The diluted solution of the diazonium salt was mixed with 700 ml. of C.P. acetone, 45 ml. of C.P. benzene, and 100 ml. of 0.50*M* cupric chloride solution. A total of 99% of the theoretical volume of nitrogen was evolved in 10 min. The procedure described above was followed with minor variations to give 5.53 g. (37%) of 1,3-dichlorobenzene, 2.63 g. (14%) of 1,2,4-trichlorobenzene, and 4.26 g. (19%) of 2,4-dichlorobiphenyl.

(*c*) *Using sodium acetate.* The quantities of reagents and procedure were identical with (b) except for the addition of an amount (12.8 g.) of anhydrous sodium acetate equivalent to the excess hydrochloric acid. A two phase reaction mixture resulted which evolved the theoretical volume of nitrogen in 17 min., yield 5.35 g. (36%) of 1,3-dichlorobenzene, 2.63 g. (14%) of 1,2,4-trichlorobenzene, and 4.74 g. (21%) of 2,4-dichlorobiphenyl.

(*d*) *By Gomberg-Bachmann reaction.* 2,4-Dichloroaniline hydrochloride (20.0 g.) was diazotized in the usual manner in a total volume of 146 ml. Excess nitrous acid was destroyed with urea and 400 ml. of C.P. benzene was added The mixture was cooled to 10°, vigorous agitation was begun, and 50 ml. of 5*N* sodium hydroxide was added over a period of 45 min. The isolation procedure previously described was followed and yielded 12.3 g. (55%) of 2,4-dichlorobiphenyl, b.p. 95–102° at 0.10–0.15 mm. A 1.49 g. sample of the biphenyl was purified by chromatography, yield 1.47 g. of colorless oil, b.p. 94–97° at 0.06–0.08 mm.

Anal. Calcd. for $C_{12}H_8Cl_2$: C, 64.6; H, 3.61; Cl, 31.8. Found: C, 64.7; H, 3.51; Cl, 31.9.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

Competitive Metalation of Diphenyl Sulfone and 4,4′-Dimethyldiphenyl Sulfone by *n*-Butyllithium

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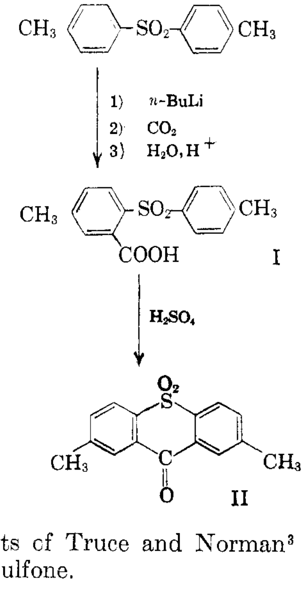
Competition between diphenyl sulfone and 4,4′-dimethyldiphenyl sulfone for an insufficient amount of *n*-butyllithium resulted in 47% metalation of diphenyl sulfone and 53% metalation of the dimethyldiphenyl sulfone. This unexpected preferential metalation of the rings supposedly deactivated by methyl groups may be due to the rapid and reversible formation of a larger concentration of the sulfone-*n*-butyllithium complex of the more basic dimethyldiphenyl sulfone. Determination of van't Hoff *i* factors in sulfuric acid for the two sulfones indicated the dimethyldiphenyl sulfone to be the more basic.

We have been studying the effect of simple alkyl substituents on the metalation of aromatic rings by *n*-butyllithium. An earlier paper[2] from this laboratory on the metalation of 4-*tert*-butyldiphenyl sulfone showed that the *tert*-butyl group caused deactivation of the ring to which it is attached, since metalation occurred predominantly in the unsubstituted ring. This result was in accord with some earlier observations by Truce[3] and Bryce-Smith[4] and the "protophilic" nature[4] of the metalation reaction. Thus, 4-methyldiphenyl sulfone was metalated[3] with *n*-butyllithium and 59% of the metalation was reported to occur in the unsubstituted phenyl ring and 41% in the ring containing the methyl group. Our work[2] with 4-*tert*-butyldiphenyl sulfone indicated an expected greater deactivating effect by the *tert*-butyl group as compared with a methyl group. These experiments were based on the intramolecular competititon of the two reactive positions adjacent to the sulfone group for the *n*-butyllithium. Intermolecular competitive metalation experiments have been used[4,5] by several workers to show relative activating and deactivating effects of functional groups toward the metalation reaction. We decided to study the intermolecular competitive metalation of diphenyl sulfone and 4,4′-dimethyldiphenyl sulfone to see how the results compared with the intramolecular competititon experiments cf Truce and Norman[3] on 4-methyldiphenyl sulfone.



