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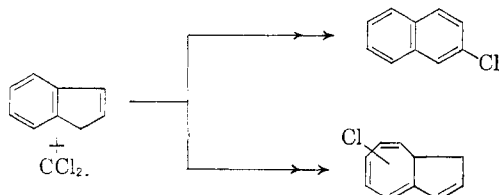
## The Reaction of Halocarbenes with Aromatic Systems: Synthesis of Chlorotropones

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The reaction of dichlorocarbene with 1-methoxynaphthalene, 2-methoxynaphthalene and 9-methoxyphenanthrene is discussed. Chlorotropones result by elimination of methyl chloride from the intermediate 1,1-dichlorocyclopropyl adducts.

We previously observed<sup>3</sup> that dichlorocarbene reacts with indenenes to give cyclopropyl adducts, which subsequently afford chloronaphthalenes, in high yield, by ring expansion and elimination of hydrogen chloride. By-products in such reactions are azulenes which establish that aromatic double

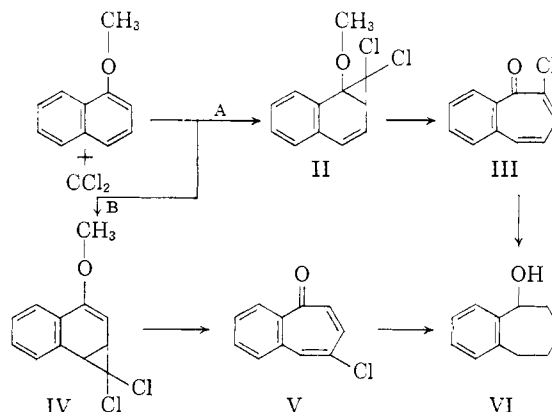


bonds, while far less reactive than aliphatic double bonds, are susceptible to reaction with dichlorocarbene. Quite recently Closs and Closs<sup>4</sup> have reported the reaction of chlorocarbene with phenoxide ions and with benzene, and Murray<sup>5</sup> has reported the reaction of dichlorocarbene with anthracene.

We now wish to report studies of the reaction of dichlorocarbene with 1- and 2-methoxynaphthalene and with 9-methoxyphenanthrene.

Dichlorocarbene was generated by reaction of ethyl trichloroacetate and sodium methoxide,<sup>6</sup> and was allowed to react with 1-methoxynaphthalene in petroleum ether at 0 to 25°. The products isolated from the reaction mixture were: recovered 1-methoxynaphthalene (*ca.* 85%), methyl chloride and a ketone (11.5%, m.p. 95–96°) with the molecular formula C<sub>11</sub>H<sub>7</sub>OCl. This ketone was characterized by conversion to the corresponding oxime, and by its infrared and ultraviolet spectra. The four peaks observed in the infrared spectrum of the ketone at 1636, 1611, 1592 and 1523 cm.<sup>-1</sup> are consistent with the benzotropone structure<sup>7–9</sup> and compare to absorptions at 1638, 1618, 1575 and 1542 cm.<sup>-1</sup> for 4,5-benzotropolone. These results sug-

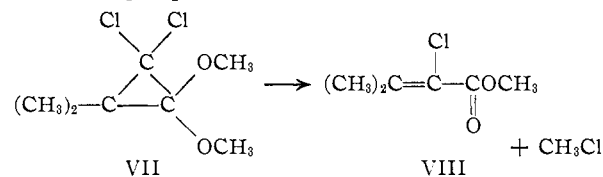
gested that ring expansion to a benz-chlorotropone (III or V) had resulted as shown in scheme A or B.



While we favor path A, and consequently structure III for the ketone, no formal decision between these structures has been possible.<sup>10,11</sup> Unequivocal evidence for the ring expansion reaction was, however, obtained by the catalytic reduction of III (or V) to benzsuberol (VI).

Unsuccessful attempts were made to isolate the intermediate cyclopropyl adduct (II or IV) by elution chromatography. It was concluded, however, that this intermediate is unstable and decomposes to methyl chloride and the benzchlorotropone under the reaction conditions (20°).

