Method of Determining O–D Shifts.—The method used was identical to that used by Searles and Tamres[24] in studying the hydrogen bonding abilities of ethers. A Perkin–Elmer model 12C double pass spectrometer, equipped with a lithium fluoride prisms was used for the determinations.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Reactions of Free Radicals with Aromatics. III. Isotope Effects in the Arylation of Deuterated Benzenes. The Mechanism of Arylation[1]

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Isotope effects have been determined for the free-radical arylation and alkylation of benzene-*d* and of benzene–benzene-d_6 mixtures with a variety of peroxides. In most cases isotope effects calculated from product deuterium content are in excess of unity. The benzene–benzene-d_6 mixture recovered from a chlorophenylation experiment (product isotope effect 1.3) is, however, unchanged in isotopic composition, indicating that the addition of the chlorophenyl radical to benzene to form an arylcyclohexadienyl radical is not freely reversible under the conditions of arylation. The product isotope effect is, therefore, ascribed to a competition between arylcyclohexadienyl radicals which go on to product biaryl and radicals which are diverted into side products (such as dimers), this competition being subject to isotopic discrimination. DeTar and Long (ref. 12) have shown that arylcyclohexadienyl radicals may disproportionate, at least in dilute solution, into arylbenzenes and aryldihydrobenzenes. In accordance with this it has now been shown that the apparent product isotope effect in biphenyl obtained from benzene-*d* and benzoyl peroxide in dilute solution is higher when the biphenyl is carefully separated from the dihydrobiphenyl than when the dihydrobiphenyl is allowed to be air-oxidized to biphenyl which becomes commingled with the primary biphenyl product. Biphenyl isolated under the latter circumstances contains biphenyl-d_2, as expected. Biphenyl-d_2 is formed also in the decomposition of benzoyl peroxide in benzene-*d* in relatively concentrated solutions, indicating that even under these conditions some biphenyl is formed by disproportionation of the phenylcyclohexadienyl intermediate, followed by dehydrogenation, rather than by direct hydrogen loss from the intermediate radical.

Introduction

The reaction of an aromatic compound with an aryldiazo acetate or hydroxide to give a biaryl was discovered almost simultaneously by Kühling[3] and by Bamberger.[4] Convenient experimental procedures for the reaction were developed by Gomberg and Bachmann[5] after whom the reaction is often named. A variation of the reaction in which the aromatic compound is allowed to react with an aroyl peroxide instead of a diazonium derivative was discovered by Gelissen and Hermans[6]; it is this variation which was studied exclusively in the present work. The free-radical character of the reaction was first recognized by Hey and Waters[7] whose school has contributed much fundamental information regarding the mechanism of the reaction.[8] Reference to their work and other pertinent publications through 1956 is found in recent reviews of the subject.[9,10] Several important papers have appeared since these reviews went to press.[8,11–13]

The sequence of events when benzoyl peroxide is decomposed in benzene has usually been considered to be the one shown in Fig. 1.

The first step in this reaction sequence is rate determining.[14] At low peroxide concentrations, this step is unimolecular, but at higher peroxide concentrations the reaction order increases, indicating the incursion of chain processes involving induced decomposition of peroxide.[14] That the second step is not concomitant with the first has been demonstrated by trapping the benzoate radicals generated in step one.[15] The third and fourth step represent the most interesting part of free-radical aromatic substitution since they are the steps which may be common to substitution reactions with such diverse radical sources as diaroyl peroxides, diazotates and nitrosoacetanilides. The finding that the isomer distribution (*ortho–meta–para* ratio) in the arylation of monosubstituted benzenes appears to be nearly independent of the nature of the radical source[9,16] suggests that step 3 is the same for all these arylations. This speaks against the possibility, sometimes suggested, that steps 2 and 3 are concomitant (extrusion of CO_2 during arylation).

The mechanism suggested above for the arylation reaction may be termed the "addition–abstraction mechanism." Two other mechanisms have been considered,[9b] namely the "abstraction–addition mechanism" and the "synchronous mech-

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[1] Paper II, S. H. Wilen and E. L. Eliel, THIS JOURNAL, **80**, 3309 (1958).

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[3] O. Kühling, *Ber.*, **28**, 41 (1895).

[4] E. Bamberger, *ibid.*, **28**, 403 (1895).

[5] M. Gomberg and W. E. Bachmann, THIS JOURNAL, **46**, 2339 (1924); *cf.* W. E. Bachmann and R. A. Hoffman in R. Adams, "Organic Reactions," Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1944, chap. 6.

[6] H. Gelissen and P. H. Hermans, *Ber.*, **58**, 285 (1925).

[7] D. H. Hey and W. A. Waters, *Chem. Revs.*, **21**, 169 (1937).

[8] Recent papers: (a) Chang Shih, D. H. Hey and G. H. Williams, *J. Chem. Soc.*, 1871 (1959); (b) B. R. Cowley, R. O. C. Norman and W. A. Waters, *ibid.*, 1799 (1959).

[9] (a) O. C. Dermer and M. T. Edmison, *Chem. Revs.*, **57**, 77 (1957); (b) D. R. Augood and G. H. Williams, *ibid.*, **57**, 123 (1957).

[10] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, Chapter 10.

[11] (a) B. M. Lynch and K. H. Pausacker, *Austral. J. Chem.*, **10**, 40 (1957); (b) K. H. Pausacker, *ibid.*, **10**, 49 (1957); (c) B. M. Lynch and K. H. Pausacker, *ibid.*, **10**, 165 (1957).

[12] D. F. DeTar and R. A. J. Long, THIS JOURNAL, **80**, 4742 (1958).

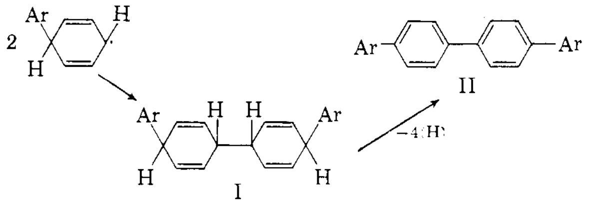
[13] A. L. J. Beckwith and W. A. Waters, *J. Chem. Soc.*, 1108 (1956); 1001, 1665 (1957); R. O. C. Norman and W. A. Waters, *ibid.*, 167 (1958); A. L. J. Beckwith, R. O. C. Norman and W. A. Waters, *ibid.*, 171 (1958); J. A. Kent and R. O. C. Norman, *ibid.*, 1724 (1959).

[14] K. Nozaki and P. D. Bartlett, THIS JOURNAL, **68**, 1686 (1946); B. Barnett and W. E. Vaughan, *J. Phys. Chem.*, **51**, 926 (1947).

[15] G. S. Hammond and L. M. Soffer, THIS JOURNAL, **72**, 4711 (1950).

[16] R. Hüisgen and R. Grashey, *Ann.*, **607**, 46 (1957).

