[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

2-Sulfonylbiphenyls and 6,7-Dihydro-2,3,4,5-dibenzothiapin-6-one-1-dioxide; a Seven-Membered Ring β-Ketosulfone[1]

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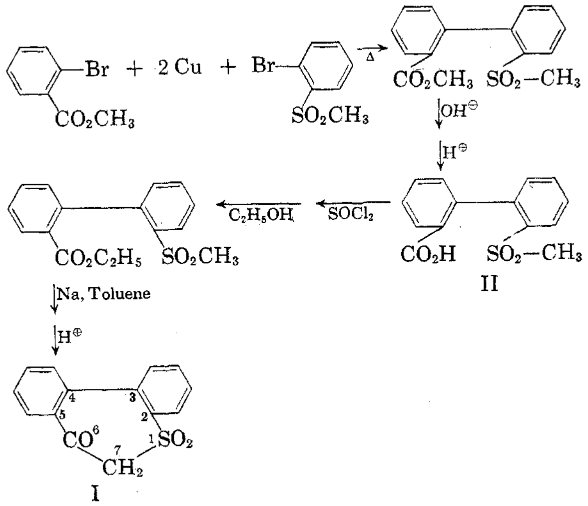
A new seven-membered ring β-ketosulfone has been synthesized in good yield by the Claisen condensation of ethyl 2′-methylsulfonylbiphenyl-2-carboxylate with sodium metal. The material resembles ω-phenylsulfonylacetophenone in its chemistry and appears to be nonplanar with respect to the seven-membered ring flanked by phenyl groups.

The synthesis of a β-ketosulfone structure of type I was of interest in view of its potential similarity to dibenzotropones. Numerous examples of the ease of formation of seven-membered ring O,O′-bridged biphenyls are noted in the literature. Among these examples are the thioketal compounds of Barber and Smiles.[3]

Also, 2,2′-diacetobiphenyl and 2′-acetobiphenyl-2-carboxaldehyde undergo aldol-type cyclizations to form seven-membered rings[4] with ease, while similar condensations in the aliphatic series produce only five- and six-membered rings.[5]

Several examples of cyclizations involving methylene hydrogens activated by sulfone groups are known.[6] These cyclizations are mixed Claisen-type condensations between alkyl sulfonyl and carbalkoxyl groups to produce β-ketosulfones. Thus, esters of *o*-carboxyphenyl benzyl sulfone readily undergo internal cyclizations in the presence of sodium ethoxide to form cyclic β-ketosulfones.[6] Such Claisen condensations have been used to prepare several cyclic β-ketosulfones in the aliphatic series.[7]

6,7-Dihydro-2,3-4,5-dibenzothiapin-6-one-1-dioxide (I) is readily prepared in good yield by such a Dieckmann type of ring closure employing the action of sodium metal upon the ethyl ester of 2′-methylsulfonylbiphenyl-2-carboxylic acid in refluxing toluene. The parent (2′-methylsulfonyl)biphenyl-2-carboxylic acid (II) is most conveniently obtained by saponifying the high boiling fraction of the products of a mixed Ullmann reaction employing methyl *o*-bromobenzoate, methyl *o*-bromophenyl sulfone and copper powder, the yield of acid after extensive purification being only 12%. Conversion of the acid to the acid chloride by means of thionyl chloride followed by treatment with ethanol gave the ethyl ester in high yield.



The Dieckmann product (I) is somewhat acidic, being readily soluble in dilute ammonia and sodium carbonate solution, but is not acidic enough to react readily with cold bicarbonate or to form stable salts with alkaloids having an ionization constant of about 1×10^{-6} or less. Like ω-phenylsulfonylacetophenone,[8] I readily reacts with phenylhydrazine. It likewise does not form a coloration with either ferric chloride or ceric sulfate nor does it react with acetyl chloride. Bright yellow or orange dyes are produced on coupling I with aromatic diazonium compounds similar to corresponding bright orange or red dyes produced from ω-phenylsulfonylacetophenone. As with the latter, bromine reacts with I to produce a colorless bromide which liberates free iodine from potassium iodide solution.

