

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

## Steric Effects and Spectra in the Tetracyclones

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Four ortho-substituted tetraphenylcyclopentadienones have been prepared: 2-(2'-chlorophenyl)-3,4,5-triphenylcyclopentadienone (VIII), 3-(2'-chlorophenyl)-2,4,5-triphenylcyclopentadienone (IX), 2,5-bis-(2'-chlorophenyl)-3,4-diphenylcyclopentadienone (X) and 3,4-bis-(2'-chlorophenyl)-2,5-diphenylcyclopentadienone (XI). Examination of the ultraviolet absorption spectra of these molecules shows two major absorption peaks. Referred to the absorption spectrum of tetracyclone it is seen that the peak at 342  $m\mu$  shifts hypsochromically and hypochromically when substituents are introduced in the 3- and 4-phenyl rings (compounds IX and XI), while substituents in the 2- and 5-phenyl rings cause the peak at 512  $m\mu$  to shift hypsochromically and hypochromically. The data also show that the unsubstituted path is shifted hyperchromically along with the hypochromic shift of the substituted path.

This investigation was designed to study the influence of ortho-substituents on the absorption spectrum of tetracyclone with specific reference to steric effects. Tetracyclone is a convenient parent molecule for making a study of this type since it has been shown<sup>3</sup> that the two major absorption peaks at 342  $m\mu$  and at 512  $m\mu$  can be related to resonance through the 3- and 4-phenyl rings and the 2- and 5-phenyl rings, respectively. This early work dealt only with parasubstituents. It was, therefore, planned to study ortho-chloro-substituted tetracyclones to determine their steric effect on the two absorption maxima.

**Synthesis of Tetracyclones.**—Most of the required intermediates were prepared according to literature procedures or by methods analogous to those in the literature with one exception.

Pyrolysis of the mixed calcium salts did not appear promising for the synthesis of 1-(2'-chlorophenyl)-3-phenyl-2-propanone (V). The reaction of a benzyl Grignard reagent with benzamide<sup>4,5</sup> appeared adaptable and after determining that unsubstituted benzyl ketone could be prepared from phenylacetamide and benzylmagnesium chloride, the reaction was extended to prepare V.

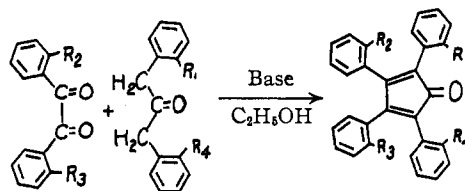
It is notable that appreciable quantities of phenylacetone nitrile and of *o*-chlorophenylacetone nitrile were recovered along with the corresponding ketones. To the authors' knowledge the conversion of an amide to a nitrile has only been effected with  $\alpha,\alpha,\alpha$ -trisubstituted acetamides.<sup>6</sup> The reported reactions were observed in boiling toluene, while those observed here took place in refluxing ethyl ether. Therefore, to establish this point firmly, the *o*-chlorophenylacetone nitrile obtained in the Grignard reaction was identified by (1) its boiling point and inability to form a 2,4-dinitrophenylhydrazone, (2) its infrared absorption band at 4.45  $\text{cm}^{-1}$ ,<sup>7</sup> and (3) hydrolysis to the amide and to the acid and comparison of these with authentic samples.

(1) From the M.S. thesis of E.L.S., June, 1953.

(2) To whom inquiries should be sent.

(3) S. B. Coan, D. E. Trucker and E. I. Becker, *THIS JOURNAL*, **75**, 900 (1953).(4) S. S. Jenkins, *ibid.*, **55**, 703 (1933).(5) S. S. Jenkins and E. M. Richardson, *ibid.*, **55**, 1618 (1933).(6) (a) Ramart-Lucas, LaClôtre and Anagnostopoulos, *Compt. rend.*, **185**, 282 (1927). (b) Professor James Cason has called our attention to the conversion of hexahydromesitoic amide to hexahydromesitoic nitrile, a highly hindered example, reported by E. P. Kohler, T. L. Jacobs and H. M. Sonnichsen, *THIS JOURNAL*, **62**, 785 (1940).(7) R. E. Kitson and N. E. Griffith, *Anal. Chem.*, **24**, 334 (1952).

The synthesis of the ortho-substituted tetracyclones was patterned after that of Dilthey and Quint<sup>8,9</sup> and consisted of the condensation of appropriately substituted benzils and benzyl ketones (equation 1). Curiously, potassium hydroxide, sodium ethoxide or the acid catalysts suggested by Dilthey<sup>10</sup> were generally ineffective in achieving the condensation. Triton B (benzyltrimethyl-



- I,  $R_2 = R_3 = H$   
 II,  $R_2 = Cl, R_3 = H$   
 III,  $R_2 = R_3 = Cl$   
 IV,  $R_1 = R_4 = H$   
 V,  $R_1 = Cl, R_4 = H$   
 VI,  $R_1 = R_4 = Cl$   
 VII,  $R_1 = R_2 = R_3 = R_4 = H$   
 VIII,  $R_2 = R_3 = R_4 = H, R_1 = Cl$   
 IX,  $R_1 = R_3 = R_4 = H, R_2 = Cl$   
 X,  $R_1 = R_4 = Cl, R_2 = R_3 = H$   
 XI,  $R_1 = R_4 = H, R_2 = R_3 = Cl$

ammonium hydroxide) did prove satisfactory.<sup>11</sup> Using it, tetracyclone itself was prepared in 89% yield and the hindered tetracyclones in somewhat lower yield. In no case was it possible to prepare the tetra-ortho-substituted tetracyclone from III and VI. In one case an interesting side reaction was observed.

When potassium hydroxide in ethanol was used as the catalyst in condensing III with IV, the properties of the only product isolated suggested that the dichlorobenzilic acid from III had been formed. Deliberate rearrangement of III did, indeed, afford *o,o'*-dichlorobenzilic acid (XII). However, the melting point was about 30° lower than that reported by Haller, *et al.*<sup>12</sup> The corresponding benzophenone and its 2,4-dinitrophenylhydrazone did agree with literature values.<sup>12</sup> Subsequently, Professor M. S. Newman and Dr. W. B. Wheatley have informed us that this acid

(8) W. Dilthey and F. Quint, *J. prakt. Chem.*, **128**, 139 (1930).(9) J. R. Johnson and O. Grummitt, *Org. Syntheses*, **23**, 92 (1943).

(10) W. Dilthey, German Patent 575,857 (November 16, 1933).

