

butane. It therefore appears safe to conclude that the  $\text{Fe}_2\text{C}$  formed during synthesis is not capable of strongly adsorbing carbon monoxide either by itself or in the presence of hydrogen. On the other hand, the carbided samples are capable of holding hydrogen by activated adsorption at temperatures close to those at which synthesis will occur. Since any likely mechanism for the synthesis would seem to involve the adsorption of the carbon monoxide as well as the hydrogen, it seems probable that the catalyst in Fischer-Tropsch synthesis is not Hägg  $\text{Fe}_2\text{C}$ . A final discussion of the relation of the adsorption measurements to the conclusions that can be drawn as to the mechanism of synthesis will be made in a forthcoming paper after the presentation of adsorption data for carbon monoxide and hydrogen both as separate gases and as mixtures on metallic iron and on  $\text{Fe}_3\text{O}_4$ .

### Summary

1. Hägg  $\text{Fe}_2\text{C}$  can be formed by carbiding finely-divided iron catalysts with a hydrocarbon such as propane, butane or pentane equally as well as carbiding with carbon monoxide. The carbiding process using a hydrocarbon is not accompanied by a lay-down of free carbon or by any strong exothermicity.

2. The samples of  $\text{Fe}_2\text{C}$  formed by using bu-

tane as a carbiding gas still contain a little residual iron after the carbiding reaction at  $300^\circ$  apparently comes to an end. Only about 7.5% carbon seems capable of being incorporated by this procedure in the catalyst employed.

3. It is possible to form hexagonal  $\text{Fe}_2\text{C}$  by carefully carbiding an iron synthetic ammonia catalyst at about  $215^\circ$  with carbon monoxide, even though the catalyst does not contain copper.

4. Carbon monoxide is still chemisorbed by a partially carbided iron catalyst at  $-195$ ,  $-78.5$  and  $-46^\circ$ , indicating that the carbiding proceeds through the formation of nuclei of carbide rather than by the formation of a smooth layer of carbide over the catalyst surface.

5. The formation of carbide eliminates most of the chemisorption of carbon monoxide at 100 and  $200^\circ$ . It also eliminates the chemisorption of hydrogen in the temperature region  $-78.5$  to  $0^\circ$ . On the other hand, it has little effect on the higher temperature type of hydrogen adsorption occurring at and above  $100^\circ$  until the catalyst samples are almost completely converted to  $\text{Fe}_2\text{C}$ .

6. The energy of activation for carbiding iron with carbon monoxide to form  $\text{Fe}_2\text{C}$  is about 32.5 kcal. per mole.

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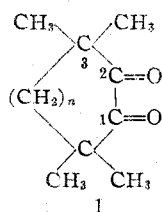
RECEIVED MARCH 24, 1950

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

## The Influence of Steric Configuration on the Ultraviolet Absorption of 1,2-Diketones

BY NELSON J. LEONARD AND PAUL M. MADER

An excellent method for arriving at the relationship between ultraviolet absorption and steric orientation of the carbonyl groups in the 1,2-dicarbonyl chromophore would appear to be through the preparation of a series of alicyclic 1,2-diketones of type I and the determination of their absorption spectra. In such a system



a,  $n = 1$ ; b,  $n = 2$ ; c,  $n = 3$ ; d,  $n = 4$ ; e,  $n = 14$

there will be a dependence of the angle between the planes of the carbonyl groups upon the size of the ring. Thus, when  $n = 1$  (Ia) the dicarbonyl groups are constrained to a *cis* relationship due to the fixity of the five-membered ring, and the absorption spectrum of the compound (Ia) should therefore be representative of *cis* coplanar dicarbonyls. As the ring size is

increased (from  $n = 1$  to  $n = 2, 3, 4$ , etc.), the angle between the carbonyls is gradually increased from  $0^\circ$ , or *cis* coplanarity, until the ring becomes large enough (*e. g.*,  $n = 14$ ) to accommodate the carbonyl groups at  $180^\circ$ , or *trans* coplanarity. The absorption spectra of these diketones with increasing ring size will therefore be representative of two adjacent carbonyl groups with regularly increasing interplanar angles. In this system (I) selected for study, there will be no extraneous influence on the absorption due to enolization<sup>1</sup> since the  $\alpha$ -carbons are completely alkyl-substituted.

### Experimental<sup>2</sup>

**Special Apparatus.**—The low-temperature crystallization apparatus shown in Fig. 1, which was necessary for

(1) (a) Schwarzenbach and Wittner, *Helv. Chim. Acta*, **30**, 663 (1947); (b) Wallach, *Ann.*, **437**, 148 (1924); (c) Wheland, *J. Chem. Phys.*, **1**, 731 (1933); (d) French and Holden, *THIS JOURNAL*, **67**, 1239 (1945).

(2) All melting points are corrected. The authors are indebted to Miss Enilly Davis, Miss Rachel Kopel, Mrs. Jane Wood and Mr. Maurice Dare for the microanalyses reported herein and to Mrs. James Johnson, Miss Elizabeth Petersen, Mrs. John C. Brantley and Mr. John Gardner for their aid in obtaining the absorption spectra data.

the purification of the many low-melting solids encountered in this study, was attached through arm b to a three-way stopcock leading to vacuum or to positive air pressure. Arm c was protected from moisture in the atmosphere by a drying tower filled with calcium chloride. While a positive pressure was maintained in d, a solution of the substance to be crystallized was introduced into tube a. Tube a was stoppered and the apparatus was lowered into a low-temperature bath to such a depth that the solution in a was submerged. When crystallization had taken place to the extent desired, d was evacuated, allowing filtration through the sintered glass plug e and effecting removal of the filtrate. The positive pressure was then restored in d, and the apparatus was removed from the freezing mixture. The recrystallized substance, after it had melted, was removed from a by means of a slender pipet, or more solvent was added and the crystallization was repeated.

**Diethyl 1,1,4,4-Tetramethyladipate.**—1,1,4,4-Tetramethyladipic acid was obtained in 67% yield by electrolysis of the potassium salt of the monoethyl ester (V) of 1,1-dimethylsuccinic acid<sup>3,4,5,6</sup> essentially according to the method of Ruzicka and Stoll,<sup>7</sup> followed by saponification of the crude diethyl ester. A solution of 92 g. (0.46 mole) of purified 1,1,4,4-tetramethyladipic acid and 1 ml. of 97% sulfuric acid in 163 ml. of absolute ethanol and 222 ml. of benzene was refluxed through an ethyl ester column for twenty-five hours, during which time 40 ml. of aqueous phase separated from the azeotrope. Ethanol and benzene were then removed by distillation, and the residue of crude ester was washed once with water, once with dilute sodium bicarbonate solution, twice with water, and was dried over sodium sulfate. The ester was fractionally distilled *in vacuo*; b. p. 86–91° (1 mm.);  $n_D^{20}$  1.4309; yield 110.7 g. (94%).

*Anal.* Calcd. for  $C_{14}H_{26}O_4$ : C, 65.08; H, 10.15. Found: C, 65.23; H, 10.26.

**Diethyl 1,1,5,5-Tetramethylpimelate.**—The procedure of Haller and Bauer<sup>8</sup> for 1,1,5,5-tetramethylpimelic acid was simplified by eliminating the isolation and purification of intermediates (46% yield). The method of esterification of the acid was identical with that described for the formation of diethyl 1,1,4,4-tetramethyladipate. From 187 g. (0.87 mole) of crude 1,1,5,5-tetramethylpimelic acid was obtained 204.7 g. (87%) of the diethyl ester, b. p. 105–106° (1.3 mm.);  $n_D^{20}$  1.4310.<sup>9</sup>

*Anal.* Calcd. for  $C_{15}H_{28}O_4$ : C, 66.14; H, 10.36. Found: C, 66.09; H, 10.48.

**1,1,6,6-Tetramethylsuberic Acid.**—This acid was made by the procedure described for the preparation of 1,1,5,5-tetramethylpimelic acid. From 104 g. (0.48 mole) of tetramethylene bromide there was obtained 45.2 g. (41%) of 1,1,6,6-tetramethylsuberic acid. Purification was effected by recrystallization from aqueous ethanol; m. p. 185.8–186.1°, after initial softening at 179°.