Buchanan[9] has confirmed the earlier suggestion of Sakan and Nakazaki[10] that the presence of

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[1] Abstracted from a portion of the Ph.D. thesis of Donald D. Emrick, Purdue University, 1956.

[2] Present address: Research Department, The Standard Oil Company (Ohio), Cleveland 28, Ohio.

[3] H. J. Barber and S. Smiles, *J. Chem. Soc.*, 1141 (1928).

[4] (a) W. Borsche and A. Herbert, *Ann.*, **546**, 293 (1941); (b) J. W. Cook, G. T. Dickson, and J. D. Loudon, *J. Chem. Soc.*, **1947**, 746 *et seq.*

[5] (a) R. G. Fargher and W. H. Perkin, Jr., *J. Chem. Soc.*, **105**, 1353 (1914); (b) E. Bauer, *Compt. rend.*, **155**, 288 (1912).

[6] (a) A. Cohen and S. Smiles, *J. Chem. Soc.*, **1930**, 406; (b) R. G. Pearson, D. H. Anderson, and L. L. Alt, *J. Am. Chem. Soc.*, **77**, 527 (1955).

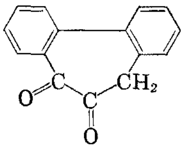
[7] W. E. Truce and R. H. Knospe, *J. Am. Chem. Soc.*, **77**, 5063 (1955).

[8] L. Field, *J. Am. Chem. Soc.*, **74**, 3919 (1952); J. Troger and O. Beck, *J. prackt. Chem.* (2) **87**, 295 (1913).

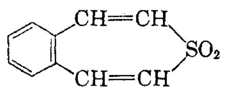
[9] G. L. Buchanan, *Chemistry & Industry*, **1952**, 855.

[10] T. Sakan and M. Nakazaki, *J. Inst. Polytech., Osaka City Univ.*, **1**, 23 (1950); *Chem. Abstr.*, **46**, 5036 (1952).

two flanking benzo groups suppresses the aromatic character of the central seven-membered ring even when highly conjugated as in the enol of the dibenzocycloheptadienedione (III).



III



IV

Truce and Lotspeich[11] prepared 3-benzothiepin-3-dioxide (IV), the sulfone analog of benzotropone. Many lines of recent evidence[12,13] indicate that the sulfone group, like the carbonyl group, is capable of conjugation by electron acceptance. However, the properties of IV were best explained by assuming more unsaturated character for the ethylenic bonds than quasi-aromatic character.[11] The inference of this essential lack of quasi-aromatic character is that the seven-membered ring is not appreciably resonance stabilized and is probably nonplanar. Although not so fully conjugated as IV, the optical resolution of 2,7-dihydro-3,4,5,6-dibenzothiepin-1-dioxide-2′,3″-dicarboxylic acid and a wealth of ultraviolet absorption spectra have been presented to indicate that such seven-membered sulfones flanked by biphenylic benzenes are definitely not coplanar.[14]

During the course of this work several 2-sulfonylbiphenyls were prepared. These 2-sulfonylbiphenyls show very characteristic maxima at 270–272 μ and 276–278 μ which are rather analogous to the maxima observed at 264–265 μ and 271–272 μ in alkyl phenyl sulfones (alkylsulfonylbenzenes).[15] This information is summarized in Table I. The interpretation of ultraviolet absorption spectrum of I is complicated by the presence of the carbonyl function adjacent to one of the aromatic nuclei (consult work of Hedden and Brown[16] dealing with the ultraviolet spectra of hindered ketones). A conjugative interaction, through the sulfone function, of the carbonyl group with *both* benzene rings of the bridged biphenyl may be possible. However, such interaction probably would occur *only* with the β-ketosulfone anion.[15] Support of this viewpoint may possibly be indicated by the existence of the remnant of the 271 μ peak in I which is present in all the *unbridged* 2-sulfonylbiphenyls discussed in Table I.

