which 0.125 mole of benzaldehyde, 0.032 mole of catalyst and sufficient anisole to give a total volume of 250 ml. was used a 77% yield of pure product was obtained.

When phenetole was used in an experiment like that described first for anisole 32.0 g. (77%) of light orange distillate of b.p. 196–204° (0.5 mm.) was obtained. A negative test for solubility in aqueous alcoholic potassium hydroxide indicated the product was free of phenols. Attempts at crystallization were unsuccessful, but a redistilled sample (b.p. 196–197° at 0.5 mm.) analyzed satisfactorily for the expected *p,p'*-diethoxytriphenylmethane. This compound has not been reported previously.

Anal.[17] Calcd. for $C_{23}H_{24}O_2$: C, 83.10; H, 7.28. Found: C, 83.01, 83.11; H, 7.37, 7.33.

Similar results were obtained with *n*-butyl phenyl ether under the same conditions. The product distilled at 234–246° (1.0 mm.) and weighed 33.7 g. (70%). A redistilled sample (b.p. 225–227° at 0.5 mm.) analyzed satisfactorily for *p,p'*-di-*n*-butoxytriphenylmethane which has not been reported previously.

Anal. Calcd. for $C_{27}H_{32}O_2$: C, 83.46; H, 8.30. Found: C, 83.39, 83.18; H, 8.31, 8.26.

In the foregoing experiments with the three phenyl ethers under the same conditions the yield of water was 98 to 100%. In each case the temperature varied about 0.8° over the first 60% of the reaction; the median temperature with anisole was 86.3°, with phenetole 86.7° and with butyl phenyl ether 87.3°. The experiments for each of these three phenyl ethers were repeated and close checks on the rate (*cf.* Discussion) were obtained.

Excess toluene served as the solvent in a study of its reactivity. A solution of 0.125 mole of benzaldehyde and 0.128 mole of catalyst in sufficient toluene to give a total volume of 250 ml. was used. A 50% yield of water was obtained in 60 hours and a 98% yield in 130 hours. The temperature decreased from 115.9 to 115.2° as the reaction progressed. A 74% yield of product (25.2 g.) distilled at 156–157° (0.7 mm.). Crystallization from methanol gave a 38% yield (13.0 g.) of *p,p'*-dimethyltriphenylmethane, m.p. 48–49°. The low yield of crystals may be due to the presence of some *p,o'*-dimethyltriphenylmethane.

Phenol reacted rapidly to give a 50% yield of water in 3 hours and a 99% yield in 10 hours when a solution of 0.125 mole of benzaldehyde, 0.625 mole of phenol and 0.008 mole of catalyst in sufficient benzene to give a total volume of 500 ml. was refluxed in the usual fashion. Only a 14% yield of *p,p'*-dihydroxytriphenylmethane was isolated, m.p. 157–159.5°.

Reactions of Other Aldehydes with Dimethylaniline.—When *n*-heptaldehyde was treated with dimethylaniline using the procedure given above for the experiments of Table I an 83% yield of water was obtained in 120 hours. An 80% yield of 1,1-bis-(*p*-dimethylaminophenyl)-heptane distilled at 206–212° (0.5 mm.). Trituration with ethanol gave a 69% yield of crystals which melted at 58.5–59.0° (lit. m.p. 59.5°).

The same conditions were employed for the reaction of α-ethylbutyraldehyde except that 0.128 mole of catalyst was used. The reaction was stopped after refluxing two weeks at which time a 90% yield of water had been evolved. A 72% yield of crude 1,1-bis-(*p*-dimethylaminophenyl)-2-ethylbutyraldehyde distilled at 180–212° (0.8 mm.). Recrystallization five times from ethanol gave a 46% yield of white crystals which melted at 103.0–104.5°.

Anal. Calcd. for $C_{22}H_{32}N_2$: C, 81.43; H, 9.93; N, 8.64. Found: C, 81.70; H, 10.21; N, 9.07.

Attempts to find a basis of calculation which would give satisfactory rate constants for these two experiments were unsuccessful.

