Photooxidation of Hexamethylbenzene and Related Aromatic Systems

HARRY H. WASSERMAN,* PATRICK S. MARIANO, AND PHILLIP M. KEEHN

Department of Chemistry, Yale University, New Haven, Connecticut 06520

Received October 8, 1970

Hexamethylbenzene, when subjected to the conditions of dye-sensitized photooxidation in methanol-benzene, forms pentamethylbenzyl methyl ether (**2**), tetramethylphthalyl bismethyl ether (**3**), and tetramethylphthalide (**4**) in high yields. The diether **3** was shown to be a product of a second-stage photooxidation of the monoether **2**. Pentamethylbenzaldehyde yields tetramethylphthalide (**4**) under the above conditions. A mechanism for these transformations is discussed.

In earlier studies,[1] we have investigated the dye-sensitized photooxidation of aromatic compounds in the cyclophane series where steric constraints result in nonplanarity of the ring systems. In the above cases, reactions of the strained aromatic systems with singlet oxygen yielded transannular peroxides which then underwent solvolysis followed by intramolecular Diels–Alder reactions.

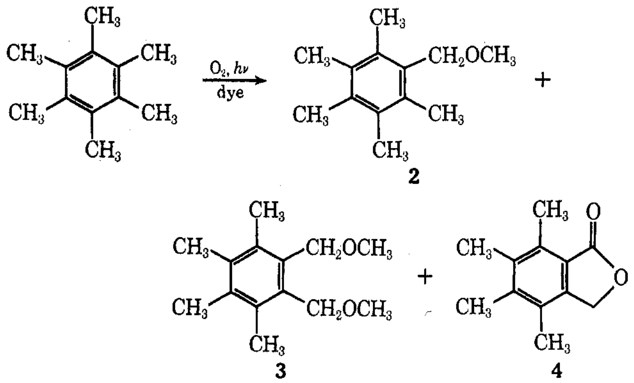
In other studies on the photooxidation of aromatic hydrocarbons, benzylic C–H groups have been oxidized,[2] phenolic systems have been hydroxylated,[3] and, in some instances, cleavage of the aromatic ring has taken place.[3] In general, the involvement of singlet oxygen in these oxidation processes has not been clearly demonstrated. In fact, the bulk of the observations may be explained in terms of a radical pathway in which the only role played by oxygen is that of a radical scavenger.[3,4] The present work describes our investigations on the dye-sensitized photooxidation of aromatic hydrocarbons containing benzylic carbon–hydrogen bonds in crowded environments.

Hexamethylbenzene, subjected to the conditions of methylene blue sensitized photooxidation in methanol–benzene (1:1) at room temperature, was converted in good yield to a mixture of three products, identified[5] on the basis of spectroscopic data as pentamethylbenzyl methyl ether (**2**, 36%), tetramethylphthalyl bismethyl ether (**3**, 42%), and tetramethylphthalide (**4**, 9%) (Scheme I).[6]

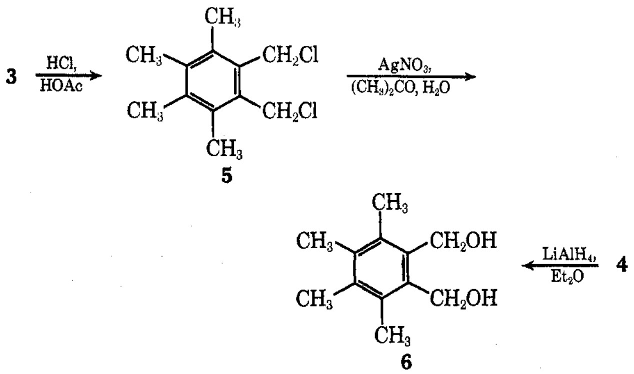
The structures **2**–**4** were confirmed by the following sequences. The bismethyl ether **3** was converted to the dichloride **5** which, on solvolysis, yielded the diol **6**. Compound **6** was identical (physical and spectroscopic properties) with the material obtained from the $LiAlH_4$ reduction of the phthalide **4** (Scheme II).

The monomethyl ether **2** was similarly converted to the monochloride **7** which underwent solvolysis to the benzyl alcohol **8**. Oxidation of the latter with MnO_2 yielded the benzaldehyde **9** (Scheme III).

