and 91–92° (23 mm.) for *trans* isomer 5] containing[16] 25% of the *cis* olefin 6 (first eluted) and 75% of the *trans* olefin 5 (second eluted). Samples of each of the pure olefins 5 and 6 were collected from the chromatograph; the mass spectra of both products exhibit a molecular ion peak at $m/e = 132$. The *trans* isomer 5, $n^{25}\text{D}$ 1.5384 (lit.[38] $n^{25}\text{D}$ 1.5387), has infrared absorption[17] at 1645 (C=C) and at 965 cm.$^{-1}$ (*trans* CH=CH) with an ultraviolet maximum[19] at 254 mμ (ϵ 19,000) and an n.m.r.[17] triplet (J = 7 c.p.s.) at δ 1.07 (3H, CH_3) with a complex multiplet centered at 2.17 (2H, CH_2), a multiplet in the region 7.0 –7.3 (5H, aryl C–H), and a partially resolved multiplet centered at 6.18 (2H, vinyl C–H).[39] The *cis* isomer 6 has infrared absorption[17] at 1635 (C=C) but lacks absorption in the region 950–1000 cm.$^{-1}$. The material has an ultraviolet maximum[19] at 242 mμ (ϵ 13,800) with an n.m.r.[17] triplet (J = 7 c.p.s.) at δ 1.03 (3H, CH_3), a multiplet centered at 2.28 (2H, CH_2), a partially resolved multiplet at 7.12 (5H, aryl C–H), a doublet of triplets (J = 11 and *ca.* 2 c.p.s.) centered at 6.28 (1H, vinyl C-H), and a doublet of triplets (J = 11 and 7 c.p.s.) centered at 5.52 (1H, vinyl C–H).

For the quantitative experiments; summarized in Table V, stock solutions of the ylid 4 in benzene were prepared using *n*-butyllithium in hexane as previously described. Negative Gilman color tests established the absence of *n*-butyllithium in these solutions. The insoluble materials were allowed to settle and aliquots of the clear, supernatant liquid were employed. For reactions in solvents other than benzene, the solvent was removed from an aliquot of the benzene solution under nitrogen and the residual red-orange solid was redissolved in the desired solvent. Titrations of aliquots of various ylid preparations with propionaldehyde indicated that the ylid concentration in the benzene solutions ranged from 0.16 to 0.43 *M*. Titration of aqueous extracts of various aliquots for chloride ion indicated that the chloride ion concentration *in solution* was in the range 0.11 to 0.15 *M*. For the experiments listed in Table V solutions of the ylid in the specified solvent and containing any specified additives were titrated with propionaldehyde until the red color of the ylid was just discharged. In cases where ethanol or methanol was used as the solvent, the red color of the ylid was discharged upon addition of the solvent. Consequently, the amount of propionaldehyde added in these cases was determined from a knowledge of the ylid concentration in the original benzene solution. Unless otherwise noted the reaction mixtures were stirred at room temperature for 30 min. and then a weighed amount of tetralin (as an internal standard) was added and the solutions were washed with water, dried, and analyzed.[16]

Fine suspensions of lithium bromide in benzene–hexane mixtures were prepared by passing dry hydrogen bromide into a solution containing 35 mmoles of *n*-butyllithium in a mixture of 15 ml. of hexane and 10 ml. of benzene until a negative Gilman color test for *n*-butyllithium was obtained.[40] Any excess hydrogen bromide was allowed to escape. Addition of this suspension to solutions of the ylid 4 in either benzene or dimethylformamide solution *did not* discharge the red color of the ylid, provided that no hydrogen bromide was present.

Solutions of the ylid 4 were also generated by reaction of benzyltriphenylphosphonium chloride with sodium ethoxide in either ethanol or dimethylformamide. The reaction mixtures were stirred at room temperature for the specified times and then worked up and analyzed as previously described. The results are summarized in Table VI.

TABLE VI

REACTION OF THE YLID 4 PREPARED USING SODIUM ETHOXIDE WITH AN EQUIMOLAR QUANTITY OF PROPIONALDEHYDE

Propionaldehyde, mmoles	Solvent (ml.)	Reaction time, hr.	Yield, %	Composition	
				% *cis* **6**	% *trans* **5**
1.81	EtOH (6)	1	95	46	54
4.6	DMF[a] (10)	2	42	46	54
		12	66	46	54
0.5	DMF[a] (4)	2	57	45	55

[a] Dimethylformamide.

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(38) C. G. Overberger and D. Tanner, *J. Am. Chem. Soc.*, **77**, 369 (1955).

(39) Except for the expected differences in multiplicity, the n.m.r. peaks for the vinyl protons in the 1-phenyl-1-butenes resemble closely the spectra of the corresponding 1-phenyl-1-propenes: see (a) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 238–240; (b) M. J. S. Dewar and R. C. Fahey, *J. Am. Chem. Soc.*, **85**, 3645 (1963).

(40) This is apparently the same procedure previously described: see ref. 4.

Transformation Products of the Photoadduct of *p*-Xylene and Phenanthrenequinone. Some Two- and Three-Atom Bridged Biphenyls[1]

MORDECAI B. RUBIN

Department of Chemistry, Carnegie Institute of Technology, Pittsburgh 13, Pennsylvania

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The photoadduct of *p*-xylene and phenanthrenequinone, 9,10-dihydro-9-hydroxy-9-(*p*-methylbenzyl)-10-ketophenanthrene (1), has been synthesized by osmium tetroxide hydroxylation of 9-(*p*-methylbenzyl)phenanthrene to *cis*-9,10-dihydro-9,10-dihydroxy-9-*p*-methylbenzylphenanthrene (5) followed by oxidation. Sodium borohydride reduction of 1 afforded the *trans* isomer (3a) of 5, cleaved by periodate to 2′-*p*-methylphenylacetyl)-biphenyl-2-carboxaldehyde (6) which underwent facile intramolecular aldol condensation on Florisil to give *cis*- and *trans*-6-*p*-tolyl-7-hydroxydibenzo[*a,c*]cycloheptan-5-one (8 and 7). Both of these isomers were readily dehydrated to 6-(*p*-tolyl)-5H-dibenzo[*a,c*]cyclohepten-5-one (9). Catalytic hydrogenation of 9 yielded a mixture of 6-(*p*-tolyl)dibenzo[*a,c*]cycloheptan-5-one (10) and *cis*-5-hydroxy-6-(*p*-tolyl)dibenzo[*a,c*]cycloheptane (11). Dehydration of 11 to 6-(*p*-tolyl)-5H-dibenzo[*a,c*]cycloheptene (12) followed by hydroboration furnished the *trans* isomer (13) of 11. The configurations assigned to 7 and 8 were based on the Karplus relationship between dihedral angle and coupling constant of vicinal protons. The presence of a skewed conformation in dibenzo-[*a,c*]cycloheptanes was suggested to account for the anomalous coupling constants observed with 11 and 13.

The revised structure 1 has recently been assigned[2] to the adduct formed by irradiation of solutions of 9,10-phenanthrenequinone in *p*-xylene[3] with ultraviolet light. This report presents the results of chemical transformations of 1 which have provided further evidence confirming the revised structure and have yielded a series of biphenyl derivatives which are of interest in themselves.

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(1) Presented in part at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April, 1964.

(2) M. B. Rubin and P. Zwitkowits, *J. Org. Chem.*, **29**, 2362 (1964).

(3) Adducts of similar structure were obtained with toluene, *o*-, and *m*-xylene among others. The *p*-xylene adduct was used in this work since the *p*-methyl substituent provided a convenient reference point for interpretation of n.m.r. spectra while not influencing the course of reaction at remote positions.

