The product was not identical with the m.p. 118° diastereomer, and not a dimorph.

Infrared Spectra.—The research spectrum was recorded, using the potassium bromide pellet method, for each new compound. The spectra showed the principal expected peaks, but have not been interpreted in detail.

Acknowledgment.—This research was made possible by generous grants to the University of San Francisco from the National Science Foundation (G-7377 and G-15839-R) and the Roscoe and Margaret Oakes Foundation. We would like to thank Professors T. Posternak (Geneva), B. Franck (Göttingen), and S. J. Angyal (New South Wales, Australia) for helpful discussions. Comparison samples were kindly provided by Professor Angyal and Dr. P. A. J. Gorin, and by Professor Rudolf Criegee (Karlsruhe).

Photochemical Reactions of Diketones. II.[1a,b] The 1,2-Addition of Substituted Toluenes to 9,10-Phenanthrenequinone

MORDECAI B. RUBIN AND PAULINE ZWITKOWITS

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

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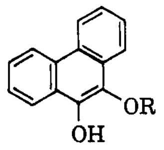
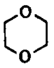
Reversible photochemical addition of substituted toluenes to phenanthrenequinone (PQ) proceeds *via* 1,2-addition to give 9,10-dihydro-9-hydroxy-9-X-benzyl-10-ketophenanthrenes (**6**) contrary to earlier reports that 1,4-addition occurs in these reactions. In addition to physical evidence, this was established by conversion of both phenanthrenequinone and the *p*-xylene–phenanthrenequinone adduct (**6d**) to *trans*-9,10-dihydro-9,10-dihydroxy-9,10-bis(*p*-methylbenzyl)phenanthrene (**7d**). Attempted synthesis of the *cis* isomer of **7d** was not successful. These results contrast with the 1,4-additions of ethers and aldehydes to phenanthrenequinone; the relative rates of addition of benzaldehyde, dioxane, and *p*-xylene to phenanthrenequinone were 48:2.7:1. The mono(*p*-methylbenzyl) ether (**2**) of 9,10-dihydroxyphenanthrene was synthesized by a new and apparently general method; photoirradiation of **2** afforded the 1,2-adduct **6d**.

In connection with the study[1b] of the photochemical addition of ethers to 9,10-phenanthrenequinone (PQ) to give products typified by the dioxane adduct (**1**), we have reinvestigated the photoaddition of *p*-xylene and related compounds to 9,10-phenanthrenequinone. This reaction was first reported in 1914 by Benrath and Von Meyer[2] and was re-examined almost 40 years later by Moore and Waters.[3] The earlier workers proposed that the 1:1 adducts obtained by sunlight irradiation of solutions of phenanthrenequinone in *o*- or *p*-xylene, mesitylene, pesudocumene, or quinaldine were substituted monobenzyl ethers (**2**) of 9,10-dihydroxyphenanthrene (**3**). This assignment was based on analogy with the photoaddition of aldehydes to phenanthrenequinone reported earlier by Klinger[4] to give monoesters (**4**) of **3** and, on degradations to **3**, phenanthrenequinone and phenanthrene quinhydrone. The surprising observation that the infrared spectrum of the *p*-xylene–phenanthrenequinone adduct exhibited both hydroxyl (2.98 μ) and carbonyl (5.96 μ) absorption was rationalized by the later workers on the assumption that appreciable tautomerization of the phenol **2** to the corresponding keto form occurred.[5]

If structure **2** were correct, the *p*-xylene–phenanthrenequinone adduct would be expected to exhibit an ultraviolet spectrum very similar to the spectra of the ether (**1**) and aldehyde (**4**) adducts. Further, the spectrum should be changed markedly in alkaline solution owing to conversion to the corresponding phenoxide ion as was observed with **1** and **4**. In fact, the ultraviolet spectrum of the *p*-xylene–phenanthrenequinone adduct (two maxima) was significantly different from the spectra of compounds of types **1** and **4** (six maxima) and remained unchanged on prolonged standing in alkaline solution. These results as well as the infrared data would be satisfactorily accommodated by the assumption that 1,2-addition of *p*-xylene to phenanthrenequinone had occurred to give 9,10-dihydro-9-hydroxy-9-(*p*-methylbenzyl)-10-ketophenanthrene (**6d**).[7a,b] The n.m.r. spectrum of the adduct exhibited singlets at τ 6.0 (hydroxyl proton, broad), 7.01 (CH_2), and 7.72 (CH_3) (relative intensities 1:2:3), and complex absorption at τ 2–3 (aromatic protons) in agreement with the revised structure.



1, R = 

2, R = $p\text{-}CH_3C_6H_4CH_2\text{-}$

3, R = H

4, R = $C_6H_5\overset{|}{C}{=}O$

Chemical evidence confirmed the correctness of this conclusion. Reaction of phenanthrenequinone with an equimolar quantity of *p*-methylbenzyl magnesium bromide led to formation, in low yield, of a substance identical with the photoadduct; the other products isolated were recovered phenanthrenequinone and 1,2-bis-*p*-tolylethane, the product of Grignard coupling.

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(1) (a) Presented in part at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1962; (b) for the previous paper in this series, see M. B. Rubin, *J. Org. Chem.*, **28**, 1949 (1963).

(2) A. Benrath and A. Von Meyer, *J. prakt. Chem.*, **89**, 258 (1914).

(3) R. F. Moore and W. A. Waters, *J. Chem. Soc.*, 3405 (1953).

(4) H. Klinger, *Ann.*, **249**, 137 (1888).

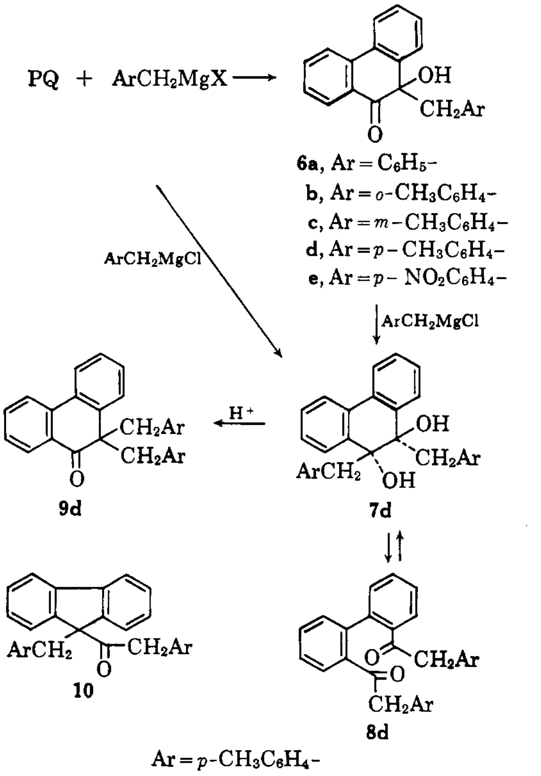
(5) 9,10-Dihydro-9-ketophenanthrene has been prepared[6] and reported to be unstable in air and to undergo rapid change in solution.

(6) E. J. Moriconi, F. T. Wallenberger, L. P. Kuhn, and W. F. O'Connor, *J. Org. Chem.*, **22**, 1651 (1957).

