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Condensation Reactions of Sulfonylcarbanion

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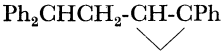
Phenylsulfonylcarbanion $PhSO_2CH_2^-$ reacts with anthracene and acridine in HMPA to afford methylated products much as does methylsulfinylcarbanion $MeSOCH_2^-$ in DMSO. The reaction mechanism is examined by following the change in the D-content during the reaction of 9-deuterioanthracene. The transformation of the negatively-charged σ-complex into the methylated product involves the concerted occurrence of a hydride shift and the elimination of the sulfinate anion. Meanwhile, the reaction of this carbanion with anthracene at a higher temperature yields the ethylated products of 9-ethyl-10-methyl- and 9,10-diethylanthracene besides 9,10-dimethylanthracene. Other condensation reactions of the carbanion investigated are those with (a) $Ph_2C{=}CH_2$, (b) $PhC{\equiv}Cph$, (c) Ph_2CO, (d) PhCOCOPh, and (e) 2-aminobenzophenone, the main products being (a)  $Ph_2CHCH_2\text{-}\underbrace{CH\text{-}CPh_2}$, (b) $Ph_2C{=}C(Ph)Me$, (c) $Ph_2C(OH)CH_2CH_2SO_2Ph$ and $Ph_2C{=}CHCH_2\text{-}SO_2Ph$, (d) $PhCOCH_2SO_2Ph$ and PhCOOH, and (e) 3-phenylindole respectively.

Synthetic reactions by means of methylsulfinylcarbanion were explored by Corey,1) Russell,2) and their co-workers.3) Previously, we recorded the attainment of the nucleophilic methylation of condensed aromatic rings with this carbanion,4,5) this reaction was reported independently by several other groups at almost the same time. The condensation reactions of sulfonylcarbanions were documented equally well6) and our previous communication7) was concerned with aromatic methylation involving the carbanion produced from methyl phenyl sulfone and sodium hydride in HMPA. The present paper will present (a) a summary of our investigations of the aromatic methylation and (b) a comparison of the behavior of sulfinyl- and sulfonylcarbanions in relation to aryl-conjugated olefinic and acetylenic bonds as well as compounds containing a benzoyl group.

Table 1 summarizes the methylation of anthracene and acridine with sulfonylcarbanions. The reaction can be effected by means of the carbanion derived from *N,N*-dimethyl(methylsulfonamide) equally well, and the solvent HMPA can be replaced with DMF. Phenanthrene, quinoline, and isoquinoline failed to be methylated with sulfonylcarbanions, whereas the reaction of these substrates with methylsulfinylcarbanion proceeded smoothly. The mechanism of the methylation with sulfinylcarbanion was outlined in the previous communication.5a) Analogous investigations have now been extended to the methylation of anthracene with sulfonylcarbanions. Scheme 1 shows two possible reaction paths, A and B. The path A implies that a concerted hydride shift and the elimination of the sulfinate anion are involved in the transformation of the negatively-charged σ-complex (IIa or IIb) into the methylated product. The other path, B,5a) assumes proton abstraction by IIa or IIb, followed by the elimination of sulfinic acid and, finally aro-

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1) a) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **84**, 866 (1962). b) *Ibid.*, **87**, 1345 (1965) and Refs. cited. c) *Ibid.*, **87**, 1353 (1965).

2) a) G. A. Russell, E. G. Janzen, H. D. Becker, and F. S. Smentowski, *ibid.*, **84**, 2652 (1962). b) G. A. Russell and H.-D. Becker, *ibid.*, **85**, 3406 (1963). For β-keto sulfoxides see: c) H.-D. Becker, G. J. Mikol, and G. A. Russell, *ibid.*, **85**, 3410 (1963). d) G. A. Russell and L. A. Ochrymowycz, *J. Org. Chem.*, **34**, 3618 (1969).

3) For detailed account see: T. Durst, "Advances in Org. Chem. Methods and Results," Vol. 6, ed. by E. C. Taylor and H. Wynberg, Interscience Publishers, New York (1969), p. 285.

4) Ordinarily a paper such as this should contain experimental details on the nucleophilic aromatic methylation with methylsulfinylcarbanion reported in our previous communication (Ref. 5a), but this will not be done. The reason is that independent reports by Russell, Argabright, and their co-workers have made such a description meaningless. Though the reaction of D-labelled aromatics was recorded only in Ref. 5a, the experimental procedure was almost the same as the methylation reaction with phenylsulfonylcarbanion in HMPA described in the "Experimental" section.