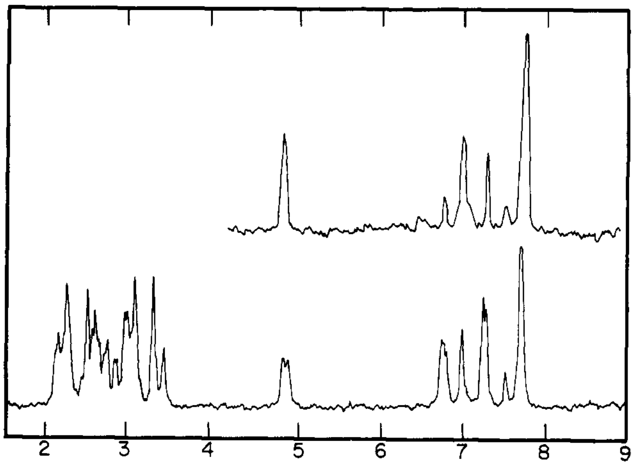
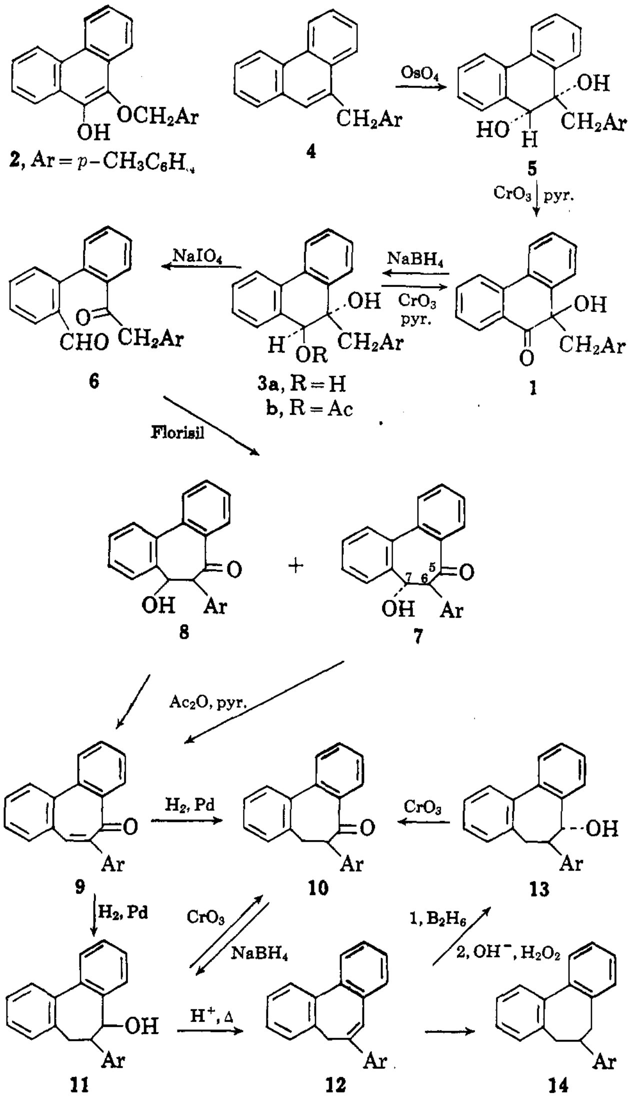


Fig. 1.—Lower curve: n.m.r. spectrum of *trans*-9,10-dihydro-9,10-dihydroxy-9-(*p*-methylbenzyl)phenanthrene (3a, 0.3 *M* in deuteriochloroform, 25°); upper curve: after crystallization from deuterium oxide.



The initial reaction in this sequence, sodium borohydride reduction of **1**, was originally performed in order to confirm the presence of a keto group in the photoadduct as opposed to the phenolic structure, 9,10-dihydroxyphenanthrene mono-*p*-methylbenzyl ether (**2**), proposed earlier.[4] The single diol, *trans*-9,10-dihydro-9,10-dihydroxy-9-(*p*-methylbenzyl)phenanthrene (**3a**), obtained by reaction with excess reagent in either diglyme or methanol solution, obviously could not have arisen from the phenol **2**. The presence of both secondary and tertiary hydroxyl groups in **3a** was confirmed by acetylation under mild conditions to a monoacetate (**3b**) which still exhibited hydroxyl absorption in the infrared. The *trans* configuration was originally assigned to **3a** on the assumption of approach of the reducing agent from the least hindered side of the carbonyl group; this assignment was confirmed by the nonidentity of **3a** with the product of osmium tetroxide hydroxylation of 9-(*p*-methylbenzyl)phenanthrene (**4**), *cis*-9,10-dihydro-9,10-dihydroxy-9-(*p*-methylbenzyl)-phenanthrene (**5**). Oxidations of both **3a** and **5** with chromium trioxide–pyridine complex[5] afforded the photoadduct **1**. The sequence starting from **4** thus provides an independent synthesis of **1**.

The n.m.r. spectra of both diols exhibited the expected complex absorption between τ 2 and 3.4 owing to the variety of aromatic protons present (*vide infra*). The remaining part of the spectrum of the *cis*-diol **5** consisted of a doublet at τ 5.78 ($J = 6$ c.p.s.), due to the C-10 proton, a singlet at 7.01 (C-9 OH), a barely resolved pair of lines centered at 7.32 with a spacing of 1.5 c.p.s. (CH_2), a singlet at 7.70 (CH_3), and a doublet at 7.86 ($J = 6$ c.p.s.) due to the C-10 hydroxyl proton. These assignments were based on relative intensity measurements and expected chemical shifts[6] and were confirmed by the observation that dilution of the sample resulted in a shift[7] of the 7.01 and 7.86 absorptions to 7.08 and 8.06, respectively, while the remainder of the spectrum remained unchanged. The spectrum of the *trans* isomer **3a** (Fig. 1) presented a complex pattern of absorption in the region between τ 6.5 and 7.5. This pattern changed appreciably with concentration and with temperature,[7] but the considerable overlap of the various lines did not allow interpretation except for the C-10 proton doublet at 4.82 ($J = 2.5$ c.p.s.) and the methyl singlet at 7.70. Marked simplification of the spectrum was observed when the hydroxyl protons were exchanged for deuterium by crystallization of **3a** from acetone–deuterium oxide mixture as can be seen in Fig. 1. The presence of a singlet at 4.86 confirmed the assignment of the doublet in the protium compound to the C-10 proton. In addition to the methyl singlet, a characteristic AB pair of doublets was observed at 6.87 and 7.40 ($J = 14$ c.p.s.) due to the methylene group, presenting a sharp contrast to the barely resolved pair of lines observed in the *cis* isomer (**5**).[8] The n.m.r. spectrum of the acetate, **3b** exhibited similar features.

Cleavage of the *trans*-glycol **3a** with sodium periodate afforded crude 2′-(*p*-methylphenylacetyl)biphenyl-2-carboxaldehyde (**6**) with infrared (3.7 μ) and n.m.r. (τ 0.20) absorption characteristic of an aldehyde. The ultraviolet absorption of this material (291 mμ) under-

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[4] A. Benrath and A. Von Meyer, *J. prakt. Chem.*, **89**, 258 (1914); R. F. Moore and W. A. Waters, *J. Chem. Soc.*, 3405 (1953).

[5] G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Am. Chem. Soc.*, **75**, 422 (1953).

[6] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, Chapters 4 and 5.

[7] The position of the hydroxyl resonance is known to vary with concentration, temperature, and solvent: ref. 5, p. 69.

[8] The pair of lines observed with **5** might again be due to observation of the methylene protons as an AB system in which the chemical shifts of the A and B protons are almost identical. In such a case only the inner lines of the AB pattern would be detectable (ref. 6).

went marked change in alkaline solution (245 and 320 mμ) (*vide infra*). A product of essentially identical spectral properties was obtained by reductive ozonolysis of **4**. When purification of this crude material by chromatography on the weakly alkaline adsorbent Florisil was attempted, two crystalline products, **7** (m.p. 165°) and **8** (m.p. 195°), were obtained in approximately equal amounts. The isolation of **8** proved to have been fortuitous since on standing for 24 hr. on Florisil both pure **7** and pure **8** afforded mixtures containing about 95% of **7**. Both isomers exhibited hydroxyl and conjugated carbonyl absorption in the infrared consistent with their formulation as the diastereomeric intramolecular aldol condensation products of **6**, *cis*- and *trans*-6-(*p*-tolyl)-7-hydroxydibenzo[*a,c*]cycloheptan-5-one, on the slightly alkaline adsorbent. The condensation also occurred on acid-washed alumina columns but not on silica gel.[9] Numerous examples[10] of formation of three-atom bridges across the *ortho–ortho'* positions of biphenyl have been recorded although the cyclization observed here involves exceptionally mild reaction conditions.