Acknowledgment.—It is a pleasure to thank du Pont de Nemours and Company for a fellowship (to L. Q. G.) and the Research Corporation for additional financial support.

COLLEGE PARK, MD.

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(17) We wish to thank Professor Mary Aldridge and Mr. Byron Baer for the microanalyses.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Reaction of *n*-Butyllithium with Dibenzothiophene-5-dioxide and with Diphenyl Sulfone

BY HENRY GILMAN AND DONALD L. ESMAY

RECEIVED AUGUST 18, 1952

Dibenzothiophene-5-dioxide reacts with *n*-butyllithium at reduced temperatures (−20 to −30°) to yield after carbonation 4-carboxy- and/or 4,6-dicarboxydibenzothiophene-5-dioxide. Similarly diphenyl sulfone yields *o*-carboxy- and/or *o,o'*-dicarboxydiphenyl sulfone.

The metalation of dibenzothiophene has been accomplished with various organometallic compounds[1] yielding derivatives substituted in the 4-position in all cases except the apparently anomalous reaction with phenylcalcium iodide which yields 3-dibenzothiophenecarboxylic acid on carbonation.[1a] The first successful nuclear metalation of a sulfoxide was recently accomplished by treating dibenzothiophene-5-oxide with *n*-butyllithium at −10°.[2] The product obtained on carbonation was established as being 4-dibenzothiophenecarboxylic acid, thereby showing that reduction of the sulfoxide group occurred along with the nuclear metalation.[3]

Initial attempts to metalate dibenzothiophene-5-dioxide with *n*-butyllithium yielded only acidic gums after carbonation.[4] We are reporting the use of reduced temperatures (−20 to −30°) to successfully accomplish the metalation of dibenzothiophene-5-dioxide with *n*-butyllithium in diethyl ether. The use of one equivalent of *n*-butyllithium yielded after carbonation 4-carboxydibenzothiophene-5-dioxide. Similarly, two equivalents of the metalating agent gave mostly 4,6-dicarboxydibenzothiophene-5-dioxide along with some 4-carboxydibenzothiophene-5-dioxide, while

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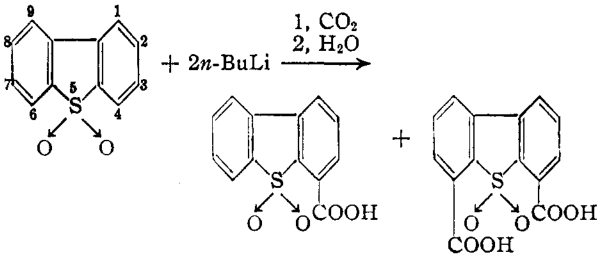
(1) (a) H. Gilman and A. L. Jacoby, *J. Org. Chem.*, **3**, 108 (1938); (b) H. Gilman and R. L. Bebb, THIS JOURNAL, **61**, 109 (1939); (c) H. Gilman, R. N. Meals, G. J. O'Donnell and L. A. Woods, *ibid.*, **65**, 268 (1943); (d) H. Gilman, A. H. Haubein, G. J. O'Donnell and L. A. Woods, *ibid.*, **67**, 922 (1945).

(2) H. Gilman and D. L. Esmay, *ibid.*, **74**, 266 (1952).

(3) H. Gilman and R. D. Nelson, *ibid.*, in press, have shown that 10-ethylphenothiazine-5-oxide undergoes a similar reaction.

(4) H. Gilman and F. J. Webb, *ibid.*, **71**, 4062 (1949).

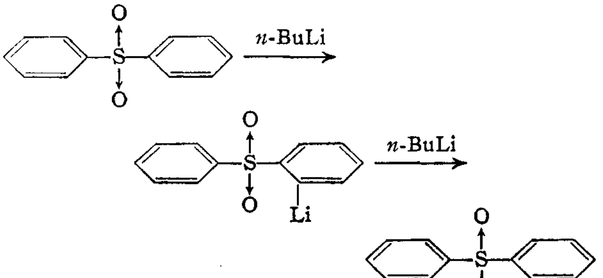
three or more equivalents gave 4,6-dicarboxydibenzothiophene-5-dioxide entirely.



