of **9**, may be assigned to the methyl group.[5] Such a peak was absent in the spectrum of the isomeric *o*-benzyl derivative **2** (see Table I).

The nmr spectrum[6] of the benzyl derivative **10** showed a singlet at 2.89 ppm (4.03 H) for the methylene protons, and a complex aromatic multiplet from 7.2 to 8.0 ppm (14.0 H). The nmr spectrum[6] of the monobenzyl derivative **15** exhibited a singlet at 2.4 ppm (3.14 H) for the methyl protons, another singlet at 2.9 ppm (3.96 H) for the methylene protons, and a multiplet from 7.2 to 7.9 ppm (13.0 H) for the aromatic protons.

Discussion

The alkylations of sodio sulfones **1′** and **9′** (Schemes I and III) were effected employing various ionization periods of the sulfones as summarized in Table III. This table shows that, with equal volumes of liquid ammonia (400 ml), much longer ionization periods were required for satisfactory yields of alkylation products **2** and **3** from *o*-tolyl sulfone **1** than of **10** and **11** from the *p*-tolyl sulfone **9**. Moreover, by using 800 ml instead of 400 ml of liquid ammonia with *p*-tolyl sulfone **9**, the ionization time to give approximately the same yield of **10** was even less. The sodio salts of both **1** and **9** were decolorized almost immediately by benzyl chloride and, since this alkylation type of reaction is irreversible, the yields of the benzyl derivative **2** and **10** may be considered a rough measure of the rel-

Table II

Assigned Infrared Peaks of Phenyl *p*-Tolyl Sulfone, and Condensation Products

(cm^{-1})

Sulfone	SO₂ stretching Asymm	SO₂ stretching Symm	*para* disubstitution	Monoaromatic substitution[a]	Other
9	1300, 1280	1155	819	756, 702	1390[b]
10	1310, 1290	1150	826	756, 702	1390[c]
11	1290	1145	809	758, *d*	
12	1290	1150	830	753, 702	3500
13	1325, 1315, 1290	1145	*d*	753, 716	1680
14	1315, 1295, 1285	1150	819	*e*	
15	1310, 1290, 1280	1145	819	751, 710	
16	1320, 1305	1155	827	*f*, 703	

[a] The spectra of all these compounds, except **14** and **15**, showed two other strong peaks in this region at 730–722 and at 693–683 cm^{-1}, possibly from C–S stretching. [b] Symmetrical methyl bending. [c] The origin of this peak is not clear. [d] Peak was absent. [e] This spectrum showed two peaks at 709 and 677 cm^{-1} which have been assigned to C–S stretching; see J. Cymerman and J. B. Willis, *J. Chem. Soc.*, 1332 (1951). [f] Other peaks in this region made assignment uncertain.

Table III

Yields of Alkylation Products of Sulfones **1** and **9** Employing Various Ionization Periods

Tolyl sulfone	Ionization period, min	Solvent volume, ml	Halide	Product	Yield, %
1 (*ortho*)	20	400	$C_6H_5CH_2Cl$	**2**	45
1	300	400	$C_6H_5CH_2Cl$	**2**	61
9 (*para*)	5	800	$C_6H_5CH_2Cl$	**10**	82
9	15	800[a]	$C_6H_5CH_2Cl$	**10**	89
9	30	400	$C_6H_5CH_2Cl$	**10**	92
1 (*ortho*)	15	400	$Br(CH_2)_4Br$	**3**	26
1	60	400	$Br(CH_2)_4Br$	**3**	58
9 (*para*	15	800	$Br(CH_2)_4Br$	**11**	61
9	30	400	$Br(CH_2)_4Br$	**11**	82

[a] 0.03 mol of phenyl *p*-tolyl sulfone used.