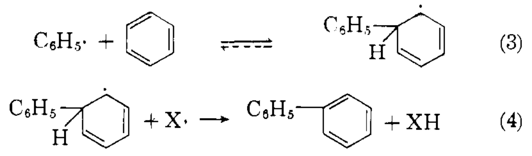
anism." In the "abstraction-addition mechanism," the phenyl (or benzoate) radical first abstracts a hydrogen atom from the aromatic substrate to produce an aryl radical which then couples with another phenyl radical to give a biaryl. Recent investigators have held this path to be unlikely on various grounds. Because of the large bond dissociation energy of the aromatic C–H bond, this mechanism would seem to entail an improbably high activation energy. For the same reason, it should give rise to a high isotope effect when deuterated substrates are used, whereas in fact the isotope effect is low or nil.[8a,17–19] Moreover, the aryl radicals formed from the substrate might be expected to couple to give a substrate-derived biaryl— for example, the decomposition of *p*-chlorobenzoyl peroxide in benzene should give biphenyl—but such substrate-derived biaryls are not found.[11] The "synchronous mechanism" is a limiting case of the "addition–abstraction mechanism" in which steps 3 and 4 are telescoped together. This mechanism appears unlikely in view of some of the side–products which have been isolated in arylation reactions. Thus the arylation of benzene gives rise to *p*-quaterphenyls[11] whose origin is most readily explained by assuming that the phenylcyclohexadienyl radicals appearing as products of step 3 above couple in the canonic forms shown[20] to give tetrahydro-*p*-quaterphenyls (I) which are then dehydrogenated to *p*-quaterphenyls (II). This path to the *p*-quaterphenyls has been elegantly confirmed by actual isolation of the tetrahydro intermediates.[12]



Brief mention must be made of the possibility that complexes may be essential intermediates in the arylation.[9b,21] It is now known that chlorine atoms[22,23] and, to a much lesser extent, *t*-butoxide radicals[24] form π-complexes with aromatic substrates and it is quite possible that aryl and methyl radicals do likewise. However, the fact, to be discussed below, that the essential intermediate in free-radical aromatic substitution is formed in a step which is not freely reversible under the conditions of the reaction speaks against such intermediate being a π-complex—unless one is willing to postulate that π-complexes involving aryl radicals can be formed in irreversible fashion.

$$(C_6H_5COO)_2 \longrightarrow 2C_6H_5COO^{\cdot} \quad (1)$$

$$C_6H_5COO^{\cdot} \longrightarrow C_6H_5\cdot + CO_2 \quad (2)$$

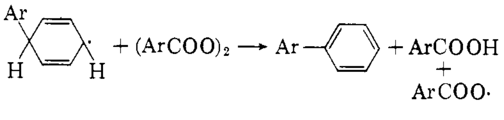


(This may be an induced decomposition—*vide infra.*)

Fig. 1.

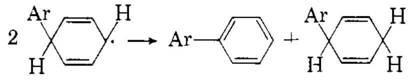
The mechanism summarized in Fig. 1 above presents at least two questions. One, already alluded to, is whether or not step 3 is freely reversible. The other concerns the nature of the hydrogen-abstracting reagent X. This latter question has been quite puzzling. Thus it is known (and has been confirmed again in the present work) that the arylation of benzene with a peroxide $(ArCOO)_2$ gives much acid ArCOOH and little hydrocarbon ArH. Thus it appears that "X·" is largely ArCOO· rather than Ar·. This seems rather strange; it is not clear why so many ArCOO· radicals should "wait around" for step 3 to occur so that they can then participate in step 4.

A "cage process"[25] involving geminate Ar· and ArCOO· reacting coöperatively with substrate has been suggested as a possibility.[21] An alternative is that X· in step 4 is not actually ArCOO· at all, but that an induced decomposition involving the diaryl peroxide is involved[11b]



Since kinetic results[14] show induced decomposition to be unimportant at low peroxide concentration, this mechanism cannot account for biphenyl formation in dilute solution. Even in more concentrated solution (*ca.* 0.2 *M*), induced decomposition seems inadequate to account for all the biaryl formed.

The results of DeTar and Long[12] provide an alternate mechanism in dilute solution. These investigators isolated 1,4-dihydrobiphenyl from the decomposition of benzoyl peroxide in benzene at low concentration (*ca.* 0.02 *M*) thus showing that disproportionation of the intermediate radicals occurs



In the present work, a study was made of the reaction of various peroxides with deuterium-labeled substrates—either benzene-d_1 or a mixture of benzene-d_0 and benzene-d_6. If there is an iso-

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(17) R. J. Convery and C. C. Price, This Journal, **80**, 4101 (1958).

(18) E. L. Eliel, Z. Welvart and S. H. Wilen, *J. Org. Chem.*, **23**, 1821 (1958) (preliminary communication); see also Table I in the present paper.

(19) D. B. Denney and P. P. Klemchuk, This Journal, **80**, 3289 (1958).

(20) If the radicals couple in the form as written in step 3, Fig. 1, o,o,-quaterphenyls should result, but these have not as yet been found. Professor M. Szwarc (personal communication) has pointed out that the corresponding tetrahydroquaterphenyls in this case would be conjugated dienes and therefore readily subject to free-radical polymerization. Such intermediate species may well be responsible for the tars usually encountered in free-radical arylation.

(21) *Cf.* C. S. Rondestvedt and H. S. Blanchard, *J. Org. Chem.*, **21**, 229 (1956).

(22) G. A. Russell, This Journal, **79**, 2977 (1957); **80**, 4987, 4997, 5002 (1958).

(23) *Cf.* also B. Miller and C. Walling, *ibid.*, **79**, 4187 (1957); H. J. den Hertog and P. Smit, *Proc. Chem. Soc.*, 132 (1959).

(24) G. A. Russell, *J. Org. Chem.*, **24**, 300 (1959).

(25) *Cf.* ref. 10, p. 76.

tope effect in the reaction —*i.e.*, if the incoming aryl radical attaches itself preferentially to a hydrogen-bearing rather than a deuterium-bearing position in the substrate[26] (or, less likely, *vice versa*) —this should reflect itself in the deuterium content of the biaryl product. Also, in the case of a benzene–benzene-d_6 substrate, an intermolecular isotope effect might result in enrichment of recovered substrate with regard to labeled material. It seemed of interest to study such effects as a function both of the nature and the concentration of the attacking peroxide, especially since similar studies in the case of electrophilic substitution[27–30] have thrown much light on the detailed mechanism of the reaction.

Several previous studies of isotope effects in free-radical aromatic substitution have been reported.[8a,17,19,31–34] Those studies[31–33] employing tritium at the tracer level and with low conversion of substrate aromatic to biaryl are inconclusive on theoretical grounds.[35] Arylations driven to high conversions, though not very clean experimentally, tend to indicate that substrate composition (C_6H_6–C_6H_5T mixture) is unchanged in the course of the arylation.[8a,17] Intramolecular free-radical substitutions did, however, show small isotope effects (1.12–1.38) in the products when deuterium was used for labeling.[19] No isotope effect was reported in the reaction of benzoyl peroxide and *p*-nitrobenzoyl peroxide with deuterated benzene and of *p*-nitrobenzoyl peroxide with deuterated nitrobenzene,[34a] but an isotope effect of 1.95 was calculated in a rather indirect manner for the reaction of *p*-nitrobenzoyl peroxide with ring-deuterated toluene.[34b]

Results and Discussion

In Table I are listed apparent isotope effects observed in the decomposition of various peroxides in benzene-*d* as well as benzene–benzene-d_6 mixtures in the course of the present work. These isotope effects are calculated for a reaction conforming to the hypothetical equation $R\cdot + C_6H_6 \rightarrow RC_6H_5 + H\cdot$ proceeding to very low conversion with the isotopic discrimination occurring by preferential extrusion of H· over D·.[36] The simplest mechanism which could account for the observation of finite though small isotope effects in free-radical substitution is that represented by Fig. 1 with step 3 appreciably reversible under the conditions of the reaction. Step 4 would have to be either rate-determining, or at least proceed at a rate not much faster than the reverse of step 3, for an isotope effect to be observed. However, on the basis of previous work[8a,17] it seemed unlikely that step 3 could be appreciably reversible under the conditions of the arylation. In the present study it was shown that in the reaction of a benzene–benzene-d_6 mixture with *p*-chlorobenzoyl peroxide to give a mixture of undeuterated and deuterated *p*-chlorobiphenyl, whereas the deuterium content of the product correspond to an isotope effect of 1.3 (Table I), *the recovered substrate* (benzene–benzene-d_6) *was completely unchanged in isotopic composition.* The pertinent data are shown in Table II, columns A-C.