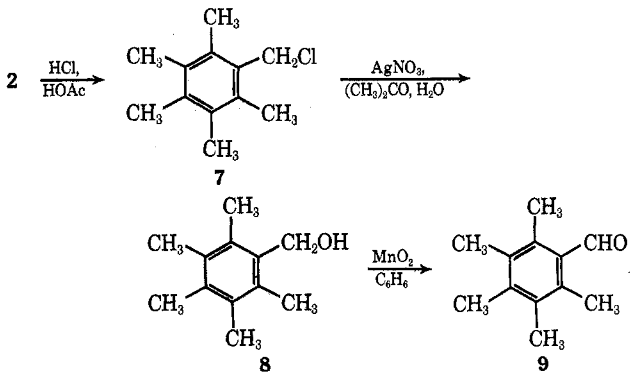
SCHEME I



SCHEME II



SCHEME III



Formation of products **2**–**4** in high yield by the above oxygenation is of interest not only in connection with the potential use of this reaction in synthesis but also in relation to possible analogies of these transformations with oxidations of aromatic nuclei in naturally occurring systems.[7] The following studies relate

---

[1] H. H. Wasserman and P. M. Keehn, *J. Amer. Chem. Soc.*, **88**, 4522 (1966); unpublished results on the photooxidation of *syn*-1,4-[2,2]-naphthalenophane.

[2] K. S. Wei and A. H. Adelman, *Tetrahedron Lett.*, 3297 (1969).

[3] T. Matsuura, N. Yoshimura, A. Nishinaya, and I. Saito, *ibid.*, 1669 (1969); T. Matsuura, A. Nishinaya, N. Yoshimura, and T. Arai, *ibid.*, 1673 (1969); I. Saito, S. Kato, and T. Matsuura, *ibid.*, 239 (1970).

[4] For a discussion of this type of process and pertinent references, see C. S. Foote, *Science*, **162**, 963 (1968).

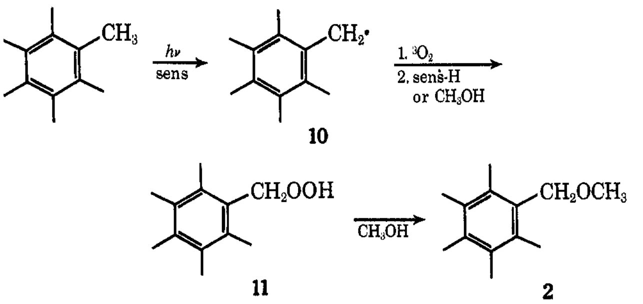
[5] Products were, in general, characterized by their nmr spectra and physical properties. Thus, for example, the bismethyl ether **3** shows a typical symmetrical pattern in the nmr for the four aryl methyl groups at τ 7.69 and 7.78 corresponding to the *o*- and *m*-methyls, respectively. The same pattern of absorption is shown for the methyl groups in the *o*-dichloride **5** (τ 7.62 and 7.75) and the diol **6** (τ 7.64 and 7.77).

[6] The yields given are based on unrecovered starting material.

[7] See, for example, J. W. Foster in "Oxygenases," Academic Press, New York, N. Y., 1962.

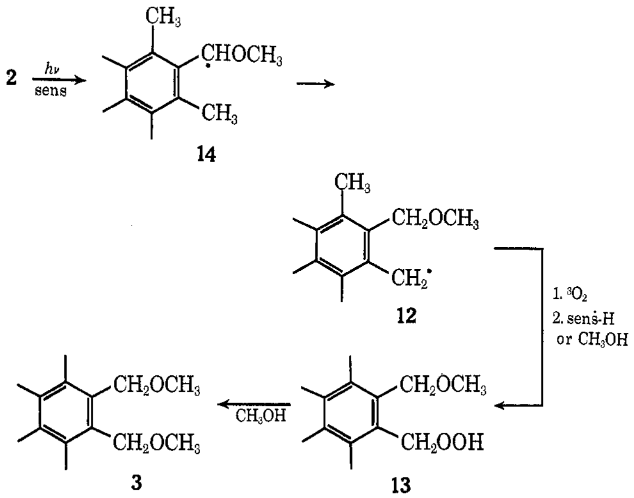
to the mechanism of this process. On varying the duration of photooxidation, we found that the yield of monomethyl ether **2**, higher at shorter times, varied inversely with that of the bismethyl ether **3**. Thus, 14-day oxidations yielded 36% **2** and 42% **3**, while 8-day reactions gave 82% **2** and 12% **3**. We have accordingly concluded that the bisether **3** arises *via* a second-stage photooxidation of the monoether **2**. This view was confirmed by the isolation of ether **2**, exclusively, in low conversion runs (20%, after 7 days). Furthermore, when pentamethylbenzyl methyl ether (**2**) was subjected to the condition of photooxidation, it was completely transformed to the tetramethylphthalyl bismethyl ether (**3**).[8]

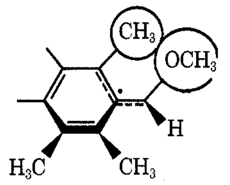
In the sequence below we suggest a mechanism for the production of the ether **2**.[9] Initial hydrogen abstraction with formation of the benzyl radical **10** is followed by uptake of triplet oxygen leading to the hydroperoxide **11**. Methanol solvolysis of the hydroperoxide then yields **2**.