5) a) H. Nozaki, Y. Yamamoto, and R. Noyori, *Tetrahedron Lett.*, **1966**, 1123. b) P. A. Argabright, J. E. Hofmann, and A. Schriesheim, *J. Org. Chem.*, **30**, 3233 (1965). c) G. A. Russell and S. A. Weiner, *ibid.*, **31**, 248 (1966). d) For aromatic methylation by means of dimethyloxosulfonium methylide see: H. König, H. Metzger, and K. Seelert, *Chem. Ber.*, **98**, 3712 (1965); V. J. Traynelis and Sr. J. V. McSweeney, O. P., *J. Org. Chem.*, **31**, 243 (1966); B. M. Trost, *Tetrahedron Lett.*, **1966**, 5761.

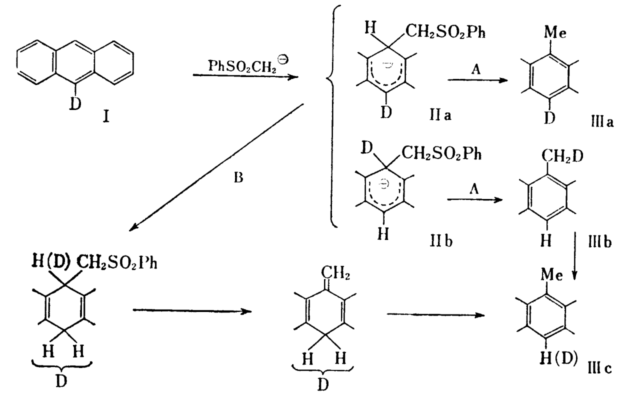
6) a) H.-D. Becker and G. A. Russell, *J. Org. Chem.*, **28**, 1896 (1963). b) H. O. House and J. K. Larson, *ibid.*, **33**, 61 (1968). c) D. F. Tavares and P. F. Vogt, *Can. J. Chem.*, **45**, 1519 (1967). d) J. M. McFarland and D. N. Buchanan, *J. Org. Chem.*, **30**, 2003 (1965).

7) H. Nozaki, Y. Yamamoto, and T. Nisimura, *Tetrahedron Lett.*, **1968**, 4625.

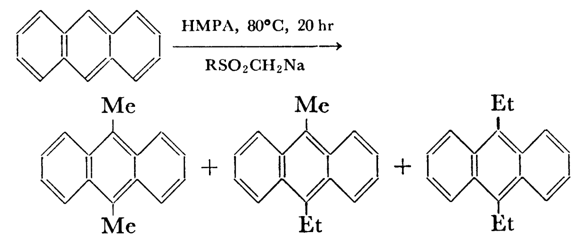
TABLE 1. METHYLATION OF ANTHRACENE AND ACRIDINE BY MEANS OF RSO_2CH_2Na

Aromatics	R	Solvent[a]	(Aromatic/Base) Mole ratio	Reaction Temp. (°C)	Reaction Time (hr)	Products (Yield %)[b]
Anthracene	Ph	HMPA	3	60	15	9-Methylanthracene (55) 9,10-Dimethylanthracene (10)
Anthracene	NMe_2	HMPA	2.1	30	20	9-Methylanthracene (35)[c]
Acridine	Ph	HMPA	1.5	25	4	9-Methylacridine (60)
Acridine	Ph	HMPA	2	80	4	9-Methylacridine (33) 9-Methylacridane (4)
Acridine	Ph	DMF	3	30	4	9-Methylacridine (67)
Acridine	NMe_2	HMPA	3	22	4	9-Methylacridine (40)

a) HMPA stands for hexamethylphosphoric triamide and DMF for *N,N*-dimethylformamide.
b) All reaction products were identified with authentic samples.
c) Yields are based on the substrates initially added, as the recoveries of unchanged materials have not determined accurately.