The ring expansion reaction noted is analogous to that involving the conversion of indene to chloronaphthalene,<sup>8</sup> and dihydropyran to 2,3-dihydro-6-chloroöxepine.<sup>12</sup> Particular reference is made to the study reported by McElvain and Weyna,<sup>13</sup> who showed that cyclopropanes such as VII are decomposed thermally to give methyl chloride and esters such as VIII, a reaction formally analogous to the ring expansion described above.



(10) It was hoped that a decision between structures III and V could be made by use of n.m.r. spectroscopy. However, due to the aromatic character of the hydrogens on the seven-membered ring no positive answer was possible due to overlap with the benzenoid hydrogens.

(11) For reaction of carbethoxycarbene with 1-methoxynaphthalene and anisole see (a) G. B. R. DeGraaff, J. H. Van Dijk-Rothuis and G. Van De Kolk, *Rec. trav. chim.*, **74**, 143 (1955); (b) N. E. Searle, U. S. Patent 2,532,575, Dec. 5, 1950; *C. A.*, **45**, 3873 (1951); (c) E. Baltazzi, *Comp. rend.*, **241**, 321 (1955).

(12) E. E. Schweizer and W. E. Parham, *THIS JOURNAL*, **82**, 4085 (1960).

(13) S. M. McElvain and P. L. Weyna, *ibid.*, **81**, 2579 (1959).

(1) In part from the Ph.D. thesis of Donald A. Bolon, The University of Minnesota, 1960. Ethyl Corporation Fellow, 1958–1959; National Science Foundation Fellow, 1959–1960.

(2) Part of this work was supported by a grant (G-7382) from the National Science Foundation.

(3) (a) W. E. Parham and H. E. Reiff, *THIS JOURNAL*, **77**, 1177 (1955); (b) W. E. Parham, H. E. Reiff and P. Swartzentruber, *ibid.*, **78**, 1437 (1956); (c) W. E. Parham and R. R. Twelves, *J. Org. Chem.*, **22**, 730 (1957); (d) W. E. Parham and C. D. Wright, *ibid.*, **22**, 1473 (1957).

(4) (a) G. L. Closs and L. E. Closs, Abstracts of the Meeting of the A.C.S., April, 1960, p. 83-O; (b) G. L. Closs and L. E. Closs, *Tetrahedron Letters*, **10**, 38 (1960).

(5) R. W. Murray, *ibid.*, **7**, 27 (1960).

(6) W. E. Parham and E. E. Schweizer, *J. Org. Chem.*, **24**, 1733 (1959).

(7) P. L. Pauson, *Chem. Revs.*, **55**, 9 (1955).

(8) D. S. Tarbell, G. P. Scott and A. D. Kemp, *THIS JOURNAL*, **72**, 379 (1950).

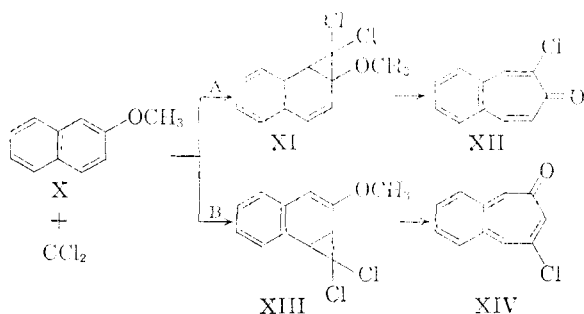
(9) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 130.

3,4-Benzotropolone (IX) was prepared, as previously described by Cook,<sup>14</sup>



and numerous unsuccessful attempts were made to convert this tropolone to 7-chloro-2,3-benzotropone (III) using thionyl chloride in benzene, and phosphorus pentachloride in phosphorus oxychloride. This behavior is in sharp contrast to the facile conversion of tropolone to 2-chlorotropone<sup>15</sup> by reaction with thionyl chloride in benzene. Attempts were also made to effect hydrolysis of III (or V) with aqueous hydrochloric acid<sup>16</sup> at 160°, and with hot potassium hydroxide in methanol<sup>14,16,17</sup>; however, no isolable products other than starting material resulted.

