

anhydrous sodium sulfate. Distillation gave 9.5 g. of the chloroester, b.p. 73–78° at 3–4 mm. The analytical sample had b.p. 81–82° at 7 mm.,  $n_D^{25}$  1.4735. The ester still contained a small amount of a ketone impurity.

*Anal.* Calcd. for  $C_8H_{11}O_2Cl$ : C, 55.0; H, 6.4; Cl, 20.3. Found: C, 54.4, 54.5; H, 6.3, 6.2; Cl, 20.6, 20.6.

**1-Chlorobicyclo[2.1.1]hexane-5-carboxylic Acid.**—A solution of 8.6 g. (0.049 mole) of methyl 1-chlorobicyclo[2.1.1]hexane-5-carboxylate in 60 ml. of methanol was treated with 5.6 g. (0.1 mole) of potassium hydroxide. The mixture was heated to reflux for 1.5 hr. and then 30 ml. of methanol was removed by distillation. The solution was diluted with 100 ml. of water and extracted with three 100-ml. portions of ether. The aqueous phase was cooled in an ice-bath, acidified with hydrochloric acid and extracted with six 100-ml. portions of ether. The ether solution was dried over anhydrous sodium sulfate and distilled giving 5.7 g. (72%) of the acid. Two recrystallizations from cyclohexane followed by sublimation at 90° and 10 mm. gave the pure acid, m.p. 101.1–103.9°.

*Anal.* Calcd. for  $C_7H_9O_2Cl$ : C, 52.4; H, 5.6; Cl, 22.1; neut. equiv., 160.5. Found: C, 52.3, 52.4; H, 5.4, 5.6; Cl, 21.8, 21.9; neut. equiv., 159.

**1-Chlorobicyclo[2.1.1]hexane-5-carbonyl Chloride.**—A mixture of 6.42 g. (40 mmoles) of 1-chlorobicyclo[2.1.1]hexane-5-carboxylic acid and 10.00 g. (84 mmoles) of thionyl chloride, protected with a drying tube, was heated on a steam-bath for 5 hours. The excess thionyl chloride was removed under reduced pressure. The residue was distilled,

giving 6.86 g. (96%), of the acid chloride, b.p. 78° at 7 mm.,  $n_D^{25}$  1.4965.

***t*-Butyl 1-Chlorobicyclo[2.1.1]hexane-5-peroxycarboxylate.**—A mixture of 6.0 g. (67 mmoles) of *t*-butyl hydroperoxide, 7.0 ml. pyridine and 40 ml. of cymene was stirred and cooled thoroughly in an ice-salt-bath. 1-Chlorobicyclo[2.1.1]hexane-5-carbonyl chloride (5.17 g., 28.9 mmoles) was added dropwise over a 1-hour period, and the solution was stirred for another hour. The mixture was poured onto 50 g. of ice, the aqueous phase extracted with 30 ml. of cymene (in two portions), the combined cymene extract was washed with two 20-ml. portions of cold 10% sulfuric acid, ice-water (10 ml.), cold 10% sodium carbonate (10 ml.) and ice-water (three 10-ml. portions). The solution was dried over magnesium sulfate.

**1-Chlorobicyclo[2.1.1]hexane.**—The same apparatus as described for the preparation of bicyclo[2.1.1]hexane preparation was used with the exception of addition of an 8" Vigreux column. The decomposition of the peroxyester was carried out at about 130°. Within 2 hours, carbon dioxide evolution ceased with the formation of 0.79 g. of carbon dioxide (62% based on the acid chloride). The solution was distilled until about 5 ml. of cymene had been collected. The product was isolated by gas phase chromatography using a silicone column at 130° giving 0.89 g. (26%) of 1-chlorobicyclo[2.1.1]hexane.

Redistillation of the chloride gave material having b.p. 122°,  $n_D^{25}$  1.4629. A sample of the compound was heated in a sealed tube at 100° for a week with 2% ethanolic silver nitrate with negative results.

*Anal.* Calcd. for  $C_6H_7Cl$ : C, 61.8; H, 7.8; Cl, 30.4. Found: C, 61.8, 61.8; H, 7.8, 7.6; Cl, 30.2, 30.5.

[CONTRIBUTION FROM FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, PRINCETON, N. J.]

## Stereochemistry of Hydroanthracenes<sup>1</sup>

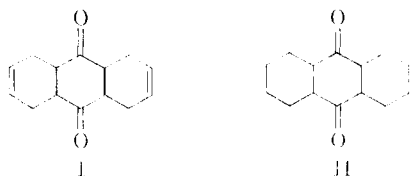
BY RICHARD K. HILL, JAMES G. MARTIN<sup>2</sup> AND WILLIAM H. STOUCH

RECEIVED DECEMBER 27, 1960

Raney nickel reduction of the bis-thioketal of the bis-butadiene-*p*-benzoquinone adduct (I) gave perhydroanthracene VIII. Several experiments proved that no epimerization occurred during this process, and I consequently has the *cis,anti,cis* configuration, in contrast to the earlier assignment of Alder and Stein. Reduction of the bis-thioketal of the stereoisomeric diketone IV gave *trans,syn,trans*-perhydroanthracene (VII), proving the configuration of IV. The four diols corresponding to I and its saturated derivative were prepared and their stereochemistry determined by infrared spectroscopy. Huang-Minlon reduction of I, III or IV, followed by hydrogenation, or of II directly, led to a mixture of VIII and IX. The perhydroanthracenes were equilibrated by aluminum bromide to a mixture composed of 96% of VII and 4% of VI.

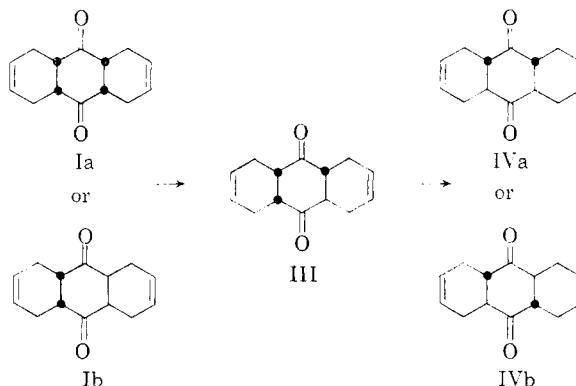
### Introduction

In 1933, Alder and Stein<sup>3</sup> prepared a bis-butadiene adduct (I) of *p*-benzoquinone, and showed, by oxidation of the tetrahydro derivative II to *cis*-cyclohexane-1,2-dicarboxylic acid, that only *cis* ring junctions were present in the adduct. Refluxing acetic anhydride epimerized I to a stereo-



isomer III, and either I or III could be further isomerized by heat, alkali or longer reflux with acetic anhydride to a third isomer IV. Both

III and IV were shown to possess at least one *trans* ring junction.