The isolation of the unreduced sulfone acids again demonstrates the greater stability toward reduction of the sulfone group over the sulfoxide group.

The progress of the reaction of *n*-butyllithium with dibenzothiophene-5-dioxide was followed by the use of color tests. Color Test I[5] was positive throughout the reaction, but Color Test II[6] did not remain positive on prolonged stirring until at least three equivalents of the *n*-butyllithium had been added. These observations indicate the possible formation of a complex between the sulfone group and the organometallic compound which suppressed the reactivity of the *n*-butyllithium for halogen-metal interconversion in Color Test II until at least three equivalents of the metalating agent were present. A similar complex formation was postulated as being an intermediate step in the metalation of dibenzothiophene-5-oxide.[2]

The achievement of satisfactory metalation of dibenzothiophene-5-dioxide suggested that other sulfones might also be successfully metalated under these conditions. Accordingly, the use of reduced temperatures for metalations was extended to diphenyl sulfone. Again it was observed that it was necessary to add at least three equivalents of *n*-butyllithium to the ether solution of diphenyl sulfone before Color Test II became permanently positive. Under these conditions the acid obtained after carbonation was identified as *o*,*o*′-dicarboxydiphenyl sulfone. While this work was in progress, Truce and Amos[7] reported the reaction of diphenyl sulfone with about one equivalent of *n*-butyllithium to yield on carbonation *o*-carboxydiphenyl sulfone (*o*-benzenesulfonylbenzoic acid). We were able to satisfactorily check their results using our reduced temperature conditions and employing only one equivalent of the *n*-butyllithium. These results indicate that the metalation of diphenyl sulfone also proceeds stepwise.



The identities of all products obtained were established by direct comparison with authentic samples except in the case of the 4,6-dicarboxydibenzothiophene-5-dioxide. Attempts to prepare a sample of 4,6-dibenzothiophenedicarboxylic acid by the metalation of dibenzothiophene with *n*-butylsodium or benzylsodium were unsuccessful, although similar metalations of dibenzofuran have been reported to give good yields of 4,6-dibenzofurandicarboxylic acid.[8] However, these results are perhaps not too surprising since dibenzofuran has been shown to be more reactive toward metalation than is dibenzothiophene.[9] The assumption that the product obtained from the reaction of dibenzothiophene-5-dioxide with two or more equivalents of *n*-butyllithium was 4,6-dicarboxydibenzothiophene-5-dioxide appears justified, however, both by analogy with the product obtained from the similar metalation of diphenyl sulfone and by an inspection of the analytical data obtained on the dibenzothiophene derivative.

Acknowledgment.—The authors are grateful to Dr. Velmer A. Fassel and Mr. Marvin Margosches for their infrared absorption measurements.

Experimental[10]

Metalation of Dibenzothiophene-5-dioxide. Run I.—A total of 3.0 equivalents of a 1.175 *M* ether solution of *n*-butyllithium[11] was added in predetermined portions to a stirred suspension of 5.8 g. (0.025 mole) of dibenzothiophene-5-dioxide[12] in 250 ml. of ether. The temperature of the reaction mixture was maintained at −20 to −25° by cooling in an acetone–Dry Ice-bath. Color test I[5] was positive throughout while Color Test II[6] did not remain positive on prolonged stirring until all three equivalents had been run in. After a total reaction time of 11 hours, the very dark red homogeneous solution was carbonated and hydrolyzed in the customary manner. Acidification of the alkaline layer caused the precipitation of a very gummy acid which was filtered off and dissolved in hot 4% sodium hydroxide. Filtration of the cooled solution yielded 0.8 g. (10.1% of a disodium salt of a dicarboxydibenzothiophene-5-dioxide) of white, flaky crystals which were soluble in water and which decomposed without burning on ignition. Acidification of the alkaline filtrate from the disodium salt yielded 0.7 g. (10.3%) of white, finely divided 4,6-dicarboxydibenzothiophene-5-dioxide, m.p. 390–391°.