The reaction of dichlorocarbene with 2-methoxynaphthalene was effected in the same manner as described for 1-methoxynaphthalene, except that benzene was used as the reaction solvent, and similar results were noted. In addition to recovered starting ether (*ca.* 75%) there was obtained a ketone (XII or XIV, 13%), isomeric with III or V. The ketone was characterized by conversion into the corresponding oxime, and by its infrared and ultraviolet spectra.



While two different ketones, XII and XIV, could result from this reaction (path A and path B), the latter appeared less likely and consequently structure XII was preferred on the basis of the following arguments: (1) The ketone is white (m.p. 105–106°), and its infrared spectrum is similar to III (or V). The quinone structure XIV would be expected to be colored, and to possess a spectrum quite different from benzotropolone. (2) The electrons of dichlorocarbene are paired and the carbene seeks centers of highest electron density.<sup>18,19</sup>

(14) J. W. Cook, A. R. M. Gibb, A. R. Somerville and R. A. Raphael, *J. Chem. Soc.*, 603 (1952).

(15) W. von E. Doering and L. H. Knox, *THIS JOURNAL*, **74**, 5681 (1952).

(16) 2-Chlorotropone is hydrolyzed under similar conditions to tropolone, *cf.* W. von E. Doering and C. E. Hiskey, *ibid.*, **74**, 5688 (1952).

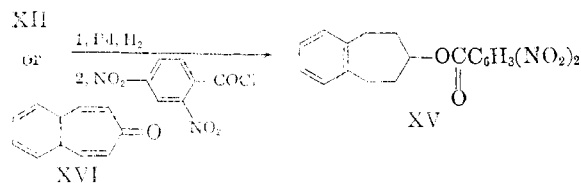
(17) Under similar conditions 2-chlorotropone is converted into sodium benzoate,<sup>15</sup> and 3,4-benzotropolone (IX) is converted into sodium 1-naphthoate.<sup>14</sup>

(18) (a) W. von E. Doering and A. K. Hoffmann, *THIS JOURNAL*, **76**, 6162 (1954); (b) W. von E. Doering and P. LaFlamme, *ibid.*, **78**, 5447 (1956).

(19) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 3409 (1956); P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956); P. S. Skell and R. C. Woodworth, *ibid.*, **78**, 4496 (1956).

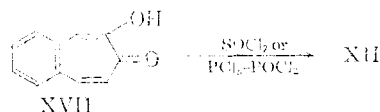
The effect of the methoxy group would be to activate the 1,2-double bond to attack by dichlorocarbene.<sup>3d</sup>

Structure XII was established for the ketone by its conversion to XV. The 3,5-dinitrobenzoate XV was identical with the product obtained from an authentic sample of 4,5-benzotropone (XVI) as shown



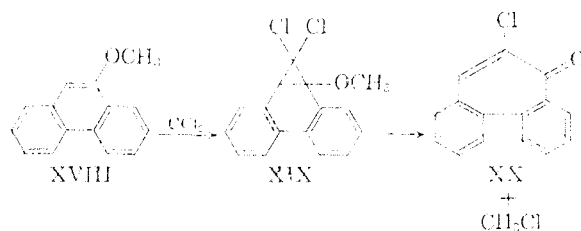
4,5-Benz-2-chlorotropone (XII) unlike the parent 2-chlorotropone,<sup>15</sup> but like III (or V), proved to be resistant to acid hydrolysis, and was recovered (97%) essentially unchanged after reaction with aqueous hydrochloric acid at 160° for 6 hours. The reaction of XII with aqueous potassium hydroxide (100°) also failed to produce a naphthoic acid.