Compound III, as the primary isomerization product of the all-*cis* adduct, was assigned the *cis,trans* configuration, but two configurations were possible for each of the other stereoisomers. Alder and Stein did not provide evidence to permit a decision between the two *cis,cis* configurations

(1) Taken from theses presented to Princeton University by J. G. Martin for the Ph.D. degree, 1960, and by W. H. Stouch for the B.A. degree, 1957. Presented, in part, at the Delaware Valley Regional Meeting, American Chemical Society, Philadelphia, Pa., February, 1960.

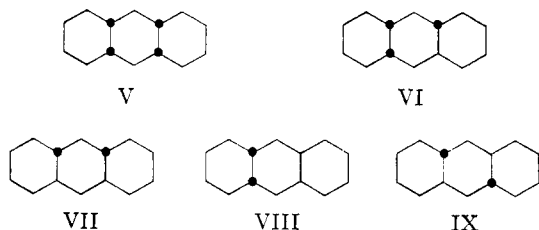
(2) Danforth Foundation Fellow, 1957–1960.

(3) K. Alder and G. Stein, *Ann.*, **501**, 247 (1933).

Ia and Ib for the adduct, nor between the two *trans,trans* configurations IVa and IVb for the stable stereoisomer. They regarded it probable, however, that the adduct possessed configuration Ia, arguing that, of the two, it would be more prone to isomerize. This assignment has been widely accepted<sup>4</sup> and an explanation offered<sup>4b</sup> for the sole formation of Ia in the Diels-Alder addition.

It seemed likely to us that the adduct was not Ia, but Ib, the *cis,anti,cis* isomer, since after one mole of butadiene has added to benzoquinone the second mole should add from the side on which the two *cis* hydrogens lie rather than from the side where a cyclohexene ring projects. Examples from the literature<sup>5</sup> support the generalization that in such additions the favored transition state is that which offers the least non-bonded repulsion between the planes of the addends.

We recently reported, in a preliminary communication,<sup>6</sup> evidence that the adduct has the *cis,anti,cis* configuration Ib; the same conclusion subsequently was reached by Crossley and Henbest.<sup>7</sup> This paper gives the details of our proof of configuration, and records some related experiments on the stereochemistry of hydroanthracenes.



### Discussion

All five of the isomeric perhydroanthracenes (V-IX) are now known. The last to be prepared, the *trans,anti,trans* isomer IX, was reported by Clarke<sup>8</sup>; references to the other four may also be found in his paper. It consequently appeared possible to show the configurations of diketones I and IV by complete reduction to perhydroanthracenes, by methods which would leave the skeletal configuration unaltered.

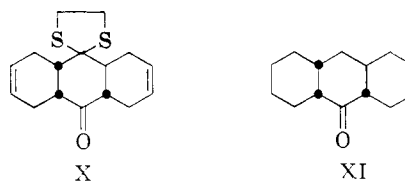
These conversions were realized by the use of the Mozingo reduction. Treatment of the adduct I with ethanedithiol and boron trifluoride etherate at room temperature for a short time gave the bis-ethylene thioketal in quantitative yield. Although formation of thioketals is rarely accompanied by epimerization at  $\alpha$ -carbon atoms,<sup>9</sup> there is at least

one report<sup>10</sup> of this phenomenon, and so it was important to show that no epimerization had occurred during the preparation of the thioketal. The following observations strongly indicate that this is true: (a) although warming the adduct with boron trifluoride etherate to 50–60° for an hour caused partial isomerization to III, at room temperature the adduct was unchanged on standing for a week with boron trifluoride etherate; (b) substituting 2-mercaptoethanol for ethanedithiol in the above reaction gave the bis-hemithioketal of I, which was reduced by Raney nickel to II, showing that the skeletal configuration remains unchanged during these steps.

Raney nickel reduction of the bis-thioketal of I yielded *cis,anti,cis*-perhydroanthracene (VIII)<sup>11</sup>; Crossley and Henbest<sup>7</sup> accomplished this reduction with lithium in ethylamine. This result demonstrates that the Diels-Alder adduct has the *cis,anti,cis* configuration Ib.

Application of the same two-step procedure to the diketone IV gave *trans,syn,trans*-perhydroanthracene<sup>12</sup> (VII), which was identical with an authentic sample kindly supplied by Dr. J. W. Cook. This transformation was also realized by Crossley and Henbest.<sup>7</sup> The stable isomer of the adduct thus has the *trans,syn,trans* configuration IVa.

When the *cis,trans*-diketone III was treated with ethanedithiol and boron trifluoride etherate, only a mono-thioketal was isolated. The observation that it is not epimerized by alkali suggests that it has structure X. Raney nickel desulfurization yielded a saturated 9-ketoperhydroanthracene, m.p. 82.5°. This ketone is also unaffected by alkali, supporting the assigned configuration XI.



**Huang-Minlon Reductions.**—Clarke<sup>8</sup> and Crossley and Henbest<sup>7</sup> have reported recently that Wolff-Kishner reduction of the tetrahydro derivative of IVa gave a mixture of VI, VIII and IX, with the *trans,anti,trans* isomer IX predominating. We have independently carried out reductions of other diketones of this series and obtained similar results. Reduction of the adduct (Ib) by the Huang-Minlon modification gave an oily mixture of unsaturated hydrocarbons, from which separated a crystalline decahydroanthracene, m.p. 96.5°. It was shown to be the *cis,anti,cis*-diene XII by dehydrogenation to anthracene and by catalytic hydrogenation to VIII.

Hydrogenation of the mother liquors from the crystallization of XII gave an additional quantity of VIII, plus a somewhat greater amount of the

(4) (a) R. A. Raphael, in "Chemistry of Carbon Compounds," Vol. IIA, edited by E. H. Rodd, Elsevier Publishing Co., New York, N. Y., 1953, p. 334; (b) J. A. Norton, *Chem. Revs.*, **31**, 319 (1942); see especially pp. 502–504.

(5) (a) K. Alder, J. Monch and H. Wirtz, *Ann.*, **627**, 47 (1959); (b) S. B. Soloway, *J. Am. Chem. Soc.*, **74**, 1027 (1952); (c) G. Stork, E. E. van Tamelen, L. J. Friedman and A. Burgstahler, *ibid.*, **75**, 384 (1953); (d) J. K. Stille and D. A. Frey, *ibid.*, **81**, 4273 (1959); (e) W. R. Vaughan and M. Yoshimine, *J. Org. Chem.*, **22**, 7 (1957); (f) R. C. Cookson and E. Crundwell, *Chemistry & Industry*, 1004 (1958); (g) K. Alder and G. Stein, *Angew. Chem.*, **50**, 510 (1937).