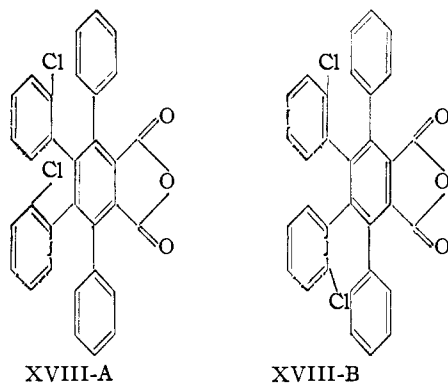
(11) We are indebted to Dr. Nathan L. Weiner for this suggestion.

(12) H. L. Haller, P. D. Bartlett, N. L. Drake, M. S. Newman, S. J. Cristol, C. M. Eaker, R. A. Hayes, G. W. Kilmer, B. Magerlein, G. P. Mueller, A. Schneider and W. Wheatley, *THIS JOURNAL*, **67**, 1591, 1601 (1945).

probably exists in three polymorphic forms, one of which is ours.<sup>13</sup>

The unusual efficacy of Triton B is not simply explained. Refluxing XI for six hours with alcoholic potassium hydroxide lowered the melting point only slightly and to about the same extent that Triton B did. Triton B was also effective in rearranging *o,o'*-dichlorobenzil to the benzoic acid.

Each of the tetracyclones was derivatized as the corresponding tetraphenylphthalic anhydride.<sup>14</sup> Anhydrides were formed without difficulty from the monohalogenated tetracyclones. X gave an anhydride XVII which appeared to exhibit a phase change to a smectic state before melting cleanly. From the reaction product XVIII, obtained from XI, two products were isolated. Infrared spectra in methylene bromide were different. These facts indicate that XVIII-A and XVIII-B are not polymorphs but geometric isomers.<sup>15</sup>



### Experimental<sup>16,17</sup>

**1,3-Bis-(2'-chlorophenyl)-2-propanone (VI).**—To 1.58 moles (270 g.) of 2-chlorophenylacetic acid, m.p. 94–95°, prepared as outlined below, was added 837 ml. of a 10% solution of sodium carbonate (0.79 mole). The solution

(13) First, Professor Newman compared the infrared spectra of the *o,o'*-dichlorobenzophenone obtained here with his reference sample; the curves were superimposable. Then Dr. Wheatley performed the following experiment: "Crude acid: 60.6 g., m.p. 74–76°. This acid was recrystallized from 200 ml. of benzene, three crops of solid being collected. Crop 1 (A-1): 33.5 g., m.p. 73.0–75.5°, solidifies and remelts at 163.0–166.0°. Crop 2 (A-2): 10.5 g., m.p. 130.5–133.5°, solidifies and remelts at 163.0–166.0°. Crop 3 (A-3): 3.6 g., m.p. 163.0–166.0°. A-1 was recrystallized from 250 ml. of benzene, giving 26.4 g. (B-1), m.p. 161.5–164.0°. A-2 was recrystallized from 100 ml. of benzene, giving 9.4 g. (B-2), m.p. 163–165°. A small portion of B-1 was recrystallized twice from benzene, m.p., 162.5–164.5° (C-1). *Anal.* Calcd. for  $C_{14}H_{10}Cl_2O_2$ : C, 56.6; H, 3.4. Found: C, 56.3; H, 3.1.

The above melting points were taken as soon as the materials were dry following recrystallization. At the present time A-1 melts completely at 129.5°, solidifies and remelts at 162.0–163.0°; A-2 melts incompletely at 130.5°, solidifies and remelts at 162.5–164.5°.

A mixture of the high-melting isomer (C-1) and the acid found here melted at 161–162.5°. When the acid obtained here was heated to 138°, it melted to a clear melt. When this was seeded with (C-1), it immediately became cloudy and viscous and became clear at 160–165°. Thus, the acid obtained here is the polymorph melting 130.5–133.5°.

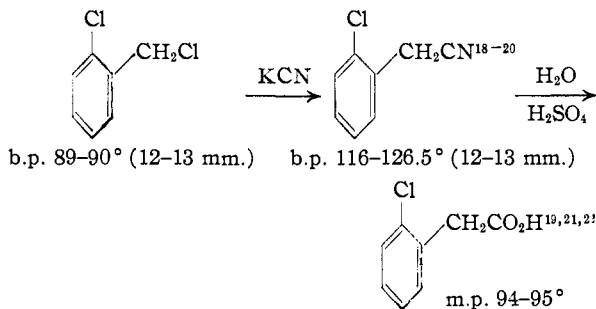
(14) M. E. Synerholm, *THIS JOURNAL*, **67**, 1229 (1945).

(15) It is suggested that the two anhydrides are isomers resulting from restricted rotation expected for ortho-phenyl rings. An examination of models shows that the two isomers could be a *cis-meso*-compound (A) and a *trans-racemate* (B).

(16) All melting points were taken in a Hersberg melting point apparatus and are corrected.

(17) The microanalyses were carried out by Drs. Weiler and Straus, 164 Banbury Road, Oxford, England; Mr. Edwin Conner of Schering Corporation, Bloomfield, N. J.; or by Dr. Francine Schwartzkopf, 62-12 79th Street, Middle Village, Long Island, New York.

was made just acid to litmus with dilute hydrochloric acid and warmed to about 70°. A solution of 88 g. (0.79 mole) of calcium chloride in 387 ml. of water was now added and a precipitate formed immediately. After chilling in an ice-bath for 3 hours, the calcium salt was collected and dried at 105° to give 220.5 g. The filtrate afforded an additional 62.2 g. (94% total).



Ninety grams of the salt in a round bottom flask was heated until liquefied, then heated for an additional 5 minutes and distilled at reduced pressure. The colorless distillate quickly solidified in the receiver. A red oil which followed afforded none of the desired product. The colorless solid was dissolved in 100 ml. benzene, washed with 10% sodium carbonate solution, then with water, dried over anhydrous sodium sulfate, filtered and concentrated. Recrystallization of the residue from 50 ml. of ethanol gave 12.9 g. (0.046 mole, 18.4% based on the acid) of colorless VI, m.p. 100.5–101.5° (reported 102°, 100.5–101°<sup>24</sup>).

The semicarbazone was obtained in 61% yield in the conventional manner,<sup>25</sup> m.p. 149–151° (reported 149°, 153–155°<sup>24</sup>).