*Anal.* Calcd. for  $C_{12}H_{22}O_4$ : C, 62.58; H, 9.63. Found: C, 62.80; H, 9.71.

The diethyl ester was prepared by the usual method in 79% yield; b. p. 104–113° (0.5–1.2 mm.),  $n_D^{20}$  1.4348. This diethyl 1,1,6,6-tetramethylsuberate was used directly in the subsequent treatment with sodium.

**2,2,7,7-Tetramethylcyclooctanol.**—This alcohol was the only product obtained, other than unchanged diethyl 1,1,6,6-tetramethylsuberate and unreacted sodium, when an attempt was made to prepare 3,3,8,8-tetramethyl-2-hy-

droxycyclooctanone using the technique described for the preparation of 3,3,6,6-tetramethyl-2-hydroxycyclohexanone (see below). From 42.2 g. of diethyl 1,1,6,6-tetramethylsuberate there was obtained 1.11 g. of a colorless fraction boiling at 73–83° (1.1–1.3 mm.) which was partially solid at room temperature and possessed a camphor-like odor. This fraction was pressed on a porous plate, and the solid which remained was observed to melt at 61.4–61.9°, after initial softening at 59°.

*Anal.* Calcd. for  $C_{12}H_{22}O$ : C, 78.19; H, 13.13. Found: C, 78.36; H, 13.38.

The infrared spectrum indicated an absorption peak at 3360  $cm^{-1}$ , in the region usually associated with hydroxyl absorption. There was no peak in the carbonyl absorption region.

**2,2,7,7-Tetramethylcyclooctanone.**—This compound was prepared by the oxidation of 0.97 g. (5.3 millimoles) of 2,2,7,7-tetramethylcyclooctanol with 0.39 g. (3.9 millimoles) of chromic anhydride in 6 ml. of glacial acetic acid and 0.25 ml. of water. The experimental procedure was the same as used for the oxidation of acyloins to diketones (see below). The crude product was distilled at 0.5 mm.; yield 0.73 g. (76%) of colorless solid, m. p. 26.2–27.0°, with a camphor-like odor. This distillate was recrystallized six times from petroleum ether (b. p. 40–45°) at –80°; m. p. 27.3–27.8°.

*Anal.* Calcd. for  $C_{12}H_{22}O$ : C, 79.05; H, 12.17. Found: C, 79.08; H, 12.29.

The compound exhibited strong typical carbonyl absorption in the infrared region (1696  $cm^{-1}$ ) and in the ultraviolet region (293  $\mu$ ).

**1,1,16,16-Tetramethyl-1,16-hexadecanedicarboxamide.**—The method of preparation was similar to that employed in making the diamide (not isolated) of 1,1,5,5-tetramethylpimelic acid.<sup>8</sup> The sodio derivative of isobutyrophenone, prepared from 37 g. (0.25 mole) of isobutyrophenone and sodamide obtained from 5.5 g. (0.24 atom) of sodium, was condensed with 42.6 g. (0.12 mole) of tetradecamethylene bromide<sup>10</sup> using toluene as the reaction medium. At the completion of the condensation, the sodium bromide was not removed by filtration because of the extreme slowness of the operation. When the mixture was agitated and heated to 80° with sodamide, prepared from 8.5 g. (0.37 atom) of sodium, there occurred a sudden solidification of the mixture to a mass having a thick, glue-like consistency. When the temperature was raised to 100°, the mass separated into a fluid toluene phase and a large blob of tar, but stirring was still impossible. The mixture was refluxed for three hours, cooled to 40°, and the toluene phase was separated from the gray, now solid, tar by decantation. When 200 ml. of water had been added to the residue and the mixture had been heated to reflux, mechanical stirring could be resumed. After one hour of refluxing and stirring, the solid mass was broken up completely and filtration was possible. The solid was powdered and then slurried with dilute hydrochloric acid solution. Filtration furnished solid material (37 g. dry weight) with fairly respectable properties. Three recrystallizations, with decolorization, from ethanol-petroleum ether (b. p. 60–100°) furnished a fluffy, colorless solid, m. p. 161–164°, with prior softening.

*Anal.* Calcd. for  $C_{22}H_{44}N_2O_2$ : C, 71.68; H, 12.03. Found: C, 71.71; H, 12.16.

(10) Chuit, *Helv. Chim. Acta*, **9**, 264 (1926).

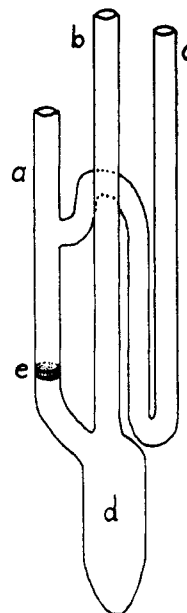


Fig. 1.—Low-temperature crystallization apparatus (constructed of "Pyrex" glass).

(3) Higson and Thorpe, *J. Chem. Soc.*, **89**, 1455 (1906).

(4) Vogel, *ibid.*, 2010 (1928).

(5) Haworth and King, *ibid.*, **105**, 1342 (1914).

(6) Bone, Sudborough and Sprankling, *ibid.*, **85**, 534 (1904).

(7) Ruzicka and Stoll, *Helv. Chim. Acta*, **16**, 493 (1933); *cf.* Farmer and Kracovskii, *J. Chem. Soc.*, 2318 (1926).

(8) Haller and Bauer, *Compt. rend.*, **152**, 1638 (1911).

(9) Diethyl 1,1,5,5-tetramethylpimelate was also prepared by an adaptation of the Hudson and Hauser (*THIS JOURNAL*, **62**, 2457 (1940)) method for the alkylation of ethyl isobutyrate in the presence of triphenylmethylsodium. The use of trimethylene bromide afforded a 23% yield of diethyl 1,1,5,5-tetramethylpimelate.

TABLE I  
ACYLOINS

Compound	B. p., °C.		M. p., °C.	$n_D^{20}$	Yield, %	Molecular formula	Carbon, %		Hydrogen, %		
	Obs.	Lit.					Calcd.	Found	Calcd.	Found	
Pivaloin (2,2,5,5-tetramethyl-4-hydroxy-3-hexanone) (VIII) <sup>15</sup>			80	80.5	56	C <sub>10</sub> H <sub>20</sub> O <sub>2</sub>					
3,3,6,6-Tetramethyl-2-hydroxycyclohexanone (IVb)	75-77	6	28.3	29.7 <sup>a</sup>	1.4566	91	C <sub>10</sub> H <sub>18</sub> O <sub>2</sub>	70.55	70.84	10.66	10.86
3,3,7,7-Tetramethyl-2-hydroxycycloheptanone (IVc)	89-90	6	19.5-21.0 <sup>a</sup>		1.4646	69	C <sub>11</sub> H <sub>20</sub> O <sub>2</sub>	71.69	71.77	10.94	10.99
3,3,8,8-Tetramethyl-2-hydroxycyclooctanone (IVd)	65-77	0.7	84.1-84.9			33	C <sub>12</sub> H <sub>22</sub> O <sub>2</sub>	72.68	72.82	11.18	11.41
3,3,18,18-Tetramethyl-2-hydroxycyclooctadecanone (IVe)	181-234 <sup>b</sup>	0.3					C <sub>22</sub> H <sub>42</sub> O <sub>2</sub>				

<sup>a</sup> After recrystallization from petroleum ether (b. p. 40-60°) at low temperature (-80°). See Fig. 1. <sup>b</sup> The infrared absorption spectra of samples taken over this wide boiling range were similar (bands at 1700 and 3470 cm.<sup>-1</sup>). The analytically impure material was used directly in the preparation of the corresponding diketone.

The same reaction was also run on a twofold and a fourfold scale.