(7) (a) W. I. Awad and A. R. A. Raouf, *ibid.*, **22**, 881 (1957), have described the related substance, 9,10-dihydro-9-hydroxy-9-phenyl-10-ketophenanthrene [λ_{max} 245, 270 (sh), and 330 mμ in reasonably close agreement with the spectrum of the photoadduct of phenanthrenequinone and *p*-xylene]; (b) Ramart-Lucas, M. J. Matti, and T. Guilmart, *Bull. soc. chim. France*, 1215 (1948), report λ_{max} 278 and 330 mμ for 9,10-dihydro-9,9-dimethyl-10-ketophenanthrene.

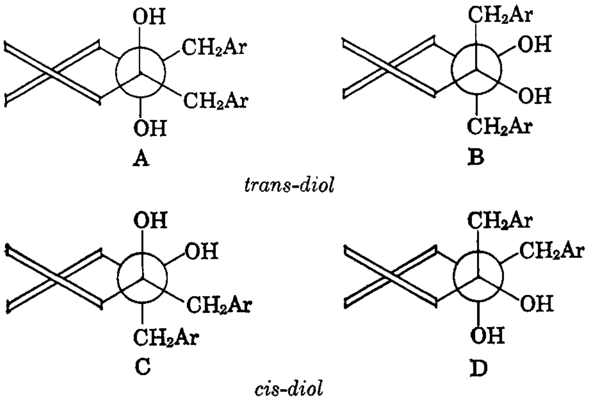
Reaction of either the photoadduct or phenanthrenequinone with excess *p*-methylbenzyl magnesium chloride furnished, in good yield in both cases, the identical product, *trans*-9,10-dihydro-9,10-dihydroxy-9,10-bis-(*p*-methylbenzyl)phenanthrene (**7d**). These results are consistent only with formulation of the adduct as **6d**.[8] (See Scheme I.)

Scheme I



The assignment of *trans* stereochemistry to the diol **7d** was based on analogy with the addition of a variety of other Grignard reagents to phenanthrenequinone.[6] In addition, the presence of a sharp hydroxyl band in the infrared suggested the absence of hydrogen bonding as had been observed[6] for *trans*-9,10-dihydro-9,10-dihydroxy-9,10-diarylphenanthrenes in contrast to the two bands (bonded and nonbonded OH) observed in the spectra of *cis* isomers. The n.m.r. spectrum of **7d** exhibited the expected complex aromatic absorption at τ 2–3.5, a pair of AB doublets due to the methylene protons at 6.79 and 7.24 (J_{AB} = 14 c.p.s.), and singlets at 7.44 (OH) and 7.70 (CH_3). The assignments were consistent with relative intensity measurements and were confirmed by the spectrum of the deuteroxy compound which was unchanged from that of **7d** except for disappearance of the singlet at τ 7.44. The observation of identical chemical shifts for the two hydroxyl protons is to be expected in the *trans* isomer since the two hydroxyl groups are equivalent in either conformation (A and B, Scheme II) of this isomer. This is not true for the *cis* isomer where the hydroxyl groups are not equivalent (*cf.* C and D), although it should be noted that exchange processes or rapid interconversion of C and D by inversion of the biphenyl could result in observation of a single hydroxyl resonance.

Scheme II



In order to obtain further evidence on the stereochemistry of **7d**, the synthesis of its *cis* isomer was attempted. Cyclizations of a number of 2,2′-diaroylbiphenyls to *cis*-9,10-dihydro-9,10-dihydroxy-9,10-diarylphenanthrenes (or mixtures in which the *cis* isomer predominated) have been reported[6,9] using a variety of pinacol-forming reagents such as magnesium–magnesium iodide couple, sodium amalgam, or zinc in acid or alkaline medium. The diketone, 2,2′-bis(*p*-methylphenylacetyl)biphenyl (**8d**), required for such cyclization attempts could be readily obtained by oxidation of **7d** with chromic anhydride in acetic acid. The methylene protons in this compound did not appear as an AB quartet in the n.m.r. spectrum, instead a broad line at τ 6.09 (half width, 5 c.p.s.) was observed. Cyclizations of **8d** with zinc in acetic acid or magnesium–magnesium iodide afforded **7d**; no isomeric pinacol could be isolated.[10] In the latter case, 1,2-bis-*p*-tolylethane (17%) and phenanthrenequinone (52%) were also isolated. These must have resulted from cleavage of **8d**[11] since the pinacol, **7d**, was recovered unchanged after treatment under the same reaction conditions. Photochemical pinacol formation[12] was also investigated; irradiation of **8d** in isopropyl alcohol solution for 24 hr. afforded quantitative recovery of starting material. This result might have been attributed to an unfavorable equilibrium[12]; however, irradiation of **7d** in acetone solution also resulted in recovery of starting material. The photochemical cleavage of **7d** could be effected by irradiation in benzene solution containing *p*-benzoquinone.[13]

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[8] After preparation of this paper was completed, the Doctoral Dissertation of G. Pfundt (Göttingen, 1962) came to our attention. Pfundt concluded that the adduct **6b** of phenanthrenequinone and *o*-xylene possessed the structure illustrated on the basis of spectroscopic evidence and conversion to an acetate exhibiting ester and conjugated carbonyl absorption in the infrared.

[9] W. E. Bachmann, *J. Am. Chem. Soc.*, **54**, 1969 (1932).

[10] A similar result has been reported by Th. Zincke and W. Tropp [*Ann.*, **363**, 302 (1908)], who observed that cyclization of 2,2′-bisphenylacetylbiphenyl with zinc and hydrochloric acid or zinc and potassium hydroxide led to a product identical with the product obtained from addition of excess benzyl magnesium chloride to phenanthrenequinone. Examination of models suggests that the conformation of the biphenyl required for cyclization to *cis* glycol is considerably more hindered when the 2,2′-substituents are benzyl ketones than when they are phenyl ketones.

[11] Cleavage of a diketone by magnesium–magnesium iodide couple has been reported by G. W. Griffin and R. B. Hager [*J. Org. Chem.*, **28**, 599 (1963)], who observed acetophenone as a by-product in cyclizations of 1,2-dibenzoylethane.

[12] A. Schönberg, "Präparative Organische Photochemie," Springer-Verlag, Berlin, 1958, pp. 111, 112. To our knowledge, no examples of intramolecular reactions of this type to give cyclic pinacols have been recorded and the stereochemical result of such a cyclization, if effected, remains an open question.

[13] A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 67 (1944); ref. 12, p. 113.

