It is curious that the values of titanium, barium and sulfate experimentally obtained by these authors should correspond not with the correct recalculated values but with the wrong ones given by them. Even assuming the formula $BaSO_4 \cdot Ti(SO_4)_2$ the figures obtained are titanium, 10.1%; barium, 29.1%; and sulfate, 61.0%, which do not agree with the experimental values given by Weinland and Kühl.

Summary

It is shown that while it is possible to prepare $CaSO_4 \cdot Ti(SO_4)_2$ described by Weinland and Kühl the strontium compound $SrSO_4 \cdot Ti(SO_4)_2$ and the barium compound $2BaSO_4 \cdot 3Ti(SO_4)_2$ described by these authors could not be obtained in spite of following the details given by these authors. It has been shown that the solid phase which separated out consisted of $TiOSO_4$.

Two more compounds of the type $RSO_4 \cdot Ti(SO_4)_2$ where R = nickel and cadmium have been prepared and described.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

The Absorption Spectra of Some Chloro-Substituted Tetracyclones

BY FLOYD J. THALLER,[1] DONALD E. TRUCKER AND ERNEST I. BECKER

Although tetracyclone[2,3,4] (tetraphenylcyclopentadienone) and a number of its substituted derivatives and analogs[5,6,7,8] have been prepared, no absorption data for any have been published. In view of the fact that these substances are all highly colored, it seemed desirable to synthesize several and measure their absorption spectra. Tetracyclones containing chlorine atoms were chosen in this report. The chlorine-containing tetracyclones were prepared employing the basic reaction of Dilthey and co-workers[4,6] in which benzil and dibenzyl ketone, or their appropriately substituted derivatives, in ethanol are condensed in the presence of potassium hydroxide. The appropriate pairs of compounds condensed readily to give the desired tetracyclones. The three new compounds—A-II, A-III and A-IV—are dark purple, dichroic, high-melting substances. Each was derivatized by conversion to its corresponding colorless tetraphenylphthalic anhydride by reaction with chloromaleic anhydride in bromobenzene, according to the elegant procedure of Synerholm.[9]

TABLE I

TETRACYCLONES (SERIES A) (FIG. 1) AND TETRAPHENYLPHTHALIC ANHYDRIDES (SERIES B)

			Analyses, %							
			Carbon			Hydrogen			Chlorine	
Compound	M. p., °C.	Yield, %	Calcd.	Found		Calcd.	Found		Calcd.	Found
A-I: $R_1 = R_2 = H$	219–220	91–96[a]								
A-II: $R_1 = H, R_2 = Cl$	239–240	92[b]	76.83	76.62	76.59	4.00	4.22	4.12	15.64	15.32
A-III: $R_1 = Cl, R_2 = H$	253–254	85[b]	76.83	76.89	76.76	4.00	4.30	4.33	15.64	15.40
A-IV: $R_1 = R_2 = Cl$	297–299	82[b]	66.69	66.81		3.09	2.96		27.16	27.09
B-I: $R_1 = R_2 = H$	288[c]	83[c]								
B-II: $R_1 = H, R_2 = Cl$	277–278	73[d]	73.71	73.77		3.48	3.53		13.60	13.70
B-III: $R_1 = Cl, R_2 = H$	299.5–300.5	27[d]	73.71	73.33		3.48	3.70		13.60	13.43
B-IV: $R_1 = R_2 = Cl$	373–374	31[d]	65.11	65.22		2.73	2.73		24.03	24.14

[a] Reference 12. [b] The yields are for the once recrystallized products. [c] Reference 9. [d] The yields are for the twice recrystallized products.

The absorption spectra were determined in a Beckman quartz spectrophotometer, Model DU, using 1-cm. quartz cells and a concentration of 1.5 × 10^{-4} molar in benzene (see Fig. 1 and Table II). It was found necessary to obtain the spectra soon after making up the solutions since the absorption characteristics changed on standing. It should be noted that the introduction of chlorine atoms into the tetracyclone molecule does not drastically alter its spectrum.

TABLE II

SPECTRAL CHARACTERISTICS OF THE TETRACYCLONES

	$\lambda(1)$	$a_m(1)$	$\lambda(2)$	$a_m(2)$
A-I	342	6760	512	1320
A-II	340	7880	514	1220
A-III	341	7080	512	1750
A-IV	341	8600	514	1580

Experimental

All melting points are corrected.