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[10] See C. R. Hauser, W. R. Brasen, P. S. Skell, S. W. Kantor, and A. E. Brodhag, *J. Amer. Chem. Soc.*, **78**, 1653 (1956).

ative ease of ionization of the starting sulfones **1** and **9**. Actually, the relative ease of ionization of the *o*-tolyl sulfone **1** must have been even less than indicated by the relative yields of the alkylation products, since this sulfone was more soluble in liquid ammonia than *p*-tolyl sulfone **9**. The relatively slow rate of ionization of the *o*-tolyl sulfone **1** suggests that a steric factor is involved. A study of a possible metallic cation effect employing various alkali amides is contemplated.

Incidentally, in one of the experiments on the benzylation of the *o*-tolyl sulfone **1** in which the yield of the benzyl derivative **2** was relatively low, a considerable amount of stilbene was detected by thin layer chromatography; this self-condensation product of the benzyl chloride was presumably produced by sodium amide that had not yet effected the ionization of **1**.[10]

The carbonyl addition reactions of sodio sulfones **1′** and **9′** (Schemes I and III) were effected employing various condensation periods as summarized in Table IV. Because of possible reversion during work-up, the reaction mixtures were neutralized inversely with ammonium chloride. Table IV shows that the yields of adducts **4** and **12** were satisfactory only when the reaction mixtures were neutralized within a relatively short time. The time was less critical with the *o*-sodio sulfone **1′** than with the *p*-sodio sulfone **9′**; with the latter, less than 5 min appeared to be required for a satisfactory yield. These results are rationalized on the basis of a kinetic *vs.* thermodynamic control as illustrated in Scheme IV for the *para* case. The kinetic control involves the initial addition reaction of sodio sulfone **9′** with benzophenone to form sodio adduct **12′**, and the thermodynamic control involves an addition reaction of sodium amide (present in equilibrium) with the ketone to form sodio adduct **17**. Such competing controls have recently been reported in the related addition reaction of disodiophenylacetamide with benzophenone, in which formation of the sodium amide adduct of the ketone (**17**) was established.[11]

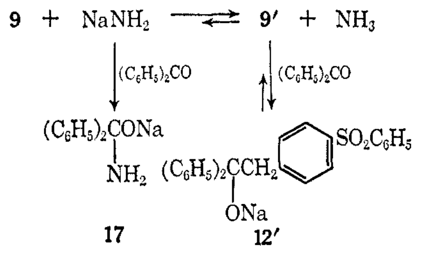
TABLE IV

YIELDS OF ADDUCTS FROM SODIO SULFONE 1′ AND 9′ WITH BENZOPHENONE ON INVERSE NEUTRALIZATION AFTER VARIOUS CONDENSATION PERIODS

Sodio sulfone	Ionization period, min	Condensation period, min	Product	Yield, %
1′ (*ortho*)	120	1	4	76
1′	120	5	4	69
1′	120	30	4	*a*
9′ (*para*)	30	1	12	51
9′	30	5	12	6
9′	30	30	12	*b*

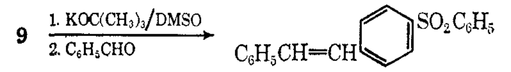
[a] No product detected; shown to be starting material by tlc; 58% starting sulfone 1 recovered. [b] No product detected; 56% starting sulfone 9 recovered.

SCHEME IV



17 **12′**

It should be mentioned that *p*-tolyl sulfone **9** previously has been condensed with certain aromatic aldehydes by means of potassium *t*-butoxide in dimethyl sulfoxide (DMSO) to form the corresponding unsaturated sulfones; the best yield (40%) was obtained with benzaldehyde (eq 3).[12]



(3)

All of the products listed in Schemes I and III (and **15**) were new. The sodium amide method employed in these syntheses could probably be extended, not only to other electrophilic compounds, but also to certain substituted *o*- and *p*-tolyl sulfones to afford various derivatives having other functional groups. Moreover, the condensations involving the *o*-tolyl sulfones should furnish derivatives which may be useful for mechanistic studies of the Truce–Smiles rearrangement and for syntheses of resulting sulfinic acids.