Scheme 1



	V	VI	VII
R=Ph (3 mol)	13%	43%	trace
R=Me (5 mol)	28%	28%	trace

Scheme 2[8]

matization. A choice between the two is made by examining the change in the D-content in the reaction of 9-deuterioanthracene (I). As the CH_2D group (IIIb) attached to the aromatic ring is rapidly changed into the CH_3 group (IIIc) under the reaction conditions, the path A gives a 50% retention, and the path B, a 25% retention, in the absence of a primary isotope effect. Mass spectrometric analyses have indicated that the original D-content (82%) is unchanged in the recovered I. In contrast, the 9-methylanthracene produced retains 45% of its D-content; therefore, nearly 50% of the deuterium is lost by methylation.

The path A is also supported by another experimental fact, the fact that the reaction of acridine with ethyl phenyl sulfone gives 9-(α-phenylsulfonylethyl)-acridane (IV). This indicates that the hydride shift in the σ-complex is slower than the protonation in this case, possibly because of the presence of a methyl substituent in the S_N center.

A remarkable feature of aromatic substitution by means of sulfonylcarbanion is the formation of ethylated by-products, as is shown in Scheme 2. *A priori*, we can not exclude the possibility of the initial formation of ethyl phenyl sulfone. However, all attempts either to detect ethyl phenyl sulfone among the recovered sulfone or to confirm the formation of monoethylated anthracene were unsuccessful. In contrast, the treatment of V under the conditions of Scheme 2 gave a 53% yield of VI and a 24% yield of VII, besides a 46% recovery of V. The ethylation would thus conceivably involve the preliminary formation of arylcarbanion by proton-abstraction from the C-methyl group.

Other condensation reactions of sulfinylcarbanion with 1,1-diphenylethylene (VIII),[9,10] tolan (XV),[11] benzophenone (XVII),[9,10] and with benzil (XXI)[12] in DMSO were recorded previously. We have examined the condensation of phenylsulfonylcarbanion with these substrates in HMPA in order to observe closely the several remarkable points of difference.

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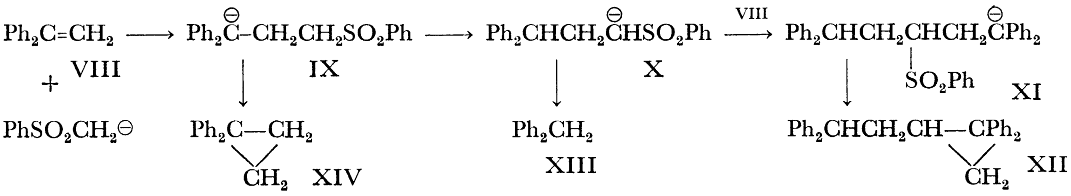
[8] As the three products could not be sharply separated, the yields were calculated as follows. On the basis of a comparison of the products with authentic samples by GLC (Apiezon L 30%), we could detect the presence of 9,10-dimethyl-, 9-ethyl-10-methyl-, and 9,10-diethylanthracene (not isolated). 9-Methylanthracene was absent. The NMR spectra indicated that the substituents of anthracene were either methyl- or ethyl-groups and that the substitution had occurred at C-9 and C-10 exclusively (This is the AA′BB′-pattern of aromatic protons). Accordingly, we calculated the yields of 9,10-dimethylanthracene and 9-ethyl-10-methylanthracene from the integral ratio of the NMR signals of the mixture, while a small amount of diethylanthracene was detected by observing the parent peak in the mass spectra.

[9] M. Chaykovsky and E. J. Corey, *J. Org. Chem.*, **28**, 254 (1963).

[10] C. Walling and L. Bollyky, *ibid.*, **28**, 256 (1963).

[11] I. Iwai and J. Ide, *Chem. Pharm. Bull.* (Tokyo), **13**, 663 (1965).

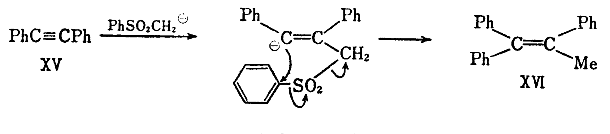
[12] a) J. C. Trisler, C. S. Aaron, J. L. Frye, and J. Y. Park, *J. Org. Chem.*, **33**, 1077 (1968). b) J. C. Trisler, J. K. Doty, and J. M. Robinson, *ibid.*, **34**, 3421 (1969).



Scheme 3

The reaction of phenylsulfonylcarbanion (15 mmol) with VIII (10 mmol) yielded mainly XII (60%), besides XIII (34%) and XIV (1%) (Scheme 3); these results are in contrast with those of methylsulfinylcarbanion, which afforded XIII (64%) and XIV (36%) only. The present reaction is, therefore, characterized by the facile isomerization of the carbanion IX into the sulfonylcarbanion X.