TABLE I

APPARENT ISOTOPE EFFECTS IN FREE RADICAL AROMATIC SUBSTITUTION AT 78° (FROM PRODUCT COMPOSITION)

Entry	Radical	Moles PhD Moles $(RCOO)_2$	Benzene-*d* % isotope purity	Product Atom % D[a]	Product Apparent isotope effect[b]
1	C_6H_5	42:1	93.7	7.81	1.0
2[c]	C_6H_5	420:1	98.2	9.10	2.6
3[d]	C_6H_5	420:1	98.1	9.49	6.6
4	*p*-$CH_3C_6H_4$	50:1	97.9	7.61	2.9
5	*p*-$CH_3OC_6H_4$	50:1	96.6	6.98	1.3
6	*p*-ClC_6H_4	25:1	93.8	9.30	1.7
7	*p*-ClC_6H_4	50:1	98.5	9.80	1.7
8	*p*-ClC_6H_4	25:1	[e]	18.77	1.3
9	*p*-$O_2NC_6H_4$	41:1	98.5	9.13	1.0
10	*p*-$O_2NC_6H_4$	47:1	[f]	27.30	1.1
11[g]	CH_3	24:1	97.9	11.05[h]	1.9
12[g]	CH_3	615:1	98.2	11.00[h]	1.7

[a] Usually average of two deuterium analyses, see Experimental. [b] Calculated by formula given in Experimental (except for entries 8 and 10). [c] No attempt made to avoid oxidation of dihydrobiphenyl. [d] Dihydrobiphenyl oxidation minimized, see Experimental. [e] Mixture of polydeuterated benzenes; see Experimental. [f] Mixture of benzene, benzene-d_5 and benzene-d_6; see Table II, A. [g] Regarding the methylation of benzene by acetyl peroxide, see E. L. Eliel, K. Rabindran and S. H. Wilen, *J. Org. Chem.*, **22**, 859 (1957). [h] Calculated from mass spectrometric analysis; see Table III.

TABLE II

ISOTOPIC COMPOSITION OF BENZENE–BENZENE-d^6 MIXTURES[37]

Mole %	A[a]	B	C	D
Benzene	48.42, 48.42	48.38, 48.34	48.39, 48.34	48.43, 48.40
Benzene-d_5	1.35, 1.34	1.34, 1.35	1.34, 1.32	1.33, 1.34
Benzene-d_6	50.23, 50.24	50.27, 50.31	50.27, 50.33	50.23, 50.26

[a] A, starting material; B, starting material recovered from blank experiment simulating isolation procedure (see Experimental); C, substrate recovered from chlorophenylation; *D*, substrate recovered from nitrophenylation.

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(26) For a general review of isotope effects, *cf.* K. B. Wiberg, *Chem. Revs.*, **55**, 713 (1955), and W. H. Saunders, "Kinetic Isotope Effects," in press.

(27) L. Melander, *Arkiv Kemi*, **2**, 211 (1950); for reservations regarding the interpretation of this excellent study see G. S. Hammond, THIS JOURNAL, **77**, 334 (1955). See also U. Berglund-Larsson and L. Melander, *Arkiv Kemi*, **6**, 219 (1954).

(28) P. B. D. de la Mare, T. M. Dunn and J. T. Harvey, *J. Chem. Soc.*, 923 (1957); E. Grovenstein and D. C. Kilby, THIS JOURNAL, **79**, 2972 (1957); E. Shilov and F. Weinstein, *Nature*, **182**, 1300 (1958).

(29) H. Zollinger, *Helv. Chim. Acta*, **38**, 1597, 1617 (1955); *Angew. Chem.*, **70**, 204 (1958).

(30) D. B. Denney and P. P. Klemchuk, THIS JOURNAL, **80**, 3285 (1958).

(31) C. C. Price and R. J. Convery, *ibid.*, **79**, 2941 (1957).

(32) G. H. Williams, Abstracts, XIVth International Congress of Pure and Applied Chemistry, Paris, France, 1957, p. 27.

(33) *Cf.* ref. 9, p. 167.

(34) (a) R. I. Milutinskaya, K. S. Bagdasaryan and E. A. Izrailevich, *J. Phys. Chem.* (*USSR*), **31**, 1019 (1957); *C. A.*, **52**, 3742c (1958). (b) R. I. Milyutinskaya, Kh. S. Bagdasaryan and Yu. Kopitovskii, *ibid.*, **32**, 428 (1958); *C. A.*, **52**, 20022c (1958).

(35) C. C. Price and R. J. Convery, THIS JOURNAL, **79**, 6579 (1957); *cf.* ref. 27.

(36) In fact, as will be shown later, this simple picture is incorrect in at least some of the arylations studied. Therefore the "apparent isotope effect" at least in those cases does not pertain to any real chemical process. Nevertheless (*vide infra*) the qualitative finding of an isotope effect in excess of unity is significant and throws considerable light on the mechanism of free-radical substitution.

(37) The data in Table II were obtained by mass spectrometry at reduced ionizing voltage at the Standard Oil Co. Research Laboratories; *cf.* D. P. Stevenson and C. D. Wagner, THIS JOURNAL, **72**, 5612 (1950); R. E. Honig, *Anal. Chem.*, **22**, 1474 (1950).

It is evident that the increase in benzene-d_6 (or decrease in benzene-d_0) in the substrate recovered from chlorophenylation or nitrophenylation[38] is less than the 0.1% margin of experimental uncertainty. Now it is clear that if the apparent isotope effect in the product biaryl is due to extensive competition of the reverse of step 3 with step 4 (Fig. 1)— in which the phenylcyclohexadienyl radical formed in step 3 has a greater tendency to go on to product biaryl when there is a hydrogen on the tetrahedral carbon than when there is a deuterium at this position–then enrichment of the product in unlabeled material must go hand in hand with enrichment of the starting material in benzene-d_6. In fact, given the experimental facts of isotopic composition of the substrate and substrate to peroxide ratio, one can calculate (see Experimental) that the recovered substrate would have been enriched in benzene-d_6 by about 0.4%. The complete absence of such enrichment rules out the possibility of any substantial fraction of the "product isotope effect" being due to the reversibility of step 3.

Another source of the product isotope effect must thus be looked for. It has already been pointed out elsewhere[11a,21] that the extensive occurrence of side reactions in free-radical arylation introduces a factor of uncertainty in the much-used "competitive method" where the relative reactivity of two chemically different substrates is gauged by allowing an equimolar mixture of the two substrates to compete for a single radical reagent.[39] By the same token, such side-reactions introduce a complication in the determination of isotope effects where two isotopically different substrates (such as benzene and benzene-d_6) or two isotopically different positions in a single substrate (benzene-*d*) compete for the radical reagent. Thus the scheme shown in Fig. 2, which is well documented by studies already cited,[11,12] may account for the observed isotope effect on the reasonable assumption that arylcyclohexadienyl radical with deuterium at the tetrahedral carbon is less prone to go on to diaryl (and more prone to go on to side products) than the corresponding radical with hydrogen at the tetrahedral carbon.

It is worth mentioning here that, just as there is an analogy between competitive arylation of two chemically different substrates and study of an intermolecular isotope effect using two isotopically different substrates (*e.g.*, C_6H_6 and C_6D_6), there is also an analogy between the study of intramolecular isotope effects (*e.g.*, in C_6H_5D) and the determination of isomer distribution in the arylation of a monosubstituted benzene (C_6H_5X). To the extent that the observed finite isotope effect in the arylation of benzene-*d* fails to reflect the lack of isotope discrimination in the first step (Fig. 2)[40] it may be argued that the observed isomer distribution in the arylation of a substituted benzene does not truly reflect whatever discrimination between positions there is in a monosubstituted benzene in the radical addition step. Attempts to make correlations between observed orientation in free-radical substitution and hypothetical transition states for the first step in Fig. 2 must therefore continue to be viewed with reserve.

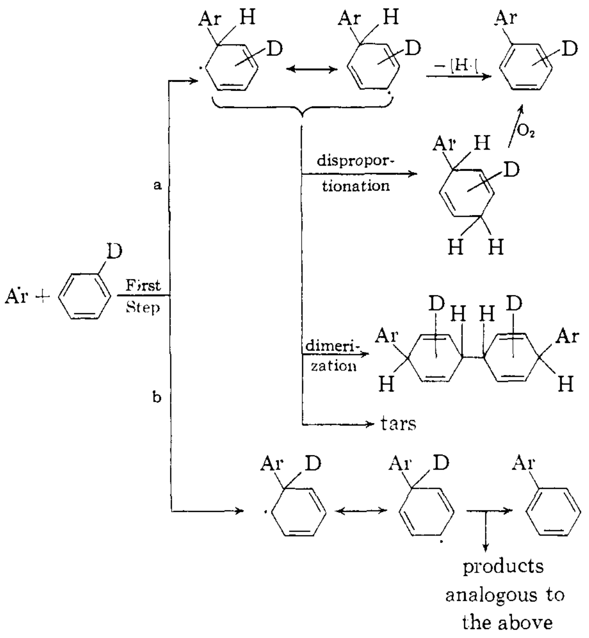

Fig. 2.