**1,1,16,16-Tetramethyl-1,16-hexadecanedicarboxylic Acid.**—A slurry of 25 g. (0.07 mole) of the crude diamide with a solution of 50 g. of potassium hydroxide in 250 ml. of methanol and 25 ml. of water in a copper flask was heated at the reflux temperature for three days. The mixture was transferred to a beaker and most of the methanol was removed by evaporation. When the residue had cooled, 650 ml. of water was added to give a cloudy solution which, when treated with 90 ml. of 12 *N* hydrochloric acid, deposited a solid material. The solid material was collected and was treated with boiling hydrochloric acid solution. After filtration the solid was washed with water and dried, and the major portion of the crude diacid was converted directly to diethyl 1,1,16,16-tetramethyl-1,16-hexadecanedicarboxylate. A small portion was purified in the following manner. The crude solid was dissolved in dilute aqueous sodium hydroxide. The aqueous solution was extracted with ether and then acidified with hydrochloric acid. The precipitate was boiled with 6 *N* hydrochloric acid, collected, and the entire process was repeated. The solid thus obtained was triturated with a warm solution of petroleum ether (b. p. 40-60°) and ether (in 40:1 proportion). The resulting mixture was filtered and the filtrate was evaporated to dryness. The residue, which was partially crystalline, was recrystallized from petroleum ether (b. p. 40-60°) to which sufficient ether had been added to effect solution at the reflux temperature. The recrystallization process was repeated until the colorless microcrystalline solid was observed to melt at 79-83°, with prior softening.

*Anal.* Calcd. for C<sub>22</sub>H<sub>42</sub>O<sub>4</sub>: C, 71.30; H, 11.43. Found: C, 71.47; H, 11.48.

**Diethyl 1,1,16,16-Tetramethyl-1,16-hexadecanedicarboxylate.**—The method of preparation from the crude 1,1,16,16-tetramethyl-1,16-hexadecanedicarboxylic acid was similar to that employed for the esterification of 1,1,4,4-tetramethyladipic acid. The purification was more difficult, necessitating repeated fractional distillation. The final distillation afforded pure diethyl 1,1,16,16-tetramethyl-1,16-hexadecanedicarboxylate, b. p. 185-187° (0.5 mm.),  $n_D^{20}$  1.4497, in 10% over-all yield from tetradecamethylene bromide.

*Anal.* Calcd. for C<sub>26</sub>H<sub>50</sub>O<sub>4</sub>: C, 73.19; H, 11.81. Found: C, 73.33; H, 11.69.

**Acyloins.**—Pivaloin was prepared by the acyloin condensation following the procedure described in "Organic Syntheses"<sup>11</sup> for the preparation of butyrolin. The same general procedure was followed for the preparation of 3,3,6,6-tetramethyl-2-hydroxycyclohexanone and 3,3,7,7-tetramethyl-2-hydroxycycloheptanone with the excep-

tions of a longer reaction period (up to forty-eight hours) and a more dilute reaction mixture. The procedure for 3,3,8,8-tetramethyl-2-hydroxycyclooctanone was adapted from that of Hansley,<sup>12</sup> and that for 3,3,18,18-tetramethyl-2-hydroxycyclooctadecanone, from the technique developed in Stoll's Laboratory.<sup>13,14</sup> The properties of the acyloins are described in Table I.

**1,2-Diketones.**—The method for the preparation of 3,3,6,6-tetramethyl-1,2-cyclohexanedione will serve as an example of the general procedure for the oxidation of the acyloins to 1,2-diketones. A solution of 20 g. (0.12 mole) of 3,3,6,6-tetramethyl-2-hydroxycyclohexanone in 53 ml. of glacial acetic acid was stirred and maintained at about 14° by cooling in an ice-bath. A solution of 9.5 g. (0.095 mole) of chromic anhydride in 53 ml. of glacial acetic acid and 6.5 ml. of water was added during one hour, and stirring was continued for an additional hour. The reaction mixture was diluted with 650 ml. of water, and the yellow crystals obtained were separated by filtration and recrystallized twice from high boiling petroleum ether (b. p. 87-102°); m. p. 114.2-114.8°; yield 12.7 g. (64%). For analysis of 3,3,6,6-tetramethyl-1,2-cyclohexanedione, see Table II. In the preparation of 3,3,7,7-tetramethyl-1,2-cycloheptanedione and of 3,3,8,8-tetramethyl-1,2-cyclooctanedione, the diketone did not separate as a solid, so that ether extraction and distillation had to be employed for isolation and purification. For the purification of the 3,3,18,18-tetramethyl-1,2-cyclooctadecanedione obtained crude from similar ether extraction and distillation, the first step was chromatography on activated alumina.<sup>16</sup> A solution of 430 mg. of the crude distilled diketone (b. p. 140-195° at 0.2 mm.) in 20 ml. of petroleum ether was passed through a 14 × 250 mm. column of alumina, and the column was percolated with 100-ml., 50-ml. and 100-ml. volumes of petroleum ether. From the last fraction on evaporation there was obtained 64.5 mg. of viscous, intensely yellow liquid. The similarity of the ultraviolet absorption spectrum with that of dipivaloyl indicated that the sample consisted of nearly optically pure diketone. The analysis was still not exact, so that a final distillation of the yellow liquid was carried out. In a small sublimation apparatus, the liquid distilled at a pressure of 0.5 mm. when the bath temperature was approximately 160°. The properties of all of the diketones are described in Table II.

**Quinoxalines.**—Quinoxalines were prepared by the general method of heating equimolar quantities of the diketone and *o*-phenylenediamine in glacial acetic acid under

(12) Hansley, *THIS JOURNAL*, **57**, 2303 (1935).

(13) Stoll and Hultskamp, *Helv. Chim. Acta*, **30**, 1815 (1947).

(14) Stoll and Rouvé, *ibid.*, **30**, 1822 (1947).

(15) Bouveault and Locquin, *Bull. soc. chim.*, [3] **35**, 641 (1906).

(11) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 114.

(16) The Eimer and Amend "Alumina Absorption" (80-200 MM) was made ready by washing with a large volume of ethanol, drying and reactivating by heating at 200° for one and one-half hours.

TABLE II  
1,2-DIKETONES<sup>a</sup>

Compound	B. p., °C. Mm.		M. p., °C.	<i>n</i> <sub>D</sub> <sup>20</sup>	Yield, %	Molecular formula	Carbon, %		Hydrogen, %	
	°C.	Mm.					Calcd.	Found	Calcd.	Found
Dipivaloyl (2,2,5,5-tetramethyl-3,4-hexanedione) (IX) <sup>17</sup>	59-62	14	-2.9 to -1.7 <sup>b</sup>	1.4144	50	C <sub>10</sub> H <sub>18</sub> O <sub>2</sub>				
3,3,6,6-Tetramethyl-1,2-cyclohexanedione (Ib)			114.2-114.8		64	C <sub>10</sub> H <sub>18</sub> O <sub>2</sub>	71.39	71.54	9.59	9.76
3,3,7,7-Tetramethyl-1,2-cycloheptanedione (Ic) <sup>c</sup>	87-91	6	16.7-17.3 <sup>b</sup>	1.4562	64	C <sub>11</sub> H <sub>18</sub> O <sub>2</sub>	72.49	72.45	9.95	10.02
3,3,8,8-Tetramethyl-1,2-cyclooctanedione (Id) <sup>d</sup>					..	C <sub>12</sub> H <sub>20</sub> O <sub>2</sub>	73.42	74.53 <sup>d</sup>	10.27	10.57
3,3,18,18-Tetramethyl-1,2-cyclooctadecanedione (Ie)	160°	0.5			..	C <sub>22</sub> H <sub>40</sub> O <sub>2</sub>	78.51	78.74	11.98	12.03
Camphorquinone (X) <sup>18</sup>			200-202			C <sub>10</sub> H <sub>14</sub> O <sub>2</sub>				

<sup>a</sup> For a detailed description of the preparation of individual 1,2-diketones, acyloins and all precursors, see Mader, Ph.D. Thesis, University of Illinois, 1950. <sup>b</sup> After recrystallization from petroleum ether (b. p. 40-60°) at low temperature (-80°). See Fig. 1. <sup>c</sup> As a proof of the structure of the dione, a 1.0-g. sample was oxidized by heating with 0.50 g. of chromic anhydride in 7 ml. of glacial acetic acid and 0.5 ml. of water. There was obtained, after recrystallization, 0.65 g. of 1,1,5,5-tetramethylpimelic acid, m. p. 169-170°, undepressed in melting point on admixture with authentic 1,1,5,5-tetramethylpimelic acid. <sup>d</sup> Physical properties are not given for this 1,2-diketone since it was not obtained analytically pure even after several distillations followed by numerous recrystallizations from petroleum ether at low temperature. Purification was followed by determination of the ultraviolet absorption spectrum at each stage. The dicarbonyl band was observed not to change in wave length (343 *mμ*) but to increase in intensity to a final  $\epsilon$  value of 21.4 during the course of purification. <sup>e</sup> Bath temperature.

