TABLE I

Alkylation of Phenol with Isobutylene[a]

Catalyst	Resin,[b] %	Di-*tert*-Butylphenol, % conv.[c]	*o*-*tert*-Butylphenol, % conv.[c]	*p*-*tert*-Butylphenol, % conv.[c]	*p*-*tert*-Butylphenol, % yield[c]
Amberlite IR-112	6 1/4	0	0	37	98
Permutite Q	6 1/4	0	4	51	83
Amberlite IR-120	6 1/4	0	0	57	87
Dowex 50 × 12	6 1/4	0	0	49	77

[a] Reactions carried out as described in Experimental. [b] Wt. % based on total charge. [c] See ref. 8.

TABLE II

Alkylation of Phenol with Diisobutylene in the Presence of Amberlite IR-112

Temp., °C.	Time, Hrs.	Resin,[a] %	*tert*-Butylphenol, % Conv.[b]	*tert*-Octylphenol, % Conv.[b]	*tert*-Octylphenol, % Conv.[b]	
83	3	14	Trace	Trace	Trace	[c]
80	2 3/4	14	10	38	63	[d]
70–5	4 1/4	1.4	6	49	100	[d,e]
70–5	8	0.4	4	53	97	[d,e]
70–5	24	3	4	73	95	[d,e]
70–5	24	7	3	88	100	[d,e]
100–5	4 1/4	1.4	11	65	91	[d,e]
100–10	18	2	14	61	77	[d,e]

[a] Wt. % based on total charge. [b] See ref. 7. [c] Air dried resin used. [d] Heat dried resin. [e] DIB dried.

The resin was then filtered off. The pale yellow filtrate had a set point of 57–60°. On distillation, the following fractions were obtained. b.p. 78–110° (20 mm.), phenol, 63 g.; b.p. 140–153° (20 mm.), *p*-*tert*-octylphenol, 390 g. (73% conversion, 95% yield), colorless liquid which soon crystallized, m.p. 82–83° (lit.[9] b.p.$_{20}$ 163°, m.p. 84°).

p-tert-Butylphenol. In a typical preparation 94 g. (1.0 mole) of phenol and 10 g. of Amberlite IR-120, prepared as described above, were heated at 80° with vigorous stirring as 58.7 g. (0.92 moles) of isobutylene (Atlantic Refining Co.) was passed in beneath the surface of the liquid over a period of 3 hr. The isobutylene was completely absorbed. After the isobutylene had all been added, the temperature was raised to 120° for 4 hr. The resin was filtered off and the colorless filtrate was distilled giving the following fractions: b.p. 175–205°, phenol, 33.5 g.; b.p. 220–228°, *o*- and *p*-*tert*-butylphenol, 1.5 g.; b.p. 230–234°, *p*-*tert*-butylphenol, 73.8 g. (57.5% conversion, 88% yield), m.p. 92° (lit.[9] b.p. 237°, m.p. 100°).

Nonylphenol. Phenol (47 g., 0.5 mole), 63 g. (0.5 mole) of nonene-1 and 5 g. of prepared Amberlite IR-112 resin were heated at 100–10° for 24 hr. with vigorous stirring. The resin was removed by filtration and the filtrate distilled giving the following fractions: b.p. 130–160°, nonene-1, 7 g.; b.p. 182–183°, phenol, 10.6 g.; b.p. 297–305°, nonylphenyl, 75.2 g., n_D^{28} 1.5060 (68% conversion, 92% yield).

Attempted alkylation of xylene. The reaction was carried out as described under the preparation of *p*-*tert*-butylphenol, except that the isobutylene was fed in more slowly. No absorption of isobutylene occurred, and the xylene was quantitatively recovered.

Attempted alkylation of benzene. Benzene (80 g.), 84 g. of propylene tetramer and 5 g. of Amberlite IR-112 were heated at reflux, with stirring for 25 hr. No reaction had occurred for the propylene tetramer was quantitatively recovered on distillation.