Acid-catalyzed rearrangement of **7d** led to 9,10-dihydro-9,9-bis(*p*-methylbenzyl)-10-ketophenanthrene (**9d**). The alternate possible structure of 9-(*p*-methylbenzyl)-9-(*p*-methylphenylacetyl)fluorene (**10**) was ruled out on the basis of the presence of a conjugated carbonyl group (6.0 μ), the similarity of the ultraviolet spectrum to that of **6d**, and the appearance of the methylene protons as a single pair of AB doublets at τ 6.32 and 6.81. Although the *trans*-diaxial relationship between a hydroxyl group and the migrating *p*-methylbenzyl group obtains in both conformations (C and D) of the *cis* isomer of **7d** and in neither conformation (A and B) of the *trans* isomer, the result of acid-catalyzed rearrangement cannot be taken as evidence in support of the *cis* configuration since previous work[6,9] has established that both *cis*- and *trans*-9,10-dihydro-9,10-dihydroxy-9,10-diarylphenanthrenes rearrange in the presence of acid to the same 9,10-dihydro-9,9-diaryl-10-ketophenanthrenes.[14]

Returning to the photochemical reaction, adducts **6a**, 90% yield, and **6c**, 95%, could be obtained from irradiation of phenanthrenequinone in toluene or *m*-xylene contrary to the earlier report.[2] Isolation of these products as well as the known[2] *o*-xylene adduct (**6b**) was conveniently effected by chromatography on Florisil. The ultraviolet spectra of **6a–d** were essentially identical; all exhibited hydroxyl and conjugated carbonyl absorption in the infrared. A broad singlet at about τ 6.0 due to the hydroxyl proton was observed (at identical concentrations) in the n.m.r. spectra of the four adducts. The adduct **6b** from *o*-xylene, in which considerable interaction between the methyl group and the adjacent aromatic ring of the dihydrophenanthrene can occur, showed a shift of the methyl singlet from the usual value of τ 7.7 to 8.08 and the methylene absorption appeared as a pair of lines (6.90, 6.97) in contrast to the singlet observed with the unsubstituted and *m*- and *p*-substituted compounds. An adduct (**6e**) was obtained by irradiation of a mixture of phenanthrenequinone and *p*-nitrotoluene in benzene solution; based on its spectral properties, this also resulted from 1,2-addition to phenanthrenequinone.

The 1,2-additions of these substituted toluenes to phenanthrenequinone provide a marked contrast to the additions of ethers and aldehydes which proceed in high yield to give products of 1,4-addition. The differences in behavior cannot be ascribed to experimental variables, since the products formed in irradiations of phenanthrenequinone with dioxane–*p*-xylene or benzaldehyde–*p*-xylene mixtures were the same adducts **1**, **4**, and **6d**, as established by chromatographic separation and spectral analysis. The relative rates of benzaldehyde, dioxane and *p*-xylene additions to phenanthrenequinone were 48:2.7:1. These values were observed at approximately 60% reaction; as would be expected of reversible processes (*vide infra*), the relative rates varied with extent of reaction. While the present lack of detailed information makes it inappropriate to speculate on the mechanism(s) of these additions, it might be noted that the currently accepted picture[1b,3,15a,b,c] of phenanthrenequinone photoadditions is not inconsistent with either 1,2- or 1,4-addition processes. Thus, the semiquinone radical resulting from abstraction of hydrogen by photoexcited phenanthrenequinone is a resonance hybrid of (among others) structures (E and F) in which the unpaired electron is localized on oxygen or carbon. Addition of an acyl, benzyl, or ether radical could then take place at either of these positions to give the two types of adducts observed.

It had previously been observed[1b] that the dioxane–phenanthrenequinone addition was photochemically reversible and the approximate composition of the photostationary state determined. Reversibility of the *p*-xylene–phenanthrenequinone addition was also established by isolation of phenanthrenequinone and *p*-xylene (detected by gas chromatography) upon irradiation of a dilute benzene solution of **6d**. Attempts to determine the composition of the photostationary state were not successful in this instance because of the accumulation of phenanthrene quinhydrone and other, unidentified by-products upon prolonged irradiation of benzene solutions containing either **6d** or an equimolar mixture of phenanthrenequinone and *p*-xylene. For example, after 24-hr. irradiation of 0.0198 *M* **6d** there was obtained 42% of recovered **6d** and 16% of phenanthrenequinone; under similar conditions 0.0198 *M* phenanthrenequinone and 0.0198 *M* *p*-xylene afforded 31% of **6d** and 20% of recovered phenanthrenequinone. The photochemical reversibility of the benzaldehyde–phenanthrenequinone addition was also demonstrated by irradiation of 0.0067 *M* **4** in benzene solution which afforded 30% of recovered **4** and 34% of phenanthrenequinone after 9 hr.

The demonstration that all of these additions are photochemically reversible suggested that equilibrium factors might be responsible for the differing modes of addition. In order to investigate this possibility, the mono(*p*-methylbenzyl) ether (**2**) of **3**, possessing the structure originally proposed[2] for the photoadduct of phenanthrenequinone and *p*-xylene, was synthesized (*vide infra*) and its photochemical behavior examined. Irradiation of 0.02 *M* **2** in benzene solution for 10 hr. afforded 28% of recovered **2** and 33% of **6d**, the 1,2-adduct. After more prolonged irradiation, the only adduct which could be isolated was **6d**. Comparison with the results obtained in the attempted determination of the photostationary state of the phenanthrenequinone–*p*-xylene addition suggests that the conversion of **2** to **6d** proceeds directly rather than *via* reversal to a mixture of phenanthrenequinone and *p*-xylene followed by 1,2-addition. This question, as well as the equilibrium between 1,2 and 1,4 adducts of benzaldehyde and dioxane, is being investigated further.

Previously reported methods[15b,16–18] for the synthesis of monoethers of **3** have afforded low (or unreported) yields and do not appear to be of general applicability. The availability of derivatives of **3**, namely the ether and aldehyde adducts with phenanthrenequinone, in which one of the hydroxyl groups is protected as an acetal or ester derivative, suggested a desirable alternative for the synthesis of **2**. Alkylation of the dioxane adduct (**1**) with *p*-methylbenzyl chloride produced a

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[14] These reactions presumably involve, for the *trans* isomer at least, the intervention of an "open" carbonium ion: *cf.* C. J. Collins, W. T. Rainey, W. B. Smith, and I. A. Kaye, *J. Am. Chem. Soc.*, **81**, 460 (1959); C. J. Collins and B. M. Benjamin, *ibid.*, **85**, 2519 (1963).

[15] (a) H. J. L. Bäckström, *Z. Physik. Chem.*, **25**, 99 (1934); *Naturwissenschaften*, **22**, 170 (1934); (b) R. F. Moore and W. A. Waters, *J. Chem. Soc.*, 238 (1953); (c) G. O. Schenck, *Z. Elektrochemie*, **64**, 997 (1960).

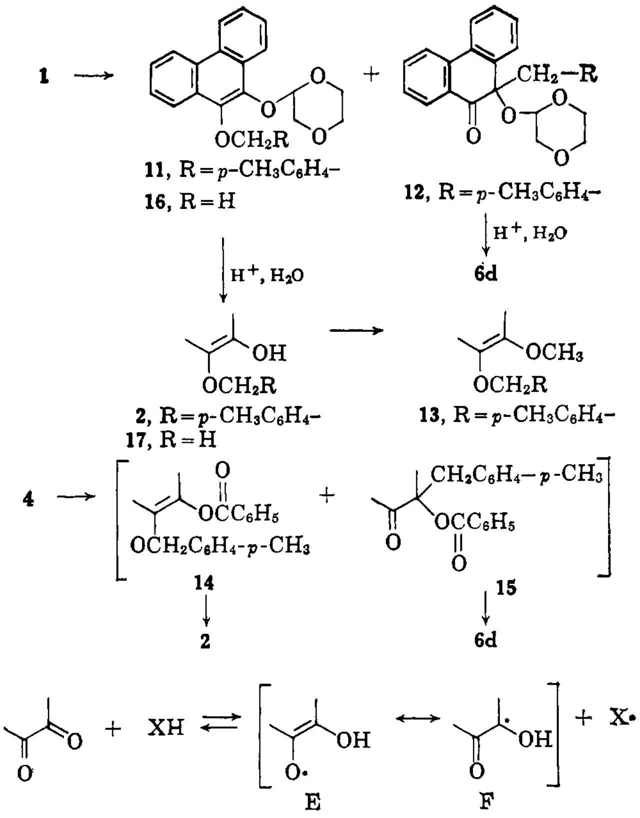
[16] F. R. Japp, *Ber.*, **12**, 1306 (1897).

