RADICAL SUBSTITUTION IN AROMATIC NUCLEI

O. C. DERMER

Department of Chemistry, Oklahoma A. & M. College, Stillwater, Oklahoma

AND

M. T. EDMISON[1]

Department of Chemistry, University of Arkansas, Fayetteville, Arkansas

Received January 13, 1956

I. INTRODUCTION

In the assignment of organic reaction mechanisms, radicals, defined as atoms or groups bearing unpaired electrons, have received far less study than ions as intermediates. The recurrent idea of polarity as a driving and orienting factor has overshadowed the line of thought traceable from Dumas, Gomberg, and Paneth. Doubtless one cause for this is simply that most preparative organic reactions are effected in solution, where ionization is favored.

[1] Present address: Research Foundation, Oklahoma A. & M. College, Stillwater, Oklahoma.

Nevertheless such radicals, well known to dominate the mechanism of gas-phase reaction, are now recognized as frequent participants in reactions in solution also. To be sure, the two environments are vastly different, but there is still profit in considering them together.

It is simpler to define radicals than to be sure that a reaction involves them. The transition from a radical mechanism to an ionic one is easy; it may occur upon change of substituents in a reactant, or addition of a polar catalyst, or use of a polar solvent (32). Moreover, it is likely that some reactions proceed by a mixture of radical and ionic mechanisms. In general, if a radical in solution is capable of being characterized by any physical means, it is too unreactive to cause direct aromatic substitution.

The presence of transient radicals is deduced from their effects. In aromatic substitution, this means (*a*) departure from the rules for activation and orientation in ionic attack and (*b*) more or less formation of biaryls. It is familiar that electron-attracting groups on a benzene ring produce deactivation of the ring toward cationic reagents and predominantly meta substitution thereby; electron-releasing groups have the same effects in anionic substitutions. If then an attacking reagent does not obey either of these rules, it must be neither cation nor anion, but a neutral atom or radical. Even in water, a solvent very favorable to ionization, radical mechanisms are quite possible (385) and indeed this solvent may be ideal for effecting radical reactions because of its great stability (100, 291).

Aromatic nuclei are defined (19, 135) so as to include the unsaturated heterocyclic compounds of special ring stability. Quinones are not considered aromatic compounds. Substitution, however, must be more arbitrarily delimited. In this paper, substitution is used to mean a *one-step reaction* (excluding intermediates that cannot be isolated) *in which a hydrogen atom on an aromatic nucleus* (ArH), *the substrate, becomes replaced by some atom or group other than another* H *or an* Ar *group derived directly from* ArH. There are few cases of replacement of an atom or group other than hydrogen in an electron-pairing reaction, so that their exclusion from this discussion is not a major one. To consider the production of symmetrical biaryls by oxidative or other elimination of hydrogen between two molecules of ArH would extend the review unduly.

Hey (200) has chosen to designate both

$$R\cdot + ArH \rightarrow ArR + H\cdot$$

and

$$R\cdot + ArH \rightarrow RH + Ar\cdot$$

as substitution processes, but it seems advisable to distinguish these as *ordinary* substitution and the first step of *transfer* substitution, respectively. This step has been called radicalotropy (129, 301). Transfer substitution in ArH is completed when the radical Ar·, recently called a "residual free radical of first order" (287), forms a bond with some atom other than hydrogen:

$$Ar\cdot + YZ \rightarrow ArY + Z\cdot$$

or

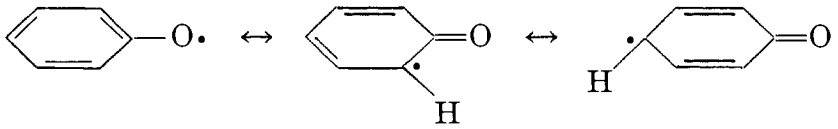
$$Ar\cdot + Y\cdot \rightarrow ArY$$

Y• may even be R•; ordinary and transfer substitutions then yield exactly the same main products, but can sometimes be distinguished by the side effects of the differing intermediates H• and Ar•.

In recent years several reviews have touched upon homolytic aromatic substitution in solution (12, 121, 199, 200, 201, 234a, 306, 333, 392, 398), the more so since quantitative comparisons of the reactivity of intramolecular positions (orientation) and also corresponding positions on unlike molecules (partial rate factors) have become available. The present paper is intended to cover the subject up to January 1, 1955 and to include as many later pertinent references as possible. The nomenclature used follows that of *Chemical Abstracts*.

Foreword on orientation

Phenols and aromatic amines differ from other aromatic substrates for radical substitution in (*a*) their susceptibility to attack by radicals not otherwise active and (*b*) their great tendency with such radicals to yield no meta-substituted products. Both of these behaviors are due to the possibilities for resonance in the substituted aryl radical:



This stabilization of the radical favors its formation, in the same way that benzyl radicals are more easily formed and more stable than phenyl radicals. In any transfer substitution thus established, it is evident that when the radical reacts as if the unpaired electron were on the ring, and prototropy reëstablishes the aromatic structure, only ortho and/or para orientation can result.

II. ALKYLATION

Benzene is slowly methylated by lead tetraacetate in boiling acetic acid; the final product is benzyl acetate, because side-chain acetoxylation occurs subsequently. Chlorobenzene is likewise converted to isomeric chlorobenzyl acetates, of which only the para isomer has been characterized (136). Nitrobenzene gives chiefly *o*- and some *p*-nitrotoluene, each in small amount, and 1,8-dinitronaphthalene yields only a trace of 2-methyl-1,8-dinitronaphthalene. About 20 per cent of *m*-dinitrobenzene is converted to a mixture of its 4-methyl, 2,4-dimethyl, and 2,6-dimethyl derivatives; 1,3,5-trinitrobenzene goes to 2,4,6-trinitrotoluene and 2,4,6-trinitro-*m*-xylene; and 2,4,6-trinitrotoluene to the same xylene (136). 2,4,6-Trinitro-*m*-xylene itself resists further methylation (136, 345).

Alternatively such methylation of polynitro compounds can be effected with acetyl peroxide (136), anode-liberated radicals from the electrolysis of sodium acetate in acetic acid (136), or phenyl iodosoacetate (345). Tetraethyllead and tetramethyllead are ineffective agents (136) for the alkylation of benzene or naphthalene at temperatures up to 300°C. (93). Mercuric acetate is also ineffective (136); it seems probable that a more strongly oxidizing acetate such as nickelic or cobaltic acetate would be better. If the aromatic substrate is not

nitrated and carries an alkyl side chain, this rather than the ring is attacked (259, 328).

The alkylation of pyridine occurs in the 2-position (predominantly) and 4-position or both, presumably by transfer substitution. The yields obtained by using diacyl peroxides are very satisfactory, whereas those from the electrolysis of a fatty acid in pyridine are only 4–14 per cent (168) (see table 1). In another example of alkylation in a heterocyclic nucleus, methyl 2-phenyloxazole-4-carboxylate with lead tetraacetate gains a methyl group in the 5-position (89).

Carboxymethylation of aromatic substrates has been observed, obviously as a transfer substitution. In the treatment of the three cresols and 2,4-xylenol with acetyl peroxide in acetic acid, a $-CH_2COOH$ group may enter any one of the unoccupied sites ortho or para to the hydroxyl group (398). The radical evidently arises from the solvent

$$CH_3COO\cdot \text{ (or } CH_3\cdot) + CH_3COOH \rightarrow \cdot CH_2COOH + CH_3COOH \text{ (or } CH_4)$$

and combines with a mesomeric radical derived from the phenol (compare page 79). In the same way the decomposition of benzoyl peroxide in acetic acid gives rise to appreciable amounts of α-carboxy-*o*-toluic acid and α-carboxy-*p*-toluic acid (164).

Other examples of the ability of benzoyl peroxide to yield such alkylated benzoic acids are available. Its decomposition in chloroform or carbon tetrachloride gives *o*- and *p*-trichloromethylbenzoic acids (48, 155, 234, 251), in *n*-octane it produces what is probably *p*-*n*-octylbenzoic acid (47), and in cyclohexane it forms *o*- and *p*-cyclohexylbenzoic acids as well as more complex ones (192).

The 2-cyano-2-propyl radical from 2,2′-azobis(2-methylpropionitrile) does not alkylate *m*-dinitrobenzene or 1,3,5-trinitrobenzene in boiling toluene (163).

Nuclear benzylation of toluene or *o*-chlorotoluene is not brought about by phenylacetyl peroxide (33), but *N*-benzyl-*N*-nitrosoacetamide does produce small yields of diarylmethanes from benzene, toluene, and chlorobenzene, by way of either benzyl or benzylidene radicals (174).

The rearrangement of benzyl phenyl ethers in quinoline produces not only

TABLE 1

Radical alkylations of pyridine (168)

Source of radical (R) introduced	Ratio of 2 isomer to 4 isomer	Overall Yield
		per cent
Electrolysis of RCOOH: R =		
CH_3	2.8:1	3.5
C_2H_5	1.3–2.8:1*	14
n-C_3H_7	5.1:1	4
Pyrolysis of $(RCOO)_2$: R =		
CH_3	7.6:1	86
C_2H_5	2.1:1*	87
n-C_3H_7	2.4:1	84
n-$C_{11}H_{23}$	3:1	38

* A small amount of 2,4-diethylpyridine was formed.

the expected benzylphenols, but benzylquinolines and hydroxyphenylquinolines also, by participation of the solvent (212, 213). Benzyl radicals from the pyrolysis of benzyl *p*-toluenesulfonate benzylate chlorobenzene in the para position but do not affect nitrobenzene so (310).

Alkylation, like phenylation, can be caused by heating an aromatic substrate with a suitable Grignard reagent (258) or its aluminum counterpart (388, 389), para orientation being observed in the few cases studied. No doubt some homolytic cleavage of such organometallic reagents does occur, especially when there is an acceptor for the radical (260). Yet it remains very uncertain whether to classify such alkylations and arylations as radical or as carbanion substitutions (149).

A remarkable alkylation of pyridine is its conversion to 4-(α-benzoyloxybenzyl)pyridine, 4-$C_6H_5CH(OCOC_6H_5)C_5H_4N$, by heating with benzaldehyde and *tert*-butyl peroxide. The steps are tentatively formulated as (*a*) generation of *tert*-butoxy radicals, (*b*) conversion thereby of benzaldehyde to benzoyl radicals, (*c*) reaction of benzoyl radicals with benzaldehyde to yield α-benzoyloxybenzyl radicals, $C_6H_5(C_6H_5COO)CH\bullet$, (*d*) 1,4-addition of either benzoyl and α-benzoyloxybenzyl or of two α-benzoyloxybenzyl radicals to pyridine, and (*e*) pyrolytic reversion to a pyridine structure (263).

The suggestion that thermal rearrangements of aryl allyl ethers, at least those yielding *p*-allylphenols, involve the migration of radicals (303) has not been accepted (69, 383). However, the arguments against a radical mechanism (232) do not necessarily apply when the reaction is caused photochemically; even diphenyl ether so rearranges to *p*-phenylphenol (264). Another classical reaction, the Elbs cyclization, may involve radicals also (20).

Triarylmethyl radicals are so stabilized that they rarely substitute directly in aromatic substrates such as benzene, although they attack the methyl group in toluene (124) and the nitro group in nitrobenzene (178). The radicals themselves interact by thermal disproportionation (411),

$$2(C_6H_5)_3C\bullet \rightarrow p\text{-}(C_6H_5)_2CHC_6H_4C(C_6H_5)_3$$

or further combine with diphenylnitrogen oxide, itself a radical (414),

$$2(C_6H_5)_3C\bullet + (C_6H_5)_2NO \rightarrow p\text{-}(C_6H_5)_3CC_6H_4C(C_6H_5)_2ON(C_6H_5)_2$$

but the mechanism of these nuclear substitutions is obscure.

The only other record of direct triphenylmethylation is that of boiling *o*-xylene and *p*-xylene. Orientation was not reported, and the anomalous failure of *m*-xylene to react similarly (411) suggests the need of further study.

Nuclear triphenylmethylation of phenol by the radical (350) surely proceeds by transfer substitution. It is doubtful whether similar substitution of phenols, phenolic ethers, amines, and acetylated amines by heating with chlorotriphenylmethane is to be assigned a radical (282) or a carbonium-ion course.

Benzene, toluene, chlorobenzene, and methyl benzoate can undergo substitution if they are first converted to aryl radicals. The necessary activating radical can come from an aroyl peroxide.

$$(ArCOO)_2 + (C_6H_5)_3C\cdot \rightarrow ArCOOC(C_6H_5)_3 + ArCOO\cdot$$

$$ArCOO\cdot + Ar'H \rightarrow ArCOOH + Ar'\cdot$$

$$Ar'\cdot + (C_6H_5)_3C\cdot \rightarrow (C_6H_5)_3CAr'$$

Little formation of carbon dioxide and none of any biaryl or $(C_6H_5)_3CAr$ was observed. Exclusively para substitution was noted (410, 412).

Only two isolated examples of nuclear acylation have been interpreted as involving radicals. The thermal reaction of either benzoyltriphenylmethyldiimide (409), $C_6H_5CON{=}NC(C_6H_5)_3$, or β-benzopinacolone (412), $C_6H_5COC(C_6H_5)_3$, yields 4-triphenylmethylbenzophenone in a rearrangement probably analogous to the noncyclizing disproportionation of triphenylmethyl itself. It is ventured here that the Fries-like rearrangement of phenolic esters such as phenyl cyclohexanecarboxylate and phenyl 3-methyl-2-butanoate into *o*-hydroxy ketones,

$$RCOOC_6H_5 \rightarrow o\text{-}HOC_6H_4COR$$

which is thermal instead of catalytic (230), proceeds by way of acyl radicals.

Under favorable circumstances an alkylidene biradical, RCH: or R_2C:, can substitute in an aromatic ring. Thus when α-toluenesulfonyl azide is thermally decomposed in aniline or dimethylaniline, some sulfur dioxide and nitrogen are evolved and 4,4′-diaminotriphenylmethane or 4,4′-bis(dimethylamino)triphenylmethane is formed (97). The diphenylmethylene radical, $(C_6H_5)_2C$:, from diazodiphenylmethane, does not attack benzene (354) and takes hydrogen from the side chain of benzyl methyl ether (28), but with phenol it gives small amounts (2 to 3 per cent) of *o*-(diphenylmethyl)phenol (61, 356). The ethoxycarbonylmethylene radical, C_2H_5OCOCH:, derived from ethyl diazoacetate, is well known to add to a benzene ring and yield a bicyclo compound containing a cyclopropane ring. This upon heating isomerizes to cycloheptane derivatives related to the tropolones (247). However, alkyl aryl ethers heated with ethyl diazoacetate yield no cyclopropane derivatives but give, among other products, small amounts of ethyl alkoxyarylacetates.

$$C_6H_5OR + N_2CHCOOC_2H_5 \rightarrow ROC_6H_4CH_2COOC_2H_5$$

Anisole was thus converted to the 4-substituted compound, 1,2-dimethoxybenzene to the 4-substituted compound, and 1-methoxynaphthalene to a similar but unidentified product, *not* ethyl 1-(4-methoxynaphthalene)acetate. 2-Methoxynaphthalene gave a 33 per cent yield of the 1-methoxycarbonylated product, and even mesitylene undergoes the substitution. A carbonium-ion sequence has been suggested for this unusual process (170), but a radical attack, comparable to sulfonamidation (see page 99), seems equally likely at present.

