Synthesis and Some Spectral Properties of Diphenyltriptycene

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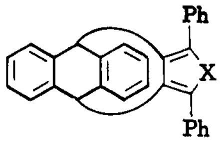
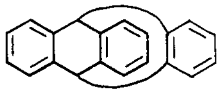
The preparation and proof of structure of 2,5-diphenyltriptycene is described. The ultraviolet spectrum of diphenyltriptycene suggests that the phenyl groups are twisted out of the plane by about 60°. This high twist angle is ascribed to steric interaction of the phenyl groups with the bridgehead hydrogens. The n.m.r. spectrum of diphenyltriptycene gives bridgehead hydrogen peaks that are shifted downfield relative to their expected positions. Possible explanations of this shift are considered.

The preparation and ultraviolet spectra of phenylated heterocyclic analogs (**1**) of triptycene (**2**) have been described previously.[2] Interpretation of the spectra of **1a** and **1b** in terms of the three constituent chromophores was complicated by the uncertainty in the twist angle of the phenyls relative to the heterocyclic ring and the resulting uncertainty in the appropriate ultraviolet absorption of this complex chromophoric unit. A solution to this question might be achieved by examination of the ultraviolet spectrum of diphenyltriptycene (**3**). Since the dependence on twist angle of the ultraviolet spectra of terphenyls is fairly well understood,[3] the spectrum of **3** would provide a calibration for analogs **1a** and **1b**.



1a, X = O
b, X = —N=N—



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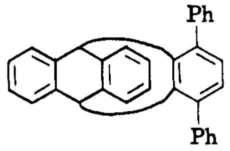

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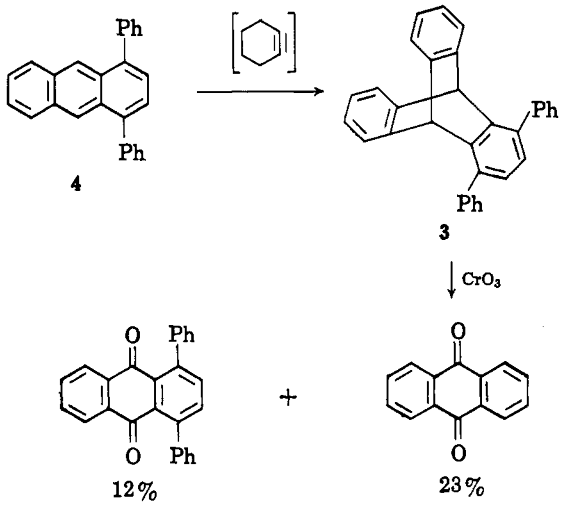
This paper presents two syntheses of diphenyltriptycene and a comparison of its ultraviolet spectrum with those of several terphenyls with different angles of twist. The n.m.r. spectrum of diphenyltriptycene is reported and compared with that of triptycene in an unsuccessful attempt to determine the twist angle from degree of shielding of the bridgehead hydrogen.

Synthesis of Diphenyltriptycene (3).—One synthesis of **3** is outlined in Chart I. The known[4] 1,4-diphenylanthracene (**4**), prepared from *trans,trans*-1,4-diphenylbutadiene and 1,4-napthaquinone, was adducted with benzyne to yield **3** directly. With benzyne generated from diphenyliodonium-2-carboxylate according to the procedure of LeGoff[5] a yield of 65% of **3** was obtained. With benzyne generated from anthranilic acid according to the method of Friedman[6] a yield of 57% of **3** was obtained. An unanticipated complication developed in the purification of **3**.

CHART I



After crystallization from carbon tetrachloride of the crude product obtained by either method, the resulting sharp-melting solid proved to be a clathrate of **3** and carbon tetrachloride, $(\mathbf{3})_2 \cdot CCl_4$. The clue that this clathrate had been formed was provided by the widely divergent molecular weights measured by the Rast[7] and the Signer[8] methods.[9] The included carbon tetrachloride was surprisingly tenacious; it was essentially unremoved even after the bulk sample had been heated for 24 hr. at 80° and 0.1-mm. pressure. Pure **3**, free of carbon tetrachloride, could be obtained, however, by fractional sublimation at 200° and 0.3-mm. pressure. The ratio of carbon tetrachloride to **3** in the clathrate was determined to be nearly 1:2 by microanalyses. Crystallization of **3** from cyclohexane yielded a new solid, which from its microanalyses was judged to be a 1:2 clathrate of cyclohexane and **3**. This cyclohexane clathrate appeared to be less stable than the carbon tetrachloride clathrate since a single crystallization of the latter from cyclohexane gave a solid of broad melting range that still contained considerable carbon tetrachloride. Only by repeated crystallization of the carbon tetrachloride clathrate from large volumes of cyclohexane with an intermediate evaporation of the cyclohexane could the pure cyclohexane adduct be

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(1) Abstracted from the Ph.D. Dissertation of F. D. Roberts submitted in January 1964 to the Graduate School of Cornell University.