[17] S. Goldschmidt and W. Schmidt, *ibid.*, **55**, 3197 (1922).

[18] E. Fourneau and J. Matti, *Bull. soc. chim. France*, **9**, 633 (1942).

mixture from which the desired O-alkylated product, 9-dioxanyloxy-10-(*p*-methylbenzyloxy)phenanthrene (**11**), could be isolated in 70% yield (Scheme III). The ultraviolet spectrum of **11** exhibited the characteristic features of a 9,10-dioxyphenanthrene[7b] and its properties in the infrared and n.m.r. were consistent with the assigned structure. A second product, 9-dioxanyloxy-9-(*p*-methylbenzyl)-10-ketophenanthrene (**12**), resulting from C-alkylation of **1**, was obtained in 13% yield. While **12** could not be obtained crystalline, the spectral properties were in agreement with the structure assigned and further confirmation was provided by acid-catalyzed hydrolysis to **6d**.

Scheme III



Similarly, acid-catalyzed hydrolysis of **11** led to isolation of **2** (54%), obtained as a low-melting solid which underwent fairly rapid decomposition in air (possibly accounting for the moderate yield) but could be stored for several months in an inert atmosphere at low temperature. **2** exhibited the expected ultraviolet spectrum, hydroxyl absorption in the infrared, and lines with the appropriate relative intensities at τ 6.0 (CH_2) and 8.18 (CH_3) as well as complex absorption at τ 2–3 due to the aromatic and phenolic protons. It was further characterized by methylation to stable 9-methoxy-10-(*p*-methylbenzyloxy)phenanthrene (**13**) which also exhibited the appropriate spectral properties. When the same reaction sequence was applied to the benzaldehyde adduct (**4**), hydrolysis of the intermediate O- and C-alkylated products (**14** and **15**) occurred in the alkylation step to give a mixture from which **2** (10%) and **6d** (19%) were isolated.

The method of synthesis described above would appear to be generally applicable for the preparation of monoethers and unsymmetrically substituted diethers of dihydric phenols provided that the appropriate quinone undergoes photoaddition reactions with ethers or aldehydes.[19] It has been utilized for the synthesis of the monomethyl ether (**17**) of **3** in 63% yield from **1**; an earlier method,[17] reaction of **3** with dimethyl sulfate in alkaline solution, afforded 7–12% of desired product.

Experimental[20]

9,10-Dihydro-9-hydroxy-9-(*p*-methylbenzyl)-10-ketophenanthrene (6d). A. By Photoirradiation.—A suspension of 2.00 g. of phenanthrenequinone in 20 ml. of *p*-xylene was irradiated for 67 hr. Unreacted quinone (0.32 g.) was removed by filtration and the filtrate adsorbed on 50 g. of Florisil. Elution with 250 ml. of 10% benzene in petroleum ether (b.p. 66–75°) afforded 60 mg. of white solid, m.p. 82–83°, identical with authentic 1,2-bis-*p*-tolylethane. Elution with 500 ml. each of 90% benzene–petroleum ether and pure benzene gave 2.00 g. (67%, 91% based on recovered quinone) of light yellow solid, m.p. 125–127°. Elution with ethyl acetate gave an additional 0.28 g. of quinone. A portion of the product crystallized from methylene chloride–petroleum ether had m.p. 129–129.5° (lit.[2,3] m.p. 129–130°); λ_{max} 242 mμ (ϵ 25,000), 248 infl. (23,400), 275 infl. (7600), and 327 (2800); 2.88 and 5.96 μ (KBr). The ultraviolet spectrum was unchanged after 6 hr. in 0.1 *N* sodium hydroxide solution (70% dioxane) at room temperature. N.m.r. showed bands at τ 6.00, 7.01, and 7.72 (relative intensities 1:2:3); complex absorption at 2–3 and 3.03 (doublet, J_{AB} = 8 c.p.s.), 3.29 (J = 8 c.p.s.).

A 64% yield (88% based on recovered phenanthrenequinone) of **6d** was obtained when a Corning C.S.-0-52 filter (<0.5% transmission at 334; <5% at 340, and 65% at 360 mμ) was used.

B. From Phenanthrenequinone and *p*-Methylbenzyl Magnesium Bromide.—The Grignard reagent prepared from 1.403 g. of freshly distilled *p*-methylbenzyl bromide and 0.179 g. of magnesium in 15 ml. of dry ether was diluted with 10 ml. of anisole and then added dropwise during 1 hr. to a stirred, refluxing solution of 1.53 g. of phenanthrenequinone in a mixture of 65 ml. of benzene and 10 ml. of anisole. After the addition was complete, the dark solution was cooled and poured onto iced 1 *M* sulfuric acid; benzene was added. The yellow phenanthrenequinone, 0.760 g., m.p. 209–210°, which separated was removed by filtration. The layers were then separated; the benzene layer was washed with water, dried over anhydrous sodium sulfate, concentrated to about 15 ml., and filtered to give 0.39 g. of additional phenanthrenequinone, m.p. 209–210°.

The filtrate was absorbed on 50 g. of Florisil. Elution with 500 ml. of benzene gave 0.62 g. of 1,2-bis-*p*-tolylethane as a white solid, m.p. 74–78°. A second benzene fraction gave 112 mg. (5%, 68% based on recovered phenanthrenequinone) of light yellow solid, m.p. 124–128°. Recrystallization from benzene–petroleum ether raised the melting point to 127.5–128.5°, which was undepressed on mixture with the product obtained by photoirradiation; infrared spectra were identical. An additional 0.27 g. of quinone was obtained by elution of the column with ethyl acetate (total recovered quinone, 1.42 g.).

***trans*-9,10-Dihydro-9,10-dihydroxy-9,10-bis-(*p*-methylbenzyl)-phenanthrene (7d). A. From 6d.**—Anisole (8 ml.) was added to 10 ml. of the Grignard solution prepared from 10.0 g. of freshly distilled *p*-methylbenzyl chloride and 1.72 g. of magnesium in 100 ml. of ether under nitrogen. **6d** (200 mg.) and 8 ml. of anisole were added and the solution then was refluxed with stirring. After 2 hr., 5 ml. of toluene were added and refluxing was continued. After a total reaction time of 7 hr., the green solution was cooled, 5% hydrochloric acid and ethyl acetate were added, and the layers were separated. The organic layer was

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[19] For a summary of quinone photoadditions see "Präparative Organische Photochemie," A. Schönberg, Springer-Verlag, Berlin, 1958; also P. de Mayo in "Advances in Organic Chemistry," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1960.

