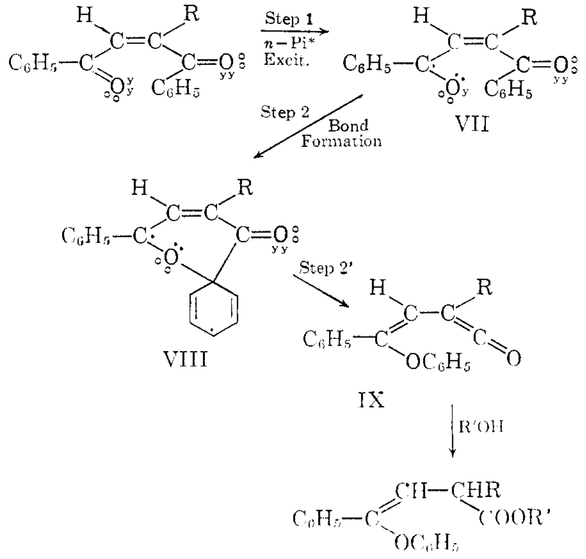
carbon atom to the C-2 carbonyl oxygen atom is reasonably formulated as proceeding *via* ketene precursors IX, which then react with ethanol and water to form the observed ester and acid products. Since filters cutting off light below 280 mμ were used in the present studies and the only absorption bands above this wavelength were n–Pi*, the photochemical reaction clearly originates with the n–Pi* excited states of the dibenzoylstyrene and dibenzoylethylene reactants.[6]

Application of the mechanistic treatment of n–Pi* reactions described earlier[1-3] leads to the sequence in Chart I. Here the odd electron-containing p_y oxygen orbital of the excited carbonyl group is envisaged as homolytically attacking the phenyl group of the second benzoyl group. Such a mechanism rationalizes the interesting selectivity in which only one of the two benzoyl phenyl groups of dibenzoylstyrene migrates. In the migration depicted in Chart I both the excited state VII (with R = C_6H_5) and the bridged intermediate VIII will have greater Pi electron delocalization than their counterparts, in which the second benzoyl group is excited and the alternative second phenyl group migrates.



II, R = C_6H_5, R' = Et
III, R = C_6H_5, R' = H
VI, R = H, R' = Et

Chart I

Further examples of this rearrangement as well as related mechanistic studies will be described in our full paper on the subject.

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[6] In any event, the n–Pi* state will be the lowest energy singlet. The same energy relationship of the triplet n–Pi* and Pi–Pi* states is probable but not certain.

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HOMOLYTIC PHENYLATION OF BENZENE, NAPHTHALENE AND ANTHRACENE IN THE PRESENCE OF COPPER SALTS. CORRELATION OF PARTIAL RATE FACTORS WITH LOCALIZATION ENERGIES[1]

Sir:

Previous correlations of theoretical indices with reactivity data for homolytic aromatic substitution have been limited to alkyl and trichloromethyl "affinities" of arenes.[2,3] Although the linearity of these relationships suggests validity, adequate test of theory requires knowledge of rates or relative rates of formation of specific compounds.

Previous publications,[4,5] which established that arylarene is a major product of Meerwein reactions with both anthracene and benene, provided a basis for the present investigation, *vide infra.* Thus phenylation was accomplished in aqueous acetone solution of arene or arenes, benzenediazonium chloride and cuprous and cupric chlorides, Table I. The reactivity of anthracene was also measured relative to naphthalene and is in excellent agreement with the value based on benzene, Table I, Runs 13–16. While both the orientation and reactivity data for anthracene are new, the phenylation of naphthalene has been studied previously using other methods of arylation and with conflicting results.[6] Since some of the analytical methods used earlier are now obsolete, we repeated the work of Huisgen and Grashey[7] and found that N-nitrosoacetanilide gives essentially the same orientation and reactivity data as the Meerwein reaction, Table I, Runs 25–28.

The partial rate factors for the 9-, 1- and 2-positions in anthracene and the 1- and 2- positions in naphthalene, calculated from the experimentally determined quantities in Table I, are 660, 55, 7.0, 22, and 3.2, respectively. A plot of the logarithms of these partial rate factors against the appropriate differences in radical localization energies[8] is linear with a slope corresponding to $\beta = -7.9$ kcal. (Fig. 1). Correlation of all positions in these arenes reinforces earlier evidence that the direction of radical attack is essentially perpendicular to the nodal plane[9] and enhances the prospects of using this β-value to predict partial rate factors, *etc.*, for homolytic phenylation of other polycyclic arenes.

Recent studies of the mechanism of the reaction of aroyl peroxides with benzene by DeTar and Long[10] and by Eliel, *et al.*,[11] have demonstrated that dimerization and other side-reactions of

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[1] Financial support from the Aeronautical Research Laboratory, Wright-Patterson Air Force Base and the assistance of M. Fryd are gratefully acknowledged.

[2] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, Chap. 11.

[3] Although free radical arylation has been studied extensively, polar factors in the usual substrates, derivatives of benzene, have frustrated attempts at theoretical interpretation; G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, New York, N. Y., 1960, Chap. 2.

[4] S. C. Dickerman, L. B. Levy and A. W. Schwartz, *Chem. and Ind.*, 360 (1958).

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[6] A review of the subject and a new determination of the total rate factor appeared recently; D. I. Davies, D. H. Hey and G. H. Williams, *J. Chem. Soc.*, 3112 (1961).