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[1] Present address: The Koppers Co., Monaca, Pa.

[2] D. A. Shirley and E. A. Lehto, *J. Am. Chem. Soc.*, **79**, 3481 (1957).

[3] W. E. Truce and O. L. Norman, *J. Am. Chem. Soc.*, **75**, 6023 (1953).

[4] D. Bryce-Smith, *J. Chem. Soc.*, 1079 (1954).

[5] (a) H. Gilman and C. G. Stuckwisch, *J. Am. Chem. Soc.*, **67**, 877 (1945). (b) H. Gilman, M. Van Ess, H. B. Willis, and C. G. Stuckwisch, *J. Am. Chem. Soc.*, **62**, 2606 (1940). (c) H. Gilman and F. Breuer, *J. Am. Chem. Soc.*, **56**, 1123 (1934).

We first carried out the metalation of 4,4′-dimethyldiphenyl sulfone itself with an equimolar amount of butyllithium, and after carbonation isolated the expected 2-carboxy-4,4′-dimethyldiphenyl sulfone (I) in 53% yield. The structure of I was indicated by its ready conversion to the corresponding thioxanthone-10-dioxide (II) with concentrated sulfuric acid.

The competitive metalation of an equimolar mixture of diphenyl sulfone and 4,4′-dimethyldiphenyl sulfone was carried out with one-half the *n*-butyllithium needed for complete monometalation. The reaction mixture was carbonated and the mixed monocarboxylic acids isolated in such manner that the isomer ratio was not disturbed. A neutralization equivalent on the mixed metalation acids indicated the composition to be 55 mole per cent 2-carboxy-4,4′-dimethyldiphenyl sulfone and 45 mole per cent of 2-carboxydiphenyl sulfone. We also constructed a melting point-composition diagram (data in Table I) from pure samples of the acids, and determined the composition of the mixture from these data. This indicated the composition to be 53 mole per cent of 2-carboxy-4,4′-dimethyldiphenyl sulfone.

TABLE I

FINAL MELTING TEMPERATURES OF MIXTURES OF 2-CARBOXYDIPHENYL SULFONE (A) AND 2-CARBOXY-4,4′-DIMETHYLDIPHENYL SULFONE (B)

Composition, Wt. Per Cent (A–B)	Final Melting Point, °C.
100–0	144
89–11	138
80–20	[a]
70–30	152
60–40	162
50–50	174
40–60	183
33–67	189
20–80	196
10–90	201
0–100	206
A and unknown mixture	167
B and unknown mixture	192
Unknown mixture (Run 1)	178
Unknown mixture (Run 2)	180
Unknown mixture (Average)	179

[a] This sample did not fully crystallize at room temperature in a vacuum desiccator.

The larger amount of metalation in the methyl substituted sulfone was surprising; such a result is not in accord with the results of the intramolecular competition experiment of Truce and Norman,[3] with another indication of the deactivating effect of the methyl group,[6] and with the probable mechanism of the metalation reaction.[4] Since our competitive metalation reaction occurred in the presence of the undissolved mixed sulfones, it was considered that the results might be influenced by a greater ether-solubility of the dimethyldiphenyl sulfone than the diphenyl sulfone, thus giving a higher effective concentration of the former compound. This was found not to be the case, since the diphenyl sulfone is actually more soluble in ether at 0° and at 25° than is the dimethyl substituted compound.