Starting Materials.—4-Chlorophenylacetic acid (m.p. 103.5–106°) was prepared through the nitrile from 4-chlorobenzyl chloride[10,11] [b.p. 109.5–111° (21–23 mm.)]. Dibenzyl ketone [b.p. 174–179° (15–17 mm.), 198–199° (24

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[1] Taken from a thesis by F. J. T. for the B.S. degree, Polytechnic Institute of Brooklyn, June, 1949.

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[8] B. A. Arbusov and Dzh. A. Akhmed-Zade, *J. Gen. Chem.* (*U. S. S. R.*), **12**, 212 (1942); *C. A.*, **37**, 2733[7] (1943).

[9] M. E. Synerholm, THIS JOURNAL, **67**, 1229 (1945).

[10] R. von Walther and A. Wetzlich, *J. prakt. Chem.*, [2] **61**, 187 (1900).

[11] F. Beilstein, A. Kuhlberg and E. Neuhof, *Ann.*, **147**, 346 (1868).

mm.)] was obtained by pyrolyzing calcium phenylacetate.[12] 4,4′-Dichlorobenzil [m.p. 195–196° (from *n*-butanol)] was prepared from 4-chlorobenzaldehyde.[13,14,15]

1,3-Bis-(4′-chlorophenyl)-2-propanone.—This compound was synthesized according to Kenner and Morton.[16] Since experimental details are lacking, they are given here.

4-Chlorophenylacetic acid (171 g., 1.0 mole) was dissolved in 500 ml. of hot water containing sodium carbonate (53 g., 0.5 mole). After making the solution just acid to litmus with acetic acid, a solution of lead acetate trihydrate (190 g., 0.5 mole) in 200 ml. of water was added. The lead salt precipitated at once. After cooling, it was filtered with suction and dried at 90–100°.

The salt was transferred to a 2-l. distillation flask and heated in a silicone oil-bath to 280–290°. After 15 minutes at this temperature, the pressure was reduced to 5 to 10 mm. and the product was collected until a red oil began to distil. Recrystallization of the distillate from 95% ethanol gave 65 g. (0.23 mole, 46%) of colorless ketone, m.p. 90–92° (reported: 93°,[16] 98–99°[17]). The semicarbazone melted 116–118° (reported[16] 118°).

Tetracyclones.—The procedure employed was that for tetracyclone reported by Dilthey and Quint[4] and modified by Johnson and Grummitt.[18] The quantities of starting materials varied from 0.05 to 0.12 mole. When 4,4′-dichlorobenzil was used, about 20% of thiophene-free benzene was added to the solvent to aid its solution. A typical procedure is given here.

A solution of 25 g. (0.119 mole) of benzil and 33.2 g. (0.119 mole) of 1,3-bis-(4′-chlorophenyl)-2-propanone in 300 ml. of 95% ethanol (purified by refluxing with and distilling from potassium hydroxide) was brought just to the boiling point. A solution of 3.6 g. of potassium hydroxide in 20 ml. of ethanol was added through the condenser. Spontaneous boiling ensued and was allowed to subside after which the mixture was refluxed for 15 minutes longer. The cooled solution was filtered to give 47.3 g. (0.104 mole, 88%) of deep purple crystals, m.p. 238–239°. Recrystallization of 5 g. by dissolving it in 250 ml. of benzene, adding 150 ml. of absolute ethanol and allowing to cool gave 4.8 g. (96%) of crystals, m.p. 239–240°.

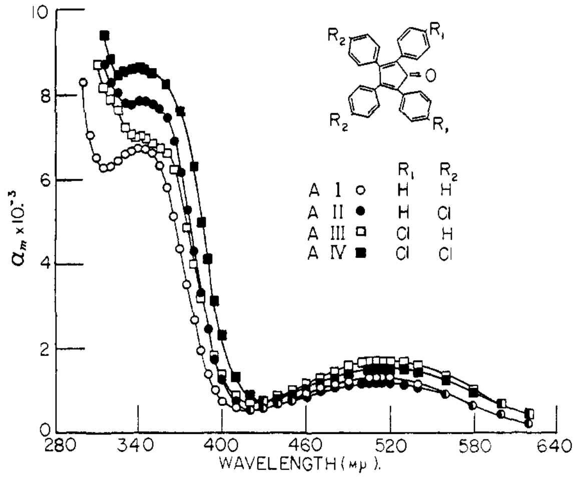

Fig. 1.