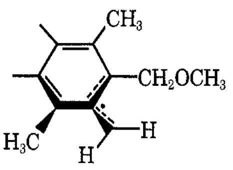
In the formation of tetramethylphthalyl bismethyl ether (**3**), initial abstraction of the most labile hydrogen (from $ArCH_2OMe$) could be followed by an intramolecular hydrogen transfer from the *o*-methyl group.[10] Subsequent oxygenation of the benzyl radical **12** and solvolysis of the intermediate hydroperoxide **13** would lead to the diether **3**.

The driving force for the 1,4 migration of hydrogen in the formation of **12** may be associated with the steric factors which bring about relatively less stabilization of the initially formed radical **14**. Thus, in **14**, the bulky methoxyl group may inhibit the achievement of coplanarity required for resonance stabilization of the radical by the aromatic ring as shown. The radical **12**, on the other hand, does not suffer from this steric restriction[11] and orbital overlap with the ring is more easily accomplished. It is also worth noting that approach of oxygen to **12** appears to be less hindered than the approach to **14**.





14



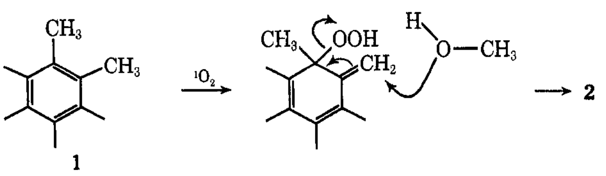
12

An important point which needs clarification in considering the above sequences is the nature of the initial hydrogen abstraction step, or more generally, the pathway for hydroperoxide formation. A high-energy C–H bond scission resulting from the excited state of hexamethylbenzene can be ruled out since the energy of light used is low[12] and the methylene blue sensitizer is present in sufficient concentration to permit no primary light absorption by the hydrocarbon. The triplet energy (33 kcal/mol) of the sensitizer is not sufficient to populate the "radical like" Σ^1 state of oxygen, therefore eliminating this species as the hydrogen abstractor. It was also possbile to demonstrate that triplet oxygen alone is not involved in the hydrogen abstraction process. Thus, in a control reaction when the oxygenation was carried out in the absence of light and sensitizer by bubbling oxygen through a methanol–benzene solution of hexamethylbenzene for 10 days at 50°, only starting material was recovered. Based on the above considerations we suggest that the excited triplet state of the sensitizer, methylene blue, may be the agent affecting

---

[8] Surprisingly, no products of further oxidation were found when the bismethyl ether **3** was subjected to the photooxidation conditions for 9 days.

[9] Since it is known that singlet oxygen is generated under the conditions of the reaction, one may not rigorously exclude the possibility of an "ene" type singlet oxygen addition mechanism for the formation of **2**, involving hydroperoxide formation followed by reaction with solvent, as shown.



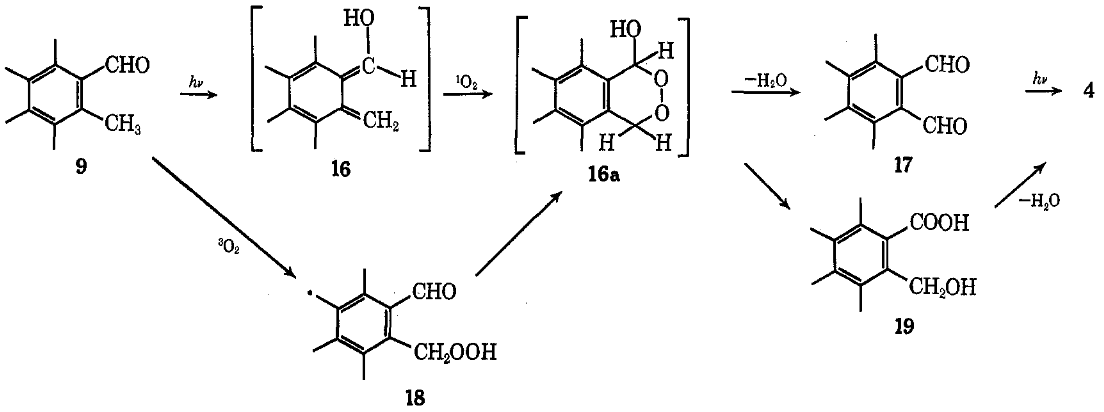
While there do not appear to be examples of the participation of an aromatic double bond in this type of oxygenation, it is conceivable that the extra crowding in hexamethylbenzene may render the system more susceptible to the ene reaction with singlet oxygen. In line with this view, we have observed that **1** undergoes photooxidation much more readily than either xylene or toluene. We thank a referee for drawing our attention to the above possibility.