A further complication must now be referred to. DeTar and Long[12] have shown that, in dilute solution, phenylcyclohexadienyl radicals disproportionate to biphenyls and 1,4-dihydrobiphenyls. In order to isolate the dihydrobiphenyl, one must work in an oxygen-free atmosphere. Under ordinary isolation conditions, dihydrobiphenyl is oxidized to biphenyl by air.[41] Two consequences follow. One is that the "first biphenyl" (formed by disproportionation in the absence of oxidation) should contain more deuterium than the "total biphenyl" (first biphenyl plus biphenyl formed by oxidation of dihydrobiphenyl). This follows from the fact that, to the extent that the biphenyl formed in the disproportionation is rich in deuterium (because $ArCHC_5H_4D\cdot$ loses hydrogen to form $ArCC_5H_4D$ more readily than $ArCDC_5H_5\cdot$ loses deuterium to form $ArCC_5H_5$) the dihydrobiphenyl formed concomitantly will contain light hydrogen in excess of the statistical amount (because more hydrogen is transferred to the arylcyclohexadienyl radical than is deuterium). As a result the isotope effect observed in the initial biphenyl formation will be so-to-speak diluted when one allows the dihydrobiphenyl formed concomitantly to oxidize to biphenyl also.[42] Experimentally this was borne

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[38] The data from nitrophenylation are less significant than those from chlorophenylation, since the product of nitrophenylation contained barely less than the statistical amount of deuterium (*cf.* Table I, entry 10).

[39] The competitive method was first developed by C. K. Ingold and F. R. Shaw, *J. Chem. Soc.*, 2918 (1927), for electrophilic aromatic substitution. Electrophilic substitution being much cleaner experimentally than radical substitution gives more clear-cut results in both the competition method and in isotope studies (ref. 27–30).

[40] The lack of change of substrate composition—Table II—incidentally rules out the possibility of an appreciable secondary isotope effect in this step.

[41] *Cf.* W. Hückel and R. Schwen, *Chem. Ber.*, **89**, 150 (1956).

[42] This statement may require some justification and elaboration. The primary products of radical addition to benzene-*d* are the species i and ii. If an isotope effect makes itself felt in the subsequent dis-

Table III

Species Present in Deuterated Biphenyl and Toluene Samples[43]

Mole %	R = C_6H_5[a]	R = C_6H_5[b]	R = CH_3[c]	R = CH_3[d]
RC_6H_5	24.90, 24.80, 24.97	17.05, 17.24, 17.16	12.60, 12.58	13.23
RC_6H_4D	74.07, 74.20, 73.95	80.86, 80.44, 80.57	85.96, 85.84	84.68
$RC_6H_3D_2$	1.03, 1.00, 1.08	1.93, 2.03, 2.01	0.96	1.28

[a] By decomposition of a 0.4 *M* solution of benzoyl peroxide in benzene-*d* of 93.7% isotopic purity. [b] By decomposition of a 0.04 *M* solution of benzoyl peroxide in 98.2% pure benzene-*d*; no effort was made to prevent air-oxidation of any dihydrobiphenyl formed. [c] By decomposition of a 0.5 *M* solution of acetyl peroxide in 97.9% pure benzene-*d*. [d] By decomposition of a 0.02 *M* solution of acetyl peroxide in 98.2% pure benzene-*d*. Added in proof (4/6/60): In order to check the possibility that the biphenyl-d_2 might have resulted from coupling of substrate benzene-*d*, we have subjected the *p*-chlorobiphenyl sample corresponding to entry 7 in Table I to mass spectrometric analysis. The result, in mole %, was: RC_6H_5, 15.58, 15.53, 15.60; RC_6H_4D, 84.01, 84.04, 84.06; $RC_6H_3D_2$, 0.40, 0.44, 0.34 where R is now *p*-ClC_6H_4. The d_2-material here is clearly not a product of substrate coupling. It must be noted, however, that the amount of dideuterated *p*-chlorobiphenyl is less than the amount of dideuterated biphenyl shown in the first column of figures in the table. *Moreover, the p-chlorobiphenyl was contaminated by biphenyl* (mass No. 154, *ca.* 1%), *about half of which was dideuterated material.* It appears, therefore, that only about half the biphenyl-d_2 in the decomposition of 0.4 *M* benzoyl peroxide in benzene-*d* is formed by the process shown in Fig. 3, the other half resulting from abstraction of hydrogen from substrate benzene-*d* to give C_6H_4D which then arylates C_6H_5D.

out; whereas the apparent isotope effect in the decomposition of 0.03 *M* benzoyl peroxide in benzene-*d* was 6.6 when maximum precautions were taken to separate the first biphenyl cleanly from the dihydrobiphenyl; the apparent isotope effect dropped to 2.6 when no precautions were taken to prevent oxidation of dihydrobiphenyl. (Under the latter circumstances, no dihydrobiphenyl was isolated as such.)

A second consequence to be forseen if some of the biphenyl is formed by dehydrogenation of dihydrobiphenyl which, in turn, results from disproportionation of the arylcyclohexadienyl radicals formed in the primary addition of aryl radicals to benzene is the occurrence of biphenyl-d_2 in the product, as shown in Fig. 3. To verify this predicted result, the biphenyl formed by phenylation of benzene-*d* at low and high benzoyl peroxide concentration and the toluene formed in the methylation of benzene with acetyl peroxide at two different concentrations were subjected to mass spectrometry at reduced ionizing voltage. The results are summarized in Table III.

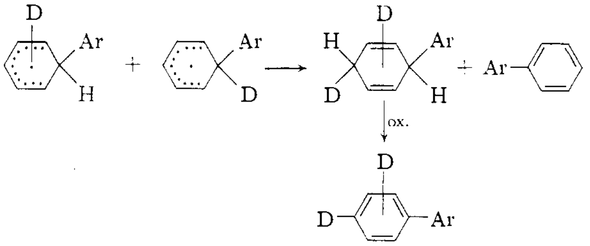

Fig. 3.

It is immediately evident from Table III that the prediction of biphenyl-d_2 formation is borne out experimentally. Two other aspects of the data are noteworthy: (1) *Biphenyl-d_2 is formed even at high benzoyl peroxide concentration (0.4 M)*, even though no dihydrobiphenyl has yet been isolated under these conditions. This suggests that even at high benzoyl peroxide concentration, disproportionation of intermediate phenylcyclohexadienyl radicals to biphenyl and dihydrobiphenyl occurs. Presumably the dihydrobiphenyl is not readily isolated under these conditions because it is rapidly dehydrogenated (through loss of the two doubly allylic hydrogens) by the benzoyl peroxide present in high concentrations.[44] (2) Less biphenyl-d_2 results at high benzoyl peroxide concentration than at low benzoyl peroxide concentration. This suggests that disproportionation–dehydrogenation[45] is a more important path at low benzoyl peroxide concentration than at high benzoyl peroxide concentration. Another path must be partly responsible for biphenyl formation at high benzoyl peroxide concentration.