Pennsalt Chemical Corporation
Philadelphia, Pa.

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[9] W. A. Pardee and W. Weinrich, *Ind. Eng. Chem.*, **36**, 595 (1944).

Metalation of Phenyl Benzyl Sulfide and Sulfone with *n*-Butyllithium

Erwin A. Lehto[1] and David A. Shirley

Received January 30, 1957

The large activating effect of a sulfone group toward metalation at an adjacent C—H bond is well known. Thus Truce and co-workers[2] have demonstrated that diaryl sulfones are metalated readily with *n*-butyllithium at the positions *ortho* to the sulfone group. Gilman and Webb[3] observed the metalation of methyl phenyl sulfone with *n*-butyllithium on the methyl group, and Grignard reagents have been shown to metalate the same position.[4,5]

It was of interest to us to observe the position of metalation of phenyl benzyl sulfone since this molecule contains two different kinds of activated C—H bonds adjacent to the sulfonyl groups. The action of a *n*-butyllithium on an equimolar amount of benzyl phenyl sulfone followed by carbonation and hydrolysis allowed formation of 65% of α-phenylsulfonylphenylacetic acid (I) indicating metalation at the —CH$_2$— group. The structure of the acid from metalation is indicated by comparison of its decarboxylation temperature of 142–

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

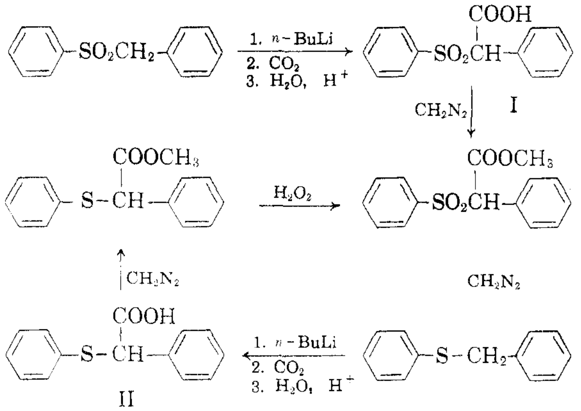
[2] W. E. Truce and M. F. Amos, *J. Am. Chem. Soc.*, **73**, 3013 (1951) and subsequent papers.

[3] H. Gilman and F. J. Webb, *J. Am. Chem. Soc.*, **71**, 4062 (1949).

[4] L. Field, *J. Am. Chem. Soc.*, **74**, 3919 (1952).

[5] W. M. Ziegler and R. Connor, *J. Am. Chem. Soc.*, 62, 2596 (1940).

143° with the similar value given by Fuchs and Breuer.[6] These latter workers have established the structure of α-phenylsulfonylphenylacetic acid by synthesis. We established that the residue remaining after heating the metalation acid was phenyl benzyl sulfone by the method of mixed melting points. Cohen and Smiles[7] have reported the melting point of the isomeric *o*-benzylsulfonylbenzoic acid as 126–128°. The *m*- and *p*-benzylsulfonylbenzoic acids have apparently never been reported, but it was considered highly unlikely that either of these positions could have been involved in the metalation in view of the very strong tendency of sulfone metalation to occur at the positions adjacent to the sulfone group.



Metalation of phenyl benzyl sulfone with an equivalent amount of methylmagnesium iodide, followed by carbonation, allowed formation of I in 28% yield.

Gilman and Webb[8] have reported the rather unexpected metalation by *n*-butyllithium of methyl phenyl sulfide on the methyl group ("lateral metalation"). We carried out the metalation of phenyl benzyl sulfide with *n*-butyllithium and obtained, subsequent to carbonation and hydrolysis, a 75% yield of α-phenylmercaptophenylacetic acid (II). The melting point of this compound corresponds to that given by Fuchs and Breuer.[6] An attempted oxidation of II to I by hydrogen peroxide in acetic acid caused decarboxylation as well as oxidation and only phenyl benzyl sulfone was isolated. The methyl ester of II, however, was oxidized under the same conditions to the methyl ester of I and comparisons by melting point and mixed melting point were made.