[10] Radical isomerizations due to 1,4- and 1,5-hydrogen transfer reactions were first reported by A. Kossiakoff and F. Rice [*J. Amer. Chem. Soc.*, **65**, 590 (1943)] and more recently by V. B. Sefton and D. J. LeRoy, *Can. J. Chem.*, **34**, 41 (1956).

[11] L. Michaelis, M. P. Schubert, and S. Granick, *J. Amer. Chem. Soc.*, **61**, 1981 (1939), have found similar effects on the rates of radical cation (Würster salt) formation of various phenylene diamines due to steric factors.

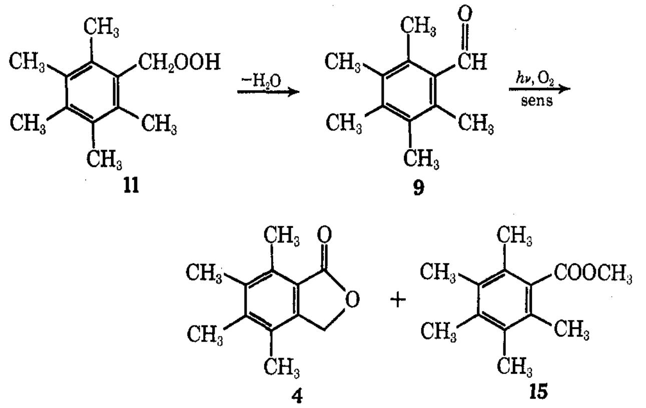
[12] Pyrex flasks were used so that light of wavelength lower than *ca.* 300 mμ is essentially filtered out.

SCHEME IV



hydrogen abstraction.[13] This possibility has been proposed by Foote[4] and Matsuura[3] for related systems.

Reasonable pathways may be suggested for the production of tetramethylphthalide (**4**). One route involves a secondary photooxidation of the probable intermediate, pentamethylbenzaldehyde (**9**), formed by dehydration of the hydroperoxide **11**.



Precedent for this type of conversion of *o*-methylphenones to phthalides under conditions of photooxidation is found in the work of Yates and coworkers.[15] Along the lines of Yates' rationale (Scheme IV), photoenolization of **9** to **16** would be followed by uptake of oxygen (presumably in singlet form) to yield the transannular peroxide **16a** which could then decompose to the dialdehyde **17**, convertible on photolysis to **4**. In this connection we have observed that **9** may be photooxidized to a mixture of the tetramethylphthalide **4** (55%) and the ethyl ester **15** (38%) under the usual conditions employed in the above oxygenation reactions. On the other hand, one would not expect our conditions to favor the photoenolization of **9** to **16** since, in the region of irradiation (>300 mμ), almost all of the light (*ca.* >99%) would be absorbed by the methylene blue. Furthermore, energy transfer from methylene blue (E_t = 33 kcal/mol) to the benzaldehyde (E_S = 72 kcal/mol) is unlikely. We therefore suggest that another process may be involved in the conversion of **9** to the hydroxy acid **19**. In this sequence, hydrogen abstraction from an *o*-methyl group leads to a radical which reacts with triplet oxygen to form the hydroperoxide **18**. Cyclization of **18** leads to **16a** which decomposes to the dialdehyde **17**. The latter, on further irradiation, rearranges to **4**. Alternatively, **16a** may break down to the hydroxy acid **19** which could then lactonize to **4**.

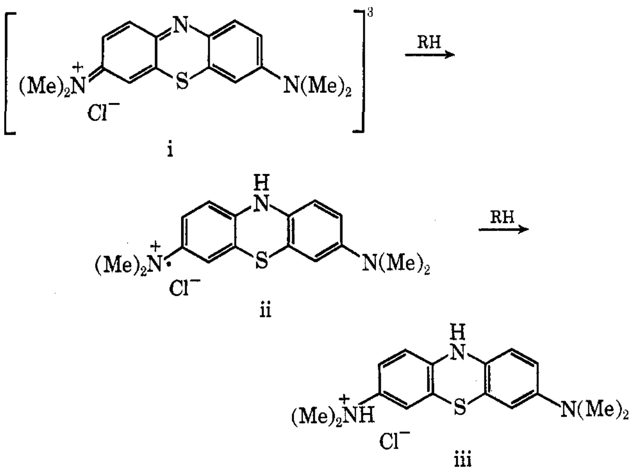
In the course of these studies we have noted a marked dependency of the oxidation reactions on the polarity of the medium. Thus, changes of solvent from methanol to methylene chloride resulted in a drastically reduced efficiency, whereby only 19% conversion to ethers **2** and **3** took place after 10 days, while only a trace of phthalide **4** was formed. By contrast, in 1:1 methanol–benzene, 93% conversion to products was observed. Similar diminished efficiency resulted when the methanol content of the solvent was reduced, although the ether to phthalide ratio remained the same. We are continuing our studies on these and related oxidation reactions in order to clarify the role of oxygen and solvent in the transformations.