Another explanation seemed more plausible. The metalation of a diaryl sulfone probably involves first the formation of a coordination complex between an *n*-butyllithium molecule and an oxygen atom of the sulfone group. Such a complex should be formed rapidly and reversibly and the more basic of two competing sulfones would be present in larger concentration as its complex with the organometallic. The subsequent step of rearrangement of the complex to the metalated product[7] is probably rate determining and irreversible. Thus a steady state of higher concentration of the complex of the more basic sulfone could lead to more metalation of this sulfone, even though the decomposition of the complex into the reaction products occurred at a somewhat slower rate in comparison with the less basic sulfone.

The question remains as to which of the two sulfones used is the more basic. The inductive and hyperconjugative electron release effects of the methyl group should render the dimethyldiphenyl sulfone more basic than the diphenyl sulfone, and this fits the interpretation of the experimental results given above. However, some work of Szmant and coworkers[8] on the determination of van't Hoff *i* factors of substituted aryl sulfones in sulfuric acid indicated that electron releasing groups rendered the sulfone less basic (lower *i* factor) while electron attracting groups had the reverse effect (higher *i* factor). We determined the *i* factors of diphenyl sulfone and 4,4′-dimethyldiphenyl sulfone and observed values of 1.19 and 1.81, respectively. Szmant and Brost[8a] report a value of 1.3 for diphenyl sulfone. These *i* factors are in line with our view of the experimental results presented above. After completion of this work, the studies of Gillespie[9] came to our attention in which is reported[9b] a redetermination of the *i* factor of 4-nitro- and 4,4′-dinitrodiphenyl sulfone and values of 1.35 and 1.28, respectively, for these two compounds. Szmant's values for these same compounds were 1.5 and 2.0. The decrease in *i* factor in going from the 4-nitro to the 4,4′-dinitro compound is indicated by Gillespie to be in line with the expected effect of the nitro group in decreasing the basicity of the sulfone

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(6) S. Gronowitz, *Arkiv Kemi*, **7**, 361 (1954).

(7) J. D. Roberts and D. Y. Curtin, *J. Am. Chem. Soc.*, **68**, 1658 (1946).

(8) (a) H. H. Szmant and G. A. Brost, *J. Am. Chem. Soc.*, **73**, 4175 (1951). (b) H. H. Szmant and R. L. Lapinski, *J. Am. Chem. Soc.*, **74**, 4395 (1952).

(9) (a) R. J. Gillespie, *J. Chem. Soc.*, 2542 (1950). (b) R. J. Gillespie and R. C. Passerini, *J. Chem. Soc.*, 3850 (1956).

group. Gillespie[9] has reported a value of 1.20 for diphenyl sulfone. Protonation of the nitro groups by the sulfuric acid makes difficult a direct comparison of diphenyl sulfone and the nitro derivatives, but Gillespie feels that the conclusion of Szmant that a nitro group increases the basicity of the sulfone is incorrect. The increase in the *i* factor from 1.19 to 1.81 when two methyl groups are introduced into the *para* positions of diphenyl sulfone indicates that the basicity of the sulfone group toward sulfuric acid is increased by such substitution. However, we also determined the *i* factor for 4-methyldiphenyl sulfone and found it to be 1.20. This indicates little, if any, increase in basicity by substitution of only one methyl group. The corresponding *i* factor for 4-*tert*-butyldiphenyl sulfone is 1.26, indicating a slight increase in basicity.

EXPERIMENTAL[10]

Metalation of 4,4′-dimethyldiphenyl sulfone. 4,4′-Dimethyldiphenyl sulfone, m.p. 159–160°, was prepared in 49% yield from *p*-toluenesulfonyl chloride and toluene by the general method of Buehler and Masters.[11] The reported melting point for this compound is 158°.[12]