(6) R. K. Hill and J. G. Martin, *Proc. Chem. Soc.*, 390 (1959).

(7) N. S. Crossley and H. B. Henbest, *J. Chem. Soc.*, 4413 (1960).

(8) R. L. Clarke, *J. Am. Chem. Soc.*, **83**, 964 (1961).

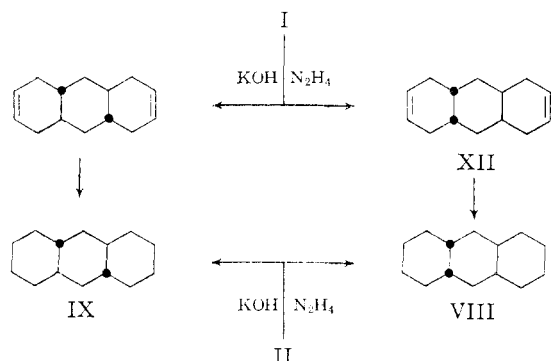
(9) See, e.g., (a) M. L. Wolfson, B. W. Lew and R. M. Goepff, Jr., *ibid.*, **68**, 1443 (1946); (b) K. Yamakawa, *J. Org. Chem.*, **24**, 897 (1959); (c) M. Yanagita and K. Yamakawa, *ibid.*, **24**, 903 (1959).

(10) R. Stevenson and L. F. Fieser, *J. Am. Chem. Soc.*, **78**, 1409 (1956).

(11) R. L. Clarke and W. S. Johnson, *ibid.*, **81**, 5706 (1959).

(12) J. W. Cook, S. Mitchell and N. A. McGinnis, *J. Chem. Soc.*, 286 (1944).

*trans,anti,trans* isomer IX. The skeleton of IX was confirmed by dehydrogenation to anthracene. Huang-Minlon reduction of II gave directly a mixture of VIII and IX. The result of these reductions makes VIII and IX, the last of the perhy-



droanthracenes to be prepared, probably the most readily available of all the isomers. Hydrocarbon IX is a particularly interesting product, since the central ring is held in a fixed boat conformation.

It is evident that the reduction products are not formed in a ratio corresponding to their thermodynamic stabilities. Johnson<sup>13</sup> has estimated the relative free energies of the five perhydroanthracenes as: VII, 0; VI, 2.4; VIII, 4.8; IX, 5.6; and V, 6.4 kcal./mole; the same values, except for a figure of 9 kcal. for V, have been assigned by Dauben and Pitzer.<sup>14</sup> The estimated 5.6 kcal. increment in going from the all chair *trans,trans* compound VII to the chair-boat-chair isomer IX has been confirmed by the recent experimental determination of 5.3 kcal. as the free energy difference between a pair of similar boat-chair isomers.<sup>15</sup> Thus, if the stability of the product were the determining factor, the *trans,syn,trans* isomer VII would have been formed in the reduction. Indeed, V and VI are isomerized in VII, though in low yield, by aluminum chloride.<sup>12</sup> We have verified that VII is the most stable perhydroanthracene by equilibrating pentane solutions of VI, VII and IX with aluminum bromide. At 0°, equilibrium is attained after about 170 hours. By the use of an infrared analytical technique, the equilibrium mixture was estimated to consist of  $96 \pm 1\%$  VII and  $4 \pm 1\%$  VI. The derived free energy difference between VI and VII, assuming negligible entropy differences,<sup>15,16</sup> is  $1.9 \pm 0.1$  kcal./mole, in good agreement with the value of 2.12 kcal./mole for the heat of isomerization of *cis*- to *trans*-decalin.<sup>17</sup>

The same mixture of VIII and IX was obtained from the Huang-Minlon reduction and subsequent hydrogenation regardless of whether the starting material was Ib, III or IVa, indicating that the diketones rapidly equilibrate in the strongly

alkaline medium. Nevertheless, the ratio of hydrocarbon products does not appear to reflect the relative stabilities of the isomeric diketodecalhydroanthracenes. The order of stability of these diketones is not expected to be the same as that of the parent hydrocarbons, since the presence of the carbonyl groups not only reduces the hydrogen-hydrogen interactions (as do the double bonds in the unsaturated derivatives), but introduces added 1,2- and 1,3-methylene-carbonyl interactions (Klyne's "2-alkylketone and 3-alkylketone effects"<sup>18</sup>). These effects have been noted previously in equilibration studies on 1,4-diketo-octalins<sup>19</sup> and in the careful work of Robins and Walker<sup>20</sup> on the 1,4-diketo-perhydrophenanthrenes. Using Klyne's values for the magnitude of the alkylketone effects and estimating the relative free energies of the isomeric diketones,<sup>21</sup> the interesting conclusion is reached that in both the saturated series (II) and unsaturated series (I), the *trans,anti,trans* configuration (corresponding to IX) is calculated to be the most stable.<sup>22</sup> The boat central ring, so costly in the hydrocarbons, becomes much less unfavorable when the eclipsed hydrogen interactions are removed by the carbonyl groups. In the unsaturated series, the *trans,anti,trans* isomer is estimated to be the most stable, followed closely by the *cis,anti,cis*, the *cis,trans* and the *trans,syn,trans* isomers. Among the saturated diketones, the predicted hierarchy is *trans,anti,trans*, then *trans,syn,trans*, followed by *cis,trans* and *cis,anti,cis*.

On the other hand, the experimental results available concerning the relative stability of the diketones do not agree with this predicted order, and are themselves contradictory. Both the adduct Ib and its *cis,trans* isomer III are rapidly and quantitatively converted to the *trans,trans*-diketone IVa by warm ethanolic potassium hydroxide,<sup>8</sup> but this surely does not represent an equilibrium situation, since the extreme insolubility of IVa in ethanol removes it from solution. Alder and Stein were able to show,<sup>3</sup> however, that refluxing acetic anhydride converts Ib, III and IVa to the same equilibrium mixture, which they estimated by melting point to contain 60% of III and 40% of IVa; a similar equilibrium mixture was reached in the saturated diketone series. In our hands, warming either Ib or IVa with potassium *t*-butoxide in pyridine, and quenching the homogeneous solution in water, gave a mixture of diketones which was estimated, by a combination of fractional crystallization and infrared analysis, to contain 66–69% IVa, 22–27% III and 7–9% Ib. These figures cannot be considered incontrovertible, since infrared curves are not available for the two unknown isomers, but a minimum of 45–50% of the equilibration mixture was crystallized as IVa.

