

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND PURDUE RESEARCH FOUNDATION, PURDUE UNIVERSITY]

Friedel-Crafts Cyclization of ω -Phenylalkanesulfonyl Chlorides¹BY WILLIAM E. TRUCE AND JERRY P. MILIONIS²

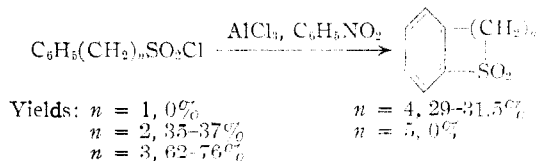
The internal Friedel-Crafts conversion of ω -phenylalkanesulfonyl chlorides to the corresponding cyclic sulfones (intramolecular sulfonylation) has been realized for three sulfonyl chlorides. 2-Phenyl-1-ethanesulfonyl chloride gave a 35-37% yield of 2,3-dihydrothianaphthene-1,1-dioxide. 3-Phenyl-1-propanesulfonyl chloride was converted to 3,4-dihydro-1,2-benzothiopyran-1,1-dioxide (thiachroman-S-dioxide) in 62-76% yield. 2,3,4,5-Tetrahydro-1-benzothiepin-1,1-dioxide (homothiachroman-S-dioxide) was formed in 29-31.5% yield from 4-phenyl-1-butanesulfonyl chloride. Several attempts to cyclize phenylmethanesulfonyl chloride and 5-phenyl-1-pentanesulfonyl chloride were unsuccessful.

Considerable work has been done in the past on the preparation of sulfones by Friedel-Crafts reactions with aromatic sulfonyl chlorides.³ The only record of an alkanesulfonyl chloride taking part in a Friedel-Crafts reaction is the report that methanesulfonyl chloride reacts with benzene to give methyl phenyl sulfone in poor yield.⁴

The present work is concerned with the internal Friedel-Crafts reaction of ω -phenylalkanesulfonyl chlorides leading to cyclic sulfones.

Phenylmethanesulfonyl chloride⁵ and 2-phenyl-1-ethanesulfonyl chloride⁶ were prepared from the corresponding sodium sulfonates and phosphorus pentachloride. 3-Phenyl-1-propanesulfonyl chloride, 4-phenyl-1-butanesulfonyl chloride and 5-phenyl-1-pentanesulfonyl chloride were synthesized by treating the appropriate disulfides with chlorine in the presence of water and glacial acetic acid.⁷ Sodium alkyl thiosulfates, prepared from the corresponding bromides and sodium thiosulfate, were converted to the desired disulfides by means of potassium hydroxide⁸ or iodine.⁹ Several attempts to prepare 3-phenyl-1-propanesulfonyl chloride from the sodium sulfonate by treatment with phosphorus pentachloride¹⁰ resulted in poor yields (3.3% and 6.7%) of thiachroman-S-dioxide only.

Results in the Friedel-Crafts cyclizations were dependent on the solvent and catalyst employed. Stannic chloride in *sym*-tetrachloroethane was not sufficiently active for the reaction to occur. Aluminum chloride in the same solvent resulted in decomposition products. However, satisfactory reactions were obtained when aluminum chloride was employed with nitrobenzene as the solvent.



(1) An abstract of a thesis submitted by Jerry P. Milionis to the Faculty of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1951. Presented at the XIIth Meeting of the International Congress of Pure and Applied Chemistry, September, 1951.

(2) American Cyanamid Fellow, 1949-1950.

(3) C. M. Suter, "The Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 673-675.

(4) J. Boeseke and H. W. von Ockenburg, *Rec. trav. chim.*, **33**, 326 (1914).

(5) T. B. Johnson and J. A. Ambler, *THIS JOURNAL*, **36**, 381 (1914).

(6) M. S. Kharasch, E. M. May and F. R. Mayo, *J. Org. Chem.*, **3**, 175 (1938).

(7) S. W. Lee and G. Dougherty, *ibid.*, **5**, 81 (1940).

(8) R. E. Stutz and R. L. Shriner, *THIS JOURNAL*, **55**, 1242 (1933).