[20] Melting points are corrected. Ultraviolet spectra were determined in methanol solution unless noted otherwise. N.m.r. spectra were determined at 60 Mc. in 0.3 *M* deuteriochloroform solution using tetramethylsilane as internal standard. Photoirradiations were performed at 30° C. in Pyrex vessels in an atmosphere of nitrogen; the light source was a 1000-w. General Electric water-cooled, high pressure mercury vapor lamp (AH-6) with Pyrex jacket.

washed with water and brine, dried over anhydrous sodium sulfate, and concentrated *in vacuo;* the oily residue was chromatographed on 25 g. of Florisil. Elution with 250 ml. of petroleum ether gave 211 mg. of 1,2-bis-*p*-tolylethane, m.p. 80–83°. Elution with 50% benzene–petroleum ether gave 250 mg. (93%) of **7d** as white needles, m.p. 146–150°. The analytical sample m.p. 149.5–150.5°, was obtained by crystallization from petroleum ether and had λ_{max} 273 mμ (ϵ 15,200), 210 (36,000); and 2.88 μ (CH_2Cl_2). N.m.r. showed bands at τ 6.79 (doublet, J_{AB} = 14 c.p.s.), 7.24 (*d*, *J* = 14 c.p.s.), 7.44, and 7.70; aromatic protons, complex absorption at 2–2.8, 2.98 (*d*, *J* = 8 c.p.s.), and 3.34 (*d*, *J* = 8 c.p.s.).

Anal. Calcd. for $C_{30}H_{28}O_2$: C, 85.68; H, 6.71. Found: C, 86.22; H, 6.58.

Crystallization of 173 mg. of **7d** from a mixture of 1 ml. of acetone and 0.5 ml. of deuterium oxide afforded white needles of deuterated **7d**. One crystallization from petroleum ether gave 107 mg., m.p. 148.5–151°, λ_{max} 3.88 μ (KBr). The n.m.r. spectrum was identical with that described above except for the almost complete disappearance of the line at τ 7.44.

B. **From Phenanthraquinone.**—To the remainder of the Grignard solution described above was added 2.00 g. of phenanthraquinone, 50 ml. of anisole, and 45 ml. of toluene. After 5-hr. stirring at reflux, the dark, blue-green solution was worked up as described above to give 2.43 g. of 1,2-bis-*p*-tolylethane and 3.60 g. (86%) of faintly yellow crystals of **7d**. Recrystallization from methylene chloride–petroleum ether gave white needles, m.p. 149–150.5°, which showed no depression on mixture with the product from procedure A; the infrared spectra were identical.

2,2′-Bis(*p*-methylphenylacetyl)biphenyl (**8d**). **A. By Chromic Acid Oxidation of 7d.**—A solution of 2.72 g. of chromium trioxide in 27 ml. of water was added during 6 min. to a stirred solution of 8.0 g. of **7d** in 80 ml. of acetic acid at 70°. After stirring for an additional 8 min., 10 ml. of water was added, and the solution was seeded and allowed to cool. Filtration afforded 7.95 g. of light yellow solid which gave 5.78 g. (82%) of **8d**, m.p. 83°, in two crops upon crystallization from isopropyl ether. The analytical sample, m.p. 83–84°, was obtained by crystallization from this solvent and had λ_{max} 290 mμ (ϵ 3100), 210 (43,000); 6.02 μ (KBr). N.m.r. showed bands at τ 6.09 (singlet, half width 5 c.p.s.) and 7.68; aromatic protons, complex absorption at 2–3 and 2.93 (doublet spacing, 3 c.p.s.).

Anal. Calcd. for $C_{30}H_{26}O_2$: C, 86.09; H, 6.26. Found: C, 85.89; H, 5.78.

B. By Photochemical Cleavage of 7d.—A solution of 330 mg. of **7d** and 259 mg. of sublimed *p*-benzoquinone in 14 ml. of benzene was irradiated for 3.5 hr. After removal by filtration of the black needles of quinhydrone (178 mg.) which had separated during the course of the irradiation, the filtrate was concentrated on the steam bath under aspirator pressure until no further sublimation of quinone was observed. The residue was chromatographed on 15 g. of alkaline alumina. Elution with 50 and 90% benzene–petroleum ether yielded 84 mg. of colorless oil which was crystallized from isopropyl ether to give 54 mg. of **8d**, m.p. 83–84°.

Elution with benzene afforded 174 mg. of crystalline material, identical with **7d** by comparison of infrared spectra. Irradiation of **7d** in acetone solution for 17 hr. resulted in quantitative recovery of starting material.

Cyclizations of 8d. A. With Zinc and Acetic Acid.—A mixture of 341 mg. of diketone **8d**, 2 g. of zinc dust, 2 ml. of methylene chloride, and 2 ml. of acetic acid was stirred at room temperature for a total of 23 hr. with additional zinc (1 g.) and acetic acid (1 ml.) being added after 17 hr. Unreacted zinc was removed by filtration and washed with methylene chloride. The filtrate and washings were concentrated under reduced pressure on the steam bath to give 336 mg. of partly crystalline product which was chromatographed on 15 g. of Florisil. Elution with 50 and 90% benzene in petroleum ether afforded 262 mg. (77%) of white crystals, m.p. 146–149°. One crystallization from petroleum ether gave 199 mg. of **7d**, m.p. 150–151°, identical by infrared analysis with the product of Grignard addition to phenanthrenequinone. Elution of the column with ethyl acetate yielded 10 mg. of phenanthrenequinone.

B. With Magnesium–Magnesium Iodide.—A mixture of 1.0 g. of iodine and 0.5 g. of magnesium powder in 10 ml. of anhydrous ether and 20 ml. of anhydrous benzene under nitrogen was stirred at room temperature for 15 min. when the iodine color had faded to a pale yellow. One gram of diketone **8d** was then added and the mixture was refluxed with stirring under nitrogen for 4 hr. and let stand at room temperature overnight. The solution was then filtered and the filtrate was shaken with cold dilute hydrochloric acid, the color changing from green to orange, After washing with water and saturated salt solution, the organic layer was dried over anhydrous sodium sulfate and taken to dryness under reduced pressure on the steam bath. The red, amorphous residue (1.03 g.) was chromatographed on 50 g. of Florisil with 500-ml. fractions being collected.

Elution with petroleum ether furnished 43 mg. (17%) of 1,2-bis-*p*-tolylethane, identified by its infrared spectrum. Elution with two fractions of 50% and one of 60% benzene in petroleum ether furnished 385 mg. of crystalline product, which afforded 154 mg. (15%) of white crystals on crystallization from isopropyl ether with m.p. 150–151°, m.m.p. (with **7d**) 149.5–150.5°; infrared spectra were identical. No additional crystalline material could be obtained from the mother liquors nor did rechromatography on Florisil afford crystalline material.

After elution of 154 mg. of amorphous material with benzene, the column was eluted with ethyl acetate to give 258 mg. (52%) of crystalline phenanthrenequinone.

C. With Light.—A solution of 197 mg. of **8d** in 15 ml. of isopropyl alcohol was irradiated for 17 hr. Removal of solvent under reduced pressure gave a light yellow solid which exhibited an infrared spectrum unchanged from that of starting material.

9,10-Dihydro-9,9-bis(*p*-methylbenzyl)-10-ketophenanthrene (**9b**).—A solution of 217 mg. of **7d** in the minimum volume of hot acetic acid (*ca.* 1 ml.) containing two drops of concentrated sulfuric acid was heated on the steam bath for 15 min. The solution was cooled and a few drops of water were added. The supernatant liquid was decanted from the resulting oil which solidified on standing. The solid was washed with water and crystallized from absolute alcohol to give 106 mg. (43%) of light yellow prisms, m.p. 148–153°. The analytical sample was obtained by crystallization from methylene chloride–methanol and had m.p. 156–156.5°; m.m.p. (with starting material) 120–137°; λ_{max} 245 mμ (ϵ 30,000), 253 infl. (25,000), 301 infl. (2500), 339 (3300); 6.0 μ (KBr). N.m.r. showed bands at τ 6.32 (doublet, J_{AB} = 14 c.p.s.), 6.81 (*d*, *J* = 14 c.p.s.), and 7.97; aromatic protons at 2–3 and 3.40 (singlet).

