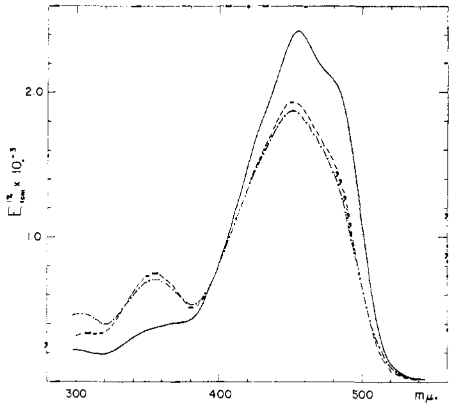

Fig. 8.—Extinction curves, in hexane, of some *cis* isomers of dehydrocarotene II: ——, neo U; ---- neo A; and –·–·–, neo B.

The interaction of dehydrocarotene II and boron trifluoride was carried out with 16 mg. of substance as described for dehydrocarotene I, but hexane +8% acetone was used as a developer. The main zone was rechromatographed and recrystallized from benzene +98% methanol; yield 1 mg., m.p. 163.5–164.5°; spectral maxima, 479, 451 mμ; maximum extinction, $E^{1\%}_{1\text{ cm.}}$ 2.42 × 10^3 at 451 mμ; and after iodine catalysis, 2.03 × 10^3 at 447 mμ (Fig. 5).

Desoxylutein "I" and Boron Trifluoride.—When 7 mg. of substance was treated with the reagent as described for dehydrocarotene I and chromatographed on lime–calcium carbonate–Celite 1:1:1 (developer, hexane + 10% acetone), two main zones were observed; both showed marked fine structure; spectral maxima: upper zone (hypophasic), 474, 447 mμ; and lower zone (epiphasic) 484, 455 mμ (Fig. 6), corresponding roughly to the location of the spectral bands of α- and β-carotene.

β-Carotene and N-Bromoacetamide.—Fifty mg. of pigment in 5 ml. of carbon tetrachloride, 15 mg. of the reagent and 2 ml. of ether were refluxed for 20 min. (during the last min. no condenser was used). The combined yields of twenty such experiments were developed with hexane + 8% acetone on ten 56 × 8 cm. lime–Celite columns. The chromatograms were similar to those obtained with N-bromosuccinimide but anhydro-eschscholtzxanthin and dehydrocarotene II were missing. The dehydro-β-carotene crystals (m.p. 192–193°; maxima at 502.5, 471.5, 445.5 mμ) showed the following composition.

Anal. Calcd. for $C_{40}H_{54}$: C, 89.84; H, 10.16. Found: C, 89.55; H, 10.33 (after correcting for 0.28% ash).

A crystalline sample of neo-dehydro-β-carotene A[13] was also isolated; m.p. 159–161°; maxima, 496, 466, 442 mμ.

Cryptoxanthin and N-Bromosuccinimide.—To a solution of 20 mg. of crystalline cryptoxanthin (*ex* persimmons)[14] in 6 ml. of carbon tetrachloride 13 mg. of the reagent and 30 mg. of sodium bicarbonate were added. The liquid was then refluxed for 45 min., diluted with hexane and developed with hexane + 8% acetone on a 24 × 4.6 cm. lime–Celite column. The corresponding zones obtained from eight such experiments (*ex* 160 mg. of cryptoxanthin) were combined and worked up as described above. Four crystalline products could be isolated: *viz.*, bisdehydro-β-carotene, anhydro-eschscholtzxanthin, a small amount of dehydrocarotene III, and a new, deep-red compound whose spectral curve was void of fine structure: $\lambda_{\max}$ at 486 mμ; and after iodine catalysis, at 476 mμ. It showed essentially epiphasic behavior and was adsorbed on lime–Celite above the bisdehydro compound (yields, Table I).

Acknowledgment.—We wish to thank Professor A. J. Haagen-Smit, Mr. G. Swinehart and Dr. A. Elek for microanalyses and Mr. K. Lunde for infrared curves.

[13] L. Zechmeister and L. Wallcave, THIS JOURNAL, **75**, 5341 (1953).

[14] H. J. Deuel, Jr., E. R. Meserve, A. Sandoval and L. Zechmeister, *Arch. Biochem.*, **10**, 491 (1946); A. Chatterjee and L. Zechmeister, THIS JOURNAL, **72**, 254 (1950).

PASADENA, CALIFORNIA

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

The Absorption Spectra of Tetracyclones. IV[1,2]

BY STEPHEN B. COAN, DONALD E. TRUCKER AND ERNEST I. BECKER

RECEIVED MAY 21, 1954

A series of tetracyclones has been synthesized in order to study absorption spectra. Substituents were introduced singly, in pairs and in quadruplet in the *p*-position of the phenyl rings. The syntheses of a number of substituted benzoins, benzils and 1,3-diphenyl-2-propanones are described as well as tetraphenylphthalic anhydrides which are derivatives for the tetracyclones. Previous observations were confirmed in that *p*-substituents in the 2- and/or 5-phenyl rings affect mainly the absorption maximum at 512 mμ, while *p*-substituents in the 3- and/or 4-phenyl ring affect mainly the maximum at 342 mμ. The shifts of the maxima are enhanced with the disubstituted compounds, while with tetrasubstituted compounds the maxima lie between those of the two corresponding disubstituted compounds. It is further suggested that the absorption maximum at 260 mμ is associated with a twinned stilbene type of resonance exclusive of the carbonyl group.