Experimental Section[13]

Conversion of Phenyl *o*-Tolyl Sulfone (1) into Sodio Salt 1′.—To a stirred suspension of 0.02 mol of sodium amide in 400 ml of liquid ammonia[14] was added 4.64 g (0.02 mol) of phenyl *o*-tolyl sulfone (1)[7] to produce immediately a deep purple solution of sodio salt **1′**. No undissolved sulfone was observed. After stirring for an appropriate time (designated ionization period), the sodio salt **1′** (maximum amount 0.02 mol) was condensed with electrophilic compounds (or rearranged) as described below.

Alkylations of Sodio Salt 1′.—In Table I are summarized the yields of products obtained employing various ionization periods. The experiments which afforded the best yields are described below.

A. With Benzyl Chloride.—To a stirred solution of sodio salt **1′** (after an ionization period of 5 hr) was added 2.79 g (0.022 mol) of benzyl chloride in 50 ml of dry ether. The purple color of **1′** was immediately discharged (to light tan). The liquid ammonia was allowed to evaporate and more (500 ml) ether was added. The resulting ethereal suspension was stirred with 50 ml of water to dissolve the inorganic salts. The two layers were separated. The ethereal solution was dried and the solvent removed. The residue was recrystallized from absolute ethanol to give 3.97 g (61%) of the benzyl derivative **2**, mp 84–87 and 86–87° after several additional recrystallizations.

Anal. Calcd for $C_{20}H_{18}SO_2$: C, 74.50; H, 5.63; S, 9.94. Found: C, 74.59; H, 5.52; S, 9.97.

The original aqueous layer of the reaction product (see above) was neutralized with 50% hydrochloric acid. The resulting solution was treated with excess aqueous ferric chloride[15] to precipitate 0.05 g (*ca.* 1%) of the red ferric derivative of 2-benzylbenzenesulfinic acid (**7b**). The infrared spectrum of this

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[11] E. M. Kaiser and C. R. Hauser, *J. Org. Chem.*, **31**, 3317 (1966).

[12] G. A. Russell, E. G. Janzen, H. D. Becker, and F. J. Smentowski, *J. Amer. Chem. Soc.*, **84**, 2652 (1962).

[13] Melting points were taken in open capillary tubes on a Thomas-Hoover melting point apparatus and are uncorrected. Elemental analyses were performed by Janssen Pharmaceutica, Beerse, Belgium, and M-H-W Laboratories, Garden City, Mich. Infrared spectra were determined with a Perkin-Elmer Model 137 Infracord using the potassium bromide pellet method. The nmr spectra were obtained on a Varian A-60 spectrometer. All chemical shifts are reported in parts per million (δ) downfield from an internal tetramethylsilane standard. Commercial, anhydrous liquid ammonia was used; it was further dried in the preparation of sodium amide by addition of small pieces of sodium until a blue color persisted. *n*-Butyllithium (*ca.* 1.5 *M* in hexane) was obtained from Foote Mineral Co. Organic fractions were dried over anhydrous magnesium sulfate, and then concentrated or removed under reduced pressure using a Roto-vac (Labline).

[14] For preparation of sodium amide, see ref 10, p 122.

[15] J. Thomas, *J. Chem. Soc.*, **95**, 342 (1909).

slightly impure sample of **7b** was nearly superimposable on that of an authenic sample obtained from the Truce–Smiles rearrangement under more appropriate conditions (see below).

B. With 1,4-Dibromobutane.—To a stirred solution of sodio salt **1′** (after an ionization period of 1 hr) was added dropwise 2.37 g (0.010 mol) of 1,4-dibromobutane in 50 ml of dry ether. The purple color of **1′** slowly changed to brownish green. The ammonia was replaced by ether and the resulting suspension stirred with water. The solid was collected and recrystallized from benzene–ethanol to give 2.99 g (58%) of the bis derivative **3**, mp 154–157 and 156–158° after further recrystallizations.

Anal. Calcd for $C_{30}H_{30}S_2O_4$: C, 69.47; H, 5.83; S, 12.36. Found: C, 69.89; H, 5.87; S, 12.36.