Anal. Calcd. for $C_{30}H_{26}O$: C, 89.51; H, 6.51. Found: C, 89.10; H, 6.65.

9,10-Dihydro-9-hydroxy-9-benzyl-10-ketophenanthrene (**6a**).—After irradiation of 1.00 g. of phenanthrenequinone in 50 ml. of toluene for 17 hr., the solvent was removed on the steam bath under reduced pressure and the dark residue (1.68 g.) was chromatographed on 60 g. of Florisil. Elution with 750 ml. of 50% and 500 ml. of 80% benzene–petroleum ether yielded 1.30 g. (90%) of light yellow crystals of **6a**, m.p. 70–75°. The analytical sample was obtained by crystallization from petroleum ether and had m.p. 81–82°; λ_{max} 242 mμ (ϵ 27,500), 248 infl. (25,000), 275 infl. (7,700), and 327 2800; 2.84, 5.94, and 6.28 μ (CH_2Cl_2). N.m.r. showed bands at τ 6.0, 6.99 and aromatic protons.

Anal. Calcd. for $C_{21}H_{16}O_2$: C, 83.98; H, 5.37. Found: C, 83.63; H, 5.40.

9,10-Dihydro-9-hydroxy-9-(*o*-methylbenzyl)-10-ketophenanthrene (**6b**).—After irradiation of 1.94 g. of phenanthrenequinone in 50 ml. of *o*-xylene at reflux under nitrogen with a General Electric S-4 lamp for 13 hr., the reaction mixture was filtered to remove a small amount (107 mg.) of phenanthrene quinhydrone; and the filtrate adsorbed on 100 g. of Florisil. Elution with 90% benzene–petroleum ether and pure benzene afforded 1.72 g. (66%, 90% based on recovered phenanthrenequinone) of **6b**, m.p. 152–154° (lit.[2] m.p. 149°). The melting point was unchanged after crystallization from benzene–petroleum ether. **6b** had λ_{max} 242 mμ (ϵ 27,000), 248 infl. (24,000), 275 infl. 8900, and 327 (2900); 2.86 and 5.93 μ (KBr). N.m.r. showed bands at τ 6.0, 6.94 (doublet, spacing 5 c.p.s.), 8.06, and aromatic protons.

Elution with ethyl acetate yielded 0.66 g. of phenanthrenequinone.

9,10-Dihydro-9-hydroxy-9(*m*-methylbenzyl)-10-ketophenanthrene (**6c**).[21]—Irradiation of 1.82 g. of phenanthrenequinone in 50 ml. of *m*-xylene for 12 hr. and chromatography as described for the *ortho* isomer afforded 1.72 g. (65%, 95% based on recovered phenanthrenequinone) of **6c** as nearly white crystals, m.p. 90–92°. The analytical sample was obtained by crystallization from benzene–petroleum ether and had m.p. 96–97°; λ_{max} 242 mμ (ϵ 25,500), 248 infl. (23,000), 275 infl. (7900), and 327

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[21] Experiment was performed by Mr. R. M. Kopchik.

(2800); 2.82 and 5.94 μ (KBr). N.m.r. showed bands at τ 6.0, 7.02, 7.80, and aromatic protons.

Anal. Calcd. for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 83.89; H, 5.87.

Elution with ethyl acetate yielded 0.64 g. of phenanthrenequinone.

9,10-Dihydro-9-hydroxy-9-(*p*-nitrobenzyl)-10-ketophenanthrene (6e).—A mixture of 1.0 g. of phenanthrenequinone and 6.0 g. of *p*-nitrotoluene in 50 ml. of benzene was irradiated for 47 hr. when all the quinone had dissolved. After removal of benzene, the brown product was chromatographed on 200 g. of Florisil. Elution with 3 l. of 2% ethyl acetate in benzene afforded 440 mg. (38%, 85% based on recovered phenanthrenequinone) of yellow crystals, m.p. 166–172°. The analytical sample was obtained by crystallization from 1:1 benzene–petroleum ether as nearly white crystals, m.p. 176°; λ_{max} 244 mμ (ε 29,600), 250 (29,000), 279 (18,000), and 325 infl. (4000); 2.82, 6.00, 6.28, 6.66, 7.50 μ (KBr). N.m.r. showed bands at τ 1.9–3.1, 5.9 and 6.90.

Anal. Calcd. for $C_{21}H_{15}NO_4$: C, 73.03; H, 4.38; N, 4.06. Found: C, 72.73; H, 4.12; N, 4.17.

Elution of the column with ethyl acetate afforded 695 mg. of unreacted phenanthrenequinone.

Competition Reactions. A. Dioxane-*p*-Xylene.—A solution of 0.500 g. (2.5 mM) of phenanthrenequinone, 325 mg. (3.7 mM) of dioxane, and 382 mg. (3.7 mM) of *p*-xylene made up to 50 ml. with benzene was irradiated under the usual conditions for 5 hr. After removal of solvent under reduced pressure, the residue was chromatographed on 40 g. of Florisil. The column was eluted with three 250-ml. fractions of 90% benzene–petroleum ether [234 (pure 1), 76, and 30 mg.]: one fraction of benzene (23 mg.), one fraction of 1% ethyl acetate–benzene (84 mg., pure 6d), and pure ethyl acetate (141 mg., phenanthrenequinone). Individual fractions were analyzed from their ultraviolet spectra using ϵ_{310} 10,400 and ϵ_{325} 900 for 1 and ϵ_{310} 2620 and ϵ_{325} 3600 for 6d. The total amount of 1 obtained was 322 mg. (43.5%) and of 6d was 125 mg. (16%), corresponding to a molar ratio of 2.73:1.

B. Benzaldehyde–*p*-Xylene.—A solution of 0.350 g. (1.75 m*M*) of phenanthrenequinone, 0.322 g. (3 m*M*) of freshly distilled benzaldehyde, and 5.168 g. (48.8 m*M*) of *p*-xylene made up to 50 ml. with benzene was irradiated for 2 hr. After concentration under reduced pressure on the steam bath, the residue was chromatographed on 30 g. of Florisil. Elution with 500 ml. of 30% benzene in petroleum ether gave 20 mg. of amorphous material; 500 ml. of 50% benzene in petroleum ether and 500 ml. of pure benzene gave 298 mg. of white crystals; additional benzene eluted only traces of material; and ethyl acetate afforded 117 mg. of recovered phenanthrenequinone. The ultraviolet spectrum of the crystalline material was determined in dioxane solution (0.0199 mg./ml.); optical densities were 4.61 at 306 mμ and 1.28 at 325 mμ. The yields, calculated using ϵ_{306} 9000 and ϵ_{325} 2500 for 4 and ϵ_{306} 1500 and ϵ_{325} 3600 for 6d, were 220 mg. (42%) of 4 and 75 mg. (14%) of 6d. Corrected for the sixteenfold excess of *p*-xylene used, the relative rates were 48:1 (benzaldehyde–*p*-xylene). Infrared spectra of mixtures exhibited the characteristic features of 4 and 6d.