Assignment of configuration to **7** and **8** was possible by application of the quantitative relationship[11a–c] between dihedral angle and coupling constant of vicinal protons. For sp^3 hybridization, carbon–carbon bond length 1.543 Å., and dihedral angle ϕ, this relationship is

$$J_{\mathrm{HH}'}(\text{c.p.s.}) = 4.22 - 0.5 \cos \phi + 4.5 \cos 2\phi$$

leading to predicted values of 1.7 c.p.s. for a dihedral angle of 60° and 9.2 c.p.s. for a dihedral angle of 180°. It has been emphasized[11c] that observed coupling constants[12] will also depend on other factors such as the presence of ionic substituents, the H–C–C bond angles, and variations in bond length, and that structural conclusions are best inferred from cases where observed values are "large" rather than "small" or *vice versa.*

Turning to the 6-(*p*-tolyl)-7-hydroxydibenzo[*a,c*]-cycloheptan-5-ones (**7** and **8**), four possible conformations (Fig. 2) can be considered. In the two (A and B) possessing the *trans* configuration, the dihedral angles are 60 and 180°. Since these conformations are interconvertible by inversion of the biphenyl, an observed coupling constant between 4 and 11.5 c.p.s. would be anticipated depending upon the rate of inversion of the biphenyl and the relative populations of the two conformers. The dihedral angles are 60° in the two interconvertible conformers possessing the *cis* configuration leading to a predicted value of about 4 c.p.s. for the vicinal proton coupling constants. Conveniently, the 165° isomer (**7**) exhibited doublets at τ 4.50 (C-7 H) and 6.05 (C-6 H), both with coupling constants of 11 c.p.s., indicating that **7** has the *trans* configuration and exists to a major extent in the conformation B. The methyl and hydroxyl protons of **7** were observed at 7.68 and 7.90, respectively. The assignments were consistent with relative intensity measurements and were confirmed by disappearance of the 7.90 resonance after exchange of the hydroxyl proton by deuterium. The 195° isomer (**8**) must then have the *cis* configuration and, in fact, its n.m.r. spectrum exhibited doublets at 4.36 and 5.57 with coupling constants of 4.5 c.p.s. in agreement with the predicted value. The hydroxyl resonance in **8** was observed at 6.22 (absent after deuterium exchange) and the methyl at 7.68.

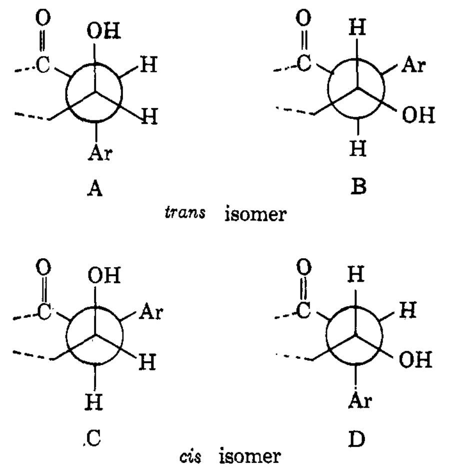

Fig. 2.—Conformations of dibenzo[*a,c*]cycloheptan-5-ones.

As noted earlier, the ultraviolet spectrum of the keto-aldehyde **6** underwent marked change in alkaline solution. Similar behavior was observed with both **7** and **8**, suggesting base-catalyzed dehydration of the aldols to 6-(*p*-tolyl)-5H-dibenzo[*a,c*]cyclohepten-5-one (**9**) as has been reported by Cook and co-workers[13] for aldehydes of similar structure. Although reaction of a mixture of **7** and **8** with methanolic potassium hydroxide did yield **9**, a superior preparative procedure consisted of treatment of either isomer with acetic anhydride and pyridine at room temperature, the usual conditions for acetylating primary and secondary alcohols. The dehydration could also be effected by reaction with acetic anhydride alone at 120° but not by acetic anhydride or pyridine at room temperature. The C-7 proton of **9** was shifted down into the aromatic region of the n.m.r. spectrum and the only readily interpretable feature of this spectrum was the methyl singlet (also shifted slightly downfield) at τ 7.59. The ultraviolet spectrum of **9** in neutral solution (247 and 320 mμ) was very similar to the spectra of its precursors (**6**, **7**, and **8**) in alkaline solution.

In a parallel investigation in this laboratory,[14] examination of n.m.r. spectra of the bridged biphenyls, 2,7-dihydrodibenz[*c,e*]oxepin and 2,7-dihydrodibenz[*c,e*]-thiepin has been performed at various temperatures. Since the methylene protons in the positions *ortho* and *ortho'* to the biphenyl system in these compounds are magnetically nonequivalent but are rendered equivalent by inversion of the biphenyl, the spectra exhibited AB quartets at sufficiently low temperatures which coa-

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[9] Attempted purification by chromatography on silica gel did not yield crystalline product.

[10] *Inter alia:* J. Kenner and E. E. Turner, *J. Chem. Soc.*, **99**, 2101 (1911); C. H. Beaven, D. M. Hall, M. S. Lesslie, and E. E. Turner, *ibid.*, 854 (1952); W. E. Truce and D. D. Emrick, *J. Am. Chem. Soc.*, **78**, 6130 (1956); J. O. Hawthorne, E. L. Mihalic, M. S. Morgan, and M. H. Wilt, *J. Org. Chem.*, **28**, 2831 (1963).

[11] (a) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); (b) H. Conroy in "Advances in Organic Chemistry. Methods and Results," Vol. II., Interscience Publishers Inc., New York, N. Y., 1960, p. 265; (c) M. Karplus, *J. Am. Chem. Soc.*, **85**, 2870 (1963).

[12] The observed values of $J_{\mathrm{HH}'}$ for a considerable variety of six-membered ring compounds have been shown to center around 11.5 c.p.s. for ϕ = 180° and 3.5–4 c.p.s. for ϕ = 60°: A. C. Huitric, J. B. Carr, W. F. Trager, and B. J. Nist, *Tetrahedron*, **19**, 2145 (1963).

[13] J. W. Cook, J. Jack, J. D. Loudon, G. L. Buchanan, and J. MacMillan, *J. Chem. Soc.*, 1397 (1951); J. W. Cook, J. D. Loudon, and R. K. Razdan, *ibid.*, 4234 (1954). The intermediate aldols were not isolated in these cases.

[14] R. J. Kurland, M. B. Rubin, and W. B. Wise, *J. Chem. Phys.*, **40**, 2426 (1964).

lesced and appeared as sharp singlets as the temperature was raised. Analysis of this behavior allowed calculation of the inversion barriers. The unsaturated ketone **9** appeared to be a suitable substance for conversion to carbocyclic compounds in which a similar phenomenon could be observed.

Hydrogenation of **9** over palladium on charcoal resulted in absorption of between one and two equivalents of hydrogen affording a mixture of di- and tetrahydro products which could be readily separated by chromatography on neutral alumina. The first product eluted was the dihydro compound, 6-(*p*-tolyl)dibenzo[*a,c*]-cycloheptan-7-one (**10**), which exhibited conjugated carbonyl absorption in the infrared and a complex group of lines between τ 5.84 and 7.07 characteristic of the ABC system as well as the sharp methyl singlet at 7.70. The second product was the alcohol, *cis*-5-hydroxy-6-(*p*-tolyl)dibenzo[*a,c*]cycloheptane (**11**), exhibiting hydroxyl absorption (2.92 μ) and no carbonyl in the infrared. Interconversion of the two reduction products could be readily achieved, sodium borohydride reduction of **10** affording **11** while chromic acid oxidation of **11** led to **10**. The formation of both compounds in the hydrogenation of **9** presumably reflects a competition between initial reduction of the double bond and of the carbonyl group. In the latter event, further reduction of the resulting allylic alcohol produced the saturated alcohol **11** accounting for the absorption of a fractional equivalent of hydrogen. The *cis* stereochemistry was assigned to **11** on the assumption of attack of borohydride from the less hindered side of the carbonyl group in **10** as had been observed in the reduction of **1**.