TABLE III  
QUINOXALINES OF 1,2-DIKETONES

Quinoxaline of	M. p., °C.	Crystal form	Molecular formula	Carbon, %		Hydrogen, %		Nitrogen, %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
Dipivaloyl <sup>a</sup>									
3,3,6,6-Tetramethyl-1,2-cyclohexanedione <sup>b</sup>	68.8-69.6	Needles	C <sub>16</sub> H <sub>20</sub> N <sub>2</sub>	79.96	80.15	8.39	8.67	11.66	11.68
3,3,7,7-Tetramethyl-1,2-cycloheptanedione	71.3-71.8	Plates	C <sub>17</sub> H <sub>22</sub> N <sub>2</sub>	80.26	80.38	8.72	8.78	11.02	10.80
Camphorquinone <sup>19</sup>	77.6-78.7	.....	C <sub>18</sub> H <sub>18</sub> N <sub>2</sub>						

<sup>a</sup> In an attempt to prepare 2,3-di-*t*-butylquinoxaline from dipivaloyl and *o*-phenylenediamine in acetic acid, the only product obtained was characterized as 2-methylbenzimidazole, m. p. 177.5-177.8° (Ladenburg, *Ber.*, **8**, 677 (1875); Valyashko and Boltina, *J. Russ. Phys. Chem. Soc.*, **46**, 1741 (1914)), identified by analysis (calcd. for C<sub>8</sub>H<sub>8</sub>N<sub>2</sub>: C, 72.70; H, 6.10; N, 21.20. Found: C, 72.49; H, 6.18; N, 21.71) and ultraviolet absorption spectrum (Behaghel and Schneider, *Ber.*, **69**, 88 (1936)). <sup>b</sup> Alternative name: 1,1,4,4-tetramethyl-1,2,3,4-tetrahydrophenazine.

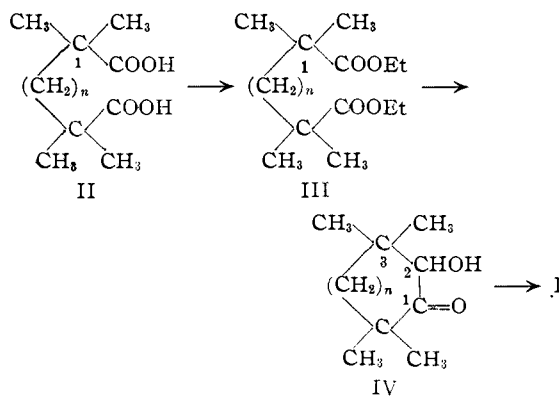
reflux for forty-five minutes. Precipitation of the quinoxaline was induced by dilution of the cooled reaction mixture with water and purification was effected by recrystallization from aqueous ethanol. The quinoxalines are listed in Table III.

**Determination of Absorption Spectra.**—All ultraviolet absorption spectra were determined using solutions of the compounds in freshly distilled 95% ethanol and employing a Beckman model DU quartz spectrophotometer. The infrared absorption spectra were determined using thin films of the pure liquid compounds or suspensions of the solids in Nujol. The spectral curves were recorded by a Perkin-Elmer model 12B infrared spectrophotometer having rocksalt optics.

### Discussion

**Synthesis.**—For this study of the relationship between ultraviolet absorption and steric configuration of 1,2-dicarbonyl groups, a new series of 1,2-diketones of type I was needed. Although acyclic analogs of this type have been

synthesized previously,<sup>3,20</sup> no alicyclic 1,2-diketone having complete substitution of the  $\alpha$ -hydrogens by methyl groups has been reported. All of the diketones studied, with the exception of camphor-



a, *n* = 1; b, *n* = 2; c, *n* = 3; d, *n* = 4; e, *n* = 14

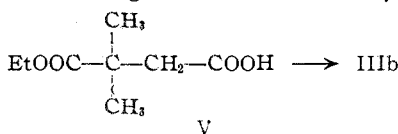
(17) Henniou and Banigan, *THIS JOURNAL*, **68**, 1202 (1946).

(18) For preparation, see Evans, Ridgion and Simonsen, *J. Chem. Soc.*, **137** (1934); for infrared absorption spectrum, see Lowry and French, *ibid.*, **125**, 1921 (1924).

(19) Singh and Mazumder, *J. Chem. Soc.*, **115**, 566 (1919).

(20) Corson, Benson and Goodwin, *THIS JOURNAL*, **52**, 3968 (1930).

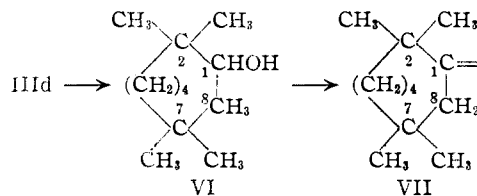
quinone, were prepared by chromic anhydride oxidation of the corresponding  $\alpha$ -hydroxyketones (IV), which were made by the acyloin condensation of the appropriate diesters (III). The dicarboxylic acids (II) from which the esters were derived were synthesized by the Kolbe electrolysis method ( $V \rightarrow IIIb$ ) in the case of 1,1,4,4-tetramethyladipic acid (IIb),<sup>7</sup> and by the method of Haller and Bauer<sup>6</sup> in the case of the other dibasic acids (IIc, d, e). We shared Haller and Bauer's experience in being unable to obtain any 1,1,3,3-



tetramethylglutaric acid (IIa) by condensation of methylene iodide with sodio isobutyrophenone.

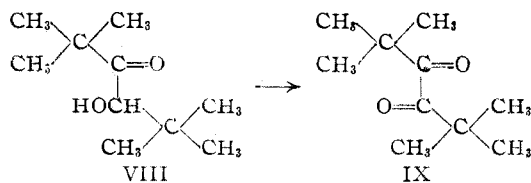
The tetramethyldicarboxylic acids (IIb, c, d, e) were transformed into their diethyl esters (IIIb, c, d, e), and the diethyl esters were converted to cyclic acyloins (IVb, c, d, e) by treatment with sodium in an anhydrous solvent. 3,3,6,6-Tetramethyl-2-hydroxycyclohexanone (IVb) was obtained in 91% yield in the cyclization of diethyl 1,1,4,4-tetramethyladipate (IIIb) by means of granular sodium in refluxing ether. The acyloin was possibly contaminated with some diketone, as indicated by the slight yellow color, but the amount was not detectable microanalytically, nor was there any change in refractive index or infrared absorption of the acyloin during the course of purification operations. 3,3,7,7-Tetramethyl-2-hydroxycycloheptanone (IVc) was prepared by the acyloin ring closure of diethyl 1,1,5,5-tetramethylpimelate (IIIc) in ether under conditions identical with those used for the homologous six-membered ring compound. However, the yield of seven-membered ring acyloin was lower (69%), probably because of competing intermolecular acyloin formation. When an attempt was made to prepare 3,3,8,8-tetramethyl-2-hydroxycyclooctanone (IVd) from diethyl 1,1,6,6-tetramethylsuberate (IIId) using the conditions which were satisfactory for the synthesis of the six- and seven-membered ring compounds, much sodium and diester remained unchanged at the end of the reaction period. Nevertheless, the reaction mixture was worked up in the usual manner and a colorless solid possessing a camphor-like odor was isolated. Analysis indicated that the product contained only one-half of the amount of oxygen expected for the acyloin (IVd). The analytical figures found for carbon and hydrogen indicated a molecular formula of  $C_{12}H_{24}O$ , which would be satisfactory for 2,2,7,7-tetramethylcyclooctanol (VI), and the infrared spectrum indicated strong hydroxyl absorption and the absence of carbonyl absorption. Additional evidence for the structure assigned (VI) was found in the oxidation of this compound in good yield to a ketone having strong carbonyl absorption in the

infrared and an elementary analysis which was satisfactory for 2,2,7,7-tetramethylcyclooctanone (VII). It was possible to obtain the eight-