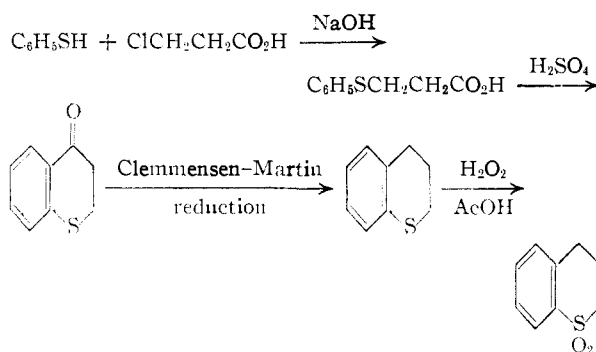
(9) H. E. Westlake and G. Dougherty, *ibid.*, **64**, 149 (1942).

(10) P. W. Clutterback and J. B. Cohen, *J. Chem. Soc.*, **123**, 2507 (1923).

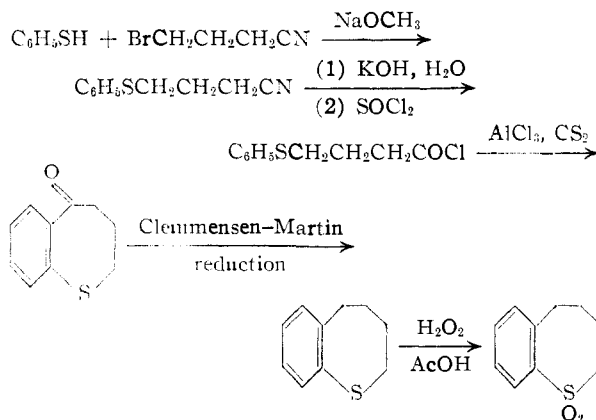
The following order of reactivity was observed $\text{C}_6\text{H}_5(\text{CH}_2)_3\text{SO}_2\text{Cl} > \text{C}_6\text{H}_5(\text{CH}_2)_2\text{SO}_2\text{Cl} \approx \text{C}_6\text{H}_5(\text{CH}_2)_4\text{SO}_2\text{Cl}$.

Work is now in progress to determine preference of ring formation between the five- and seven-membered rings by the cyclization of 1,5-diphenyl-2-pentanesulfonyl chloride.

The proof of structure of the product obtained from 2-phenyl-1-ethanesulfonyl chloride consisted of comparing it with an authentic sample of 2,3-dihydrothianaphthene-1,1-dioxide which was prepared from thianaphthene.^{11,12} The product obtained from 3-phenyl-1-propanesulfonyl chloride was shown to be 3,4-dihydro-1,2-benzothiopyran-1,1-dioxide (thiachroman-S-dioxide) by the independent synthesis^{13,14}



2,3,4,5-Tetrahydro-1-benzothiepin-1,1-dioxide (homothiachroman-S-dioxide) was shown to be the product from 4-phenyl-1-butanesulfonyl chloride by the series of reactions¹⁵



(11) F. C. Bordwell, B. B. Lampert and W. H. McKellin, *THIS JOURNAL*, **71**, 1702 (1949).

(12) F. Challenger and P. H. Clapham, *J. Chem. Soc.*, 1615 (1948).

(13) F. Krollpfeiffer, *et al.*, *Ber.*, **56**, 1819 (1923).

(14) F. Arndt, *et al.*, *ibid.*, **56**, 1269 (1923).

(15) P. Cagniant and A. Deluzarche, *Compt. rend.*, **223**, 677 (1946).

The isolation of the ω -phenylalkanesulfonamides makes it possible to cite the series $C_6H_5(CH_2)_nSO_2NH_2$ as another in which there is an alternation in melting points. This observation was originally made by Evans, *et al.*,¹⁶ for the first four members (n , 0-3). The next two members of the series (n , 4 and 5) comply with the rule.

n	M.p., °C., observed	M.p., °C., reported
0	153 ¹⁷
1	103.5-104.0	105 ¹⁰
2	122.0-123.0	121.5-122.5 ¹³
3	60.5-61.0	35 ¹⁰
4	103.0-104.5	..
5	80.5-81.0	..

