

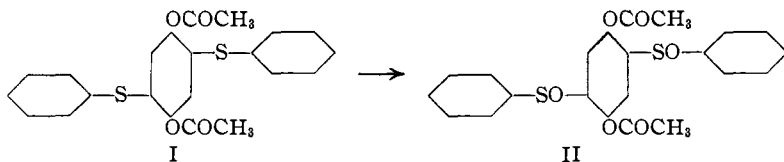
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Diastereoisomers of 2,5-Diphenylsulfinylhydroquinone Diacetate

BY MARION E. MACLEAN¹ AND ROGER ADAMS

Phillips² in 1925 first demonstrated that a sulfur atom in combination with three dissimilar groups could be resolved. His investigations³ involved the preparation of optically active sulfinic esters and of sulfoxides. Bell and Bennett⁴ and their associates extended the study to the isomerism of aliphatic and aliphatic-aromatic disulfoxides and to cyclic di- and trisulfoxides. These authors are confident that the semi-polar linkage between oxygen and sulfur is an important factor in producing asymmetry. Others⁵ urge caution in adopting this as an official explanation. Bergmann⁶ on the other hand opposes the idea of a semi-polar bond and believes the resolution due to the fact that the oxygen atom lies in a different plane from that of the bonds holding the other two groups to the sulfur atom and states that all the cases given can be explained on this basis.

An additional pair of stereoisomers among the disulfoxides is described in this communication. It is the first example of such isomerism in a diarylsulfoxide. A meso and a racemic form of 2,5-diphenylsulfinyl-1,4-hydroquinone diacetate (II) were obtained by oxidizing the corresponding disulfide (I) with hydrogen peroxide. The α - and β -disulfoxides differ in m. p. by approximately 30° and are markedly different in solubility. They have strikingly different crystalline forms. Both the α and β forms are readily reduced to the parent disulfide and oxidized to the same disulfone. In the preparation of the disulfoxides a small amount of monosulfoxide was always produced.



Experimental

α - and β -2,5-Diphenylsulfinylhydroquinone-1,4-diacetates (II).—To a suspension

(1) The junior author held during 1931-32 the Julia C. G. Piatt fellowship awarded by the A. A. U. W. She desires to express her thanks for this aid.

(2) Phillips, *J. Chem. Soc.*, **127**, 2552 (1925).

(3) Harrison, Kenyon and Phillips, *ibid.*, 2079 (1926); Clarke, Kenyon and Phillips, *ibid.*, 188 (1927); Holloway, Kenyon and Phillips, 3000 (1928); Kenyon and Phillips, *ibid.*, 1676 (1930).

(4) Bell and Bennett, *ibid.*, 1798 (1927); 86, 3189 (1928); 15 (1929); 1 (1930); Bell and Waddington, *ibid.*, 2832 (1929); Bell, Mosses and Statham, *ibid.*, 1668 (1930); Bennett and Statham, *ibid.*, 1684, 1690 (1931); Bennett and Waddington, *ibid.*, 1692 (1931).

(5) Sidgwick, "Electronic Theory of Valency," Oxford-Clarendon Press, 1927; deVries and Rodebush, *THIS JOURNAL*, **53**, 2888 (1931).

(6) Bergmann, Engel and Sandor, *Z. physik. Chem.*, **B10**, 397 (1930); Bergmann and Tschudnowsky, *Ber.*, **65**, 457 (1932).

of 24 g. of diphenylthiohydroquinone diacetate⁷ (I) in 750 cc. of glacial acetic acid was added 12.5 cc. of perhydrol and with mechanical stirring, the mixture left for five days. An additional 100 cc. of glacial acetic acid was added after three days. About 5 g. of solid (the disulfide) still remaining after five days was filtered off.

The filtrate was diluted with about 2 liters of water. On settling, 12.6 g. of a pale cream solid was obtained (Part A).

A large amount of water added to the filtrate from Part A gave 4.9 g. (Part B).

The total yield, calculating as disulfoxide and correcting for the disulfide recovered, was 83%. (A.) Three grams of (A) was digested with 200 cc. of carbon tetrachloride to remove impurities. The residue, 1.9 g., was dissolved in 130 cc. of 95% alcohol and gave 1.65 g. of colorless plates which melted with decomposition at 207–208° (corr.), with signs of decomposition from 179°.

Anal. (α -form, m. p. 207–208°) Calcd. for $C_{22}H_{18}O_6S_2$: C, 59.73; H, 4.07; S, 14.48. Found: C, 60.26; H, 4.16; S, 14.50.

On evaporation of the carbon tetrachloride solution, a solid was obtained which was purified from alcohol, m. p. 142.5–145.5° with softening at 140° (corr.). This on analysis proved to be a monosulfoxide.

Anal. (Compound m. p. 142.5–145.5°) Calcd. for $C_{22}H_{18}O_6S_2$: C, 61.97; H, 4.23; S, 15.02. Found: C, 61.98; H, 4.28; S, 14.93.