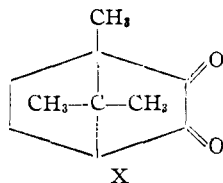
membered ring acyloin (IVd) by operating under the more vigorous conditions suggested for certain acyloin condensations by Hansley.<sup>12</sup> The acyloin ring closure was run in xylene at 105° under an atmosphere of nitrogen. Fractional distillation of the product gave some 2,2,7,7-tetramethylcyclooctanol, but also a satisfactory quantity of 3,3,8,8-tetramethyl-2-hydroxycyclooctanone (IVd). The structure of the acyloin was established by elementary analysis and by the infrared spectrum, which exhibited strong carbonyl and hydroxyl absorption. The preparation of 3,3,18,18-tetramethyl-2-hydroxycyclooctadecanone (IVe) from 1,1,16,16-tetramethyl-1,16-hexadecanedicarboxylate (IIIe) was accomplished by applying the general technique of Stoll and his co-workers.<sup>13,14</sup> Refluxing xylene was employed as the reaction medium, rapid agitation was used, and as long as the reaction mixture was strongly alkaline, it was maintained under an atmosphere of oxygen-free nitrogen. Fractional distillation of the product failed to give cyclic acyloin (IVe) of analytical purity although the major portion of the product was apparently the desired compound, as indicated by the facts that the molecular weight was in the correct range and that the infrared spectrum exhibited strong carbonyl and hydroxyl absorption peaks.

Transformation of the acyloins (IV) to the 1,2-diketones (I) was effected by oxidation with chromic anhydride in acetic acid. The open-chain model compound, dipivaloyl (IX),<sup>17</sup> was likewise obtained by chromic anhydride oxida-

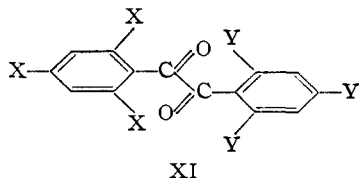


tion of pivaloin (VIII),<sup>15</sup> and some of the diketone (IX) was also formed in the condensation of ethyl pivalate which led to pivaloin (VIII) as the major product. Although no difficulty was experienced in obtaining pure samples of 3,3,6,6-tetramethyl-1,2-cyclohexanedione (Ib) and 3,3,7,7-tetramethyl-1,2-cycloheptanedione (Ic) by oxidation of the corresponding cyclic acyloins, it was not possible to obtain 3,3,8,8-tetramethyl-1,2-cyclooctanedione (Id) in a pure form. Chromic anhydride oxidation of 3,3,8,8-tetra-

methyl-2-hydroxycycloöctanone (IVd) gave a mixture which contained a considerable amount of 1,1,6,6-tetramethylsuberic acid (IIId), a small amount of unchanged acyloin, some diketone, and other materials containing less oxygen than the diketone. The purification of the crude diketone was followed by means of the ultraviolet absorption spectrum, and as the purity of the diketone increased the intensities of the absorption maxima (at 343 and 295.5  $m\mu$ ) were observed to increase, but with no attendant shift in wave length. The diketone Id was not obtained in a state of analytical purity, but it is considered that the wave lengths, if not the extinction coefficients, of the ultraviolet absorption maxima are representative of this eight-membered cyclic diketone. 3,3,18,18-Tetramethyl-1,2-cycloöctadecanedione (Ie) was obtained by the oxidation of impure 3,3,18,18-tetramethyl-2-hydroxycycloöctadecanone (IVe). The pure diketone Ie was finally isolated after a series of purification steps involving distillation, chromatography and again distillation. Since we were not successful in synthesizing 3,3,5,5-tetramethyl-2-hydroxycyclopentanone (IVa), the precursor of 3,3,5,5-tetramethyl-1,2-cyclopentanedione (Ia), another diketone had to be used for a model of the five-membered ring 1,2-diketone type. Camphorquinone (X) was selected since it is well-characterized and can be prepared readily by the selenium dioxide oxidation of camphor.<sup>18</sup>



**Configuration and Spectra.**—In an earlier examination of the ultraviolet absorption spectra of benzil (XIa), mesityl phenyl diketone (XIb) and mesityl (XIc), and similarly related series of



a, X = Y = H; b, X = CH<sub>3</sub>, Y = H; c, X = Y = CH<sub>3</sub> compounds, it was shown that the wave length of the dicarbonyl absorption maximum is qualitatively dependent upon the angle between the planes of the carbonyl groups.<sup>21,22</sup> Specifically, the dicarbonyl absorption maximum is shifted to longer wave length with increasing hindrance at the ortho carbons of benzil (dicarbonyl maxima,  $\lambda_{XIa} < \lambda_{XIb} < \lambda_{XIc}$ ), corresponding to increasing tendency to coplanarity of the two carbonyl

(21) Leonard, Rapala, Herzog and Blout, *THIS JOURNAL*, **71**, 2997 (1949).

(22) Leonard and Blout, *ibid.*, **72**, 484 (1950).

groups ( $90^\circ \rightarrow 180^\circ$ ). In considering a study of the benzil system as a means of arriving at a quantitative relationship between ultraviolet absorption and steric orientation of the carbonyl groups in 1,2-diketones, there are two important deficiencies. First, the presence in the benzil system of aromatic groups attached to the carbonyls introduces extraneous phenyl-carbonyl absorption into the spectrum. Second, the benzil system does not lend itself readily to a systematic and determinable variation in the value of the inter-carbonyl angle.

The compounds selected for the present study (I) do not suffer from these deficiencies. No aromatic group is present. The systematic variation in the value,  $\theta$ , of the intercarbonyl angle is possible by means of the systematic variation in the ring size of the alicyclic 1,2-dicarbonyl system (I). Enolization of the carbonyl groups in the 1,2-diketones, which would be expected to introduce an extraneous factor into the ultraviolet absorption,<sup>23</sup> is prevented by the complete methyl-substitution on the  $\alpha$ -carbon atoms (I).

Compounds of type I containing six- (Ib), seven- (Ic), eight- (Id) and eighteen-membered (Ie) rings have been prepared and their ultraviolet absorption spectra have been determined. The spectrum of the analogous acyclic diketone, dipivaloyl (IX), has also been determined. Since we did not prepare the five-membered ring compound Ia, we have included for the purpose of comparison the spectrum of camphorquinone (X), a compound which possesses two vicinal, non-enolizable<sup>1b</sup> carbonyl groups in a five-membered ring. The ultraviolet absorption maxima and the infrared absorption peaks for these diketones and for related compounds prepared in the course of this study are recorded in Table IV. The ultraviolet absorption maxima designated as B-bands are identified as those associated with the activation of the individual carbonyl groups on the basis that these bands occur in the region of ketone absorption in the ultraviolet, and—more specifically—in the range of the absorption maxima of the closely analogous cyclic monoketones, 2,2,7,7-tetramethylcycloöctanone (VII) and 3,3,8,8-tetramethyl-2-hydroxycycloöctanone (IVd) (Table IV, Fig. 3).