III. INTERMOLECULAR ARYLATION

There are several reasons why arylation is the best-studied radical substitution. The radical source—most commonly some form of a diazo compound or an aroyl peroxide—is readily obtainable, the products are usually crystalline and

reasonably identifiable, and there is no abundance of syntheses for biaryls. Radicals are almost surely involved also in the Ullmann reaction and the production of biaryls by dehydrogenation, but these will not be considered here.

A. Arylation with diazotates and diazoacetates

Reactions of this category have been reviewed in detail (16). Table 2 supplements the earlier data primarily by description of work published since 1944. No doubt some of the reactions tabulated are partially ionic in character, e.g., those of diazonium trifluoroacetates, which are discussed below. In some instances wherein metal powders or metallic salts were added, proof of a homolytic course of reaction is lacking.

In table 4 ratios of isomeric arylation products from these reactions and from the pyrolysis of peroxides have been tabulated. It should be noted that these ratios do not show a preponderance of the para compounds, as formerly believed. In this respect recent work is more reliable because new analytical tools and techniques have become available. Indeed, the ratios of isomers obtained from preparative experiments are not safe to use in the derivation of partial rate factors (211).

A recent study (315) has been made of the formation of biphenyls from arylamines nitrosated with alkyl nitrite–trifluoroacetic anhydride mixtures, from aqueous diazonium trifluoroacetates, from diazonium chlorides with added trifluoroacetate ions, and from diazonium salts stabilized as the water-insoluble acid trifluoroacetates (see table 2). An equilibrium probably exists between an ionic and some covalent type of structure, the latter producing homolytic substitutions. There must be, however, only a little of the covalent material, since diazonium acid trifluoroacetates appear to be largely dissociated in dilute aqueous solutions.

Whatever the mechanisms of copper-catalyzed reactions of diazo compounds, little doubt exists that homolytic substitution is sometimes involved. Thus, when benzenediazonium formate is decomposed in acetic acid containing copper powder (161), *p*-terphenyl is produced. The addition of copper powder and glacial formic acid to aniline diazotized in glacial acetic acid results in the formation of *p*-terphenyl, *p*-quaterphenyl, and *p*-quinquephenyl. Benzenediazonium sulfate in the presence of alcohol and copper powder (162) gives the same products. Biphenyl, *p*-terphenyl, and *p*-quaterphenyl are produced when *p*-biphenyldiazonium sulfate is decomposed in a mixture of benzene, glacial formic acid, and copper powder.

The exceptional reactivity of ferrocene as a substrate for arylation (312a) deserves notice.

B. Arylation with triazenes (diazoamino compounds)

The pyrolysis of 1,3-diphenyltriazene yields a mixture of 2- and 4-biphenylamines; the orientation is characteristic of homolytic as well as electrophilic substitution (197, 215). 1,3-Di-*p*-tolyltriazene behaves similarly, yielding about

TABLE 2

Arylated products from diazo compounds[a]

Product	Component A	Component B	Method[b]	Yield	Reference
Monosubstituted biphenyls, $RC_6H_4C_6H_5$					
				per cent	
R =					
H	$C_6H_5NH_2$	C_6H_6	A-1	19	(174)
				15	(359)
			A-2	19	(174)
				22	(130)
			A-3	16	(130)
			A-6	5-30	(315)
			A-7	7-19	(315)
			A-9	33	(299)
			B-1	40-80	(174)
			B	5	(227)
			B-3	32-49	(315)
2-, 3-, and 4-CH_3	$C_6H_5NH_2$	$C_6H_5CH_3$	B-2	9, 27	(342)
4-CH_3	*p*-$CH_3C_6H_4NH_2$	C_6H_6	A-1	14	(64)
			A-4	43	(315)
			A-7	8	(315)
	$C_6H_5NH_2$	$C_6H_5CH_3$	A-9	—	(298)
	p-$CH_3C_6H_4NH_2$	C_6H_6	B-3	16–37	(315)
(?)-CH_3	$C_6H_5NH_2$	$C_6H_5CH_3$	B-1	49	(174)
2-, 3-, and 4-$(CH_3)_2CH$	$C_6H_5NH_2$	$C_6H_5CH(CH_3)_2$	B-2	22, 24	(342)
2-, 3-, and 4-$(CH_3)_3C$	$C_6H_5NH_2$	$C_6H_5C(CH_3)_3$	B-2	22, 25	(342)
4-$(CH_3)_3C$	*p*-$(CH_3)_3CC_6H_4NH_2$	C_6H_6	B-1	—	(66)
2-HO	$C_6H_5NH_2$	C_6H_5OH	A-6	2	(309)
2- and 4-HO	$C_6H_5NH_2$	C_6H_5OH	A-6	>27	(214)
4-HO	$C_6H_5NH_2$	C_6H_5OH	A-4[c]	26	(216)
			A-6	27	(309)
(?)-C_2H_5OOC	$C_6H_5NH_2$	$C_6H_5COOC_2H_5$	B-1	—	(174)
2-C_6H_5CO	2-$H_2NC_6H_4COC_6H_5$	C_6H_6	A-1	15	(117)
			B-2	15	(118)
2-CH_3O	$C_6H_5NH_2$	$C_6H_5OCH_3$	A-2	15	(126)
4-CH_3O	*p*-$CH_3OC_6H_4NH_2$	C_6H_6	A-6	25	(315)
			B-3	12	(315)
2-C_6H_5O	*o*-$C_6H_5OC_6H_4NH_2$	C_6H_6	A-1	25	(117)
2- and 4-O_2N	$C_6H_5NH_2$	$C_6H_5NO_2$	A-1	6	(174)
			A-2	8	(174)
2-, 3-, and 4-O_2N	$C_6H_5NH_2$	$C_6H_5NO_2$	A-1	—	(11)
				13–15	(359)
			B-2	39-53	(119)
			B	30-37	(359)
3-O_2N	*m*-$O_2NC_6H_4NH_2$	C_6H_6	A-1	21	(243)
			A-2	18	(130)
			A-3	—	(116)
			B-1	63	(146)
4-O_2N	*p*-$O_2NC_6H_4NH_2$	C_6H_6	A-2	26	(130)
			A-6	11	(315)
			B-3	6, 14	(315)
			B[d]	—	(270)
3-F_3C	*m*-$CF_3C_6H_4NH_2$	C_6H_6	B-1	35	(314)
4-F_3C	*p*-$CF_3C_6H_4NH_2$	C_6H_6	A-6	17	(315)
			B-3	23	(315)
2-Cl	*o*-$ClC_6H_4NH_2$	C_6H_6	A-1	13	(14)
(?)-Cl	$C_6H_5NH_2$	C_6H_5Cl	A-1	16, 33	(14)
3-Cl	*m*-$ClC_6H_4NH_2$	C_6H_6	A-1	22	(14)
4-Cl	*p*-$ClC_6H_4NH_2$	C_6H_6	A-1	28	(14)
			A-4	18-25	(315)
			A-6	12	(315)
			A-7	9	(315)
			B-3	17, 33	(315)

TABLE 2—*Continued*

Product	Component A	Component B	Method[b]	Yield	Reference
Disubstituted biphenyls, $RR'C_6H_3C_6H_5$					
R and R′ =				*per cent*	
2-CH_3-4-HO	$C_6H_5NH_2$	*m*-$CH_3C_6H_4OH$	A-6	10-15	(74)
3-CH_3-4-HO	$C_6H_5NH_2$	*o*-$CH_3C_6H_4OH$	A-6	10-15	(74)
3-CH_3-4-O_2N	3-CH_3-4-$O_2NC_6H_3NH_2$	C_6H_6	A-2	—	(174)
4-CH_3-2-O_2N	4-CH_3-2-$O_2NC_6H_3NH_2$	C_6H_6	A-3	40	(337)
				—	(68)
3,4-$(HO)_2$	$C_6H_5NH_2$	*o*-$C_6H_4(OH)_2$	A-6	11	(309)
3-O_2N-2-CH_3OOC	2-H_2N-6-$O_2NC_6H_3COOCH_3$	C_6H_6	A-1	7	(228)
3,4-$(C_2H_5OOC)_2$	4-H_2N-1,2-$C_6H_3(COOC_2H_5)_2$	C_6H_6	B-2	45	(184)
3,4-$(CN)_2$	4-H_2N-1,2-$C_6H_3(CN)_2$	C_6H_6	A-1	57	(184)
4-O_2N-3-CF_3	4-O_2N-3-$CF_3C_6H_3NH_2$	C_6H_6	A-3	22	(314)
Disubstituted biphenyls, $RC_6H_4C_6H_4R'$					
R and R′ =					
4,4′-$(CH_3)_2$	*p*-$CH_3C_6H_4NH_2$	$C_6H_5CH_3$	A-4	2	(315)
4′-CH_3-4-CH_3OOC	*p*-$CH_3C_6H_4NH_2$	$C_6H_5COOCH_3$	A-4	1	(315)
4-CH_3-2′- and 4′-O_2N	*p*-$CH_3C_6H_4NH_2$	$C_6H_5NO_2$	A-2	—	(204)
4-CH_3-2′-, 3′-, and 4′-O_2N	*p*-$CH_3C_6H_4NH_2$	$C_6H_5NO_2$	A-1	27-45	(204)
			B-2	28-32	(204)
2- and 4-CH_3-3′-O_2N	*m*-$O_2NC_6H_4NH_2$	$C_6H_5CH_3$	A-3	19	(204)
2- and 4-CH_3-4′-O_2N	*p*-$O_2NC_6H_4NH_2$	$C_6H_5CH_3$	B[d]	—	(270, 272)
4,4′-$(HO)_2$	*p*-$HOC_6H_4NH_2$	C_6H_5OH	A-4[c]	41	(216)
4′-CH_3O-4-HO	*p*-$CH_3OC_6H_4NH_2$	C_6H_5OH	A-4[c]	36	(216)
2′- and 4′-HO-2-HOOC	*o*-$H_2NC_6H_4COOH$	C_6H_5OH	A-6[e]	—	(171, 173)
4′-Cl-4-HO	*p*-$ClC_6H_4NH_2$	C_6H_5OH	A-4[c]	31	(216)
4′-O_2N-4-HOOC	*p*-$O_2NC_6H_4NH_2$	C_6H_5COOH	B	—	(271)
4′-O_2N-4-$HOCH_2$	*p*-$O_2NC_6H_4NH_2$	$C_6H_5CH_2OH$	B	—	(271)
4′-O_2N-4-HCO	*p*-$O_2NC_6H_4NH_2$	C_6H_5CHO	B	—	(271)
4′-O_2N-4-CH_3CO	*p*-$O_2NC_6H_4NH_2$	$C_6H_5COCH_3$	B	—	(271)
2,4′- and 4,4′-$(O_2N)_2$	*p*-$O_2NC_6H_4NH_2$	$C_6H_5NO_2$	B	—	(272)
3,4′-$(O_2N)_2$	*m*-$O_2NC_6H_4NH_2$	$C_6H_5NO_2$	B-2	12	(70)
2-CH_3O-3′-O_2N	*m*-$O_2NC_6H_4NH_2$	$C_6H_5OCH_3$	A-2	50	(126)
			B-1	47	(126)
4-C_2H_5O-4′-O_2N	*p*-$O_2NC_6H_4NH_2$	$C_6H_5OC_2H_5$	B[f]	—	(271)
4-Br-2′-, 3′-, and 4′-O_2N	*p*-$BrC_6H_4NH_2$	$C_6H_5NO_2$	A-1	16-25	(204)
			B-2	34-44	(204)
2,4′-$(CH_3O)_2$	*p*-$CH_3OC_6H_4NH_2$	$C_6H_5OCH_3$	B-1	—	(126)
Fluorenone	2-$C_6H_5COC_6H_4NH_2$		A-1	1	(117)
3-Chlorofluorenone	2-(4-$ClC_6H_4CO)C_6H_4NH_2$		A-6	—	(44)
Polysubstituted biphenyls					
5,2′-$(CH_3)_2$-2-HO	*o*-$CH_3C_6H_4NH_2$	*p*-$CH_3C_6H_4OH$	A-6	10-15	(74)
5,3′-$(CH_3)_2$-2-HO	*m*-$CH_3C_6H_4NH_2$	*p*-$CH_3C_6H_4OH$	A-6	10-15	(74)
5,4′-$(CH_3)_2$-2-HO	*p*-$CH_3C_6H_4NH_2$	*p*-$CH_3C_6H_4OH$	A-6	10-15	(74)
2,2′-$(CH_3)_2$-4-HO	*o*-$CH_3C_6H_4NH_2$	*m*-$CH_3C_6H_4OH$	A-6	10-15	(74)
2,3′-$(CH_3)_2$-4-HO	*m*-$CH_3C_6H_4NH_2$	*m*-$CH_3C_6H_4OH$	A-6	10-15	(74)
2,4′-$(CH_3)_2$-4-HO	*p*-$CH_3C_6H_4NH_2$	*m*-$CH_3C_6H_4OH$	A-6	10-15	(74)
3,2′-$(CH_3)_2$-4-HO	*o*-$CH_3C_6H_4NH_2$	*o*-$CH_3C_6H_4OH$	A-6	10-15	(74)
3,3′-$(CH_3)_2$-4-HO	*m*-$CH_3C_6H_4NH_2$	*o*-$CH_3C_6H_4OH$	A-6	10-15	(74)
3,4′-$(CH_3)_2$-4-HO	*p*-$CH_3C_6H_4NH_2$	*o*-$CH_3C_6H_4OH$	A-6	10-15	(74)
2′-HO-3-Cl-2-HOOC	2-H_2N-6-ClC_6H_3COOH	C_6H_5OH	A-6	3	(229)
2′-HO-4-Cl-2-HOOC	2-H_2N-4-ClC_6H_3COOH	C_6H_5OH	A-6	10	(229)
3,4,5-$(CH_3OOC)_3$	5-H_2N-1,2,3-$C_6H_2(COOCH_3)_3$	C_6H_6	B-2	60	(317)
2′-, 3′-, and 4′-CH_3O-3,4-$(CN)_2$	4-H_2N-1,2-$C_6H_3(CN)_2$	$C_6H_5OCH_3$	A-1	—	(184)

