

a singlet of the type of form II, referred to⁶ as the "charge-transfer" band. Addition of hydrogen chloride to the 2-propanol solution leads to no change in the 249-m μ band, but to marked decrease of the band at 352 m μ . The pK_a of DMABP, estimated from the decrease in this absorption with addition of hydrogen chloride, is 1.7 in 2-propanol. At 2 *N* HCl the long wave length band is at 344 m μ and of low intensity ($\log \epsilon$ 2.25), comparable to the corresponding band of benzophenone at 334 m μ ($\log \epsilon$ 2.18); it appears to arise from an $n-\pi^*$ transition which leads to a chemically reactive state, presumably the triplet.⁸

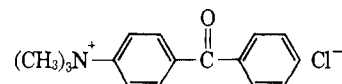
Photoreduction of 0.1 *M* DMABP in 2-propanol in Pyrex by a G. E. 85W A3 ultraviolet lamp proceeds very slowly, about 0.003 the rate of benzophenone. The rate however rises regularly with addition of hydrogen hydrochloride, while the absorption at long wave length decreases, leveling at *ca.* 0.7 *N* HCl at a rate about 0.2 that of benzophenone, indicating a quantum yield of about 0.4. The rate of photoreduction of benzophenone in 2-propanol is unaffected by 0.5 *N* HCl. The rate of photoreduction of DMABP in 2-propanol appears to rise more rapidly than the "charge-transfer" band is suppressed with addition of hydrogen chloride, indicating that the ground state may be a weaker base than is the $n-\pi^*$ excited triplet. In 1:1 2-propanol-water the rate of photoreduction of DMABP is negligible and is again greatly increased by addition of hydrogen chloride. Higher concentrations of the acid are required to reach maximum rate of photoreduction than in the absence of water, reflecting the lower protonating power of the aqueous system. Water reduces the maximum rate of photoreduction of DMABP and also that of benzophenone itself, effects which will be described in a subsequent report.

The product of photoreduction of 0.1 *M* DMABP in 0.5 *N* HCl in 2-propanol, formed quantitatively, is 4,4'-bis(dimethylaminobenzpinacol) dihydrochloride, m.p. 150-154° dec. This was converted quantitatively to the free base, m.p. and m.m.p. 181-183°, identical with an authentic sample prepared by reduction of DMABP by magnesium-magnesium iodide.⁹ *Anal.* Calcd. for $C_{30}H_{32}N_2O_2$: C, 79.7; H, 7.08; N, 6.19. Found: C, 80.0; H, 7.10; N, 6.21. The pinacol was readily distinguished from *p*-dimethylaminobenzhydrol, m.p. 66°, prepared by reduction of the ketone by sodium borohydride. *Anal.* Calcd. for $C_{15}H_{17}NO$: C, 79.3; H, 7.40; N, 6.16; mol. wt. 227. Found: C, 79.5; H, 7.24; N, 6.19; mol. wt. 230.

Preliminary experiments have shown that *p*- and *o*-aminobenzophenone are also reduced readily in 2-propanol in the presence of acid. A 0.01 *M* solution of the *para* compound was reduced less than 7% in the absence of hydrogen chloride after irradiation for 24 hr. and was completely reduced in less than this time in the presence of 0.5 *N* HCl. *o*-Aminobenzophenone, 0.01 *M*, showed no reduction after irradiation for 17 hr. in the absence of acid and was almost completely reduced after irradiation for 1 hr. in the presence of 0.5 *N* HCl. The *ortho* compound is of particular interest since its reduction might normally be prevented

both because of an unreactive low triplet of structure related to that of form II and because of intramolecular hydrogen abstraction related to photoionization.¹⁰ The observed photoreduction in acid medium indicates that the *o*-NH₃⁺ group, unlike -CH₃, does not transfer hydrogen rapidly to the oxygen of the $n-\pi^*$ triplet-carbonyl group, and that the latter is relatively positive and its activity in hydrogen atom abstraction is electrophilic in character.