Since the products of the Huang-Minlon reduction correspond to the stability hierarchy of neither

(13) W. S. Johnson, *J. Am. Chem. Soc.*, **75**, 1498 (1953).

(14) W. G. Dauben and K. S. Pitzer, in "Steric Effects in Organic Chemistry," edited by M. S. Newman, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 34.

(15) W. S. Johnson, J. L. Margrave, V. J. Bauer, M. A. Frisch, L. H. Dreger and W. N. Hubbard, *J. Am. Chem. Soc.*, **82**, 1255 (1960).

(16) R. M. Gascoigne, *J. Chem. Soc.*, 876 (1958).

(17) G. F. Davies and E. C. Gilbert, *J. Am. Chem. Soc.*, **63**, 1585 (1941).

(18) W. Klyne, *Experientia*, **12**, 119 (1956).

(19) H. B. Henbest, M. Smith and A. Thomas, *J. Chem. Soc.*, 3293 (1958).

(20) P. A. Robins and J. Walker, *ibid.*, 1789 (1955).

(21) Values for the other interactions were taken from ref. 14, pp. 13–35; for details, see the thesis of J. G. M.

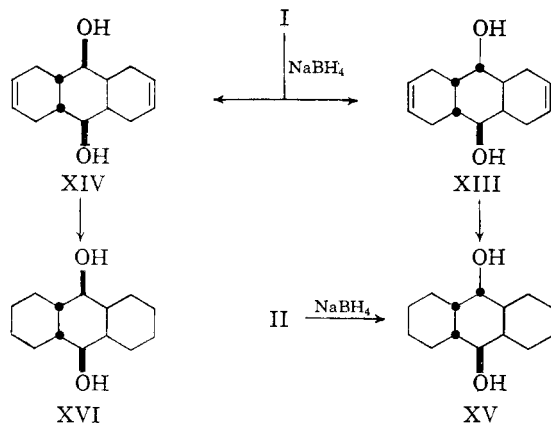
(22) Cf. ref. 11, footnote 19, where the same conclusion is reached.

the perhydroanthracenes nor the diketones, one must conclude, in agreement with Clarke,<sup>8</sup> that the decisive factor is a kinetic one, the rates at which each of the diketones is converted into its hydrazone. This explanation has been offered for the products obtained from Wolff-Kishner reduction of 10-methyldecalone-1<sup>23</sup> and 15-ketosteroids.<sup>24</sup>

**9,10-Diols.**—Several other methods of determining the configuration of the adduct (I) were investigated, in addition to the successful route described above.

(a) Reduction of the carbonyl groups of I could conceivably yield *three* isomeric diols if the adduct were Ia, but only two diols are possible from Ib. The isolation of three diols would thus be an unambiguous solution, but any other result would be inconclusive. In practice, sodium borohydride reduction of I gave a mixture of two diols: XIII, m.p. 256–259°, and XIV, m.p. 134–136°, easily separated by virtue of the insolubility of the higher-melting isomer in chloroform. The ratio of diols formed varied strikingly with temperature: at 0°, 5° and 23° the ratio of XIII to XIV was, respectively, 16:75, 21:62 and 30:53. Both diols could be oxidized to the original diketone I using the mild chromic acid-acetone reagent,<sup>25</sup> showing that no stereochemical isomerization had occurred during reduction.

Compound XIII was hydrogenated to a saturated diol XV, m.p. 276–276.5°, which was also the sole product of sodium borohydride reduction of II. Clarke and Johnson<sup>11</sup> have reported a diol, m.p. 273–274°, formed by lithium aluminum hydride reduction of II, undoubtedly the same compound. Hydrogenation of XIV gave an isomeric saturated diol XVI, m.p. 174–175°. Both XV and XVI were oxidized by chromic acid to II.



The configurations of these diols were established unequivocally by examining their infrared spectra in dilute carbon tetrachloride solution. In the O–H stretching region, all four diols showed multiple peaks at 3631–3632 and 3618–3619 cm.<sup>-1</sup>;

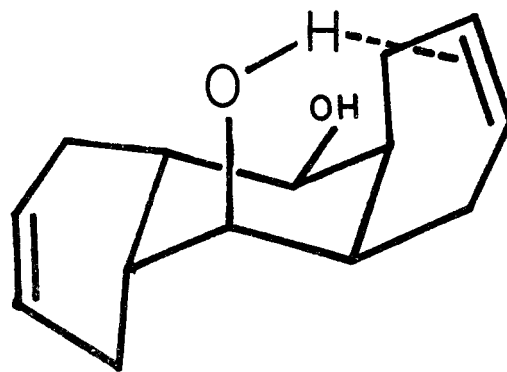


Fig. 1.

the multiplicity and splitting of 12–14 cm.<sup>-1</sup> are characteristic of alcohols with configurational or conformational heterogeneity.<sup>26</sup> Diol XIV showed, in addition, a strong absorption peak at 3584 cm.<sup>-1</sup>. This shift of 47 cm.<sup>-1</sup>, unaffected by dilution, is characteristic of intramolecularly hydrogen bonded hydroxyls. It cannot be due to bonding between two hydroxyls, since the shift in such cases is twice as large, and since the shift disappears on hydrogenating the double bonds, and so is assigned to hydrogen bonding with the double bond in an adjacent ring<sup>27</sup> (see Fig. 1). Diol XIV must consequently have an axial hydroxyl, and is assigned the *cis*(a,e) configuration, while XIII is the *trans*, diequatorial diol. These assignments are confirmed by the infrared spectra of the two saturated diols in Nujol: XV shows strong bands at 9.57 and 9.70  $\mu$  indicative of equatorial hydroxyls, but no absorption in the axial hydroxyl region around 9.9  $\mu$ <sup>28</sup>; XV has bands in both the axial and equatorial hydroxyl regions. The higher melting points and lower solubilities in chloroform of the two diequatorial diols are probably due to superior intermolecular hydrogen bonding.

We may call attention, in passing, to the observation that sodium borohydride reduction of the adduct I yields predominantly the *cis*-diol XIV, while reduction of the saturated diketone II gives only the *trans*-diol XV.

(b) Another possible solution to the problem of the adduct configuration was the resolution of a monoester of one of the diols. It can be seen that monoesters of any of the three diols derivable from Ia all possess a plane of symmetry, while monoesters of either of the diols from Ib are theoretically resolvable; a similar approach was employed recently by Winstein and co-workers<sup>29</sup> in elucidating the stereochemistry of the bis-cyclopentadiene-benzoquinone adduct. We were unable, however, to prepare monophthalates from XIII or XIV. Attempted partial hydrolysis of the diacetate of XIV gave only starting diester plus diol. A monotosylate was prepared from XIII and was

(23) F. Sondheimer and D. Rosenthal, *J. Am. Chem. Soc.*, **80**, 3995 (1958).