TABLE 2—*Continued*

Product	Component A	Component B	Method[b]	Yield	Reference
Terphenyls and derivatives					
				per cent	
o-Terphenyl, 2-CH_3-6-O_2N	*o*-(2-CH_3-6-$O_2NC_6H_3$)$C_6H_4NH_2$	C_6H_6	A-1	13–16	(115)
m-Terphenyl	*m*-$C_6H_5C_6H_4NH_2$	C_6H_6	B-2	35	(70)
4,4′,4″-$(O_2N)_3$ and others	5-O_2N-1,3-$C_6H_3(NH_2)_2$	$C_6H_5NO_2$	B-2	19	(70)
p-Terphenyl[g]	$C_6H_6NH_2$	$C_6H_5C_6H_5$	A-9	—	(298)
4,4″-$(O_2N)_2$-3-(4-$O_2NC_6H_4$)-2′,5′-$(H_2N)_2$	*p*-$O_2NC_6H_4NH_2$	*p*-$C_6H_4(NH_2)_2$	A-6	27	(6)
2,2″-$(O_2N)_2$-3′,6′-(2-$O_2NC_6H_4$)-2′,5′-$(H_2N)_2$	*o*-$O_2NC_6H_4NH_2$	*p*-$C_6H_4(NH_2)_2$	A-6	81	(6)
2,5,2″,5″-Cl_4-3′-(2,5-$Cl_2C_6H_3$)-2′,5′-$(H_2N)_2$	2,5-$Cl_2C_6H_3NH_2$	*p*-$C_6H_4(NH_2)_2$	A-6	23	(6)
Quaterphenyls, 4-CH_3	*p*-$CH_3C_6H_4NH_2$	C_6H_5	A-1	—	(64)
Arylnaphthalenes					
1- and 2-C_6H_5	$C_6H_5NH_2$	$C_{10}H_8$	A-9	—	(297)
			B	38[h]	(227)
1-(4-HOC_6H_4)	1-$C_{10}H_7NH_2$	C_6H_5OH	A-4	29	(216)
2-(4-HOC_6H_4)	2-$C_{10}H_7NH_2$	C_6H_5OH	A-4	35	(216)
2-(2- and 4-$O_2NC_6H_4$)	2-$C_{10}H_7NH_2$	$C_6H_5NO_2$	B-1, B-2	—	(202)
(?)-(4-$O_2NC_6H_4$)	*p*-$O_2NC_6H_4NH_2$	$C_{10}H_8$	B	—	(272)
2-CH_3-(?)-C_6H_5[i]	$C_6H_5NH_2$	2-$CH_3C_{10}H_7$	B	—	(227)
2,7-$(C_6H_5)_2$	2,7-$C_{10}H_6(NH_2)_2$	C_6H_6	B-1	—	(202)
6-CH_3O-2-C_6H_5	6-CH_3O-2-$C_{10}H_6NH_2$	C_6H_6	B-1	41	(202)
7-CH_3O-2-C_6H_5	7-CH_3O 2-$C_{10}H_6NH_2$	C_6H_6	B-1	44	(202)
1-O_2N-2-C_6H_5	1-O_2N-2-$C_{10}H_6NH_2$	C_6H_6	A-1	—	(202)
5-O_2N-2-C_6H_5	5-O_2N-2-$C_{10}H_6NH_2$	C_6H_6	B-1	40	(202)
6-O_2N-2-C_6H_5	6-O_2N-2-$C_{10}H_6NH_2$	C_6H_6	B-1	52	(202)
8-O_2N-2-C_6H_5	8-O_2N-2-$C_{10}H_6NH_2$	C_6H_6	B-1	47	(202)
6-Br-2-C_6H_5	6-Br-2-$C_{10}H_6NH_2$	C_6H_6	B-1	44	(202)
2,6-$(CH_3)_2$-1-C_6H_5	$C_6H_5NH_2$	2,6-$(CH_3)_2C_{10}H_6$	B	49.5[j]	(227)
Arylfurans					
2-C_6H_5	$C_6H_5NH_2$	Furan	A-1	22	(246)
2-(4-$O_2NC_6H_4$)	*p*-$O_2NC_6H_4$	Furan	A-3	20	(246)
2-(4-ClC_6H_4)	*p*-$ClC_6H_4NH_2$	Furan	B-2	19	(246)
2- and 3-(4-ClC_6H_4)	*p*-$ClC_6H_4NH_2$	Furan	A-1	29	(246)
2-(4-BrC_6H_4)	*p*-$BrC_6H_4NH_2$	Furan	A-1	15	(246)
2-(1-$C_{10}H_7$)	1-$C_{10}H_7NH_2$	Furan	A-3	18	(246)
Arylthiophenes					
3-C_6H_5	$C_6H_5NH_2$	C_4H_4S	A-9	—	(298)
2-(4-$CH_3C_6H_4$)	*p*-$CH_3C_6H_4NH_2$	C_4H_4S	A-1	13	(63)
2-(2-$O_2NC_6H_4$)	*o*-$O_2NC_6H_4NH_2$	C_4H_4S	A-3	51	(364)
2-(4-ClC_6H_4)	*p*-$ClC_6H_4NH_2$	C_4H_4S	A-1	33	(63)
2,5-(4-$CH_3C_6H_4)_2$	*p*-$CH_3C_6H_4NH_2$	C_4H_4S	A-1	3	(63)
2,5-(4-$ClC_6H_4)_2$	*p*-$ClC_6H_4NH_2$	C_4H_4S	A-1	2	(63)
2-C_6H_5-thianaphthene	$C_6H_5NH_2$	Thianaphthene	B-1	5	(150)
Dibenzothiophene	2-$C_6H_5SC_6H_4NH_2$		A-1	10	(117)

TABLE 2—*Continued*

Product	Component A	Component B	Method[b]	Yield	Reference
Arylated heterocyclic nitrogen compounds					
				per cent	
Pyridines:					
2- and 4-C_6H_5	$C_6H_5NH_2$	C_5H_5N	A-5	21	(298)
3-C_6H_5	3-$H_2NC_5H_4N$	C_6H_6	B-2[k]	39	(323)
2-(2- and 4-HOC_6H_4)	2-$H_2NC_5H_4N$	C_6H_5OH	A-2	—	(75, 76)
2-(4-$O_2NC_6H_4$)	*p*-$O_2NC_6H_4NH_2$	C_5H_5N	B	—	(272)
4-(4-$O_2NC_6H_4$)	*p*-$O_2NC_6H_4NH_2$	C_5H_5N	A-5	28	(391)
2-(4-BrC_6H_4) and isomers	*p*-$BrC_6H_4NH_2$	C_5H_5N	B-2	7	(208a)
2-, 3-, and 4-(4-$(CH_3)_3C$-2-$O_2NC_6H_3$)	4-$(CH_3)_3C$-2-$O_2NC_6H_3NH_2$	C_5H_5N	A-5	30	(82)
2-, 3-, and 4-(4-$(CH_3)_3C$-3-$O_2NC_6H_3$)	4-$(CH_3)_3C$-3-$O_2NC_6H_3NH_2$	C_5H_5N	A-5	59	(82)
2-, 3-, and 4-(3,4-$(C_2H_5OOC)_2C_6H_3$)	4-H_2N-1,2-$C_6H_3(COOC_2H_5)_2$	C_5H_5N	A-5	40	(184)
2-, 3-, and 4-(3,4-$(CN)_2C_6H_3$)	4-H_2N-1,2-$C_6H_3(CN)_2$	C_5H_5N	A-5	—	(184)
2-, 3-, and 4-(5-CH_3O-2-$O_2NC_6H_3$)	5-CH_3O-2-$O_2NC_6H_3NH_2$	C_5H_5N	A-5	22	(82)
4-(4-$(CH_3)_2NC_6H_4$)	*p*-$(CH_3)_2NC_6H_4NH_2$	C_5H_5N	A-5	—	(266)
2-(4-$C_6H_5NHC_6H_4$)	*p*-$C_6H_5NHC_6H_4NH_2$	C_5H_5N	A-5	—	(86)
(*m*-C_6H_4=)di-	(?)-(*m*-$H_2NC_6H_4$)C_5H_4N	C_5H_5N	A-5	—	(85)
(*p*-C_6H_4=)di-	(?)-(*p*-$H_2NC_6H_4$)C_5H_4N	C_5H_5N	A-5	—	(85)
2-, 3-, and 4-(3-*o*-$\underline{CONHCOC_6H_4}$)	3-Aminophthalimide	C_5H_5N	A-5	85	(184)
2-, 3-, and 4-(4-*o*-$\underline{CONHCOC_6H_4}$)	4-Aminophthalimide	C_5H_5N	A-5	56	(184)
2-, 3-, and 4-(2-phthalimido-5-methoxyphenyl)	*N*-(2-Amino-4-methoxyphenyl)phthalimide	C_5H_5N	A-5	—	(82)
2-, 3-, and 4-(3,4-$Cl_2C_6H_3$)	3,4-$Cl_2C_6H_3NH_2$	C_5H_5N	A-5	—	(184)
2-, 3-, and 4-(3,4-$Br_2C_6H_3$)	3,4-$Br_2C_6H_3NH_2$	C_5H_5N	A-5	—	(184)
2-*n*-C_4H_9O-5-C_6H_5	5-H_2N-2-*n*-$C_4H_9OC_6H_3N$	C_6H_6	A-1	14	(3)
2-Cl-3-C_6H_5	3-H_2N-2-ClC_6H_3N	C_6H_6	B-2	—	(3)
2-Cl-5-C_6H_5	5-H_2N-2-ClC_6H_3N	C_6H_6	A-3	—	(3)
			B-2	22	(3)
Quinolines:					
3-C_6H_5	3-$H_2NC_9H_6N$	C_6H_6	B-2	33	(3)
(?)-(3-$O_2NC_6H_4$)	*p*-$O_2NC_6H_4NH_2$	C_9H_7N	B	—	(272)
3-(2- and 3-C_5H_4N)	3-$H_2NC_3H_6N$	C_5H_5N	A-5	48	(81)
3-(2- and 4-C_5H_4N)	3-$H_2NC_9H_6N$	C_5H_5N	A-5	39	(1)
5-(2- and other C_5H_4N)	5-$H_2NC_9H_6N$	C_5H_5N	A-5	29	(81, 83)
8-(2-, 3-, and 4-C_5H_4N)	8-$H_2NC_9H_6N$	C_5H_5N	A-5	15	(81, 83)
4-CH_3-3-(?-C_5H_4N)	3-H_2N-4-$CH_3C_9H_5N$	C_5H_5N	A-5	—	(355)
6-CH_3O-8-(2-, 3-, and 4-C_5H_3N)	8-H_2N-6-$CH_3OC_2H_5N$	C_5H_5N	A-5	—	(82, 83)
8-CH_3O-6-(2-, 3-, and 4-C_5H_3N)	6-H_2N-8-$CH_3OC_9H_5N$	C_5H_5N	A-5	—	(83)
8-Br-6-(2-, 3-, and 4-C_5H_3N)	6-H_2N-8-BrC_9H_5N	C_5H_5N	A-5	—	(83)
6-(2,6-$(CH_3)_2$-3- and 4-C_5H_2N)	6-$H_2NC_9H_6N$	2,6-$(CH_3)_2C_5H_3N$	B-2	12	(87)
3-(4-C_2H_5OOC-2-C_5H_3N)	3-$H_2NC_9H_6N$	4-$C_5H_4NCOOC_2H_5$	A-5	—	(210)
8-(2-, 3-, and 4-(C_5H_4N)-6-(2-C_5H_4N)	8-H_2N-6-(2-C_5H_4N)C_9H_5N	C_5H_5N	A-5	—	(85)
Pyrroles:					
N-C_2H_5OOC-2-C_5H_5	$C_5H_5NH_2$	$C_5H_4NCOOC_2H_5$	B-1	29	(336)
Phthalocyanines:					
(?-C_5H_4N)$_4$	$(H_2N)_4$-phthalocyanine	C_5H_5N	A-5	—	(168)

TABLE 2—*Continued*

Product	Component A	Component B	Method[b]	Yield	Reference
		Ferrocenes			
				per cent	
C_6H_5	$C_6H_5NH_2$	Ferrocene	A-8	65	(54)
			A-6[i]	17	(393)
			B	46	(54)
o-$CH_3C_6H_4$	*o*-$CH_3C_6H_4NH_2$	Ferrocene	A-8	43	(54)
p-$CH_3C_6H_4$	*p*-$CH_3C_6H_4NH_2$	Ferrocene	A-6	57	(306b)
p-HOC_6H_4	*p*-$HOC_6H_4NH_2$	Ferrocene	A-8	14	(54)
			A-6[l]	60	(393)
o-$HOOCC_6H_4$	*o*-$H_2NC_6H_4COOH$	Ferrocene	A-8	7	(54)
			A-6[l]	15	(393)
p-$CH_3OC_6H_4$	*p*-$CH_3OC_6H_4NH_2$	Ferrocene	A-8	35	(54)
			A-6	40	(306b)
o-$O_2NC_6H_4$	*o*-$O_2NC_6H_4NH_2$	Ferrocene	A-8	5	(54)
p-$O_2NC_6H_4$	*p*-$O_2NC_6H_4NH_2$	Ferrocene	A-8	18	(54)
			A-6	64	(306b)
			A-6[l]	10	(393)
m-ClC_6H_4	*m*-$ClC_6H_4NH_2$	Ferrocene	A-8	34	(54)
p-$HO_3SC_6H_4$	*p*-$H_2NC_6H_4SO_3H$	Ferrocene	A-8	—	(54)
8-$HOOCC_{10}H_6$	8-H_2N-1-$C_{10}H_6COOH$	Ferrocene	A-6[l]	6	(393)
$(C_6H_5)_2$	$C_6H_5NH_2$	Ferrocene	A-8	9	(54)
			A-6[l]	20	(393)
			B	8	(54)
	$C_6H_5NH_2$	Phenylferrocene	A-8	52	(54)
(*p*-$CH_3OC_6H_4)_2$	*p*-$CH_3OC_6H_4NH_2$	Ferrocene	A-8	7	(54)
			A-6	—	(306b)
(*p*-$O_2NC_6H_4)_2$	*p*-$O_2NC_6H_4NH_2$	Ferrocene	A-6[l]	60	(393)
(*m*-$ClC_6H_4)_2$	*m*-$ClC_6H_4NH_2$	Ferrocene	A-8	0.4	(54)
$(C_6H_5)_3$	$C_6H_5NH_2$	Phenylferrocene	A-8	10	(54)
$(C_6H_5)_5$	$C_6H_5NH_2$	Ferrocene	A-6	42	(306b)
(4-$C_6H_5C_6H_4)_3$	4-$C_6H_5C_6H_4NH_2$	Ferrocene	A-6[l]	50	(393)
(8-$HOOCC_{10}H_6)_2$	8-H_2N-1-$C_{10}H_6COOH$	Ferrocene	A-6[l]	30	(393)

[a] Excepting the products of quantitatively studied arylations recorded in table 4A.

[b] The procedures are designated by letters and numbers:

A-1 = diazohydroxide reaction (NaOH)
A-2 = sodium diazotate procedure
A-3 = sodium acetate modification
A-4 = stabilized diazonium salt procedure
A-5 = pyridine method
A-6 = use of aqueous diazonium salt
A-7 = use of aqueous diazonium chloride + trifluoroacetate ions
A-8 = use of aqueous diazonium salt + acetic acid
A-9 = use of diazonium chloride + aluminum chloride
B = nitrosoacetylamine reaction (not further specified)
B-1 = nitrosoacetylamine reaction (N_2O_3)
B-2 = nitrosoacetylamine reaction (NOCl)
B-3 = nitrosoacetylamine reaction [RONO + $(CF_3CO)_2O$]

[c] Without alkali.