In a comparable experiment, the ratio was 36:1 after 3-hr. irradiation.

Attempted Determination of the Composition of the Photostationary State in the *p*-Xylene–Phenanthrenequinone Reaction. A. Forward Reaction.—A solution of 413 mg. (1.98 m*M*) of phenanthrenequinone and 209 mg. (1.98 m*M*) of *p*-xylene in 100 ml. of benzene was irradiated in the usual manner and 20-ml. aliquots were withdrawn after 21 and 41 hr. After removal of solvent under reduced pressure, the residues (104 and 106 mg.) were chromatographed on 6 g. of Florisil and four fractions were collected. Fraction 1, eluted with petroleum ether and 30% benzene in petroleum ether consisted of unidentified oils having no selective ultraviolet absorption. Fraction 2, eluted with 30 and 90% benzene in petroleum ether and pure benzene, consisted of the adduct 6d (the amount was checked by ultraviolet analysis). Fraction 3, eluted with ethyl acetate, consisted of phenanthrenequinone, and fraction 4, eluted with methanol, consisted of phenanthrene quinhydrone. The mixture after 21 hr. contained 22 mg. of fraction 1, 48 mg. of fraction 2, 21 mg. of fraction 3, and 8 mg. of fraction 4. After 41 hr. the corresponding quantities were 30, 28, 19, and 19 mg.

B. Reverse Reaction.—Irradiation of a solution of 622 mg. (1.98 m*M*) of 6d followed by analysis as described above gave the following results: after 24 hr. (117-mg. total wt.), 33, 44, 11, and 13 mg.; after 48 hr. (118 mg.), 29, 34, 15, and 17 mg.; and, after 72 hr. (110 mg.), 21, 29, 18, and 22 mg. A sample of the solution after 48-hr. irradiation was chromatographed on a silicone oil column (DC-200) at 100°. The only peak observed (except for solvent benzene) had a retention time of 5.2 min. identical with the retention time observed under the same conditions with an 0.5% solution of *p*-xylene in benzene.

Photoirradiation of 9,10-Dihydroxyphenanthrene Monobenzoate (4).—A solution of 100 mg. of 4[1b] in 50 ml. of benzene was irradiated for 9 hr. After removal of solvent the residue was chromatographed on 5 g. of Florisil. Elution with 80 and 90% benzene in petroleum ether and pure benzene afforded 30 mg. of recovered 4a. Elution with ethyl acetate gave 23 mg. (34%) of phenanthrenequinone, m.p. 205–208°.

9-Dioxanyloxy-10-(*p*-Methylbenzyloxy)phenanthrene (11) and 9-Dioxanyloxy-9-(*p*-methylbenzyl)-10-keto-9,10-dihydrophenanthrene (12).—A mixture of 500 mg. of dioxane–phenanthrenequinone adduct (1), 260 mg. of *p*-methylbenzyl chloride, and 234 mg. of anhydrous potassium carbonate in 10 ml. of dry acetone was refluxed with stirring for 29 hr. After removal of the acetone under reduced pressure, the residue was treated with dilute hydrochloric acid and benzene. The organic layer was separated, washed with water and saturated salt solution, dried over anhydrous magnesium sulfate, and concentrated to dryness under reduced pressure on the steam bath. Crystallization of the residue from 5 ml. of petroleum ether gave 480 mg. (71%) of 11, m.p. 109–112°. The analytical sample of 11 was obtained by crystallization from benzene–petroleum ether and had m.p. 114–115°; λ_{max} (dioxane) 280 mμ infl. (ε 10,500), 293 (10,500), 305 (10,900), 324 infl. (520), 340 (810), and 357 (840); 6.18, 6.25, and no absorption at 2.5–3.05 μ (CH_2Cl_2). N.m.r. showed bands at τ 5.65 (multiplet), 6.00, 6.92–7.10 (complex absorption), 8.16, and complex absorption at 2–3.

Anal. Calcd. for $C_{26}H_{24}O_4$: C, 77.98; H, 6.04; mol. wt., 400. Found: C, 77.34; H, 6.07; mol. wt., 386.

The crude product (2.8 g.) from reaction of 2.2 g. of 1 as above was chromatographed on 150 g. of Florisil. Elution with 2 l. of 1:1 benzene–petroleum ether afforded 2.0 g. (67%) of 11. Elution with ethyl acetate gave 0.383 g. (13%) of 12 as an orange oil which could not be obtained crystalline and which had λ_{max} (dioxane) 330 mμ (ε 2900); 5.95 and 6.28 μ (CH_2Cl_2). N.m.r. showed bands at τ 5.5 (multiplet), 6.0–6.5 (complex absorption), 7.02, and 7.85.

Hydrolysis of 9,10-Dihydro-9-dioxanyloxy-9-(*p*-methylbenzyl)-10-ketoanthrene (12).—A solution of 570 mg. of crude 12 in 50 ml. of methanol was treated with 20 drops of concentrated hydrochloric acid. After 15 min. at 50°, the acid was neutralized by addition of solid sodium bicarbonate, the solution was diluted with 50 ml. of water, and methanol was removed under reduced pressure on the steam bath. The aqueous residue was worked up in the usual manner affording a crude product which was crystallized once from petroleum ether to give 402 mg. (90%) of light yellow solid, m.p. 100–110°, identical by infrared spectral comparison with 6d.

9,10-Dihydroxyphenanthrene Mono(*p*-methylbenzyl) Ether (2). A. From 11.—A solution of 2.0 g. of 11 in 200 ml. of methanol containing 3 ml. of concentrated hydrochloric acid was heated at 50° for 0.5 hr. Excess solid sodium bicarbonate was added followed by 10 ml. of water and the solution was concentrated under reduced pressure. The oily residue was extracted with ethyl acetate which was then washed with water and saturated salt solution, dried over anhydrous sodium sulfate, and concentrated to dryness under reduced pressure on the steam bath. The residue was chromatographed on 80 g. of Florisil. Elution with 2 l. of 1:9 benzene–petroleum ether gave 0.85 g. (54%) of 2, m.p. 63–64°; λ_{max} (dioxane) 272 mμ infl. (ε 12,700) 299 (7200), 309 (7200), 330 infl. (700), 347 (1000), and 363 (1100); 2.80, 6.15, and 6.25 μ (CH_2Cl_2). N.m.r. showed bands at τ 6.0 and 8.18. A portion was crystallized from petroleum ether to give the analytical sample as white crystals, m.p. 72–73°. This material was stable in an inert atmosphere at 0–5° C. but darkened rapidly in air and became gummy after less than 1 day.

Anal. Calcd. for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 83.45; H, 5.81.

Elution of the column with ethyl acetate furnished 0.15 g. of phenanthrenequinone.

B. From 4.—A mixture of 630 mg. of benzaldehyde–phenanthrenequinone adduct (4), 310 mg. of *p*-methylbenzyl chloride, and 280 mg. of anhydrous potassium carbonate in 10 ml. of dry acetone was refluxed with stirring for 23 hr. After removal of acetone under reduced pressure, the residue was dissolved in benzene and washed with dilute hydrochloric acid; the aqueous layer was washed with three portions of benzene. The combined benzene solutions were washed with water and saturated salt solution, dried over anhydrous sodium sulfate solution, and concentrated under reduced pressure on the steam bath. The residue (524 mg., 2.8, 5.95, 6.18 and 6.28 μ) was chromatographed on 25 g. of Florisil. Elution with 150 ml. of 20% and 200 ml. of 30% benzene–petroleum ether afforded 66 mg. (10%) of **2**, identical by infrared analysis with material described above.