(24) C. Djerassi, T. T. Grossnickle and L. B. High, *ibid.*, **78**, 3166 (1956); see also D. H. R. Barton and G. F. Laws, *J. Chem. Soc.*, 52 (1954), and C. S. Barnes, D. H. R. Barton and G. F. Laws, *Chemistry & Industry*, 616 (1953).

(25) K. Bowden, I. M. Heilbron, E. R. H. Jones and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

(26) R. Piccolini and S. Winstein, *Tetrahedron Letters*, **13**, 4 (1959).

(27) P. v. R. Schleyer, D. S. Trifan and R. Bacskaï, *J. Am. Chem. Soc.*, **80**, 6691 (1958). We are very grateful to Prof. Schleyer for his aid in obtaining and interpreting these spectra.

(28) (a) R. A. Pickering and C. C. Price, *J. Am. Chem. Soc.*, **80**, 4931 (1958); (b) R. L. Clarke and C. M. Martini, *ibid.*, **81**, 5716 (1959).

(29) L. de Vries, R. Heck, R. Piccolini and S. Winstein, *Chemistry & Industry*, 1416 (1959).

converted to the acid phthalate, but this could not be resolved with quinine or brucine.

(c) Finally, several methods of converting the diols to perhydroanthracenes were investigated. Compound XIII readily formed a bis-methanesulfonate, but lithium aluminum hydride reduction regenerated the diol. Attempts to convert the bis-mesylate to a diiodide or bis-benzyl thioether were unavailing; these results are paralleled by similar unsuccessful experiments on the bis-tosylate of XV by Clarke and Johnson.<sup>11</sup> Refluxing XV with phosphorus and hydriodic acid gave a low yield of a crystalline moniodoperhydroanthracene, which was not investigated further.

**Acknowledgments.**—The authors are indebted to the Danforth Foundation for financial support to J. G. M. and to the Standard Oil Co. of New Jersey for a summer grant to J. G. M. We express our thanks to Drs. J. W. Cook and J. D. Loudon for providing samples of several perhydroanthracenes, and Dr. Robert L. Clarke for sending us a copy of his manuscript before publication.

### Experimental

Melting points were determined in open capillaries, and are uncorrected. Infrared spectra were obtained on a Perkin-Elmer recording spectrophotometer, model 21-C; the high-resolution spectra of the diols were obtained on a similar instrument using lithium fluoride optics.

***cis,anti,cis*-Perhydroanthracene (VIII).**—A mixture of 1.0 g. of the bis-butadiene-benzoquinone adduct<sup>3</sup> (I) and 2.0 ml. of ethanedithiol was chilled and treated with 2.0 ml. of redistilled boron trifluoride etherate. The adduct dissolved and a precipitate formed after 2 minutes. After 25 minutes at room temperature the thick paste was diluted with methanol and filtered, affording 1.8 g. of the colorless, powdery bis-thioether, m.p. 249–250°. The crude product was recrystallized from dioxane and washed with methanol, and melted then at 257–259° (reported<sup>7</sup> m.p. 254–255°). An infrared spectrum of the thioether in Nujol suspension showed no carbonyl absorption.

*Anal.* Calcd. for  $C_{18}H_{24}S_2$ : C, 58.65; H, 6.56. Found: C, 58.68; H, 6.68.

In the absence of ethanedithiol, a suspension of the adduct I in boron trifluoride etherate was kept 1 week at room temperature, and recovered unchanged. Warming the suspension for an hour at 50° caused partial isomerization to III.

A mixture of 3.0 g. of the bis-thioether and 9–10 g. of Raney nickel catalyst in 250 ml. of ethanol was refluxed for 2 hours, then filtered and the catalyst washed with ethanol. A faint yellow color with tetranitromethane on an aliquot of the product isolated at this point indicated that the double bonds were nearly saturated, so the filtrate was hydrogenated over fresh Raney nickel at 45 p.s.i. to ensure complete reduction. Concentration of the filtrate, after removing the catalyst, yielded 0.36 g. of colorless needles of VIII, m.p. 123–124° (lit.<sup>11</sup> m.p. 122–122.5°), which gave no color with tetranitromethane. An analytical sample was prepared by sublimation at 100° and 20 mm.

*Anal.* Calcd. for  $C_{18}H_{24}$ : C, 87.42; H, 12.58. Found: C, 87.20; H, 12.39.

**Bis-ethylene Hemithioether of I.**—A mixture of 2.0 g. of the adduct I and 2.0 ml. of 2-mercaptoethanol with 4.0 ml. of boron trifluoride etherate was kept at room temperature for 1 day. The resulting paste was diluted with methanol and filtered, giving 3.1 g. of crude product, m.p. 230–249°, which showed no carbonyl absorption in the infrared. Recrystallization from dioxane gave the analytical sample, m.p. 252–256°.

*Anal.* Calcd. for  $C_{18}H_{24}O_2S_2$ : C, 64.23; H, 7.19. Found: C, 64.07; H, 7.40.

**Raney Nickel Hydrogenolysis of the Bis-ethylene Hemithioether.**—A 0.94-g. sample of the hemithioether was suspended with 5 g. of Raney nickel catalyst in 150 ml. of ethanol and refluxed for 2.5 hours. The filtered, cooled solution deposited 0.41 g. of unreacted or partially hydro-

genated starting material first, then 0.05 g. of *cis,anti,cis*-perhydroanthraquinone<sup>3</sup> (II), m.p. 176–181°. The melting point was not depressed by admixture with an authentic sample, m.p. 183°, and the infrared spectrum was identical with that of authentic material.

***trans,syn,trans*-Perhydroanthracene (VII).** (a) **From IVa.**—The unsaturated *trans,syn,trans*-diketone IVa<sup>3</sup> was converted to its bis-ethylenethioether<sup>7</sup> by the procedure described above. The thioether (0.2 g.) was refluxed in 150 ml. of ethanol with 2 g. of Raney nickel catalyst for 2 hours. Concentration of the filtrate gave 23 mg. of crystals, m.p. 83–86°. Hydrogenation over fresh Raney nickel in ethanol, to ensure complete reduction, and crystallization of the product from acetone, gave 4 mg. of *trans,syn,trans*-perhydroanthracene (VII), m.p. 86–88.5°. Its identity was shown by infrared comparison with an authentic sample, m.p. 90–92°, generously furnished by Drs. J. W. Cook<sup>12</sup> and J. D. Loudon; a mixture of the two samples melted at 86–91°.