(2) C. F. Wilcox, Jr., and M. P. Stevens, *J. Am. Chem. Soc.*, **84**, 1258 (1962).

(3) J. Derkosch and F. Sanger, *Monatsh. Chem.*, **86**, 928 (1955).

(4) C. Weizmann, E. Bergmann, and L. Haskelberg, *J. Chem. Soc.*, 391 (1939).

(5) E. LeGoff, *J. Am. Chem. Soc.*, **84**, 3786 (1962).

(6) L. Friedman and F. Logullo, *ibid.*, **85**, 1549 (1963).

(7) E. L. Skau and H. Wakeam, "Technique of Organic Chemistry," Vol. I, "Physical Methods of Organic Chemistry," Part I, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1949, p. 96, and references contained therein.

(8) E. P. Clark, *Ind. Eng. Chem., Anal. Ed.*, **13**, 820 (1941).

(9) Both methods are a measure of the number of particles formed on dissolving a known weight of sample in a determined volume of solvent. In the Rast procedure the included carbon tetrachloride of the clathrate contributes extra particles that lead to a low calculated molecular weight. In the Signer procedure the included carbon tetrachloride becomes a part of the volatile solvent and thereby yields a high calculated molecular weight.

TABLE I

Compd.	Solvent	λ_{max}, mμ (log ε)	Ref.
p-Terphenyl	95% ethanol	278 (4.51)	*a*
2′,3′,5′-Trimethylterphenyl	95% ethanol	219 (4.46), 245 (4.15), 278 sh (3.20)	*a*
Triptycene	95% ethanol	264 (3.3), 271 (3.55), 279 (3.67)	*b*
	Isooctane	263 (3.25), 271 (3.66), 278 (3.56)	*c*
2,5-Diphenyltriptycene	95% ethanol	241 (4.50), 252 (4.44), 261 (4.41), 277 sh (4.14)	
	Cyclohexane	241 (4.52), 253 (4.43), 262 (4.38), 277 (4.10)	

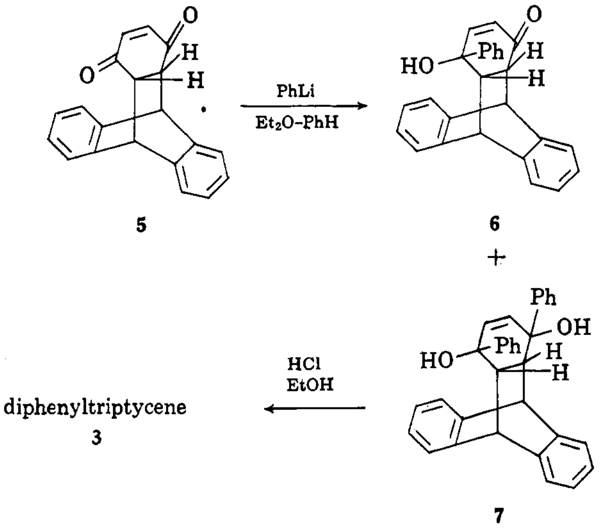
[a] Reference 3. [b] Reference 11. [c] P. D. Bartlett and E. S. Lewis, *J. Am. Chem. Soc.*, **72**, 1005 (1950).

obtained. In contrast, a single crystallization of the cyclohexane clathrate from carbon tetrachloride produced apparently pure carbon tetrachloride clathrate. Attempts to determine the upper size limitations on the included solvent were rendered ambiguous by the lack of assurance that these necessarily higher boiling solvents were not simply adhering mechanically to the crystals.

Other clathrates of triptycene derivatives have been reported although none have been described as being as tight as the present case. Bartlett and Greene[10] obtained a 2:1 complex of 1-carboxy-2-hydroxytriptycene with water and Wittig and Tochtermann[11] observed a 2:1 complex of 1,1-ditriptycylmercury with the recrystallization solvent, dimethylformamide.

The second synthesis of **3** was from the benzoquinone adduct of anthracene (**5**) and is outlined in Chart II.

CHART II



Although this approach was initiated before the benzyne method its completion was delayed by difficulties in purifying the intermediates. Addition of a threefold excess (mole ratio of 6:1) of phenyllithium to **5** gave a mixture of the mono- and diphenylated products (**6** and **7**,[12] respectively) which could be separated most easily by fractional sublimation in a large-scale temperature-gradient sublimator (see Experimental). The monophenylated keto alcohol **6** could be converted to the diol **7**[12] by further treatment with a large excess of phenyllithium. Dehydration of **7** with concentrated ethanolic hydrochloric acid[13] gave an 11% yield of diphenyltriptycene along with a 54% yield of anthracene. The other fragmentation products were not identified.