The reaction of XV with methylsulfinylcarbanion is known to produce 2,3-diphenyl-1,3-butadiene.[11] Meanwhile, the reaction with phenylsulfonylcarbanion proceeded according to Scheme 4 to give 1,1,2-triphenylpropene (XVI) (21%), possibly *via* Truce-Smiles rearrangement.[13]



Scheme 4

Scheme 5 shows the reactions of XVII with phenylsulfonylcarbanion, affording XIX (21%) and XX (22%). The condensation of XVII with methylsulfinylcarbanion[9,10] gives mainly VIII (47%), in addition to such by-products as XIII (30%), XIV (3%), and diphenylacetaldehyde (20%). The aldehyde may be ascribed to intermediary 2,2-diphenyloxirane (XVIII) (not isolated). In contrast, the reaction of phenylsulfonylcarbanion with XVIII gave XIX (44%), whose dehydration with trifluoroacetic acid afforded XX.

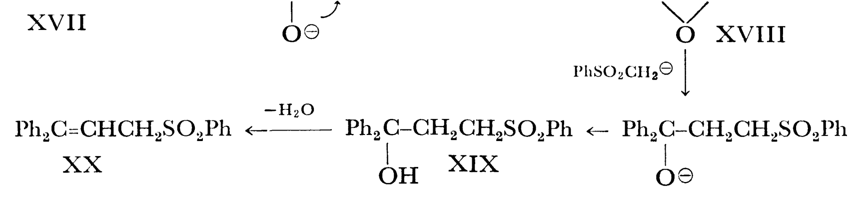
The reaction of phenylsulfonylcarbanion with benzil (XXI) afforded mainly phenacyl phenyl sulfone (XXII) (22%) and benzoic acid (XXIII) (26%), besides desoxybenzoin (XXIV) (17%) and the Kostanecki compound (XXV) [14] (11%). This is in contrast to that of methylsulfinylcarbanion, which has been recorded to produce 2,4,5-triphenyl-3-benzoylfuran and XXIII.[12] The condensation of phenylsulfonylcarbanion with 2-aminobenzophenone (XXVI) yielded 3-phenylindole (XXVII) (59%), while that with salicylaldehyde (XXVIII) gave not benzofuran, but *o*-hydroxystyryl phenyl sulfone (XXIX) (73%).

On the basis of these observations, we may summarize the points of difference between sulfinyl- and sulfonylcarbanions as follows: the sulfinylcarbanion has a higher reactivity than the sulfonylcarbnion, as is evident from the comparison of the methylation reaction of condensed aromatics and from the reaction temperature required for the condensation with olefinic and acetylenic compounds. It is also to be noticed that higher temperatures are generally required for the reaction of sulfonylcarbanion and that products retaining the sulfonylgroup are obtained more frequently, although it has often been demonstrated that sulfinic acid is a better leaving group than the sulfenic acid.[16] The reason for this remains to be clarified.

Experimental

All the mps are uncorrected. The microanalyses were performed at the Elemental Analyses Center of Kyoto University and by Mrs. K. Fujimoto at Prof. K. Sisido's Laboratory. The NMR spectra were obtained in $CDCl_3$, CCl_4, or D_3CSOCD_3 on a 60 MHz instrument (JEOL C-60H spectrometer). The mass spectra were obtained on a Hitachi RMU-6E or RMU-6D spectrometer, lent by the Sagami Chemical Research Center and the Toray Co. respectively.

Reaction of Phenylsulfonylcarbanion with Anthracene. A solution of sodium phenylsulfonylcarbanion was prepared under N_2 from sodium hydride (0.41 g, 16.8 mmol) and methyl phenyl sulfone (5.3 g, 33.6 mmol) in HMPA (30 m*l*). Into this solution, at room temperature, anthracene (1.0 g, 5.6 mmol) in HMPA (30 m*l*) was stirred over a period of



Scheme 5

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[13] a) G. P. Crowther and C. R. Hauser, *ibid.*, **33**, 2228 (1968). b) W. E. Truce, C. R. Robbins, and E. M. Kreider, *J. Amer Chem. Soc.*, **88**, 4027 (1966).