(b) **From Tetralin.**—The procedure of Schroeter<sup>30</sup> was modified as follows: A mixture of tetralin (30 g.) and aluminum chloride (10 g.) was stirred and heated at 125° for 12 hours, cooled, poured onto ice and 25 ml. of concentrated hydrochloric acid, and extracted with 100 ml. of ether. An equal volume of acetone was added, and the dense, black oil which separated was discarded. The remaining solution was concentrated to 50 ml. and added dropwise to an aqueous solution of excess potassium permanganate. Aqueous sodium hydroxide was added until the mixture was alkaline, and the mixture stirred 1 more hour at 75°, then cooled, and the excess permanganate reduced with acetone. The manganese dioxide was filtered and washed with acetone and ether; the aqueous filtrate was extracted with ether. The combined organic solutions were concentrated and steam distilled, and the distillate extracted with ether. Concentration of the extracts and recrystallization of the residue from acetone gave 0.80 g. of VII, m.p. 88–89.5°; another crystallization from acetone raised the melting point to 91–92.5° (reported<sup>30</sup> 93°). The identity of this compound, which has been assumed, but never proved, to be VII, was shown by mixed melting point and comparison of infrared spectra with an authentic sample of VII.

**Mono-thioether of III (X).**—A mixture of 0.5 g. of the unsaturated *cis,trans*-diketone III, 1.0 ml. of ethanedithiol and 1.0 ml. of boron trifluoride etherate was kept at room temperature for 7 hours, cooled well and filtered, and the solid washed with cold ether, affording 0.62 g. of the mono-thioether X, m.p. 123–126°. Recrystallization from methanol raised the melting point to 128.5–131.5°. The infrared spectrum in Nujol suspension showed a sharp ketone band at 5.86 $\mu$ . The thioether (55 mg.) was recovered unchanged after refluxing in ethanol with 10 drops of 1% potassium hydroxide under nitrogen for 5 minutes.

*Anal.* Calcd. for  $C_{18}H_{20}OS_2$ : C, 65.71; H, 6.89; S, 21.93. Found: C, 65.72; H, 7.05; S, 21.75.

***cis,syn,trans*-9-Ketoperhydroanthracene (XI).**—A solution of 0.50 g. of the thioether X in 100 ml. of ethanol was refluxed with 6 g. of Raney nickel catalyst for 2.5 hours. Evaporation of the filtrate gave 0.24 g. of crystalline ketone, m.p. 80.5–81.5°; three recrystallizations from acetone brought the melting point to 81.5–82.5°. The ketone was recovered unchanged after refluxing with 1% potassium hydroxide in ethanol for 2 minutes. The infrared spectrum showed a carbonyl band at 5.86 $\mu$ .

*Anal.* Calcd. for  $C_{14}H_{22}O$ : C, 81.49; H, 10.75. Found: C, 81.58; H, 10.75.

***cis,trans*-Perhydroanthracene (VI).**—A solution of 1.0 g. of *trans-asym*-octahydroanthrone<sup>12</sup> in 120 ml. of ethanol and 3 ml. of saturated ethanolic hydrogen chloride was hydrogenated over 0.5 g. of platinum dioxide at 3.9 atm. for 72 hours at room temperature. The mixture was filtered and neutralized with aqueous sodium bicarbonate. Evaporation of the solvent under reduced pressure caused the separation of flaky crystals of VI, 0.39 g., m.p. 31–34°. Several recrystallizations from acetone raised the melting point to 36–39.5° (reported<sup>12</sup> 39°).

*Anal.* Calcd. for  $C_{14}H_{24}$ : C, 87.42; H, 12.58. Found: C, 87.29; H, 12.71.

**Huang-Minlon Reductions.** (a) **Ib.**—A solution of 10.0 g. of Ib, 35 ml. of 85% aqueous hydrazine hydrate and 35 g.

(30) G. Schroeter, *Ber.*, **57**, 1990 (1924).

of sodium hydroxide in 400 ml. of triethylene glycol was refluxed for 1 hour, then slowly distilled until the temperature reached 190°. A fragrant, water-soluble oil distilled from 165–190° and hindered recovery of the product, so it was best collected separately; it did not occur in later runs which used ethylene glycol as solvent. The reaction mixture was refluxed at 190° for 3 hours, cooled and diluted with water, then steam distilled. The combined distillates were extracted with ether and the extracts evaporated to dryness and hydrogenated in ethanol over 0.3 g. of platinum dioxide at 3.2 atm. for 1.5 hours. Evaporation of the filtered reaction mixture gave 1.05 g. of *cis,anti,cis*-perhydroanthracene (VIII), m.p. 121–123°, identified by mixed melting point and infrared comparison with the sample described above. Concentration of the filtrate gave 0.80 g. of colorless crystals of *trans,anti,trans*-perhydroanthracene (IX), m.p. 32–44°, which melted at 45–46° after recrystallization from ethanol (reported<sup>8</sup> m.p. 48.5–49.7°). Its infrared spectrum was different from those of the other four perhydroanthracenes, and a mixture with the 39° *cis,trans* isomer melted below 25°.

*Anal.* Calcd. for C<sub>14</sub>H<sub>24</sub>: C, 87.42; H, 12.58. Found: C, 87.42; H, 12.58.

(b) IVa.—A solution of 7.0 g. of the *trans,syn,trans*-diketone IVa in 300 ml. of triethylene glycol was refluxed with 24 g. of sodium hydroxide and 24 ml. of 85% hydrazine hydrate for 2 hours, cooled and diluted with an equal volume of water, and steam distilled. The distillate was extracted with ether, the extracts evaporated and the residue crystallized from acetone to afford 0.38 g. of the *cis,anti,cis*-diene XII, m.p. 93–96°; recrystallization from acetone raised the melting point to 95–96.5°. In later experiments XII was also isolated from Huang-Minlon reduction of the adduct Ib.

*Anal.* Calcd. for C<sub>14</sub>H<sub>20</sub>: C, 89.29; H, 10.71. Found: C, 88.99; H, 10.71.

The mother liquor from the separation of XII was evaporated to dryness and hydrogenated in ethanol over platinum dioxide. Evaporation of the filtered solution gave 0.305 g. of VIII, m.p. 120–122°, and 0.850 g. of IX, m.p. 41–44°.

(c) III.—A 14.8-g. mixture of stereoisomeric ketones, consisting mostly of the *cis,trans* isomer III, was mixed with 400 ml. of ethylene glycol, 60 g. of sodium hydroxide and 60 ml. of 85% hydrazine hydrate and promptly distilled until a pot temperature of 193° was reached. The mixture was refluxed at this temperature for 4 hours, cooled and steam distilled. The combined distillates were extracted with ether, and the extracts hydrogenated as described above. The saturated products were crystallized from acetone to yield 2.27 g. (17%) of VIII, m.p. 121–123°, and 2.92 g. (22%) of IX, m.p. 43–45°, along with 0.5 g. of an oil. This procedure appeared to be the best of those tried.