An attempt was made to prepare XII by replac-



ing the hydroxyl group of 4,5-benzotropolone<sup>20</sup> (XVII) by chlorine; however, as was the case with 3,4-benzotropolone, these attempts were unsuccessful. It was concluded from these studies that the facile interchange noted for tropolone  $\rightleftharpoons$  2-chlorotropone is not evident in the fused 3,4- and 4,5-benzotropolone and benzchlorotropone system.

Finally, the reaction of dichlorocarbene with 9-methoxyphenanthrene was studied. A significantly higher yield of addition product was obtained—probably not only the result of the greater double bond character of the 9,10-unsaturation in XVIII,



as compared with the double bonds in naphthalene, but also of the fact that fewer side reactions are possible<sup>21</sup> which permitted the use of excess dichlorocarbene precursor.

The product XIX isolated from this reaction (52% by partition chromatography) was the cyclopropyl adduct, for which structure XIX is assigned. The molecular formula and spectra obtained are consistent with structure XIX; furthermore, thermal decomposition of this product gave methyl

(20) D. S. Tarbell and J. C. Bill, *ibid.*, **74**, 1234 (1952).

(21) The adducts II (or IV) and XI (or XIII) possess a double bond which may be of comparable or greater reactivity toward dichlorocarbene than the starting ether; however, the adduct XIX possesses only aromatic unsaturation.

chloride and a ketonic material ( $C_{15}H_9OCl$ ) assumed to be XX. The ketone XX was characterized by its composition and infrared spectrum, and by its conversion to the corresponding 2,4-dinitrophenylhydrazone. As with the other benzchlorotropones, we were unable to effect the hydrolysis of XX to the corresponding tropolone.

### Experimental

**The Reaction of 1-Methoxynaphthalene with Dichlorocarbene.**—Distilled commercial ethyl trichloroacetate (57.3 g., 0.3 mole) was rapidly added, under dry nitrogen, to a stirred, cold (0–5°) slurry of sodium methoxide (16.2 g., 0.3 mole), 1-methoxynaphthalene (63.2 g., 0.4 mole) and olefin-free petroleum ether (b.p. 66–67°, 200 ml.). The reaction was stirred 10 hours in the cold, and then allowed to warm to room temperature. Water (200 ml.) was added to the mixture and the organic layer which separated was then dried ( $MgSO_4$ ), and the solvent removed by distillation. The residue was chromatographed on a column of alumina (5 cm.  $\times$  45 cm.), and eluted with petroleum ether (30–60°) until no unreacted 1-methoxynaphthalene was recovered. Further elution with a 1:1 petroleum ether (30–60°)-benzene mixture gave discolored crystals of 7-chloro-2,3-benzotropolone<sup>22</sup> (III, m.p. 88–92°, 6.6 g., 11.5%). Recrystallization of this product from petroleum ether (60–68°) or sublimation gave white crystals melting at 95–96°; ultraviolet spectrum (95% ethanol):  $\lambda_{max}$  230 m $\mu$  (log  $\epsilon$  4.50),  $\lambda_{max}$  263 m $\mu$  (log  $\epsilon$  4.02),  $\lambda_{max}$  315 m $\mu$  (log  $\epsilon$  3.90),  $\lambda_{max}$  324 m $\mu$  (log  $\epsilon$  3.90); infrared spectrum: included bands at 1636 (m), 1611(m), 1592(s), 1523(s) cm.<sup>-1</sup>.

*Anal.* Calcd. for  $C_{11}H_7ClO$ : C, 69.30; H, 3.70; Cl, 18.60; mol. wt., 191. Found: C, 69.18; H, 3.91; Cl, 18.82; mol. wt., 189.

**Identification of Methyl Chloride. Hexamethylenetetramine-Methyl Iodide Salt.**—A cold (0°) saturated solution of methyl chloride in petroleum ether (65–66°) was prepared. This solution was shaken with a mixture of hexamethylenetetramine (0.5 g.), sodium iodide (0.5 g.) and 95% ethanol (6 g.) for 30 minutes. After the mixture had stood for 48 hours blades of the salt precipitated. This product was recrystallized from absolute ethanol to yield fine white needles melting at 198–199°; ultraviolet spectrum:  $\lambda_{max}$  220 m $\mu$ , log  $\epsilon$  4.16.