Anal. Calcd. for $C_{14}H_8O_6S$: S, 10.5; neut. equiv., 304. Found: S, 10.5, 10.4; neut. equiv., 308.

These data thus indicate a dicarboxydibenzothiophene-5-dioxide. The infrared spectrum of the acid showed absorption at 5.92, 8.65 and 13.1 μ, characteristic of the carbonyl group, the sulfone group and 1,2,3-substitution of a benzene ring, respectively. The absence of a band between 13 and 14 μ, characteristic of 1,2-substitution, indicates substitution in both benzene rings. The absorption band commonly observed for the sulfoxide group was also absent.

Run II.—This run was the same in all respects as run I except that 2.0 equivalents of *n*-butyllithium were used. Carbonation, hydrolysis and acidification were carried out

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(5) H. Gilman and F. Schulze, This Journal, **47**, 2002 (1925).

(6) H. Gilman and J. Swiss, *ibid.*, **62**, 1847 (1940).

(7) W. E. Truce and M. F. Amos, *ibid.*, **73**, 3013 (1951).

(8) H. Gilman and R. V. Young, *ibid.*, **57**, 1121 (1935).

(9) H. Gilman, M. W. Van Ess, H. B. Willis and C. G. Stuckwisch, *ibid.*, **62**, 2606 (1940).

(10) All melting points are uncorrected.

(11) H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, This Journal, **71**, 1499 (1949). It has been found advantageous to modify the reported procedure slightly by adding the solution of *n*-butyl bromide rather rapidly while controlling the temperature by raising or lowering an acetone–Dry Ice-bath containing excess Dry Ice. In this way, the time required for the addition of a solution of 0.5 mole of *n*-butyl bromide can be reduced from about 30 minutes to less than 10 minutes. It is necessary, however, to stir the mixture for at least one hour after addition of the *n*-butyl bromide is complete in order to obtain the maximum yield.

(12) H. Gilman and D. L. Esmay, *ibid.*, **74**, 2021 (1952).

in the usual manner. Filtration of the acidified alkaline layer gave 7.8 g. of product melting at 330–334°. Two digestions with methanol left 1.9 g. of residue melting at 378–384° which was recrystallized from dioxane to give 0.6 g. (4.0%) of 4,6-dicarboxydibenzothiophene-5-dioxide, m.p. and mixed m.p. with the product from run I 391–392°. From the methanol filtrates there was isolated 2.6 g. (20.1%) of pure 4-carboxydibenzothiophene-5-dioxide, m.p. and mixed m.p. 337–338°.

Run III.—To a stirred suspension of 10.8 g. (0.05 mole) of dibenzothiophene-5-dioxide in 400 ml. of ether cooled to −30° was added 40.9 ml. of a 1.221 *M* ether solution of *n*-butyllithium (0.05 mole). The mixture was stirred at −20° to −25° for 6 hours during which Color Test I was positive, Color Test II was negative, and the solution gradually became deep red in color. Carbonation and hydrolysis were effected as usual. Filtration of the acidified water layer yielded 10.3 g. of white product melting at 295–305°. Recrystallization from methanol gave 2.8 g. (21.5%) of 4-carboxydibenzothiophene-5-dioxide melting at 328–331°. Recrystallization from dioxane gave 2.3 g. of pure product (17.7%), m.p. and mixed m.p. 338–339°. Removal of the solvent from the dried ether layer gave, after recrystallization from glacial acetic acid, 2.2 g. (20.4% recovery) of dibenzothiophene-5-dioxide melting at 231–232°; identified by the method of mixed melting points. The yields of acid based on the amount of dibenzothiophene-5-dioxide which actually reacted were 27.0% crude and 22.3% pure.