(d) II.—A mixture of 2.4 g. of the saturated diketone II, 8.0 g. of sodium hydroxide and 8 ml. of 85% hydrazine hydrate in 100 ml. of diethylene glycol was refluxed for 75 minutes, then distilled until the pot temperature reached 195°. The mixture was refluxed for 4 hours and steam distilled; the combined distillates were extracted with ether. Evaporation of the ether left about 0.5 g. of crude solid, m.p. 30–75°. Recrystallization from methanol gave a crop of small, colorless needles of VIII, m.p. 102–111°, which, after recrystallization from ethanol, melted at 121–123°. The filtrate from the separation of VIII then deposited fluffy crystals of IX, m.p. 47–49°.

**Hydrogenation of XII.**—A solution of 280 mg. of the diene XII in 100 ml. of ethanol was hydrogenated over Raney nickel at 3.1 atm. for 25 minutes. After removal of the catalyst, the filtrate afforded 245 mg. of *cis,anti,cis*-perhydroanthracene (VIII), m.p. 121–123°.

**Dehydrogenation of Hydroanthracenes XII and IX.** (a) XII.—A mixture of 130 mg. of diene XII and 0.05 g. of 10% palladium-charcoal was heated at 225–240° in an evacuated glass vessel for 1.5 hr., cooled and triturated with hot ethanol. The solution was treated with ethanolic picric acid and concentrated at reduced pressure; on standing, it deposited red crystals of anthracene picrate, m.p. 136–138° (reported<sup>21</sup> m.p. 138°).

(b) IX.—A 0.27-g. sample of IX was heated with 0.10 g. of 10% palladium-charcoal in a sealed, evacuated glass tube

at 265° for 1 hour, then at 235° for 3 hours. After cooling, the contents of the tube were extracted with hot ethanol and crystallized to yield 20 mg. of anthracene, m.p. 214–217°. The melting point was not depressed on admixture with an authentic sample of anthracene, m.p. 218°.

**Isomerization of Perhydroanthracenes.** (a) With Aluminum Chloride.—A solution of 0.50 g. of IX in 20 ml. of pentane was treated with 1.0 g. of anhydrous aluminum chloride in a stoppered flask and shaken intermittently at room temperature for 14 days. The mixture was poured into 50 ml. of water, separated, and the pentane layer washed with water and dried. Evaporation left a waxy solid, which was recrystallized from acetone to provide 10 mg. of a solid, m.p. 62–67°. The infrared spectrum was very similar to that of *sym*-octahydroanthracene, m.p. 74°.

(b) With Aluminum Bromide.—Solutions of 0.40 g. of VII, VIII and IX, each containing 1.00 ml. of a stock solution of 30.27 g. of aluminum bromide in a total volume of 96.8 ml. of cyclohexane (1.17 moles/ml.), and made up to a volume of 50.0 ml. in pentane, were kept in the refrigerator at 0–5°. At measured intervals 5.0-ml. aliquots were pipetted from the solutions and run into a mixture of 3.0 ml. of a 7.72 M sodium fluoride aqueous suspension, 0.5 ml. of N sodium hydroxide and 20 ml. of ethanol, and shaken vigorously for 1 minute. Water (100 ml.) and ether (40 ml.) were added, shaken, and the layers separated. The ether layer was dried over calcium chloride and evaporated; several samples were weighed and showed the hydrocarbon residue to be 0.030–0.035 g. (75–88% recovery). Infrared spectra of the aliquots, taken from 0 to 441 hours, showed: that no VIII was detectable at 54 hours, that little change in the ratio of VII to VI was evident after 169 hours, and that bands not present in any of the perhydroanthracenes became significant at 312 hours. At 169 hours, the spectra of the reaction mixtures from all three starting hydrocarbons were virtually identical. Aliquots at 104, 166 and 196 hours were combined and concentrated to give crystalline VII, m.p. 87–88.5°.

For each aliquot taken at 169 hours and at 441 hours, absorbances were measured at three pairs of wave lengths characteristic of VI and VII, which appeared to be the only perhydroanthracenes present in detectable quantity: 10.31 and 10.36  $\mu$ , 11.55 and 11.58  $\mu$ , and 11.80 and 11.86  $\mu$ . The ratio of VI to VII was obtained from graphs plotted by measuring absorbances at the same wave lengths for a series of standard mixtures; Table I shows the results. The figures are believed to be accurate to  $\pm 1\%$ .

Starting isomer	VII/VI ratio at 169 hr.	VII/VI ratio at 441 hr.
VIII	96.3/3.7	96.5/3.5
VII	95.2/4.8	95.6/4.4
IX	95.9/4.1	95.6/4.4

**Isomerization of the Unsaturated Diketones.**—Solutions of 0.45 g. of Ib and of IVa in 25 ml. of pyridine were heated to 85  $\pm$  2° under nitrogen. Three drops of a 5% solution of potassium *t*-butoxide in *t*-butyl alcohol was added and the temperature maintained at 85° for 2 minutes. The hot, amber solutions were stirred into 800 ml. of ice and water and left overnight to coagulate. In each case, 0.410–0.415 g. of solid, m.p. 200–220°, was collected by filtration and triturated with 35 ml. of hot ethanol. Fairly pure IVa, m.p. 240–244°, was left undissolved; it amounted to 53% of the ketones recovered from Ib and 45% of the recovered product from IVa. The composition of the remaining ketone mixtures was estimated by infrared analysis, comparing the Nujol spectra with standard mixtures, and using the following bands for analysis: IVa: 7.63, 7.75, 8.26 and 12.4  $\mu$ ; III: 7.85, 8.70, 10.85, 11.85 and 12.2  $\mu$ ; Ib: 8.55, 8.64, 11.10 and 12.65  $\mu$ . The composition of the total recovered ketone mixture was thus estimated at: from Ib: 66% IVa, 27% III and 7% Ib; from IVa: 69% IVa, 22% III and 9% Ib.

**Sodium Borohydride Reduction of Ib.**—A solution of 5.00 g. of Ib in 400 ml. of methanol at 0–23° was treated with 2.0 g. of sodium borohydride in small portions, and allowed to stand overnight. The solution was concentrated to 100 ml. and diluted with water to the cloud point; on cooling, a solid mixture of diols precipitated. It was collected and boiled

(31) Elsevier's "Encyclopedia of Organic Chemistry," Vol. 13, series III, 1946, p. 199.

with chloroform; the insoluble portion was recrystallized from aqueous methanol to yield colorless needles of XIII, m.p. 256–259°.