Since this work is part of a study of photoreduction and its inhibition by sulfur compounds¹¹ in aqueous media, we have prepared the quaternary methochloride from DMABP, 4-benzoylphenyltrimethylammonium chloride, m.p. 187-189° dec. *Anal.* Calcd. for C_{16}



$H_{18}NOCl$: C, 69.3; H, 6.53; N, 5.08; Cl, 13.0. Found: C, 69.3; H, 6.42; N, 5.17; Cl, 13.1. It showed λ_{max} 340 m μ ($\log \epsilon$ 2.20), presumably due to an $n-\pi^*$ transition, similar to that of benzophenone, and no high intensity long wave length absorption characteristic of the unquaternized and unprotonated aminoketones. This quaternary compound was also readily photoreduced in 1:1 2-propanol-water, at a rate about 0.35 that of benzophenone in this solvent pair, with estimated quantum yield *ca.* 0.25.

(10) N. C. Yang and C. Rivas, *ibid.*, **83**, 2213 (1961).

(11) S. G. Cohen, S. Orman, and D. A. Laufer, *ibid.*, **84**, 3905 (1962).

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RECEIVED AUGUST 21, 1964

Homolytic Aromatic Substitution. V.¹ Phenylation of Phenanthrene

Sir:

Electrophilic and homolytic aromatic substitutions of phenanthrene have been investigated to evaluate predictions, based on molecular orbital theory, that the reactivities of the five positions in this arene follow the sequence 9 > 1 > 4 > 3 > 2.² For example, nitration has been found to give the order 9 > 1 > 3 > 2 > 4,³ and homolytic phenylation with two sources (benzoyl peroxide and diazoaminobenzene) has been reported to correspond to the sequence 9 > 1 > 3 > 2.⁴ The latter studies failed to reveal 4-phenylphenanthrene among products from either source, and steric hindrance has been suggested by way of explanation. We now report that the reactions of phenanthrene with three sources of phenyl radicals, including diazoaminobenzene, produce the 4-isomer in substantial amounts and that at least one source yields 4-phenylphenanthrene in amounts that are indicative of steric

(1) Paper IV: S. C. Dickerman, M. Klein, and G. B. Vermont, *J. Org. Chem.*, in press; paper III: S. C. Dickerman, A. M. Felix, and L. B. Levy, *ibid.*, **29**, 26 (1964).

(2) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961.

(3) M. J. S. Dewar, T. Mole, and E. W. T. Warford, *J. Chem. Soc.*, 3531 (1956), and earlier papers.

(4) A. L. J. Beckwith and M. J. Thompson, *ibid.*, 73 (1961).

(8) G. S. Hammond and W. M. Moore, *J. Am. Chem. Soc.*, **81**, 6334 (1959).

(9) M. Gomberg and W. E. Bachman, *ibid.*, **49**, 241 (1927).

acceleration rather than retardation. Other findings are relevant to problems concerning mechanisms of homolytic aromatic substitution.

Authentic samples of the five phenylphenanthrenes were prepared by the photochemical method of Mallory and co-workers⁵ and were used to establish that g.l.c. would suffice for individual analysis of the 4-, 3-, and 2-isomers and for mixtures of 9- and 1-phenylphenanthrenes. Meerwein, N-nitrosoacetanilide, and diazoaminobenzene phenylations of phenanthrene were studied and gave the data presented in Table I. The identity and homogeneity of that reaction product which has the same retention time as authentic 4-phenylphenanthrene were confirmed by ultraviolet and infrared analysis of samples collected from the gas chromatograph. Infrared analysis also served to establish the presence of both the 9- and 1-isomers in the single peak exhibited by these compounds.

Examination of the data in Table I reveals that all three sources of phenyl radicals produce 4-phenylphenanthrene in amounts up to a third of the total.