Experimental¹⁹

Phenylmethanesulfonyl Chloride.—This compound was prepared in 55% yield from sodium phenylmethanesulfonate and phosphorus pentachloride⁵; m.p. 92-93°; reported²⁰ m.p. 92-93°.

By adding dry gaseous ammonia to a small quantity of phenylmethanesulfonyl chloride dissolved in anhydrous diethyl ether, the sulfonamide was prepared. Recrystallization from diethyl ether gave a solid, m.p. 103.5-104.0°; reported¹⁰ m.p. 105°.

2-Phenyl-1-ethanesulfonyl Chloride.—Ninety grams (0.43 mole) of sodium 2-phenyl-1-ethanesulfonate¹⁶ and 33.3 g. of phosphorus pentachloride gave 47 g. (53.6%) of the sulfonyl chloride⁶, b.p. 134-135° (4 mm.), n_D^{20} 1.5457.

2-Phenyl-1-ethanesulfonamide, prepared from the sulfonyl chloride and aqueous ammonia, was recrystallized from ethanol, m.p. 122-123°; reported¹⁸ m.p. 121.5-122.5°.

Attempted Preparation of 3-Phenyl-1-propanesulfonyl Chloride.—Fifty-one and one-half grams (0.25 mole) of phosphorus pentachloride was added gradually to 111 g. (0.5 mole) of sodium 3-phenyl-1-propanesulfonate¹⁰ suspended in 600 ml. of dry chloroform. A vigorous reaction occurred after each addition. The mixture was heated on a steam-bath for three hours and then was cooled before it was poured on ice and the chloroform layer separated. Evaporation of the chloroform gave an oil which solidified with difficulty. This solid, thiachroman-S-dioxide (3,4-dihydro-1,2-benzothiazopyran-1,1-dioxide), was recrystallized from ether, m.p. 89.0-89.5° (uncor.); yield 3.0 g., 3.3%. None of the desired sulfonyl chloride was obtained.

A second experiment, starting with 62 g. (0.28 mole) of the sulfonate, gave 3.4 g. (6.7%) of thiachroman-S-dioxide, m.p. 88.5-89.0° (uncor.). The m.p. was not depressed when mixed with an authentic sample prepared as described below.

Bis-(3-phenyl-1-propyl) Disulfide.—A mixture of 99.5 g. (0.5 mole) of 1-bromo-3-phenylpropane, 250 ml. of ethanol, 150 g. of sodium thiosulfate pentahydrate and 250 ml. of water was refluxed for two hours. Seventy grams of potassium hydroxide in 150 ml. of water was then added and the solution was refluxed for an additional hour. The mixture was diluted with water and was extracted with ether. Distillation of the ethereal solution gave 44.0 g. (58.3%) of bis-(3-phenyl-1-propyl) disulfide, b.p. 194-195° (1.5 mm.), 165-166° (0.03-0.04 mm.), n_D^{20} 1.5877.

Anal. Calcd. for $C_{13}H_{22}S_2$: C, 71.49; H, 7.33. Found: C, 71.59; H, 7.23.

This compound was also prepared employing a slight modification of the method of Westlake and Dougherty.⁹ A mixture of 99.5 g. (0.5 mole) of 1-bromo-3-phenylpropane, 124 g. (0.5 mole) of sodium thiosulfate, 250 ml. of ethanol and 250 ml. of water was refluxed with stirring for two hours. One hundred and fifty milliliters of ethanol was removed by distillation and iodine was added in small portions to the hot

reaction mixture until the color remained. A small excess of iodine was then added and the mixture was allowed to stand overnight at room temperature. The mixture was diluted with water and was extracted with ether. The ethereal solution, after being washed with dilute sodium bisulfite solution, water, and dried, gave 72.5 g. (96%) of crude disulfide, n_D^{20} 1.5872.