**$\alpha$ -(2'-Chlorophenyl)-acetophenone (XIII).**—The procedure is essentially that for the preparation of desoxybenzoin.<sup>26</sup>

A mixture of 90 g. (0.53 mole) of 2-chlorophenylacetic acid and 24.0 ml. (0.275 mole) of phosphorus trichloride was heated on the steam-bath for 1 hour. Benzene (432 ml.) was added, stirred, and the supernatant benzene solution decanted from the insoluble phosphorous acid onto 86.4 g. (0.65 mole) of aluminum chloride. After chilling during the addition, the mixture was refluxed for 1 hr., cooled and poured onto a mixture of 540 g. of ice and 216 g. of concentrated hydrochloric acid. The aqueous phase was separated and extracted with a 1:1 mixture of benzene and ether. The combined organic solutions were washed with 10% sodium carbonate solution, then with water, dried over calcium sulfate, filtered and concentrated. Crystallization of the residue from 300 ml. of methanol (Darco G-60) afforded 97.7 g. of white needles, m.p. 69–70.0° (reported m.p. 70.5°). The mother liquor gave an additional 5.9 g. (total 103.6 g., 0.45 mole, 85%) of product, m.p. 69.4–70.2°.

The oxime melted at 85–87° (reported 85–86°<sup>25</sup>).

**2-Chlorobenzil (II).**—The general procedure of Hatt, *et al.*,<sup>27</sup> for the selenium dioxide oxidation of desoxybenzoin was followed.

A mixture of 72.5 g. (0.314 mole) of XIII, 69.4 g. (0.63 mole) of sublimed selenium dioxide and 125 ml. of acetic anhydride was heated with an oil-bath at 140–150° for 4 hours. The reaction mixture was filtered hot, using 15 ml. of acetic anhydride for washing the cake of selenium. The filtrate was cooled to room temperature and poured into 1 l. of water. After warming the mixture for 1 hr. on the steam-

(18) H. Mehner, *J. prakt. Chem.*, **62**, 554 (1900).

(19) G. S. Misra and J. S. Shukla, *J. Indian Chem. Soc.*, **28**, 480 (1951); *C. A.*, **46**, 11149a (1952).

(20) M. J. Zimmermann, *J. prakt. Chem.*, **66**, 376 (1902).

(21) W. F. J. Dippy and F. R. Williams, *J. Chem. Soc.*, 1888 (1934).

(22) P. R. Austin and J. R. Johnson, *THIS JOURNAL*, **54**, 657 (1932).

(23) J. Kenner and F. Morton, *J. Chem. Soc.*, 679 (1934).

(24) J. A. King and F. H. McMillan, *THIS JOURNAL*, **73**, 491 (1951).

(25) S. M. McElvain, "The Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., 1945, p. 198.

(26) C. F. H. Allen and W. E. Barker, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 156.

(27) H. N. Hatt, A. Pilgrim and W. J. Hurran, *J. Chem. Soc.*, 93 (1936).

bath, the yellow-brown solid was filtered and dissolved in 500 ml. of ethanol containing 100 ml. of 0.5 *N* hydrochloric acid and 5 g. of Darco G-60. Filtration and concentration at reduced pressure gave an oil which was taken up in benzene, washed successively with dilute hydrochloric acid, water, 10% sodium carbonate solution and water, and then dried over anhydrous sodium sulfate. Filtration and concentration gave a residue which was crystallized from 300 ml. of ethanol to afford 54.9 g. of yellow II, m.p. 47.5–48.9°. An additional 13.7 g. was obtained from the mother liquor, m.p. 47–49° (total 68.6 g., 0.28 mole, 89.5%). The analytical sample was crystallized successively from ethanol and from petroleum ether (b.p. 30–75°) and melted at 47.2–49°.

*Anal.* Calcd. for  $C_{14}H_{13}ClO_2$ : C, 68.71; H, 3.71; Cl, 14.50. Found: C, 68.90; H, 3.47; Cl, 14.02.

**2-(2'-Chlorophenyl)-3-phenylquinoxaline (XIV).**—A solution of II (4.0 g., 0.0164 mole) and *o*-phenylenediamine dihydrochloride<sup>28</sup> (3.1 g., 0.0173 mole) (prepared by passing dry hydrogen chloride into an ether solution of the free base) in 44 ml. of 91% ethanol was refluxed for 3 hr. After adding 9 ml. of water and standing, the solution deposited 5.1 g. (0.016 mole, 98%) of colorless crystals of XIV, m.p. 123–125°. Recrystallization from 91% ethanol raised the melting point to 124–125.8°.

*Anal.* Calcd. for  $C_{20}H_{19}ClN_2$ : C, 75.82; H, 4.14; Cl, 11.20; N, 8.85. Found: C, 76.15; H, 4.38; Cl, 11.20; N, 8.95.

**2,2'-Dichlorobenzilic Acid (XII).**—A solution of 4.0 g. (0.071 mole) of potassium hydroxide and 4.0 g. (0.0143 mole) of 2,2'-dichlorobenzil (III)<sup>29</sup> (m.p. 133–134°<sup>32</sup>) in 8 ml. of water and 8 ml. of ethanol was refluxed for 12 minutes. After concentrating the solution to a sirup with a stream of air, the residue was diluted with 25 ml. of water and extracted with 25 ml. of chloroform which was discarded. After filtering, the aqueous layer was acidified with 1:1 hydrochloric acid to precipitate a gummy solid. Extraction of the mixture with 100 ml. of benzene, drying the benzene solution with anhydrous sodium sulfate, filtering and concentrating to 13 ml. gave 2.1 g. (7.07 mmoles, 49.5%) of white needles, softening 131–133°, m.p. 133–134.5°.

*Anal.* Calcd. for  $C_{14}H_{10}Cl_2O_2$ : C, 56.59; H, 3.39; Cl, 23.86; neut. equiv., 297. Found: C, 57.15, 56.39; H, 3.43, 3.80; Cl, 23.64; neut. equiv., 297.

When this experiment was repeated using Triton B in place of potassium hydroxide, *o,o'*-dichlorobenzilic acid again was obtained. Qualitatively, this appeared to be a slower reaction than with potassium hydroxide.

The 2,2'-dichlorobenzophenone was obtained according to Haller, *et al.*,<sup>12</sup> in 71% yield, m.p. 50–51.5° (reported 50–52°<sup>33</sup>). The 2,4-dinitrophenylhydrazone melted at 207–209° (reported 206–208°<sup>12</sup>).