[14] This is 1,2,3-tribenzoylpropene (and tautomers). For details see: Y. Yamamoto and H. Nozaki, The 23rd Annual Meeting of Chem. Soc. Japan, No. 14305, Tokyo (1970), and Ref. 15.

[15] a) P. Yates, D. G. Farnum, and G. H. Stout, *Chem. & Ind.*. **1956**, 821. b) P. E. Devitt, E. M. Philbin, and T. S. Wheeler, *Ibid.*, **1956**, 822.

[16] J. L. Kice, *Accounts Chem. Res.*, **1**, 58 (1968) and Refs. cited.

2 min. The dark-brown reaction mixture was then stirred at 65°C for 15 hr. The products were isolated and confirmed by chromatography on a silica-gel column and GLC (Apiezon L 30%). 9-Methylanthracene was obtained in a 55% yield as prisms; mp and mixed mp 81°C (EtOH) (lit,[17] 81°C). The recovery of anthracene was 4%.[18] GLC of the mother liquor indicated the presence of 9,10-dimethylanthracene (*ca.* 10%).

An equimolar mixture of 9-deuterioanthracene (I) (D-content 82%, obtained by the treatment of the Grignard reagent of 9-bromoanthracene with D_2O), and phenylsulfonylcarbanion in HMPA was allowed to react at 65°C for 15 hr. The reaction mixture was separated by preparative GLC (Apiezon L 30%). The D-contents of the recovered anthracene and 9-methylanthracene were estimated to be 82% and 45% respectively, on the basis of the molecular peaks in the mass spectra.

Meanwhile, the reaction of anthracene (1.0 g, 5.6 mmol) in HMPA (30 m*l*) with the phenylsulfonylcarbanion obtained from sodium hydride (0.4 g, 17 mmol) and methyl phenyl sulfone (5.25 g, 34 mmol) in HMPA (40 m*l*) yielded 0.59 g of a mixture of 9,10-dimethylanthracene (13%) and 9-ethyl-10-methylanthracene (43%) as yellow needles; mp 145—146°C upon chromatography on a silica-gel column. The yields were calculated by the method described in the footnote.

The Reaction of Phenylsulfonylcarbanion with 9,10-Dimethylanthracene. 9,10-Dimethylanthracene (0.52 g, 2.5 mmol), dissolved in HMPA (30 m*l*), was added to a solution of carbanion prepared from sodium hydride (0.24 g, 10 mmol) and methyl phenyl sulfone (1.56 g, 10 mmol) in HMPA (30 m*l*); the mixture was then allowed to react at 85°C for 24 hr. A subsequent work-up gave 53% of 9-ethyl-10-methylanthracene and 24% of 9,10-diethylanthracene, besides 46% of the recovered 9,10-dimethylanthracene.

The Reaction of Phenylsulfonylcarbanion with Acridine. Acridine (2.0 g, 11 mmol), dissolved in HMPA (10 m*l*), was added to a solution of carbanion prepared from sodium hydride (0.40 g, 17 mmol) and methyl phenyl sulfone (2.6 g, 17 mmol) in HMPA (30 m*l*); the mixture was then allowed to react at 25°C for 4 hr. A subsequent work-up and isolation by chromatography on a silica-gel column gave 9-methylacridine (1.3 g, 60%); mp 118—119°C (lit,[19] 117—118°C) (EtOH).

The heating of a solution of the same components (2 : 2 : 1 ratio) at 80°C for 4 hr gave 9-methylacridine (33%) and 9-methylacridane (4%); mp 123—125°C (lit,[19] 124—125.5°C). IR (Nujol): 3400 cm^{-1} (NH). NMR (CCl_4): δ 1.34 (d, 3H, Me), 4.02 (q, 1H, -CH-), 5.83 (s (broad), 1H, NH) and 6.43—7.25 (m, 8H, aromatic protons).

9-(α-Phenylsulfonylethyl)acridane (IV). Acridine (2.0 g, 11 mmol), dissolved in HMPA (10 m*l*), was treated with a solution of carbanion obtained from ethyl phenyl sulfone (3.0 g, 18 mmol) and sodium hydride (0.41 g, 17 mmol) in HMPA (40 m*l*) under N_2 at 50°C for 4 hr. A subsequent work-up gave IV (2.11 g, 54%). The analytical sample crystallized from benzene as colorless prisms; mp 209—212°C (dec.). IR (Nujol): 3300 cm^{-1} (NH), 1300, 1140 cm^{-1} (SO_2). NMR (CD_3SOCD_3 at 72°C using hexamethyldisilane as an internal standard): δ 0.82 (d, 3H, Me, J=8 Hz), 3.16 (d of q, 1H, -C*H*(Me)SO_2-, J=2 and 8 Hz), 4.94 (d, 1H, -C*H*-CH(Me)SO_2-, J=2 Hz), 6.7—8.0 (m, 13H, aromatic protons) and 8.60 (s (broad), 1H, NH).