Metalation of Diphenyl Sulfone. Run I.—To a stirred suspension of 11.0 g. (0.05 mole) of diphenyl sulfone in 500 ml. of ether was added 4.0 equivalents of *n*-butyllithium during 3.5 hours. The temperature was maintained at −25 to −30° by an acetone–Dry Ice-bath. Color Test I was positive throughout, but Color Test II did not remain positive on prolonged stirring until 3.0 equivalents of the organometallic compound had been added. The mixture became yellow-orange in color during the addition of the first equivalent of *n*-butyllithium, orange-red during the addition of the second equivalent and a deep red by the time three equivalents had been run in. Carbonation, hydrolysis, acidification and filtration yielded 3.9 g. (25.5%) of *o,o'*-dicarboxydiphenyl sulfone melting at 216–219° which was recrystallized from glacial acetic acid to yield 3.3 g. (21.9%) of pure product; m.p. and mixed m.p. 220–221°.

Anal. Calcd. for $C_{14}H_{10}O_6S$: S, 10.48; neut. equiv., 306. Found: S, 10.54, 10.57; neut. equiv., 308, 313, 308, 307.

Infrared absorption measurements on this compound gave bands at 5.77 and 5.9 μ, 8.73 μ, and 13.17 and 13.9 μ, characteristic of the carbonyl group, sulfone group and 1,2-substitution of the benzene rings, respectively.

Run II.—This run was made with two equivalents of *n*-butyllithium under the same conditions of run I with a total reaction period of 4.5 hours. Nine grams (58.2%) of very crude acid sulfone was isolated which melted at 165–174°. Digestion with benzene and filtration while hot left 7.5 g. of product melting at 200–210°. Three recrystallizations from glacial acetic acid yielded 4.0 g. (25.9%) of pure *o,o'*-dicarboxydiphenyl sulfone; m.p. and mixed m.p. 221–222°. From the benzene filtrate there was isolated 1.2 g. (9.2%) of *o*-carboxydiphenyl sulfone melting at 141–143°. Recrystallization from benzene yielded 0.7 g. (5.3%) of pure material, m.p. and mixed m.p. 146–147°.

Run III.—The procedure of run I was followed in this experiment using one equivalent of *n*-butyllithium and a total reaction time of 1.5 hours. The crude acid weighed 6.3 g. and melted at 132–138°. Digestion with benzene and filtration while hot left a small amount of insoluble residue which was recrystallized from glacial acetic acid diluted with xylene to give 0.2 g. of nearly pure *o,o'*-dicarboxydiphenyl sulfone melting at 217–218.5°. From the benzene filtrate there was isolated 5.4 g. (41.2%) of nearly pure *o*-carboxydiphenyl sulfone melting at 145–146.5°; identified by the method of mixed melting points. Further recrystallizations raised the melting point to 146–147°. Removal of the solvent from the reaction mixture ether layer gave 2.4 g. (21.8% recovery) of slightly impure diphenyl sulfone, m.p. 124–125.5°. Based on the amount of sulfone actually used, the yield of acid was 52.5%.

4-Carboxydibenzothiophene-5-dioxide.—A stirred suspension of 4.6 g. (0.02 mole) of 4-dibenzothiophenecarboxylic acid[1a] in 100 ml. of glacial acetic acid was heated to reflux without effecting complete solution. Ten ml. of 30% aqueous hydrogen peroxide was added to the hot mixture, and stirring and refluxing were continued. The mixture became homogeneous by the end of 8 minutes and a precipitate began to form at the end of 15 minutes. After a total of one hour of stirring and refluxing an additional 10 ml. of peroxide was added and the reaction was allowed to proceed one hour longer. The mixture was cooled overnight, then filtered to yield 5.1 g. (98.1%) of finely divided, shiny crystalline material melting at 334–337°. The compound was insoluble in hot methanol, glacial acetic acid and acetone, and only slightly soluble in hot dioxane. Digestion with 100 ml. of acetone and filtration while hot left 4.9 g. of insoluble pure 4-carboxydibenzothiophene-5-dioxide, m.p. 337–338°. The melting point of a small sample was not raised on recrystallizing from dioxane.