TABLE I

HOMOLYTIC PHENYLATION OF PHENANTHRENE^a

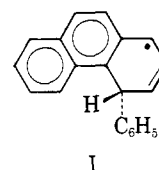
Source ^b	Temp., °C.	Solvent	Isomers, %				Con- version, ^c %	Recov- ery ^d %
			9 + 1	4	3	2		
M	30	Acetone ^e	56	31	7.4	5.8	4.3	97
NAA	30	Acetone ^e	56	24	11	8.2	0.34	82
NAA	30	Benzene	56	21	13	11	3.5	101
NAA	4	Benzene	61	15	12	12		
NAA	60	Benzene	57	25	10	7.6		
DAB	156	Bromo- benzene	53	23	15	10		
DAB	152	None ^f	44	28	16	12		

^a Analyses by g.l.c. with a probable error of 4–5% per 100. ^b M (Meerwein), NAA (N-nitrosoacetanilide), DAB (diazoaminobenzene). ^c Conversion to phenylphenanthrenes based on phenanthrene. ^d Recovery of phenanthrene as phenanthrene and phenylphenanthrenes. ^e Plus 20 vol. % water and 2.8 vol. % benzene. ^f Essentially a duplicate of the reaction conditions employed by Beckwith and Thompson.⁴

In fact, Meerwein phenylation must correspond to a reactivity sequence $9 > 4 > 1 > 3 > 2$ or $4 > 9 > 1 > 3 > 2$. Such discrepancy with theory is similar to that observed in studies of rates of deuterioprotonation and basicities of phenanthrene and phenanthrene-like hydrocarbons.⁶ Steric acceleration has been suggested to account for these results and we infer that relief of nonbonded interaction is the most reasonable explanation for the enhanced reactivity of the 4,5-positions of phenanthrene in homolytic phenylation. Although steric acceleration has not been observed previously in reactions of radicals with aromatic hydrocarbons, it is not entirely unexpected in view of earlier work which has indicated that addition of aryl radicals must be directed essentially perpendicular to the nodal plane.^{7,8}

The data in Table I provide a direct comparison of radical sources and reveal that Meerwein and N-

nitrosoacetanilide phenylations of phenanthrene, in aqueous acetone and at 30°, do not yield identical mixtures of phenylphenanthrenes. Differences of this kind may arise through the intervention of side reactions which selectively alter the composition of isomers.^{9,10} Such side reactions have not been detected in Meerwein phenylations of anthracene, although other radical sources invariably yield dimers, etc.⁸ The mechanism of Meerwein arylation of arenes has been discussed,⁸ and the absence of these types of side reactions has been attributed to the presence of an internal oxidizing agent, cupric chloride, which efficiently aromatizes intermediate radicals, e.g., I. On the other hand, the mechanism of N-nitrosoacetanilide phenylation is not well understood. Recent



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developments may be summarized as follows: (a) the cage mechanism has been eliminated from consideration,^{11,12} (b) evidence of induced decomposition has been given,¹¹ and (c) an analogy has been drawn to the diazoanhydride mechanism of the Gomberg-Bachmann reaction.¹³ A noncage mechanism for N-nitrosoacetanilide phenylation, accompanied by side reactions, offers an explanation for the observed differences in isomer distribution of phenylphenanthrenes between this and Meerwein phenylation (Table I). Isolation of 1,4-dihydrobiphenyl from decompositions of N-nitrosoacetanilide in benzene at 60° confirms the occurrence of such reactions, at least at this temperature, and provides additional evidence against the cage mechanism.¹⁴

The effect of temperature on the reactions of N-nitrosoacetanilide with phenanthrene in benzene was investigated and it was found that an increase in temperature favored formation of 4-phenylphenanthrene largely at the expense of the 3- and 2-isomers (Table I). These results are unusual in that an increase in reaction temperature is normally accompanied by an increase in those isomers whose formation requires the largest energies of activation. Present speculations concerning the origin of the temperature effect include the more favorable entropy of activation associated with formation of radical I relative to the isomeric intermediates and/or to changes in the selectivity of the side reactions.

(9) These side reactions involve dimerization and disproportionation of intermediate radicals and were discovered in peroxide arylations of benzene; D. F. DeTar and R. A. Long, *ibid.*, **80**, 4742 (1958).

(10) Whether such side reactions selectively alter the "true" composition of isomeric biaryls has been a subject of considerable controversy. The original presumption of general selectivity, which was based on a *priori* reasoning, has been shown to be incorrect through a comprehensive study of peroxide arylations of derivatives of benzene: R. T. Morrison, J. Cazes, N. Samkoff, and C. A. Howe, *ibid.*, **84**, 4152 (1962). Present findings indicate that each system must be evaluated separately, that is, the absence of selective side reactions in arylations of derivatives of benzene does not imply that such reactions will not alter the composition of phenylphenanthrenes or *vice versa*.