We were unsuccessful in carrying out the metalation of phenyl benzyl sulfide with an equivalent amount of methylmagnesium iodide at 35–40°.

EXPERIMENTAL[9]

Phenyl benzyl sulfone. Phenyl benzyl sulfide was prepared in accordance with the procedure of Shriner, Struck and Jorison[10] and unrecrystallized product, m.p. 39–40°, was used. To a warm solution of crude phenyl benzyl sulfide (from 57 g. or 0.52 mole of thiophenol) in 300 ml. of acetic acid was added slowly with stirring 150 ml. of 30% hydrogen peroxide. External cooling was necessary during the addition, but after the exothermic reaction had subsided, the mixture was heated on the steam bath for 1 hr. A further 75 ml. of 30% hydrogen peroxide was added, and heating on the steam bath continued for another hr. After addition of another 75 ml. of 30% hydrogen peroxide, the reaction mixture was heated to reflux for 1 hr. The resulting solution was added to 300 ml. of cold water. The precipitated colorless crystalline solid was collected by filtration. The weight of product, melting at 148–149°, was 111.3 g., or 92% based on the original amount of thiophenol used. The melting point given by Shriner, Struck, and Jorison[10] for phenyl benzyl sulfone, prepared from sodium benzenesulfinate and benzyl chloride, was 146–146.5°.

Metalation of phenyl benzyl sulfone with n-butyllithium. To the well-stirred suspension of 11.6 g. (0.05 mole) of phenyl benzyl sulfone and 100 ml. of dry ether was added slowly at ice-bath temperature an equimolar amount of an ethereal solution of *n*-butyllithium.[11] A nitrogen atmosphere was used. 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 ether and carbon dioxide had been removed, excess water was added and the resulting mixture was filtered. The residue from filtration was recrystallized from 95% ethanol to give 2.8 g. (24%) of crystalline phenyl benzyl sulfone. The aqueous filtrate was acidified with dilute hydrochloric acid and the colorless crystalline solid which precipitated was collected by filtration. This solid was treated with aqueous sodium carbonate solution, the solution was filtered, the aqueous filtrate was acidified with dilute hydrochloric acid, and the resulting precipitated crystalline solid was collected by filtration. It weighed 9.0 g. (65 per cent) and decomposed at 142–143°. The residue from this decomposition melted at 148–149°. A mixed melting point of this residue with phenyl benzyl sulfone, m.p. 148–149°, was 148–149°. Fuchs and Breuer[6] have reported the same melting point behavior for α-phenylsulfonylphenylacetic acid, whereas Cohen and Smiles[7] have indicated that the melting point of the isomeric *o*-benzylsulfonylbenzoic acid is 126–128°. The *m*- and *p*-benzylsulfonylbenzoic acids have not been reported.

Anal. Calcd. for $C_{14}H_{12}O_4S$: C, 60.15; H, 4.35; neut. equiv., 276. Found: C, 60.26; H, 4.54; neut. equiv., 270.

Metalation of phenyl benzyl sulfone with methylmagnesium iodide. The Grignard reagent was prepared from 2.0 g. of magnesium, 7.1 g. methyl iodide and 50 ml. of ether. A solution of 11.6 g. (0.05 mole) of phenyl benzyl sulfone in 50 ml. of ether was added. The mixture was stirred at room temperature for 1 hr. and then heated under reflux for 1.5 hr. Carbonation and hydrolysis in the usual manner gave crude acidic product which was dissolved in aqueous sodium carbonate solution, filtered and acidified to give 3.9 g. (28%) of crystalline solid decomposing at 142–143°. The residue from the decomposition melted at 148–149°.

Methyl α-phenylsulfonylphenylacetate. A solution of 5.0 g.

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(6) K. Fuchs and F. Breuer, *Monatsh.*, **53,** 438 (1929).

(7) A. Cohen and S. Smiles, *J. Chem. Soc.*, 406 (1930).