Introduction

This investigation is a continuation of a study which has already indicated that the two major absorption peaks of tetracyclone at 342 and 512 mμ can be related to resonance through the 3- and 4-phenyl rings and through the 2- and 5-phenyl rings, respectively. The earlier work dealt with several *p*-chlorosubstituted tetracyclones[1a]: a series of singly, *p*-substituted tetracyclones with electron-releasing groups[1b] and a series of *o*-chlorosubstituted tetracyclones.[1c] The purpose of the present work was to examine tetracyclones with substituents in pairs and in quadruplet employing electron-attracting as well as electron-releasing groups.

Syntheses of Tetracyclones

Most of the required intermediate benzils and 1,3-diphenyl-2-propanones were prepared by methods already in the literature. The preparation of 1,3-

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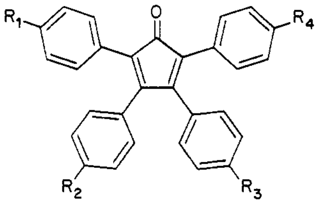
[1] (a) Part I, F. J. Thaller, D. E. Trucker and E. I. Becker, THIS JOURNAL, **73**, 228 (1951); (b) part II, S. B. Coan, D. E. Trucker and E. I. Becker, *ibid.*, **75**, 900 (1953); (c) part III, E. L. Shapiro and E. I. Becker, *ibid.*, **75**, 4769 (1953).

[2] Taken from part of the Dissertation of D.E.T. (1951) and S.B.C. (1954) presented to the Graduate Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the Ph.D. degree. The spectra referred to in this paper have been deposited as Document number 4331 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting in advance $2.50 for photoprints, or $1.75 for 35 mm. microfilm payable to: Chief Photoduplication Service, Library of Congress.

TABLE I

p-SUBSTITUTED TETRACYCLONES



No.	*p*,*p*-R$_1$,R$_4$-diphenylpropanone, mole	*p*,*p*-R$_2$R$_3$ benzil, mole	M.p., °C.	Yield,[a] %	Carbon, %		Hydrogen, %		Hal./S	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
I	0.10	0.10	220.0–221.0	79.0	90.59	90.58	5.24	4.93	...	...
				Methyl substitution						
IV	.05	.05	179.5–180.2	66.0	90.26	90.28	5.86	6.00	...	...
V	.03	.03	221.8–222.6[b]	75.0	90.26	90.62	5.86	6.00	...	...
VI	.029	.029	250.4–251.4	61.0	89.96	90.17	6.41	6.77	...	...
				Methoxyl substitution						
IX	.01	.01	195.0–195.4	34.0	83.76	84.00	5.44	5.60	...	...
X	.10	.10	226.8–227.2[c]	63.0	83.76	83.53	5.44	5.58	...	...
XI	.01	.01	255.0–256.0	55.6	78.55	78.55	5.58	5.68	...	...
				Halogen substitution						
XIV	.01	.01	249.5–250.0	76.0[d]	64.22	64.37	3.34	3.17	29.43	29.22
XV	.02	.02	249.0–249.5	50.0[d]	64.22	63.99	3.34	3.57	29.43	29.21
XVI	.01	.01	312.5–313.2	54.5[d]	49.75	49.82	2.29	2.47	45.67	45.05
				Sulfur substitution						
XIX	.0025	.0025	203.8–204.5	74.0[d]	83.68	83.70	5.15	5.38	7.45	7.18
XX	.0025	.0025	169.5–170.0	67.0	83.68	83.50	5.15	5.56	7.45	7.24
XXI	.005	.005	254.8–255.5	60.0	77.89	77.62	4.79	4.82	6.93	6.59
XXII	.005	.005	124.3–126.0	43.5	77.89	77.97	4.79	4.82	6.93	6.53
				Amine substitution						
XXIII	.01	.01	248.0–249.2	62.0	76.31	76.23	5.72	5.72	...	...

[a] Yields are for twice recrystallized products. [b] Reported 218–219° (W. Dilthey, O. Trösken, K. Plum and W. Schommer, *J. prakt. Chem.*, **141**, 331 (1934)). [c] Reported 222–223°, see reference in footnote *b*. [d] Finally recrystallized from pyridine.

di-(*p*-tolyl)-2-propanone, 1,3-di-(*p*-anisyl)-2-propanone, 4-methylmercaptobenzoin, 4-methylmercaptobenzil, 4-methylsulfonylbenzil and 4-trimethylammoniumbenzil tosylate are new and are described. The necessary unsymmetrically substituted 1,3-diphenyl-2-propanones have already been reported.[3] It should be noted that all attempts to introduce a nitro group into 1,3-diphenyl-2-propanone by base-catalyzed reactions either returned the starting materials or afforded intractable tars. However, the ultimate purpose of the nitro group was to prepare a tetracyclone possessing an electron-attracting group and since the methylsulfonyl group had been successfully introduced in the 1,3-diphenyl-2-propanone[3] and in benzil in this paper, the search for the nitro compounds was obviated.

The syntheses of the tetracyclones were carried out according to the well-established procedure of Dilthey.[4,5] Thus by condensing the appropriately substituted benzil with the appropriately substituted 1,3-diphenyl-2-propanone, the desired tetracyclones were prepared (see Table I). Most of the tetracyclones were derivatized as the corresponding tetraarylphthalic anhydrides by reaction with chloromaleic anhydride[6] (see Table II).

Experimental[7]

Substituted 1,3-Diphenyl-2-propanones.—The unsymmetrically substituted 1,3-diphenyl-2-propanones have already been described.[3]

1,3-Di-(*p*-tolyl)-2-propanone.—In view of the paucity of details in the original reference, this preparation is described.