Structure Proof.—The structure assigned to **3** follows in part from the two independent modes of synthesis. As shown in Chart I additional chemical evidence was provided by oxidation of **3** with chromium trioxide to give a mixture (in low yield) of anthraquinone and 1,4-diphenylanthraquinone. If it is accepted that **3** must be some phenylated triptycene, these two oxidation products uniquely identify the three rings. Supporting evidence for the structure of **3** is provided by its n.m.r. spectrum which shows absorption at τ 4.36 (singlet of relative area 1) and a complex of bands near 2.5 (relative area 10).

Ultraviolet Spectrum.—The interpretation of the ultraviolet spectrum of diphenyltriptycene is complicated by the uncertainty in angle of twist between the outer phenyl groups and the central benzene ring to which they are attached. The 250-mμ band of diphenyl undergoes a shift to 230 mμ when the phenyl groups are rotated out of conjugation and into perpendicularity.[14,15] A similar displacement would be expected[16] for terphenyl and this is borne out by the first pair of compounds in Table I. The spectrum of diphenyltriptycene appears to be a superposition of the benzene α-bands of triptycene[17] on a more intense peak that can be assigned to a twisted terphenyl chromophore. From the similarity of this latter peak position with that of the trimethylterphenyl it seems that both molecules have similar angles of twist. This twist angle can be estimated indirectly to be roughly 60° from planarity by combining a comparison of the electron-diffraction[18] and dipole-moment[19] determination of twist angles of diphenyl and various halogenated diphenyls with their ultraviolet spectra and those of methylated diphenyls. Some support for this crude estimate comes from approximating the angle of twist as that angle that places the interacting phenyl and bridgehead hydrogens at their van der Waals contact distance. The value of 63° obtained by this procedure is high since it makes no correction for the increased conjugation energy that accompanies

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(10) P. D. Bartlett and F. D. Greene, *J. Am. Chem. Soc.*, **76**, 1088 (1954).

(11) G. Wittig and W. Tochtermann, *Ann.*, **660**, 23 (1962).

(12) The stereochemistry of **7** shown in Chart II is speculative. It is consistent with attack from the least hindered side.

(13) A. C. Craig and C. F. Wilcox, Jr., *J. Org. Chem.*, **24**, 1619 (1959). The dehydration procedure of W. Theilacker, U. Berger-Brose, and K. Beyer [*Ber.*, **93**, 1658 (1960)] was not attempted.

(14) A review of steric effects on ultraviolet spectra of diphenyl compounds is contained in G. H. Beaven, "Steric Effects in Conjugated Systems," G. W. Gray, Ed., Academic Press Inc., New York, N. Y., 1958, Chapter 3.

(15) In terms of the coupled chromophore model of H. C. Longuet-Higgins and J. N. Murrell [*Proc. Phys. Soc.* (London), **68A**, 601 (1955)], this blue shift results from a diminished contribution of the interbenzene charge-transfer excitations.

(16) J. N. Murrell and H. C. Longuet-Higgins, *J. Chem. Soc.*, 2552 (1955).

(17) C. F. Wilcox, *J. Chem. Phys.*, **33**, 1874 (1960).

(18) O. Bastiansen, *Acta Chem. Scand.*, **3**, 408 (1949); **4**, 926 (1950); O. Bastiansen and L. Smedvik, *ibid.*, **8**, 1593 (1954).

(19) A. C. Littlejohn and J. W. Smith, *J. Chem. Soc.*, 2552 (1954).

approach to planarity.[20] The required correction can be estimated by subtraction of the observed twist angle of 42° for diphenyl from the value of 47° calculated using the same van der Waals contact-angle model. Using this deviation of 5° the corrected estimate of the twist angle in diphenyltriptycene is 58°, which is in good agreement (perhaps fortuitous) with the estimate of 60° from the ultraviolet spectrum.

N.m.r. Spectra.—The n.m.r. spectrum of triptycene in $CDCl_3$ shows a complex set of peaks (relative area of 6) in the aromatic proton region in addition to a sharp singlet at τ 4.65 (relative area of 1). Diphenyltriptycene has a more complicated aromatic proton spectrum (relative area of 10) and an analogous sharp singlet at τ 4.36 (relative area of 1). It is apparent that the high-field peak of both molecules arises from the bridgehead protons so that the consequence of introduction of the phenyl groups is to *deshield* these hydrogens by *ca.* 0.3 γ unit. This is striking when it is considered that for all phenyl twist angles greater than 42° (the observed twist angle of biphenyl, a molecule less hindered than diphenyl triptycene) the ring current model of Johnson and Bovey[21] predicts an *upfield* shift. For the previously estimated twist angle of 56° an upfield shift of *ca.* 0.5 γ unit is predicted. The observed downfield shift cannot be accommodated unless the phenyls are twisted to an unreasonably low angle of about 30°.