(8) H. Gilman and F. J. Webb, *J. Am. Chem. Soc.*, **62,** 987 (1940).

(9) Microanalyses are by Galbraith Microanalytical Laboratories of Knoxville, Tenn.

(10) R. L. Shriner, H. C. Struck, and W. J. Jorison, *J. Am. Chem. Soc.*, **52,** 2060 (1930).

(11) H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn, and L. S. Miller, *J. Am. Chem. Soc.*, **71,** 1499 (1949).

(0.018 mole) of α-phenylsulfonylphenylacetic acid (obtained from the metalation of phenyl benzyl sulfone) in 100 ml. of ether was treated with an excess of an ethereal solution of diazomethane at ice-bath temperature. After the addition of the ethereal solution of diazomethane, the reaction mixture was allowed to stand at room temperature for 1 hr. After the ether and excess diazomethane had been removed by evaporation, the residue was extracted with dilute aqueous sodium carbonate and recrystallized from aqueous methanol. The recrystallized material weighed 4.7 g. (90%) and melted at 109–110°.

Anal. Calcd. for $C_{15}H_{14}O_4S$: C, 62.07; H, 4.83. Found: C, 61.88; H, 5.10.

Metalation of phenyl benzyl sulfide. Ten grams (0.05 mole) of phenyl benzyl sulfide was dissolved in 150 ml. of dry ether and filtered into the reaction flask which had been previously flushed with nitrogen. To this solution was added slowly with stirring an equimolar amount of *n*-butyllithium in ether. The addition caused an immediate color change and reflux of the ether. After the reflux had somewhat subsided, the reaction mixture was heated at reflux temperature for 5 hr. The reaction mixture was then carbonated by pouring over a slurry of ether and crushed solid carbon dioxide. After the removal of the carbon dioxide, water was added and the aqueous layer was separated, filtered, and acidified with dilute hydrochloric acid. This gave 9.2 g. of solid material melting at 100–102°. After treatment of this solid with dilute aqueous sodium carbonate, filtration, and acidification of the aqueous filtrate, there was obtained 8.8 g. (75%) of solid melting at 102–103°, neutralization equivalent 249. The melting point of this compound corresponds to that reported by Fuchs and Breuer[6] for α-phenylmercaptophenylacetic acid, prepared from α-chlorophenylacetic acid and sodium thiophenolate. The ether layer was dried over anhydrous calcium chloride, filtered, and the ether removed. A yellow oil remained, which on cooling solidified. After recrystallization from methanol, the crystalline solid weighed 1.3 g. (13%) and melted at 41–42°. A mixed melting point with a sample of phenyl benzyl sulfide, melting point 42–43°, was 41–42°.

To 1.6 g. (0.007 mole) of α-phenylmercaptophenylacetic acid in 50 ml. of dry ether was added an excess of an ethereal solution of diazomethane. After the ether and excess diazomethane had been removed, the residue was taken up in 60 ml. of glacial acetic acid and treated with 10 ml. of 35% hydrogen peroxide. The reaction mixture was heated on the steam bath for 1 hr. After the addition of a further 10 ml. of hydrogen peroxide, the reaction mixture was heated to reflux for 0.5 hr. and was then poured into an excess of cold water. The precipitated solid was collected by filtration and recrystallized from aqueous methanol. The recrystallized material weighed 1.3 g. (67%) and melted at 109–110°. A mixture melting point with the methyl ester prepared from α-phenylsulfonylphenylacetic acid, m.p. 109–110°, was 109–110°.

α-Phenylmercaptophenylacetamide. One gram (0.004 mole) of α-phenylmercaptophenylacetic acid was heated on the steam bath with 5 ml. of thionyl chloride for 20 min. The reaction mixture was then poured into 20 ml. of ice-cold concentrated ammonia. The precipitated solid was collected by filtration and recrystallized from dilute aqueous ethanol. This gave 0.8 g. (82%) of crystalline solid melting at 174–175°.