Anal. Calcd. for $C_{13}H_8O_4S$: S, 12.32. Found: S, 12.19, 12.26.

The infrared spectrum of this acid showed absorption at 5.81, 8.68, 13.05 and 13.9 μ, characteristic of the carbonyl group, the sulfone group, 1,2,3-substitution and 1,2-substitution of the benzene ring, respectively.

Dimetalation of Dibenzothiophene (Attempted). Run I.—The directions followed in this experiment were those given by Gilman and Young[8] for the preparation of 4,6-dibenzofurandicarboxylic acid in over 70% yields. A solution of 5.9 g. (0.032 mole) of dibenzothiophene in 75 ml. of ether was treated with 1.84 g. (0.08 g. atom) of sodium and 10.0 g. (0.032 mole) of di-*n*-butylmercury. Only a trace of acidic material was isolated from the carbonated reaction mixture and 94.8% of the starting dibenzothiophene was recovered. A repeat run in which benzene was substituted for the ether gave essentially the same results.

Run II.—A suspension of 18.4 g. (0.1 mole) of dibenzothiophene in 80 ml. of toluene was treated for 11 hours at 100–105° with a solution of benzylsodium prepared from 120 ml. of toluene, 11.5 g. (0.5 g. atom) of sodium and 22.5 g. (0.2 mole) of chlorobenzene. Only a trace of acidic material was isolated from the reaction mixture after carbonation and 87.4% of the starting dibenzothiophene was recovered.

***o*-Carboxydiphenyl Sulfone.**—About 0.1 g. of *o*-carboxydiphenyl sulfide (*o*-phenylmercaptobenzoic acid[1b]) was dissolved in 5 ml. of glacial acetic acid. One ml. of 30% aqueous hydrogen peroxide was added and the solution was allowed to stand at room temperature for 48 hours. The solvent was removed under a water-pump vacuum by warming on a steam-bath. The remaining residue was recrystallized from 5 ml. of benzene to give nearly 0.1 g. of *o*-carboxydiphenyl sulfone melting at 139–142°. Two recrystallizations from benzene raised the melting point to 146–147°. The reported melting point was 143–144°.[7]

***o,o'*-Dicarboxydiphenyl Sulfide.**—To a filtered solution of 2.8 g. (0.05 mole) of potassium hydroxide in 75 ml. of ethanol was added a filtered solution of 7.8 g. (0.05 mole) of *o*-chlorobenzoic acid in 25 ml. of ethanol. After reducing the volume to about 25 ml. the hot solution was added to a warm mixture of the disodium salt of thiosalicylic acid and ethanol prepared by adding a solution of 7.7 g. (0.05 mole) of thiosalicylic acid in 75 ml. of ethanol to a solution of 2.3 g. (0.1 g. atom) of sodium in 50 ml. of ethanol. The solvent was removed by evaporation under a water-pump vacuum while warming slightly to remove the last traces. The residue was warmed to 120°, a pinch of copper bronze was stirred in, and heating was continued under an air condenser until the temperature reached 250°. The mixture remained solid throughout and after heating at 250° for 5 minutes, it was cooled and digested with 100 ml. of 10% sodium hydroxide. The nearly black solution was digested with Norit, filtered hot, cooled and carefully neutralized with 6 *N* hydrochloric acid. Filtration yielded a slightly yellow product which melted at 218–223°. The slightly wet material was recrystallized from glacial acetic acid to give 10.3 g. (75.1%) of nearly pure *o,o'*-dicarboxydiphenyl sulfide melting at 228–231°. Further recrystallizations raised the melting point to 233–234°.

Anal. Calcd. for $C_{14}H_{10}O_4S$: S, 11.7; neut. equiv., 274. Found: S, 11.4, 11.7; neut. equiv., 275.

Initial attempts to prepare *o,o'*-dicarboxydiphenyl sulfide by the method of Mayer[13] (two runs), by the method of

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(13) F. Mayer, *Ber.*, **43**, 584 (1910).