Eighty-five grams of calcium *p*-tolylacetate was pyrolyzed at 230–250° and 5 mm. pressure. The distillate, which crystallized in the receiver, was dissolved in ether and washed with sodium carbonate solution and then with water. After drying with anhydrous sodium sulfate, the solvent was distilled and the solid residue recrystallized from ethanol. There was obtained 22 g. (0.09 mole, 37% from starting acid), m.p. 53.2–54.4°; oxime, m.p. 106–107° (reported melting points 54 and 106°, respectively[8]).

1,3-Di-*p*-anisyl-2-propanone.—Self-condensation of ethyl *p*-methoxyphenylacetate (b.p. 108–110° (1 mm.), n^{23}_{D} 1.5062) was effected according to the procedure of Conant and Blatt.[9] To a chilled solution of isopropylmagnesium bromide, prepared from 50.1 g. (0.42 mole) of isopropyl bromide and 10.1 g. (0.42 atom) of magnesium in 250 ml. of anhydrous ether, was added dropwise 46.6 g. (0.24 mole) of ethyl *p*-methoxyphenylacetate. The reaction mixture was allowed to stand at room temperature overnight and was then decomposed by the addition of 10% ammonium chloride solution followed by 10% aqueous hydrochloric acid. The layers were separated and the aqueous phase extracted with ether. The combined ether extracts were washed with water, 10% sodium hydroxide solution and then with water again. After drying over anhydrous sodium sulfate, the solvent was distilled on a steam-bath leaving 40 g. of a non-

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[3] S. B. Coan and E. I. Becker, THIS JOURNAL, **76**, 501 (1954).

[4] W. Dilthey and F. Quint, *J. prakt. Chem.*, **128**, 139 (1930).

[5] J. R. Johnson and O. Grummitt, *Org. Syntheses*, **23**, 92 (1943).

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

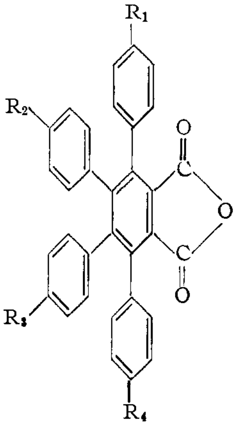
[7] All melting points are corrected.

[8] G. Errara, *Gazz. chim. ital.*, **21I**, 102 (1892).

[9] J. B. Conant and A. H. Blatt, THIS JOURNAL, **51**, 1227 (1929).

TABLE II

TETRAPHENYLPHTHALIC ANHYDRIDES



Compound				M.p., °C.	Yield,[a] %	Carbon, %		Hydrogen, %	
R₁	R₂	R₃	R₄			Calcd.	Found	Calcd.	Found
H	H	H	H	297.0–297.4[b]	54.5	84.93	85.38	4.46	4.47
CH_3	H	H	H[c]	260.5–261.3	22.8	84.96	85.04	4.75	4.77
H	CH_3	H	H[c]	264.8–265.4	42.4	84.96	85.20	4.75	4.68
CH_3	H	H	CH_3	303.2–304.2	29.0	84.98	85.23	5.03	5.07
H	CH_3	CH_3	H	289.4–289.8	47.4	84.98	85.39	5.03	5.04
CH_3	CH_3	CH_3	CH_3	280.4–280.8	41.8	85.01	85.14	5.55	5.32
Cl	H	H	H[c]	246.2–246.5	35.8	78.93	79.06	3.93	4.14[d]
F	H	H	H[c]	219.2–220.8	58.3	81.69	81.95	4.07	3.87
Br	H	H	H[c]	254.2–255.0	19.1	72.32	72.61	3.60	3.69[e]
H	Br	H	H[c]	307.8–308.3	19.0	72.32	72.55	3.60	3.67[f]
Br	H	H	Br	302.5–303.0	56.0	62.97	63.23	2.97	3.27[g]
H	Br	Br	H	316.4–316.8	55.8	62.97	63.28	2.97	3.20[h]
Br	Br	Br	Br	372.5–374.0	19.0	50.03	50.21	2.10	2.42[i]
H	OCH_3	H	H[c]	267.2–277.0	5.89	82.14	82.40	4.60	4.35
OCH_3	H	H	OCH_3	267.4–268.0	83.2	79.67	79.53	4.72	4.90
H	OCH_3	OCH_3	H	301.8–302.0	8.0	79.67	79.62	4.72	4.34
OCH_3	OCH_3	OCH_3	OCH_3	297.7–298.0	29.1	75.51	75.20	4.93	5.20
SCH_3	H	H	H	159.0–160.3	58.7	79.49	79.35	4.45	4.50
SO_2CH_3	H	H	H	258.8–259.2	44.3	74.70	74.34	4.18	4.15
H	SO_2CH_3	H	H	285.0–286.0	40.0	74.70	74.74	4.18	4.58

[a] Yields are for twice recrystallized products. [b] Reported[6] 288°. [c] The cyclone has been described in reference 1b. [d] Calcd. for $C_{32}H_{19}ClO_3$: Cl, 7.28. Found: Cl, 7.50. [e] Calcd. for $C_{32}H_{19}BrO_3$: Br, 15.03. Found: Br, 14.90. [f] Calcd. for $C_{32}H_{19}BrO_3$: Br, 15.03. Found: Br, 15.19. [g] Calcd. for $C_{32}H_{18}Br_2O_3$: Br, 26.17. Found: Br, 26.38. [h] Calcd. for $C_{32}H_{18}Br_2O_3$: Br, 26.17. Found: Br, 26.18. [i] Calcd. for $C_{32}H_{16}Br_4O_3$: Br, 41.63. Found: Br, 41.32.

crystallizable oil, which gave a colored complex with alcoholic ferric chloride solution.