Reaction of **11** with *p*-toluenesulfonic acid in refluxing toluene resulted in dehydration to 6-(*p*-tolyl)-5H-dibenzo[*a,c*]cycloheptene (**12**) in 80% yield. The C-7 proton in this compound appeared at τ 3.21 (*cf.* **9**) and the methyl singlet at 7.65. Significantly, the methylene absorption appeared as a broad line (half-width 11 c.p.s.) at 6.55. The assumption that this broadening was due to relatively slow inversion of the biphenyl was confirmed by determination of the spectrum at −30°; the methylene protons then appearing as a characteristic AB pair of doublets with coupling constants of about 14 c.p.s.

The availability of **12** suggested the possibility of confirming the *cis* configuration of **11** by independent synthesis of its *trans* isomer. Hydroboration of unsymmetrical alkenes followed by reaction with alkaline hydrogen peroxide[15] results in *cis* addition of the elements of water across the double bond with anti-Markovnikov orientation.[16] Application of this procedure to **12** should then result in the formation of *trans*-5-hydroxy-6-(*p*-tolyl)dibenzo[*a,c*]cycloheptane (**13**), an expectation which was realized. The single product, isomeric with **11**, obtained in good yield by hydroboration of **12** followed by peroxide treatment was shown to be the product of anti-Markovnikov addition by oxidation to **10** and presumably has the *trans* configuration as well. In order for these assignments to be incorrect, both the hydroboration of **12** and the sodium borohydride reduction of **10** would necessarily have proceeded in abnormal fashion.

The relationship between dihedral angle and coupling constants of vicinal protons which was discussed in connection with the assignment of stereochemistry to **7** and **8** can be applied equally well to the isomeric alcohols **11** and **13**. A coupling constant of about 4 c.p.s. would be predicted for the C-5,C-6 proton–proton coupling in the *cis* isomer **11** and a value between 4 and 11 c.p.s., depending on the equilibrium between the two possible conformers, for the *trans* isomer **13**. The spectrum of **11** exhibited a triplet at τ 5.10 (J = 8 c.p.s.) due to the C-5 proton (coupled with the adjacent hydroxyl and C-6 protons), a complex group of lines between 6.05 and 7.3, a methyl singlet at 7.67, and a doublet (J = 8 c.p.s.) at 8.27 due to the hydroxyl proton. These assignments were confirmed by determination of the spectrum after exchange of the hydroxyl proton for deuterium when the C-5 proton appeared as a doublet (J = 8 c.p.s.) and the 8.27 absorption had disappeared. The spectrum of the *trans* isomer **13** showed considerable similarity to that of **11** except that the C-5 proton appeared as a doublet (J = 8 c.p.s.) and the hydroxyl proton appeared at 8.30 as a broad singlet. Again, exchange of the hydroxyl proton for deuterium confirmed the assignments; only the 8.3 line disappearing. In both cases, the absorption of the C-6 proton could not be interpreted in terms of coupling constant due to the additional splitting by the adjacent C-7 methylene protons. While the value of 8 c.p.s. for the coupling constant in the *trans* isomer (**13**) suggests a rapid inversion of the biphenyl and appreciable population of both possible conformations, the observation of an identical coupling constant for the *cis* isomer (**11**) is anomalous. As noted earlier,[12] a number of examples of deviations from the dihedral angle–coupling constant relationship have been recorded, particularly when the ethane moiety is substituted by electronegative groups; the results in this instance may simply represent an additional deviation of this type. Interestingly, however, examination of Drieding models suggested an alternative explanation. In models of dibenzo[*a,c*]cycloheptan-5-one, the ethane moiety (C-6 and C-7) appears in the normal, staggered conformation with the usual 60° dihedral angles between bonds on the vicinal carbon atoms. However, in dibenzo[*a,c*]cycloheptane, lacking the carbonyl group in the three-atom bridge,[17] a skewed conformation is observed in which the dihedral angles between vicinal protons are either 30 or 150°. The calculated values for the coupling constants would then be 6.0 and 6.9 c.p.s., respectively, in reasonable agreement with the values observed.[18] The hazards of attempting to assign precise values for dihedral angle from observed coupling constants have been noted earlier; this is particularly true for seven-membered rings where relatively little data are available and further investigation is required.

The final compound in the synthetic sequence was the symmetrical hydrocarbon, 6-(*p*-tolyl)dibenzo[*a,c*]-

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[15] H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, Chapters 7 and 8.

[16] For example, reaction of 1-phenylcyclohexene produces *trans*-2-phenylcyclohexanol: H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 2544 (1961).

[17] Similar observation is made upon examination of Dreiding models of cycloheptadienone and cycloheptadiene although the deviation from the staggered conformation in the latter compound appears to be somewhat less than in the dibenzo case.

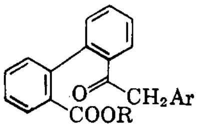
[18] It should be noted that Dreiding models are particularly resistant to deviations from the angles for which they were constructed and might not present a realistic representation of the actual molecule.

cycloheptane (**14**), which was obtained without difficulty by catalytic hydrogenation of **12**. The n.m.r. spectrum of **14** exhibited the usual methyl singlet at τ 7.68, a group of four or five lines between 6.19 and 6.64 attributable to the methine proton, and four lines between τ 7.19 and 7.34 due to the methylene protons. Variable temperature studies with this compound are also in progress.

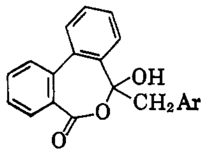
In the preceding discussions of n.m.r. spectra, the presence of aromatic protons has been ignored although absorption in this region of the spectrum is obviously present and may be considered as the sum of absorption of biphenyl and *p*-tolyl moieties. Since the aromatic protons of biphenyl itself appear at lower field than the corresponding protons of *p*-xylene,[19] these protons might be distinguishable from one another. Further, all of the compounds described may be regarded as *para*-substituted toluenes whose protons might appear as an AB quartet or as a singlet (as in *p*-xylene) depending upon the effect of the *para* substituent on the chemical shifts of the A and B protons. While the lower field portion of the aromatic proton absorption consisted of a complex group of lines in all cases, the expected pair of AB doublets at somewhat higher field was observed in spectra of the photoadduct **1** (3.03, 3.29), the glycols **3a** (3.03, 3.38) and **5** (3.00, 3.21), the acetate **3b** (3.03, 3.33), the *cis*-aldol **8** (2.92, 3.42), and the *cis* alcohol **11** (2.91, 3.09). The coupling constants were 8 c.p.s. in all cases. In four compounds a sharp singlet (corresponding in intensity to four protons), rather than a pair of doublets, was observed; these were the *trans*-aldol **7** (τ 2.7), the ketone **10** (2.92,) the *trans* alcohol **13** (3.05), and the hydrocarbon **14** (2.95).

Since the predominant conformation of **7** was known from n.m.r. data, it appeared possible to relate the conformations of **10** and **13** to **7** on the basis of this portion of the n.m.r. spectrum. However, examination of models showed that the relationship of the *p*-tolyl group to the biphenyl moiety is identical in both possible conformers. The observation of singlet *vs.* quartet absorption must then be due to the nature of the three-atom bridge and no correlations of conformation appear warranted.

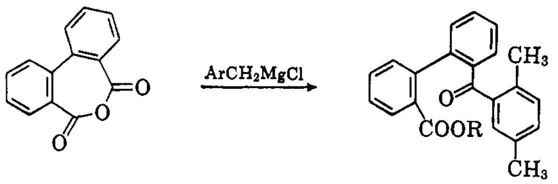
The facility with which the ketoaldehyde **6** underwent intramolecular cyclization to the aldols **7** and **8** strongly suggested that the acid, 2′-(*p*-methylphenylacetyl)biphenyl-2-carboxylic acid (**15a**), derived from **6** might exist to an appreciable extent as the ring tautomer[20] **16**. Accordingly **6** was treated with chromic acid in acetone[21] to give the (more stable) condensation product **7** and a carboxylic acid with properties in agreement with those anticipated for **15a**. Thus it exhibited absorption in the infrared at 3–4 μ characteristic of the carboxyl group as well as carbonyl absorption at 5.85 and 5.95 μ. The n.m.r. spectrum consisted of a broad singlet at τ -1.15 due to the carboxyl proton, a pair of lines at 6.12 and 6.18 due to the methylene protons,[22] and a singlet at 7.72 (CH_3) (relative intensities 1:2:3) in addition to complex absorption due to the aromatic protons. The n.m.r. spectrum offered no evidence for the presence of a second substance, such as **16** in deuteriochloroform solution at room temperature.[23] This was confirmed by examination of the ultraviolet spectrum of the methyl ester **15b**, which was essentially identical with the spectrum of the free acid.