Hinsberg[14] (two runs), and following the general directions of Reinhalt[15] (one run) and of Hunter[16] (one run) were unsuccessful.

***o,o'*-Dicarboxydiphenyl Sulfoxide. By Peroxide Oxidation.**—A mixture of 1.4 g. (0.005 mole) of *o,o'*-dicarboxydiphenyl sulfide and 25 ml. of ethanol was refluxed on a steam-bath until solution was complete. To the hot solution was added 2 ml. of 30% aqueous hydrogen peroxide. After refluxing for 3.0 hours an additional 1 ml. of peroxide was added and refluxing was continued for 3.0 hours more. An equal volume of hot water was added slowly to the hot solution and heating was discontinued. Filtration of the cooled mixture gave 1.0 g. (71.4%) of pure *o,o'*-dicarboxydiphenyl sulfoxide melting at 310–311°.

By Permanganate Oxidation.—The following procedure is essentially that used by Mayer[13] for the reported preparation of *o,o'*-dicarboxydiphenyl sulfone except that the solution was left slightly basic and only a slight excess of permanganate was used. One gram (0.0036 mole) of *o,o'*-dicarboxydiphenyl sulfide was dissolved in a very slight excess of 2% sodium hydroxide and the resulting solution was diluted to 50 ml. with water. A warm solution of 0.8 g. (0.005 mole) of potassium permanganate in 100 ml. of water was added and the resulting solution was warmed overnight on a steam-bath. The precipitated manganese dioxide was filtered off to leave a clear, colorless solution. The filtrate was acidified with a solution of sodium bisulfite to which had been added excess 6 *N* hydrochloric acid. No solid product was obtained until the volume of the solution was reduced to about 25 ml. Filtration gave 0.8 g. of brown flakes which melted at 215–229°. Repeated recrystallizations from glacial acetic acid diluted with xylene resulted in a total yield of pure *o,o'*-dicarboxydiphenyl sulfoxide of 38.1%, m.p. 312–313°. An extensive search of the various filtrates did not reveal the presence of any other compound.

***o,o'*-Dicarboxydiphenyl Sulfone. By Peroxide Oxidation of *o,o'*-Dicarboxydiphenyl Sulfide.**—A mixture of about 1.0 g. of *o,o'*-dicarboxydiphenyl sulfide and 15 ml. of glacial acetic acid was refluxed to give complete solution of the sulfide. To the slightly cooled solution was added 3 ml. of 30% aqueous hydrogen peroxide. After refluxing for 30 min., an additional 1.0 ml. of peroxide was added, refluxing was continued for 30 min. longer, and the solution was allowed to stand overnight at room temperature. No product was obtained until the volume of the solution had been reduced to about 1 ml. The crystals were dissolved in 5 ml. of glacial acetic acid and the resulting solution was digested with Norit, filtered hot and cooled. Filtration yielded 0.3 g. of small rectangular plates which melted at 220–221°.

By Permanganate Oxidation of *o,o'*-Dicarboxydiphenyl Sulfide.—The following procedure is essentially that reported by Mayer.[13] One gram (0.0036 mole) of *o,o'*-dicarboxydiphenyl sulfide was dissolved in a very slight excess of 2% sodium hydroxide and the solution was back-titrated with 3 *N* hydrochloric acid until the precipitated acid just redissolved. A warm solution of 0.9 g. (0.006 mole) of potassium permanganate in 100 ml. of water was added and the resulting solution was warmed overnight on a steam-bath. The precipitated manganese dioxide was filtered off giving a clear permanganate colored filtrate. A solution of sodium bisulfite which had been made strongly acid with 6 *N* hydrochloric acid was added until the filtrate was colorless and acid in reaction. The solution was evaporated to a volume of about 25 ml., filtered hot and cooled in air. Filtration yielded 0.7 g. (63.6%) of impure material melting at 216–219°. One recrystallization from glacial acetic acid diluted with an equal volume of xylene gave 0.4 g. (36.4%) of pure *o,o'*-dicarboxydiphenyl sulfone melting sharply at 220–221°. A check run following this same procedure gave essentially identical results.