To a solution of 40.0 g. of the crude acetoacetic ester in 500 ml. of glacial acetic acid was added 70 ml. of 18% hydrochloric acid and the mixture was refluxed for 5 hours during which time there was a copious evolution of carbon dioxide. The mixture was concentrated to a low volume by distillation *in vacuo* and the residue taken up in ether. After washing with 10% sodium hydroxide solution and water, the ether solution was dried over anhydrous sodium sulfate and evaporated to dryness. There was obtained 30 g. (0.11 mole, 92%) of a clear, colorless oil which crystallized on standing, m.p. 80–82°. Recrystallization from 250 ml. of hexane afforded 23 g. (0.085 mole, 71%), of 1,3-di-*p*-anisyl-2-propanone, m.p. 86.0–86.2°.

Anal. Calcd. for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.85; H, 7.00.

Its 2,4-dinitrophenylhydrazone melted at 121.0–121.2° after recrystallization from ethanol.

Anal. Calcd. for $C_{23}H_{22}N_4O_6$: N, 12.31. Found: N, 12.55.

Its oxime melted at 103.5–104.2° after recrystallization from aqueous ethanol.

Anal. Calcd. for $C_{17}H_{19}NO_4$: N, 4.91. Found: N, 5.04.

Substituted Benzils.—With the exception of the following, the benzils were either obtained commercially or prepared according to methods in the literature.

4-Methylmercaptobenzil.—In a 2-l. flask equipped with a condenser, dropping funnel and stirrer were placed 700 ml. of carbon bisulfide, 37.2 g. (0.30 mole) of thioanisole and 79.8 g. (0.60 mole) of powdered anhydrous aluminum chloride. The mixture was cooled to 0° and then held at 0° during the dropwise addition of a solution of 40.2 g. (0.30 mole) of phenylglyoxal[10] in 200 ml. of carbon bisulfide (one hour). After stirring for an additional 6 hours at 0°, the mixture was decomposed with ice and hydrochloric acid, the organic layer separated, and the aqueous layer extracted with three 300-ml. portions of ether. The combined organic layers were washed successively with water, dilute sodium hydroxide solution and finally with water. Drying over anhydrous sodium sulfate was followed by filtration and crystallization to give 19 g. (0.074 mole, 24.5%) of cream colored solid, m.p. 122–124°. Recrystallization from methanol raised the melting point of the 4'-methylmercaptobenzoin to 129.8–130.5°.

Anal. Calcd. for $C_{15}H_{14}O_2S$: C, 69.73; H, 5.46. Found: C, 69.91; H, 5.69.

A mixture of 4.0 g. (0.0155 mole) of 4'-methylmercaptobenzoin, 2.5 g. of ammonium nitrate and 100 mg. of cupric acetate in 18 ml. of 80% acetic acid was refluxed for 1.5 hours according to the procedure of Weiss and Appel.[11]

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(10) H. D. Riley and A. R. Gray, "Organic Syntheses," Coll. Vol. II, edited by A. H. Blatt, John Wiley and Sons, Inc., 1943, p. 509.

(11) M. Weiss and M. Appel, THIS JOURNAL, **70**, 3666 (1948).

The solution was cooled, seeded with a crystal of the benzil and water was added to complete the precipitation. After filtering and drying *in vacuo*, there was obtained 3.7 g. (0.0144 mole, 93%) of yellow needles, m.p. 55–56°. Recrystallization from 10 ml. of ethanol yielded 4-methylmercaptobenzil as yellow crystals, 2.5 g. (0.0098 mole, 63%) m.p. 58.8–59.0°.

Anal. Calcd. for $C_{15}H_{12}O_2S$: C, 70.28; H, 4.72. Found: C, 70.31; H, 4.98.

A quinoxaline was prepared according to the procedure of Kohler and Weiner,[12] m.p. 106.6–107.8°.

Anal. Calcd. for $C_{21}H_{16}N_2S$: N, 8.53. Found: N, 8.32.

4-Methylsulfonylbenzil.—To a stirred solution of 13.0 g. (0.105 mole) of thioanisole and 18.0 g. (0.104 mole) of phenylacetyl chloride in 75 ml. of anhydrous 1,1,2,2-tetra chloroethane was added, portionwise, 14.5 g. (0.108 mole) of anhydrous aluminum chloride. The temperature of the mixture was maintained at 0–5° throughout. An intense green color developed as the aluminum chloride complex was formed. After stirring several hours, the mixture was allowed to stand overnight at room temperature, after which it was decomposed by pouring onto a mixture of 500 g. of ice and 500 ml. of concentrated hydrochloric acid. The precipitated crystals were removed by filtration and dried affording 25 g. (0.103 mole, 100%), m.p. 99–100°. Recrystallization from 125 ml. of ethanol yielded 20.5 g. of α-phenyl-4-methylmercaptoacetophenone (0.085 mole, 82.5%), m.p. 99.4–99.8°.

Anal. Calcd. for $C_{15}H_{14}OS$: C, 74.34; H, 5.82. Found C, 74.17; H, 6.06.

The 2,4-dinitrophenylhydrazone melted at 201.0–202.8° after recrystallization from ethanol.

Anal. Calcd. for $C_{21}H_{18}O_4N_4S$: N, 13.28. Found: N, 12.99.