15a, R = H
b, R = CH_3



16



17a, R = H
b, R = CH_3

An alternate synthesis of **15a** addition of a limited amount of *p*-methylbenzyl magnesium chloride to diphenic anhydride,[24] was also explored. When the solution obtained after hydrolysis of the reaction mixture was shaken with aqueous sodium carbonate, separation into three phases occurred. The top and bottom phases afforded diphenic anhydride and diphenic acid, respectively, after the appropriate work-up. A carboxylic acid (35%, **17a**) obtained from the middle layer had the expected absorption (3–4, 5.9, 6.0 μ) in the infrared but was clearly not identical with **15a**; the methyl ester (**17b**) derived from this acid was also not identical with **15b**. The n.m.r. spectrum of **17a** did not exhibit absorption at about τ 7 which would be expected if a methylene group flanked by a carbonyl group and an aromatic ring were present. Instead two singlets of equal intensity (each corresponding to three protons relative to the carboxyl proton at τ -1.20) were observed with chemical shifts characteristic of aromatic methyl groups (τ 7.77 and 7.90). On this basis **17a** was assigned the structure, 2′-(2,5-dimethylbenzoyl)biphenyl-2-carboxylic acid, the product of allylic attack by the Grignard reagent. Although numerous examples of this type of behavior have been recorded,[25] the present instance is remarkable in that no trace of the normal product **15a** or its derived ester **15b**, pure samples of which were at hand, could be detected. As in the case of **15a**, there was no evidence in the n.m.r. spectrum of **17a** for the presence of a ring tautomer. Unlike **15a**, neither **17a** nor **17b** exhibited selective absorption in the ultraviolet

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(19) In carbon disulfide solution, biphenyl protons have chemical shifts in the range τ 2.5–2.7 while *p*-xylene exhibits a singlet at 3.1.

(20) For a recent review of ring-chain tautomerism, see P. R. Jones, *Chem. Rev.*, **63**, 461 (1963).

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

(22) These lines probably represent the inner lines of a pair of AB doublets.

(23) Although n.m.r. analysis would seem to offer a considerable improvement over earlier methods for investigation of ring-chain tautomerism, to our knowledge the only instance of its application to this problem has been recorded by P. T. Lansbury and J. F. Bieron, *J. Org. Chem.*, **28**, 3564 (1963).

(24) This method has been successfully employed for the synthesis of 2′-benzoylbiphenyl-2-carboxylic acid by R. L. Shriner and L. Geipel, *J. Am. Chem. Soc.*, **79**, 227 (1957); *cf.* also D. V. Nightingale, W. S. Wagner, and R. H. Wise, *ibid.*, **75**, 4701 (1953).

(25) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, pp. 1133–1145.

Experimental[26]

***trans*-9,10-Dihydro-9,10-dihydroxy-9-(*p*-methylbenzyl)phenanthrene (3a).**—A solution of 520 mg. of the photoadduct **1**[2] in 10 ml. of diglyme was treated with 148 mg. of sodium borohydride for 2 hr. at room temperature. Acetic acid was then added until the yellow color which had developed during the reduction disappeared. The colorless solution was diluted with ethyl acetate, washed with water and saturated salt solution, dried over anhydrous sodium sulfate, and concentrated to dryness on the steam bath under reduced pressure. The thick, oily residue crystallized slowly on standing. Crystallization from 2 ml. of isopropyl ether afforded 339 mg. (65%) of white crystals of **3a**, m.p. 126–127°, m.m.p. 110–120° with starting **1**. The analytical sample was obtained by crystallization from methylene chloride–isopropyl ether: m.p. 131–132°, $\lambda_{\max}$ 271 mμ (ϵ 14,500) and 300 infl. (3100), 2.85 μ (CH_2Cl_2).

Anal. Calcd. for $C_{22}H_{20}O_2$: C, 83.50; H, 6.37. Found: C, 83.77; H, 6.44.

Chromatography of the mother liquors on Florisil furnished an additional 15% of **3a** eluted with benzene and 1% ethyl acetate in benzene. No other crystalline product could be isolated.

Comparable results were obtained using methanol as the solvent instead of diglyme.

The bis deuteroxy compound was obtained by crystallization of 90 mg. of **3a** from 1 ml. of acetone and 0.4 ml. of deuterium oxide, $\lambda_{\max}$ (KBr) 3.7 μ.

Reaction of 277 mg. of **3a** with 2 ml. of acetic anhydride and 5 ml. of pyridine overnight at room temperature followed by the usual work-up procedure afforded 300 mg. of light yellow oil which crystallized spontaneously, m.p. 163–170°. One crystallization from ethyl acetate–petroleum ether gave 239 mg. of white crystals of the acetate **3b**, m.p. 168.5–170.5°. The analytical sample was obtained by further crystallization from the same solvent mixture: m.p. 171–171.5°; $\lambda_{\max}$ (CH_2Cl_2) 2.80, 5.72, and 8.1 μ; n.m.r. τ 3.03 (d, J = 8 c.p.s.), 3.33 (d, J = 8), 6.90 (d, J = 14), 7.28 (d, J = 14), 7.66, 7.71, and complex absorption 2–2.7.

Anal. Calcd. for $C_{24}H_{22}O_3$: C, 80.42; H, 6.19. Found: C, 80.23; H, 6.47.

9-(*p*-Methylbenzyl)phenanthrene (4).—The following procedure was based on the procedure reported by Bachmann[27] for the synthesis of 9-benzylphenanthrene. Magnesium (645 mg.), 50 mg. of iodine, and 6.46 g. of 9-bromophenanthrene in a mixture of 15 ml. of benzene and 15 ml. of ether were stirred at reflux under nitrogen for 5 hr. when almost all the magnesium had reacted. The solution was transferred to a second flask under nitrogen pressure and 4.5 ml. of *p*-methylbenzyl chloride was added. After a few minutes a vigorous, exothermic reaction set in; the solution became orange and a light-colored solid began to separate. The mixture was stirred at reflux for 3 hr. and cooled; 5% hydrochloric acid was added with stirring. The layers were separated; the aqueous layer was extracted twice with ethyl acetate; the combined organic layers were washed with water and saturated salt solution, dried over anhydrous sodium sulfate, and concentrated *in vacuo*. The resulting orange oil crystallized on addition of benzene.

Recrystallization from benzene afforded 3.01 g. of white needles, m.p. 133–138°. A second crop, 0.64 g. (total yield 51%), m.p. 130–137°, was obtained with benzene–petroleum ether. The analytical sample was obtained by crystallization from acetone: m.p. 141–142°; $\lambda_{\max}$ 252 mμ (ϵ 60,000), 275 (14,000), 285 (11,000), 296 (13,000), 316 (300), 325 (300), 331 (400), 339 (300), 347 (440); n.m.r. τ 5.51, 7.66, and aromatic protons.

Anal. Calcd. for $C_{22}H_{18}$: C, 93.58; H, 6.42. Found: C, 93.36; H, 6.24.