*Anal.* Calcd. for  $C_6H_{12}N_4I$ : C, 29.80; H, 5.36; N, 19.89. Found: C, 29.83; H, 5.38; N, 19.87.

The first 20 ml. from the distillation of the solvent in the preparation of 7-chloro-2,3-benzotropolone (III) was treated as above. A small amount of white crystalline material was formed, which upon recrystallization from ethanol gave white needles which were identical with the salt prepared from authentic methyl chloride (m.p. 196–197°, mixed m.p. 198–199°,  $\lambda_{max}$  220 m $\mu$  (log  $\epsilon$  4.21). Vapor phase chromatograms of the methyl chloride-solvent solution also confirmed the presence of methyl chloride.

**Reactions of III (or V).** 1. **Reduction to Benzuberol.**—A sample of the ketone (0.2 g., 0.00105 mole) dissolved in absolute ethanol (20 ml.) was hydrogenated in a micro apparatus with Pd-BaCO<sub>3</sub> (5%, 1.0 g.) catalyst (95% of four molar equivalents of hydrogen was absorbed). When hydrogen absorption was complete, the catalyst was removed by filtration through filter-cel. After evaporation of the solvent a slightly pinkish solid (yield = 100%) was left, which upon recrystallization from ethanol-water gave white needles melting at 98–100°. This material caused no depression in melting point when admixed with authentic benzuberol<sup>23</sup> (m.p. 100–101°); the infrared spectrum of this material was identical to that of benzuberol.

2. **Reaction with Alkali.**—The procedure used was that described by Doering and Knox<sup>16</sup> for the conversion of chlorotropone to benzoic acid. Tars were obtained from the basic solution obtained when potassium hydroxide-methanol, sodium hydroxide-water, or sodium ethoxide-ethanol were employed, and no evidence for the formation of sodium naphthoate was evident. A small amount of acidic material

(m.p. 244–247° dec.) was isolated when KOH and methanol was employed. This material was not characterized; however, it could not have been 1-naphthoic acid (m.p. 160–161°) or 2-naphthoic acid (m.p. 182–182.5°).<sup>24</sup>

3. **Reaction with Acid.**—The procedure used by Doering and Hiskey<sup>16</sup> for the hydrolysis of chlorotropone to tropolone was adapted. A mixture of the ketone (0.30 g., 0.00157 mole) and hydrochloric acid (3 N, 20 ml.) was heated in a Pyrex Carius tube for varying times (6 hr. to 5 days). With shorter reaction time only starting material was recovered. With longer reaction time little starting material, and only trace amounts of impure base-soluble material, were recovered. This small quantity of base-soluble material did not sublime; 3,4-benzotropolone sublimes readily.

4. **Reaction with Hydroxylamine.**—The oxime of III was prepared in the usual manner and recrystallized from ethanol-water. Light yellow needles were obtained which melted at 196–198.5°.

*Anal.* Calcd. for  $C_{11}H_9NOCl$ : C, 64.24; H, 3.92; N, 6.81. Found: C, 63.97; H, 4.11; N, 6.59.

3,4-Benzotropolone (IX).—3,4-Benzotropolone was prepared by the method described by Cook, *et al.*<sup>14</sup> Repeated attempts were made to convert IX into 7-chloro-2,3-benzotropolone (III) by reaction with thionyl chloride in benzene,<sup>15</sup> and by reaction with phosphorus pentoxide in phosphorus oxychloride. Red glassy residues which resisted crystallization, and which contained no sublimable component, resulted. No material was eluted with common solvents when the red residue was chromatographed. Infrared spectra of 3,4-benzotropolone included bands at 1668(s) and 1582(m) cm.<sup>-1</sup>; of 7-chloro-3,4-benzotropolone: 1668(m), 1662(m), 1580(m) and 1547(m) cm.<sup>-1</sup>.