Since neither "exocyclic strain"<sup>24</sup> nor the steric

(23) For example, it has been established that 1,2-cyclohexanedione exists largely as the mono-enol,<sup>1a,b,c</sup> and its ultraviolet absorption spectrum is essentially that of an  $\alpha,\beta$ -unsaturated carbonyl compound.<sup>1d</sup>

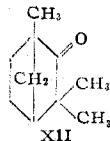
(24) "Exocyclic strain" is evidenced in the spectrum of a compound by a shift in the position of the absorption band of an unsaturated chromophore when that chromophoric group is placed in an exocyclic position (Ramart-Lucas, *Bull. soc. chim.*, [5] **1**, 1133 (1934); [5] **3**, 723 (1936); Lewis and Calvin, *Chem. Revs.*, **26**, 273 (1939); Woodward, *THIS JOURNAL*, **64**, 72 (1942)). The direction and magnitude of the shift for a 1,3-diene system has been worked out empirically, but the corresponding data for the 1,2-dicarbonyl system are not at all precise. Biquard (*Bull. soc. chim.*, [5] **7**, 894 (1940)) has found, in a comparison of the ultraviolet absorption spectra of the cyclic ketones from cyclobutanone to cycloöctanone with those of the analo-

TABLE IV  
 ULTRAVIOLET AND INFRARED ABSORPTION

Compound	Maxima in the ultraviolet <sup>a</sup>				Peaks in the infrared <sup>c</sup> $\nu$ , cm. <sup>-1</sup>
	A-band <sup>b</sup>		B-band <sup>b</sup>		
	$\lambda$ , m $\mu$	$\epsilon$	$\lambda$ , m $\mu$	$\epsilon$	
Camphorquinone (X)	466	30.7	...	..	1753 (s) <sup>e,g</sup> 3490 (w) <sup>e</sup>
3,3,6,6-Tetramethyl-2-hydroxycyclohexanone (IVb)	~457 <sup>d</sup>	28.5			1705 (s) 3484 (s)
3,3,6,6-Tetramethyl-1,2-cyclohexanedione (Ib)	380	11.1	297.5	28.9	1709 (s) 3403 (w)
3,3,7,7-Tetramethyl-2-hydroxycycloheptanone (IVc)					1693 (s) 3470 (s)
3,3,7,7-Tetramethyl-1,2-cycloheptanedione (Ic)	337	33.8	299	34.5	1710 (s)
2,2,7,7-Tetramethylcyclooctanol (VI)			~288	28	3397 (w)
2,2,7,7-Tetramethylcyclooctanone (VII)			293	28.7	3360 (s)
3,3,8,8-Tetramethyl-2-hydroxycyclooctanone (IVd)			295	33.9	1696 (s) 1692 (s) 3430 (s)
3,3,8,8-Tetramethyl-1,2-cyclooctanedione (Id)	343	21.4 <sup>f</sup>	295.5	43.2 <sup>f</sup>	1697 (s)
			~287	34.5	3541 (w)
					3384 (w)
3,3,18,18-Tetramethyl-1,2-cyclooctadecanedione (Ie)	384	21.7	296	50.6	1698 (s)
			286.5	59	3363 (w)
			~278	48	
Pivaloin (VIII)					1700 (s) 3464 (s)
Dipivaloyl (IX)	365	21.0	294	47.0	1700 (s)
			285	52.5	3376 (w)
			~275	38	
Quinoxalines derived from		$\lambda$ , m $\mu$		$\epsilon$	
Camphorquinone		~323		6600	
		314		8800	
		242		26000	
3,3,6,6-Tetramethyl-1,2-cyclohexanedione		323		9800	
		310		7900	
		238		31000	
3,3,7,7-Tetramethyl-1,2-cycloheptanedione		323		7700	
		~314		6000	
		236		30000	

<sup>a</sup> Ultraviolet spectra were determined using solutions of the compounds in 95% ethanol. <sup>b</sup> Merely for convenience in discussing the spectra, the long wave length bands are referred to as A-bands, those of short wave length, as B-bands. <sup>c</sup> Infrared spectra were determined using thin films of the liquid compounds and thin films of suspensions of the solid compounds in Nujol. Only maxima in the carbonyl and hydroxyl regions of the infrared spectra are listed. <sup>d</sup> ~ Indicates an inflection point. <sup>e</sup> (s) indicates high intensity; (w) low intensity. <sup>f</sup> The correct  $\epsilon$  values for this compound are probably higher than those recorded since the material was not obtained in the pure state. <sup>g</sup> No splitting of the carbonyl bands (1692–1753 cm.<sup>-1</sup>) was observed (cf. Rasmussen, Tunnicliff and Brattain, THIS JOURNAL, 71, 1068 (1949)).

gous acyclic ketones, that the absorption band of the cyclic ketones is shifted toward the red. By contrast, fenchone (XII) has an ab-



sorption maximum at 293 m $\mu$  ( $\epsilon = 19.9$ ) (Donle and Volkert, Z. physik. Chem., B8, 80 (1930)), representing a shift toward shorter wave length from that (296.2 m $\mu$ ,  $\epsilon = 19.5$ ) of the analogous band for the acyclic analog, di-*t*-butyl ketone (Wolf and Lederle, *ibid.*, B2, 39 (1929)). In view of these conflicting shifts, it is not possible to apply an empirical correction to the carbonyl absorption maxima exhibited by the cyclic 1,2-diketones here studied (I), in relating these maxima to that of the acyclic analog, dipivaloyl (IX). As a matter of fact, empirical correction is evidently unnecessary since the carbonyl absorption bands (B-bands) for all of the cyclic diketones (Ib, c, d, e) and also for dipivaloyl (IX) occur at practically the same wave length, 294–299 m $\mu$  (Table IV). There is no regular shifting

relation of the dicarbonyl group to the  $\alpha$ -methyl groups<sup>25</sup> can account for the large differences ob-

of the band toward the red as the ring size is reduced; however, there is an attendant regular decrease in the intensity of the B-band (see Fig. 2), which would appear to be associated with the steric relation of the two carbonyls rather than with any "exocyclic strain." Since, from the data available, it is not evident that "exocyclic strain" has any large effect on the wave length of the carbonyl absorption band, it may also be argued that such strain would not cause any large shifts in the wave lengths of the bands associated with dicarbonyl absorption.

(25) In the acyclic member of the series studied, dipivaloyl (IX), the *t*-butyl groups are able to rotate about the bonds connecting them to the carbonyl carbons, while in the cyclic molecules such motion is essentially restricted. The relative orientations of the carbonyl groups and adjacent hydrocarbon portions of the molecule may thus be different in the acyclic and cyclic structures. It seems unlikely, however, that the resulting environmental differences will be responsible for any appreciable alteration of the absorption spectra in the ultraviolet region.

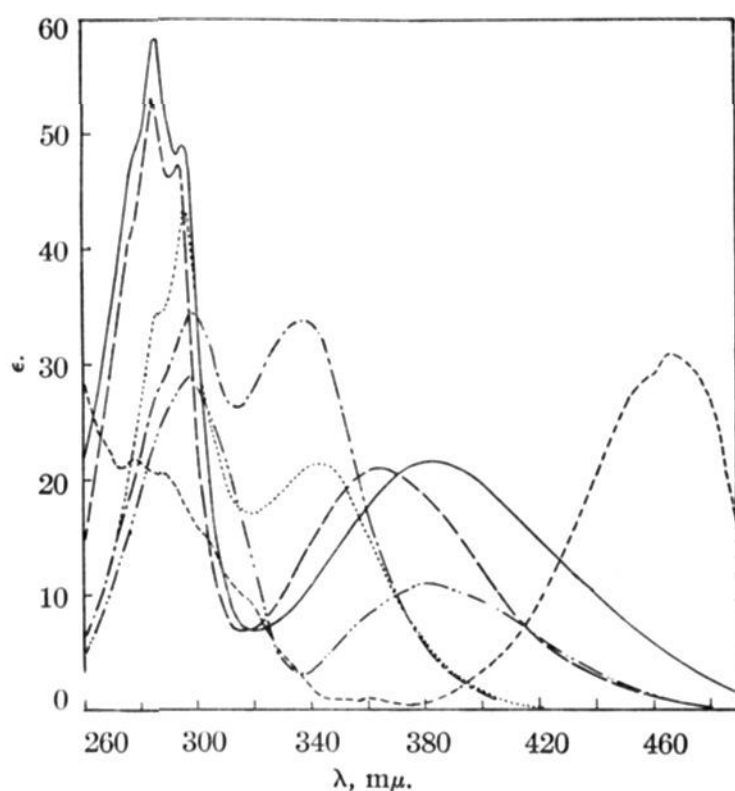


Fig. 2.—Camphorquinone, -----; 3,3,6,6-tetramethyl-1,2-cyclohexanedione, -·-·-·-; 3,3,7,7-tetramethyl-1,2-cycloheptanedione, ———; 3,3,8,8-tetramethyl-1,2-cyclooctanedione (impure), ·······; 3,3,18,18-tetramethyl-1,2-cyclooctadecanedione, ———; dipivaloyl, — — —; (solvent 95% ethanol).