***cis*-9,10-Dihydro-9,10-dihydroxy-9-(*p*-methylbenzyl)phenanthrene (5).**—A solution of 1 g. of 9-(*p*-methylbenzyl)phenanthrene, 1 g. of osmium tetroxide, 1 ml. of pyridine, 30 ml. of anhydrous ether, and 20 ml. of dry benzene was allowed to stand at room temperature for 6 days. A dark solid separated slowly from the reaction mixture. After addition of 15 ml. of petroleum ether, the solid was filtered, washed with petroleum ether and dissolved in 100 ml. of chloroform. The chloroform solution was stirred for 19 hr. at room temperature with a solution of 23 g. of mannitol and 1.5 g. of sodium hydroxide in 200 ml. of water. The layers were then separated, the nearly colorless chloroform layer was washed with water and saturated salt solution, dried over anhydrous sodium sulfate, and concentrated under reduced pressure on the steam bath to give 672 mg. of dark oil. This was chromatographed on 30 g. of Florisil. Elution with 250-ml. portions of benzene, 1, 2, and 3% ethyl acetate in benzene afforded 511 mg. of colorless crystals, m.p. 132–133°. The analytical sample was obtained by crystallization from methylene chloride–isopropyl ether: m.p. 132–133°; m.m.p. 110–118° with *trans* isomer (**3a**); $\lambda_{\max}$ 273 mμ (ϵ 16,300); n.m.r. (0.3 M) τ 5.78 (d, J = 6 c.p.s.), 7.01, 7.32 (d, J = 1.5), 7.70, 7.86 (d, J = 6); (0.15 M) 5.77 (d, J = 6 c.p.s.), 7.08, 7.31 (d, J = 1.5), 7.72, 8.06 (d, J = 6).

Anal. Calcd. for $C_{22}H_{20}O_2$: C, 83.50; H, 6.37. Found: C, 83.74; H, 6.33.

9,10-Dihydro-9-hydroxy-9-(*p*-methylbenzyl)-10-ketophenanthrene (1). A. From *trans*-Glycol 3a.—A solution of 118 mg. of **3a** in 1 ml. of pyridine was added to the complex[5] prepared from 106 mg. of chromium trioxide and 1 ml. of pyridine, and the dark solution was stirred briefly. It was allowed to stand overnight at room temperature and then poured into cold, dilute hydrochloric acid and extracted three times with ethyl acetate. The combined extracts were washed with water, saturated potassium bicarbonate solution, water, and saturated salt solution and then dried over anhydrous sodium sulfate and evaporated to dryness on the steam bath under reduced pressure. The residue was washed through 5 g. of Florisil with 150 ml. of benzene and 50 ml. of 1% ethyl acetate in benzene to give 113 mg. of light yellow crystals, m.p. 128–130° (lit.[2] m.p. 129–129.5°). The infrared spectrum was identical with that of the photoadduct of *p*-xylene and phenanthrenequinone.

B. From *cis*-Glycol 5.—Similar treatment of 89 mg. of **5** afforded 41 mg. of solid product identical with **1**.

2′-(*p*-Methylphenylacetyl)biphenyl-2-carboxaldehyde (6). A. From Glycol 3a.—A cooled solution of 730 mg. of sodium metaperiodate in 18 ml. of distilled water was mixed with a solution of 600 mg. of **3a** in 35 ml. of methanol. After 15 min. at room temperature needles began to separate from the clear solution. After 21 hr. the solution which contained a mass of long needles was diluted with 100 ml. of saturated salt solution and 100 ml. of ethyl acetate. The layers were separated, the aqueous layer was washed twice with ethyl acetate, and the combined organic layers were washed with saturated salt solution, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residual oil could not be induced to crystallize: $\lambda_{\max}$ plateau 285–295 mμ (ϵ 3000), end absorption 210 (34,000); (0.1 N KOH in MeOH) 245 mμ (ϵ 32,000), 320 (10,000); 3.7, 5.96 μ (CH_2Cl_2); n.m.r. τ 0.20, 6.19, 7.74, and aromatic protons.

B. From 9-(*p*-Methylbenzyl)phenanthrene (4).—Ozone-enriched oxygen was bubbled through a solution of 3.00 g. of **4** in 150 ml. of methylene chloride at Dry Ice–acetone temperature until a faint blue tinge was observed. The dissolved ozone was swept out with oxygen and 3 g. of zinc dust, and 10 ml. of acetic acid were added. The solution was stirred for 2 hr., an additional 2 g. of zinc being added after 1 hr. The zinc was removed by filtration and the filtrate was washed with water and brine, dried over anhydrous sodium sulfate, and concentrated *in vacuo*. The residual light yellow oil had infrared and ultraviolet spectra very similar to those of the material obtained by periodate cleavage.

***trans*- and *cis*-6-(*p*-Tolyl)-7-hydroxydibenzo[*a*,*c*]cycloheptan-5-one (7 and 8).**—The crude aldehyde (**6**) from 2.17 g. of glycol **3a** was adsorbed in benzene solution on 100 g. of Florisil and let stand for 12 hr. The column was then eluted with 500-ml. fractions of 90% benzene–petroleum ether, benzene (two fractions), and 2% ethyl acetate–benzene (two fractions).

The first three fractions were combined (1.13 g.) and recrystallized from methylene chloride–methanol to give 765 mg. of *trans* isomer (**7**), m.p. 163–165°. The analytical sample was obtained by crystallization from methanol: m.p. 164.5–165°; $\lambda_{\max}$ 230 mμ (ϵ 28,000), 295 (1700), end absorption 212 (35,000); (0.01 N KOH in MeOH) 248 mμ (ϵ 38,000), (12,000), end absorption 220 (21,000); $\lambda_{\max}$ (CH_2Cl_2) 2.77 and 5.95 μ; n.m.r. τ 2.70, 4.50 (d, J = 11 c.p.s.), 6.05 (d, J = 11), 7.68, 7.90, and complex absorption 2–2.6.

Crystallization of 108 mg. of **7** from 1 ml. of acetone and 0.3 ml. of deuterium oxide afforded 89 mg. of needles: m.p. 161.5–

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[26] Melting points are corrected. Ultraviolet spectra were determined in methanol solution. N.m.r. spectra were determined at 60 Mc. on approximately 0.3 M solutions in deuteriochloroform using tetramethylsilane as internal standard.

[27] W. E. Bachmann, *J. Am. Chem. Soc.*, **56**, 1363 (1934).

164.5°; $\lambda_{\max}$ (KBr) 3.84 μ; n.m.r., τ 2.72, 4.54 (d, J = 11 c.p.s.), 6.09 (d, J = 11), 7.66.

Anal. Calcd. for $C_{22}H_{18}O_2$: C, 84.04; H, 5.77. Found: C, 83.93; H, 5.84.

The last two fractions were combined (1.19 g.) and crystallized from methylene chloride–methanol to give 537 mg. of *cis* isomer (**8**), m.p. 191–194°. The analytical sample was obtained by crystallization from the same solvent pair: m.p. 193–195°; $\lambda_{\max}$ 235 mμ (ϵ 24,500), 256 (sh) (10,000), 301 (2200), end absorption 210 (34,000); (0.01 N KOH in MeOH) 245 mμ (ϵ 37,000), 320 (11,000), end absorption 220 (22,000); (CH_2Cl_2) 2.78 and 5.95 μ; n.m.r. τ 2.92 (d, J = 8 c.p.s.), 3.42 (d, J = 8), 4.36 (d, J = 4.5), 5.57 (d, J = 4.5), 6.22, 7.68, and complex absorption 2–2.9.

Crystallization of **8** from acetone and deuterium oxide as above gave product, $\lambda_{\max}$ (KBr) 3.85 μ; n.m.r. unchanged except for disappearance of 6.22 absorption.

Anal. Calcd. for $C_{22}H_{18}O_2$: C, 84.04; H, 5.77. Found: C, 83.83; H, 5.91.

Compounds identical with **7** and **8** resulted from Florisil chromatography of crude aldehyde obtained *via* reductive ozonolysis of 9-(p-methylbenzyl)phenanthrene. The isomerization was also effected by acid-washed alumina but not by silica gel, as evidenced by infrared spectra.

Equilibration of 7 and 8 on Florisil.—A solution of 101 mg. of **8** in the minimum volume of benzene (*ca.* 2 ml.) was adsorbed on 5 g. of Florisil. An additional 8 ml. of benzene was used to wash the material into the Florisil and the column then allowed to stand at room temperature for 24 hr. It was then eluted with three 50-ml. fractions of benzene, one 50-ml. of fraction of 2% ethyl acetate in benzene, and one of 5% ethyl acetate in benzene. The first two fractions (75 and 19 mg.) consisted of pure **7** (comparison of infrared spectra), the third fraction (5 mg.) was a mixture containing approximately equal amounts of **7** and **8**, and the fourth fraction (3 mg.) consisted of pure **8**.