A solution of 20 g. (0.083 mole) of α-phenyl-4-methylmercaptoacetophenone in 125 ml. of glacial acetic acid and 29 g. (0.28 mole) of 30% aqueous hydrogen peroxide was refluxed for 20 hours. After cooling, water was added to induce crystallization. The precipitated solids were filtered and dried giving 15 g. (0.055 mole, 66.3%), m.p. 158–163°. Recrystallization from benzene–ethanol gave 10 g. (0.037 mole, 44.5%) of α-phenyl-4-methylsulfonylacetophenone, m.p. 164.5–166.0°.

Anal. Calcd. for $C_{15}H_{14}O_3S$: C, 65.68; H, 5.14. Found: C, 65.82; H, 5.42.

Its phenylhydrazone melted at 194.0–194.5° after recrystallization from ethanol.

Anal. Calcd. for $C_{21}H_{20}N_2O_2S$: N, 7.68. Found: N, 7.44.

A mixture of 9.0 g. (0.033 mole) of α-phenyl-4-methylsulfonylacetophenone and 4.35 g. (0.039 mole) of selenium dioxide in 20 ml. of acetic anhydride was refluxed for 4 hours. After cooling the solution was filtered and the solid discarded. The filtrate was cautiously added to 150 ml. of water and then boiled for a few minutes. Filtration gave 6.5 g. of solid, m.p. 129–131°. Recrystallization from ethanol–benzene afforded 5.0 g. (0.0173 mole, 54%) of yellow 4-methylsulfonylbenzil, m.p. 131.8–132.3°.

Anal. Calcd. for $C_{15}H_{12}O_4S$: C, 62.49; H, 4.19; S, 11.12. Found: C, 62.52; H, 4.41; S, 11.00.

A quinoxaline was prepared by reaction of the benzil with *o*-phenylenediamine dihydrochloride in ethanol, m.p. 255.0–256.0°.

Anal. Calcd. for $C_{11}H_{16}N_2O_2S$: N, 7.77. Found: N, 7.45.

***p*-Tosylate of 4-Trimethylammoniumbenzil.**—A mixture of 10 g. (0.039 mole) of 4-dimethylaminobenzil and 7.8 g. (0.042 mole) of methyl *p*-toluenesulfonate was heated at 140° for one hour. At first, the mixture melted and then resolidified. The cooled mass was triturated with 100 ml. of warm benzene, filtered and finally recrystallized from 100 ml. of ethanol to give 11 g. (0.025 mole, 63%) of the quaternary salt, m.p. 229.4–229.6°.

Anal. Calcd. for $C_{24}H_{25}NO_5S$: C, 65.58; H, 5.73. Found: C, 65.41; H, 5.96.

Tetracyclones

The desired tetracyclones were prepared from the appropriate diphenylpropanone and appropriate benzil without particular difficulty according to the general procedure of Dilthey[4,5] (see Table I).

However, when benzil was condensed with 1-*p*-methylsulfonylphenyl-3-phenyl-2-propanone in the presence of potassium hydroxide, the usual red coloration was observed without formation of crystals. Chromatographic analysis on Alumina F-20 showed the presence of the tetracyclone as a distinct colored band. Repeating the condensation adding an equivalent amount of Triton B (35% methanolic solution of benzyltrimethylammonium hydroxide, Rohm and Haas) to the refluxing solution of reactants caused a violent immediate reaction with the yellow solution changing color to purple with the insoluble tetracyclone appearing within 1–2 minutes.

The crude tetracyclones were recrystallized from benzene–ethanol and then from glacial acetic acid except that 2,5-di-*p*-bromophenyl-3,4-diphenylcyclopentadienone and *p*-tetrabromophenylcyclopentadienone were finally recrystallized from pyridine while the quaternary ammonium tetracyclone (compound XXIII) was finally recrystallized from ethanol.

The tetracyclones were derivatized by reaction with chloromaleic anhydride to yield the appropriately substituted tetraphenylphthalic anhydride according to the procedure of Synerholm.[6] The reaction was performed in bromobenzene and the products were generally recrystallized from chlorobenzene–petroleum ether or toluene–petroleum ether (see Table II).

Discussion of Spectra

Single Substituents.—In extending the study of the effects of single substituents on the absorption spectrum of tetracyclone, the methylmercapto group was examined. As expected, when this group is in the 2-phenyl ring (XIX) the peak at 512 mμ is shifted hyperchromically and bathochromically (see Table III). When the substituent is in the 3-phenyl ring (XX), the peak at 340 mμ responds similarly. Thus, the order of decreasing influence of interaction of groups in this series becomes: $CH_3S– > CH_3O > CH_3 > Br > Cl,F$. Having thus confirmed the previous notion of the effect of single, electron-releasing groups on the absorption spectrum of tetracyclone, attention was next directed to the effect of electron-attracting groups. It was hypothesized that such a group would cause a hypsochromic and hypochromic shift of the resonance path to which it is attached in accord with the known effects of electron-withdrawing groups in opposed positions of a conjugated chain.

With methylsulfonyl in the 2-phenyl ring (Table III, compound XXI), the peak at 342 mμ has shifted bathochromically and hyperchromically while the peak at 510 mμ has shifted to 505 mμ. The intensity of the peak at 505 mμ is still higher than that for tetracyclone. Although this appears not to be in accord with the theory, it would be more accurate to compare XXI with the corresponding *o*-substituted compound, one which has not yet been synthesized.[10]

Introduction of methylsulfonyl in the 3-phenyl ring, compound XXII, effects a hypsochromic and hypochromic shift of the peak at 342 mμ. The intensity of the peak at 510 mμ is increased only slightly over that for I.