Addition Reaction of Sodio Salt 1′ with Benzophenone.—In Table II are summarized the yields of product obtained employing various condensation periods; the 2-hr ionization period allowed is considered sufficient to form approximately 0.02 mol of sodio salt **1′**. The experiment which gave the best yield is described below.

To a stirred solution of sodio salt **1′** was added, during 1 min, 4.01 g (0.022 mol) of benzophenone in 50 ml of dry ether. The purple color of **1′** changed to red during the 1 min, after which the reaction mixture was poured into a solution of 2.36 g (0.044 mol) of ammonium chloride in liquid ammonia. The ammonia was replaced by ether. The resulting suspension was stirred with water and the mixture filtered. The solid (4.67 g), mp 166–168°, was combined with more (1.65 g) of solid, mp 162–165°, isolated from the filtrate to give 6.32 g (76%) of benzophenone adduct **4**, which melted at 166–167° after several recrystallizations from benzene–hexane.

Anal. Calcd for $C_{26}H_{22}SO_3$: C, 75.33; H, 5.35; S, 7.73. Found: C, 75.42; H, 5.39; S, 7.68.

Dehydration of 2 g (0.00483 mol) of adduct **4** was accomplished by refluxing with a catalytic amount (<0.1 g) of *p*-toluenesulfonic acid monohydrate in 100 ml of benzene for 14 hr; the azeotrope of water and benzene was removed using a Dean–Stark water trap. The resulting solution was diluted with ether, washed with sodium bicarbonate solution, and dried. The solvent was removed to give 1.66 g (86%) of unsaturated sulfone **6**, mp 170–173 and 171–172.5° after recrystallization from benzene–hexane.

Anal. Calcd for $C_{26}H_{20}SO_2$: C, 78.76; H, 5.08. Found: C, 79.12; H, 5.19.

Benzoylation of Sodio Salt 1′.—To a stirred solution of sodio salt **1′** (ionization period of 4 hr to form presumably 0.02 mol of **1′**) was added 1.36 g (0.01 mol) of methyl benzoate in 50 ml of dry ether. The purple color of **1′** changed to reddish brown and finally to yellowish green. After neutralization with excess ammonium chloride (1.77 g, 0.033 mol), the ammonia was replaced by ether, and the resulting ethereal suspension was stirred with 50 ml of water. The layers were separated. The ethereal layer was dried and concentrated. The resulting precipitate (1.94 g), mp 117–124°, was collected by filtration and recrystallized from absolute ethanol to give 1.69 g (50%) of keto sulfone **5**, mp 128–130°.

Anal. Calcd for $C_{20}H_{16}SO_3$: C, 71.41; H, 4.80; S, 9.53. Found: C, 71.12; H, 4.78; S, 9.55.

Further concentration of the filtrate afforded 1.59 g (34%) of the crude starting sulfone **1**, mp 65–75°.

When 0.044 mol of sodium amide in 400 ml of liquid ammonia was treated with 0.02 mol of sulfone **1**, followed, after 5 hr, by 0.03 mol of methyl benzoate in 50 ml of dry ether, there was obtained, on working up the reaction mixture as described above, the keto sulfone **5**, mp 128–130°, in 34% yield (based on **1**).

Rearrangement of Sodio Salt 1′.—To a stirred suspension of 0.022 mol of sodium amide in 400 ml of liquid ammonia was added 0.02 mol of phenyl *o*-tolyl sulfone (**1**) and the ammonia replaced by freshly distilled tetrahydrofuran (THF). The resulting dark red solution of sodio salt **1′** was refluxed for 7 hr; the red color gradually faded and a tan solid precipitated. The solid was collected by filtration to give 2.73 g (54%) of crude sodio salt **7a** of 2-benzylbenzenesulfinic acid (**7**). The filtrate was diluted with ether, and water added. The layers were separated. The aqueous layer was neutralized with 50% hydrochloric acid and treated with aqueous ferric chloride to precipitate 0.82 g (16%) of the known[7a] red ferric derivative **7b**.