Nearly identical results were obtained upon treatment of 105 mg. of **7** in the same manner.

6-(*p*-Tolyl)-5H-dibenzo[*a*,*c*]cyclohepten-5-one (9). A. From 7.—A solution of 189 mg. of **7** in 1 ml. of acetic anhydride and 2 ml. of pyridine was allowed to stand at room temperature for 18 hr. It was then poured onto iced, dilute hydrochloric acid, and extracted twice with ethyl acetate; the combined ethyl acetate solutions were washed with water, saturated potassium bicarbonate solution, water, and saturated salt solution. The crude product obtained after drying and concentration on the steam bath under reduced pressure was chromatographed on 10 g. of Florisil. Elution with 200 ml. of 50% and 200 ml. of 70% benzene in petroleum ether gave 161 mg. (90%) of light oil which crystallized after long standing at room temperature, m.p. 105–111°. The analytical sample was obtained by crystallization from petroleum ether: m.p. 113–114°, $\lambda_{\max}$ 247 mμ (ϵ 35,900) and 320 (10,500), (KBr) 6.09 μ, n.m.r. τ 7.60 and aromatic protons at 2–3.4.

Anal. Calcd. for $C_{22}H_{16}O$: C, 89.16; H, 5.44. Found: C, 89.14; H, 5.63.

Reaction of 224 mg. of **7** with acetic anhydride alone at 120° for 1.5 hr. followed by removal of solvent under reduced pressure and chromatography as described afforded 154 mg. of oily solid which was crystallized from 5 ml. of petroleum ether to give 97 mg. of **9**, m.p. 112.5–113°, identical with the material described above.

No reaction was observed on treatment of **7** with pyridine or acetic anhydride at room temperature.

B. From 8.—Reaction of 148 mg. of **8** under the same conditions afforded an oil which was crystallized from 5 ml. of petroleum ether to give 91 mg. (65%) of **9**, m.p. 110–111°. The infrared spectrum was identical with the spectrum of the material described in A and the mixture melting point showed no depression.

Catalytic Hydrogenation of 12. 6-(*p*-Tolyl)dibenzo[*a*,*c*]cycloheptan-5-one (10) and *cis*-5-Hydroxy-6-(*p*-tolyl)dibenzo[*a*,*c*]cycloheptane (11).—A mixture of 733 mg. of **9** and 291 mg. of 10% palladium on charcoal in 30 ml. of ethyl acetate was hydrogenated at atmospheric pressure and room temperature. Reaction proceeded rapidly and stopped completely after 1.5 hr. with absorption of 95 ml. of hydrogen (1.5 equiv.). The catalyst was filtered and washed with ethyl acetate. The residue (757 mg.) remaining after evaporation of the ethyl acetate was chromatographed on 20 g. of neutral alumina. Elution with 600 ml. of benzene afforded 291 mg. (39%) of the ketone **10** as white crystals. One crystallization from petroleum ether gave 214 mg., m.p. 90–93°. The analytical sample was obtained by further crystallization from the same solvent: m.p. 94–95.5°; $\lambda_{\max}$ 232 mμ (ϵ 28,200), 255 infl. (10,200), 299 (1940); (KBr) 5.96, 6.16 μ; n.m.r. τ 2.92, 5.84, 5.89, 6.01, 6.08, 6.35, 6.56, 6.74, 6.84, 6.92, 7.07, 7.70, and complex absorption 2–2.9.

Anal. Calcd. for $C_{22}H_{18}O$: C, 88.56; H, 6.08. Found: C, 88.37; H, 6.59.

Elution with 200 ml. of 2, 3, and 4% ethyl acetate in benzene gave 299 mg. (40%) of the alcohol **11** as white crystals. One crystallization from ethyl acetate–petroleum ether gave 278 mg. of large prisms, m.p. 143–144.5°. The analytical sample was obtained by crystallization from methanol: m.p. 150–151°; $\lambda_{\max}$ 250 mμ (ϵ 15,400); 2.82 μ (CH_2Cl_2); n.m.r., τ 5.10 (t, J = 8 c.p.s.), 6.13 (multiplet), 7.13, 7.28 (broad), 7.67, 8.27 (d, J = 8), 2.91 (d, J = 8), 3.09 (d, J = 8), and complex adsorption 2–2.9.

Anal. Calcd. for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 88.19; H, 7.18.

The deuteroxy compound was prepared by crystallization of 54 mg. of **11** from 1 ml. of acetone and 0.3 ml. of deuterium oxide: m.p. 148–150°, $\lambda_{\max}$ (KBr) 3.75 μ; n.m.r. τ 5.11 (d, J = 8 c.p.s.), 6.13 (multiplet), 7.13, 7.26, 7.29, and 7.67.

Oxidations of *cis*- and *trans*-5-Hydroxy-6-(*p*-tolyl)dibenzo[*a*,*c*]cycloheptane.—Five drops of 8 N chromic acid solution[21] were added to a solution of 42 mg. of **11** in 2 ml. of acetone. An immediate green color developed. After 1 min., a few drops of methanol were added, the solution was poured into water and extracted with ethyl acetate. The organic layer was washed with water and saturated salt solution, dried over anhydrous sodium sulfate, and concentrated on the steam bath under reduced pressure. The crude product crystallized on standing, m.p. 90–93°; the infrared spectrum was identical with the spectrum of the ketone **10**.

Application of the same procedure to 74 mg. of the *trans* alcohol **13** afforded 80 mg. of crude product which crystallized on seeding with **10**. The infrared spectrum was identical with that of **10**.

Reduction of 6-(*p*-Tolyl)dibenzo[*a*,*c*]cycloheptan-5-one (10).—A solution of 94 mg. of the ketone **10** in 1.5 ml. of methanol was treated with 109 mg. of sodium borohydride. After 1 hr. at room temperature, an additional 50 mg. of borohydride was added. After 2 hr. the solution was neutralized with acetic acid and poured into water. The white solid which precipitated was collected (84 mg.) and afforded an infrared spectrum identical with that of the *cis* alcohol **11**.

6-(*p*-Tolyl)-5H-dibenzo[*a*,*c*]cycloheptene (12).—A solution of 569 mg. of **11** and 380 mg. of p-toluenesulfonic acid monohydrate in 45 ml. of toluene was refluxed for 3 hr. After cooling, the light yellow solution was washed with saturated potassium bicarbonate solution, water, and saturated salt solution, dried over anhydrous sodium sulfate and then concentrated on the steam bath under reduced pressure. The residual dark oil was washed through 25 g. of Florisil with 250 ml. of petroleum ether to give 426 mg. (80%) of **12** which crystallized spontaneously. One crystallization from isopropyl ether gave 355 mg., m.p. 121–121.5°. The analytical sample was obtained by two further crystallizations from the same solvent, m.p. 121.5–122°; $\lambda_{\max}$ 229 mμ (ϵ 24,500), 250 (29,400) 294 (19,100); n.m.r. τ 3.21, 6.55 (half-width 11 c.p.s.), 7.65, and aromatic protons.

Anal. Calcd. for $C_{22}H_{18}$: C, 93.58; H, 6.42. Found: C, 93.41; H, 6.87.

***trans*-5-Hydroxy-6-(*p*-tolyl)dibenzo[*a*,*c*]cycloheptane (13).**—The diborane generated by addition of 1 ml. of boron trifluoride etherate to a solution of 135 mg. of sodium borohydride in 2 ml. of diglyme was passed into a solution of 99 mg. of **12** in 3 ml. of diglyme. The solution was then stirred for 2 hr. at room temperature, cooled in an ice bath, and 1 ml. of 3 N sodium hydroxide and 1 ml. of 30% hydrogen peroxide were added. After stirring for 1 hr., the solution was poured into water which was then extracted with ethyl acetate. This was washed with water and saturated salt solution, dried over anhydrous sodium sulfate, and concentrated on the steam bath under reduced pressure. The residue (110 mg.) crystallized spontaneously, m.p. 123–138°. One crystallization from 0.5 ml. of methanol afforded 59 mg. of white needles of **13**, m.p. 143–145°, m.m.p. 118–128° with *cis* isomer (**11**). The analytical sample was obtained by crystallization from methylene chloride–petroleum ether: m.p. 143.5; $\lambda_{\max}$ 250 mμ (ϵ 20,600), 2.82 μ (CH_2Cl_2); n.m.r. τ 3.05, 5.27 (d,

J = 8 c.p.s.), 6.58, 6.71, 6.87, 7.08, 7.22, 7.37, 7.68, 8.30 (broad), and 2–3.