[d] Nitrosated amides of acetic, butyric, and benzoic acids gave the same results.

[e] Isolated as the lactone.

[f] Isolated as the hydroxy compound.

[g] An isomer was also produced.

[h] The 2-isomer comprised 16.6 per cent of the phenylated product.

[i] The 1-phenyl isomer predominated.

[j] Percentage of arylated product rather than of theoretical yield. Smaller amounts of two isomers were present; one was thought to be the 3-phenyl isomer.

[k] The isobutyryl derivative was used.

[l] In strongly acid solution.

15 per cent of dimethylbiphenylamines, mostly 4′,5-dimethyl-2-biphenylamine (299).

A 1-aryl-3,3-dimethyltriazene is more frequently used for generating radicals to attack an aromatic substrate. This kind of triazene is made by coupling an arenediazo compound and dimethylamine. The decomposition of 1,3-bis(4-methoxy-2-nitrophenyl)triazene in benzene gives the expected 4-methoxy-2-nitrobiphenyl, and that of 1-(3,4-dimethylphenyl)-3,3-dimethyltriazene similarly yields 3,4-dimethylbiphenyl (233). The reaction has been used in the study of isomer ratios in the homolytic arylation of toluene, cumene, and *tert*-butylbenzene (342). Either 3,3-dimethyl-1-(3,4,5-trimethoxyphenyl)triazene or the methoxy-free compound arylates methyl 3,4,5-trimethoxybenzoate by displacing a nuclear methoxyl group instead of hydrogen; a methyl 4-aryl-3,5-dimethoxybenzoate is obtained (313). Sometimes the reaction is effected in acid solution; biphenyl was thus obtained in 25–37 per cent yield (131) and 3-nitrobiphenyl in 34–42 per cent yield (252). 3,3-Dimethyl-1-phenyltriazene upon decomposition in nitrobenzene through which hydrogen chloride was bubbled produced a 35 per cent yield of 2- and 4-nitrobiphenyls (131). Perhaps the presence of hydrogen chloride or even acetic acid favors a polar mechanism, but the reactivity of nitrobenzene can hardly be explained on this basis. Under similar conditions 3,3-dimethyl-1-(3-quinolyl)triazene and benzene give the expected 3-phenylquinoline (3).

C. Arylation with other diazo compounds

Diazoanhydrides, $(ArN_2)_2O$, made by careful addition of acetic acid to potassium arenediazotates, react vigorously, even explosively, with aromatic substrates. Arylamines are converted to triazenes, but benzene and toluene yield biaryls, albeit in low yields because of the violence of the reaction. Diazoanhydrides derived from toluene, chlorobenzene, bromobenzene, and nitrobenzene behave thus (23).

The most stable of the diazo ethers, *p*-nitrodiazobenzene methyl ether, upon long boiling with benzene and toluene arylates them to 4-nitrobiphenyl and 4-methyl-4′-nitrobiphenyl, respectively (22).

The decomposition of diazocyanides in nonaqueous media is believed to be homolytic (371). *p*-Chlorobenzenediazocyanide in benzene gave a 1.5 per cent yield of 4-chlorobiphenyl; the ortho isomer gave a 3 per cent yield of 2-chlorobiphenyl, and *p*-bromobenzenediazocyanide gave a 1 per cent yield of 4-bromobiphenyl.

p-Nitrodiazobenzene sulfide, like its oxygen counterpart, the anhydride, yields 4-nitrobiphenyl on reacting with benzene (27).

Potassium benzenediazocarboxylate in refluxing benzene containing bismuth trichloride yields some biphenyl (334). With benzophenone it is reported to produce phenylbenzophenones in 10.5 per cent yield (307).

In the deamination of arenediazonium salts with hypophosphorous acid, some *p*-terphenyl is formed; this must represent radical substitution (5).

D. Arylation with azo compounds

When 1′,1′,1′-triphenylbenzeneazomethane (phenylazotriphenylmethane) was first pyrolyzed in benzene the products were shown (198) to include tetraphenylmethane, biphenyl, and some triphenylmethyl peroxide. The first two compounds could occur by attack on the benzene or by combination of free radicals, and the last by oxidation of the triphenylmethyl radicals. That biphenyl was probably formed through substitution of benzene is indicated by the fact that no biphenyl was found when the decomposition was carried out in chlorobenzene or in nitrobenzene. Some 4-chlorobiphenyl was formed from chlorobenzene, but no biphenyl derivative at all from nitrobenzene. This is not surprising in view of the tendency of triphenylmethyl radicals to attack the nitro group rather than the ring in nitrobenzene (178). Nevertheless, recent work has shown that nitrobiphenyl *can* be obtained in 25 per cent yield (226). Toluene undergoes the same reaction to yield at least 2- and 4-methylbiphenyls (408, 409). Pyridine as substrate has been examined repeatedly; at first only 2- and 4-phenylpyridines were found as arylated products (408, 409), but later the 3-phenyl isomer (3) and a compound that may be either (triphenylmethyl)-phenylpyridine (226) or *p*-2-pyridyltetraphenylmethane (208a) were also characterized. From reaction at 65–70°C. the amounts of isomeric phenylpyridines were 4- > 3- > 2-, whereas at 20°C. (in a much slower process) the order was 3- > 4- > 2- (226). The ratio of the 2-, 3- and 4-phenyl isomers formed at 105°C. was more precisely established (208a) as 29.3–30.6 per cent, 46.4–47.0 per cent, and 23.0–23.7 per cent, respectively. The singularly low proportion of the 2-phenyl isomer in comparison to the relative amounts formed in phenylations of pyridine with diazotized aniline, *N*-nitrosoacetanilide, benzoyl peroxide, lead tetrabenzoate, and phenyl iodosobenzoate is attributed to preferential further substitution of the 2-phenyl isomer by triphenylmethyl radicals and is normal after correction for this (208a).

The photolytic decomposition of 1′,1′,1′-triphenylbenzeneazomethane in benzene apparently follows the same course but has been less investigated (220, 226). A detailed consideration of alternative sequences of reactions, including (*a*) direct decomposition of 1′,1′,1′-triphenylbenzeneazomethane into free radicals, (*b*) a chain or induced decomposition, and (*c*) a "kryptoradical" route in which no truly free radicals occur, resulted in a decision for sequence (a) (226):

$$C_6H_5N{=}NC(C_6H_5)_3 \rightarrow C_6H_5\cdot + N_2 + (C_6H_5)_3C\cdot$$

$$C_6H_5\cdot + ArH \rightarrow C_6H_5Ar + H\cdot$$

$$H\cdot + (C_6H_5)_3C\cdot \rightarrow (C_6H_5)_3CH$$

$$C_6H_5\cdot + (C_6H_5)_3C\cdot \rightarrow (C_6H_5)_4C \text{ (small amount)}$$

The arylation is inhibited in the presence of excess *p*-benzoquinone, which traps the radicals efficiently. Nitric oxide similarly prevents the formation of triphenylmethane by uniting with triphenylmethyl radicals, as does also iodine (in the presence of ethanol, to prevent reversal of the trapping).

Benzenediazoacetate at 20°C. and 1′,1′,1′-triphenylbenzeneazomethane at 50°C. give different relative amounts of biphenyl and phenyldimethylquinoline when they attack a mixture of benzene and dimethylquinoline (226). This was taken to indicate a difference in the phenyl radicals generated, but since such

TABLE 3

Arylations with aroyl peroxides[a]

Peroxide	Aromatic Substrate	Positions Taken by Aryl Groups	References
Benzoyl	Benzene	Any[b]	(13, 155, 319, 321, 326)
	Toluene	2, 3, 4	(101, 122, 156)
	Chlorobenzene	2, 3, 4	(13, 101, 105, 234, 341)
	Bromobenzene	2, 3, 4	(105)
	Iodobenzene	2, 3, 4	(105)
	Nitrobenzene	2, 3, 4	(10, 14, 65, 66, 101, 114, 198, 207, 326)
	Phenol	2, 3, 4	(11)
	Methyl benzoate	4	(101)
	Ethyl benzoate	3, 4	(198)
	Biphenyl	2, 3, 4	(157)
	p-Dichlorobenzene	2	(14)
	1,3,5-Trichlorobenzene	2	(14)
	p-Di-*tert*-butylbenzene	2	(66)
	Pyridine	2, 3, 4	(13, 101, 105, 207, 208a, 209, 312)
	Quinoline	4, 5, and others	(209)
	Benzothiazole	2	(305)
p-Chlorobenzoyl	Benzene	Any	(155)
	Pyridine	2, 4	(209)
p-Methoxybenzoyl	Benzene	Any	(209)
	Pyridine	2, 4	(209
o-Nitrobenzoyl	Benzene	Any	(209)
	Pyridine	None	(209)
m-Nitrobenzoyl	Benzene	Any	(209)
	Benzoic acid	3, 4	(209)
	Pyridine	None	(209)
p-Nitrobenzoyl	Benzene	Any	(209)
	Pyridine	None	(209)
o-Carboxybenzoyl	Benzene	None	(209)
	Nitrobenzene	2, 4	(209)
o-Methoxycarbonylbenzoyl	Benzene	Any	(209)
	Pyridine	?	(209)
4-Methoxy-4′-nitrobenzoyl	Benzene	Any	(275)
2-Methoxycarbonyl-4-nitrobenzoyl	Benzene	Any	(209)
2-Methoxycarbonyl-5-nitrobenzoyl	Benzene	Any[c]	(73, 209)
5-Methoxycarbonyl-2-nitrobenzoyl	Benzene	Any	(73)
2-Methoxycarbonyl-3-nitrobenzoyl	Benzene	Any	(73)
4-Methoxycarbonyl-2-nitrobenzoyl	Benzene	Any	(73)
Phthaloyl	Benzene	Any	(172)
Cinnamoyl	Benzene	[d]	(209)
	Pyridine	[e]	(209)
1-Naphthoyl	Benzene	None	(209)
	Pyridine	?	(209)
2-Naphthoyl	Benzene	Any	(209)
	Pyridine	2, 3, 4	(209)
o-(2-Methyl-6-nitrophenyl)benzoyl	Benzene	Any	(115)

[a] Excepting self-arylations by benzoyl peroxide, which are noted separately, and the quantitatively studied arylations recorded in table 4B.

[b] The products are biphenyl, terphenyls, and quaterphenyls.

[c] The product is a mixture of methyl 4- and 5-nitrobiphenyl-2-carboxylates.

[d] Not strictly arylation; the product is stilbene.

[e] The product is α-stilbazole.

difference is not otherwise observed (13, 14, 119, 208a, 261), the lack of agreement is probably due to the temperature difference (*cf.* 15). The observation that radicals from diazonium salts phenylate ferrocene, whereas those from 1′,1′,1′-triphenylbenzeneazomethane do not, remains unexplained (54). It is possible, but not probable, that this involves the difference between a nonradical and a radical mechanism.

E. Arylation with aroyl peroxides

Studies of the kinetics of thermal decomposition of aroyl peroxides have been extensive and will not be reviewed here. Suffice it to say that both benzoyloxy

TABLE 4

Isomer ratios in arylations

A. With diazo compounds

Product	Component A	Component B	Method[a]	Isomer[b] 2-	Isomer[b] 3-	Isomer[b] 4-	Reference
				per cent	*per cent*	*per cent*	
Nitro-4-methoxybiphenyls	*p*-$CH_3OC_6H_4NH_2$	$C_6H_5NO_2$	B-1	*45*	*0*	*55*	(360a)
Nitro-*p*-terphenyls	*p*-$C_6H_5C_6H_4NH_2$	$C_6H_5NO_2$	B-1	*54*	*0*	*46*	(144)
Methyl-4-nitrobiphenyls	*p*-$O_2NC_6H_4NH_2$	$C_6H_5CH_3$	B-1	*67*	*0*	*33*	(145)
p-Nitrophenylpyrimidines	*p*-$O_2NC_6H_4NH_2$	Pyrimidine[c]		10	0	14	(281)
Methoxy-4-bromobiphenyls	*p*-$BrC_6H_4NH_2$	$C_6H_5OCH_3$	A-1	20	0	7	(181)
Methyl-*p*-terphenyls	*p*-$C_6H_5C_6H_4NH_2$	$C_6H_5CH_3$	B-1	*50*	*6*	*44*	(144)
Bromo-*p*-terphenyls	*p*-$C_6H_5C_6H_4NH_2$	C_6H_5Br	B-1	*33*	*15*	*53*	(144)
Nitrobiphenyls	$C_6H_5NH_2$	$C_6H_5NO_2$	A-1	*55–61*	*0–4*	*39–41*	(119)
				12–16	0–1	7–12	
				54 ± 4	*9 ± 2*	*37 ± 4*	(204)
				46	*18*	*36*	(359)
		$C_6H_5NO_2 + C_6H_6$ (1:2)	A-1		*34*	*20*	(359)
		$C_6H_5NO_2$	B	*17*	*23*	*60*	(359)
		$C_6H_5NO_2 + C_6H_6$ (1:2)	B		*22*	*19*	(359)
Chloro-*p*-terphenyls	*p*-$C_6H_5C_6H_4NH_2$	C_6H_5Cl[d]	B-1	*32*	*20*	*48*	(144)
(?)′,4-Dinitrobiphenyls	*p*-$O_2NC_6H_4NH_2$	$C_6H_5NO_2$	A-3	*34 ± 6*	*23 ± 3*	*43 ± 3*	(116)
(?)′,3-Dinitrobiphenyls	*m*-$O_2NC_6H_4NH_2$	$C_6H_5NO_2$	A-3	*31 ± 2*	*25 ± 1*	*44 ± 1*	(116)
Methylbiphenyls	$C_6H_5NH_2$	$C_6H_5CH_3$	B-2	*62*	*20*	*18*	(342)
Chlorobiphenyls	$C_6H_5NH_2$	C_6H_5Cl	A-1	*64*	*22*	*14*	(359)
p-Nitrophenylpyridines	*p*-$O_2NC_6H_4NH_2$	C_5H_5N	A-5	15	5	2	(143)
				24	9	4.5	(183)
Isopropylbiphenyls	$C_6H_5NH_2$	$C_6H_5CH(CH_3)_2$	B-2	*26*	*53*	*21*	(342)
tert-Butylbiphenyls	$C_6H_5NH_2$	$C_6H_5C(CH_3)_3$	B-2	*15*	*63*	*22*	(342)
Phenylpyridines	$C_6H_5NH_2$	C_5H_5N	A-5	*54*	*23*	*23*	(183)
			B-1	*46*	*43*	*11*	(208a)
o-Nitrophenylpyridines	*o*-$O_2NC_6H_4NH_2$	C_5H_5N	A-5	*44.9*	*51.7*	*3.4*	(183)
(?)′,3-Dimethyl-4-nitrobiphenyls	3-CH_3-4-$O_2NC_6H_3NH_2$	$C_6H_5CH_3$	A-3	*82*	*17*	*0*	(415)
				9.5	2	0	
				1-	2-		
Phenylnaphthalene	$C_6H_5NH_2$	$C_{16}H_8$	A-9	*90*	*10*		(297)
			B	*84*	*16*		(227)
(?)-Phenyl-2-ethoxynaphthalene	$C_6H_5NH_2$	2-$C_2H_5OC_{10}H_7$	B	17.1 of 1- 3.1 of 3- 2.3 of 6-			(227)