To a well-stirred suspension of 24.6 g. (0.10 mole) of 4,4′-dimethyldiphenyl sulfone in 200 ml. of dry ether was added slowly at ice-bath temperature an equimolar amount of an ethereal solution of *n*-butyllithium. A nitrogen atmosphere was used. The mixture was stirred for 2 hr. at ice-bath temperature and then for 1 hr. after removal of the ice-bath. The mixture was carbonated by pouring over a slurry of ether and crushed solid carbon dioxide. After removal of the ether and carbon dioxide, water was added and the insoluble material was separated by filtration. The residue weighed 6.7 g. and melted at 155–157°. After recrystallization from benzene it melted at 156–157°. A mixture melting point with a sample of 4,4′-dimethyldiphenyl sulfone, m.p. 159–160°, was 157–158°. The aqueous filtrate from the above filtration was acidified with 1:1 hydrochloric acid and the resulting solid precipitate was collected by filtration. It weighed 21.8 g. and melted at 208–211°. This material was dissolved in aqueous sodium carbonate, filtered, and the filtrate was acidified with dilute hydrochloric acid. The precipitated solid was collected by filtration and recrystallized from 95% ethanol. The yield of crystalline solid melting at 205–206° was 15.3 g. (53%).

Anal. Calcd. for $C_{15}H_{14}O_4S$: C, 62.07; H, 4.83; neut. equiv., 290. Found: C, 61.87; H, 5.06; neut. equiv., 291.

Methyl ester of 2-carboxy-4,4′-dimethyldiphenyl sulfone. A mixture of 5.0 g. (0.017 mole) of 2-carboxy-4,4′-dimethyldiphenyl sulfone and 100 ml. of dry ether was treated with an excess of an ethereal solution of diazomethane. After removal of the ether and excess diazomethane, the residue was recrystallized from aqueous ethanol. There was obtained 4.3 g. (83%) melting at 95–96°. Recrystallization of a small amount of this material from aqueous methanol did not raise the melting point.

Anal. Calcd. for $C_{16}H_{16}O_4S$: C, 63.16; H, 5.26. Found: C, 63.06; H, 5.35.

Hydrazide of 2-carboxy-4,4′-dimethyldiphenyl sulfone. Two grams (0.007 mole) of the methyl ester was heated to reflux with 4 ml. of 99–100 per cent hydrazine hydrate for 15 min. and then just enough absolute ethanol was added to cause complete solution. The solution was heated to reflux for 2 hr. on the steam bath, after which the ethanol was removed by evaporation and the residue was recrystallized from very dilute aqueous ethanol. The resulting material weighed 1.5 g. (75%) and melted at 153–154°.

Anal. Calcd. for $C_{15}H_{16}N_2O_3S$: N, 9.21. Found: N, 9.19.

2,7-Dimethylthioxanthone-10-dioxide. II. One gram (0.003 mole) of 2-carboxy-4,4′-dimethyldiphenyl sulfone was heated at 185–195° with 20 ml. of concentrated sulfuric acid for 15 min. according to the procedure described by Ullmann and Lehner.[13] The solution was cooled and poured into an excess of cold water. Recrystallization of the resulting precipitated solid from a mixture of methanol and 95% ethanol gave 0.5 g. (61%) of a solid melting at 237–238°.

Anal. Calcd. for $C_{15}H_{12}O_3S$: C, 66.18; H, 4.41. Found: C, 66.19; H, 4.54.

Metalation of diphenyl sulfone. The procedure followed was due to Truce and Amos[14] for metalation of the same compound. A 42% yield of 2-carboxydiphenyl sulfone, m.p. 143–144° was obtained. Truce and Amos[14] report a 61% yield of acid melting at the same temperature.

Competitive metalation between diphenyl sulfone and 4,4′-dimethyldiphenyl sulfone. (*a*) *Run 1.* To a well-stirred suspension of 21.8 g. (0.10 mole) of diphenyl sulfone and 24.6 g. (0.10 mole) of 4,4′-dimethyldiphenyl sulfone in 300 ml. of dry ether under an atmosphere of nitrogen was added slowly at ice-bath temperature 0.10 mole of an ethereal solution of *n*-butyllithium. After the addition of *n*-butyllithium was complete, the reaction mixture was stirred for 2 hr. at ice-bath temperature and for 1 hr. after removal of the ice-bath. Carbonation of the reaction mixture was accomplished by pouring over a slurry of ether and crushed solid carbon dioxide. After the removal of the ether and carbon dioxide, water was added, and the resulting mixture was filtered. The insoluble residue weighed 35.1 g. and melted at 97–109°. The aqueous filtrate on acidification with 1:1 hydrochloric acid gave an oily precipitate which slowly crystallized on standing. The crystalline solid which was collected by suction filtration melted at 120–176°. It was dissolved in aqueous sodium carbonate solution, filtered, and the aqueous filtrate acidified with dilute hydrochloric acid. The precipitated crystalline material collected by filtration weighed 11.9 g. and melted at 115–178°. The neutralization equivalent of this material was found to be 278, which corresponds to a weight per cent composition of 57% of 2-carboxy-4,4′-dimethyldiphenyl sulfone and 43% of 2-carboxydiphenyl sulfone, or a mole per cent composition of 55 and 45%, respectively.