Numerous factors could be proposed to explain the 0.8-τ-unit discrepancy between the expected and observed n.m.r. shifts accompanying introduction of the phenyl groups in triptycene. Foremost, perhaps, is the question of the quantitative reliability of the particular ring-current model employed. Little can be said that is definite except to note that it gives generally good fits for other molecules.[22] In order to check partially the applicability of this model to these bicyclic systems the observed influence of successive removal of benzo groups from triptycene has been compared with the calculated shifts to see if there was any evidence of a super ring current operating between the benzene rings of the triptycene system. If such a ring current were present in triptycene, its possible impairment by the additional phenyl of **3** could account for the downfield shift. In Table II are recorded the n.m.r. peak positions of the four related compounds, triptycene (**2**), 9,10-etheno-9,10-dihydroanthracene (**8**), 1,4-etheno-1,4-dihydronaphthalene (**9**), and bicyclo[2.2.2]octatriene (**10**). Since all four of these compounds either were available or had their n.m.r. spectra recorded, the only difficulty was to assign unambiguously the bridgehead-hydrogen peaks of **8**. In this compound the bridgehead hydrogens form one-half of an A_2B_2 subsystem and both halves of this subsystem lie close together at relatively low field and straddle the bridgehead-hydrogen peak position found for triptycene. The ambiguity was resolved directly by synthesis of 9,10-etheno-9,10-dihydroanthracene-9,10-d_2 (**11**) (see Experimental).

TABLE II

N.M.R. PEAK POSITIONS

Compd.	Bridgehead hydrogens[a]	Vinyl hydrogens[a]
2	4.65	. . .
8	4.95	*ca.* 3.1
9	5.2[b]	3.2[b]
10[c]	5.31[d]	3.36[d]

[a] Chemical shifts are in τ units measured with reference to TMS as internal standard (τ = 10.00). Unless specified otherwise the solvent is carbon tetrachloride. [b] F. G. Miller and M. Stiles, *J. Am. Chem. Soc.*, **85**, 1798 (1963). [c] No solvent given. [d] H. E. Zimmerman and G. L. Gruenwald, *J. Am. Chem. Soc.*, **86**, 1434 (1964).

It can be seen that the peak positions of the four compounds increase with some regularity.[23] The ring-current model of Johnson and Bovey predicts a downfield shift of τ *ca.* 0.6 for each benzene ring present. This is in plausible agreement with the observed increments of τ *ca.* 0. 3 when it is considered that the structural change involved in this series is *replacement* of a benzene ring by a double bond which itself introduce a partially compensating shift.[24] The origin of the smaller increment observed between **9** and **10** is not clear since the solvent used to dissolve **10** was not specified. The presence of a super ring current would presumably act in the opposite direction. It is concluded that either no significant super ring current is induced in triptycene or that such a ring current is similar for all four of the molecules. The latter possibility has not been excluded, but it seems most unlikely. In either case it would be difficult to invoke any difference in super ring current as a possible explanation of the downfield shift of **3** relative to **2**.

A second interpretation of the low n.m.r. peak position of the bridgehead hydrogens of diphenyltriptycene might be to postulate different degrees of solvation for it and triptycene itself. In deuteriobenzene the difference in the bridgehead peak positions between these two molecules is enhanced by an additional 0.4 τ unit. Solvent cannot be the entire explanation, however, since in cyclohexane, which should be a relatively inert molecule, the spread in the bridgehead peak position is about the same as it is in carbon tetrachloride.

A third possible explanation for the n.m.r. shift of diphenyltriptycene might be a steric effect of the sort

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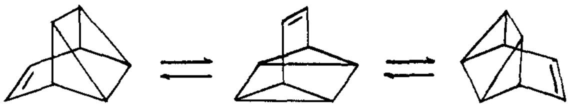
[20] For a recent sophisticated treatment of diphenyl along these lines, see I. Fischer-Hjalmars, *Tetrahedron*, **19**, 1805 (1963).

[21] C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

[22] However, because the bridgehead proton is close to and above the benzene ring it seems possible that the predicted shift might be more sensitive to the choice of separation of the split rings of current than most of the molecules used to calibrate the model (see ref. 21 for details). No systematic examination of this possibility has been made; however, in the limiting case of zero separation the predicted shifts for 30 and 60° twist angles do not change significantly from the Johnson and Bovey values.