Experimental Section

Photooxidation of Hexamethylbenzene.—Pure, dry oxygen was passed through a stirred, cooled (25°) solution of 1.000 g of

---

(13) Hydrogen abstraction by the triplet excited state of methylene blue (i) should be a favorable process,[4] since the radical cation formed (ii) would have a high degree of delocalization of the odd electron. Analogous systems, like the Würster salts, having a similar electronic and atomic constitution, are known to possess high stability. This rationale would also account for the efficient bleaching of methylene blue during the photooxidation of systems containing easily abstractable hydrogen atoms (1,4-cyclohexadiene and 1,4,5,8-tetralin), since transfer of a hydrogen atom to the radical cation (ii) would lead to the amine hydrochloride (iii).[14]



(14) Photobleaching of methylene blue by water has been studied by Y. Usui, H. Obata, and M. Koizumi, *Bull. Soc. Chem. Jap.*, **34**, 1049 (1961).

(15) P. Yates, A. C. MacKay, and F. X. Garmeaux, *Tetrahedron Lett.*, 5389 (1968); see also S. A. Pappar and J. E. Blackwell, *ibid.*, 3337 (1968).

hexamethylbenzene (Aldrich Chemical Co.) and 0.050 g of methylene blue in 700 ml of 1:1 methanol–benzene while irradiating with a 275-W sun lamp for 14 days. Concentration of the solution *in vacuo* gave an oil which was subjected to column chromatography on silica gel (Davison, grade 923, 100–200 mesh). Elution with benzene gave 0.116 g (11%) of recovered hexamethylbenzene.

Elution with 25% ether–benzene gave 0.368 g (31%) of a crystalline material, mp 65–67° (from 95% methanol), which was characterized as pentamethylbenzyl methyl ether on the basis of the following spectral and physical properties: nmr ($CDCl_3$) τ 5.50 (s, 3 H, methylene), 6.61 (s, 3 H, methoxyl), 7.68 (s, 6 H, *o*-methyls), 7.80 (s, 9 H, *m*- and *p*-methyls); ir (KBr) 3.54, 9.01 μ; mass spectrum *m/e* 192 (P), 176, 161 ($-OCH_3$), 160, 146 ($-CH_3OCH_3$). *Anal.* Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 80.98; H, 10.19.

Elution with 50% ether–benzene gave 0.499 g (37%) of a crystalline solid, mp 71–73° (from 95% methanol), which was characterized as tetramethylphthalyl bismethyl ether on the basis of the following spectral and physical properties: nmr ($CDCl_3$) τ 5.47 (s, 4 H, methylenes), 6.56 (s, 6 H, methoxyls), 7.69 (s, 6 H, *o*-methyls), 7.78 (s, 6 H, *m*-methyls); ir ($CHCl_3$) 3.55, 9.10 μ; mass spectrum *m/e* 222 (P), 190 ($-CH_3OH$), 165, 150, 137. *Anal.* Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.82; H, 10.22.

Elution with chloroform gave 0.087 g (8%) of a crystalline solid, mp 224–226° (from 95% methanol), which was characterized as tetramethylphthalide on the basis of the following spectral and physical properties: nmr ($CDCl_3$) τ 4.87 (s, 2 H, methylene), 7.35 (s, 3 H, *o*-methyl to C=O), 7.69 (s, 6 H, *o*-methyl and *p*-methyl to C=O), 7.78 (s, 3 H, methyl); ir (KBr) 5.75, 8.93, 9.86 μ; mass spectrum *m/e* 190 (P), 162 ($-CO$), 161, 133. *Anal.* Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.99; H, 7.76.

Irradiation, utilizing the above conditions, with the exception of shortening the time to 8 days, gave, after column chromatography, the following: recovered hexamethylbenzene, 0.049 g (5%); pentamethylbenzyl methyl ether, 0.913 g (78%); tetramethylphthalyl bismethyl ether, 0.184 g (11%).

Irradiation, utilizing the above conditions, with the exception of using a 100-W flood lamp for 16 days gave the following: pentamethylbenzyl methyl ether, 0.656 g (49%); tetramethylphthalyl bismethyl ether, 0.716 g (52%).

When the solvent for photooxidation was changed to 1:9 methanol–benzene, the product ratio after 8 days was as follows: recovered hexamethylbenzene, 0.834 g (83%); pentamethylbenzyl methyl ether, 0.165 g (14%); tetramethylphthalide, 0.029 g (1%).