TABLE I

ULTRAVIOLET ABSORPTION OF SULFONYLBENZENES AND 2-SULFONYLBIPHENYLS

Compound (in 95% ethanol)	λ_{max}, μ^a	ϵ
2-Biphenylylmercaptoacetic acid	232	ca. 15,000
Methylsulfonylbenzene[b]	264	980
	271	890
2-Methylsulfonylbiphenyl	270	2,240
	276	2,490
Ethyl phenylsulfonylacetate[b]	266	1,050
	272	890
2-Biphenylylsulfonylacetic acid	(271)	2,330
	276	2,570
2′-Methylsulfonylbiphenyl-2-carboxylic acid (II)	272	—
	277	—
Ethyl 2′-methylsulfonylbiphenyl-2-carboxylate	271	—
	277	—
2,6-Dihydro-2,3,4,5-dibenzothiapin-6-one-1-dioxide (I)	240	—
	(271)	—
Phenylsulfonylacetone[b]	219	8,700
	265	1,120
	272	1,000
α-Phenylsulfonylisopropyl methyl ketone[b]	218	10,000
	266	1,150
	273	1,000

[a] Secondary maxima in all cases, primary maxima being in region 210–217 μ. [b] See ref. 15.

Papanastassiou[17] has observed that nonplanar dibenzo[a,c][1,3]cycloheptadiene-5-one (carbonyl adjacent to aromatic nucleus) shows a principal absorption peak at 233 μ. If the sulfone function adjacent to a benzene ring produces a bathochromic and hyperchromic displacement of the benzenoid absorption[15] towards longer wave lengths, the principal absorption maximum at 240 μ for 6,7-dihydro-2,3,4,5-dibenzothiapin-6-one-1-dioxide (I) would seem in accord with the value observed by Papanastassiou for dibenzo[a,c][1,3]cycloheptadiene-5-one.[17] Admittedly, the situation may be more complex, however.

In view of the work of Bergmann,[18] the infrared spectrum of I also indicates nonplanarity of the seven-membered ring. Thus, both I and nonplanar nonaromatic dibenzotropones[18] display carbonyl absorption bands at 6.0 μ while planar aromatic tropone displays a carbonyl band at 6.1 μ.

In summary, the chemistry and properties of I are in accord with a nonplanar configuration, the material resembling ω-phenylsulfonylacetophenone more than a fully conjugated coplanar biphenyl. The much greater chemical stability of I as contrasted to its β-diketone analog dibenzo-

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(11) W. E. Truce and F. J. Lotspeich, *J. Am. Chem. Soc.*, **78**, 848–850 (1956).

(12) F. G. Bordwell and G. D. Cooper, *J. Am. Chem. Soc.*, **74**, 1058 (1952); F. G. Bordwell and H. M. Anderson, *J. Am. Chem. Soc.*, **75**, 6019 (1953).

(13) W. von E. Doering, et al., *ibid.*, **77**, 509 (1955); *J. Am. Chem. Soc.*, **77**, 514 (1955); *J. Am. Chem. Soc.*, **77**, 521 (1955).

(14) W. E. Truce and D. D. Emrick, *J. Am. Chem. Soc.*, **78**, 6130–6137 (1956).

(15) E. A. Fehnel and M. Carmack, *J. Am. Chem. Soc.*, **71**, 231 (1949); *J. Am. Chem. Soc.*, **72**, 1292–1297 (1950); *cf.* W. E. Truce and R. H. Knospe, *op. cit.*

(16) G. D. Hedden and W. G. Brown, *J. Am. Chem. Soc.*, **75**, 3744–3748 (1953).

(17) Z. B. Papanastassiou, Ph.D. Thesis, University of West Virginia, Morgantown, West Virginia, June 1954.