[23] At the time this study was undertaken, the n.m.r. data reported for "barrelene" (**10**) in the report of its synthesis [H. E. Zimmerman and R. M. Paufler, *J. Am. Chem. Soc.*, **82**, 1514 (1960)] did not fit this series of compounds. Both kinds of protons were reported to absorb at abnormally high field; the bridgehead protons centered about τ 7.72 and the vinyl hydrogens centered about 6.7. On this basis, it was thought that **10** might be a rapidly equilibrating mixture of the three equivalent quadricyclenes shown below. The estimated n.m.r. spectrum of such a mixture is consistent with the original n.m.r. data. The mixture is also compatible with the reported chemistry of **10** and is not inconsistent with its unique ultraviolet spectrum.



[24] The combined ring current and inductive effects of vinyl groups are about half the magnitude of those found for phenyl groups (see L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press Inc., New York, N. Y., 1959). Recently, K. Tori, *et al.* [*Can. J. Chem.*, **42**, 926 (1964)], have observed downfield increments of τ 0.39 ± 0.05 for the bridgehead hydrogens of the dihydro and tetrahydro analogs of **8**, **9**, and **10**.

proposed by Reid[25] to account for the τ 1.0 downfield shift of the sterically crowded 4- and 5-hydrogens of phenanthrene. Such a sterically induced shift would be consistant with the proposed crowding of the phenyls against the bridgehead hydrogens and the authors consider it to be the most probable explanation of the shift.

Experimental

Melting points were determined in a Hoover melting point apparatus and all are uncorrected. The infrared absorption spectra were taken on a Perkin-Elmer Infracord spectrophotometer. The mode of measurement is indicated in all cases. The ultraviolet spectra were taken on a Cary Model 14 spectrophotometer. The n.m.r. spectra were obtained on a Varian A-60 spectrometer at 60 Mc. The chemical shifts are in τ values relative to tetramethylsilane as an internal standard (τ = 10.00). Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y., or Scandinavian Microanalytical Laboratory, Copenhagen, Denmark.

Fractional Sublimation. A. Apparatus.—A length of copper tubing (40 in. × 0.5 in.) was fitted with two electrically insulated thermocouples, one at the end of the tube and one in the middle. A layer of asbestos was applied to the tube and then heater A (No. 26 Chromel-A heating wire) wrapped over this to a length of 4 in. from the end. Another layer of asbestos and then heaters B and C (No. 18 Nichrome heating wire) were applied to the tube. Heater B overlapped A and extended 24 in. down the tube. Heater C covered another 12 in. of the tube.

The advantage of this apparatus is that it maintains a nearly linear temperature gradient in the tube without requiring the usual nonlinear winding.

B. Operation.—The sample was inserted into a small (approximately 2 in.) piece of 7-mm.-o.d. tubing, which had been sealed at one end. This sample tube was then slid down into a 4-ft. length of 10-mm.-o.d. tubing, which had been sealed at one end. The 4-ft. piece of tubing was then inserted into the heating apparatus, the heaters were set at the desired temperatures by means of Variacs, and a vacuum system was connected to the open end of the tube.

Isolation of the fractions was effected by cutting the glass tubing in the appropriate places and either scraping or washing out the solid material.

1,4-Diphenylanthraquinone.—This compound was prepared from *trans,trans*-1,4-diphenylbutadiene[26] and 1,4-naphthoquinone according to the procedure of Weizmann, Bergmann, and Haskelberg[4] in 20% yield, m.p. 209–211° (lit.[4,27] m.p. 212°).

1,4-Diphenylanthracene.—This compound was prepared from 1,4-diphenylanthraquinone according to the procedure of Weizmann, Bergmann, and Haskelberg[4] in 71% yield, m.p. 170–172° (lit.[4] m.p. 170°).

Diphenyliodonium-2-carboxylate.—This compound was prepared according to the method of LeGoff[5] in 84% yield, m.p. 226–228° dec. (lit. m.p. 220.5–221°,[5] 229–230°[28].

2,5-Diphenyltriptycene (3). Method A.[5]—A solution of 3.00 g. (0.009 mole) of 1,4-diphenylanthracene and 4.55 g. (0.014 mole) of diphenyliodonium-2-carboxylate in 40 ml. of diglyme (purified by refluxing over sodium for 2 hr. and subsequent distillation) was refluxed for 3.25 hr. The solution was allowed to cool to room temperature and the solvent was removed by vacuum distillation. The residue, after it had been dried under vacuum, was dissolved in *ca.* 75 ml. of carbon tetrachloride and then the solution was concentrated. This yielded upon standing 2.36 g. of solid, m.p. 208–216° dec.