(B) A solution of 2.5 g. of (B) in 60 cc. of alcohol, on cooling gave 1.6 g. of short, colorless crystals, melting 173.5–175° (corr.) to a dark red liquid with darkening from 166°. Recrystallization did not change the melting point.

Anal. (β -form, m. p. 173.5–175°) Calcd. for $C_{22}H_{18}O_6S_2$: C, 59.73; H, 4.07; S, 14.48. Found: C, 60.48; H, 4.16; S, 14.27.

Mixed melting points of various proportions of the α - and β -disulfoxides were determined. In every case the mixture melted over a range intermediate between the melting points of the separate α - and β -forms.

Repetition of the isolation of α - and β -forms on a larger scale gave essentially the same results except that the presence of a larger amount of the monosulfoxide rendered the separation more difficult.

2,5-Diphenylsulfonylhydroquinone Diacetate from α -Disulfoxide.—To a solution of 2 g. of the α -disulfoxide in 50 cc. of glacial acetic acid was added 5 cc. of perhydrol. Upon heating overnight on the steam-bath under reflux, a large quantity of small crystals deposited. After about twenty-six hours the crystals were filtered from the still hot solution and washed with a little glacial acetic acid, then alcohol. The precipitate weighed 1.2 g. A part was recrystallized from dioxane and part from glacial acetic acid. Both solutions were violet by reflected light. The recrystallized compound melted when pure with decomposition at 270–271°, darkening beginning about 220°.

Anal. Calcd. for $C_{22}H_{18}O_6S_2$: C, 55.69; H, 3.79; S, 13.50. Found: C, 55.37; H, 3.99; S, 13.67.

A similar reaction with the β -disulfoxide gave the same compound.

2,5-Diphenylthiohydroquinone Diacetate by Reduction of α -2,5-Diphenylsulfonylhydroquinone Diacetate.—To a solution of 1 g. of α -disulfoxide in 40 cc. of glacial acetic acid, 5 g. of zinc dust was added, and the mixture refluxed for seventeen hours. The solution was filtered hot into about 200 cc. of water. The slightly gummy precipitate which settled after about two hours was filtered and recrystallized from alcohol. The

(7) Posner, *Ann.*, **336**, 134 (1904).

(8) The exact m. p. of the α - and β -forms varied with the rate of heating and the temperature of the bath when samples were inserted. But samples of the two, melted simultaneously, always showed a difference such as that indicated here.

product showed exactly the same slender needle form and melting point as 2,5-diphenylthiohydroquinone diacetate. The identity was confirmed by a mixed melting point.

In a similar way the β -form was also reduced to 2,5-diphenylthiohydroquinone.

Summary

The meso and racemic forms of 2,5-diphenylsulfinylhydroquinone have been isolated. These represent a pair of diastereoisomers in the class of di-diarylsulfoxides.

URBANA, ILLINOIS

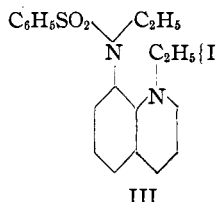
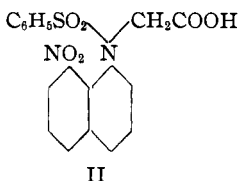
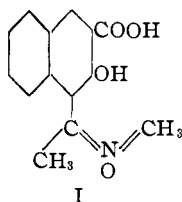
RECEIVED JULY 24, 1933
PUBLISHED NOVEMBER 7, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Study of Certain Analogs of Resolvable Diphenyls

BY MARION E. MACLEAN¹ AND ROGER ADAMS

The cause of optical activity in properly substituted diphenyls is now generally ascribed to restricted rotation of the two rings.² Meisenheimer³ has observed in certain substituted oximes (I) and Mills⁴ in certain nitronaphthalenes (II) and quinoline derivatives (III), optical isomerism which may also be explained on the basis of restricted rotation due to the interference of groups.



Similar possibilities⁵ in substituted aryl aliphatic compounds have been suggested but none have as yet been prepared in which resolution has been realized.

It is clear from the work cited above that other cases of optical activity caused by interference of adjacent groups are to be anticipated. Compounds related to the diphenyl series of the general structure indicated in IV, V and VI have now been investigated.

From experience in the diphenyl series, the methyl group may be assumed to be relatively large.² Consequently, if (a) in the above formulas represents a methyl group, the 2,2' groups in these molecules should pro-

(1) Submitted as part of a thesis for the degree of Doctor of Philosophy at the University of Illinois. The junior author held during 1931-1932 the Julia C. G. Piatt Memorial Fellowship of the A. A. U. W. She desires to express her thanks for this aid.

(2) Adams and Yuan, *Chem. Rev.*, **12**, 261 (1933).

(3) Meisenheimer, Theilacker and Beisswenger, *Ann.*, **495**, 249 (1932).

(4) Mills, *Trans. Faraday Soc.*, **26**, 431 (1930); Mills and Breckenridge, *J. Chem. Soc.*, 2209 (1932); Mills and Elliott, *ibid.*, 1291 (1928).

(5) Hyde and Adams, *THIS JOURNAL*, **50**, 2499 (1928); Maxwell and Adams, *ibid.*, **52**, 2959 (1930).