Anal. Calcd. for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 87.91; H, 6.87.

The n.m.r. spectrum determined after crystallization of a sample of **13** from acetone–deuterium oxide was identical with that described above except for the appearance of a singlet at τ 5.25 and disappearance of the 8.30 absorption.

6-(*p*-Tolyl)dibenzo[*a*,*c*]cycloheptane (14).—A mixture of 300 mg. of **12** and 110 mg. of 10% palladium on charcoal in 20 ml. of ethyl acetate was hydrogenated at room temperature and atmospheric pressure. Absorption was complete after 30 min. The catalyst was filtered and washed with ethyl acetate, and the filtrate and washings were concentrated under reduced pressure on the steam bath to give 306 mg. of colorless oil which crystallized after long standing in the refrigerator with a few drops of methanol. One crystallization from 8 ml. of methanol afforded 246 mg. (82%) of **14**, m.p. 84–84.5°. The analytical sample was obtained by further crystallization from the same solvent: m.p. 84–85°; λ_{max} 249 mμ (ϵ 15,100); n.m.r. τ 2.95, 6.19, 6.32, 6.42, 6.54, 6.64, 7.19, 7.22, 7.29, 7.33, 7.68, and 2–2.9.

Anal. Calcd. for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 92.59; H, 7.16.

2′-(*p*-Methylphenylacetyl)biphenyl-2-carboxylic Acid (15a).—A solution of 1.06 g. of crude aldehyde (**6**) in 60 ml. of acetone was mixed with 5 ml. of solution prepared from 10.3 g. of chromium trioxide, 30 ml. of water, and 8.7 ml. of concentrated sulfuric acid. After 10 min. at room temperature, the dark solution was treated with excess methanol and then poured into a mixture of 100 ml. of water and 50 ml. of saturated salt solution which was extracted three times with ethyl acetate. The ethyl acetate extracts from four such reactions were washed with water, three times with 10% sodium carbonate solution, then with water and saturated salt solution. After drying over anhydrous sodium sulfate and concentration under reduced pressure on the steam bath, the neutral fraction weighed 1.75 g. Chromatographic purification as described for the preparation of **7** and **8** yielded 1.16 g. (27%) of **7**. A portion, recrystallized once from benzene–petroleum ether, had m.p. 163.5–165°, infrared spectrum identical with that of material described earlier.

The sodium carbonate extracts were run into iced 1:1 hydrochloric acid which was then extracted three times with ethyl acetate. The combined ethyl acetate extracts were washed with water, dried over anhydrous sodium sulfate, and concentrated under reduced pressure on the steam bath to give 2.45 g. of thick, light yellow oil. This was washed through 20 g. of silicic acid with 180 ml. of chloroform to give 2.24 g. (50%) of colorless oil which crystallized after long standing, m.p. 121–124°. A portion was crystallized from ethyl acetate to give the analytical sample of **15a** as white prisms: m.p. 125–126°; λ_{max} 286 mμ (ϵ 3100), 210 (40,000); (0.1 M methanolic potassium hydroxide) only end absorption, 286 mμ (ϵ 3300); 3–4 (CH_2Cl_2) (broad), 5.85, 5.95, 6.3, and 6.4 μ; n.m.r. τ 1.15, 6.12, 6.18, 7.74, and aromatic protons 2–3.

Anal. Calcd. for $C_{22}H_{18}O_3$: C, 79.96; H, 5.49. Found: C, 79.58; H, 5.56.

The methyl ester (**15b**) was prepared by addition of excess ethereal diazomethane to a suspension of 203 mg. of **15a** in 10 ml. ether. The product (194 mg., m.p. 60–63°) was obtained by concentration in an air stream and was crystallized from 0.5 ml. of methanol to give the analytical sample: m.p. 66–67°; λ_{max} 285 mμ (ϵ 3200), 220 (30,000); 5.83, 5.93, 6.3, 6.4 μ (CH_2Cl_2); n.m.r. τ 6.19, 6.31, 7.70, and aromatic protons.

Anal. Calcd. for $C_{23}H_{20}O_3$: C, 80.21; H, 5.85. Found: C, 79.83; H, 5.69.

2′-(2,5-Dimethylbenzoyl)biphenyl-2-carboxylic Acid (17a).—The Grignard reagent prepared from 8 ml. of freshly distilled *p*-methylbenzyl chloride and 1.38 g. of magnesium in 100 ml. of ether was diluted with 80 ml. of anisole and transferred under nitrogen pressure to a Hershberg dropping funnel.[28] This solution was added during 5 hr. to a stirred, refluxing solution of 9.64 g. of diphenic anhydride in 100 ml. of benzene and 80 ml. of anisole under nitrogen. The yellow solution was allowed to stand overnight at room temperature and then poured into a mixture of hydrochloric acid and ice. The organic layer was separated, the aqueous layer was extracted twice with benzene, and the organic phases were combined. When 100 ml. of 10% sodium carbonate solution were added, three layers were observed; these were separated.

The bottom (sodium carbonate) layer was acidified with dilute hydrochloric acid and worked up in the usual manner to give a white solid. This was crystallized from chloroform to give, in two crops, 2.08 g. (20%, based on diphenic anhydride) of diphenic acid, m.p. 228–232°.

The top, organic layer was washed with water and worked up in the usual manner to give 4.92 g. of light-colored semisolid which was crystallized from ethyl acetate to give, in two crops, 1.33 g. (14%) of diphenic anhydride, m.p. 212–216°. Chromatography of the mother liquors on Florisil gave 1.12 g. of bis-*p*-tolylethane eluted with petroleum ether.

The middle layer was a viscous, orange-red oil which dissolved in hot water (oiled on cooling) but not in ethyl acetate. When covered with ethyl acetate and acidified with dilute hydrochloric acid, it dissolved in the organic phase. The layers were separated; the organic layer was washed with water and saturated salt solution, dried over anhydrous magnesium sulfate, and concentrated under reduced pressure on the steam bath to give 5.52 g. of red oil which was washed through 50 g. of silicic acid with 600 ml. of chloroform to give 5.01 g. (35%) of crystalline product, m.p. 115–140°. Crystallization of 522 mg. of this from 2 ml. of ethyl acetate gave 212 mg. of white solid, m.p. 152–159°. The analytical sample was obtained by crystallization from methylene chloride–ethyl acetate: m.p. 165–166°; λ_{max} 240 infl. mμ (ϵ 18,000), 290 infl. (4900), 205 (52,000); (KBr) 3–4, 5.90, 6.00, 6.25, 6.35 μ; n.m.r. τ −1.20, 7.77, 7.90, and aromatic protons.

Anal. Calcd. for $C_{22}H_{18}O_3$: C, 79.96; H, 5.49. Found: C, 79.82; H, 5.45.

Seeding of mother liquors with **15a** or rechromatography on silicic acid did not furnish any other crystalline product.

The methyl ester **17b** was prepared by reaction of a suspension of 63 mg. of the above acid in 10 ml. of anhydrous ether with excess ethereal diazomethane. The residue remaining after removal of solvent in an air stream was crystallized from 0.5 ml. of isopropyl ether to give 41 mg. (63%) of white crystals, m.p. 89–93°. The analytical sample was obtained by further crystallization from the same solvent: m.p. 92.5–93°; λ_{max} 255 mμ infl. (12,000), 290 infl. (4400), 210 (42,000); (KBr) 5.85, 5.96 μ; n.m.r. τ 6.25, 7.70, 7.78 and aromatic protons.

Anal. Calcd. for $C_{23}H_{20}O_3$: C, 80.21; H, 5.85. Found: C, 79.76; H, 5.97.

Repetition of the above esterification with mother liquors from crystallization of the acid, **17a**, did not lead to isolation of crystalline product.

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[28] E. B. Hershberg, *Org. Syn.*, **18**, 16 (1938).