Tetraphenylphthalic Anhydrides.[9]—The tetracyclone (6.6 mmoles.) and chloromaleic anhydride[19] (b.p. 88° (14 mm.)) (1.0 g., 7.6 mmoles.) were refluxed in 15 ml. of bromobenzene (b.p. 156.2–157.0°) for 8 hr. (B-II), 10 hr. (B-III) and 6 hr. (B-IV). The solution was cooled in an ice–salt-bath, filtered, washed with cold bromobenzene and recrystallized from chlorobenzene (b.p. 132–134°). The crystals were freed from solvent by grinding and drying at reduced pressure at 156°.

Summary

2,5-Diphenyl-3,4-bis-(4′-chlorophenyl)-cyclopentadienone, 3,4-diphenyl-2,5-bis-(4′-chlorophenyl)-cyclopentadienone and tetrakis-(4-chlorophenyl)-cyclopentadienone have been synthesized. Reaction with chloromaleic anhydride converted these compounds to 3,6-diphenyl-4,5-bis-(4′-chlorophenyl)-phthalic anhydride, 4,5-diphenyl-3,6-bis-(4′-chlorophenyl)-phthalic anhydride, and tetrakis-(4-chlorophenyl)-phthalic anhydride, respectively. The absorption spectra of tetracyclone and of the three chlorotetracyclones have been presented.

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[12] H. Apitzsch, *Ber.*, **37**, 1428 (1904); see also A. Popow, *ibid.*, **6**, 560 (1873).

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[15] We are indebted to the Heyden Chemical Company, Garfield, N. J., for generous samples of 4-chlorobenzyl chloride and 4-chlorobenzaldehyde.

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[19] Kindly supplied by the General Chemical Division, Allied Chemical and Dye Corporation, New York 6, N. Y.

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[CONTRIBUTION FROM THE RESEARCH DIVISION, BRISTOL LABORATORIES, INC.]

Terpene Derivatives. Basic Ethers[1]

BY WILLIAM B. WHEATLEY, WILLIAM E. FITZGIBBON, LEE C. CHENEY AND S. B. BINKLEY[2]

Despite the tremendous amount of research that has been carried out in the field of terpene chemistry there have been few publications on basic ethers of the terpene alcohols. A patent issued to Rothenberger[3] describes the reaction of terpene haloalkyl ethers with various amines to give terpene basic ethers. In another patent, which covers the reaction of terpenes and alcohols to give ethers,[4] the use of aminoalcohols is indicated. Except for these patents, the literature appears to be devoid of references to such compounds.

The lack of investigation of terpene basic ethers is even more surprising in view of the long use of some terpene alcohols as medicinal agents; *e.g.*, menthol.[5] These considerations, together with the availability of several useful intermediates, led to the preparation of a series of terpene basic ethers.

Isobornyl β-chloroethyl ether served as the starting material for the preparation of a number of basic ethers, being caused to react with both primary and secondary amines. It reacted readily in all cases tried, with the exception of diisopropylamine. However, isobornyl β-iodoethyl ether, prepared from the chloro compound by means of

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[1] Presented before the Division of Medicinal Chemistry of the American Chemical Society, Chicago, September 3–8, 1950.

[2] Department of Biochemistry, University of Illinois College of Medicine, Chicago, Ill.

[3] Rothenberger, U. S. Patent 2,316,625 (*C. A.*, **37**, 5806 (1943)).

[4] Borglin, U. S. Patent 2,321,978 (*C. A.*, **37**, 6674 (1943)).

[5] A patent issued to Kropp in 1930 (U. S. Patent 1,733,462 (*C. A.*, **24**, 469 (1930)) claims basic oxime ethers as pharmaceutical compounds suitable for subcutaneous injection. Included in the examples is the O-β-diethylaminoethyl ether of camphor oxime.