TABLE 4—*Continued*

B. With benzoyl peroxides

Product	Substrate	Isomer[e]			Reference
		2-	3-	4-	
		per cent	*per cent*	*per cent*	
Nitrobiphenyls	$C_6H_5NO_2$	*46.3*	*0.7*	*53*	(204)
		72	*2*	*26*	(119)
		58	*10*	*32*	(13)
		59.5 ± 4	*8.5 ± 2,* *11.5 ± 2*	*32.4 ± 4,* *29 ± 4*	(11)
		56	*16*	*28*	(208)
Cyanobiphenyls	C_6H_5CN	*60*	*10*	*30*	(103)
Biphenylcarboxylic acids	C_6H_5COOH	*59*	*15*	*26*	(104)
		49[f]	*20*[f]	*31*[f]	
Terphenyls	$C_6H_5C_6H_5$	*48.5*	*23.0*	*28.5*	(65)
α-Trifluoromethylbiphenyls	$C_6H_5CF_3$	*18*	*40*	*42*	(106)
Ethylbiphenyls	$C_6H_5C_2H_5$	*50*	*25*	*25*	(107)
Methoxybiphenyls	$C_6H_5OCH_3$	*67*	*18*	*15*	(374)
Methylbiphenyls	$C_6H_5CH_3$	*65*	*19*	*16*	(107)
		64	*20*	*16*	(342)
		70.8	*16.7*	*12.4*	(207)
α-Trichloromethylbiphenyls	$C_6H_5CCl_3$	*0*	*60*	*40*	(106)
Chlorobiphenyls	C_6H_5Cl	*62.2*	*24.0*	*13.8*	(14)
		64	*23*	*13*	(103)
Bromobiphenyls	C_6H_5Br	*48.5*	*33.0*	*18.5*	(103)
		49.3	*33.3*	*17.4*	(10)
Iodobiphenyls	C_6H_5I	*51.7*	*31.6*	*16.7*	(10)
Fluorobiphenyls	C_6H_5F	*54.1*	*30.7*	*15.2*	(10)
Phenylpyridines	C_5H_5N	*64.3*	*0*	*35.7*	(312)
		58	*28*	*14*	(104)
		54	*32*	*14*	(208a)
Isopropylbiphenyls	$C_6H_5CH(CH_3)_2$	*10*	*60*	*30*	(107)
		29	*50*	*21*	(342)
Methyl biphenylsulfonates	$C_6H_5SO_3CH_3$	*53*	*33*	*14*	(103)
tert-Butylbiphenyls	$C_6H_5C(CH_3)_3$	*24*	*49*	*27*	(66)
		17	*61*	*22*	(342)
4-Chloro-α-trichloromethylbiphenyls[g]	$C_6H_5CCl_3$	*0*	*85*	*17*	(106)
4-Nitro-α-trichloromethylbiphenyls[h]	$C_6H_5CCl_3$	*0*	*100*	*0*	(106)

[a] The system used for designating the methods used is explained in footnote (b) of table 2.

[b] The numbers set in italics indicate the relative amounts of arylated products rather than the theoretical yields. For any given combination of components A and B, the isomer percentage values are arranged in increasing order of the ratio of the 3-isomer to the 4-isomer.

[c] Statistically there are twice as many chances of forming 4-monosubstituted pyrimidines as 2-monosubstituted products.

[d] Bromobenzene by method A-1 or B gives isomers in the agreeing ratio (qualitative only) ortho > meta > para (360).

[e] All the numbers are given in italics and indicate the relative amounts of arylated products only and not the theoretical yields. For any given substrate, the isomer products are arranged in increasing order of the ratio of the 3-isomer to the 4-isomer.

[f] In the presence of pyridine.

[g] Made with *p*-chlorobenzoyl peroxide.

[h] Made with *p*-nitrobenzoyl peroxide.

and aryl radicals are usually produced; decarboxylation and consequent formation of aryl radicals are favored by increase in temperature. These conclusions from rates of reaction are borne out by preparative work, in which benzoyloxylation is preferred at lower temperatures (321) and with especially reactive aromatic nuclei (102, 341). Table 3 presents a literature summary of all such arylations except self-arylations. These occur, often as minor reactions, when benzoyl peroxide is heated in various solvents. The formation of *o*- and *p*-phenylbenzoic

acids in this way has been noted in acetic acid (164) and alkylbenzenes (107, 156, 207). *p*-Phenylbenzoic acid alone has been identified more frequently among products of reaction in 2,2,4-trimethylpentane (209), 1,2-dichloroethane (329), 1,1,2,2-tetrachloroethane (329), 2-methyl-1-propanol (158), 2,3-butanediol (208), acetic acid (158, 159), diethyl malonate (375), cyclohexane (160), cyclopropyl methyl ketone (180), phenylcyclopropane (180), and pyridine (105, 312). Recently the pyrolysis of acyl peroxides of the form $C_6H_5CO_2OCO(CH_2)_nCOOR$ has also been shown to yield *p*-phenylbenzoic acid (167).

Because arylation with aroyl peroxides is cleaner than arylation with diazo compounds, it has been preferred as a way for studying competition between nuclear positions (orientation) and between molecules (relative reactivities). The results of the former are summarized in table 4 and interpreted in the accompanying paper (15). The Ingold (235) competitive method for comparing rates of reaction is being applied systematically and successfully in several laboratories. The topic has been reviewed recently (199, 201, 211) and further theoretical treatment is presented by Augood and Williams (15).

F. Arylation with metalloörganic compounds

It has been postulated (257) that aryl radicals are involved when halogen atoms of aryl halides are displaced by the action of Grignard reagents in the presence of organic halides and metal salts. Certainly the formation of terphenyls, quaterphenyls, and probably higher polyphenyls constitutes substitution under the current definition. When butylmagnesium bromide was decomposed in the presence of chlorobenzene and cobaltous chloride, biphenyl was produced in only 3 per cent yield, but there was an 11 per cent yield of polyphenyls (262). Similarly, phenylaluminum diiodide and bromobenzene heated in benzene generate biphenyl, terphenyls, quaterphenyls, and quinquephenyls (388, 390).

Phenylmagnesium bromide when sufficiently heated in toluene causes phenylation in the 4-position; *o*-xylene is substituted in an undetermined position, probably the 4-position also (258) (*cf.* page 81). In chlorobenzene the decomposition of phenylmagnesium bromide gave chlorobiphenyl in 5 per cent and biphenyl in 39 per cent yield. Obviously the high reactivity of Grignard reagents toward most functional groups prevents much extension of this work. Similarly, the known arylation of pyridines and quinolines by these reagents probably involves a polar, additive route instead of a radical mechanism.

The photochemical decomposition of phenylmercuric hydroxide in toluene produces methylbiphenyls among other products (330), and that of diphenylmercury in bromobenzene produces 4-bromobiphenyl (327). Free phenyl radicals are thought to be responsible for the ortho and para phenylation of ethyl benzoate when that liquid is used as solvent during the Ullmann treatment of iodobenzene with copper (324). The same radicals from diphenyliodonium chloride heated with pyridine and sodium hydroxide (344), or from phenyl iodosobenzoate with pyridine (208a), give 2-, 3-, and 4-phenylpyridines.

When lead tetrabenzoate is decomposed at low temperatures the reaction does not appear to involve free radicals (208) and aromatic substitution does not

occur. However, at higher temperatures radical substitutions of chlorobenzene and nitrobenzene produce mixtures of isomeric chlorobiphenyls and of isomeric nitrobiphenyls. Under the same conditions, the reactions of lead tetrabenzoate and of benzoyl peroxide with nitrobenzene yield almost identical ratios of isomers (208).

It appears that aryl radicals are involved in the decomposition of silver iodide dibenzoate in chlorobenzene at 130°C., which produces chlorobiphenyls (22 per cent), *p*-chlorophenyl benzoate, benzoic acid, and silver iodide (58). Reaction with nitrobenzene produces nitrobiphenyls and *m*-nitrophenyl benzoate. It seems not improbable that silver benzoate itself may phenylate aromatic nuclei.

Somewhat similarly, heating a solution of *tert*-butyl peroxide and triphenylsilane in chlorobenzene forms *o*- and *p*-chlorobiphenyls, along with triphenylchlorosilane (96).

G. Other intermolecular arylations

The rearrangement of benzyl phenyl ethers (212, 213) in quinoline, as already noted (page 81) produces hydroxyphenylquinolines, evidently by way of the mesomeric phenoxy radical.

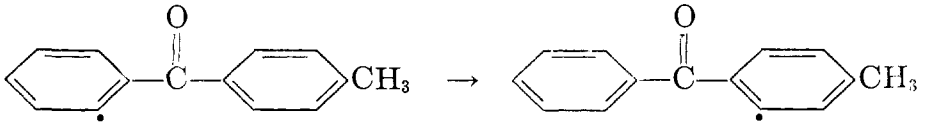
Besides the hydroxylation of benzene by Fenton's reagent (368), water irradiated with x-rays (368), or gaseous oxygen (217) (see page 101), these reagents cause some formation of *p*-terphenyl (368). Indeed, the decomposition of individual compounds by radiation often leads to the formation of radicals which can arylate the original material or some new substance formed. This kind of process has been reviewed exhaustively for aromatic hydrocarbons (128) and somewhat earlier for all classes of aromatic compounds (230). The field is an extensive one, and its treatment here is restricted by the arbitrary exclusion of the coupling of like nuclei, e.g., the benzene–biphenyl conversion, from consideration. Nevertheless, a few examples of substitutions of this type will be given.

Benzene has repeatedly been shown to yield about equal amounts of *m*-terphenyl and *p*-terphenyl (besides, of course, many other products) when subjected to high temperatures; the absence of the ortho isomer is probably due to steric effects. Upon prolonged exposure to red heat, phenol yields *p*-hydroxybiphenyl (293). The pyrolysis of benzoic acid yields some phenylbenzoic acids, and methyl benzoate gives methyl *m*-phenylbenzoate and methyl *p*-phenylbenzoate (230); again the orientation is noteworthy.

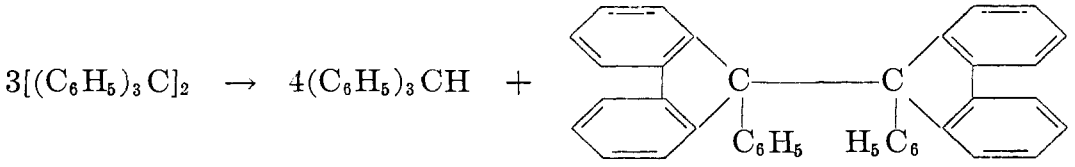
IV. INTRAMOLECULAR ARYLATION

The pyrolysis of cyclic diazoamino compounds, i.e., benzotriazoles, has long been known to yield carbazoles (80, 227, 253, 384), but the subject has already been adequately reviewed (348). Carbazoles are obtained also from diazotized *N*-alkyl-*N*-aryl- and *N*,*N*-diaryl-*o*-phenylenediamines, which cannot yield triazoles as intermediates (125, 320, 373). The Pschorr synthesis of phenanthrenes is recognizable as a counterpart of the Gomberg preparation of biaryls and thus deserves attention, but again an extensive bibliography and studies of modifications of the reaction have been made recently (186, 187, 188, 203, 205, 206, 347).

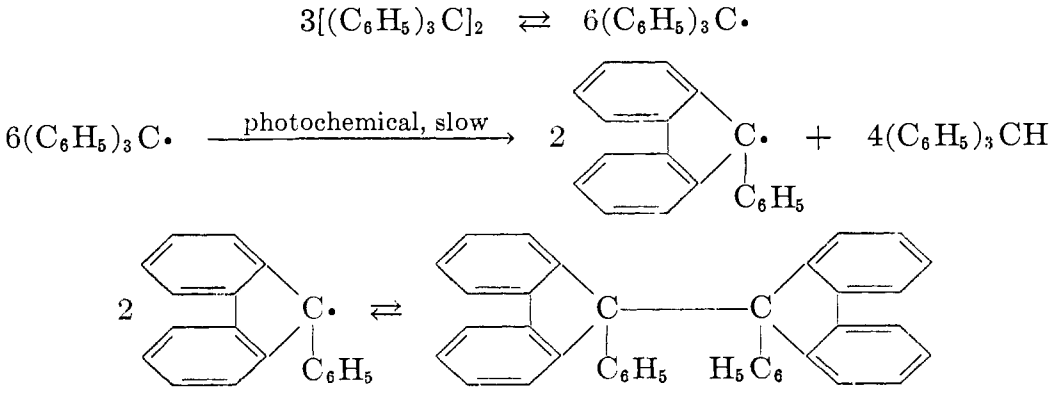
Of especial interest is the discovery of evidence for internuclear chain transfer within molecules. In the course of investigations of radical intermediates (118, 332), 2-benzoyl-*N*-nitrosoacetanilide in benzene was found to react to give 15 per cent of 2-phenylbenzophenone and 7 per cent of fluorenone, as might be expected. However, decomposition in carbon tetrachloride of the diazonium fluoborate derived from 2′-amino-4-methylbenzophenone gave not only 10 per cent of 3-methylfluorenone and 10 per cent of 2′-chloro-4-methylbenzophenone but also 10 per cent of 2-chloro-4-methylbenzophenone. The last-named product would appear to be formed only as the result of a transfer of radical status from one nucleus within the molecule to the other. Evidence for this type of product was not found in heterolytic reactions under acid conditions, but it was also obtained in the Sandmeyer reaction using cuprous bromide. It seems clear that the Sandmeyer reaction also proceeds at least in part by a course which allows for some intramolecular transfer substitution:



The disproportionation of triphenylmethyl free radicals involves ortho attack to cause cyclization. For cyclization of triphenylmethyl on long standing in most organic solvents in diffuse light (50, 351) the overall reaction is



which takes place stepwise (50, 276) as follows:

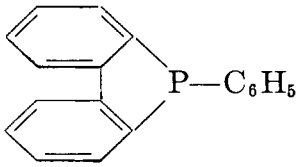


In alkaline dioxane the products are 9-phenylfluorene and triphenylmethane (276).