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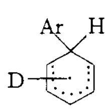
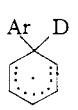
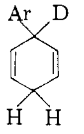
proportionation, it is clear that i will preferentially lose hydrogen to give deuterated "first" biphenyl and ii, by default, becomes the principal hydrogen acceptor to give the dihydrobiphenyl iii. Upon dehydrogenation iii will give *un*deuterated "second" biphenyl. A complica-



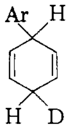
i



ii



iii



iv

tion is, however, introduced by the fact that the dehydrogenation of the dihydrobiphenyl is also affected by an isotope effect. Thus species iv, formed by radical addition in the *para* position of benzene-*d* followed by hydrogen acceptance will preferentially yield biphenyl-*d* because of an isotope effect in dehydrogenation. As a result, if the isotope effect in the "first biphenyl" formation were low, the "second biphenyl" might actually be richer in deuterium than the "first biphenyl." Fortunately, it turned out that the apparent isotope effect in the formation of the "first biphenyl" was high (6.6). It is therefore reasonable to assume that the isotope effect in the dehydrogenation of the dihydrobiphenyl is at least no greater than that. A statistical calculation *made with this assumption* shows that the "second biphenyl" should indeed be considerably poorer in deuterium than the "first biphenyl."

(43) The biphenyl analyses were carried out in a high-mass instrument at the Standard Oil Co. Research Laboratories. Small peaks at masses just above that corresponding to $RC_6H_3D_2$ were found in *b*, *c* and *d*, but these may have been caused by traces of deuterated dihydrobiphenyls or dihydrotoluenes. These peaks were more prominent in the toluene samples (*c* and *d*) which, because of their liquid nature, were harder to purify. Extraneous peaks were absent in the biphenyl sample *a* formed at high peroxide concentration—conditions under which dihydrobiaryls do not seem to survive. The deuterium content of this sample (*a*) as calculated from the mass analysis (7.62% D) is in satisfactory agreement with that obtained by a combustion—falling drop method (7.81% D). In the case of sample *b* which may have been contaminated, the mass analysis (8.57% D) and elementary analysis (9.10% D) were not in such good agreement.

(44) The reaction of 1,4-dihydrobiphenyl with benzoyl peroxide is under investigation in Professor DeTar's laboratory.

(45) At high benzoyl peroxide concentration, the dehydrogenation is probably produced by benzoyl peroxide[45] whereas at low benzoyl peroxide concentration it is mainly produced by air oxidation if at all. Accordingly, DeTar and Long[12] as well as ourselves have found that the ratio of benzoic acid to biphenyl in the arylation products is much smaller at low benzoyl peroxide concentration than at high benzoyl peroxide concentration.

a likely possibility being the already mentioned induced decomposition process.

It is clear, now, why the data in Table I were labeled "*apparent* isotope effect." These data were calculated on the assumption that the biaryls contained one deuterium atom and that they were formed by the addition of an aryl group to and the loss of a hydrogen or deuterium atom from the benzene-*d*. It is now evident that at least in the case of the reaction of phenyl radicals with benzene-*d* the process is more complicated than that, and in view of that and the fact that the biphenyl contains higher deuterated species, the figures shown in Table I (entries 1 and 2) do not represent real isotope effects. The same may be true of the other figures in Table I, although in their case mass spectrometric analyses are not available.[46] The question may be raised whether the deuterium analyses reported in Table I correspond to any isotopic discrimination altogether. Now, in the case of the phenylation of benzene-*d* (93.7% isotopic purity) at high benzoyl peroxide concentration (first entry), a process giving biphenyl exclusively by addition of a phenyl radical, followed by disproportionation, followed by dehydrogenation (Fig. 2) without any isotope effect at all should lead to a product containing biphenyl-d_0, 24.4%; biphenyl-d_1, 73.2%; biphenyl-d_2, 2.4%; atom % deuterium, 7.8%. If only biphenyl-d_0 and biphenyl-d_1 were formed without an isotope effect by the simpler process mentioned above, the calculated product composition would be biphenyl-d_0, 21.9%; biphenyl-d_1, 78.1%; atom deuterium 7.8%. It is clear that the statistically calculated atom % deuterium assuming no isotope effect is the same for the simple addition–hydrogen loss mechanism (Fig. 1) and the more complex addition – disproportionation – dehydrogenation mechanism (Fig. 3). Hence, whenever there is an isotope effect in excess of unity reported in Table I, it still means that hydrogen and deuterium are not lost in statistical fashion, regardless of whether the arylation process is simple or complex.

Another way in which the isotope effect manifests itself is in the deuterium content of the species XH (or XD) in eq. 4, Fig. 1. This deuterium content and the apparent isotope effect calculated from it are shown in Table IV. If Fig. 1 correctly represented the course of events in arylation, the apparent isotope effect in Tables I and IV should agree, but in fact they do not. The more complicated scheme (Fig. 2) now believed to represent the course of arylation does not, of course, necessitate identity of the "apparent" isotope effects in Tables I and IV. This scheme may also account for the fact that, contrary to what Fig. 1 might suggest, the hydrocarbon ArH is formed in only *very small amounts* in the decomposition of $(ArCOO)_2$ in benzene.

In the process shown in Fig. 3 one would expect an isotope effect either in the disproportionation or the dehydrogenation or both. The expectation is borne out with almost all the peroxides included in Table I with the exception of *p*-nitrobenzoyl peroxide and benzoyl peroxide. In the case of *p*-nitrobenzoyl peroxide it has already been suggested[11b] that because of the high susceptibility of the peroxide to induced decomposition[47] arylation may proceed cleanly by the process shown in Fig. 1 with step 4 (the hydrogen abstraction step) being

$$p\text{-}O_2NC_6H_4C_6H_6\cdot + (p\text{-}O_2NC_6H_4COO)_2 \longrightarrow p\text{-}O_2NC_6H_4C_6H_5 + p\text{-}O_2NC_6H_4COOH + p\text{-}O_2NC_6H_4COO\cdot$$

thus making the arylation reaction essentially a chain reaction. If the substrate is cleanly and quantitatively converted to product by a process such as in Fig. 1 with step 3 being essentially irreversible (*cf.* Table II), no isotope effect would be expected. In confirmation, it has already been observed[11b] and was confirmed in the present work that little tar is formed in arylation of benzene with *p*-nitrobenzoyl peroxide. However, in the nitrophenylation of benzene-d_6, where the isotope effect slows down hydrogen abstraction from the intermediate nitrophenylcyclohexadienyl radical, tar formation is appreciable and there is a slight apparent isotope effect in the product (Table I, entry 10).

TABLE IV

APPARENT ISOTOPE EFFECTS IN FREE RADICAL AROMATIC SUBSTITUTION FROM ISOTOPIC COMPOSITION OF HYDROGEN ABSTRACTION PRODUCT

Entry[a]	Product	% R-D	Apparent isotope effect[c]
4	$CH_3C_6H_5$	7.75[b]	2.2
5	$CH_3OC_6H_5$	5.29[b]	3.4
6	ClC_6H_5	6.9[b]	2.3
6	ClC_6H_4COOH	5.91[d]	3.0

[a] Entries correspond to those in Table I. [b] By mass spectrometry at reduced ionizing voltage. [c] Calculated by formula in Experimental. [d] By mass spectrometry on HD obtained by treating the acid with $LiAlH_4$.

With benzoyl peroxide itself the situation is more complicated. Although the product (biphenyl) contains the statistical amount of deuterium, it does contain biphenyl-d_2 thus precluding the exclusive operation of the process shown in Fig. 1. Exclusive operation of the process shown in Fig. 3 without an isotope effect is in disagreement with the mass spectrometric analysis (24.9% d_0, 74.1% d_1, 1.0% d_2 *vs.* the statistical 24.4% d_0, 73.2% d_1, 2.4% d_2). The superposition of an isotope effect in the disproportionation (as demonstrated by the experiment in dilute solution, Table I, entry 3) would tend to diminish the amount of d_2 species below the statistical, but it would also diminish the expected amount of d_0 species. If the process shown in eq. 4, Fig. 1, (leading to product containing 21.9% d_0 and 78.1% d_1) contributes appreciably, it makes the high amount of d_0 species in the product even harder to understand. A possible explanation here is that some light biphenyl is formed by dimerization of phenyl radicals from benzoyl peroxide and that some of these radicals give rise to benzene which dilutes the substrate. Biphenyl as well as benzene was indeed obtained (see Experimental) in small amount when benzoyl

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(46) The general proposition that the calculation of an isotope effect in a reaction may be meaningless unless the reaction steps are understood may be worth noting; *cf.* ref. 1 and F. H. Westheimer, Abstr., 14th Natl. Org. Chem. Symposium, Lafayette, Ind., 1955.