(11) D. B. Denney, N. E. Gershman, and A. Appelbaum, *ibid.*, **86**, 3180 (1964).

(12) E. L. Eliel and J. G. Saha, *ibid.*, **86**, 3581 (1964).

(13) C. Rüchardt and E. Merz, *Tetrahedron Letters*, 2431 (1964).

(14) S. C. Dickerman and N. Milstein, unpublished results.

(5) F. B. Mallory, C. S. Wood, and J. T. Gordon, *J. Am. Chem. Soc.*, **86**, 3094 (1964).

(6) G. Dallinga, P. J. Smit, and E. L. Mackor in "Steric Effects in Conjugated Systems," G. W. Gray, Ed., Butterworths and Co., London, 1958, Chapter 13; see also ref. 2, p. 344.

(7) H. Weingarten, *J. Org. Chem.*, **26**, 730 (1961).

(8) S. C. Dickerman and G. B. Vermont, *J. Am. Chem. Soc.*, **84**, 4150 (1962).

Acknowledgments.—We are indebted to Professors Mallory and Newman for generous gifts of authentic samples of 9- and 2-phenylphenanthrenes and to the former for detailed procedures in advance of publication. We also wish to thank Dr. Robert Gore of the Perkin-Elmer Corp. for technical assistance.

(15) This investigation was supported by a Public Health Predoctoral Fellowship (5F1-GM-22, 577-02) from the National Institute of General Medical Sciences.

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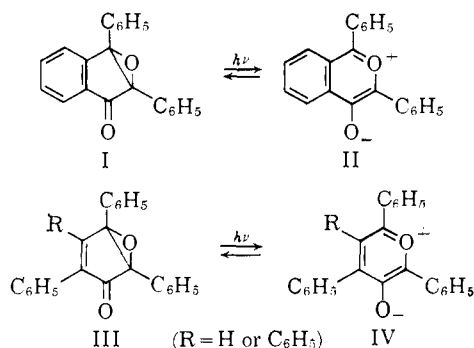
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RECEIVED AUGUST 13, 1964

Photochemical Valence Tautomerization Mechanism of Indenone and Cyclopentadienone Oxides. III

Sir:

Reversible photochemical valence tautomerizations have recently been described for 2,3-diphenylindenone oxide (I)^{1a} and the cyclopentadienone oxides III, R = H^{1b} and R = C₆H₅,^{1c} with the red pyrylium oxides II and IV, R = H and C₆H₅, respectively. We now describe data bearing on the mechanism of these reactions.



The indenone oxide I exists in thermal equilibrium with II ($K_{II/I}^{25^\circ} = 7 \times 10^{-5}$) in deoxygenated benzene. Irradiation (365 mμ) in this solvent produces a photostationary state, II/I = 0.097, which slowly diminishes on prolonged exposure. Addition of enough benzophenone (triplet energy, $E_T = 68.7$ kcal.)² to absorb initially most of the light produces shifts in the photostationary state, up to II/I = 0.35, which appear limited by the direct unsensitized photochemical reconversion to I of the strongly absorbing II ($\epsilon_{365\text{m}\mu}$ 7800) and by thermal reconversion of II to I. Sensitizers of lower triplet energies (<68 kcal.) in sufficient quantities to absorb nearly all the light no longer sensitize the forward reaction and thus produce complete bleaching by sensitized reaction of II.³ These data suggest that II can be formed from triplet

(1) (a) E. F. Ullman and J. E. Milks, *J. Am. Chem. Soc.*, **84**, 1316 (1962); *ibid.*, **86**, 3814 (1964); (b) E. F. Ullman, *ibid.*, **85**, 3529 (1963); (c) J. M. Dunston and P. Yates, *Tetrahedron Letters*, 505 (1964).