Correspondingly, 9-phenylfluorene and ammonia are among the products of the pyrolysis of 1,2-bis(triphenylmethyl)hydrazine in the presence of anhydrous zinc chloride. They are produced also in the reaction of triphenylmethylamine with zinc chloride (372); this observation suggested that the same amine is an

intermediate in the first reaction. The belief that radicals are involved is strengthened by the observation that phenol is formed when the hydrazine is heated in air or oxygen, but not in carbon dioxide. The triphenylmethyl radical appears to participate in all of these reactions.

Evidently related is the decomposition of pentaphenylphosphorus (416) to form benzene, biphenyl, triphenylphosphine, and *o*-diphenylenephenylphosphine.



V. AMINATION

The direct substitution of an amino group in an aromatic nucleus by a radical sequence is not common. The action of the imino radical, generated by irradiation of hydrazoic acid, on liquid toluene or nitrobenzene gives traces of primary arylamines (254), but the substitution fails for benzene vapor (335). However, benzene and ammonia give aniline in 28 per cent yield, besides many byproducts, when subjected to a silent electrical discharge (376). Reducing agents acting upon hydroxylamine in acid solution generate the free amino radical, which can substitute in benzene or toluene by way of an addition compound barely stable enough to be isolated (110, 357).

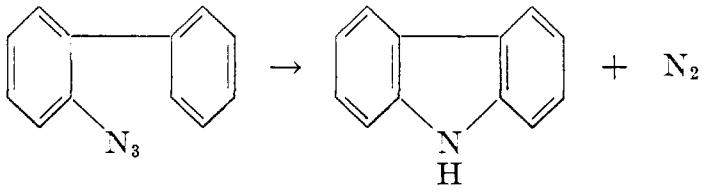
$$HONH_3^+ + Ti^{3+} \rightarrow H_2N\cdot + Ti^{4+} + H_2O$$

$$H_2N\cdot + C_6H_6 \rightarrow H_2NC_6H_6\cdot$$

$$H_2NC_6H_6\cdot \rightarrow \text{a primary arylamine } \textit{inter alia}$$

The reaction is comparable to hydroxylation by means of Fenton's reagent.

Independently binuclear aromatic compounds containing an azido group in the position ortho to a linking bond are sterically well suited to ring closure. Thermal or photochemical decomposition of *o*-azidobiphenyls gives carbazoles in excellent yields except when the azido group is flanked by a nitro group (365):



The reaction succeeds also for 2-(*o*-azidophenyl)thiophene and 3-(*o*-azidophenyl)-pyridine but fails for 2-(*o*-azidophenyl)pyridine, 1-azidonaphthalene (364), and 2,2′-diazidobiphenyl (366). When the two nuclei are separated by one other atom, Y, the cyclization is normal for Y = —S— and —SO_2— but not for Y = —O—, —N($COCH_3$)—, or —CO— (366).

Although there is considerable evidence of the generation of phenylimino radicals, C_6H_5N:, by the pyrolysis of azidobenzene or phenylhydroxylamine,

such radicals do not affect benzene or nitrobenzene and attack *p*-xylene only in a side chain (45, 343). Only by heating *p*-azidotoluene in phenol at 160°C. has substitution been accomplished (24).

$$p\text{-}CH_3C_6H_4N_3 + C_6H_5OH \rightarrow 4\text{-}(p\text{-}CH_3C_6H_4NH)C_6H_4OH + N_2$$

p-Anilination of aromatic compounds has been effected with azidobenzene and aluminum chloride and even assigned a radical course (49), but a polar route seems at least as likely.

To be mentioned here are the remarkable thermal disproportionations of diarylamino radicals, since further ring substitution is involved. They are illustrated for the diphenylamino radical (406):

$$4(C_6H_5)_2N\cdot \rightarrow \text{[5,10-Dihydro-5,10-diphenylphenazine]} + 2(C_6H_5)_2NH$$

$$2(C_6H_5)_2N\cdot \rightarrow o\text{-}C_6H_5NHC_6H_4N(C_6H_5)_2$$

The action of certain mild reducing agents, notably potassium ferrocyanide or cuprous ion, upon aqueous diazonium salts leads in part to arylazo-substituted aromatic compounds. This has been tentatively represented as involving the arylazo radical:

(a) $C_6H_5N_2^+ + e^- \rightarrow C_6H_5N_2\cdot$

(b) $C_6H_5N_2\cdot \rightarrow C_6H_5\cdot + N_2$

(c) $C_6H_5\cdot + C_6H_5N_2^+ \rightarrow C_6H_5C_6H_4N_2^+ + H\cdot$

(d) $C_6H_5\cdot + C_6H_5C_6H_4N_2^+ + e^- \rightarrow C_6H_5C_6H_4N{=}NC_6H_5$

(e) $C_6H_5\cdot + H \text{ source} \rightarrow C_6H_6$

(f) $C_6H_5N_2\cdot + C_6H_6 \rightarrow C_6H_5N{=}NC_6H_5 + H\cdot$

Equations (c) and (d) are supposed to explain the observed formation of arylazobiaryls (142, 346). Equation (d) is essentially that recently preferred over combination of $ArN_2\cdot$ and $Ar\cdot$ to account for the production of a little azobenzene from benzenediazonium salts decomposed in acetate-buffered methanol (120). Substitution by the arylazo radical (equation (f)) (217) appears rather unlikely. To explain the observed formation of azobenzene-2-carboxylic acid from a diazotized mixture of aniline and anthranilic acid, it is necessary only to postulate that the dipolar-ion form of the 2-carboxybenzenediazonium salt is

sufficiently stabilized as such to await attack by phenyl radicals as in equation (d).

$$o\text{-}^{-}OOCC_6H_4N_2^{+} + C_6H_5\cdot + e^{-} \rightarrow o\text{-}^{-}OOCC_6H_4N{=}NC_6H_5$$

VI. AMIDATION, INCLUDING SULFONAMIDATION

A. Amidation

There are only two examples of formation of *N*-aryl carboxamides by radical substitution. The radicals generated from benzoyl azide do not attack benzene, even in the presence of triphenylmethyl (316), but *N*-bromosuccinimide acting upon acridine yields among other products 9-succinimidoacridine, several of its bromo derivatives, and probably a disuccinimidoacridine (349). Similarly, the succinimido radical from *N*-bromosuccinimide does produce a little *N*-phenylsuccinimide in the presence of olefins (225).

B. Sulfonamidation

When aromatic sulfonyl azides are heated in various aromatic liquids the ensuing reaction is not a typical Curtius rearrangement (97). On the contrary, the nature of the compounds that can be isolated from the reaction mixtures after cessation of nitrogen evolution, which begins at approximately 100°C., shows that substitution of the aromatic liquid occurs in nearly every case. The isolable products consist primarily of simple and *N*-arylated arenesulfonamides. The reactions can be conceived as follows, (b) and (c) being alternatives:

$$\text{(a)}\quad ArSO_2N_3 \rightarrow ArSO_2N\text{:} + N_2$$

$$\text{(b)}\quad ArSO_2N\text{:} + Ar'H \rightarrow ArSO_2NHAr'$$

$$\text{(c)}\quad ArSO_2N\text{:} + 2Ar'H \rightarrow ArSO_2NH_2 + 2Ar'\cdot$$

The fate of the free aryl radicals in (c) is not clear. A benzidine was believed formed when aniline was used as the aromatic substrate (105), but the compound could not be fully characterized.

The results of an extensive series of experiments on sulfonamidation are reviewed in table 5. They are corrected by later work only for pyridine and quinoline. It was suggested (4) and soon confirmed (9, 59, 108) that the compounds earlier supposed to be *N*-pyridylarenesulfonamides in fact constitute a remarkable kind of dipolar compound, $C_5H_5\overset{+}{N}\text{—}\overset{-}{N}SO_2Ar$, and that *C*-sulfonamidation of the pyridine nucleus does not occur. The *N*-(*N*-pyridyl)arenesulfonimides so obtained can even be hydrolyzed to *N*-iminopyridine, but this substance is very short-lived (108). Thus the decomposition of sulfonyl azides in pyridine (and by analogy, in quinoline) is like the conversion of tertiary amines to amine oxides.

$$R_3N + [O] \rightarrow R_3NO$$

$$R_3N + ArSO_2N\text{:} \rightarrow R_3NNSO_2Ar$$

A systematic investigation of the ratios of isomeric benzenesulfonanilides produced by the thermal decomposition of benzenesulfonyl azide in selected mono-

TABLE 5

Sulfonamidations with sulfonyl azides (97)

A. Normal reaction of type (b)[a]; isomers not possible or not specified
$C_6H_5SO_2N_3$ + C_6H_6, $C_6H_5CH_3$, $C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5N(CH_3)_2$, $(C_6H_5)_2NH$
p-$CH_3C_6H_4SO_2N_3$ + C_6H_6, p-$C_6H_4(CH_3)_2$, $C_6H_5NH_2$, $C_6H_5NHCH_3$
p-$ClC_6H_4SO_2N_3$ + p-$C_6H_4(CH_3)_2$
1,3-$C_6H_4(SO_2N_3)_2$ + p-$C_6H_4(CH_3)_2$
p-$CH_3CONHC_6H_4SO_2N_3$ + p-$C_6H_4(CH_3)_2$
1-$C_{10}H_7SO_2N_3$ + p-$C_6H_4(CH_3)_2$
2-$C_{10}H_7SO_2N_3$ + p-$C_6H_4(CH_3)_2$, $C_6H_5NHCH_3$, $C_6H_5N(CH_3)_2$
1,5-$C_{10}H_6(SO_2N_3)_2$ + p-$C_6H_4(CH_3)_2$
2-Anthraquinonesulfonyl azide + p-$C_6H_4(CH_3)_2$

B. Normal reaction of type (b)[a]; orientation as noted
$C_6H_5SO_2N_3$ + $C_6H_5CH_3$ → 2.4 ortho: no meta: 1 para
$C_6H_5SO_2N_3$ + $C_6H_5N(CH_3)_2$ → 1 ortho: 2 para
p-$CH_3C_6H_4SO_2N_3$ + $C_6H_5N(CH_3)_2$ → ortho only
p-$CH_3C_6H_4SO_2N_3$ + $C_6H_5NH_2$ or $C_6H_5NHCH_3$ or $C_6H_5N(CH_3)_2$ → ortho only
p-$CH_3C_6H_4SO_2N_3$ + $C_{10}H_8$ → 1-isomer only
2-$C_{10}H_7SO_2N_3$ + $C_6H_5NH_2$ → ortho only
2-$C_{10}H_7SO_2N_3$ + $C_{10}H_8$ → 1-isomer only

C. Failure of normal reactions; (c)[a] may occur, but no sulfonamidation
$C_6H_5SO_2N_3$ + C_6H_5CHO, $C_6H_5NO_2$, pyridine,[a][b] quinoline[a][b]
p-$CH_3C_6H_4SO_2N_3$ + pyridine[a][b]
1,3-$C_6H_4(SO_2N_3)_2$ + $C_6H_5N(CH_3)_2$
2-$C_{10}H_7SO_2N_3$ + pyridine,[a][b] quinoline[a][b]

[a] See text.
[b] From results of later work.

TABLE 6

Isomer ratios in sulfonamidation at 105–115°C.

Aromatic Substrate	Average Ratio of Isomeric Anilines[a]			Aromatic Substrate	Average Ratio of Isomeric Anilines[a]		
	Ortho	Meta	Para		Ortho	Meta	Para
Toluene	60	12	28	Anisole	49	21	30
Chlorobenzene	56	15	29	Phenol	58	20	22
Bromobenzene	57	10	33				

[a] Produced by hydrolysis of the sulfonanilides.

substituted benzenes (113) gave the results shown in table 6. Benzonitrile, benzoyl chloride, and methyl benzoate gave mixed crystalline products of sulfonamidation, but the results as regards isomer ratio were indecisive. No such sulfonamide could be isolated from the reaction mixture made with nitrobenzene. However, nitric oxide was evolved, presumably from attack on the nitro group by the benzenesulfonimino radical.

The behavior of arenesulfonyl azides toward aromatic substrates suggested trial of sulfuryl azide. The analogy fails, however; in an amazing and surely very

complex process, sulfuryl azide and benzene yield pyridine (99, 352, 353). Carbonyl azide with benzene acts similarly.

VII. HYDROXYLATION

A. Hydroxylation with hydrogen peroxide

While benzene can be hydroxylated in aqueous solution or suspension by hydrogen peroxide alone (43), better results are obtained with Fenton's reagent (hydrogen peroxide and a ferrous salt). Oxidations of this type have been reviewed recently (40a, 385). The reagent generates hydroxyl radicals by the reaction

$$Fe^{2+} + HOOH \rightarrow Fe^{3+} + OH^- + HO\cdot$$

and these readily hydroxylate aromatic nuclei. It has been supposed that the process is not a chain reaction (290) but in the presence of much ferric ion the process goes by the following steps:

(a) $ArH + HO\cdot \rightarrow Ar\cdot + H_2O$

(b) $Fe^{3+} + H_2O + Ar\cdot \rightarrow ArOH + Fe^{2+} + H^+$
(and *not* $Ar\cdot + HO\cdot \rightarrow ArOH$)

(c) $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO\cdot$

These constitute a chain mechanism for transfer substitution (41, 42). Biaryl formation evidently competes with hydroxylation, and so does reconversion to the substrate (41, 290).

(d) $Ar\cdot + Ar\cdot \rightarrow ArAr$

(e) $Ar\cdot + Fe^{2+} + H^+ \rightarrow ArH + Fe^{3+}$

In air or oxygen biaryl formation is suppressed entirely (41, 368); otherwise the primary products are phenols and biaryls. The ability of ferric ions to promote aromatic hydroxylation had been noted before (7, 370). Cupric ions are even more effective for oxidizing phenyl radicals to phenol (42, 268).

Since phenols themselves are readily further substituted, hydroxylation usually gives mixtures; thus phenol itself goes to pyrocatechol and hydroquinone (283, 285). A further complication is the well-known tendency of ferric ions to form complexes with phenols; this can be minimized by adding fluoride or pyrophosphate ions to remove ferric ions (41, 370).

The complications due to iron can be avoided by generating hydroxyl radicals merely by the photolysis of aqueous hydrogen peroxide. The ratio of phenol to biphenyl is then nearly independent of the concentrations of hydrogen peroxide and benzene and of the light intensity, but is greatly increased by decreasing the pH to about 1. These observations are not yet explained (40a).