Elution with 200 ml. of 50% and 150 ml. of 80% benzene–petroleum ether gave 121 mg. (19%) of **6d**, m.p. 115–125°, identical by infrared analysis with authentic sample.

Finally, elution with ethyl acetate gave 146 mg. of phenanthrenequinone.

9-Methoxy-10-(*p*-methylbenzyloxy)phenanthrene (**13**).—A mixture of 500 mg. of **2** from Florisil chromatography, 250 mg. of methyl iodide, and 220 mg. of anhydrous potassium carbonate in 7 ml. of acetone was refluxed with stirring for 46 hr. After removal of acetone under reduced pressure, the residue was treated with dilute hydrochloric acid which was then extracted with benzene. The benzene layer was washed with water and saturated salt solution, dried over anhydrous sodium sulfate, and concentrated under reduced pressure on the steam bath. One crystallization of the crude product from methanol gave 460 mg. (88%) of **13**, m.p. 85–89°. Further crystallization from methanol furnished the analytical sample, m.p. 87–89°; λ_{max} (dioxane) 292 mμ (ϵ 10,000), 305 (12,000), 324 (900), 341 (1200), and 358 (1200); 6.15, 6.25, and no absorption at 2.5–3.1 μ (CH_2Cl_2). N.m.r. showed bands at τ 5.97, 6.82, 8.18, and complex absorption at 2–3.

Anal. Calcd. for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14. Found: C, 83.75; H, 6.66.

Photoirradiation of 9,10-Dihydroxyphenanthrene Mono(*p*-methylbenzyl) Ether (**2**).—A solution of 132 mg. of **2** in 21 ml. of benzene was irradiated for 10 hr. at 30° in a nitrogen atmosphere. The yellow solution was then taken to dryness under reduced pressure on the steam bath and the residue chromatographed on 6 g. of Florisil. Eluion with increasing proportions of benzene in petroleum ether to pure benzene afforded a series of amorphous fractions (88-mg. total), which were analyzed from their ultraviolet spectra. The early fractions consisted predominantly of starting material **13** and the later fractions were mainly **6d**; the yields were 36 mg. (28%) of **2** and 43 mg. (33%) of **6d**.

A comparable experiment in which **13** was irradiated for 19 hr. afforded 27% of crystalline **6d**, m.p. 118–126°, identical by infrared analysis with an authentic sample. Only a trace of unreacted **13** could be detected in this experiment.

9-Dioxanyloxy-10-methoxyphenanthrene (**16**).—A mixture of 2.0 g. of the adduct **1**, 1.0 g. of methyl iodide, and 0.9 g. of anhydrous potassium carbonate in 20 ml. of acetone was refluxed for 26 hr. with stirring. The crude product obtained by work-up similar to that described for the preparation of **11** was chromatographed on 100 g. of Florisil. Elution with 2.5 l. of 50%, 500 ml. of 70%, and 500 ml. of 90% benzene in petroleum ether afforded 1.59 g. (76%) of crystalline **16**, m.p. 78–79°. The analytical sample of **16** was obtained by crystallization from petroleum ether and had m.p. 80–81°; λ_{max} (dioxane) 272 mμ infl. (ϵ 19,000), 281 infl. (12,000), 293 (11,000), 304 (12,000), 326 infl. (500), 341 (850), and 357 (850); 6.15, 6.25, and no absorption at 2.5–3.1 μ (CH_2Cl_2). N.m.r. showed bands at τ 4.42 (broad), 5.86–6.28 (complex), 6.00, and complex absorption 2–3.

Anal. Calcd. for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85. Found: C, 73.64; H, 5.92.

Further elution with pure benzene and ethyl acetate afforded 255 mg. of yellow oil (λ_{max} 2.84, 5.8, and 6.25 μ), which could not be induced to crystallize.

9,10-Dihydroxyphenanthrene Monomethyl Ether (**17**).—A solution of 794 mg. of **16** in 70 ml. of methanol was treated with 1 ml. of concentrated hydrochloric acid at 50° for 15 min. Work-up as described for the preparation of **13** gave 480 mg. (83%) of crystalline **17**, m.p. 106–107° (lit.[17] m.p. 103°); λ_{max} 255 mμ (ϵ 44,000), 272 infl. (13,000), 298 (7400), 308 (7200), 330 infl. (1100), 346 (1200), and 362 (1100); 2.83, 6.18, 6.28 μ (CH_2Cl_2). N.m.r. showed bands at τ 6.04 and complex absorption 2–3. This compound was considerably more stable than **2** but darkened in color after several months.

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The Separation of Ketimine Isomers[1,2]

STANLEY C. BELL, GEORGE L. CONKLIN, AND SCOTT J. CHILDRESS

Wyeth Laboratories, Inc., Philadelphia 1, Pennsylvania

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The separation of the geometric isomers of ketimines derived from 2-amino-5-chlorobenzophenone has been achieved by fractional crystallization. Configuration has been assigned by relating ultraviolet absorption spectra of the ketimine isomers with those of the corresponding oximes. The validity of this approach is discussed.

The separation of the geometric isomers of ketimines[3] has been claimed a number of times in the past. A review of these claims appeared in the recent paper of Curtin and Hausser[4] wherein the evidence for the presence of both *syn* and *anti* forms of some benzophenone methylimines was given. However, these authors were able to separate only one form of each imine as a stable solid. We have accomplished the preparation and separation of both forms of a number of substituted benzophenone imines. The orientation of the isomers has been established by comparison of their ultraviolet absorption spectra with those of related oximes of known configuration.[5]

The reaction between a number of *o*-aminobenzophenones and a group of primary amines led in several cases to mixtures of two products. The preparations were carried out by heating the reactants together in the presence of zinc chloride. A solvent such as xylene was used to permit azeotropic removal of the water formed as a by-product. Fractional crystallization of

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[1] Presented at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April, 1964.

[2] A preliminary communication has appeared: S. C. Bell, G. L. Conklin, and S. J. Childress, *J. Am. Chem. Soc.*, **85**, 2868 (1963).

[3] A review on imines has recently been published: R. W. Layer, *Chem. Rev.*, **63**, 489 (1963).

[4] D. Y. Curtin and J. W. Hausser, *J. Am. Chem. Soc.*, **83**, 3474 (1961).

[5] After this work had been completed, a publication appeared by G. Saucy and L. H. Sternbach [*Helv. Chim. Acta*, **45**, 2226 (1962)] that described both forms of 2-methylamino-5-trifluoromethylbenzophenone methylimine. These authors attributed the longer wave-length ultraviolet absorption band of their lower melting isomer to the expanded conjugation system arising from hydrogen bonding between $NHCH_3$ and $C{=}NCH_3$. We prefer the twisted ring explanation given in the present paper since *o*-dimethylaminobenzophenone, without hydrogen bonding, has λ_{max} 385 mμ and *o*-methylaminobenzophenone is only slightly shifted to λ_{max} 392 mμ [P. Grammaticakis, *Bull. soc. chim. France*, 93 (1953)].