3-Phenyl-1-propanesulfonyl Chloride.—A solution of 30.2 g. (0.1 mole) of bis-(3-phenyl-1-propyl) disulfide, 200 ml. of glacial acetic acid and 7.2 g. (0.4 mole) of water was treated with 30 ml. (0.67 mole) of gaseous chlorine at room temperature (25°). The solution was then poured on ice, extracted with ether and the ethereal solution washed with dilute solutions of sodium bisulfite and sodium bicarbonate, water, and dried over anhydrous sodium sulfate. Distillation gave 30 g. (69%) of 3-phenyl-1-propanesulfonyl chloride, b.p. 121.0-123.5° (1.5 mm.), 113.0-113.5° (0.2 mm.), n_D^{20} 1.5401. Considerable difficulty was encountered in the purification of this material.

Anal. Calcd. for $C_9H_{11}O_2SCl$: C, 49.42; H, 5.07. Found: C, 48.49; H, 4.57.

A small amount of the sulfonyl chloride was redistilled at 127° (2.0 mm.), n_D^{20} 1.5388.

Anal. Calcd. for $C_9H_{11}O_2SCl$: C, 49.42; H, 5.07; Cl, 16.21. Found: C, 50.56; H, 5.37; Cl, 16.18.

Treatment of a few grams of the sulfonyl chloride with aqueous ammonia gave 3-phenyl-1-propanesulfonamide. This was also prepared by addition of dry ammonia gas to the sulfonyl chloride dissolved in ether. Both products were recrystallized from low boiling petroleum ether, m.p. 60.5-61.0°, reported¹² m.p. 35°.

Anal. Calcd. for $C_9H_{11}O_2NS$: C, 54.23; H, 6.57; N, 7.03. Found: C, 54.45; H, 6.53; N, 7.28.

Bis-(4-phenyl-1-butyl) Disulfide.—4-Phenylbutanoic acid²¹ was reduced with lithium aluminum hydride by the method of Nystrom and Brown²² to 4-phenyl-1-butanol (71.5%); b.p. 125-126° (8 mm.), n_D^{20} 1.5220. Two hundred and thirty-four grams (1.56 moles) of the alcohol was treated with 500 g. of phosphorus tribromide to give 1-bromo-4-phenylbutane (239 g., 71.8%); b.p. 129-130° (12 mm.), n_D^{20} 1.5400.

A mixture of 213 g. (1.0 mole) of 1-bromo-4-phenylbutane, 300 g. of sodium thiosulfate pentahydrate, 500 ml. of ethanol and 400 ml. of water was refluxed with stirring for two hours. One hundred and forty grams of potassium hydroxide in 300 ml. of water was then added and the solution refluxed an additional hour. The reaction product was diluted with water, extracted with ether, and the ethereal solution dried over sodium sulfate. Distillation of the product, after removal of ether, yielded bis-(4-phenyl-1-butyl) disulfide (110.4 g., 66.7%); b.p. 195° (0.2 mm.), n_D^{20} 1.5750.

*Anal.*²³ Calcd. for $C_{20}H_{26}S_2$: C, 72.70; H, 7.93. Found: C, 73.35; H, 8.11.

4-Phenyl-1-butanensulfonyl Chloride.—A solution of 63 g. (0.18 mole) of bis-(4-phenyl-1-butyl) disulfide, 14.4 g. (0.8 mole) of water and 500 ml. of glacial acetic acid was treated with 70.8 g. (1.0 mole) of chlorine at room temperature. The reaction mixture was diluted with water and extracted with ether. The ether extract was washed with dilute sodium bisulfite solution, dilute sodium bicarbonate solution, water, and dried over sodium sulfate. Distillation of the product, after removal of ether, gave 4-phenyl-1-butanensulfonyl chloride (58.5 g., 71.0%); b.p. 151-153° (1.5 mm.), n_D^{20} 1.5370.

Anal. Calcd. for $C_{10}H_{13}O_2SCl$: C, 51.61; H, 5.63. Found: C, 51.51; H, 5.64.