Found: C, 72.1; H, 5.2%. Calcd for $C_{21}H_{19}NO_2S$: C, 72.2; H, 5.5%.

The Reaction of Phenylsulfonylcarbanion with 1,1-Diphenylethylene (VIII). A solution of phenylsulfonylcarbanion was prepared under N_2 with sodium hydride (0.36 g, 15 mmol) and methyl phenyl sulfone (2.3 g, 15 mmol) in HMPA (40 m*l*). A solution of VIII (1.6 g, 9 mmol) in HMPA (10 m*l*) was stirred into this carbanion solution at room temperature over a period of 5 min. After subsequent stirring at 85°C for 20 hr, the mixture was separated from the recovered sulfone by chromatography on an alumina column and was distilled at 70—90°C/2.5 mmHg. The distillate was isolated by GLC (Apiezon L 30%) and was identified as being composed of diphenylmethane (XIII) and 1,1-diphenylcyclopropane (XIV). The yields were 34% and 1% respectively. A work-up of the mother liquor gave 1.01 g (60%) of 1,1-diphenyl-2-(β,β-diphenylethyl)cyclopropane (XII) as white prisms; mp 109—110°C. IR (Nujol): 1030 cm^{-1} (cyclopropane). NMR ($CDCl_3$): δ 1.00—2.35 (m, 5H, cyclopropane hydrogens and those of ring-attached methylene), 3.95 (t, 1H, Ph_2C*H*-) and 6.99, 7.06, 7.12 and 7.28 (four s, total 20 H, aromatic protons). Mass *m/e* (rel intensity): 374 (7), 296 (trace), 270 (7), 207 (17), 194 (33), 180 (26), 167 (15) and 91 (100).

Found: C, 92.9; H, 6.9%. Calcd for $C_{29}H_{26}$: C, 93.0; H, 7.0%.

The Reaction of Phenylsulfonylcarbanion with Tolan (XV). A solution of XV (0.90 g, 5 mmol) in HMPA (20 m*l*) was stirred into a carbanion solution prepared from sodium hydride (0.35 g, 15 mmol) and methyl phenyl sulfone (1.95 g, 13 mmol) in HMPA (30 m*l*). After stirring at 95°C for 18 hr, the reaction mixture was treated as above. 1,1,2-Triphenylpropene (XVI) (0.28 g, 21%) was thus obtained as white crystals; mp 85—86°C (lit,[20] 86—89°C). NMR ($CDCl_3$): δ 2.12 (s, 3H, Me), 6.95, 7.12, 7.28 (three s, 15H, aromatic protons). Mass *m/e*: 275 (M^+).

Found: C, 93.0; H, 6.7%. Calcd for $C_{21}H_{18}$: C, 93.3; H, 6.7%.

The Reaction of Phenylsulfonylcarbanion with Benzophenone (XVII). The treatment of benzophenone (1.82 g, 10 mmol) with a solution of carbanion prepared from sodium hydride (0.36 g, 15 mmol) and methyl phenyl sulfone (2.34 g, 15 mmol) in HMPA (20 m*l*) at 60°C for 20 hr gave a mixture of 3,3-diphenyl-3-hydroxypropyl phenyl sulfone (XIX) and 3,3-diphenyl-2-propenyl phenyl sulfone (XX). XIX (0.73 g, 21%), mp 200—201°C, was isolated as a product which did not resolve in benzene. IR (Nujol): 3500 cm^{-1} (OH), 1300, 1150 cm^{-1} (SO_2).

Found: C, 71.9; H, 5.8%. Calcd for $C_{21}H_{20}O_3S$: C, 71.6; H, 5.7%.

XX (0.73 g, 22%), isolated from the mother liquor by chromatography on a silica-gel column (benzene), showed a mp of 109—110°C. IR (Nujol): 1300, 1140 cm^{-1} (SO_2). NMR ($CDCl_3$): δ 3.90 (d, 2H, -CH_2-), 6.14 (t, 1H, =CH-) and 6.53—7.80 (m, 15H, aromatic protons).