Method B.[6]—A solution of 2.00 g. (0.015 mole) of anthranilic acid in 15 ml. of acetone was added dropwise over a period of 0.75 hr. to a stirred solution of 3.3 g. (0.023 mole) of *n*-butyl nitrite in 40 ml. of methylene chloride. The low-boiling solvents were removed by distillation and replaced by 20 ml. of xylene. Maleic anhydride (1.25 g.) was added and the solution was refluxed for 0.5 hr. The solution was allowed to cool slightly and poured into 60 ml. of water. The aqueous layer was separated. The organic layer was diluted with additional methylene chloride and then washed four times with 75-ml. portions of 15% aqueous potassium hydroxide solution and twice with 100-ml. portions of water, dried over anhydrous magnesium sulfate, and filtered. The solvent was removed and the residue was dissolved in carbon tetrachloride. The solution was concentrated and the resultant solid was separated by filtration and washed with ice-cold methanol. This gave 3.23 g. of tan solid. Its infrared spectrum showed that it still contained maleic anhydride. Recrystallization from carbon tetrachloride yielded 2.30 g. (57%) of solid, m.p. 219–225° dec. The infrared spectrum of this material was identical with the spectrum of the solid obtained in method A.

An analytical sample was obtained by recrystallization from carbon tetrachloride and drying for 24 hr. in a vacuum pistol at 80° and 0.10 mm., m.p. 228–229.5°; the infrared spectrum (KBr) includes peaks at 6.28, 6.82, 6.90, 8.60, 9.78, 12.66, 13.22, and 14.28 μ.

Anal. Calcd. for $2C_{32}H_{22} \cdot 1CCl_4$: C, 80.74; H, 4.59; Cl, 14.67; mol. wt., 322. Calcd. for $2.15C_{32}H_{22} \cdot 1CCl_4$: C, 81.70; H, 4.65; Cl, 13.65; mol. wt., 328. Found: C, 81.80; H, 4.75; Cl, 13.69; mol. wt., 358.

Another analytical sample was obtained by recrystallization twice from cyclohexane and drying overnight in a vacuum pistol at 80° and 0.10 mm., m.p. 215–218° dec.; infrared spectrum (KBr) includes peaks at 6.28, 6.82, 6.90, 8.60, 9.78, 12.24, 13.22, 13.60, and 14.28 μ. A large excess of solvent was boiled off before recovery of product for each recrystallization.

Anal. Calcd. for $2C_{32}H_{22} \cdot 1C_6H_{12}$: C, 93.71; H, 6.29. Found: C, 93.93; H, 6.07.

A third sample was purified for analysis by fractional sublimation at 200° and 0.3 mm., m.p. 210–211.5°; the infrared spectrum (KBr) includes peaks at 6.28, 8.82, 6.90, 8.60, 9.78, 12.24, 13.22, and 14.28 μ; ultraviolet spectrum (EtOH) 241 mμ (log ϵ 4.50), 252 (4.44), and 261 (4.41); the n.m.r. spectrum (CCl_4) shows a complex multiplet from τ 2.5 to 3.3 and a singlet at 4.36.

Anal. Calcd. for $C_{32}H_{22}$: C, 94.54; H, 5.46; mol. wt., 407. Found: C, 94.32; H, 5.50; mol. wt., 403.

Chromic Acid Oxidation of 2,5-Diphenyltriptycene.—To a mixture of 0.5326 g. (0.00131 mole) of 2,5-diphenyltriptycene (3) in 80 ml. of glacial acetic acid was added 0.80 g. of chromic acid. The resulting deep red mixture was heated at 95–100° for 9 hr. At the end of the heating period all of the solid had dissolved and the solution had turned green. The solution was allowed to cool to room temperature, poured into 240 ml. of water, and allowed to stand for 2 hr. The precipitated solid was separated by filtration, washed thoroughly with water, and dried in a vacuum desiccator overnight. This material, 0.3105 g., was dissolved in *ca.* 15 ml. of benzene and chromatographed on 40 g. of alumina (Merck chromatographic grade) using benzene as eluent to give the following fractions after evaporation of the solvent.

Fraction 2–3: This white solid, 0.1186 g., m.p. 223–225°, had an infrared spectrum identical with that of starting material. A mixture of this material and pure starting material (m.p. 228–229.5°) had m.p. 226–227°.

Fractions 6–8: This light yellow solid, 0.0283 g., m.p. 283–284°, had an infrared spectrum identical with that of an authentic sample of pure anthraquinone. A mixture of this material and anthraquinone (m.p. 284–285°) had m.p. 283–285°.