*Anal.* Calcd. for  $C_{14}H_{20}O_2$ : C, 76.32; H, 9.15. Found: C, 76.06; H, 9.14.

The chloroform solution was concentrated and cooled, giving an isomeric diol (XIV), m.p. 127–133°; recrystallization from carbon tetrachloride raised the melting point to 134–136°.

*Anal.* Calcd. for  $C_{14}H_{20}O_2$ : C, 76.32; H, 9.15. Found: C, 76.40; H, 9.36.

The relative yields of the two diols varied with the reaction temperature, as follows: at 0°, 16% XIII and 75% XIV; at 5°, 21% XIII and 62% XIV; at 23°, 30% XIII and 53% XIV.

**Chromic Acid Oxidation of Diols XIII and XIV.**—A solution of 0.4 g. of XIII in acetone was treated with 1.0 ml. of a 7.63 *N* solution of chromic oxide in 7.74 *N* aqueous sulfuric acid and kept for 4 hours. The mixture was diluted with 200 ml. of water, the precipitate collected and recrystallized from methanol to give 0.3 g. of Ib, m.p. 148–151°. The infrared spectrum was identical with that of Ib, and the melting point of their mixture was not depressed. Oxidation of XIV in the same manner also yielded Ib, m.p. 150–152°, again identified by infrared spectra and mixed melting point.

**Hydrogenation of the Unsaturated Diols.**—A solution of 0.5 g. of XIII in 130 ml. of ethanol was shaken for 12 hours over 0.1 g. of Adams catalyst at 3.4 atm. of hydrogen. Filtration of the catalyst and concentration of the filtrate left colorless needles of XV, m.p. 276–276.5°; the yield was 0.45 g.

The same diol was obtained by sodium borohydride reduction of the saturated diketone II; 0.5 g. of II was reduced with an equal weight of sodium borohydride as described above, and the product recrystallized from ethanol to afford in 75% yield the same diol, m.p. 273–275°. Their identity was demonstrated by mixed melting point.

*Anal.* Calcd. for  $C_{14}H_{14}O_2$ : C, 74.95; H, 10.78. Found: C, 74.72; H, 10.74.

A solution of 1.0 g. of XIV in 50 ml. of ethanol was hydrogenated as described above. After filtration of the catalyst, the filtrate was concentrated, diluted with water, and cooled, giving 1.0 g. of XVI, m.p. 169–174°. Recrystallization from chloroform afforded 0.75 g., m.p. 174–175°.

*Anal.* Calcd. for  $C_{14}H_{24}O_2$ : C, 74.95; H, 10.78. Found: C, 74.96; H, 10.83.

**Chromic Acid Oxidation of Saturated Diols.**—Acetone solutions of XV and XVI were oxidized with chromic acid as described above. Dilution of the reaction mixtures with water yielded about 70% of II, m.p. 178.5–182.5°, in each case. The product was identified by mixed melting point with an authentic sample of II, m.p. 183°.

**Derivatives of Diols.** (a) **Diacetate of XIV.**—A solution of 5.5 g. of XIV in 100 ml. of acetic anhydride and 35 ml. of pyridine was refluxed 2 hours, kept overnight, evaporated to a small volume at reduced pressure and distributed between water and ether. The aqueous layer was twice extracted with ether, and the combined ether extracts washed

successively with aqueous sodium carbonate, dilute hydrochloric acid, and saturated salt solution. The solution was dried and concentrated, and the residue recrystallized from aqueous ethanol to give 7.0 g. of the diacetate, m.p. 114–116°; recrystallization from ether raised the melting point to 117–118°.

*Anal.* Calcd. for  $C_{18}H_{24}O_4$ : C, 71.02; H, 7.95. Found: C, 71.30; H, 8.08.

(b) **Monotosylate of XIII.**—A solution of 4.55 g. of XIII in 400 ml. of dry pyridine was cooled in ice and treated with 3.95 g. of *p*-toluenesulfonyl chloride in 30 ml. of pyridine. The solution was kept for 3 days, poured into water, and the precipitate collected and extracted with chloroform. The chloroform-soluble portion, after removal of the chloroform, was crystallized from benzene-hexane, giving 1.73 g. of the tosylate, m.p. 149–151° dec. Recrystallization from benzene gave purer material, m.p. 153–153.5° dec.

*Anal.* Calcd. for  $C_{21}H_{26}O_4S$ : C, 67.34; H, 6.99. Found: C, 66.97; H, 7.08.

(c) **Phthalate of Monotosylate.**—The above tosylate (1.5 g.) and phthalic anhydride (1.5 g.) were refluxed in 30 ml. of pyridine for 2 hours, then kept overnight and distributed between dilute aqueous hydrochloric acid and chloroform. The organic layer was washed with saturated salt solution and dried, then diluted with hexane, precipitating 1.54 g. of crude product. Recrystallized from benzene, the phthalate melted at 184–185°. Attempted resolution of this acid phthalate with quinine and brucine was unsuccessful.

*Anal.* Calcd. for  $C_{29}H_{30}O_7S$ : C, 66.64; H, 5.79. Found: C, 66.38; H, 5.84.

(d) **Bis-methanesulfonate of XIII.**—A solution of 1.1 g. of XIII in 22 ml. of pyridine was cooled and treated, with stirring, with 1.4 g. of methanesulfonyl chloride, then kept in the cold for 3 hours. The mixture was poured into cold dilute hydrochloric acid and the precipitated solid collected and dried. Two recrystallizations from chloroform-hexane gave fine colorless crystals of the bis-methanesulfonate, m.p. 142–143°.

*Anal.* Calcd. for  $C_{16}H_{24}O_6S_2$ : C, 51.04; H, 6.43. Found: C, 50.50; H, 6.61.

When the bis-methanesulfonate was refluxed overnight with a solution of lithium aluminum hydride in tetrahydrofuran, in an attempt to prepare the hydrocarbon, the only product recovered was impure XIII, m.p. 240–245°.

**9-Iodoperhydroanthracene.**—Red phosphorus (0.3 g.) and 10 ml. of 47% hydriodic acid were added to a solution of 0.20 g. of XV in 3 ml. of glacial acetic acid, and the mixture refluxed for 4 hours. The mixture was cooled, diluted with water and extracted with ether. The extracts were filtered, washed with dilute sodium hydrosulfite and sodium bicarbonate, dried and evaporated. The residue was recrystallized from acetone, yielding 30 mg. of colorless needles of a moniodo compound, m.p. 102–103°. The infrared spectrum showed no hydroxyl, carbonyl or olefin bands.

*Anal.* Calcd. for  $C_{14}H_{22}I$ : C, 52.83; H, 7.28. Found: C, 52.79; H, 7.52.