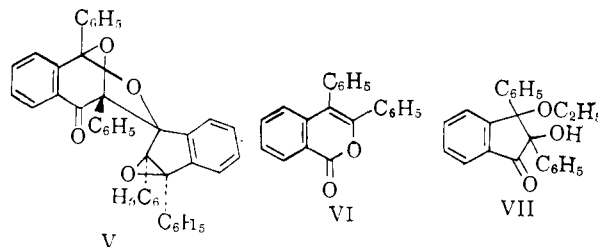
(2) G. S. Hammond and J. Saltiel, *J. Am. Chem. Soc.*, **84**, 4883 (1962).

(3) Additives having $E_T \leq 68$ kcal. which did not absorb light such as fluorene (E_T 68 kcal.)⁴ and naphthalene ($E_T = 60.5$ kcal.)⁴ were without effect, showing that the described phenomena are due to sensitization rather than quenching processes. As would be expected, when benzophenone was also added, these additives in high concentration competed successfully with I for triplet energy and behaved similarly to other low-energy sensitizers.

(4) D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949).

I (T_1) which is populated by sensitizers having $E_T > 68$ kcal., i.e., $E_{T_1} \geq 68$ kcal. Moreover, I can be formed from T_{II} , where $E_{T_{II}} < 50$ kcal. since T_{II} must be less energetic than singlet II ($E_{S_{II}} \leq 50$ kcal. = 570 mμ).⁵

On prolonged unsensitized irradiation (365 mμ) of benzene or ethanol solutions of I there were formed the dimer V,^{1a} 3,4-diphenylisocoumarin (VI) and, in ethanol, the stereoisomeric ethers VII. The isocoumarin VI was found to arise exclusively from II. Thus on irradiation of a thermally equilibrated mixture



of I and II in hot (125°) ethanol using light (>450 mμ) absorbed only by II (i.e., population of S_{II}), high conversions to VI were obtained. Moreover, VI was not formed by irradiation (365 mμ) of I alone (i.e., population of S_I).⁶⁻⁸ Therefore, S_I does not rearrange to S_{II} , a precursor of the isocoumarin VI.

A less rigorous argument suggests that similarly T_I does not rearrange to T_{II} . On using sensitizers with progressively lower triplet energies an abrupt drop in the efficiency of sensitization of reaction I → II is observed at $E_{T(\text{sens})} \sim 68$ kcal. Thus, for example, a sharp change is observed in the benzophenone ($E_T = 68.7$ kcal.) sensitized photostationary state from II/I ≥ 0.35 down to II/I ≤ 0.001 on addition of fluorene ($E_T = 68$ kcal.).⁹ This striking behavior of reaction I → II toward small changes in sensitizer triplet energy stands in sharp contrast to the slow, erratic dropoff in sensitizer efficiency observed for reactions capable of sensitization by a process described as "nonvertical" energy transfer.¹⁰ This process, which probably involves sensitized triplet excitation and concerted rearrangement of the reactant to give a new triplet species, appears to be characteristic of photochemical reactions which proceed by exothermic triplet rearrangements.^{10,11} Since the process $T_I \rightarrow T_{II}$ is highly exothermic ($\Delta E_T > 12$ kcal.), such a nonvertical energy transfer process to give the lower energy T_{II} might be expected. The absence of this abnormal

(5) The lowest observable absorption maximum at -190° is given. This represents a maximum energy for the 0-0 band, since II showed no vibrational structure in the long wave length band.

(6) This was shown by irradiation of tritium-labeled indenone oxide (1) in the presence of norbornadiene, an efficient scavenger for 11a.^{1b} An isotopic dilution method was used to detect small quantities of isocoumarin VI in the presence of up to 98% yields of the norbornadiene adduct of 11.

(7) These results cannot presently be reconciled with the assumption of H. E. Zimmerman and R. D. Simkin [*Tetrahedron Letters*, 1847 (1964)] that 3-methyl-4-phenylisocoumarin is formed by direct photochemical rearrangement of 2-methyl-3-phenylindenone oxide.

(8) The ethers VII were likewise produced only from 11 but in a multistep process which does not shed light on the present problem.

(9) Cf. ref. 3.

(10) G. S. Hammond and J. Saltiel, *J. Am. Chem. Soc.*, **85**, 2516 (1963).

(11) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *ibid.*, **86**, 3197 (1964).