Fractions 9–13: The infrared spectrum of this yellow solid, 0.0291 g., showed that it was a mixture of anthraquinone and 1,4-diphenylanthraquinone. Analysis by means of ultraviolet spectroscopy using the method of Jones and Thatcher[29] showed that the mixture contained 0.0202 g. of anthraquinone and 0.0008 g. of 1,4-diphenylanthraquinone.

Fractions 14–26: The infrared spectrum of the golden yellow solid, 0.0420 g., m.p. 198–205°, was identical with that of pure 1,4-diphenylanthraquinone. A mixture of the above solid with pure 1,4-diphenylanthraquinone (m.p. 209–211°) had m.p. 206–209°.

The yield of anthraquinone was 0.0485 g. (23% based on consumed starting material) and the yield of 1,4-diphenylanthraquinone was 0.0428 g. (12% based on consumed starting material).

2,5-Diketo-2,5,15,16-tetrahydrotiptycene.[5]—This compound was prepared from anthracene and *p*-benzoquinone in 88%

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[25] C. Reid, *J. Am. Chem. Soc.*, **78**, 3225 (1956).

[26] B. B. Corson, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 229.

[27] E. Bergmann, L. Haskelberg, and F. Bergmann, *J. Org. Chem.*, **7**, 303 (1942).

[28] F. Beringer and I. Lillien, *J. Am. Chem. Soc.*, **82**, 725 (1960).

[29] M. Jones and R. L. Thatcher, *Anal. Chem.*, **23**, 957 (1951).

yield according to the procedure of Bartlett, *et al.*,[30] m.p. 227–232° (lit.[31] m.p. 217–220°).

Reaction of Adduct 5 with Phenyllithium.—A slurry of 5.75 g. (0.020 mole) of adduct **5** in 125 ml. of benzene was added to a stirred ethereal solution of 10.5 g. (0.125 mole) of phenyllithium.[32] The reaction mixture was stirred at room temperature for 20 hr. and poured into 150 ml. of water which contained *ca.* 150 g. of ice and 30 ml. of concentrated hydrochloric acid. The organic layer was separated and then washed twice with 200-ml. portions of 10% hydrochloric acid and twice with 200-ml. portions of water. It was dried over anhydrous magnesium sulfate and filtered. Concentration of the filtrate to *ca.* 50 ml. and subsequent filtration afforded 4.03 g. of white solid, m.p. 205–208°. The solid had to be washed two or three times with benzene in order to obtain white material.

Further concentration of the mother liquor yielded 0.29 g. of white solid (after washing), m.p. 265–270°.

Still further concentration of the mother liquor gave 1.10 g. of white solid (after washing), m.p. 205–210°.

The infrared spectrum of the third crop of material was identical with that of the first. The infrared spectrum of the second crop was different from those of the first and third, which might be due to a variation in the degree of washing.

An analytical sample of the first crop (mostly **6**) was obtained after three recrystallizations from benzene and subsequent drying at 80° and 0.10 mm.: m.p. 207–209°; infrared spectrum (KBr) 2.95, 6.06, 6.82, 9.38, 13.12, and 14.31 μ.

Anal. Calcd. for $C_{26}H_{20}O_2$: C, 85.69; H, 5.53. Found: C, 85.65; H, 5.66.

Another sample of the first crop was purified by fractional sublimation at 260° and 0.10 mm., m.p. 208–210°.

Anal. Calcd. for $C_{26}H_{20}O_2$: C, 85.69; H, 5.53. Found: C, 85.73; H, 5.73.

The total yield was 69%.

The second crop (mostly **7**) of solid was purified by fractional sublimation at 260° and 0.10 mm.: m.p. 279–282°; infrared spectrum (KBr) 3.12, 6.25, 9.70, 13.31, and 14.40 μ.

Anal. Calcd. for $C_{32}H_{26}O_2$: C, 86.85; H, 5.92. Found: C, 86.66; H, 5.94.

The total yield of the second crop was 3%.

Reaction of Phenyllithium with 6.—A slurry of 0.2538 g. (0.00070 mole) of **6** in 20 ml. of benzene was added to a stirred ethereal solution of 0.689 g. (0.0082 mole) of phenyllithium. The reaction mixture was then refluxed for *ca.* 24 hr. The mixture was added to 25 ml. of water which contained 25 g. of ice and 5 ml. of concentrated hydrochloric acid. The mixture was shaken and the aqueous layer was separated. The aqueous layer was extracted with 30 ml. of ether, and the organic solution was then washed twice with 50-ml. portions of 10% hydrochloric acid and then three times with 50-ml. portions of water, dried over anhydrous magnesium sulfate, and filtered. The filtrate was concentrated to *ca.* 5 ml. which upon standing yielded 0.0654 g. of white solid after washing with benzene, m.p. 233–240°. The infrared spectrum of this solid was identical with that of **7**. Purification of a sample by fractional sublimation at 220° and 0.10 mm. afforded material that had m.p. 273–277° and showed no depression of melting point (276–278°) upon mixing with **7** obtained directly.