Attempted Autoxidation of Hexamethylbenzene.—A solution of 0.50 g of hexamethylbenzene in 500 ml of 1:1 methanol–benzene was heated at 50° while pure, dry oxygen was passed through for 10 days. All light was rigorously excluded. Concentration *in vacuo* yielded a crystalline solid, shown by its spectral and physical properties to be unreacted hexamethylbenzene.

Photooxidation of Pentamethylbenzyl Methyl Ether (2).—Pure, dry oxygen was passed through a stirred, cooled (25°) solution of 1.750 g of pentamethylbenzyl methyl ether and 0.050 g of methylene blue in 700 ml of 1:1 methanol–benzene while irradiating with a 275-W sun lamp for 9 days. Concentration *in vacuo* gave an oil which was subjected to column chromatography on silical gel (Davison, grade 923, 100–200 mesh). Elution with 25% ether–benzene gave 1.605 g (86%) of tetramethylphthalyl bismethyl ether, characterized by its known spectral and physical properties (*vide supra*).

Photooxidation of Tetramethylphthalyl Bismethyl Ether (3).—Pure, dry oxygen was passed through a stirred, cooled (25°) solution of 0.300 g of tetramethylphthalyl bismethyl ether and 0.050 g of methylene blue while irradiating with a 250-W sun lamp for 9 days. Concentration of the solution *in vacuo* gave recovered, pure starting diether, mp 65–70°, with no traces of other products detectable by nmr, tlc, glc, or mass spectrum.

Photooxidation of Pentamethylbenzaldehyde (9).—Pure, dry oxygen was passed through a stirred, cooled solution of 100 mg of pentamethylbenzaldehyde (*vide infra* for preparation) and 50 mg of methylene blue in 200 ml of 1:1 methanol–benzene while irradiating with a 275-W sun lamp for 10 days. The solvent was removed *in vacuo* giving an oil which was subjected to preparative layer chromatography (2-mm silica gel plates) giving the following results. Cut 1 (R_f 0.75) gave 57 mg (38%) of an oil characterized as methyl pentamethylbenzoate by the following spectral properties: nmr ($CDCl_3$) τ 6.71 (s, 3 H, methoxyl), 7.83 s and 7.86 s (15 H, methyls); ir (CS_2) 3.40, 3.45, 5.82, 7.85, 9.07, 10.5, 13.6 μ; mass spectrum *m/e* 206 (P), 175 ($-CH_3O$), 154, 147 ($-CO_2CH_3$), 134, 119, 94. Cut 2 (R_f 0.35) gave 61 mg (55%) of a crystalline solid, mp 224–226°, the spectral properties of which were indistinguishable from those of tetramethylphthalide obtained above.

Pentamethylbenzyl Chloride (7).—To a stirred solution of 1.40 g of pentamethylbenzyl methyl ether in 20.0 ml of glacial acetic acid at 22° was added 5.0 ml of concentrated hydrochloric acid. A crystalline precipitate appeared instantaneously which was separated by filtration and dissolved in ether. The ethereal solution was washed with water, dried, and concentrated *in vacuo* giving a white crystalline solid. Recrystallization from hexane gave 1.32 g (93%) of pure pentamethylbenzyl chloride, mp 80–82°, which has the following spectral and physical properties: nmr ($CDCl_3$) τ 5.26 (s, 2 H, methylene), 7.63 (s, 6 H, *o*-methyls), 7.75 (s, 9 H, *m*- and *p*-methyls); ir (CS_2) 3.35, 3.43, 7.30, 7.30, 7.75, 7.93, 12.6, 13.5, 14.9 μ; mass spectrum *m/e* 198 and 196 (P), 162 and 160 ($-HCl$), 147 ($-CH_2Cl$), 130, 128. *Anal.* Calcd for $C_{12}H_{17}Cl$: C, 73.28; H, 8.71. Found: C, 73.23; H, 8.92.

Pentamethylbenzyl Alcohol (8).—A solution of 1.30 g of pentamethylbenzyl chloride and 3.00 g of silver nitrate in 50.0 ml of 50% aqueous acetone was stirred at 22° for 2.0 hr, after which time a voluminous white precipitate had formed. Ether was added and the ethereal layer separated by filtration, washed with water, dried, and concentrated *in vacuo* giving a crystalline white solid. Recrystallization from 1:1 benzene–hexane gave 0.95 g (79%) of pure pentamethylbenzyl alcohol, mp 162–163°, which has the following spectral and physical properties: nmr ($CDCl_3$) τ 5.28 (s, 2 H, methylene), 7.68 (s, 6 H, *o*-methyls), 7.78 (s, 9 H, *m*- and *p*-methyls), 8.46 (br s, 1 H, hydroxyl); ir ($CHCl_3$) 2.78, 2.92 br, 3.34, 3.44, 6.90, 7.25, 7.73, 9.07, 10.5, 10.9 μ; mass spectrum *m/e* 178 (P), 161 ($-OH$), 160 ($-H_2O$), 149, 147, 136, 134, 119, 105, 91. *Anal.* Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.63; H, 10.03.