By adding dry ammonia gas to a small amount of 4-phenyl-1-butanensulfonyl chloride in anhydrous ether, the sulfonamide was prepared. Recrystallization from 35-37° petroleum ether gave a solid, m.p. 103.0-104.5°.

Anal. Calcd. for $C_{10}H_{13}O_2NS$: C, 56.30; H, 7.09; N, 6.58. Found: C, 56.39; H, 7.12; N, 6.91.

(16) E. B. Evans, E. E. Mabbott and E. E. Turner, *J. Chem. Soc.*, 1159 (1927).

(17) J. Stenhouse, *Ann.*, **140**, 294 (1866).

(18) T. B. Johnson and J. M. Sprague, *THIS JOURNAL*, **58**, 1348 (1936).

(19) All melting points are corrected unless otherwise indicated.

(20) E. Fromm and J. Palma, *Ber.*, **39**, 3312 (1906).

(21) E. L. Martin, *THIS JOURNAL*, **58**, 1438 (1936).

(22) R. F. Nystrom and W. C. Brown, *ibid.*, **69**, 2548 (1947).

(23) Disulfides have been known to disproportionate to sulfides and trisulfides when heated to high temperatures, O. Hinsberg, *Ber.*, **43**, 1874 (1910). This is probably the reason for the discrepancy in the analysis for carbon.

TABLE I
 FRIEDEL-CRAFTS REACTIONS OF 2-PHENYL-1-ETHANESULFONYL CHLORIDE

Sulfonyl chloride mole	Catalyst, mole	Solvent, g.	Temp., °C.	Time, min.	Product	Recovered sulfonyl chloride, mole		
0.049 ^a	SnCl ₄	0.108	CHCl ₂ CHCl ₂	100	100	120	0.0357
.1 ^b	AlCl ₃	.1	CHCl ₂ CHCl ₂	200	22	120	Decomposition products, free S	Trace
.1 ^a	AlCl ₃	.2	CHCl ₂ CHCl ₂	200	25	60	Decomposition products, free S	0.0046
.086 ^b	AlCl ₃	.2	CHCl ₂ CHCl ₂	190	8-11	300605
.1 ^b	AlCl ₃	.11	C ₆ H ₅ NO ₂	150	40	600229
.1 ^b	AlCl ₃	.11	C ₆ H ₅ NO ₂	150	80	60	Sulfone ^c
.1 ^b	AlCl ₃	.11	C ₆ H ₅ NO ₂	150	90	75	Sulfone ^c

^a Catalyst was added to a cold solution of the sulfonyl chloride in the solvent. ^b The sulfonyl chloride dissolved in the solvent was added to a cold solution of the catalyst in the same solvent. ^c See Table II.

 TABLE II
 FRIEDEL-CRAFTS REACTIONS OF ω-PHENYLALKANESULFONYL CHLORIDES

Sulfonyl chloride	Mole	AlCl ₃ , mole	C ₆ H ₅ NO ₂ , g.	Temp., °C.	Time, min.	Product	Yield, %	Recovered sulfonyl chloride, mole
Phenylmethane-	0.10	0.11	250	25	30	Decomposition products
	.053	.06	200	7	300	Decomposition products
2-Phenyl-1-ethane-	.10	.11	150	40	60	2,3-Dihydrothianaphthene-		
				80	60	1,1-dioxide ^{a,b}	37.0	0.023
3-Phenyl-1-propane-	.10	.11	150	90	75		35.1
	.05	.06	75	50-60	210	Thiachroman-S-dioxide ^{a,c}	61.6
4-Phenyl-1-butane-	.034	.05	150	87-90	150		76.2
	.065	.08	150	85-90	75	Homothiachroman-S-	31.5	0.0047
5-Phenyl-1-pentane-	.045	.06	150	100	120	dioxide ^{a,d}	27.6	.0039
	.051	.065	150	90-94	60	Decomposition products ^e	..	.0053
	.05	.05	150	60	120	Decomposition products	..	.0105