Upon further concentration of the mother liquor a second crop of solid, 0.1137 g., m.p. 198–204°, was obtained. Purification of a sample by recrystallization from benzene gave solid with m.p. 205–207°, and an infrared spectrum identical with that of starting material.

The yield of **7** based on consumed starting material was 38%.

Dehydration of 7.—A mixture of 0.11 g. (0.00025 mole) of **7** in 30 ml. of 95% ethanol and 10 ml. of concentrated hydrochloric acid was refluxed for 2 hr. The solid dissolved completely after *ca.* 1 hr. The solution was cooled to room temperature and poured into 30 ml. of water. The resultant white solid was separated by filtration and washed a number of times with water. This yielded 0.354 g. of material. Fractional sublimation of this material at 200° and 0.10 mm. gave two solids.

Fraction 1: This white solid, 0.0104 g. (11%), m.p. 210–212°, had an infrared spectrum identical with that of 2,5-diphenyltriptycene. A mixture of this material with 2,5-diphenyltriptycene showed no melting point depression, m.p. 212–214°.

Fraction 2: This white solid, 0.0237 g. (54%), m.p. 211–214°, had an infrared spectrum identical with that of anthracene. A mixture of the solid with anthracene showed no melting point depression, m.p. 213–215°.

Dibenzobicyclo[2.2.2.]octatriene (8).—This compound was prepared from anthracene according to the procedure of Cristol and Bly[33] to give a product of melting point 119.5–121° (lit.[33] m.p. 119–120.5). The n.m.r. spectrum in carbon tetrachloride showed a complex multiplet from τ 2.6 to 3.3 (relative 1.0).

Anthracene-9,10-d_2.—This deuterioanthracene was prepared by the method used by Applequist[34] to make 9-bromoanthracene-10-*d* and is analogous to the procedure used by Petukhov[35] to prepare anthracene-9,10-d_2. An ethereal solution of phenyllithium was added to a mixture of 9,10-dibromoanthracene and anhydrous ether. The mixture was shaken thoroughly and allowed to stand for a short time (*ca.* 30 min.). Deuterium oxide was added slowly to the ether solution and the solution was allowed to stand at room temperature for *ca.* 4 hr. The precipitated solid was removed by filtration and the solvent was evaporated from the filtrate. The residue was purified by sublimation and subsequent recrystallization of the sublimate from 95% ethanol. This gave white flakes, m.p. 214–217° (lit.[36] m.p. 217° [213°] for anthracene). The n.m.r. spectrum of this solid dissolved in carbon tetrachloride was exactly the same as that of anthracene except for the complete disappearance of the singlet at τ 3.35 which has been assigned to the 9- and 10-hydrogens.[37]

A mixture of 1.10 g. (0.0061 mole) of anthracene-9,10-d_2 and 5.92 g. (0.061 mole) of *cis*-dichloroethylene was heated at 186–200° for 24 hr. in a sealed 40-ml. ampoule. The ampoule was allowed to cool, then opened, and the contents were rinsed out with carbon tetrachloride. This solution was chromatographed on 50 g. of alumina (Merck chromatographic grade) using carbon tetrachloride as eluent to give the following fractions.

Fraction 1: The infrared spectrum of this solid, 1.38 g., m.p. 163–195°, showed that it contained mainly a product with a small amount of starting material.

Fraction 2: This white solid, 0.13 g., m.p. 203–206°, had an infrared spectrum [(KBr) 6.12, 6.88, 8.01, 9.62, 12.39, 13.05, and 13.16 μ] that showed no peaks due to starting material. This solid was used without further purification for the next reaction.

9,10-Etheno-9,10-dihydroanthracene-9,10-d_2 (11).—To a refluxing mixture of 0.13 g. (0.00048 mole) of *cis*-dichlorodibenzobicyclo[2.2.2]octadiene-9,10-d_2 in 25 ml. of *n*-amyl alcohol were added small pieces of sodium until the particles no longer floated on the surface. The addition required 2 hr. The solution was allowed to cool and extracted three times with 35-ml. portions of water. The last two washes required the addition of ammonium chloride to facilitate separation of the layers. The organic layer was dried over anhydrous sodium sulfate and filtered, and the solvent was removed by vacuum distillation. The residue was recrystallized from 95% ethanol to give 0.0331 g. (23%) of pure product, m.p. 120–121°. The n.m.r. spectrum of this compound was exactly the same as that of 9,10-dihydroanthracene except for the complete disappearance of the triplet centered about τ 4.95.

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