**Reaction of 2-Methoxynaphthalene with Dichlorocarbene.**—The reaction of 2-methoxynaphthalene (63.2 g., 0.4 mole), ethyl trichloroacetate (57.4 g., 0.3 mole) and sodium methoxide (16.2 g., 0.3 mole) was carried out in dry, olefin-free benzene (250 ml.) as described above for 1-methoxynaphthalene. The reaction mixture was processed essentially as described for I. There was obtained recovered 2-methoxynaphthalene (ca. 73%), methyl chloride (identified as described above) and ketone XII (7.24 g., 13%, m.p. 100.6–102.6°).

The ketone was further purified by vacuum sublimation and white crystals melting at 105–106° were obtained; ultraviolet spectrum (95% ethanol):  $\lambda_{max}$  236 m $\mu$  (log  $\epsilon$  4.47),  $\lambda_{max}$  275 m $\mu$  (log  $\epsilon$  4.66),  $\lambda_{max}$  341 m $\mu$  (log  $\epsilon$  3.57),  $\lambda_{max}$  358 m $\mu$  (log  $\epsilon$  3.31); infrared spectrum: bands at 1627(s), 1605(m), 1545(w) and 1520(s) cm.<sup>-1</sup>.

*Anal.* Calcd. for  $C_{11}H_7OCl$ : C, 69.30; H, 3.70; Cl, 18.60; mol. wt., 191. Found: C, 69.40; H, 3.87; Cl, 18.38; mol. wt., 201.

**Proof of Structure of XII.**—A sample of the ketone XII (0.3 g., 0.0016 mole) was reduced following the procedure described for the reduction of III. After evaporation of the ethanol an oil remained. This oil was taken up in benzene. To the benzene solution was added pyridine (1.5 ml.) and 3,5-dinitrobenzoyl chloride, and the resulting mixture was refluxed for 2 hours. The benzene was washed with three 20-ml. portions of 5% sodium carbonate. The organic layer was dried ( $MgSO_4$ ), and the benzene distilled. The residue was crystallized from ethanol-water. Cream-colored crystals were obtained which melted at 163–165°.

*Anal.* Calcd. for  $C_{12}H_8N_2O_6$ : C, 60.67; H, 4.53; N, 7.86. Found: C, 60.74; H, 4.66; N, 7.57.

4,5-Benzotropolone (XVI) was prepared according to the procedure of Thiele and Weitz<sup>25</sup>; m.p. 65–66° (reported 66–67°). The benzotropolone XVI was hydrogenated over palladium-on-charcoal in ethanol and the 3,5-dinitrobenzoate of reduction product was prepared in the same manner as described above. The cream-colored crystals had m.p. 164–166°, mixed m.p. 162–164° with the 3,5-dinitrobenzoate of the reduction product of compound XII.

**Reactions of Ketonic Material XII.** 1. **Reaction with Acid.**—A mixture of the ketone (0.30 g.) and hydrochloric acid (20 ml., 3 N) was heated<sup>16</sup> for 9 hours at 160°. Starting material (0.29 g., 97%) was recovered. With longer reaction time (to 60 hr.) more tars and less starting material were recovered.

(24) A. Kailan, *Monatsh.*, **28**, 1069 (1900).

(25) J. Thiele and E. Weitz, *Ann.*, **377**, 1 (1910).

(22) This material is assumed to be III, and is so designated in the Experimental section; however, as pointed out in the Discussion, no formal decision between III and V is possible at this time.

(23) G. Baddeley and J. Chadwick, *J. Chem. Soc.*, 308 (1951).

2. **Reaction with Base.**—The reaction of ketone (0.47 g.) and aqueous sodium hydroxide was carried out as described for III (or V). A small amount of starting material, but no base-soluble component, was recovered.