The quaternary group, trimethylammonium, also was examined in compound XXIII. With this substituent in the 3-phenyl ring, the peak at 342 mμ is decreased to only an inflection, while the peak at 510 mμ is changed but little in

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[12] E. P. Kohler and N. Weiner, THIS JOURNAL, **56**, 434 (1934).

TABLE III

SPECTRAL CHARACTERISTICS OF TETRACYCLONES

Cmpd.	Substituent R_1	R_2	R_3	R_4	Solvent	λ_1[a]	α_{m1}[b, c]	λ_2	α_{m2}	λ_3	α_{m3}
I	H	H	H	H	I[d]	262	27.8	333	7.20		
					B[e]			342	6.60	512	1.25
					ID[f]	260	25.0	332	7.20		
					MD[g]	258	26.2	330	7.70		
					MD			330	6.85	510	1 34
II	CH_3	H	H	H	I	263	28.0	340	6.60		
					B			341	6.31	515	1.51
III	H	CH_3	H	H	I	262	29.4	345	8.25		
					B			350	7.50	510	1.07
IV	CH_3	H	H	CH_3	I	267	29.5	350	5.85		
					B			341[h]	7.20	518	2.26
V	H	CH_3	CH_3	H	I	262	28.2	345	8.25		
					B			354	8.95	510	1.25
VI	CH_3	CH_3	CH_3	CH_3	I	267	31.6				
					B			350	8.30	520	1.90
VII	OCH_3	H	H	H	I	267	30.4	350[h]	6.90		
					B			343[h]	6.10	525	1.88
VIII	H	OCH_3	H	H	I	261	29.1	361	10.3		
					B			370	8.95	510	0.87
IX	OCH_3	H	H	OCH_3	I	272	31.8	370	5.45		
					B			340[h]	6.66	545	2.26
X	H	OCH_3	OCH_3	H	I	262	29.0	360	10.5		
					B			375	10.4	510	0.87
					ID	260	26.7	362	12.2		
XI	OCH_3	OCH_3	OCH_3	OCH_3	I	270	31.2	350[i]	11.4		
								384[i]	10.4		
					B			362[i]	10.4		
								385[j]	9.6	560	1.46
XII	Br	H	H	H	I	265	32.8	339	8.70		
					B			340	6.85	510	1.46
XIII	H	Br	H	H	I	260	26.0	339	8.20		
					B			342	7.75	510	1.26
XIV	Br	H	H	Br	ID	270	31.6	337	7.00		
					B			336[h]	7.32	515	1.91
XV	H	Br	Br	H	ID	255	25.6	340	9.50		
					B			343	8.55	511	1.21
XVI	Br	Br	Br	Br	ID	271	32.2	340	10.2		
					B			342	9.42	518	1 74
XVII	F	H	H	H	I	259	28.3	330[h]	7.80		
					B			340	7.10	510	1.53
XVIII	Cl	H	H	H	I	264	30.6	338	7.45		
					B			340	7.10	510	1.46
XIX	SCH_3	H	H	H	I	272	31.8	..			
					B			..		530	2.16
XX	H	SCH_3	H	H	I	258	28.7	378	9.05		
					B			388	9.20	510	1.29
XXI	SO_2CH_3	H	H	H	ID	268	25.8	338	6.20		
					B			345	7.11	505	1.60
XXII	H	SO_2CH_3	H	H	ID	270	19.0	340	7.30		
					B			342[h]	6.12	510	1.37
XXIII	H	$Y_3\overset{+}{N}\overset{-}{X}$[k]	H	H	MD	258	25.0	330[h]	6.65		
					MD			320[h]	6.17	510	1.26

[a] Millimicrons. [b] See M. G. Mellon, *Anal. Chem.*, **21**, 3 (1949). [c] All α_m values are 10^{-3}. [d] Isoöctane. [e] Benzene. [f] Isoöctane–dioxane, 1:1. [g] Methanol-dioxane, 1:1. [h] Inflection. [i] Split peak. [j] Shoulder. [k] $Y = CH_3$, $X = O_3SC_6H_4\text{-}CH_3\text{-}p$.

agreement with the effect of the methylsulfonyl group.[13]

Substituents in Pairs.—It was logically predicted that the introduction of groups in the 2- and the 5-phenyl rings simultaneously or in the 3- and 4-phenyl rings simultaneously would effect changes similar to, and larger than, those effected by a single substituent. That this is the case is borne out by the data of Table III. With methyl groups in the 2- and 5-phenyl rings, IV, the peak at 512 mμ is intensified and shifted bathochromically

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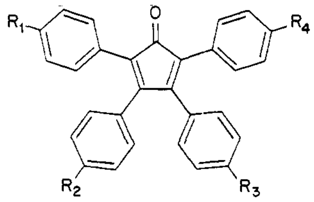
(13) It is recognized by the authors that the amine cation is known to be devoid of resonance contribution in benzenoid structures, yet the definite decrease in intensity for the peak at 342 mμ speaks for some interaction, be it polar or resonance, for the group.