**Benzyl Ketone (IV).**—The procedure is adapted from that of Jenkins.<sup>4,5</sup> To a stirred ether solution of benzylmagnesium chloride (from 7.3 g. (0.30 atom) of magnesium and 41.8 g. (0.33 mole) of benzyl chloride) in 150 ml. of anhydrous ether under nitrogen was added 10.0 g. (0.074 mole) of phenylacetamide m.p. 164° (reported 157°<sup>34</sup>). Gentle reflux with intermittent stirring was maintained for 44 hr. Hydrolysis with a mixture of 300 g. of ice and 30 g. of concentrated sulfuric acid was followed by separation of the aqueous phase, which was extracted with ether. The organic layers were combined, washed with 10% sodium carbonate solution, dried over anhydrous sodium sulfate, filtered, concentrated and distilled to give two fractions: 2.9 g. of a colorless liquid, b.p. 110° (11–12 mm.) (reported<sup>35</sup> boiling point for phenylacetone nitrile, 115–120° (10 mm.)),

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

(29) The product was obtained in better yield when the intermediate benzoin was not isolated<sup>12</sup> than when it was.<sup>30,31</sup>

(30) H. Hodgson and W. Rosenberg, *J. Chem. Soc.*, **14** (1930).

(31) A. Weissberger, E. Strasser, H. Mainz and W. Schwartz, *Ann.*, **478**, 112 (1930).

(32) Reported m.p. 128°<sup>30</sup> and 133–135°.<sup>12</sup>

(33) Dr. M. S. Newman has told us that the compound initially melted 45–46° (footnote 12), but melted as cited above after storage.

(34) W. Braren and E. Büchner, *Ber.*, **34**, 985 (1901).

(35) R. Adams and A. F. Thal, in "Organic Syntheses" Coll. Vol. I, second edition, edited by H. Gilman and A. H. Blatt, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 107.

and 7.6 g. (0.036 mole, 49%) of a light yellow liquid, b.p. 164° (3–5 mm.), which solidified.

The higher boiling fraction was characterized as benzyl ketone by its m.p. 31–32° (authentic m.p. 34–35°), conversion to the oxime, m.p. 122–125° (reported 123°<sup>36</sup>, 125°<sup>37</sup>), conversion to the 2,4-dinitrophenylhydrazone, m.p. 110° (reported 100°<sup>38</sup>, 108°<sup>39</sup>, 110°<sup>40</sup>), and conversion to tetracyclone, m.p. 219–220.5° (no depression with an authentic sample).

**1-(2'-Chlorophenyl)-3-phenyl-2-propanone (V).**—This ketone was prepared in the same manner as IV using 50 g. (0.294 mole) of 2-chlorophenylacetamide, m.p. 177–179° (reported 175°<sup>18</sup>) (prepared either from 2-chlorophenylacetic acid through the acyl chloride and ammonium hydroxide, or from the nitrile with aqueous sulfuric acid<sup>41</sup>) and benzylmagnesium chloride (from 164 g. (1.30 moles) of benzyl chloride and 28.6 g. (1.18 atom) of magnesium). As in the case of IV two fractions were isolated: (1) 34 g., b.p. 110–118° (5–6 mm.) and (2) 27 g. (0.11 mole, 37.5%), b.p. 184–188° (3–4 mm.).

Redistillation and recrystallization of fraction 2 from hexane afforded colorless V, m.p. 38–39.5°. The analytical sample melted at 39.0–39.7°.

*Anal.* Calcd. for  $C_{14}H_{13}ClO$ : C, 73.62; H, 5.35; Cl, 14.49. Found: C, 73.40; H, 5.05; Cl, 14.64.

The 2,4-dinitrophenylhydrazone was prepared without difficulty<sup>38</sup> and crystallized as orange platelets from ethanol in 57.5% yield, m.p. 111.0–112.0°.

*Anal.* Calcd. for  $C_{21}H_{17}ClN_4O_4$ : C, 59.37; H, 4.03; Cl, 8.35; N, 13.19. Found: C, 58.79; H, 4.08; Cl, 8.58; N, 12.90.

The lower-boiling fraction gave no precipitate on boiling with 2,4-dinitrophenylhydrazine in acetic acid. A micro-boiling point gave 263°. Hydrolysis with concentrated sulfuric acid gave 45% of *o*-chlorophenylacetamide, m.p. 175–178.5°, which did not depress the authentic material. Hydrolysis with sulfuric acid in acetic acid–water gave 58.2% of *o*-chlorophenylacetic acid, m.p. 92–95°, which did not depress the melting point of the authentic acid.

**Tetracyclone (VII) with Triton B as Catalyst.**—A solution of 1.0 g. (4.8 mmoles) of benzyl ketone and 1.0 g. (4.8 mmoles) of benzil in 10 ml. of ethanol was heated to incipient reflux and 0.55 ml. (1.1 mmoles) of Triton B was added all at once. The yellow solution immediately turned brown-red, then purple-black and deposited crystals within one minute. After refluxing for 15 minutes, the reaction mixture was cooled in ice-water and filtered to afford 1.64 g. (4.27 mmoles, 89%) of purple-black VII, m.p. 218.5–220° (reported 91–96% with potassium hydroxide as catalyst<sup>8,9</sup>).

**Synthesis of Ortho-substituted Tetracyclones.**—VIII, IX, X and XI were all prepared employing Triton B as catalyst. Where the isolation of the product proved difficult, chromatography was essential. The preparation of XI is described herein (see Table I for physical constants of these tetracyclones).

**3,4-Bis-(2'-chlorophenyl)-2,5-diphenylcyclopentadienone (XI).**—To 50 ml. of ethanol were added 3.75 g. (0.018 mole) of IV and 5.0 g. (0.018 mole) of III, m.p. 132–134° (prepared from 2-chlorobenzaldehyde with isolation of intermediate 2,2'-dichlorobenzoin<sup>30,31</sup> or more directly, without isolation of the intermediate<sup>12</sup>). The solution was heated to just under reflux and 2.75 ml. (5.5 mmoles) of Triton B was added all at once. The solution became black within 30 seconds and was refluxed for 10 minutes. After cooling, 250 ml. of benzene was added and the solution was washed with dilute hydrochloric acid, water, and then dried over anhydrous sodium sulfate. The filtered solution was concentrated at reduced pressure to near dryness while protecting the flask from light. The oily residue was chromatographed on activated alumina using a 1:4 mixture of benzene and petroleum ether (b.p. 30–75°) as the eluant. A red-purple band rapidly moved away from a green and a brown-yellow band. The eluate containing the red-purple

(36) G. Goldschmiedt and H. Krczmar, *Monatsh.*, **22**, 664 (1901).

(37) F. E. Francis, *J. Chem. Soc.*, **75**, 878 (1899).