(47) C. G. Swain, W. H. Stockmayer and J. T. Clarke, THIS JOURNAL, **72**, 5426 (1950).

peroxide (0.4 *M*) was decomposed in chlorobenzene. The intrusion of this extraneous biphenyl and the dilution of the substrate may explain why the apparent isotope effect in the phenylation with benzoyl peroxide is lower than the effects observed with most substituted benzoyl peroxides (with the exception of the *p*-nitro compound referred to earlier). The attractiveness of this explanation is, however, impaired by the fact that no peroxide derived biaryls [Ar–Ar from $(ArCOO)_2$] were found in any other instance (although they were searched for) and that the amount of biphenyl found in the decomposition of benzoyl peroxide in cyclohexane[48] is very slight. Moreover, the formation of biphenyl in the phenylation of chlorobenzene may be due to attack of phenyl radicals at the chlorinated position of C_6H_5Cl followed by loss of a chlorine atom (similar to the formation of quaterphenyl in the phenylation of chlorobenzene[11c]) rather than to coupling of phenyl radicals. The exact cause of the apparent isotope effect of unity in the decomposition of benzoyl peroxide in benzene-*d* (mole ratio 42:1) cannot yet be considered as settled.

It is evident that free radical arylation is a considerably more complex reaction than had been hitherto believed. The simple process shown in Fig. 1 (X = ArCOO·) previously thought to be the major, if not the only path, to arylation product now appears to be at best of minor significance.

Experimental

Mass spectra were recorded by Mr. George Young on a Consolidated model 21-103A analytical mass spectrometer unless otherwise noted. Carbon-hydrogen and deuterium analyses by Mr. Josef Nemeth, University of Illinois, Urbana, Ill. The hydrogen analyses were calculated in two ways. The first way assumes that complete hydrogen-deuterium exchange of the combustion water takes place in the analyst's train before the water is collected and weighed. The second way (indicated in parentheses) assumes that to the extent that the sample contains deuterium, the water collected is actually HDO. Inspection of the figures shows that the agreement (or lack thereof) for the calculated and experimental figures is about the same on either basis, suggesting that the actual situation may correspond to a partial H–D exchange. Given this result it would seem simpler to report the figures on the basis of complete H–D exchange, since this allows one to use the experimental percentage of hydrogen as reported by the analyst. The alternative way of reporting the hydrogen percentage (figures in parenthesis) requires either a knowledge of the weight of sample burnt and weight of water collected by the analyst or a calculation of the ratio of these figures from the reported analysis. If *w* is the weight of sample burnt, *a* the weight of water collected, *h* the reported % hydrogen and *d* the atom % deuterium (determined separately), then % hydrogen plus deuterium = $100\ a/w \times (100.1 + d)/(894.5 + d) = 8.937h \times (100.1 + d)/(894.5 + d)$.

Peroxides.—Benzoyl peroxide was recrystallized commercial material, m.p. 107–107.5° (lit. 108° dec.), equiv. wt. by iodimetric titration[49] 121 (calcd. 121). Other aromatic peroxides were prepared by the standard method.[50] *p*-Toluyl peroxide had m.p. 137–138° (lit.[48] 136–137°), equiv. wt. 135.3 (calcd. 135.1); anisoyl peroxide had m.p. 127° (lit.[50] 126–127°), equiv. wt. 152.5 (calcd. 151.1); *p*-chlorobenzoyl peroxide had m.p. 140–141° (lit.[48] 140–141° dec.), equiv. wt. 158.2 (calcd. 155.6); *p*-nitrobenzoyl peroxide had m.p. 156° (lit.[50] 155–156°), equiv. wt. 166.5 (calcd. 166). Acetyl peroxide, prepared from sodium peroxide and acetic anhydride,[51] was dissolved in the substrate (benzene-*d*) and the solution titrated.[49]

Benzene-*d* was prepared by a modification of the known method.[52] An excess of heavy water was employed (1.15–1.5 moles per mole of bromobenzene) and it was not found necessary to use ether-free phenyl Grignard reagent, although removal of the major part of the ether prior to addition of D_2O seemed to facilitate isolation of the product. Stirring was continued for 12 hours after the addition of D_2O and the material was then distilled without attempt to decomposes any remaining Grignard reagent. The major part of the operation was carried out under nitrogen dried over phosphorus pentoxide. Benzene-*d* was obtained in about 56–59% yield, b.p. 78.9–79.2°, $n^{20}D$ 1.5008. The material was analyzed by mass spectrometry at reduced ionizing voltage,[53] the voltage being chosen such that a sample of benzene-d_0 showed only the parent peak at *m/e* 78 (and isotopic peaks at 79 and 80) but no fragmentation peaks. It was assumed that the peak heights at 78, 79, 80 etc. (the latter after correction for naturally occurring isotopes) were directly proportional to the mole per cent. benzene-d_0, -d_1, -d_2 etc. Isotopic purity of the benzene-*d* ranged from 93.5 to 98.5%. Benzene-d_2 was absent (less than 0.1%).

Benzene-d_6.—A heterogeneous sample of polydeuterated benzene, b.p. 79° (744 mm.), $n^{20}D$ 1.4999, was prepared by shaking benzene with deuteriosulfuric acid.[54] This sample had benzene-d_0, 1.8%; -d_1, 4.9%; -d_2, 8.6%; -d_3, 12.7%; -d_4, 17.2%; -d_5, 22.2%; -d_6, 32.7%. A nearly pure sample was purchased from Merck & Co., Ltd., Montreal, Canada, and had benzene-d_6, 97.4%; -d_5, 2.6%.

Decomposition of Peroxides in Deuterated Benzenes.[11a,b] ***p*-Chlorobenzoyl Peroxide and Benzene-*d*.**—A suspension of 3.44 g. (0.01105 mole) of *p,p'*-dichlorobenzoyl peroxide (elsewhere in this paper referred to as *p*-chlorobenzoyl peroxide) in 21.82 g. (0.276 mole) of benzene-*d* (93.8% isotopic purity) (mole ratio 1:25) was de-aerated by bubbling argon through it and was then heated at 79 ± 1° for 25 hours in a flask equipped with a reflux condenser connected to a sulfuric acid bubbler. At the end of this period, reaction was complete as evidenced by the cessation of gas evolution. After cooling, a solid was filtered from the reaction mixture. In some runs this solid was treated with aqueous sodium bicarbonate in which most of it dissolved. The insoluble part was not investigated but may have been *p,p'*-dichloroquaterphenyl.[11b] The acid, reprecipitated from the carbonate solution by acidification, had m.p. 221–229° and was undoubtedly *p*-chlorobenzoic acid (m.p. 240°).[11b] The liquid reaction product was flash-distilled at 84–100 mm. to give a distillate and a residue. The distillate was fractionally redistilled to give benzene-*d* and a residue (0.5 g., b.p. above 78.9°). Ultraviolet, infrared, gas chromatographic and mass spectra analyses showed this residue to contain chlorobenzene. Mass analysis indicated chlorobenzene-d_0, 91.7%; chlorobenzene-d_1, 6.9%; chlorobenzene-d_2, 1.4%. The origin of the dideuterated material is not clear and the C_6H_5Cl:C_6H_4DCl ratio (Table IV) corresponds to an isotope effect[55] of 2.3, higher than the apparent product isotope effect (Table I).

The solid residue was chromatographed and then vacuum sublimed until it had a sharp melting point, 76.0–76.7° (Kofler Block) (lit. 77.5° for *p*-chlorobiphenyl).

Anal. Calcd. for $C_{12}D_{0.84}H_{8.16}Cl$: Cl, 76.06; H, 4.79 (5.27). Found: C, 76.12; H, 4.93 (5.36); 9.25, 9.34 atom % D (absolute).[56]

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[48] C. G. Swain, L. J. Schaad and A. J. Kresge, This Journal, **80**, 5313 (1958).