The combined yield of **7a** and **7b** was 70%. The sodio salt **7a** was identified by its infrared spectrum: 1435, 1025 (SO_2),[16] 952 (SO_2),[16] 879, 757, 726, and 695 cm^{-1}, and by conversion of a sample into the red ferric derivative **7b**. The latter derivative was identified by infrared spectrum [1590, 1485, 1465, 1445, 960–920 (very broad SO_2), 755, 728, and 679 cm^{-1}], and by conversion of a 1-g sample into the free sulfinic acid[7] and the mercuric chloride derivative[7,17] as described previously. The sulfinic acid **7**, isolated in 40% yield, melted at 68–76 and 74.5–76° after recrystallization from ether–petroleum ether (bp 30–65°) (lit.[7] mp 70–72°): infrared, 2830 OH,[16] 2470 (OH),[16] 1480, 1465, 1445, 1435, 1120, 1080, 1070 (SO_2),[16] 1035 (SO_2),[16] 833, 763, 747, 724, and 697 cm^{-1}. The mercuric chloride derivative melted at 142–144° (lit.[7] mp 147–148°).

When the sodio sulfone **1′** was prepared in liquid ammonia as described above, and the ammonia replaced by ether followed by 10 hr of refluxing, the red color of **1′** was still present and, on working up the reaction mixture, there was obtained sulfinic acid **7** as its ferric derivative **7b** in 12% yield; 38% of the sulfone **1** was recovered.

Results with Sulfone 1 and *n*-Butyllithium.—The rearrangement of sulfone **1** with this reagent was effected in ether–hexane as described by Truce and Ray[7] (refluxed 6 hr). There was obtained 2-benzylbenzenesulfinic acid (**7**), isolated as its ferric derivative **7b** in 54% yield. The infrared spectrum of a sample of this product was identical with that of **7b** obtained from the rearrangement of sulfone **1** with sodium amide as described above.

The intermediate lithio salt of sulfone **1** was trapped by treating 0.01 mol of sulfone **1** in 300 ml of dry ether at −80° with 0.011 mol of *n*-butyllithium in hexane (7.34 ml) and, after 6 hr, adding 0.011 mol of benzophenone in ether. After 30 min, the ethereal solution was washed with water, dried, and concentrated (reduced pressure) to give 0.55 g (13%) of slightly impure benzophenone adduct **4**, mp 155–160°. Admixture with a sample of authentic **4** did not depress the melting point; the infrared spectra of the two samples were superimposable.

Rearrangement of Benzyl Derivative 2.—Into a solution of 0.82 g (0.0025 mol) of **2** in 100 ml of dry ether was syringed 2 ml (0.0028 mol) of approximately 1.5 *M* *n*-butyllithium to form a deep red solution. After refluxing for 4 hr under nitrogen, the reaction mixture was stirred with 50 ml of iced water until all the solid dissolved. The two layers were separated. The cooled aqueous layer was acidified with 50% hydrochloric acid to form an oil, which was taken up in ether. The ethereal solution was extracted with sodium bicarbonate. This bicarbonate solution was neutralized with 50% hydrochloric acid and treated with aqueous ferric chloride to precipitate a red solid which was collected by filtration to give 0.49 g (60%) of the ferric derivative of sulfinic acid **8**: infrared, 1620, 1510, 1460, 970–940 (broad), 759, and 700 cm^{-1}.

An aqueous suspension of this ferric derivative was treated with excess concentrated ammonium hydroxide to leave a brown suspension of ferric hydroxide, which was removed by filtration. The cooled aqueous filtrate was acidified with concentrated hydrochloric acid to form an oil, which failed to crystallize. This oil was dissolved in absolute ethanol, and the solution treated with excess *p*-toluidine. The resulting solution was warmed slightly and then added dropwise to 75 ml of chilled stirred, dry ether. The solid which precipitated was collected by filtration to give the *p*-toluidine salt of sulfinic acid **8**: mp 160–163 and 162–163° after two recrystallizations from ethanol–ether; infrared, 3400, 2830, 2580, 1510, 1435, 1020 (SO_2),[16] 915 (SO_2),[16] 808, 760, 754, and 695 cm^{-1}.