(18) E. D. Bergmann, E. Fischer, D. Ginsberg, Y. Hirshberg, D. Lavie, M. Mayot, A. Pullman, and B. Pullman, *Bull. soc. chim., France*, (5) **18**, 684 (1951).

[a,c] [1,3]cycloheptadiene-5,7-dione[19] is also noteworthy.

EXPERIMENTAL

Biphenylthiol. The general procedure for converting Grignard reagents to magnesium mercaptides was that of Taboury.[20]

A solution of 60 g. (0.214 mole) of 2-iodobiphenyl in 150 ml. of anhydrous ether was added slowly, with refluxing, to a well stirred suspension of 5.21 g. (0.214 g.-atom) of fine magnesium turnings in 100 ml. of anhydrous ether, employing a crystal of iodine to initiate the reaction. The resulting mixture was refluxed for an additional hour. Eight grams of powdered rhombic sulfur was added to the Grignard solution causing a vigorous reaction to take place. Refluxing was continued for 45 more min. and the mixture was then cautiously acidified with 15% sulfuric acid. The ethereal layer was separated and extracted with two 200-ml. portions of cold 15% sodium hydroxide. The combined sodium hydroxide solutions were then extracted with 100 ml. ether. The sodium hydroxide layer was then acidified with a mixture of ice and concd. hydrochloric acid to precipitate a thick light-greenish oil which was taken up in 200 ml. ether. The ethereal solution was shaken with 60 ml. water and evaporated to give nearly white crystals, m.p. 32–37°. Distillation gave 22.1 g. (56%) of product, b.p. 143° (4 mm.), m.p. 39–40.

Anal. Calcd. for $C_{12}H_{10}S$: C, 77.4; H, 5.38. Found: C, 77.12; H, 5.37.

2-Biphenylyl methyl sulfone. A solution of sodium ethoxide was prepared by dissolving 1.24 g. (0.054 g.-atom) of sodium metal in 25 ml. of absolute ethanol. To this solution was added 5.0 g. (0.027 mole) of 2-biphenylthiol and then a solution of 11.5 g. (0.081 mole) of methyl iodide in 10 ml. of ethanol was run in with vigorous stirring. The mixture was refluxed with stirring for 2 hr. and then the excess alcohol (and methyl iodide) was distilled at 100°. The residue was taken up with 50 ml. water and the oily 2-methylmercaptobiphenyl was separated from the aqueous phase. All of the oily sulfide was oxidized by refluxing for 1 hr. with a mixture of 30 ml. of 30% hydrogen peroxide (about 0.27 mole) and 60 ml. of glacial acetic acid. Upon pouring the resulting solution into excess sodium hydroxide solution and allowing to stand at 0° overnight, crude crystals of sulfone were obtained. Recrystallization from 70% ethanol gave pure white flat platelets of the desired 2-biphenylyl methyl sulfone; yield 5.4 g. (87%), m.p. 100–101°.

Anal. Calcd. for $C_{13}H_{12}SO_2$: C, 67.2; H, 5.17. Found: C, 67.46; H, 5.06.

2-Biphenylylmercaptoacetic acid. A solution of sodium ethoxide was prepared by dissolving 1.92 g. (0.083 g.-atoms) of sodium metal in 150 ml. of absolute ethanol. To this solution was added 15.5 g. (0.083 mole) of 2-biphenylthiol to form the sodium mercaptide. Twenty milliliters (0.19 mole) of ethyl chloroacetate was added slowly with vigorous stirring. After refluxing for 6 hr., most of the ethanol was distilled and the residue was extracted with chloroform. After drying overnight with 10 g. of anhydrous calcium sulfate, the chloroform was removed by distillation and the residue distilled to yield 16.4 g. of pale yellow-oil (70%), b.p. 205–208° (16 mm.), n_D^{20} 1.5952.

Anal. Calcd. for $C_{16}H_{16}SO_2$: C, 70.6; H, 5.88. Found: C, 68.51; H, 6.16.