(38) C. F. H. Allen and J. H. Richmond, *J. Org. Chem.*, **2**, 224 (1937).

(39) G. G. Smith, *THIS JOURNAL*, **75**, 1134 (1953).

(40) S. B. Coan, Dissertation.

(41) W. J. Hickinbottom, "Reactions of Organic Compounds," 2nd edition, Longmans, Green and Co., London, 1948, p. 282.

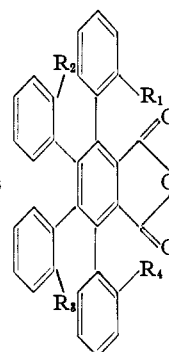
TABLE I  
 ORTHO-SUBSTITUTED TETRACYCLONES

Compound	M.p., °C.	Yield, %	Color	Formula	Analyses, %					
					Carbon		Hydrogen		Chlorine	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
VII	218.5-220	90 <sup>a</sup>	Black-purple	C <sub>29</sub> H <sub>20</sub> O						
VIII	170.5-172	68.8 <sup>b</sup>	Brown-red	C <sub>29</sub> H <sub>19</sub> ClO	83.16	82.80	4.57	4.53	8.46	8.68
						83.15		4.28		
IX	192.5-193.8	54.6 <sup>b</sup>	Rust-brown	C <sub>29</sub> H <sub>19</sub> ClO	83.16	83.19	4.57	4.60	8.46	8.59
X	208.0-209.4 (sintering-204)	47.3 <sup>b</sup>	Red-orange	C <sub>29</sub> H <sub>18</sub> Cl <sub>2</sub> O	76.83	77.06	4.00	4.49	15.64	15.18
						77.16		3.97		15.48
						76.96		3.87		
XI	177-178.8 (sinter-164-165)	14 <sup>b</sup>	Black-brown	C <sub>29</sub> H <sub>18</sub> Cl <sub>2</sub> O	76.83	76.80	4.00	3.78	15.64	15.64
						76.85		3.89		
						76.91		4.09		

<sup>a</sup> J. R. Johnson and O. Grummitt<sup>9</sup> report 91-96% using potassium hydroxide as catalyst. <sup>b</sup> After chromatography.

TABLE II

SUBSTITUTED TETRAPHENYLPHTHALIC ANHYDRIDES



No.	Compound				M.p., °C.	Yield, %	Formula	Analyses					
	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>				Carbon		Hydrogen		Chlorine	
							Calcd.	Found	Calcd.	Found	Calcd.	Found	
XV	Cl	H	H	H	246-247.5 (sinter-238)	75	C <sub>32</sub> H <sub>19</sub> ClO <sub>3</sub>	78.91	78.71	3.94	3.73	7.29	7.33
XVI	H	Cl	H	H	294.3-295.8	79	C <sub>32</sub> H <sub>19</sub> ClO <sub>3</sub>	78.91	79.09	3.94	3.97	7.29	7.41
								78.60		3.80			
XVII	Cl	H	H	Cl	Soft 264.5 liq. 275-276.5	44.5	C <sub>32</sub> H <sub>18</sub> Cl <sub>2</sub> O <sub>3</sub>	73.70	74.08	3.48	3.81	13.61	13.25
								74.12		3.47			13.18
XVIII	H	Cl	Cl	H	Approx. 270-310	73							
XVIII-A	H	Cl	Cl	H	330-331.2		C <sub>32</sub> H <sub>18</sub> Cl <sub>2</sub> O <sub>3</sub>	73.70	73.51	3.48	3.61	13.61	14.04
													13.65
XVIII-B	H	Cl	Cl	H	271.8-274		C <sub>32</sub> H <sub>18</sub> Cl <sub>2</sub> O <sub>3</sub>	73.70	74.26	3.48	3.72	13.61	13.81
								74.26		3.57			13.43

band was filtered and concentrated to near-dryness. Residual solvent was exchanged with ethanol to give 1.1 g. (2.44 mmoles, 14%) of black-brown crystals, m.p. 177-178.6° (sintering 164-165°). Recrystallization from acetic acid or aqueous pyridine and drying at 144° under 1 mm. pressure did not change the melting point.

A solution of 50 mg. of XI in 100 ml. of ethanol was refluxed with 0.2 ml. of 0.2 N alcoholic potassium hydroxide for 6 hr. The color was the same. Distillation to dryness, trituration with water, filtering and drying under vacuum gave 50 mg. of deep purple crystalline solid, m.p. 163-164°, sintering at 155°. In admixture with the starting material, the substance melted 173-174°, sintering 163°.

**Synthesis of Ortho-chloro-substituted Tetraphenylphthalic Anhydrides.**—The preparation from the corresponding tetracyclones proceeded according to Synerholm<sup>14</sup> without difficulty for compounds XV (from VIII) and XVI (from IX). In the preparation of compound XVII (from X) complete decolorization of the reaction solution was not achieved, the yield was poor, and a sharp melting product was not obtained. In the reaction of chloromaleic anhydride with XI, two products were obtained and therefore the reaction is described in detail. (See Table II for data concerning these anhydrides.)

**4,5-Bis-(2'-chlorophenyl)-3,6-diphenylphthalic Anhydride (XVIII-A) and (XVIII-B).**—A solution of 2.0 g. (44.2

mmoles) of XI and 0.425 ml. (4.95 mmoles) of chloromaleic anhydride (b.p. 85° (14-15 mm.)) in 5 ml. of bromobenzene was refluxed for 7 hr. at which time the solution had turned yellow. Upon chilling, 1.7 g. (3.26 mmoles, 73%) of crude product separated and was filtered, m.p. 207-310°. A second crop weighed 0.3 g., m.p. 254-256° (sintering at 224° and softening at 230°). Repeated recrystallizations from chlorobenzene gave two materials—A and B. A was less soluble in chlorobenzene than B. Fraction A melted 330-331.2° but, after solidification, the melting point was 315-325°. Fraction B was isolated from the chlorobenzene mother liquors and recrystallized from benzene and petroleum ether (b.p. 30-75°) to a white solid, m.p. 271.8-274.0°. After solidifying, the melting point was 270-300°.

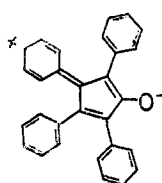
### Spectra

Many examples of steric effects are to be found in the literature including an interesting article by Beale and Roe<sup>42</sup> in which important references are cited. Perhaps the compounds most closely related to tetracyclone are the biphenyls, the phenyl-naphthalenes and the 2,6-disubstituted-dimethyl-aminoanilines.