Found: C, 75.3; H, 5.6%. Calcd for $C_{21}H_{18}O_2S$: C, 75.5; H, 5.4%.

The Reaction of Phenylsulfonylcarbanion with 2,2-Diphenyloxirane (XVIII). The treatment of XVIII (2.76 g, 15 mmol) with a solution of carbanion prepared from sodium hydride (0.72 g, 30 mmol) and methyl phenyl sulfone (4.64 g, 30 mmol) in HMPA (20 m*l*) at 60°C for 20 hr gave XIX (2.32 g, 44%).

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[17] A. Sieglitz and R. Marx, *Ber.*, **56**, 1619 (1923).

[18] All the yields are based on the starting materials consumed unless otherwise stated.

[19] O. Blum, *ibid.*, **62**, 881 (1929).

[20] J. Bornstein and F. Nunes, *J. Org. Chem.*, **30**, 3324 (1965).

The Reaction of Phenylsulfonylcarbanion with Benzil (XXI). To a solution of carbanion prepared from sodium hydride (0.72 g, 30 mmol) and methyl phenyl sulfone (4.7 g, 30 mmol) in HMPA (30 m*l*), we added XXI (3.15 g, 15 mmol) in HMPA (10 m*l*) at room temperature; the mixture was then allowed to react at 85°C for 20 hr. The reaction mixture was treated with water and extracted with benzene. A subsequent work-up of the benzene solution gave the Kostanecki compound (XXV) (11%) and desoxybenzoin (XXIV) (17%) upon chromatography on a silica-gel column. The water solution was neutralized with acetic acid and extracted with benzene. Phenacyl phenyl sulfone (XXII) (22%) and benzoic acid (XXIII) (26%) was obtained upon chromatography on a silica-gel column. Sulfone XXII showed a mp of 92—93.5°C (lit,[21] 93—94°C). IR (Nujol): 1670 cm^{-1} (CO), 1300, 1150 cm^{-1} (SO_2). NMR ($CDCl_3$): δ 4.30 (s, 2H, $-CH_2-$) and 7.20—8.15 (m, 10 H, aromatic protons). The Kostanecki compound, XXV, showed a mp of 122—123°C (lit,[15] 120°C) and was identical with the authentic sample.

The Reaction of Phenylsulfonylcarbanion with 2-Aminobenzophenone (XXVI). The reaction of carbanion, prepared from sodium hydride (0.96 g, 40 mmol), and the sulfone (6.2 g, 40 mmol) in HMPA (30 m*l*) with XXVI (2.23 g, 11 mmol) in HMPA (10 m*l*) was carried out at 110°C for 48 hr. Chromatography on a silica-gel column (hexane) gave 3-phenylindole (XXVII) (1.25 g, 59%); mp 88—89°C (lit,[22] 88—89°C).

Found: C, 87.0; H, 5.7; N, 7.1%. Calcd for $C_{14}H_{11}N$: C, 87.0; H, 5.7; N, 7.3%.

The Reaction of Phenylsulfonylcarbanion with Salicylaldehyde (XXVIII). The reaction of carbanion, prepared from sodium hydride (0.72 g, 30 mmol), and the sulfone (4.68 g, 30 mmol) in HMPA (25 m*l*) with salicylaldehyde (2.64 g, 22 mmol) in HMPA (10 m*l*) gave *o*-hydroxystyryl phenyl sulfone (XXIX) (4.17 g, 73%); mp 171—172°C. IR (Nujol): 3350 cm^{-1} (OH), 1280, 1130 cm^{-1} (SO_2) and 965 cm^{-1} (–CH=CH–). NMR (CD_3SOCD_3 using sodium 3-(trimethylsilyl)propylsulfonate as the internal standard): 6.70—8.31 (m, 11H, aromatic and olefinic protons) and 10.65 (s (broad), 1H, OH).

Found: C, 64.6; H, 4.7%. Calcd for $C_{14}H_{12}O_3S$: C, 64.6; H, 4.7%.

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[21] E. H. Holst and W. C. Fernelius, *ibid.*, **23**, 1881 (1958).

[22] E. Fischer and T. Schmidt, *Ber.*, **21**, 1811 (1888).