(*b*) *Run 2.* The procedure was similar to that of Run 1, except that 10.9 g. (0.05 mole) of diphenyl sulfone and 12.3 g. (0.05 mole) of 4,4′-dimethyldiphenyl sulfone in 200 ml. of dry ether were allowed to react with approximately 0.05 mole of an ethereal solution of *n*-butyllithium. The nonacidic material recovered from the reaction mixture weighed 12.1 g., while the acidic material, isolated as in Run 1, weighed 8.7 g. and melted over the range 127–180°, neutralization equivalent 278 ± 1. A mixture melting point with the acidic mixture obtained from Run 1 had a final melting point of 179°.

Mixture melting points of 2-carboxydiphenyl sulfone and 2-carboxy-4,4′-dimethyldiphenyl sulfone. Samples of these two acids were weighed together to give mixtures of varying composition. These were dissolved in acetone and the resulting solutions evaporated slowly to dryness. Melting points of these mixtures were determined by means of a Köfler micro hot stage melting point apparatus, and the final melting points (representing complete melt) were plotted *versus* composition (weight per cent). The unknown mixture (taking an average of the final melting points of the mixtures obtained from both Run 1 and Run 2) corresponded

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[10] Microanalyses by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

[11] C. A. Buehler and J. E. Masters, *J. Org. Chem.*, **4**, 262 (1939).

[12] H. Beckurts and R. Otto, *Ber.*, **11**, 2066 (1878).

[13] F. Ullmann and A. Lehner, *Ber.*, **38**, 729 (1905).

[14] W. E. Truce and M. F. Amos, *J. Am. Chem. Soc.*, **73**, 3013 (1951).

to a 55–45, weight per cent composition (53–47 mole per cent) of 2-carboxy-4,4′-dimethyldiphenyl sulfone and 2-carboxydiphenyl sulfone, respectively, according to the plotted data of Table I. Furthermore, a mixture melting point of 2-carboxy-4,4′-dimethyldiphenyl sulfone with the unknown mixture raised the melting point, while a mixture melting point of 2-carboxydiphenyl sulfone with the unknown mixture lowered the melting point, which information supports the composition designated from the plot. The above procedure was used by Truce and Norman[8] to determine the percentage composition of a mixture of isomeric carboxylic acids resulting from the metalation of 4-methyldiphenyl sulfone with *n*-butyllithium, followed by carbonation.

Determination of i factors. The diphenyl sulfone used was Eastman White Label sample recrystallized from benzene. The 4-*tert*-butyldiphenyl sulfone was prepared as described previously.[2] The 4-methyldiphenyl sulfone was prepared from *p*-toluenesulfonyl chloride and benzene in the presence of aluminum chloride. The product melted at 124–125° (reported[11] 125–125.5°). The apparatus, technique, and solvent for the cryoscopic measurements have been described previously.[15] The solvent was prepared with care so that the freezing point of the 100% sulfuric acid was on the linear portion on the water side of the freezing point-composition curve as shown by Gillespie.[16] The apparatus was allowed to stand several hours for the sulfuric acid to absorb the moisture from the air in the cell before the initial freezing point of the acid was determined. The supercooling of the solutions was controlled to ±0.1°. The solutions in the cryostat were held below 18° throughout the period in which freezing point measurements were being made.[17] For diphenyl sulfone, three independent runs gave *i* factors of 1.19, 1.20, and 1.17, calculated from freezing points taken 15 to 20 min. after addition of the sulfone to the cryostat. Single runs gave corresponding values of 1.20 for 4-methyldiphenyl sulfone, 1.26 for 4-*tert*-butyldiphenyl sulfone, and 1.81 for 4,4′-dimethyldiphenyl sulfone.