^a The m.p. of the sulfone was not depressed when mixed with an authentic sample prepared as described below. ^b Recrystallized from absolute ethanol, m.p. 90.5-91.5°. *Anal.* Calcd. for C₈H₉O₂S: C, 57.14; H, 4.79. Found: C, 57.11; H, 4.76. ^c Recrystallized from 60-70° petroleum ether, m.p. 87-88°. *Anal.* Calcd. for C₉H₁₀O₂S: C, 59.31; H, 5.53. Found: C, 59.45; H, 5.57. ^d Recrystallized from 60-70° petroleum ether, m.p. 77-78°. *Anal.* Calcd. for C₁₀H₁₂O₂S: C, 61.17; H, 6.16. Found: C, 61.20; H, 6.15. ^e A few crystals of a white solid were obtained which sublimed at 191-193°.

Bis-(5-phenyl-1-pentyl) Disulfide.—5-Phenyl-1-pentanol²⁴ was synthesized from 3-phenyl-1-propylmagnesium bromide and excess ethylene oxide in 55.5% yield; b.p. 128.0-128.5° (6 mm.), *n*_D²⁰ 1.5160. Two hundred and forty grams (1.46 moles) of the alcohol was treated with 400 g. of phosphorus tribromide to give 241.3 g. (73%) of 1-bromo-5-phenylpentane,²⁴ b.p. 99.0-101.5° (1.5 mm.), *n*_D²⁰ 1.5328.

A mixture of 100 g. (0.44 mole) of 1-bromo-5-phenylpentane, 109 g. of sodium thiosulfate pentahydrate, 250 ml. of ethanol and 250 ml. of water was refluxed for two hours. Iodine, in small portions, was added while the solution was hot until the color remained. The product was diluted with water and extracted with ether. The aqueous layer was heated to remove the ethanol and then extracted again with ether.

Crop	Yield, g.	<i>n</i> _D ²⁰
1	40.0	1.5630
2	25.3	1.5663

The yield of crude disulfide was 82.6%. Attempts to purify this compound by distillation under reduced pressure were unsuccessful. Purification was finally achieved by low temperature crystallization from low boiling petroleum ether, m.p. 23-24°.

Anal. Calcd. for C₂₂H₃₀S₂: C, 73.66; H, 8.43. Found: C, 73.80; H, 8.37.

5-Phenyl-1-pentanesulfonyl Chloride.—A solution of 25 g. (0.07 mole) of crude bis-(5-phenyl-1-pentyl) disulfide, 5.04 g. (0.28 mole) of water and 250 ml. of glacial acetic acid was treated with 25.4 g. of chlorine. The reaction mixture was subjected to the same procedure used for 4-phenyl-1-butanesulfonyl chloride. Distillation gave 27.5 g. (80%) of 5-phenyl-1-pentanesulfonyl chloride, b.p. 131-132° (0.5 mm.), *n*_D²⁰ 1.5300.

Anal. Calcd. for C₁₁H₁₅O₂SCl: C, 53.55; H, 6.13. Found: C, 53.70; H, 6.23.

A small amount of sulfonyl chloride was treated with aqueous ammonia to give 5-phenyl-1-pentanesulfonamide. The sulfonamide, after recrystallization from benzene, melted at 80.5-81.0°.

Anal. Calcd. for C₁₁H₁₇O₂NS: C, 58.11; H, 7.54; N, 6.16. Found: C, 58.09; H, 7.40; N, 6.24.

General Friedel-Crafts Procedure.—The sulfonyl chloride, dissolved in nitrobenzene, was added with stirring to a cold solution of anhydrous aluminum chloride and nitrobenzene. The ice-bath was removed and the reaction was allowed to proceed at the temperature and for the time indicated in Table II for each sulfonyl chloride. An ice-bath was used to cool the mixture before it was poured into an ice-water-hydrochloric acid mixture. Vigorous agitation was necessary to decompose the addition complex. The reaction mixture was extracted with ether and the ethereal solution was washed with dilute sodium bicarbonate solution, water, and dried over anhydrous sodium sulfate. Ether and nitrobenzene were removed by distillation under reduced pressure. Distillation was continued in order to recover any unreacted sulfonyl chloride and the residue was extracted with petroleum ether (60-70°). Evaporation of the solvent gave the solid sulfone.