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TABLE I

ORIENTATION AND TOTAL REACTIVITY OF ANTHRACENE AND NAPHTHALENE IN HOMOLYTIC PHENYLATION[a]

Runs	Arene(s)[b]	Reaction[c]	Conversion	Recovery[d]	Orientation 9-	1-	2-	Total rate factor[e]
1–6	A	M			84.3 ± 0.5	14.0 ± 0.5	1.8 ± 0.1	
7–12	A,B	M	8 A	94 A	84.4 ± .8	13.9 ± .8	1.6 ± .1[f]	263 ± 18
13–16	A,N	M	34 A	82 A	84.6 ± .3	13.9 ± .4	1.6 ± .1[f]	16.2 ± 0.7[g]
			3 N	97 N		84.2 ± .7	15.8 ± .7	
17–20	N	M	2	90		87.1 ± .5	12.9 ± .5	
21–24	N,B	M	3 N	94 N		86.3 ± .8	13.7 ± .8	16.5 ± .5
25–28[h]	N,B	NNA	3 N	94 N		84.3 ± .4	15.7 ± .4	16.5 ± .6

[a] Analyses by G. L. C.; all data are expressed as percentages and represent averages of the indicated number of runs. [b] A (anthracene), B (benzene), N (naphthalene). [c] M (Meerwein reaction): benzenediazonium chloride, cuprous and cupric chloride in 80% aq. acetone at 25–26°; NNA (N-nitrosoacetanilide): benzene at 25–30°. [d] Arene plus phenylarenes. [e] Calculated from the ratio of the differential forms of the rate expressions using time average concn. of A and/or N. [f] Estimated. [g] A relative to N, compare calculated value of 15.9. [h] Huisgen and Grashey, ref. 7, report 79.5, 20.5 and 14.

arylcyclohexadiene radicals do occur and thus should contribute to the observed orientation and total reactivity in any competitive arylation. Although isolation of dimer from reactions of benzene and benzoyl peroxide is a relatively new development,[10] the formation of dimers in radical reactions involving the more reactive arene, anthracene, is well documented.[12a,b,c] In particular, Norman and Waters reported that reactions of anthracene with phenyl radicals, generated from benzenediazonium zincichloride with zinc dust (Waters reaction), yield comparable amounts of 9,10-diphenylanthracene and dimer, a bianthryl, but not 9-phenylanthracene. Since Meerwein arylations of anthracene routinely yield arylanthracenes and not dimers[4,13] it follows that copper salts must effectively suppress dimerization in a system prone to this side-reaction.

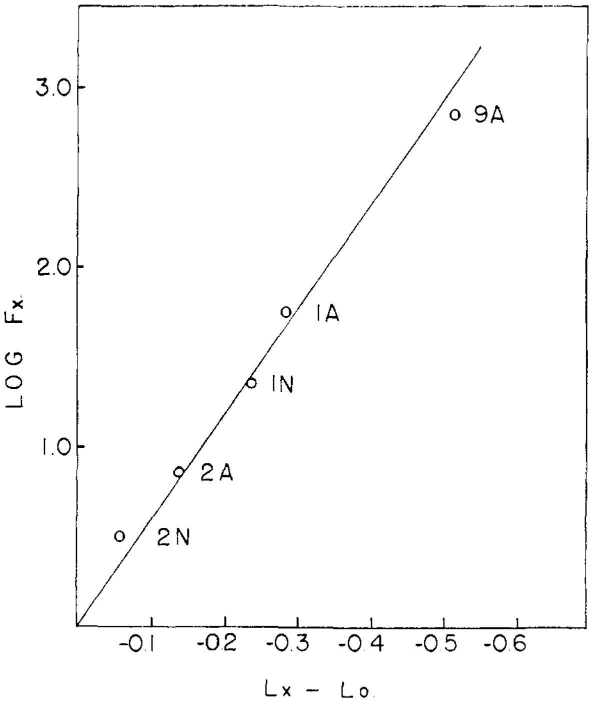

Fig. 1.—Partial rate factors for homolytic phenylation of anthracene (A) and naphthalene (N) against respective localization energies (L_X) minus that of benzene (L_0).

The first interpretation of the mechanistic roles of cuprous and cupric chlorides in these systems appeared in previous publications[14] and has now been incorporated by Kochi[15] into a comprehensive treatment of the effects of metal salts on reactions of radicals. The particular application indicated here is the ability of one or more species of cupric copper to convert intermediate radicals, *e.g.* the 10-phenyl-9,10-dihydro-9-anthryl radical, into phenylarene by oxidative elimination. A recent report by Eberhardt and Eliel[16] to the effect that the presence of oxygen virtually eliminates side-reactions in the system benzene–benzoyl peroxide is presumably another example of selective oxidation of intermediate radicals in which oxygen, rather than cupric chloride, acts as the oxidizing agent. The suggestion by these authors that orientation determined in the presence of oxygen should be more reliable than existing data has now been evaluated experimentally. Morrison and coworkers[17] have investigated the phenylation of a representative group of substituted benzenes both in the presence and absence of oxygen and have found no change in the partial rate factors. Obviously the dimerization and disproportionation reactions that occur in these peroxide arylations are non-selective with respect to both isomeric and competitive products. These findings not only reestablish the validity of much of the earlier peroxide work but also demonstrate that the occurrence of side-reactions in any homolytic arylation does not necessarily invalidate competitive rate data from that system.

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