B. Hydroxylation with irradiated water

Vigorous irradiation of water also produces hydroxyl radicals

$$H_2O(l) \xrightarrow{\sim} H\cdot + HO\cdot$$

TABLE 7

Hydroxylations with water or hydrogen peroxide

Aromatic Substrate	Product[a]	Source of Hydroxyl[b]	References
C_6H_6	C_6H_5OH	I	(41, 95, 291, 311)
		II	(268)
		III	(111, 147, 367, 368, 382)
		IV	(367, 369)
		V	(42)
		VII	(88, 294, 295)
	o-$C_6H_4(OH)_2$	I	(95)
		IV	(367, 369)
	p-$C_6H_4(OH)_2$	IV	(369)
$C_6H_5CH_3$	$CH_3C_6H_4OH$ isomers	I	(291)
		VII	(294)
C_6H_5Cl	Ortho meta para isomers of ClC_6H_4OH	I	(291)
	40–45% 20–25% 20–25%	All I	(248)
	25–30% 20–30% 40–45%	All III	(248)
$C_6H_5NO_2$	Ortho meta para isomers of $O_2NC_6H_4OH$	I	(291)
	25–30% 20–25% 50–55%	All I	(278)
	28–36% 27–31% 34–45%	All III at pH 2–12	(279)
C_6H_5OH	*o*-$C_6H_4(OH)_2$ and *p*-$C_6H_4(OH)_2$ only, in following ratios:		
	90:10	I, Fe^{3+} only	(370)
	70:30	I, no addition	(78, 166, 284, 285, 370)
	30:70	I, NaF addition	(356)
	65–80:20–35	III, pH 2–12	(370)
	1,2,3-$C_6H_3(OH)_3$	I	(166)
$C_6H_5OCH_3$	*o*-$CH_3OC_6H_4OH$	I	(284)
$C_6H_5CONH_2$	*o*-$HOC_6H_4CONH_2$	I	(291)
m-$CH_3C_6H_4COOH$	*x*-HO-3-$CH_3C_6H_3COOH$	V	(36)
p-$CH_3C_6H_4COOH$	2-HO-4-$CH_3C_6H_3COOH$	V	(35, 36)
o-HOC_6H_4COOH	2,5-$(HO)_2C_6H_3COOH$	I	(52, 304)
		VI	(52)
p-HOC_6H_4COOH	3,4-$(HO)_2C_6H_3COOH$	I	(52)
		VI	(52)
$C_6H_5SO_2H$	*o*- and/or *p*-$HOC_6H_4SO_3H$	I	(291)
Coumarin	Umbelliferone	I	(52)
o-$HOOCC_6H_4CH{=}CHCOOH$	*x*-HO-2-$HOOCC_6H_3CH{=}CHCOOH$	I	(52)
		VI	(52)
$C_{10}H_8$	1-$C_{10}H_7OH$ (*80%*) and 2-$C_{10}H_7OH$ (*20%*)	I	(52)
		VI	(52)
	$C_{10}H_7OH$	VII	(294)
C_6H_5COOH	HOC_6H_4COOH: *o-* I (52, 291); *m-*; *p-* I (52, 367, 368); $(HO)_2C_6H_3COOH$: 2,5- I (52); 3,4- I (52)		
	II (268)		
	III (111, 368)		
	30% 10% 60%	All III	(280)
	40% 40% 20%	All V	(35, 36)
	38% 17% 17% 7% 24%	All VI	(52)

[a] Percentage yields in italics refer not to efficiency of conversion of substrate but to ratio of products, usually isomers, shown in the same horizontal line. Efficiencies of conversion are neglected because the reaction is of little or no preparative value.

[b] The Roman numerals designate methods as follows:

I = Fenton's reagent
II = $H_2O_2 + Cu^{++}$
III = H_2O + x-rays or gamma rays alone
IV = H_2O + neutrons or alpha particles
V = H_2O + ultraviolet light + Fe^{3+}
VI = H_2O_2 + ultraviolet light
VII = H_2O_2 in $R_3COH + V_2O_5$, CrO_3, or OsO_4

without limiting the pH range as the Fenton method does. It has been shown both theoretically and experimentally that the reaction of ArH and HO•, whether by way of an adduct or not, is very much more likely to yield Ar• + H_2O —that is, to react by transfer substitution—than H• + ArOH. Phenols are then formed from Ar• and HO•, and biaryls from 2Ar•; the reaction

$$Ar\bullet + ArH \rightarrow ArAr + H\bullet$$

is less probable, since the yield of biaryl is sometimes independent of the concentration of ArH (42, 368). Neutrons and α-particles give somewhat more energetic attack than x-rays and gamma rays, and more polyphenols and ring-cleavage products are formed (369).

In general there is good agreement among isomer ratios for the several hydroxylations of the same substrate (see table 7). An exception is the production of hydroxybenzoic acids from aqueous benzoic acid, which has given the ortho-meta-para ratio 5:2:10 with x-rays (280), 2:2:1 with ultraviolet light in the presence of ferric ions (35, 36), and 2:1:1 with hydrogen peroxide irradiated with ultraviolet light (52). These determinations were very approximate, and perhaps better agreement may be obtained in the future.

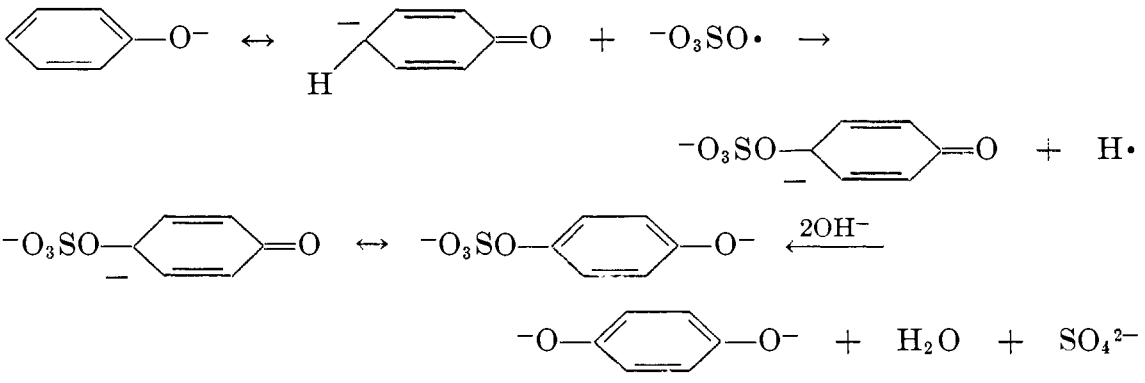
The formation of *o*-nitrosophenols from aromatic substrates, air or hydrogen peroxide, and hydroxylamine (37, 38, 39, 94) or sodium nitroprusside (40) is probably the result of hydroxylation and then nitrosation (269).

Tetralin hydroperoxide does not hydroxylate an aromatic nucleus, even so susceptible a one as *m*-dinitrobenzene (338), but it might do so in the presence of a reducing ion such as Fe^{+2} or Cu^{+1}.

C. Hydroxylation with peroxy acids

The Elbs alkaline persulfate oxidation of monohydric phenols to dihydric phenols, which has been lately reviewed (358), may well proceed by a radical mechanism. The radical-ion $^{-}O_3SO\bullet$ is supposed to attack the phenoxide anion, although such an anion–anion approach seems unlikely.

$$Fe^{2+}\ (\text{trace}) + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{2-} + {}^{-}O_3SO\bullet$$



Substitution occurs in the para position unless that is blocked, when some ortho hydroxylation (hydrolysis being assumed) occurs (21, 304). 2-Naphthol becomes substituted in the 1-position (306). However, the supposed radical-ion

$^{-}O_2SO\cdot$ does not affect benzene, toluene, naphthalene, benzoic acid, nor nitrobenzene (53), so it cannot be very active. The Elbs reagent causes exclusively ortho hydroxylation of arylamines (51, 53), just as the undoubtedly radical generator benzoyl peroxide does (127). This is additional evidence for a radical reaction but it leaves the problem of the difference in orientation between phenols and arylamines completely unsettled.

The silver-catalyzed oxidation of various aromatic compounds with persulfate often gives phenols in 1–5 per cent yield (17, 18). In acid solution *p*-cresol yields *p*-toluhydroquinone by an unusual rearrangement (273).

Monoperoxysulfuric acid oxidizes phenol to catechol and hydroquinone (26), *m*-nitrophenol to 3- and 4-nitrocatechols, and *p*-nitrophenol to 4-nitrocatechol (25).

Other inorganic peroxy acids besides those derived from sulfur can cause aromatic hydroxylation. The catalytic effects of vanadium and chromium oxides (294) and osmium tetroxide (295) have been attributed to the formation of such peroxy acids. Benzene is hydroxylated in trace amounts by peroxychromic acid, but not by peroxyboric or peroxycarbonic acid (195). The best studied case is that of peroxynitrous acid, HOONO, most readily derivable from hydrogen peroxide and nitrous acid. The radicals from peroxynitrous acid may cause hydroxylation or nitration or both (176, 196, 274). Substitution products formed (always in small yield) with peroxynitrous acid are shown in table 8. The hydroxyl group tends to enter in the ortho or para position, and the nitro group in the meta position, with respect to the original substituent. When both groups enter, they become ortho or para to each other. This is considered to favor a process whereby first a hydroxyl and then a nitro radical adds to the ring, after which the ring reverts to aromatic structure by loss of water, nitrous acid, or hydrogen. The homolytic character of the reaction is confirmed by the unusual orientation of nitro groups in the reaction of quinoline (274).

The oxidation of phenols with a mixture of 30 per cent hydrogen peroxide and

TABLE 8

Substitutions with peroxynitrous acid

Aromatic Substrate	Products[a] (Major Ones in Italics)	Reference
C_6H_6	*$C_6H_5NO_2$*, *o-$HOC_6H_4NO_2$*, *p*-$HOC_6H_4NO_2$, *p*-$C_6H_4(NO_2)_2$, C_6H_5OH, 2,4-$(O_2N)_2C_6H_3OH$, 2-O_2N-4-$C_6H_5C_6H_3OH$	(177)
$C_6H_5CH_3$	*$CH_3C_6H_4NO_2$* (isomers), 2-*CH_3-4-$O_2NC_6H_3OH$*, 4-CH_3-2-$O_2NC_6H_3OH$	(177)
$C_6H_5NO_2$	*o- (35%)*, *m- (12%)*, and *p-*(51%)nitrophenols; *o- (5%)*, *m- (91%)*, and *p-(5%)* dinitrobenzenes, 2-O_2N-4-(*p*-$O_2NC_6H_4$)C_6H_3OH (?)	(177)
C_6H_5Cl	*o-ClC_6H_4OH*, *m-$ClC_6H_4NO_2$*, *2-O_2N-4-ClC_6H_3OH*, *p*-$ClC_6H_4NO_2$	(177)
C_6H_5OH	*o-$C_6H_4(OH)_2$*, *p-$C_6H_4(OH)_2$*, *o-* and *p*-$O_2NC_6H_4OH$	(177)
$C_6H_5N(CH_3)_2$	*o-* and *p-$O_2NC_6H_4N(CH_3)_2$*	(177)
$C_6H_5OCH_3$	*o-$O_2NC_6H_4OH$*, *4-CH_3O-2-$O_2NC_6H_3OH$*, 6-CH_3O-2-$O_2NC_6H_3OH$	(177)
$C_6H_5OC_2H_5$	*o-$C_2H_5OC_6H_4OH$*, *6-C_2H_5O-2-$O_2NC_6H_3OH$*, 6-C_2H_5O-2,4-$(O_2N)_2C_6H_2OH$	(196)
$C_6H_5OC_3H_7$	6-C_3H_7O-2,4-$(O_2N)_2C_6H_2OH$	(196)
$C_6H_5COCH_3$	*m-$O_2NC_6H_4COCH_3$*, *2-HO-5-$O_2NC_6H_3COCH_3$*, *o*-$HOC_6H_4COCH_3$	(196)
Quinoline	6- and 7-$O_2NC_9H_6N$, $(O_2N)_2C_9H_5N$ (?)	(274)

[a] Percentage yields in italics refer not to the efficiency of conversion of the substrate, but to the ratio of isomers formed in a single run. The efficiency of conversion of the substrate to substituted products is usually <10 per cent.

glacial acetic acid at room temperature probably involves peroxyacetic acid. The reagent converts phenol to pyrocatechol and hydroquinone, *o*-cresol to *p*-toluhydroquinone, *m*-cresol to the same compound and orcinol, *p*-cresol to 4-methylpyrocatechol, *p-tert*-butylphenol to 3-*tert*-butyl-1,2,4,5-benzenetetrol, and either thymol or carvacrol to 3-isopropyl-6-methyl-1,2,3,5-benzenetetrol (190).

Benzothiazole heated with benzoyl peroxide yields a little 4-hydroxybenzothiazole among other products (305).

D. Electrolytic hydroxylation

Electrochemical oxidations frequently proceed by a radical mechanism. A characteristic behavior of the aromatic nucleus in such processes is hydroxylation (55, 133, 134), although subsequent conversion to quinones and further degradation products enormously complicates matters. Thus benzene yields, among other things, a little phenol, catechol, and *o*-phenoxyphenol (302), toluene gives cresols or at least their conversion products (296, 302), and benzoic acid produces 2-, 4-, 2,5-, and 3,4-hydroxylated benzoic acids (302). Benzonitrile is hydroxylated in the 2- and 5-positions, benzenesulfonic acid in the 3- and 4-positions, and naphthalene in the 1-position (55, 133, 134). However, the failure of nitrobenzene to undergo hydroxylation shows that electrolytic oxidation is not fully comparable to phenylation. At best, like other electrolytic substitutions, it is liable to give poor yields because the high concentration of radicals at the surface of the electrode favors side reactions and consecutive reactions (168).

E. Other hydroxylations

There are scattered observations on the nonpreparative but surely radical oxidation of liquid benzene to phenol by chlorine monoxide, air in the presence of water and palladium, and air in the presence of the rays from radium (43). Irradiation with radium produces *o*- and *p*-nitrophenol from nitrobenzene (250), and the related conversion to *p*-nitrophenol by exposure of nitrobenzene vapor to ultraviolet light probably involves oxygen atoms (182):

$$C_6H_5NO_2 \xrightarrow{h\nu} C_6H_5NO + O$$

$$C_6H_5NO_2 + O \longrightarrow p\text{-}HOC_6H_4NO_2$$

Little is known of the way in which aqueous potassium ferricyanide oxidizes polynitro aromatic compounds to phenols, e.g., 1,3,5-trinitrobenzene to picric acid (191). The ease of methylating such compounds with radicals and the conversion of 2-naphthol to 1-(2-naphthyloxy)-2-naphthol by the ferricyanide reagent (318) suggest that the hydroxylation also involves radicals. The same may be said of the remarkable production of nitrophenols, including *o*-nitrophenol, by the decomposition of 1′,1′,1′-trinitrobenzeneazomethane in benzene, 2-ethoxyethanol, or carbon tetrachloride (325).