[49] V. R. Kokatnur and M. Jelling, *ibid.*, **63**, 1432 (1941).

[50] C. C. Price and E. Krebs, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 649.

[51] C. C. Price and H. Morita, This Journal, **75**, 3686 (1953).

[52] L. H. P. Weldon and C. L. Wilson, *J. Chem. Soc.*, 235 (1946).

[53] *Cf.* ref. 1, footnote 10.

[54] C. K. Ingold, C. G. Raisin and C. L. Wilson, *J. Chem. Soc.*, 915, 1637 (1936).

[55] The formula for calculating the apparent isotope effect from the composition of the ArH–ArD or ArCOOH–ArCOOD mixture formed from $(ArCOO)_2$ and C_6H_5D is I.E. = $n \times h/(600\text{-}n) \times d$ where *h* is the mole % light material (ArH or ArCOOH), *d* is the mole % monolabeled material (ArD or ArCOOD) and *n* is the isotopic purity of the benzene-*d* substrate used.

[56] We have not distinguished between absolute and excess atom % deuterium in the calculations, since the difference (*ca.* 0.02%) is considerably less than experimental error and is blurred by the differences between duplicate analyses.

The isotope effect entered in Table I was calculated from the deuterium analysis making the assumption of infinitesimal conversion (*i.e.*, no change of substrate composition during reaction—this is justified by the high substrate: peroxide ratio) and assuming that the intramolecular and intermolecular isotope effects are equal. Furthermore it entails the assumption, explained in the Discussion, that the arylation process is simply PhH + Ar. → PhAr + H·. On the basis of these assumptions one may derive the formula I.E. = $Anq/(500n–600Aq + Anq)$ where I.E. is the apparent isotope effect, n is the isotopic purity (in %) of the substrate, A is the atom % deuterium in the product and q is the total number of hydrogenated and/or deuterated positions in the biphenyl. In the above instance, n = 93.9, A = 9.3 (average of duplicate analyses) and q = 9 (chlorobiphenyl has nine hydrogens).

A duplicate run at a benzene-*d* (98.5% isotopic purity): *p*-chlorobenzoyl peroxide mole ratio of 50:1 gave *p*-chlorobiphenyl, melting at 78.5–79°, isolated in this instance by steam distillation and purified by vapor phase chromatography (5-ft. silicone oil column, 148°, He flow rate 50 ml./min., retention time 9 min. 10 sec.)

Anal. Calcd. for $C_{12}D_{0.88}H_{8.12}Cl$: C, 76.04; H, 4.79 (5.25). Found; C, 75.64; H, 5.31 (5.77); atom % D 9.75, 9.86.

The deuterium content of the *p*-chlorobenzoic acid, ClC_6H_5COOD, formed in an experiment using 93.8% pure benzene-*d* (mole ratio 25:1) was measured in a small scale run (one-fifth the above) on the assumption that no other active hydrogen compound is present. To the total reaction product was added an excess of lithium aluminum hydride in diethylene glycol dimethyl ether after the system had been fitted with a gas bulb and evacuated until the benzene solvent began to boil. The hydrogen gas evolved was collected in the bulb and analyzed mass spectrometrically. Found: 5.91 mole % HD corresponding to an isotope effect[55] of 3.0.

Control experiments were carried out to check (a) that no *p*-chlorobenzoic acid was present in the *p*-chlorobenzoyl peroxide used for this experiment and (b) that chlorobenzene did not result from decarboxylation of *p*-chlorobenzoic acid. A solution of 0.20 g. of *p*-chlorobenzoyl peroxide in 45 ml. of ether was extracted with 2 × 10 ml. of 10% aqueous sodium carbonate. Acidification with hydrochloric acid (total final volume *ca.* 30 ml.) produced no precipitate of *p*-chlorobenzoic acid. Since the solubility in water of the acid[57] is only 6.8 mg./100 ml., the peroxide contained less than 1–2% free acid. (b) *p*-Chlorobenzoic acid (3 g.) was heated in 35 ml. of benzene in the presence of 3 g. of benzoyl peroxide under the conditions previously employed to decompose *p*-chlorobenzoyl peroxide. The reaction mixture was worked up as described above. Chlorobenzene could not be found either gas chromatographically or mass spectrometrically.

***p*-Chlorobenzoyl Peroxide and Benzene–Benzene-*d*$_6$ (A).**—The experiment was carried out as described above, but using as a substrate the mixed deuterated benzene described earlier diluted with ordinary benzene. The substrate analysis (by mass spectrometry) was: benzene-d_0, 49.5%; -d_1, 2.5%; -d_2, 4.4%; -d_3, 6.5%; -d_4, 8.9%; -d_5, 11.5%; -d_6, 16.7%. The chlorobenzene formed in this experiment had: C_6H_5Cl, 81.9%; C_6H_4DCl, 17.5%; $C_6H_3D_2Cl$, 0.5%. The chlorobiphenyl melted at 78.6–79°.

Anal. Calcd. for $C_{12}H_{1.67}H_{7.33}Cl$: C, 75.72; H, 4.77 (5.66). Found: C, 75.83; H, 5.05 (5.88); atom % D, 18.77%.

The calculation of the apparent isotope effects is slightly more involved in this case. From the chlorobiphenyl analysis one calculates an apparent isotope effect of 1.26, from the chlorobenzene analysis, 2.8.

(B).—A second experiment was carried out with a benzene-d_6–benzene-d_5–benzene-d_0 mixture of composition indicated in Table II, A. In this experiment 0.0960 g. of *p*-chlorobenzoyl peroxide was decomposed in 1.3 ml. of benzene mixture in a carbon dioxide atmosphere. The benzene (1.0745 g.) was recovered by distillation, 0.0884 g. of peroxide was added and the decomposition repeated. This time 1.0089 g. of benzene was recovered and to it was added 0.0830 g. of peroxide which was decomposed in the usual way. By distillation, 0.9774 g. of benzene was recovered, composition indicated in Table II, C. Unfortunately, not enough pure *p*-chlorobiphenyl could be isolated from the distillation residues to permit deuterium analysis. A blank experiment was carried out in which the substrate was three times distilled on a vacuum line (Table II, B).

The total amount of peroxide decomposed in this experiment is 0.2674 g. or 0.853 mmole. Assuming an isotope effect of 1.25 for a simple process such as shown in Fig. 1 with step 3 reversible and taking into account that 48.42% of the substrate was benzene-d_0, 50.24% was benzene-d_6 and 1.34% benzene-d_5, the chances of consuming benzene-d_0 should be proportional to 1.25 × 48.42 or 60.53, that of consuming benzene-d_6 to 50.24 and that of consuming benzene-d_5 to 1.04 × 1.34 or 1.39. Hence the amount of benzene-d_0 consumed would be 0.853 × 60.53/112.16 or 0.4604 mmole (112.16 = 60.53 + 50.24 + 1.39); the amount of benzene-d_6 consumed would be 0.853 × 50.24/112.16 or 0.3821 mmole and the amount of benzene-d_5 consumed would be 0.853 × 1.39/112.16 or 0.0106 mmole. Since the original amount of substrate was approximately 14 mmoles containing 14 × 0.5842 or 6.779 mmole of benzene-d_0, 14 × 0.5024 or 7.034 mmole of benzene-d_6 and 14 × 0.0134 or 0.188 mmole/benzene-d_5, there will be left, at the end of the experiment, 6.779 – 0.460 or 6.319 mmoles of benzene-d_0, 7.034 – 0.382 or 6.652 mmoles of benzene-d_6 and 0.188 – 0.011 or 0.177 mmole of benzene-d_5. This would correspond to a composition of 48.06% benzene-*d*, 50.59% benzene-d_6 and 1.35% benzene-d_5 which is clearly different from the analysis experimentally found and shown in Table II, C.