3. **Attempted Nitration.**—The procedure described by Fernholz<sup>26</sup> for the nitration of 4,5-benzotropolone (nitric acid in glacial acetic acid) only led to high recovery of starting material XII.

4. **Reaction with Hydroxylamine.**—The oxime of the ketone was prepared in the usual manner; yellow crystals, m.p. 216–217° (from ethanol-water).

*Anal.* Calcd. for  $C_{11}H_8NOCl$ : C, 64.24; H, 3.92; N, 6.81. Found: C, 64.08; H, 4.16; N, 7.21.

4,5-Benzotropolone was prepared as described by Tarbell and Bill<sup>27</sup> (m.p. 158–160°, reported 158–160°; acetate m.p. 105–106°, reported 103–104°), and numerous unsuccessful attempts to replace the hydroxyl group by chlorine were made as described above for 3,4-benzotropolone. Recovered starting material was generally obtained; Infrared spectrum: bands at 1638(m), 1618(m), 1575(s) and 1542(m).  $cm^{-1}$ .<sup>28</sup>

**Reaction of Dichlorocarbene with 9-Methoxyphenanthrene.**—A modification in the procedure described for reaction with 1-methoxynaphthalene using two equivalents of dichlorocarbene precursor was possible since the initial adduct XIX contains unsaturation relatively inert to further attack by dichlorocarbene. From 9-methoxyphenanthrene<sup>29</sup> (m.p. 90–92°, reported 95–97°, 6.07 g., 0.029 mole), pentane (120 ml.), sodium methoxide (3.24 g., 0.06 mole) and ethyl trichloroacetate (11.46 g., 0.06 mole), there was obtained by chromatography: recovered 9-methoxyphenanthrene (eluted with petroleum ether, b.p. 30–60°) and the cyclopropyl adduct XIX (glassy solid, eluted with the same solvent shortly after starting ether). The glassy solid was recrystallized from petroleum ether (b.p. 68°) and XIX was ob-

tained as dense white crystals (m.p. 116–118°, 4.36 g., 52% yield). Further recrystallization of this solid from the same solvent afforded material melting at 120.5–122°; ultraviolet spectrum (95% ethanol):  $\lambda_{max}$  306  $m\mu$  ( $\log \epsilon$  3.18),  $\lambda_{max}$  275  $m\mu$  ( $\log \epsilon$  4.05),  $\lambda_{max}$  246  $m\mu$  ( $\log \epsilon$  4.26),  $\lambda_{max}$  239  $m\mu$  ( $\log \epsilon$  4.32),  $\lambda_{max}$  218  $m\mu$  ( $\log \epsilon$  4.48).

*Anal.* Calcd. for  $C_{16}H_{12}OCl_2$ : C, 66.00; H, 4.15; Cl, 24.35; mol. wt., 291. Found: C, 65.99; H, 4.43; Cl, 24.23; mol. wt., 283.

**Thermal Decomposition of XIX.**—A sample of XIX (1.11 g., 0.0058 mole) was heated (140°) for 1 hour under vacuum (0.2 mm.). The effluent gases were trapped in petroleum ether, b.p. 65°, cooled to 75°. The petroleum ether, after the pyrolysis, was subsequently shown, by vapor phase chromatography, to contain appreciable quantities of methyl chloride.

The solid residue from the pyrolysate was separated by elution chromatography (using petroleum ether, b.p. 60–68° as eluent) into two fractions: (1) starting material, 0.29 g.; and (2) a ketonic fraction, 0.76 g.

The ketonic fraction was further purified by recrystallization from petroleum ether (b.p. 65°), and was obtained as a solid melting at 95.5–97°. This product is considered to be XX; ultraviolet spectrum (95% ethanol):  $\lambda_{max}$  315  $m\mu$  ( $\log \epsilon$  3.58),  $\lambda_{max}$  265  $m\mu$  ( $\log \epsilon$  4.19),  $\lambda_{max}$  238  $m\mu$  ( $\log \epsilon$  4.33); infrared spectrum: bands at 1665(s), 1610(m) and 1595(m)  $cm^{-1}$ .