Determination of solubilities. Samples of diphenyl sulfone and 4,4′-dimethyldiphenyl sulfone were placed in dry ether which was then refluxed for a short time. The solutions were decanted into glass-stoppered Erlenmeyer flasks which were placed in a thermostat at 25 ± 0.02° and allowed to reach temperature equilibrium. The sulfones, in excess of the amount required to saturate the ether, precipitated during this period. Samples of the clear supernatant liquid were withdrawn into a gravimetric pipet, and 10 ml. of the saturated solutions delivered into a weighing bottle. The solvent was evaporated, and the weights of the sulfones determined gravimetrically. The Erlenmeyer flasks containing the solutions were then placed in an ice bath and allowed to stand until equilibrium conditions were reached. Samples of the saturated solutions were withdrawn and their sulfone content determined as before. The results of duplicate determinations expressed in moles per liter of solution are as follows:

Diphenyl sulfone	25°	.0830, .0829
	0°	.0400, .0396
4,4′-Dimethyldiphenyl sulfone	25°	.0436, .0443
	0°	.0207, .0208

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[15] C. M. Welch and H. A. Smith, *J. Am. Chem. Soc.*, **72**, 4748 (1950).

[16] R. J. Gillespie, *J. Chem. Soc.*, 2496 (1950).

[17] H. A. Smith and R. G. Thompson, *J. Am. Chem. Soc.*, **77**, 1778 (1955).

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF MARYLAND AND WAYNE STATE UNIVERSITY]

Pyrolysis of Esters. XI. A New Synthesis of α-Alkylacrylonitriles[1,2]

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The selectivity in the direction of elimination during the pyrolysis of tertiary esters has been used to prepare a series of α-alkylacrylonitriles. Thus α-ethyl-, α-*n*-propyl-, α-isobutyl-, and α-*n*-hexylacrylonitriles were prepared in 73 to 94% yields by the pyrolysis of the acetates derived from the corresponding methyl ketone cyanohydrins. Each of these monomers was polymerized by peroxide to a moderately high molecular weight polymer, with the poly-α-ethylacrylonitrile softening at 110–140°. One must conclude that previous preparations of these monomers were not free from inhibitors. These present results are additional evidence for the high degree of selectivity during the pyrolysis of esters.

Previous work in these laboratories has shown that the pyrolysis of esters proceeds in a highly selective manner to produce almost exclusively the least highly alkylated olefin according to the Hofmann rule.[6,7] For example, the pyrolysis of methylisopropylcarbinyl acetate gave almost exclusively 3-methyl-1-butene with little or no formation of the other possible isomer, 2-methyl-2-butene. It was shown that the presence of an unsaturated electron-withdrawing group in the β-position to the acyloxy group resulted in the formation of primarily the

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[1] Previous paper in this series, *J. Org. Chem.*, **21**, 858 (1956).

[2] (a) Presented in part before the Division of Polymer Chemistry at the 128th National Meeting of the AMERICAN CHEMICAL SOCIETY, Minneapolis, Minn., September 1955; (b) Abstracted in part from a dissertation submitted by John J. Hewitt to the Graduate Council of Wayne State University, December 1952, and from a thesis submitted by Floyd E. Naylor to the faculty of the Graduate School of the University of Maryland, December 1955, in partial fulfillment of the requirements of the degrees of Doctor of Philosophy.

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[5] Research Corporation Fellow, Wayne State University, 1951–1952.

[6] W. J. Bailey and C. King, *J. Am. Chem. Soc.*, **77**, 75 (1955).

[7] W. J. Bailey, C. King, and J. J. Hewitt, *J. Am. Chem. Soc.*, **77**, 357 (1955).