Anal. Calcd. for $C_{14}H_{13}NOS$: N, 5.76. Found: N, 5.87.

α-Phenylsulfonylphenylacetamide. A solution composed of 0.3 g. (0.001 mole) of α-phenylmercaptophenylacetamide, 50 ml. of acetone and 10 ml. of 35% hydrogen peroxide was heated to reflux on the steam bath for 1 hr., after which an additional 10 ml. of 35% hydrogen peroxide was added and the solution was again heated at reflux temperature for 3 hr. The reaction mixture was then poured over an excess of ice and the acetone was removed by evaporation on the steam bath. The colorless solid which precipitated was collected by filtration. It weighed 0.2 g. (65%) and melted at 195–197°. Recrystallization from dilute aqueous ethanol brought the melting point up to 203–204°.

Anal. Calcd. for $C_{14}H_{13}NO_2S$: N, 5.41. Found: N, 5.56.

Hydrazide of α-phenylmercaptophenylacetic acid. An ethereal solution of 3 g. (0.012 mole) of α-phenylmercaptophenylacetic acid was converted to the methyl ester with diazomethane. The crude ester was converted to the hydrazide, m.p. 85–86°. The yield was 1.1 g. and crystallization was from water.

Anal. Calcd. for $C_{14}H_{14}N_2OS$: N, 10.85. Found: N, 10.88.

Hydrazide of α-phenylsulfonylphenylacetic acid. A mixture of 0.6 g. (0.002 mole) of methyl α-phenylsulfonylphenylacetate, 100 ml. of absolute ethanol, and 5 ml. of 85% hydrazine hydrate was allowed to stand at room temperature in a stoppered flask for one week. The ethanol was removed by evaporation on the steam bath and the residue was recrystallized from aqueous ethanol. The yield of solid material melting at 182–183° was 0.5 g. (83%).

Anal. Calcd. for $C_{14}H_{14}N_2O_3S$: N, 9.66. Found: N, 9.48.

α-Phenylsulfonylphenylacetamide. One gram (0.0036 mole) of the acid was converted to the amide, m.p. 278°, with thionyl chloride and ammonia. The yield was 40% and crystallization was from aqueous ethanol.

Anal. Calcd. for $C_{14}H_{13}NO_3S$: N, 5.09. Found: N, 5.19.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF TENNESSEE
KNOXVILLE, TENN.

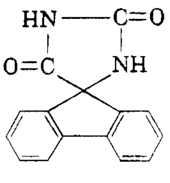
Alkaline Condensation of Phenanthraquinone with Urea

W. R. DUNNAVANT[1]

Received February 12, 1957

In a previous publication[2] the results of a study of the alkaline condensation of benzil with urea was reported. The products of this reaction were 3a,6a-diphenyl glycoluril, and the rearrangement product 5,5-diphenylhydantoin. The results from a series of 4,4′-disubstituted benzils used in this reaction gave relative migratory aptitudes of *p*-substituted phenyl groups which indicated that the rearrangement involved in the hydantoin formation is closely allied with the benzilic acid rearrangement.

Since phenanthraquinone undergoes the benzilic acid rearrangement,[3] it was supposed that the



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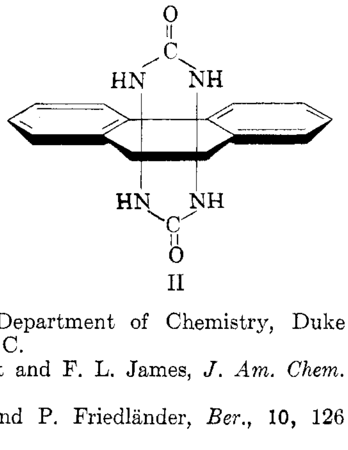

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[1] Present address Department of Chemistry, Duke University, Durham, N. C.

[2] W. R. Dunnavant and F. L. James, *J. Am. Chem. Soc.*, **78,** 2740 (1956).

[3] A. von Baeyer and P. Friedländer, *Ber.*, **10,** 126 (1877).