Anisoyl Peroxide and Benzene-*d*.—Anisoyl peroxide (1.80 g., 6 mmoles) was decomposed in 25 ml. of benzene-*d* (96.5% isotopically pure) as described for *p*-chlorobenzoyl peroxide. The excess benzene-*d* was removed by distillation and the residue taken up in ether in which a considerable amount of material (0.77 g.) was insoluble. The ether solution was extracted with aqueous sodium hydroxide, concentrated, subjected to saponification with 10% alcoholic potassium hydroxide and the remaining product (non-saponified fraction) steam distilled. The steam distillate was extracted with ether, concentrated and the residue purified by gas chromatography on a silicone column at 215°. Two recrystallizations from 95% ethanol followed by two recrystallizations from petroleum ether (b.p. 60–90°) gave *p*-methoxybiphenyl, m.p. 89° (lit. 90°).

Anal. Calcd. for $C_{13}D_{0.85}H_{11.15}O$: C, 84.36; H, 6.54 (6.99). Found; C, 84.23; H, 6.79 (7.21); atom % D, 6.98, 7.14.

The benzene-*d* recovered from this reaction was subjected to gas chromatography (silicone) and anisole was isolated. Mass spectral analysis indicated 5.29% anisole-*d* corresponding to an apparent isotope effect[55] of 3.4.

p-Toluyl Peroxide and Benzene-*d*.—The peroxide (2.025 g., 7.5 mmoles) was decomposed in 35 ml. of benzene-*d* (97.86% isotopic purity). The solid product was worked up as described for anisoyl peroxide, except that the steam-distilled material was purified by column chromatography on alumina. *p*-Methylbiphenyl melted at 47.5–48° (lit. 47–48°).

Anal. Calcd. for $C_{13}D_{0.91}H_{11.09}$: C, 92.31; H, 7.15 (7.69). Found; C, 92.32; H, 7.35 (7.85); atom % D, 7.55, 7.67.

From the recovered benzene-*d*, toluene was isolated by gas chromatography (silicone column). It contained 7.75% toluene-*d* corresponding to an apparent isotope effect[55] of 2.3.

Benzoyl Peroxide and Benzene-*d*, (a).—One gram (1 mmole) of benzoyl peroxide was decomposed in 12 ml. of benzene-*d* (93.73% isotopic purity) and the product was worked up as described for anisoyl peroxide, except that chromatography of the biphenyl product was not needed. Two recrystallizations of the crude product (0.22 g., 1.4 mmoles) from ethanol gave material melting at 71–72° (lit. 70.5°).

Anal. Calcd. for $C_{12}D_{0.78}H_{9.22}$: C, 92.99; H, 6.50 (7.01). Found: C, 92.92; H, 6.56 (7.13); atom % D, 7.85, 7.77.

The benzoic acid isolated by sodium carbonate extraction weighed 0.172 g. (1.4 mmoles).

(b).—One-half gram (2 mmoles) of benzoyl peroxide was decomposed in 65 ml. of benzene-*d* (98.18% isotopic purity). Upon concentration of the solution, here as in the previous experiment, *p*-quaterphenyl (m.p. 312°, lit.[112] 312°) precipi-

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[57] A. Osol and M. Kilpatrick. THIS JOURNAL, **55**, 4430 (1933).

tated in small amount (*ca.* 0.011 g.) and was removed by filtration. Extraction of the ether solution of the solid residue (after benzene removal) with sodium bicarbonate yielded benzoic acid upon acidification. The crude acid melting at 109–110° (lit. 121°) weighed 81 mg. (0.65 mmole). A further 37 mg. (0.31 mmole) of benzoic acid was produced in the saponification step. The biphenyl obtained by steam distillation weighed 0.225 g. (1.48 mmoles and melted at 71–72° after recrystallization.

Anal. Calcd. for $C_{12}D_{0.91}H_{9.09}$: C, 92.91; H, 6.50 (7.09). Found: C, 92.60; H, 7.03 (7.60); atom % D: 9.07, 9.13.

No dihydrobiphenyl was found in this experiment (by gas chromatography).

(**c**).—The decomposition of benzoyl peroxide in benzene-*d* (98.10% isotopic purity) in dilute solution was repeated using the technique of DeTar and Long[12,58] using precautions to avoid oxidation of the product by isolating and storing it under an atmosphere of carbon dioxide. The product was purified by chromatography on alumina. The early fractions (pentane eluent) contained a mixture of dihydrobiphenyl and biphenyl and were subjected to gas chromatography on Ucon (polar) at 205°. There were two peaks of retention time 340 sec. and 550 sec. The latter peak contained the biphenyl which was collected and purified by three crystallizations from isopropyl alcohol and 96% ethanol, m.p. 71.5°.

Anal. Calcd. for $C_{12}D_{0.95}H_{11.05}$: C, 92.89; H, 6.50 (7.09). Found: C, 93.13; H, 6.63 (7.18); atom %, 9.47, 9.50.

***p*-Nitrobenzoyl Peroxide and Benzene-*d*.**—The peroxide (0.92 g., 2.8 mmoles) was decomposed in 12 ml. of benzene-*d* (98.54% isotopic purity) and worked up as described for anisoyl peroxide. No nitrobenzene was found among the products although it was searched for carefully both by mass spectrometry and by vapor phase chromatography in material whose boiling point ranged from that of benzene to that of *p*-nitrobiphenyl. The *p*-nitrobiphenyl was crystallized from isopropyl alcohol; m.p. 115.5–116° (lit. 113–114°).

Anal. Calcd. for $C_{12}D_{0.82}H_{8.18}NO_2$: C, 72.05; H, 4.54 (4.94). Found: C, 71.99; H, 4.44 (4.80); atom % D, 9.16, 9.10.

***p*-Nitrobenzoyl Peroxide and Benzene-d_6.**—The peroxide (0.0996 g.) was decomposed in 1.3 ml. of benzene–benzene-d_6 mixture (see Table II, A). To the recovered benzene (1.1057 g.) was added 0.0919 g. of peroxide and the decomposition repeated. This time 1.0412 g. of benzene was recovered and 0.865 g. of peroxide was decomposed in it. The final recovered benzene weighed 0.9742 g.; its composition is indicated in Table II, D. The combined distillation residues were steam distilled. Unlike in the case of decomposition in benzene-d_1, considerable resin (0.1837 g.) remained.[59] The steam-distilled *p*-nitrobiphenyl weighed 0.1234 g. and was purified as indicated above, m.p. 116.5–117°.

Anal. Calcd. for $C_{12}D_{2.46}H_{6.54}NO_2$: C, 71.46; H, 4.50 (5.73). Found: C, 71.27; H, 4.45 (5.50); atom % D, 27.30.

Acetyl Peroxide and Benzene-*d*.—The solution of acetyl peroxide in benzene-*d* (for isotopic purity see Table I) was decomposed by slow addition to a reaction flask heated at 78° and subsequent heating at this temperature until gas evolution ceased. Anisole (purity checked by gas chromatography) was added as a chaser and the mixture fractionated. A fraction boiling between 82 and 125° was subjected to gas chromatography and the toluene peak collected and analyzed mass spectrometrically.

In one experiment the mole ratio of benzene to acetyl peroxide was 24:1, in a second 615:1. The toluene analyses are shown in Table III. In both instances titration showed the formation of appreciable amounts of acetic acid in solution, suggesting that hydrogen abstraction involves a process of induced decomposition of the acetyl peroxide.

Decomposition of Benzoyl Peroxide in Chlorobenzene.—Benzoyl peroxide (2.5 g., 0.01 mole) was decomposed in 56 g. (0.5 mole) of chlorobenzene by the standard method. The chlorobenzene was recovered by distillation and the early fraction was shown to contain benzene by both mass spectrometric and gas chromatographic analysis. The distillation residue was worked up as previously described and the steam-distilled product was subjected to gas chromatographic analysis on both a silicone and a polar Ucon column. In both cases three peaks resulted. The area of the first peak (about 4% of the total) was greatly enhanced when authentic biphenyl was added to the mixture prior to gas chromatography.

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[58] D. F. DeTar, private communication.

[59] In a model experiment with light benzene we obtained 0.1313 g. of crude *p*-nitrobiphenyl and only 0.0165 g. of tar, in accordance with a previous report (ref. 11b).