TABLE IV

COMPARISON OF THE 262 AND 512 Mμ PEAKS OF SOME TETRACYCLONES[a]



Cmpd.[b]	Substituent	λ_1[c]	α_{m1}[d]	λ_3[c]	α_{m3}[d]
		R_1-Substitution			
I	H	262	27.8	512	1.25
	H	260[e]	25.0		
	H	258[f]	26.2	510[f]	1.34
II	CH_3	263	28.0	515	1.51
VII	OCH_3	267	30.4	525	1.88
XII	Br	265	32.8	510	1.46
XVII	F	259	28.3	510	1.53
XVIII	Cl	264	30.6	510	1.46
XIX	SCH_3	272	31.8	530	2.16
XXI	SO_2CH_3	268[e]	25.8	505	1.60
		R_2-Substitution			
III	CH_3	262	29.4	510	1.07
VIII	OCH_3	261	29.1	510	0.87
XIII	Br	260	26.0	510	1.26
XX	SCH_3	258	28.7	510	1.29
XXII	SO_2CH_3	270[e]	19.0	510	1.37
XXIII	$Y_3\overset{+}{N}\overset{-}{X}$[g]	258[f]	25.0	510[f]	1.26
		R_1,R_4-Substitution			
IV	CH_3	267	29.5	518	2.26
IX	OCH_3	272	31.8	545	2.26
XIV	Br	270[e]	31.6	515	1.91
		R_2,R_3-Substitution			
V	CH_3	262	28.2	510	1.25
X	OCH_3	262	29.0	510	0.87
XV	Br	255[e]	25.6	511	1.21
		R_1,R_2,R_3,R_4-Substitution			
VI	CH_3	267	31.6	520	1.90
XI	OCH_3	270	31.2	560	1.46
XVI	Br	271[e]	32.2	518	1.74

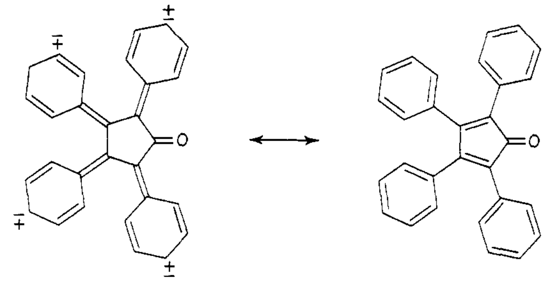
[a] Unless otherwise indicated λ_1 and λ_3 were evaluated in isoöctane solvent and benzene solvent, respectively. [b] The numbers correspond to those in Table III. [c] Millimicrons. [d] All α_m values are 10^{-3}. [e] Isoöctane–dioxane, 1:1 solvent. [f] Methanol–dioxane, 1:1 solvent. [g] Y = CH_3, X = $O_3SC_6H_4CH_3$-*p*.

while the peak at 340 mμ becomes an inflection. With methyl groups in the 3- and 4-phenyl rings, V, the peak at 342 mμ is shifted bathochromically and hyperchromically, while the peak at 512 mμ is shifted hypochromically as compared to that of IV. These shifts are paralleled by the intensities of the analogous chloro compounds,[1a] bromo compounds and methoxy compounds.

Substituents in Quadruplets.—In Table III are plotted the data for tetrasubstituted tetracyclones. The curve for a given tetrasubstituted tetracyclone exhibits maxima between those for the two disubstituted compounds with the same substituent. As expected, the curve lies above that for tetracyclone. It is interesting that the absorption maximum at 512 mμ has been shifted to 560 mμ in the tetramethoxytetracyclone XI. Thus, non-fused ring tetracyclones have now been prepared which vary in color from orange (2,5-diphenyl-3,4-di-(*o*-chlorophenyl)-cyclopentadienone[1c]) to blue, compound XI.

The Absorption Maximum at 262 mμ.—The peak at 262 mμ shifts bathochromically whenever a substituent is introduced in either the 2- and 5-phenyl rings or in the 3- and 4-phenyl rings. These facts imply that the carbonyl group is not taking part in the absorption path associated with the peak at 262 mμ. Other possible resonance structures which have been considered are phenyl absorption, benzil absorption, styrene absorption and *cis*-stilbene absorption.[14] All but the latter have been eliminated.

cis-Stilbene absorption requires resonance structures such as XXIV.



XXIV I

Further evidence in favor of this assignment is the fact that 1,2,3,4-tetraphenylfulvene, 2,3,4,5-tetraphenylcyclopentadiene[15] and 2,3,4,5-tetraphenylcyclopentadien-1-ol all exhibit a high intensity peak in the neighborhood of 260 mμ. Saturation of the central ring obliterates this maximum.

The intensity of this maximum is also in agreement with the *cis*-stilbene assignment. The two stilbene resonance paths are essentially independent of one another. This would be true if the 2,3- and 4,5-bonds of the central ring were foreshortened.[16] Thus, the intensity of the peak at 260 mμ would be expected to be roughly twice that of *cis*-stilbene since isolated chromophores are additive.[17] The absorption maximum for *cis*-stilbene is 13,500, that for tetracyclone is 27,800. The fact that electron-releasing substituents effect a bathochromic shift is also in accord with the effect of such substituents in *cis*-stilbene.[18]

The absorption spectrum of 2,5-diethyl-3,4-diphenylcyclopentadienone also bears on the assignment of the peak at 260 mμ to *cis*-stilbene structures. Although the spectrum available extends only to 280 mμ, it is seen from the direction of the curve at this wave length that the absorption is decreasing or approaching a minimum. From the general shape of the curves of other tetracyclones it

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(14) D. E. Trucker, Dissertation presented to the Graduate Faculties of the Polytechnic Institute of Brooklyn, 1951.

(15) N. O. V. Sonntag, S. Linder, E. I. Becker and P. E. Spoerri, THIS JOURNAL, **75**, 2283 (1953).

(16) See reference 1c for a discussion of the geometry of the tetracyclone molecule.

(17) E. A. Braude, *Ann. Repts. on Progress Chem.* (*Chem. Soc. London*), **42**, 126 (1945).

(18) E. A. Braude, *J. Chem. Soc.*, 1902 (1949).

can be inferred that a maximum will not be reached in the vicinity of 260 mμ. This is in agreement with the hypothesis of a twinned stilbene-type of resonance structure since this type of structure is not possible for the molecule.