A mixture of 14 g. (0.0514 mole) of the above ethyl 2-biphenylylmercaptoacetate, 18 ml. of water, 18 ml. of ethanol, and 6 g. (0.15 mole) of sodium hydroxide were refluxed for 5 hr. The resulting solution was poured into 50 g. of ice and was acidified with excess hydrochloric acid. After standing 15 min., the precipitated acid was filtered and washed with cold water. The yield of white crystals was 12.4 g. (98%), m.p. 169–170°.

Anal. Calcd. for $C_{14}H_{12}SO_2$: C, 68.8; H, 4.92; neut. eq. 244. Found: C, 68.50; H, 5.25; neut. eq. 249.

2-Biphenylylsulfonylacetic acid. A mixture of 6.0 g. (0.025 mole) of 2-biphenylylmercaptoacetic acid, 17 ml. of glacial acetic acid, and 7.6 ml. (about 0.07 mole) of 30% hydrogen peroxide were refluxed for 1 hr. and then poured into a cold solution of 15 g. of sodium hydroxide dissolved in 60 ml. of water. After standing at 0° for 1 hr., the solution was filtered and the filtrate was acidified to congo red with concd. hydrochloric acid. The resulting paste was allowed to stand at 0° for 10–12 hr. to complete the precipitation of the white crystalline acid which was filtered and washed with ice water. The yield of glistening white needles was 5.7 g. (84%), m.p. 117–119°. Recrystallization from a minimum of a mixture of benzene and petroleum ether (b.p. 70–90°) gave a product melting at 119–120° (the melted material evolved carbon dioxide at about 185° and turned black at 230°); experimental equivalent weight, 277 (calcd. 276).

Anal. Calcd. for $C_{14}H_{12}SO_4$: C, 60.90; H, 4.37. Found: C, 61.21; H, 4.29.

All attempts to prepare the seven-membered ring *O,O'*-bridged biphenyl, 6,7-dihydro-2,3-4,5-dibenzothiapin-6-one-1-dioxide, (XXIX) by treatment of 2-biphenylylsulfonylacetic acid with concd. sulfuric acid or polyphosphoric acid failed, 2-biphenylyl methyl sulfone being produced with loss of carbon dioxide. The preparation of 2-biphenylylsulfonylacetyl chloride from the free acid under mild conditions (with low boiling oxalyl chloride) and attempted Friedel Crafts cyclization of this material with aluminum chloride or stannic chloride under very mild conditions gave extensive degradation, the only product isolated being impure 2-biphenylyl methyl sulfone.

2'-Methylsulfonylbiphenyl-2-carboxylic acid. (II) *o*-Bromophenylmethyl sulfone[21] was prepared by alkylating sodium *O*-bromobenzenesulfinate[22] with methyl iodide by the general method of Todd and Shriner;[23] 92% yield, m.p. 108–108.5°; Martin[21] reports m.p. 108–108.5°.

Forty-four grams (0.20 mole) of methyl *O*-bromobenzoate and 32 g. (0.136 mole) of *O*-bromophenyl methyl sulfone were heated to 180°, with stirring, by means of an external oil bath. In four portions, 50 g. (0.785 g.-atom) of #445 copper bronze powder was added, maintaining the temperature at 220–230° after each addition for 20 min. and then cooling to 180–190° before adding more copper powder. The resulting mixture was then stirred at 230–240° for 1 hr. and then cooled. The residue was extracted with several portions of refluxing chloroform; the combined extracts were filtered and evaporated on a steam cone to give a brown oil. The resulting oily residue was distilled at 2 mm. until a pot temperature of 200° was achieved, unchanged starting materials and dimethyl diphenate, b.p. 158° (2 mm.), being collected in the distillate to this point. The residue, which was essentially a mixture of 2,2'bis(methylsulfonyl)biphenyl and the desired methyl 2'-methyl-sulfonylbiphenyl-2-carboxylate, was then refluxed with 200 ml. of 15% aqueous potassium hydroxide. The resulting solution was cooled to 0° for 24 hr., filtered, decolorized by boiling with 2 g. of activated charcoal, refiltered, and acidified to give a crude acid. The product was grossly impure but was easily purified by extraction with hot benzene, the desired 2-methylsulfonylbiphenyl-2-carboxylic acid (II) being nearly insoluble in boiling benzene while the other acidic materials were very soluble in benzene. The purified sulfone carboxylic acid was recrystallized from a large volume of a mixture of ben-