Pentamethylbenzaldehyde (9).—A solution of 0.50 g of pentamethylbenzyl alcohol in 150 ml of dry benzene with 5.00 g of suspended, freshly prepared manganese dioxide was heated at 85° under nitrogen for 5.0 hr, cooled, and filtered through Celite. The resulting benzene solution was concentrated *in vacuo* giving a crystalline solid. Recrystallization from hexane gave 0.42 g (86%) of pure pentamethylbenzaldehyde, mp 148–150°, which has the following spectral and physical properties: nmr ($CDCl_3$) τ 0.60 (s, 1 H, aldehyde), 7.65 (s, 6 H, *o*-methyls), 7.80 (s, 3 H, *p*-methyl), 7.83 (s, 6 H, *m*-methyls); ir ($CHCl_3$) 3.33, 3.43, 3.64, 5.95, 6.20, 6.90, 7.22, 7.86, 9.28, 11.75 μ; mass spectrum *m/e* 176 (P), 175, 161 ($-CH_3$), 149, 147 ($-CHO$), 133, 119, 115, 105, 91. *Anal.* Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.55; H, 9.26.

Tetramethylphthalyl Dichloride (5).—Tetramethylphthalyl bismethyl ether (1.00 g) was treated under the same conditions described above for the monoether **2** to monochloride **7** conversion yielding, after recrystallization from hexane, 0.85 g (83%) of pure tetramethylphthalyl dichloride, mp 133–135°, which has the following spectral and physical properties: nmr ($CDCl_3$) τ 5.20 (s, 4 H, methylenes), 7.62 (s, 6 H, *o*-methyls), 7.75 (s, 6 H, *m*-methyls); ir (CHCl) 3.40, 6.45, 7.70, 8.00, 10.0, 10.5 μ; mass spectrum *m/e* 232 and 230 (P), 197, 196, and 195 ($-Cl$), 160 ($-2Cl$), 130, 115, 91. *Anal.* Calcd for $C_{12}H_{16}Cl_2$: C, 62.35; H, 6.98. Found: C, 62.10; H, 7.02.

Tetramethylphthalyldiol (6).—Tetramethylphthalyl dichloride (0.85 g) was reacted under same conditions described above for the monochloride **7** to monoalcohol **8** conversion yielding, after recrystallization from benzene, 0.76 g (93%) of pure tetramethylphthalyldiol, mp 173–175°, which has the following spectral and physical properties: nmr (acetone-d_6) τ 5.17 (s, 4 H, methylenes), 6.52 (br s, 2 H, hydroxyls), 7.64 (s, 6 H, *o*-methyls), 7.76 (s, 6 H, *m*-methyls); ir ($CHCl_3$) 2.79, 2.98 br, 3.35, 3.46, 6.15, 6.39, 7.76, 8.15, 9.39, 10.25, 10.50 μ; mass spectrum *m/e* 194 (P), 193, 175 ($-H_3O$), 160 ($-H_2O_2$), 146 132, 104, 90. *Anal.* Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.00; H, 9.01.

Lithium Aluminum Hydride Reduction of Tetramethylphthalide.—To a suspension of 0.50 g of lithium aluminum hydride in 50.0 ml of anhydrous ether was added a solution of 0.05 g of tetramethylphthalide in 10.0 ml of anhydrous ether. After addition, the solution was stirred for 1.0 hr at 22° and quenched with water. The ether layer was separated, dried, and concentrated *in vacuo* yielding a crystalline solid which after recrystallization from benzene gave 0.04 g of pure material, mp 171–173°, whose spectral and physical properties were indistinguishable from those of tetramethylphthalyldiol prepared by another route (*vide supra*).

Registry No.—**2,** 20145-50-0; **3,** 29002-53-7; **4,** 29002-54-8; **5,** 29002-55-9; **6,** 3205-92-3; **7,** 484-65-1; **8,** 484-66-2; **9,** 17432-38-1; **15,** 28195-45-1; hexamethylbenzene, 87-85-4.

Acknowledgment.—This work was supported in part by Grant GM-13854 from the National Institutes of Health. One of us (P. S. M.) would like to thank the National Institutes of Health for a postdoctoral fellowship.