Finally, the possible excitation of twinned stilbene paths would appear to depend upon the extent to which these paths can be excited independent of the carbonyl group. Although no exact measure of this is available, from the infrared studies of Bergmann, *et al.*,[19] and the measurement of dipole moments of tetracyclone[20,21] and several chlorotetracyclones,[21] it does appear that the carbonyl group is not very highly polarized. It seems feasible that for a molecule in which the carbonyl group is not highly polarized, excited states excluding the carbonyl group may be possible.

(19) E. D. Bergmann, J. Berthier, D. Ginsburg, Y. Hirschberg, D. Lavie, S. Pinchas, B. Pullman and A. Pullman, *Bull. soc. chim. France*, **17**, 661 (1951).

(20) E. D. Bergmann and E. Fischer, *ibid.*, **17**, 1084 (1950).

(21) A. Di Giacomo and C. P. Smyth, THIS JOURNAL, **74**, 4441 (1952).

BROOKLYN 1, NEW YORK

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

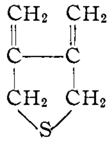
An Attempted Synthesis of 3,4-Dimethylenethiophane[1]

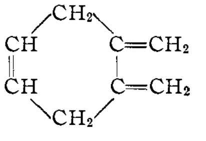
BY C. S. MARVEL AND E. E. RYDER, JR.

RECEIVED JULY 22, 1954

An attempt to prepare 3,4-dimethylenethiophane by the pyrolysis of 3,4-bis-(acetoxymethyl)-thiophane has given only 3,4-dimethylthiophene.

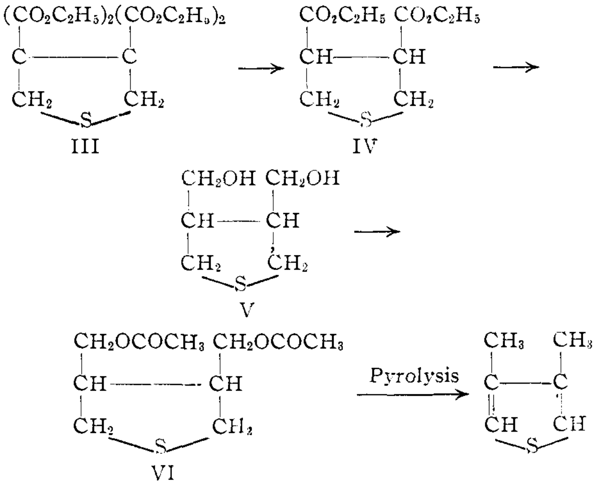
In the course of an attempt to prepare an all-*cis* polymer we had occasion to undertake the preparation of 3,4-dimethylenethiophane (I). Since Bailey[2] has been able to prepare 4,5-dimethylenecyclohexane (II) by the pyrolysis of the corresponding diacetate, this general method was decided upon as the most promising route to the desired thiophane derivative.


I


II

Accordingly tetraethyl thiophane-3,3,4,4-tetracarboxylate[3] (III) was hydrolyzed, decarboxylated and esterified to yield diethyl thiophane-3,4-dicarboxylate (IV). This ester was reduced to the glycol with lithium aluminum hydride and the glycol V converted to the diacetate VI.

Pyrolysis of the diacetate gave a single product which was established to be 3,4-dimethylthiophene. It was thought that some acidic decomposition products formed on the glass helices during pyrolysis might be responsible for the isomerization of the thiophane to the thiophene. But pyrolysis in the presence of a base (triethylamine) did not change the course of the reaction. Thiophane itself was subjected to pyrolysis under the same conditions used for the diacetate and no appreciable decomposition was noticed. In order to learn if some pyrolytic product might be formed which was responsible for the aromatization of our compound, we pyrolyzed a mixture of a small amount of the thiophane diacetate (VI) and 4,5-bis-(acetoxymethyl)-cyclohexene. The cyclohexene derivative gave Bailey's dimethylenecyclohexene but none was rearranged to *o*-xylene. Thus, none of the thiophane cleavage products seem to be aromatization catalysts. It appears, therefore, that dimethylenethiophane is not stable at the temperatures needed for the pyrolysis of the diacetate.



We used a modified procedure for the condensation of bis-chloromethyl sulfide with tetraethyl ethane-1,1,2,2-tetracarboxylate[3] and obtained a better yield than we were able to obtain by the original directions. The tetraester was further characterized by conversion to the sulfone. The anhydride of thiophane-3,4-dicarboxylic acid is also reported.

Experimental[4]

Tetraethyl Thiophane-3,3,4,4-tetracarboxylate.—This compound was prepared by a variation of the method of Mann and Pope.[3] A mixture of 50 g. (2.08 moles) of sodium hydride, 333 g. (1.05 mole) of tetraethyl ethane-1,1,2,-2-tetracarboxylate and 2500 ml. of dry dioxane was refluxed with stirring for one hour at which time 138 g. (1.05 mole) of bis-chloromethyl sulfide[3] was added and refluxing continued 24 hours. Following the usual work-up 350 g. of

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[1] The work discussed herein was performed as a part of the research project sponsored by the Reconstruction Finance Corporation, Office of Synthetic Rubber, in connection with the Government Synthetic Rubber Program.

[2] W. J. Bailey, *et al.*, THIS JOURNAL, **77**, 73 (1955).

[3] F. G. Mann and W. J. Pope, *J. Chem. Soc.*, **123**, 1172 (1923).

[4] All melting points and boiling points are uncorrected.