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[19] H. W. Lucien and A. Taurins, *Can. J. Chem.*, **30**, 208 (1952).

[20] M. Taboury, *Bull. soc. chim., France*, **29**, 761–2 (1903).

[21] G. A. Martin, *Iowa State Coll. J. Sci.*, **21**, 38–40 (1946); *Chem. Abstr.*, **41**, 952 (1947).

[22] M. E. Hanke, *J. Am. Chem. Soc.*, **45**, 1321–1323 (1923).

[23] H. R. Todd and R. L. Shriner, *J. Am. Chem. Soc.*, **56**, 1383 (1934).

zene and petroleum ether to give pure white crystals, m.p. 187–188°. Two more recrystallizations from 65% ethanol gave beautiful golden-flecked crystals m.p. 194–195°. The crystals showed moderate yellow fluorescence and in strong ethanol solutions showed moderate green fluorescence. The yield of highly purified acid was 4.5 g. (12%); experimental equivalent weight 274 (calcd. 276).

Anal. Calcd. for $C_{14}H_{12}SO_4$: C, 60.90; H, 4.35. Found: C, 60.97; H, 4.49.

The structure of the 2′-methylsulfonylbiphenyl-2-carboxylic acid (II) was confirmed as follows. 2′-Methyl-2-nitrobiphenyl was prepared[24] and reduced to 2-amino-2′-methylbiphenyl.[24] The latter was diazotized and upon treatment with potassium iodide produced 2-iodo-2′-methylbiphenyl[24] in fair yield. The Grignard of 2-iodo-2′-methylbiphenyl upon treatment with sulfur and subsequent acidification (see above preparation of 2-biphenylthiol) produced 2′-methylbiphenyl-2-thiol in 51% yield, b.p. 110–113° (1 mm.), n_D^{20} 1.6272.

2′-Methylbiphenyl-2-thiol treated with sodium ethoxide in ethanol and then methyl iodide produced 2′-methyl-2-methylmercaptobiphenyl as a noncrystallizable oil. Oxidation of the latter sulfide with 30% hydrogen peroxide in glacial acetic acid produced waxy low melting 2′-methyl-2-methylsulfonylbiphenyl which could not be readily recrystallized for analysis. Oxidation with strong sodium dichromate and sulfuric acid in aqueous acetic acid produced fair yields of the desired 2′-methylsulfonylbiphenyl-2-carboxylic acid upon diluting with water and standing for 10 days at 0°. From about 3 g. of starting 2′-methylbiphenol-2-thiol about 0.6 g. of crude acid was obtained. After recrystallization from benzene-petroleum ether mixture and then from 56% ethanol, the material melted at 192–194°; the material failed to depress the melting point of the acid obtained from the mixed Ullman reaction, confirming the structure of the latter.

Two grams of the above highly purified 2′-methylsulfonylbiphenyl-2-carboxylic acid were refluxed for 16 hr. with 5 ml. of thionyl chloride to convert it to the acid chloride. The excess thionyl chloride was distilled *in vacuo* at 100° and the cooled residual acid chloride was then cautiously treated with 6 ml. of ethanol under reflux. After refluxing for 15 min., the resulting solution was poured into ice and the oil shaken first with 5% sodium bicarbonate solution and then water. The oil spontaneously crystallized to form white crystals of ethyl 2′-methylsulfonylbiphenyl-2-carboxylate which was recrystallized from petroleum ether (b.p. 70–90°); yield was 2.0 g. (91%), m.p. 70.5–72°.