*Anal.* Calcd. for  $C_{15}H_9OCl$ : C, 74.85; H, 3.77; Cl, 14.78; mol. wt., 240. Found: C, 74.60; H, 3.85; Cl, 14.71; mol. wt., 239.

The 2,4-dinitrophenylhydrazone of XX was prepared by the standard procedure. A reaction time of 48 hours was required for the dinitrophenylhydrazone to precipitate. The orange crystals that formed were recrystallized from acetone-water to yield blocky prisms, m.p. 264–267° (uncor.).

*Anal.* Calcd. for  $C_{21}H_{13}O_4N_4Cl$ : C, 59.93; H, 3.11; N, 13.31. Found: C, 59.82; H, 3.40; N, 13.16.

Attempts to hydrolyze XX with aqueous hydrochloric acid, as described for III (or V) and XII, resulted in recovered starting material.

- (26) H. Fernholz, E. Hartwig and I. C. Salfeld, *Ann.*, **576**, 131 (1952).  
 (27) D. S. Tarbell and J. C. Bill, *This Journal*, **74**, 1234 (1952).  
 (28) Infrared data in part from D. S. Tarbell, G. P. Scott and A. D. Kemp, *ibid.*, **72**, 379 (1950).  
 (29) R. F. Schultz, E. D. Schultz and J. Cochran, *ibid.*, **62**, 2902 (1940).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN, MADISON 6, WISC.]

## The Energy Difference between the Chair and Boat Forms of Cyclohexane. The Twist Conformation of Cyclohexane

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A pair of stereoisomeric lactones (formulas A and B) have been prepared by a stereo-rational synthesis, and they have been submitted to combustion calorimetric and heat of vaporization determinations. These results showed that the enthalpy of B is greater than that of A by  $4.1 \pm 0.4$  kcal./mole in the vapor phase at 25°. Since A and B differ mainly in that the central ring in the former is a chair while that in the latter is a boat, this value can be used to estimate the difference in energy between the chair and boat forms of cyclohexane as about 5.5 kcal./mole. The consequences of these findings are discussed, and arguments are advanced in favor of the stability of the *twist* conformation of cyclohexane as compared with the severe boat form.

The application of conformational principles to systems containing six-membered rings<sup>1</sup> depends upon the basic rule that cyclohexane is more stable in the chair than in the boat conformation. This premise derives conclusive, if only qualitative, support from Raman, infrared and electron diffraction spectroscopy, as well as from thermodynamic considerations.<sup>2</sup> Several theoretical and semi-

empirical estimates of the magnitude of this energy difference have been reported; however, the approximations and assumptions implicit in these calculations have led to values ranging from as low as 1.31<sup>3</sup> to as high as 10.6<sup>4</sup> kcal./mole.<sup>5</sup> We disclose, in the present paper, the details<sup>6</sup> of an experimental

- (1) D. H. R. Barton, *Experientia*, **6**, 316 (1950); *Chemistry & Industry*, 664 (1953).  
 (2) (a) K. W. F. Kohrausch and W. Stockmair, *Z. physik. Chem.*, **B31**, 382 (1936); (b) R. S. Rasmussen, *J. Chem. Phys.*, **11**, 249 (1943); (c) O. Hassel and H. Viervoll, *Acta Chem. Scand.*, **1**, 149 (1947); (d) C. Beckett, K. S. Pitzer and R. Spitzer, *This Journal*, **69**, 2488 (1947).

- (3) The lower value of the range calculated by D. H. R. Barton, *J. Chem. Soc.*, 340 (1948).  
 (4) The higher value of a range calculated by the Turner semi-empirical method (ref. 5).  
 (5) For a complete review, see W. G. Dauben and K. S. Pitzer in M. S. Newman's "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956.  
 (6) Preliminary communication, W. S. Johnson, J. L. Margrave, V. J. Bauer, M. A. Frisch, L. H. Dreger and W. N. Hubbard, *This*