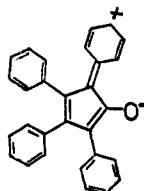
(42) R. N. Beale and E. M. F. Roe, *THIS JOURNAL*, **74**, 2302 (1952).

In the biphenyls it has been shown<sup>43,44</sup> that substitution in the 2,2'-positions by groups, such as CH<sub>3</sub> or Cl, prevents coplanarity of the two phenyl rings, thus obliterating biphenyl resonance and causing emergence of the spectrum of the substituted benzene derivative. With 1- and 2-phenylnaphthalenes, substitution in the ortho-position of the phenyl rings, or in a corresponding position in the naphthalene ring may so hinder phenylnaphthalene resonance as to effect reappearance of the fine structure of naphthalene.<sup>45</sup> Klevens and Platt<sup>46</sup> have also studied oscillator strengths of *o*- and *o,o'*-substituted N,N-dimethylanilines. Their conclusion was that with two ortho-substituents, the dimethylamino group was twisted out of the plane of the benzene ring and the spectrum of the meta-substituted benzene derivative appeared.

As stated earlier, the selection of tetracyclone for studying steric effects was predicated on the assumption that with two resonance paths assigned to definite absorption maxima in the molecule,<sup>8</sup> it would be possible to observe changes in both maxima with substituents in one path.



X-path  
 $\lambda_{\max}$  342 m $\mu$



Y-path  
 $\lambda_{\max}$  512 m $\mu$

It would be helpful to know the extent of overlap of the ortho-hydrogens of the phenyl groups. However, the exact dimensions of tetracyclone are not known. It seems reasonable that since the central angle formed by two adjacent phenyl rings is near 72°, the overlap will be less than that for ortho-terphenyl<sup>47</sup> in which the central angle is 60°. Further, the smaller overlap should permit

(43) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, 1951, no. 167, 182 and 183.

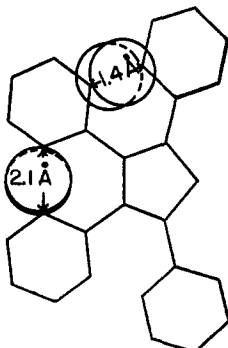
(44) M. T. O'Shaughnessy and W. H. Rodebush, *THIS JOURNAL*, **62**, 2906 (1940).

(45) Footnote 43, nos. 290 and 291.

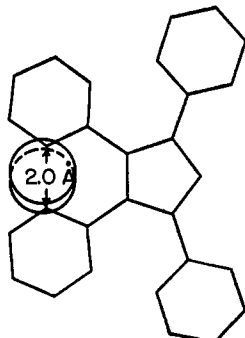
(46) H. B. Klevens and J. R. Platt, *THIS JOURNAL*, **71**, 1714 (1949).

(47) C. J. B. Clews and K. Lonsdale, *Proc. Roy. Soc. (London)*, **A161**, 493 (1937).

(48) If the dimensions of the central ring of tetracyclone are taken as those for cyclopentadiene<sup>49</sup> and the C<sub>ar</sub>-C<sub>s</sub> distance taken as 1.48 Å.,



A



B

less twisting out of the plane of the central ring than for ortho-terphenyl, where this angle is approximately 54°. <sup>47</sup>

The absorption spectra of the tetracyclones investigated here are shown in Table III and Fig. 1. For comparison the absorption spectra for tetracyclone and for the *p*-chloro-substituted tetracyclones are shown in Table IV.

TABLE III

SPECTRA OF HINDERED TETRACYCLONES IN BENZENE

No.	Compound <sup>a</sup> Chlorine as noted	$\lambda_{(1)}$ m $\mu$	$\epsilon_{(1)}$	$\lambda_{(2)}$ m $\mu$	$\epsilon_{(2)}$
VIII	2-(2'-Chloro-)	334.5	7980	464	850
IX	3-(2'-Chloro-)	332	6000	492.5	1590
X	2,5-Bis-(2'-chloro-)	332	8850	436.5	610
XI	3,4-Bis-(2'-chloro-)	325	4750	500	2110

<sup>a</sup> Concentration -  $1.5 \times 10^{-4}$  molar.

TABLE IV

ANALYSIS OF SPECTRAL DATA<sup>a</sup>

Para-compounds	Ortho-compounds	$\Delta\epsilon$
2-(4'-Chlorophenyl)- <sup>b</sup>	Tetracyclone <sup>c</sup>	
7020 at 340 m $\mu$	6760 at 342 m $\mu$	+ 260
1460 at 510	1320 at 512	+ 140
2,5-Bis-(4'-chlorophenyl)- <sup>c</sup>	Tetracyclone <sup>c</sup>	
7080 at 341 m $\mu$	6760 at 342 m $\mu$	+ 320
1750 at 512	1320 at 512	+ 430
2-(4'-Chlorophenyl)- <sup>b</sup>	2-(2'-Chlorophenyl)-	
see above	7980 at 334.5 m $\mu$	- 960
	850 at 464	+ 610
3-(4'-Chlorophenyl)- <sup>b</sup>	Tetracyclone <sup>c</sup>	
7740 at 345 m $\mu$	see above	+ 980
1360 at 510		+ 40
3,4-Bis-(4'-chlorophenyl)- <sup>c</sup>	Tetracyclone <sup>c</sup>	
7880 at 340 m $\mu$	see above	+ 1120
1220 at 514		- 100
3-(4'-Chlorophenyl)- <sup>b</sup>	3-(2'-Chlorophenyl)-	
see above	6000 at 332 m $\mu$	+ 1740
	1590 at 492.5	- 230
3,4-Bis-(4'-chlorophenyl)- <sup>c</sup>	3,4-Bis-(2'-chloro-phenyl)-	
see above	4750 at 324 m $\mu$	+ 3130
	2110 at 500	- 890

<sup>a</sup> Concentration of  $1.5 \times 10^{-4}$  M in benzene. <sup>b</sup> Footnote 3. <sup>c</sup> F. J. Thaller, D. E. Trucker and E. I. Becker, *THIS JOURNAL*, **73**, 228 (1951).