Anal. Calcd for $C_{27}H_{27}NSO_2$: C, 75.49; H, 6.34; N, 3.26; S, 7.46. Found: C, 75.33; H, 6.27; N, 3.28; S, 7.29.

Conversion of Phenyl *p*-Tolyl Sulfone (9) into Sodio Salt 9′.—To a stirred suspension of 0.022 mol of sodium amide in 400–800 ml of liquid ammonia was added 0.02 mol of phenyl *p*-tolyl sulfone **9**,[18] mp 125–127° (lit.[19] mp 125°), to produce a deep red solution of sodio salt **9′**. All of the sulfone appeared to dissolve within 15 and 30 min when the volume of liquid ammonia was 800 and 400 ml, respectively. After stirring for an appropriate time (designated ionization period), the sodio salt **9′** was condensed with electrophilic compounds as described below.

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[16] S. Detoni and D. Hadzi, *J. Chem. Soc.*, 3163 (1955).

[17] See F. C. Whitman, F. H. Hamilton, and N. Thurman, *J. Amer. Chem. Soc.*, **45**, 1066 (1923).

[18] Prepared in 77% yield from thiophene-free benzene (dried over sodium) and *p*-toluenesulfonyl chloride by means of aluminum chloride as described for similar sulfones; see ref 7.

[19] J. T. Braunholtz and F. G. Mann, *J. Chem. Soc.*, 4174 (1957).

Alkylations of Sodio Salt 9′.—In Table III are summarized yields of products obtained employing various ionization periods; the experiments which gave the best yields are described below.

A. **With Benzyl Chloride.**—To a stirred solution of sodio salt 9′ in 400 ml of liquid ammonia (ionization period, 30 min) was added 2.79 g (0.022 mol) of benzyl chloride in 50 ml of dry ether. The color of 9′ was changed immediately to a brighter red which faded slowly. The reaction mixture was worked up as described above for benzylation of sodio salt **1′** to give a white solid, mp 124–128°, upon removal of the ether. One recrystallization from absolute ethanol afforded 5.89 g (92%) of benzyl derivative **10**, mp 130–132.5 and 133.5–135° after several more recrystallizations from absolute ethanol.

Anal. Calcd for $C_{20}H_{18}SO_2$: C, 74.51; H, 5.63; S, 9.94. Found: C, 74.52; H, 5.73; S, 9.95.

B. **With 1,4-Dibromobutane.**—To a stirred solution of sodio salt 9′ in 400 ml of liquid ammonia (ionization period, 30 min) was added 0.01 mol of 1,4-dibromobutane in dry ether. The color changed to dark brown. The reaction mixture was worked up as described above for the corresponding reaction of the sodio salt **1′** to give, after trituration with water and benzene, 4.24 g (82%) of the bis derivative **11**, mp 224–228 and 229.5–231° after four recrystallizations from large volumes of benzene.

Anal. Calcd for $C_{30}H_{30}S_2O_4$: C, 69.47; H, 5.83; S, 12.36. Found: C, 69.62; H, 5.83; S, 12.04.

Addition Reaction of Sodio Salt 9′ with Benzophenone.—In Table IV are summarized the yields of products obtained employing various condensation periods; the experiment which gave the best yield is described below.

To a stirred solution of sodio salt 9′ in 800 ml of liquid ammonia (ionization period, 30 min) was added, during 1 min, 4.01 g (0.022 mol) of benzophenone in 50 ml of dry ether. The dark color became lighter red. After 1 min the reaction mixture was inversely neutralized and worked up as described above for the addition reaction of sodio salt **1′** to give, after recrystallization from THF–ethanol, 4.01 g (51%) of benzophenone adduct **12**, mp 203–205 and 208–210° after further recrystallizations.