Anal. Calcd. for $C_{16}H_{16}SO_4$: C, 63.1; H, 5.26. Found: C, 62.96; H, 5.23.

6,7-Dihydro-2,3-4,5-dibenzothiapin-6-one-1-dioxide (I). Two grams (0.0066 mole) of ethyl 2′-methylsulfonyl-biphenyl-2-carboxylate, 11 ml. of toluene, and 0.30 g. (0.0132 g.-atom) of sodium metal were refluxed with stirring for 18 hr. After cooling, the toluene layer was decanted cautiously into 4*N* aqueous ammonia and shaken. The ammoniacal layer, containing the desired compound, was decolorized by boiling with 0.3 g. of activated charcoal, filtered, and acidified with hydrochloric acid. After standing at 0° for 24 hr., the resulting 6,7-dihydro-2,3-4,5-dibenzothiapin-6-one-1-dioxide was filtered and recrystallized from a minimum of 70% ethanol to give white crystals; yield 1.3 g. (76%), m.p. 167–168°.

The material was stable to hot hydrochloric acid and was reprecipitated unchanged upon acidifying a hot sodium hydroxide solution of the material.

Anal. Calcd. for $C_{14}H_{10}SO_3$: C, 65.1; H, 3.88. Found: C, 65.27; H, 3.86.

The infrared absorption spectrum shows characteristic bands at 5.95μ (6.26μ) (benzoyl type aryl ketone bands); 7.57μ, 8.66μ, and 8.85μ (sulfone bands); and 12.88μ, 13.16μ, and 13.81μ (apparently, substituted phenyl bands). Compare with significant bands in ethyl 2′-methylsulfonylbiphenyl-2-carboxylate at 5.88μ, (aryl ester band), 7.68–7.76μ, 8.69μ (8.79 and 8.86μ) (12.63–12.74μ), 13.09μ, and 13.24μ; and also the significant bands in 2-methylsulfonylbiphenyl at 7.71μ, 8.71μ, 8.90μ, 12.77μ, 13.19μ, and 13.33μ. Planar, aromatic, seven-membered ring, tropone displays carbonyl band at *ca.* 6.1μ while dibenzotropones (believed to contain non-planar, nonaromatic seven-membered rings) have bands at *ca.* 6.0μ.

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[24] R. G. Shuttleworth, W. S. Ropson, E. T. Stewart, *J. Chem. Soc.*, 1944, 71–73.

[CONTRIBUTION FROM THE CHEMISTRY RESEARCH LABORATORY OF THE DEPARTMENT OF SURGERY, UNIVERSITY OF WASHINGTON SCHOOL OF MEDICINE]

Derivatives of Fluorene. IX. 4-Hydroxy-2-fluorenamine; New 3,4-Benzocoumarin Derivatives[1]

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Synthesis of 4-hydroxy-2-fluorenamine, 4-hydroxyfluorene, and related compounds is described. New 7- and 6-substituted 3,4-benzocoumarins were synthesized; the first series was obtained in an alternate attempt to synthesize 4-hydroxy-2-fluorenamine. Ultraviolet and infrared spectral data for several of these new compounds are reported.

Although several ring-hydroxylated metabolites of the carcinogen, *N*-2-fluorenylacetamide have been identified,[3] *N*-2-(4-hydroxyfluorenyl)acetamide has not been reported, nor is there any recorded synthesis. The following describes the preparation of this substance and of 4-hydroxyfluorene, also new to the literature, and of several related derivatives. One approach failed to give the fluorene nucleus when facile splitting of the methoxyl group

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[3] E. K. Weisburger and J. H. Weisburger in J. P. Greenstein and A. Haddow (eds.), *Advances in Cancer Research, Vol. V*, Academic Press, Inc., New York, N.Y., 1958, pp. 409–418.