The Pschorr Reaction by Electrochemical Generation of Free Radicals. I. Phenanthrene Synthesis

R. M. ELOFSON* AND F. F. GADALLAH

Contribution No. 530 from the Research Council of Alberta, Edmonton 7, Alberta, Canada

Received November 23, 1970

Diazonium tetrafluoroborates of 2-amino-α-(R-phenyl)cinnamic acids have been reduced electrolytically at 0 V *vs.* sce and nonelectrolytically in aprotic solvents to produce substituted and nonsubstituted phenanthrene-10-carboxylic acids in near-quantitative yields. These cyclized products were produced by other methods in lower yields. The efficacy of a homolytic pathway through generation of phenyl σ radicals by a number of schemes is discussed.

Pschorr and Pschorr-like reactions have been the subject of numerous investigations since they were discovered by Graebe and Ullman[1] in 1894 and Pschorr[2] in 1896. These reactions are of importance not only as synthetic tools but from a mechanistic viewpoint as well. De Tar[3] and others[4–6] have pointed out that some of these reactions appear to proceed by a heterolytic and others by a homolytic pathway. We have recently developed a new route to intermolecular arylation by the electrochemical reduction of diazonium salts in aprotic solvents.[7] Since this method, as carried out in our laboratories, occurs under mild conditions, 0°, and goes by exclusively homolytic pathway, we decided to investigate two intramolecular reactions (*i.e.*, phenanthrene and fluorenone synthesis) to obtain improved yields and/or new information on mechanisms. How far we have succeeded with these objectives in cyclization to phenanthrene is the subject of this paper.

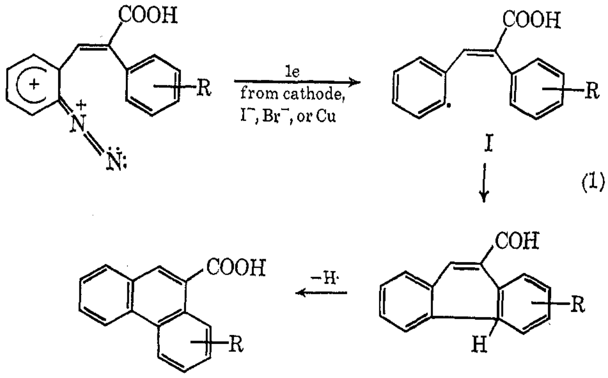
Results

The results of electrochemical reduction of diazonium salts of 2-amino-α-arylcinnamic acids are presented in Table I. For comparison, results of cyclizations of the same diazonium salts in aqueous fluoroboric acid (with and without copper) are included, as are results of one reduction of diazotized unsubstituted acid using iodide ion as the reducing agent, and, finally, results from other laboratories.

Yields from the electrochemical method were consistently high. Examination of products by melting points and infrared and mass spectral analysis gave no indication of by-products from such usual side reactions as replacement of the diazonium with hydrogen or fluoride ions. Substitution by hydroxyl group, not anticipated in an aprotic medium, was absent. Substituent effects on yields were insignificant within limits of experimental error incurred during isolation of products. The iodide ion cyclization also gave an excellent yield but about 10% of the by-product, 2-iodo-α-phenylcinnamic acid, was recovered. Replacing iodide with bromide gave high yields of cyclization comparable to the iodide reaction. The low (62%) yield obtained from cyclization by heating with aqueous fluoroboric acid was increased to 93% by the addition of copper powder.

Discussion

Intermolecular arylations by electrochemical reduction of benzenediazonium tetrafluoroborate in acetonitrile and monosubstituted benzenes produced considerable amounts of benzene (50–60%) due to abstraction of hydrogen atoms from the solvent.[7] No detectable hydrogen abstraction or dimerization occurred during intramolecular arylation of cinnamic acid derivatives, suggesting that conditions strongly favored cyclization (eq 1).



(1)

For the unstrained α-phenylcinnamic acid molecule, Hey and Mulley[8] have calculated the distance between positions to be linked by intramolecular bond formation to be 1.5 Å, and, hence, very favorable to cyclization. Since 1.5 Å applies only to the molecular configuration in which the rings are coplanar, the lifetimes of the

---

(1) C. Graebe and F. Ullmann, *Ber.*, **27**, 3483 (1894).

(2) R. Pschorr, *ibid.*, **29**, 496 (1896).

(3) D. F. De Tar, *Org. React.*, **9**, 409 (1957).

(4) G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, London, 1960.

(5) R. Huisgen and R. E. Zahler, *Ber.*, **96**, 736 (1963).

(6) R. A. Abramovitch, *Advan. Free-Radical Chem.*, **2**, 87 (1966).

(7) F. F. Gadallah and R. M. Elofson, *J. Org. Chem.*, **34**, 3335 (1969).

(8) D. H. Hey and R. D. Mulley, *J. Chem. Soc.*, 2276 (1952).