By Peroxide Oxidation of *o,o'*-Dicarboxydiphenyl Sulfoxide.—To a solution of about 0.1 g. of *o,o'*-dicarboxydiphenyl sulfoxide in 5 ml. of glacial acetic acid was added 1 ml. of 30% aqueous hydrogen peroxide. After standing for 48 hours the solvent was removed under a water-pump vacuum by distillation from a steam-bath. The residue was recrystallized from glacial acetic acid diluted with an equal volume of xylene to give nearly 0.1 g. of product melting at 212–215°. Two recrystallizations from the same solvent pair raised the melting point to 220–221°. A mixed melting point with the sulfone prepared by permanganate oxidation showed no depression.

In view of the above evidence, the melting point of 137° reported for *o,o'*-dicarboxydiphenyl sulfone by Mayer[13] is believed to be in error. As described above, the sulfone was prepared by peroxide and permanganate oxidation of the corresponding sulfide, by peroxide oxidation of the corresponding sulfoxide and by metalation of diphenyl sulfone with subsequent carbonation, and in all cases the compound melted at 220–221°.

AMES, IOWA

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[14] O. Hinsberg, *ibid.*, **43**, 1877 (1910).

[15] F. E. Reinhalt, *J. Franklin Inst.*, **249**, 248 (1950).

[16] B. A. Hunter, *Iowa State Coll. J. Sci.*, **15**, 215 (1941).

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

Reactions of *cis*- and *trans*-1,2-Dibenzoylpropenes with Hydrogen Halides, Bromine and Phenylmagnesium Bromide[1]

BY PHILIP S. BAILEY AND SEYMOUR H. POMERANTZ[2]

RECEIVED JULY 31, 1952

A comparison is made of the reactions of the *cis*- and *trans*-1,2-dibenzoylpropenes with hydrogen bromide and hydrogen chloride under various conditions. These propenes react with bromine in chloroform solution to form 3-(dibromomethyl)-2,5-diphenylfuran. This involves a substitution reaction with bromine, the 1,3-shift of hydrogen which has been found to be common in the reaction of the dibenzoylpropenes and similar substances, addition of the hydrogen bromide by-product and cyclization. The addition of phenylmagnesium bromide does not involve a 1,3-shift of hydrogen. The equilibria involved in these reactions are discussed.

In previous papers,[3] the novel reactions of *cis*- and *trans*-1,2-dibenzoylpropene (IV) with amines to give 1-amino-2,3-dibenzoylpropanes (Ic) and with hydrogen chloride in ether solution to give 1-chloro-2,3-dibenzoylpropane (Ia) or in chloroform solution to give 3-(chloromethyl)-2,5-diphenylfuran (IIa) were described. In these reactions, III, formed from IV by a 1,3-shift of hydrogen, is an intermediate.[3b]

In the present paper reactions of IV with hydrogen bromide, bromine and phenylmagnesium bromide are described. In ether solution the *trans* isomer of IV reacted with hydrogen bromide in the same manner as it did with hydrogen chloride

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[1] Presented before the Organic Division at the Atlantic City Meeting of the American Chemical Society, September, 1952. This is the seventh in a series of papers dealing with 1,3-shifts of hydrogen in the reactions of dibenzoylalkenes and related compounds. For the sixth see P. S. Bailey, G. Nowlin, S. H. Pomerantz, J. V. Waggoner and E. E. Kawas, THIS JOURNAL, **73**, 5560 (1951).

[2] From the Ph.D. dissertation of S. H. Pomerantz.

[3] (a) R. E. Lutz and P. S. Bailey, THIS JOURNAL, **67**, 2229 (1945); (b) P. S. Bailey, G. Nowlin, S. H. Pomerantz, J. V. Waggoner and E. E. Kawas, *ibid.*, **73**, 5560 (1951).