served in the ultraviolet absorption spectra of the 1,2-diketones (Table IV, Fig. 2), we conclude that the differences in the absorption spectra are due mainly to variation in ring size, *i. e.*, variation in the value of the inter-carbonyl angle, in the 1,2-dicarbonyl compounds. It is possible to arrive at the most probable values for the inter-carbonyl angles in the series of 1,2-diketones

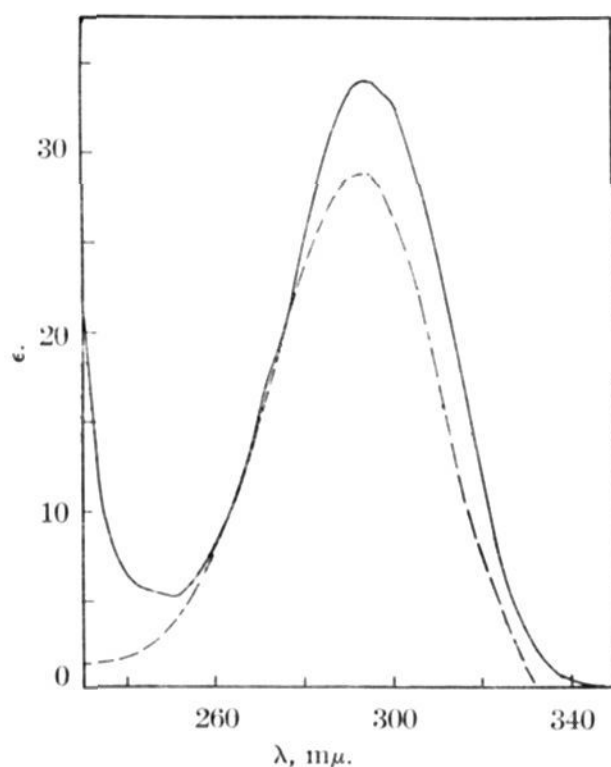


Fig. 3.—2,2,7,7-tetramethylcyclooctanone, - - - -; 3,3,8,8-tetramethyl-2-hydroxycyclooctanone, ———; (solvent 95% ethanol).

by consideration of accurate molecular models of these compounds. There seems to be little doubt concerning the relative orientation of the carbonyl groups in camphorquinone (X). The carbonyl groups must be held tightly in a *cis* configuration by the bicyclic ring system so that the angle,  $\theta$ , between the carbonyl groups is  $0^\circ$  or nearly so<sup>26</sup> (Table V). A consideration of the Fisher-Hirschfelder-Taylor model of 3,3,6,6-tetramethyl-1,2-cyclohexanedione (Fig. 4, Ib—arrows point

TABLE V  
RELATION OF INTER-CARBONYL ANGLE TO DICARBONYL ABSORPTION

Diketones, size of ring	$\theta$	A-band, $\lambda_{\max.}, m\mu$
5-Membered (X)	$0-10^\circ$	466 <sup>a</sup>
6-Membered (Ib)	$0-60^\circ$	380
7-Membered (Ic)	$90-110^\circ$	337
8-Membered (Id)	$100-140^\circ$	343
Acyclic (IX)	$90-180^\circ$	365
18-Membered (Ie)	$100-180^\circ$	384

<sup>a</sup> No empirical correction has been applied to the absorption maximum for camphorquinone (X), although for the purpose of comparison with the other models (I, IX) it might be expedient since the former is effectively a trialkyl-1,2-diketone whereas the others are tetraalkyl-1,2-diketones.

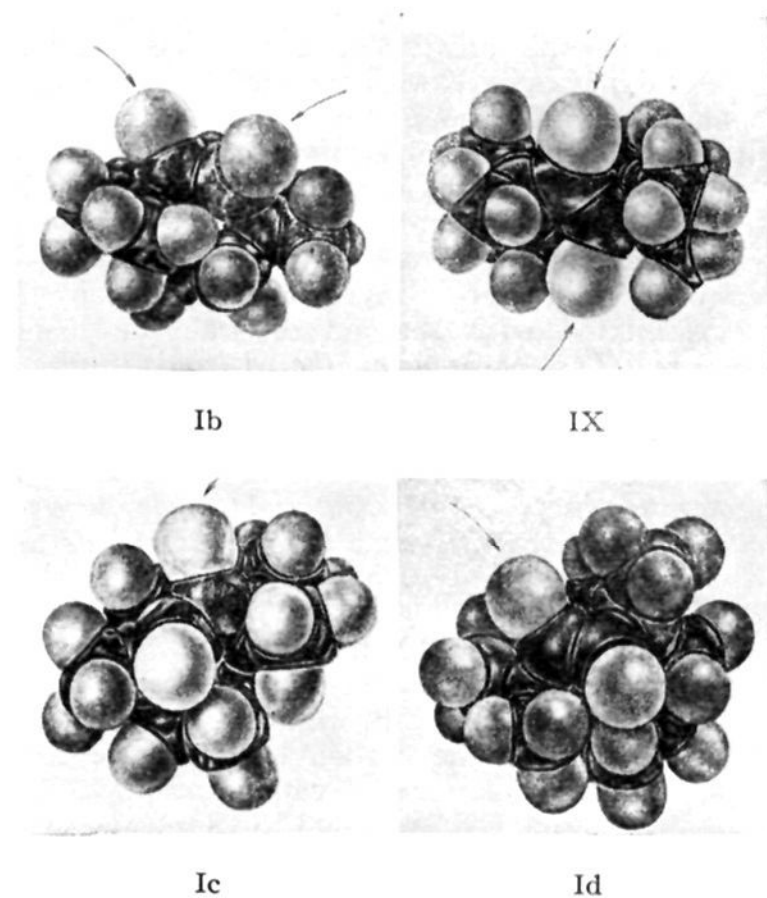


Fig. 4.

(26) Although it has been demonstrated by Kilpatrick, Pitzer and Spitzer (THIS JOURNAL, **69**, 2483 (1947)) and by Aston, Schumann, Fink and Doty (*ibid.*, **63**, 2029 (1941)) that the carbon atoms of cyclopentane are not coplanar but that the ring is puckered, similar demonstration is lacking in the case of a five-membered alicyclic 1,2-diketone here considered (Ia, X). The deviation from coplanarity would be expected to be smaller for the 1,2-dicarbonyl compound than for the hydrocarbon. Accordingly, the value of  $10^\circ$  is set as a conservative upper limit for the angle,  $\theta$ , between the carbonyl groups in camphorquinone (X) (see Table V).



to the oxygen atoms) indicates that most of the molecules of this compound are probably in configurations such that the angle,  $\theta$ , between the planes of the carbonyl groups lies between 0 and 60°. A similar consideration of models of 3,3,7,7-tetramethyl-1,2-cycloheptanedione (Fig. 4, Ic) and 3,3,3,8-tetramethyl-1,2-cyclooctanedione (Fig. 4, Id) shows that the most probable configurations of these molecules are represented by inter-carbonyl angles of 90–110° and 100–140°, respectively. In the model of 3,3,18,18-tetramethyl-1,2-cyclooctadecanedione, the *trans* orientation ( $\theta = 180^\circ$ ) is readily attainable, and the bulk of the molecules are probably represented by configurations in which  $\theta = 100\text{--}180^\circ$ . In the model of dipivaloyl (Fig. 4, IX) also, the *trans* orientation of the two carbonyls is readily attainable, while the *cis* is not, and the bulk of the molecules are probably represented by configurations in which  $\theta = 90\text{--}180^\circ$ . The existence of a large portion of the dipivaloyl molecules in the *trans* configuration is in accord with the electron diffraction data of LuValle and Schomaker,<sup>27</sup> which indicated existence of analogous glyoxal and biacetyl molecules in the *trans* configuration.