When the spectrum of tetracyclone is compared with that of VIII, it is seen that the substituent in the 2-phenyl ring has effected a hypsochromic and hypochromic shift of the peak at 512 m $\mu$ . At the same time the maximum at 342 m $\mu$  has been shifted hyperchromically. Comparing the spectrum of tetracyclone with that of IX, the effects are reversed; the peak at 342 m $\mu$  is now the one which has been shifted hypsochromically and

similar to biphenyl,<sup>50</sup> then the *o,o'*-distance for the 2- and 3-phenyl rings is 1.4 Å. and for the 3- and 4-phenyl rings 2.1 Å. (A). Assuming a symmetrical central ring with a C-C bond length of 1.44 Å. (average of the distances given in footnote 49) and C<sub>ar</sub>-C<sub>s</sub> of 1.48 Å., then the *o,o'*-distances are all 2.0 Å. (B). Figures A and B show the overlap using 1.1 Å. as the van der Waals radius for hydrogen.<sup>51</sup>

(49) V. Schomaker and L. Pauling, *THIS JOURNAL*, **61**, 1769 (1939).

(50) J. Dhar, *Indian J. Phys.*, **7**, 43 (1932); *C. A.*, **33**, 467 (1939).

(51) L. Pauling, "Nature of the Chemical Bond," 2nd edition, Cornell University Press, Ithaca, N. Y., 194, p. 217 ff.

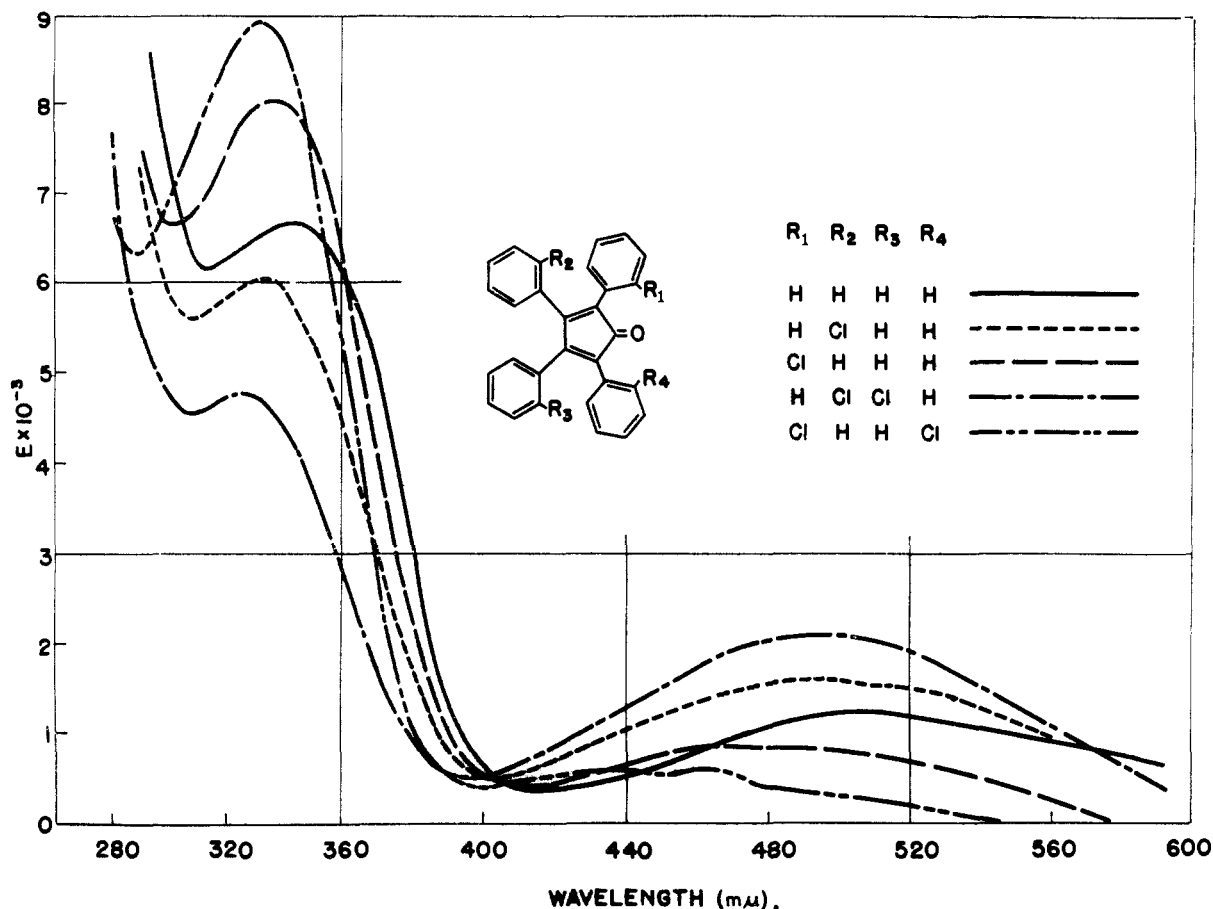


Fig. 1.—Ultraviolet absorption spectra of tetracyclones in benzene.

hypochromically, while the peak at 512  $m\mu$  has shifted hyperchromically. In comparing the di-substituted tetracyclones, this effect is enhanced. These observations are highlighted by comparing directly the extinction coefficients of the *para*-compounds with those of the *ortho*-compounds.

The significance of the data is (1) that the assignment of electronic paths to absorption maxima as postulated by Coan, *et al.*,<sup>3</sup> is reaffirmed, and (2) that, if the intensities can be used as a qualitative measure of the statistical weight of the two canonical structures, then the introduction of an *ortho*-substituent twists the path out of planarity diminishing its weight and simultaneously increasing the contribution to the absorption maximum of the other path. One weakness of the present argument is that both absorption maxima are affected somewhat with each substitution. This effect is insufficient to alter the conclusions, but it puts further off any attempt at an absolute evaluation of the effect of the substituent.

It should be noted that the peak at 342  $m\mu$  is not shifted largely with one substituent in the 3-phenyl ring, but it is shifted significantly with substituents in the 3- and 4-phenyl rings. In both instances the intensities are shifted greatly. Therefore, it may be that intensities are, in general, more sensitive to slight changes in the angle between the rings than wave lengths.

The interpretations deduced above are in con-

trast with those of Bergmann, *et al.*<sup>52-54</sup> Bergmann assigned the ultraviolet absorption maxima of tetracyclone from 2500–3500 Å. to C=C absorption and the maximum at 5100 Å. to C=O absorption.<sup>52</sup> Upon comparing the infrared absorption bands for the carbonyl group of tetracyclone (1710  $\text{cm}^{-1}$ ) with those for benzophenone (1663  $\text{cm}^{-1}$ ) and dibenzalacetone (1655  $\text{cm}^{-1}$ ), he concluded that in tetracyclone the carbonyl group was non-interacting and a "true" carbonyl group.<sup>53</sup> Similar conclusions were also reached from the dipole moment of tetracyclone.<sup>55</sup>

Although it is tempting to make correlations by comparing molecules of different structural classes, the results are apt to be misleading. Thus, it may be granted that the carbonyl group of tetracyclone is less polar than in benzophenone or in dibenzalacetone without granting that it is non-interacting or "true." The interaction is, indeed, implied by the deep red color of tetracyclone which is observed in no other class of doubly  $\alpha,\beta$ -unsaturated ketones. Further, based upon geometric considera-

(52) E. D. Bergmann and Y. Hirshberg, *Bull. soc. chim. France*, **17**, 1091 (1950).