Anal. Calcd for $C_{26}H_{22}SO_3$: C, 75.33; H, 5.35; S, 7.73. Found: C, 75.04; H, 5.36; S, 8.40.

Dehydration of 2 g of adduct **12** was effected as described for dehydration of adduct **4** to give (in two crops) 1.53 g (80%) of unsaturated sulfone **16**, mp 181–184 and 182.5–184° after several recrystallizations from benzene–hexane.

Anal. Calcd for $C_{26}H_{20}SO_2$: C, 78.76; H, 5.08. Found: C, 78.88; H, 5.14.

Benzoylation of Sodio Salt 9′.—To a stirred solution of 0.02 mol of sodio salt 9′ in 400 ml of liquid ammonia (ionization period, 30 min) was added dropwise 1.36 g (0.01 mol) of methyl benzoate in dry ether. The red color gradually changed to yellow. After 1 hr the reaction mixture was worked up as described for the benzoylation of sodio salt **1′** to give, on recrystallization of the product from acetonitrile, 2.37 g (70% based on the ester) of keto sulfone **13**, mp 213–216 and 215–217° after several recrystallizations from large volumes of acetonitrile.

Anal. Calcd for $C_{20}H_{16}SO_3$: C, 71.41; H, 4.80; S, 9.53. Found: C, 71.01; H, 4.82; S, 9.30.

There was recovered from the original filtrate 1.44 g (30%) of the starting sulfone **9**, mp 123–125°.

When 0.044 mol of sodium amide in 400 ml of liquid ammonia was treated with 0.02 mol of sulfone **9** in a manner described before for sulfone **1**, 3.59 g (53%) of crude ketone sulfone **13**, mp 205–215°, was obtained. Further purification was not attempted since the yield was low.

Monobenzylation of Di-*p*-tolyl Sulfone (14).—To a stirred suspension of 0.022 mol of sodium amide in 400 ml of liquid ammonia was added 4.94 g (0.02 mol) of commercial sulfone **14** to form a deep red solution. After 30 min, 2.79 g (0.022 mol) of benzyl chloride in 50 ml of dry ether was added. The reaction mixture was worked up as usual to give, after one recrystallization from absolute ethanol, 5.91 g (81%) of monobenzyl derivative **15**, mp 120–130°; a second recrystallization gave 4.54 g (67%) of **15**, mp 126–130 and 135–136° after several recrystallizations from absolute ethanol.

Anal. Calcd for $C_{21}H_{20}SO_2$: C, 74.97; H, 5.99; S, 9.53. Found: C, 74.74; H, 6.00; S, 9.63.

Attempted Dibenzylation of Di-*p*-tolyl Sulfone (15).—To a stirred suspension of 0.066 mol of sodium amide in 800 ml of liquid ammonia was added 0.03 mol of di-*p*-tolyl sulfone (**15**) which gradually dissolved. After 30 min, 0.066 mol of benzyl chloride was added. The purple color characteristic of stilbene formation was observed.[10] The reaction mixture was worked up to give a mixture of solids which was indicated by thin layer chromatography to consist of monobenzyl derivative **16**, stilbene, starting sulfone **15**, and a trace of an unidentified compound.

Registry No.—**1,** 7018-84-0; **1′,** 16425-98-2; **2,** 16425-99-3; **3,** 16426-00-9; **4,** 16426-01-0; **5,** 16426-02-1; **6,** 16426-03-2; **7,** 16426-04-3; **8** *p*-toluidine salt, 16426-05-4; **8** ferric derivative, 16426-14-5; **9,** 640-57-3; **9′,** 16426-07-6; **10,** 16426-08-7; **11,** 16426-09-8; **12,** 16426-10-1; **13,** 16426-11-2; **15,** 16426-12-3; **16,** 16426-13-4; sodium amide, 7782-92-5.