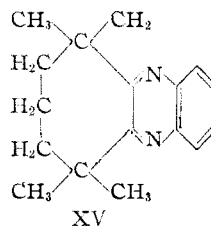
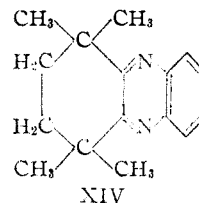
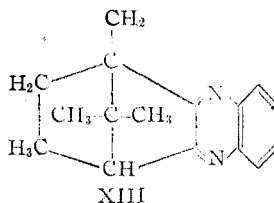
In Table V are recorded the probable ranges of values for the inter-carbonyl angles in the 1,2-diketones (Ib, c, d, e, IX, X), along with the wave lengths of the ultraviolet absorption maxima (A-bands) associated with the dicarbonyl system. As has been indicated previously, the B-bands are associated with the absorption of a single carbonyl group. A consideration of the values in Table V indicates that the positions of the A-bands vary in a systematic way with the relative orientations of the carbonyl groups in the molecule as estimated with the aid of scale molecular models. *The position of the A-band shifts to shorter wave lengths as the carbonyl groups rotate out of a coplanar cis configuration ( $\theta = 0^\circ$ ), reaches a minimum wave length when the carbonyl groups lie in planes at about right angles to each other, and then shifts back toward the red as the carbonyl groups approach a coplanar trans configuration ( $\theta = 180^\circ$ ).*

Camphorquinone (X) represents a compound in which the carbonyl groups are held essentially in *cis* configuration, but we have provided no example wherein the carbonyl groups are held equally firmly in a *trans* configuration. With both dipivaloyl (IX) and 3,3,18,18-tetramethyl-1,2-cyclooctadecanedione (Ie), at any instant a considerable proportion of the molecules will have configurations other than *trans* or near-*trans*, and the departure from the coplanar *trans* configuration is probably greater for dipivaloyl than for the eighteen-membered ring ketone. The absorption maximum for neither compound can be considered to be characteristic of pure-*trans* molecules. The maximum for such a theoretical pure-*trans* type should be much closer to that

for camphorquinone, representative of the pure-*cis* type.

Our findings on the relation between  $\theta$  and  $\lambda_{\max}$  in dicarbonyls constitute an extension of the principle developed by Klevens and Platt,<sup>28</sup> in their study of substituted dimethylanilines, that changes in spectrum are quantitatively related to the angle of twist between potentially conjugable groups. Their examples permitted spectral reference to angles of twist from 0 to 90°, whereas the present study on 1,2-dicarbonyls has allowed correlation of absorption maxima with angles of twist ( $\theta$ ) from 0° through 90° toward 180°. The chromophoric dicarbonyls are "insulated" when the inter-carbonyl angle is 90°, and the wave length of the absorption maximum is then at its lowest value. The *cis* or *trans* coplanar forms ( $\theta = 0^\circ$  or  $180^\circ$ ) have higher energy in the ground state relative to that of the excited state; hence their absorption maxima are found at the longest wave lengths.

Quinoxalines were prepared from camphorquinone (XIII), 3,3,6,6-tetramethyl-1,2-cyclohexanedione (XIV) and 3,3,7,7-tetramethyl-1,2-cycloheptanedione (XV), and the ultraviolet absorption curves are shown in Fig. 5. The spectra are all very similar. The large differences which are present in the spectra of the corresponding



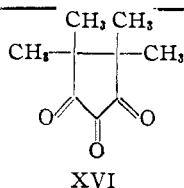
diketones (X, Ib, Ic) are not present in the spectra of the quinoxalines. This fact constitutes corroborative evidence that the differences in the spectra of the diketones are due mainly to variations in the relative orientation of the carbonyl groups. When these steric variations are eliminated partially or completely by formation of the quinoxalines, with C=N bonds essentially forced into coplanar *cis* configuration, the differences in the spectra become much smaller. The minor differences which do exist between the spectra of the three quinoxalines are probably related to varying amounts of strain or distortion produced in the aromatic quinoxaline system due to the steric demands of the attached saturated rings.

It is apparent from existing information in the

(27) LuValle and Schomaker, *THIS JOURNAL*, **61**, 3520 (1939).

(28) Klevens and Platt, *ibid.*, **71**, 1714 (1949).

literature that a similar analysis of the relation between inter-carbonyl angles and ultraviolet absorption maxima could be extended to the 1,2,3-triketone system. The absorption spectrum of triketopentane is not much different from that of biacetyl. Calvin and Wood<sup>29</sup> have provided the logical suggestion that this is due to one of the end carbonyl groups lying out of the plane ( $\theta' = \text{ca. } 90^\circ$ ) of the other two ( $\theta = 180^\circ$ ). As a result, the interaction between the two non-coplanar groups is hindered, and the compound exhibits absorption at shorter wave length than would be anticipated for a completely coplanar triketone. (The color of triketopentane is described as orange-yellow.) The absorption spectrum for a model coplanar triketone has not yet been determined, but 4,4,5,5-tetramethyl-1,2,3-cyclopentanetrione (XVI) has been synthesized by Shoppee<sup>30</sup> and has been described as a blue com-



pound. This indicates that XVI, which is non-enolizable and in which the three carbonyl groups are in the *cis-cis* coplanar configuration, absorbs at much longer wave length than does the acyclic triketone. From the present study, it is concluded that the bathochromic shift in absorption is due to the ring structure in XVI rather than to the complete methyl-substitution on the  $\alpha$ -carbons. Both factors were proposed by Shoppee as possible explanations when the unique blue triketone was first synthesized.

### Summary

Six 1,2-diketones (camphorquinone, 3,3,6,6-tetramethyl-1,2-cyclohexanedione, 3,3,7,7-tetra-

(29) Calvin and Wood, *THIS JOURNAL*, **62**, 3152 (1940).

(30) Shoppee, *J. Chem. Soc.*, 269 (1936).

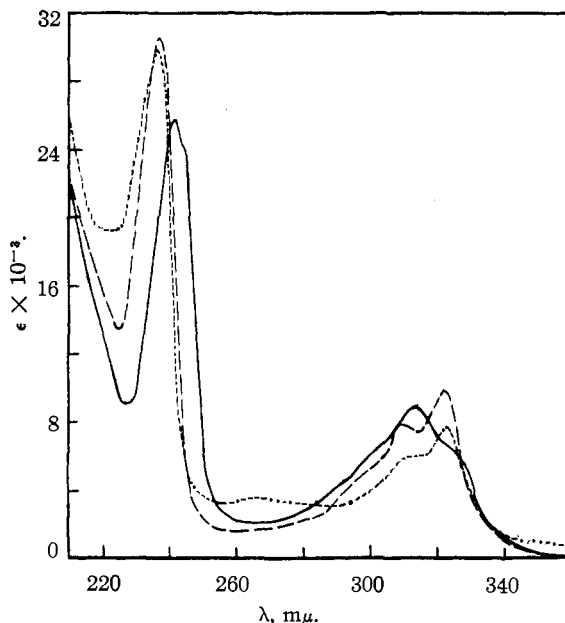


Fig. 5.—Quinoxalines of: camphorquinone, —; 3,3,6,6-tetramethyl-1,2-cyclohexanedione, - - -; 3,3,7,7-tetramethyl-1,2-cycloheptanedione, - · - ·; (solvent 95% ethanol).

methyl-1,2-cycloheptanedione, 3,3,8,8-tetramethyl-1,2-cyclooctanedione, 3,3,18,18-tetramethyl-1,2-cyclooctadecanedione and dipivaloyl) have been prepared and their ultraviolet absorption spectra have been determined. The position of the long wave length absorption bands of these diketones has been correlated with the relative steric orientation of the carbonyl groups as estimated with the aid of molecular models. The position of the band varies in a regular way with the angle between the planes of the carbonyl groups. The band moves toward shorter wave lengths as the angle increases from  $0^\circ$  to about  $90^\circ$  and shifts back again toward longer wave lengths as the angle increases beyond  $90^\circ$ .

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RECEIVED MARCH 29, 1950