(53) E. D. Bergmann, G. Berthier, D. Ginsberg, Y. Hirshberg, D. Lavie, S. Pinchas, B. Pullman and A. Pullman, *ibid.*, 661 (1951).

(54) E. D. Bergmann and S. Pinchas, *Bull. Research Council Israel*, **1**, 87 (1952).

(55) E. D. Bergmann and E. Fischer, *Bull. soc. chim. France*, **17**, 1084 (1950).

tions and comparison with tropone, Smyth<sup>56</sup> has interpreted the dipole moment as showing a small but definite interaction between the phenyl rings and the central ring.

(56) A. Di Giacomo and C. P. Smyth, *THIS JOURNAL*, **74**, 4411 (1952).

**Acknowledgment.**—The authors hereby express their thanks to Mr. Edwin Conner and to Misses Cecelia Vitiello and Betty Blasko, all of the Schering Corporation, for the infrared and ultraviolet spectra and for help in interpreting the spectra.

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## Isomerization of Saturated Hydrocarbons. XII.<sup>1</sup> The Effect of Experimental Variables, Alkyl Bromides and Light upon the Isomerization of Methylcyclopentane in the Presence of Aluminum Bromide

BY HERMAN PINES, EUGENE ARISTOFF<sup>2</sup> AND V. N. IPATIEFF<sup>3</sup>

RECEIVED APRIL 17, 1953

The effect of temperature, contact time and concentration of reactants upon the isomerization of methylcyclopentane in the presence of aluminum bromide-hydrogen bromide has been investigated. The effect of alkyl bromides as chain initiators for the isomerization reaction has been studied and it was found that methyl bromide and ethyl bromide do not act as chain initiators. The effect of ultraviolet light upon the isomerization of methylcyclopentane in the presence of methyl bromide has been investigated. The mechanism of the isomerization of methylcyclopentane is discussed.

In the previous papers of this series it was shown that under certain controlled experimental conditions methylcyclopentane does not undergo isomerization to cyclohexane unless small amounts of olefins, alkyl halides or other chain initiators are present. This investigation was now extended to study the effect of experimental variables upon the isomerization and the type of alkyl bromides which can act as promoters for the reaction.

The experiments were made using a high vacuum apparatus for the purification of the reactants and for charging and discharging the reaction tubes.<sup>4</sup> The experimental procedure was the same as described previously.<sup>5</sup>

**1. Effect of Time and Temperature.**—The study of the effect of time and temperature upon the isomerization of methylcyclopentane was made in an attempt to determine the kinetics of this reaction. *s*-Butyl bromide was used as a chain initiator since it seems to be the most efficient of all the alkyl bromides investigated. The results obtained are represented graphically in Fig. 1. The rate of isomerization tends to approach a limit after a certain period of time, and the levelling off occurs much sooner as the temperature at which the reaction occurs is increased. It seems that the chain initiator or the chain propagator is destroyed through secondary reactions such as a condensation reaction which involves a transfer of hydrogen<sup>6</sup> or conjunct polymerization.<sup>7</sup> The latter re-

action occurs more readily at higher temperatures and involves the conversion of the olefinic hydrocarbons into highly unsaturated cyclic hydrocarbons which form complexes with the aluminum bromide. These complexes cannot function as chain propagators or initiators.

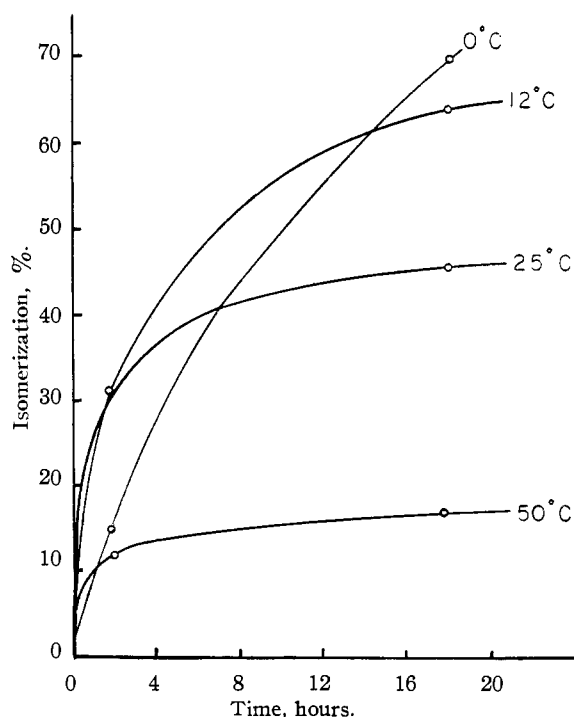


Fig. 1.—Effect of temperature: 100 moles methylcyclopentane, 2 moles aluminum bromide, 0.9 mole hydrogen bromide and 0.1 mole *s*-butyl bromide.

The data as shown in Fig. 1 indicate that the study of the kinetics of the isomerization of saturated hydrocarbons might lead to erroneous conclusions, unless the disappearance of a chain initiator or a chain propagator is taken into consideration.

(1) For paper XI of this series see H. Pines, W. D. Huntsman and V. N. Ipatieff, *THIS JOURNAL*, **75**, 2315 (1953).

(2) Universal Oil Products Company Predoctoral Fellow 1947-1949.

(3) Deceased, November 29, 1952.

(4) H. Pines, B. H. Abraham and V. N. Ipatieff, *THIS JOURNAL*, **70**, 1742 (1948).

(5) H. Pines, F. J. Pavlik and V. N. Ipatieff, *ibid.*, **73**, 5738 (1951).

(6) V. N. Ipatieff and H. Pines, *J. Org. Chem.*, **6**, 242 (1941); *THIS JOURNAL*, **70**, 531 (1948).

(7) V. N. Ipatieff and H. Pines, *J. Org. Chem.*, **1**, 464 (1936); L. Schermerling and V. N. Ipatieff, "The Mechanism of the Polymerization of Alkenes" in "Advances in Catalysis," Vol. II, Academic Press, Inc., New York, N. Y., p. 63.