In the case of homothiachroman-S-dioxide, obtained from 4-phenyl-1-butanesulfonyl chloride, distillation of the residue gave a mixture of the sulfone and unreacted sulfonyl chloride, b.p. 151-159° (1.5 mm.). The distillate was treated with petroleum ether (60-70°), placed in the refrigerator for several hours, and the sulfone was filtered off.

The results of the exploratory experiments to determine the proper solvent and catalyst are given in Table I.

2,3-Dihydrothianaphthene-1,1-dioxide.—A solution of thianaphthene in glacial acetic acid was treated with 30% hydrogen peroxide to give thianaphthene-1,1-dioxide,¹¹ m.p. 139.0-140.5°. The latter compound was reduced with zinc in sodium hydroxide solution to the 2,3-dihydrothianaphthene-1,1-dioxide¹² (69%); recrystallized from boiling water, m.p. 90.5-91.5°.

Thiachroman-S-dioxide (3,4-Dihydro-1,2-benzothiapyrans-1,1-dioxide).—3-Phenylmercaptopropanoic acid,¹⁴ prepared from thiophenol and 3-chloropropanoic acid, was converted by means of concentrated sulfuric acid to 4-thiachromanone¹⁵ (67.7%); b.p. 112–114° (1.5 mm.), m.p. 29.0–29.5°, n_D^{20} 1.6397. Semicarbazone: recrystallized from dilute alcohol melted at 215–216° (uncorrected). The reported m.p. is 219–220°.¹⁵

Fifty-nine grams (0.36 mole) of the ketone was reduced by the Clemmensen–Martin procedure²¹ to thiachroman (32.1 g., 59.5%); b.p. 121–122° (11 mm.), n_D^{20} 1.6148. The cyclic sulfide was then oxidized with 30% hydrogen peroxide to give thiachroman-S-dioxide; recrystallized from boiling water, m.p. 87.5–88.0°.

Homothiachroman-S-dioxide.—4-Phenylmercaptobutanenitrile²⁶ was prepared from 134.7 g. (0.91 mole) of 4-bromobutanenitrile,²⁶ 100 g. (0.91 mole) of thiophenol and 51.3 g. (0.95 mole) of sodium methoxide, b.p. 132–133° (1.5 mm.), n_D^{20} 1.5667; yield 108.2 g., 67.3%.

One hundred and five grams (0.594 mole) of 4-phenylmercaptobutanenitrile, 89 g. (1.59 moles) of potassium hydroxide, 70 ml. of water and 340 ml. of absolute ethanol was refluxed for 18 hours. The ethanol was removed by distilla-

tion, water was added to the residue, and the solution was acidified with concentrated hydrochloric acid. 4-Phenylmercaptobutanoic acid was filtered off and dried; 107.3 g., 91.5%; m.p. 68.0–68.5°. Treatment of the acid with thionyl chloride gave a 96.5% yield of 4-phenylmercaptobutanoyl chloride, b.p. 129–130° (1.5 mm.), n_D^{20} 1.5695. The amide melted at 96.0–96.5°.

A solution of 100 g. (0.467 mole) of 4-phenylmercaptobutanoyl chloride and 550 ml. of carbon disulfide was treated with 110 g. of aluminum chloride over a period of one-half hour. The temperature was maintained at 5° during the addition of the catalyst and then the reaction mixture was allowed to stand for three hours at room temperature. Distillation of the product gave 65.5 g. (79%) of 5-homothiachromanone, b.p. 119.5–120.0° (1.5 mm.), n_D^{20} 1.6228. Semicarbazone: recrystallized from dilute alcohol melted at 222° (uncorrected). The reported¹⁵ m.p. is 213°.

The ketone was converted by means of the Clemmensen–Martin reduction²¹ to homothiachroman (55.5%), b.p. 103–104° (3 mm.).

Ten grams of homothiachroman was refluxed with 40 ml. of 30% hydrogen peroxide and 150 ml. of glacial acetic acid for four hours. The mixture was cooled, poured on ice, and the sulfone was filtered off and recrystallized from 60–70° petroleum ether, m.p. 77–78°; yield 8.1 g., 67.5%.

(25) A. A. Goldberg and W. Kelly, *J. Chem. Soc.*, 1369 (1947).

(26) O. K. Behrens, *et al.*, *J. Biol. Chem.*, **175**, 789 (1948).

LAFAYETTE, INDIANA

RECEIVED AUGUST 29, 1951

[CONTRIBUTION NO. 101 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

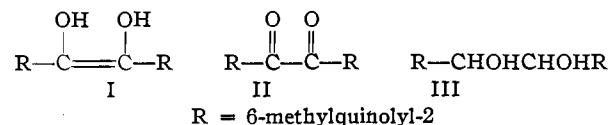
The Benzin Condensation of 6-Methylquinaldehyde

BY C. A. BUEHLER AND S. PAUL EDWARDS

The benzin condensation of 6-methylquinaldehyde produced 1,2-di-(6-methylquinolyl-2)-1,2-ethenediol, 1,2-di-(6-methylquinolyl-2)-1,2-ethanediol and 6-methylquinaldic acid. A *trans* chelated formula has been assigned to the enediol on the basis of its physical and chemical properties.

In a recent publication¹ it was shown that quinaldehyde when subjected to the benzin condensation does not give the benzin, but instead the enediol and the reduced enediol or glycol. The enediol, in contrast to the proposal of Brown and Hammick,² was assigned a *trans* chelated structure from a study of its physical and chemical properties.

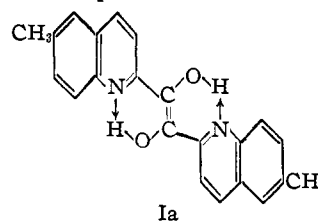
A similar study of 6-methylquinaldehyde produced parallel results. The enediol I is a brown-black solid, m.p. 258° (dec.), which decolorized sodium 2,6-dichlorobenzeneoneindophenol and reduced Tollens reagent in the cold. It formed a



dibenzoate, m.p. 280° (dec.), and in bubbling air through a dioxane solution a yellow benzil (II), m.p. 278° (dec.), not in agreement with Brown and Hammick's value² of 250–251°, was obtained. The presence of the hydroxyl group in the enediol is not shown by infrared absorption.³ All these properties of the enediol are best explained on the basis of the *trans* chelated form Ia.

A comparison of ultraviolet absorption spectrum of the enediol with that of *trans*-9,9'-diphenanthryl-

ethylene⁴ and that of the *trans*-enediol of 9,9'-phenanthroin⁴ (Fig. 1) shows sufficient similarity to offer some support for the presence of the ethylenic double bond conjugated with condensed ring systems. The first maxima of the curves agree well, although the intermediate shoulder does not appear in the enediol and the second maximum of the enediol exhibits a pronounced hypsochromic effect over that shown by the reference compounds. Insufficient data are available to say whether this effect is due even in part to chelation, which might be expected to reduce the basic character of the ring nitrogens and thus decrease the contribution of the charge separation forms possible for the excited state. It is of interest to note, however, that Ewing and Steck⁵ were unable to detect any chelation in 8-quinolol by ultraviolet absorption.



As in the case of quinaldil, whose proposed structure also differed from that suggested by Brown and Hammick,² the benzil II appears to have the conventional structure in that it formed a

(1) C. A. Buehler and J. O. Harris, *THIS JOURNAL*, **72**, 5015 (1950).

(2) B. Brown and D. L. Hammick, *J. Chem. Soc.*, 623 (1950).

(3) The hydroxyl group absorption failed to make its appearance even in a special experiment in which a saturated solution of the enediol in carbon tetrachloride using a cell thickness of 5 mm. was employed.

(4) Y. Hirschberg and F. Bergmann, *THIS JOURNAL*, **72**, 5118 (1950); R. N. Jones, *ibid.*, **67**, 1956 (1945).

(5) G. W. Ewing and E. A. Steck, *ibid.*, **68**, 2182 (1946).