Much effort has been expended upon the direct vapor-phase oxidation of benzene to phenol because of its commercial attractiveness, and some recent re-

views are available (77, 112). Thermal conversion of benzene and air, with either homogeneous or heterogeneous catalysts, has been most studied. The best yield (10 per cent per pass, 77 per cent ultimate) has been achieved by passing excess benzene with oxygen, sulfur dioxide, and an inert carrier gas over a supported catalyst containing copper, silver, or gold and also a transition metal at 350–550°C. and a pressure of 100–300 lb./sq. in.; toluene thus gives chiefly *m*-cresol (331). Air and excess benzene at 370–450°C. and a pressure of 500–2000 lb./sq. in. produce up to 30 per cent of phenol per pass when aliphatic compounds are present as promoters, to supply initiating radicals (112, 223, 224a). The same kind of promoters are more or less effective also at 1 atm. (238, 249). Some kinetic studies of the reaction uncatalyzed except by reactor surfaces have been reported (237a, 239, 276a). Alternatively the oxygen may be made atomic by electric discharge; at 6–12 mm. pressure, such oxygen oxidizes benzene to phenol in about 10–12 per cent yield per pass at 100–340°C., the extent of side reactions being unknown (77). At lower conversions (<4 per cent) and higher pressure (750 mm.), air and benzene give 18–30 per cent yields of phenol and some catechol, resorcinol, and hydroquinone, but the consumption of electric power is prohibitive (376, 377, 378, 379). Under approximately similar conditions toluene gives some cresols, mostly *o*-cresol (4–7 per cent overall yield), besides products of side-chain attack (236, 380, 381). Toluene and air at 210°C. and 1500 lb./sq. in. produce a little 4-methylresorcinol (308); here, as from benzene (378), the formation of resorcinols is unexpected, since almost no other radical substitution meta to a hydroxyl group is known. More typically, the oxidation of phenol by air at 610–650°C. yields dibenzofuran and traces of 2,2′-biphenol, along with other products (237).

The greater resistance of nitrobenzene to oxidative destruction suggested its vapor-phase oxidation by air, but only a 1.5 per cent yield of *o*-nitrophenol was obtained. Probably this was the only phenol volatile enough to escape destruction on the heterogeneous catalyst (288).

The mechanism of the biological hydroxylation of aromatic nuclei is not understood, and some similarities to hydroxylation by radical attack have been pointed out (52, 339, 363). An ascorbic acid–iron complex–oxygen model system for such hydroxylation gave the products and yields shown in table 9 (56).

TABLE 9

Hydroxylated aromatic compounds produced in an ascorbic acid system (56)

Substrate	Product	Yield
		per cent
$C_6H_5NHCOCH_3$	*p*-$CH_3CONHC_6H_4OH$	17
	o-$CH_3CONHC_6H_4OH$	12
$C_6H_5NH_2$	*p*-$H_2NC_6H_4OH$	9
o-HOC_6H_4COOH	2,5-$(HO)_2C_6H_3COOH$	55
C_9H_7N	3-HOC_9H_6N	15
p-$HOC_6H_4CH_2CH_2NH_2$	3,4-$(HO)_2C_6H_3CH_2CH_2NH_2$	25

VIII. ALKOXYLATION

Direct attack of alkoxyl radicals on an aromatic nucleus is unknown. No alkoxylation is caused by tetralin hydroperoxide (338), di-*tert*-butyl peroxide (132, 322, 386), cyclohexenyl peroxide (34), and bis(triphenylmethyl) peroxide (407). Electrolytic methoxylation of benzene also fails (267).

Two instances of alkoxylation by transfer substitution have been reported, both for benzoic acid. In one case the generating radicals came from benzoyl peroxide and the alkoxyl radicals from isobutyl alcohol; *o*- and *p*-isobutoxybenzoic acids were produced (157). Some doubt of the accuracy of this observation has been expressed, since no alkoxyl radicals are formed from diacetyl peroxide and alcohols (261). Nevertheless, autoxidizing tetralin in ethanol converted benzoic acid to ethoxybenzoic acids (148).

IX. ACETOXYLATION

Acyloxylations must necessarily compete with decarboxylation:

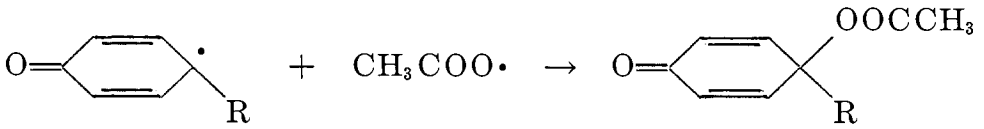
$$R\cdot + CO_2 \leftarrow RCOO\cdot \xrightarrow{ArH} RCOOAr, \text{ etc.}$$

It follows that the substitution will be most successful with very reactive substrates such as polynuclear compounds and phenols. Indeed, no acetoxylation of noncondensed-ring aromatic hydrocarbons is established, although there is evidence of nuclear attack in diphenylmethane and triphenylmethane during the electrolysis of sodium acetate in acetic acid (277). Otherwise, acyloxy radicals do not affect benzene (33, 84, 141, 413), and they abstract hydrogen from any side chain present (259).

Naphthalene is substituted in the 1-position by acetoxy radicals generated either electrolytically (277) or from lead tetraacetate (136). Evidence for an ionic rather than a radical mode of decomposition of lead tetraacetate in carboxylic acids has been presented (300), but the radical mechanism of attack on aromatic substrates is still generally accepted. Anthracene with lead tetraacetate yields the 9-acetoxy derivative (292), 1,2-benzanthracene the 10-acetoxy (137), and 3,4-benzpyrene the 5-acetoxy (138, 139), but the others may resemble anthracene in going through an isolable dihydro diacetoxy adduct (140), so that calling the reaction a substitution is questionable. 10-Acetamino-3,4-benzpyrene is acetoxylated in the 5-position, 5-acetamino-3,4-benzpyrene probably in the 10-position (139), and phenanthrene (by manganese triacetate) in the 9-position (417).

The acetoxylation of some para-substituted *N*-arylacetamides by phenyl iodosoacetate appears, by its orientation and otherwise, to be ionic in character (29).

Phenols are attacked as usual by way of transfer substitution. The quinonoid forms of the radicals derived from ortho- and para-alkylated phenols tend to become stabilized as quinol derivatives by addition of acetoxy radicals (71, 394, 395, 397).



Even for structures in which tautomerization to phenols is not thus blocked, the reaction does not often stop at simple acetoxylation. Nevertheless such substitution by means of acetyl peroxide in acetic acid has been observed: *o*-cresol is acetoxylated in the 4- or 6-position, *p*-cresol in the 2- or 6-position, *m*-cresol in the 2-, 4- or 6-position, and 2,4-xylenol in the 5- (?) or 6-position (396).

At 80°C. anisole is slowly acetoxylated by lead tetraacetate in acetic acid but not by acetyl peroxide in ethyl ether–acetic acid. This has been taken to disprove the ability of acetoxy radicals to attack phenyl ethers (72), but the relatively rapid destruction of such radicals by the aliphatic ether makes any such conclusion unjustified. The reaction with lead tetraacetate doubtless involves both acetoxy and *p*-methoxyphenyl radicals, for the latter substitute in added benzene or nitrobenzene, yielding 4-methoxybiphenyl or its 4′-nitro derivative. The aryl radicals do not affect carbon tetrachloride, in which *p*-methoxyphenyl anisate is an unexpected product (72). In the absence of solvent, lead tetraacetate also causes *p*-acetoxylation of phenetole, isopropyl phenyl ether, and benzyl phenyl ether, but benzyl *p*-tolyl ether is substituted in the methyl group (31, 72). In 1-methoxynaphthalene the 4-position reacts, and in 2-methoxynaphthalene the 1-position (394).

Substitution in anisole during the electrolysis of potassium alkanoates in alkanoic acids with graphite or platinum electrodes has been observed. Mixed methoxyphenyl propionates (24 per cent yield) and valerates (13 per cent) were thus obtained, and the ortho–para ratio for acetoxylation was about 70:30 (185). The *o*-, *m*-, and *p*-methoxyanisoles also react in this way.

X. BENZOYLOXYLATION

It has been reported that benzoyloxy (benzoxy, benzoate) radicals, $C_6H_5COO\cdot$, do not substitute in benzene (179) or chlorobenzene (341) at 80°C., although they strip hydrogen therefrom. The production of mixed chlorophenyl benzoates from chlorobenzene and silver iodide dibenzoate at 130°C. (58) and from benzoyl peroxide decomposed in carbon tetrachloride (234) is apparently due to transfer substitution. Substituted phenyl benzoates are also obtained from aromatic substrates and silver bromide dibenzoate. However, the formation of mainly *m*-nitrophenyl benzoate from nitrobenzene and of *p*-chlorophenyl benzoate from chlorobenzene suggests that the substituting entity is then the benzoyloxy cation (58). Since there is evidence for the production of radicals from silver benzoates and bromine, at least in carbon tetrachloride (30, 109), the type of reaction may be mixed.

Benzoyloxylations with benzoyl peroxide occur in favorable circumstances, as shown in table 10.

A transfer-substitution course has been proposed to account for one product

TABLE 10

Benzoyloxylation of aromatic nuclei[a] *by benzoyl peroxide*

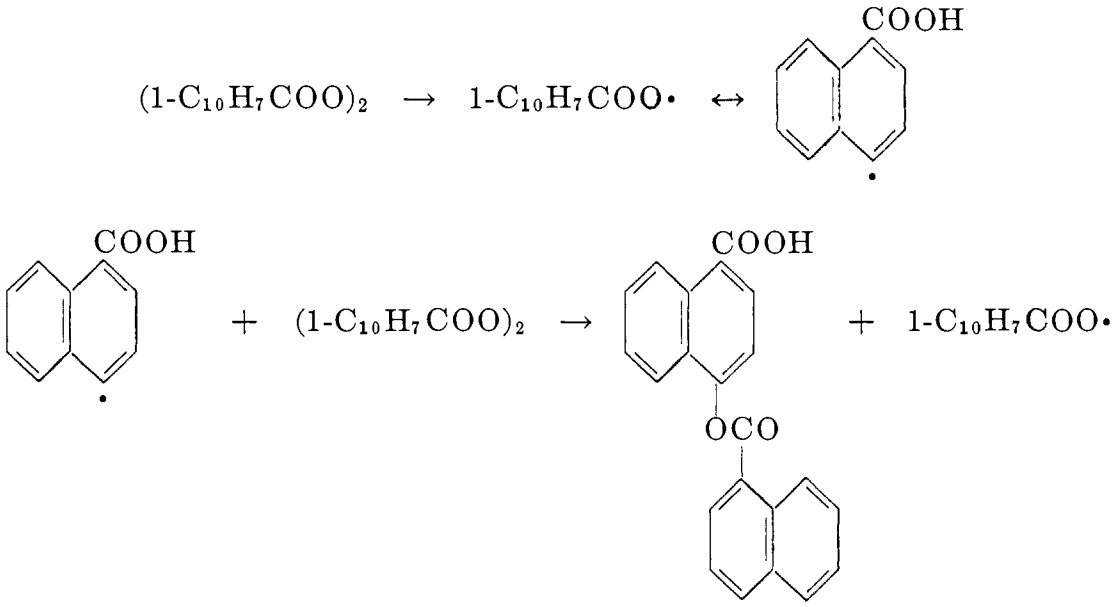
Substrate	Positions of Benzoyloxylation and Yield[b]	Reference
1,2,3-$C_6H_3(OCH_3)_3$	4 and 5 (*ca.* 20%)	(313)
$C_{10}H_8$	1 and 2	(52)
1-$ClC_{10}H_7$	2 (0.9%), 4 (16%), and 5 (14%)	(102)
1-$BrC_{10}H_7$	2 (0.7%), 4 (41%), and 5 (20%)	(102)
1-$O_2NC_{10}H_7$	2 (3%), 4 (18%), and 5 (10%)	(102)
Anthracene	9 (15%)	(341)
9-Methylanthracene	10[c]	(341)
1,2-Benzanthracene	10	(341)
3,4-Benzpyrene	5 (33%)	(341)

[a] Except phenols and amines.

[b] Based on benzoyl peroxide.

[c] Along with another benzoyloxylated product, 10-[2-(9-anthryl)ethyl]anthranol benzoate.

of the thermal decomposition of 1-naphthoyl peroxide (but not the 2-isomer) in carbon tetrachloride (256).



As with other radical sources, phenols and amines characteristically react with benzoyl peroxide by transfer substitution. Sometimes transbenzoylation modifies the original hydroxyl or amino group. Phenols (90, 91), *N*-alkylanilines (127), and the one *N*-arylaniline studied (151) yield almost entirely *o*-benzoyloxylated products unless the ortho positions are blocked, when para substitution occurs (see table 11). If the para position also is occupied, as in mesitol, no aromatic substitution products are formed (92, 395).

The mechanism for reaction of dialkylanilines is slightly different, since no

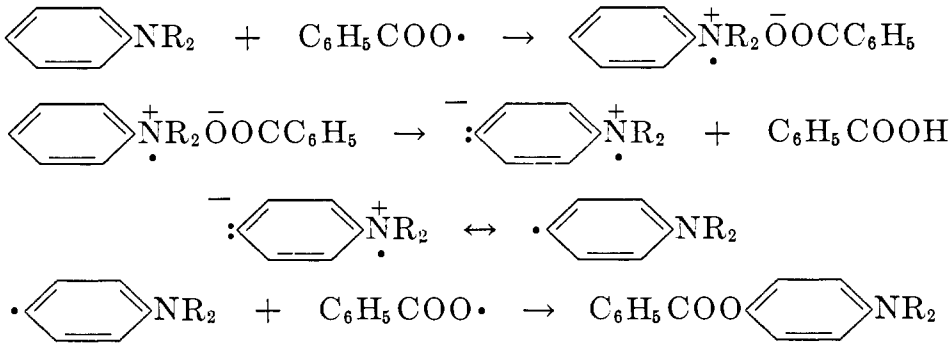
TABLE 11

Benzoyloxylation of phenols and amines with benzoyl peroxide

Substrate	Positions of Benzoyloxylation	Yields[a]	Reference	Substrate	Positions of Benzoyloxylation	Yields[a]	Reference
		per cent				*per cent*	
C_6H_5OH	2 and 4	2% total, in ratio *ca.* 4:1	(90)	$C_6H_5NHC_4H_9$-*n*	2	35	(127)
				$C_6H_5NHCH_2CH_2CH(CH_3)_2$	2	20	(127)
o-$CH_3C_6H_4OH$	6	Trace	(90)	$C_6H_5NHCH_2C_6H_5$	2	8	(127)
m-$CH_3C_6H_4OH$	6	15–20	(90)	*o*-$CH_3C_6H_4NHCH_3$	6	8	(127)
p-$CH_3C_6H_4OH$	2	30–40	(90)	*m*-$CH_3C_6H_4NHCH_3$	6	10	(127)
2,4-$(CH_3)_2C_6H_3OH$	6	30–40	(90)	*p*-$CH_3C_6H_4NHCH_3$	2	31	(127)
3,5-$(CH_3)_2C_6H_3OH$	2	15–20	(90)				
2,6-$(CH_3)_2C_6H_3OH$	4	10	(92)	*p*-$ClC_6H_4NHCH_3$	2	19	(127)
m-$CH_3OC_6H_4OH$	6	15–20	(92)	1-$C_{10}H_7NHC_2H_5$	2	40	(127)
p-$CH_3OC_6H_4OH$	2	30–40	(92)	1,2,3,4-Tetrahydroquinoline	8	16	(127)
$C_6H_5NHCH_3$	2	30	(127)	$(C_6H_5)_2NH$	2	—	(151)
$C_6H_5NHC_2H_5$	2	37	(127)	$C_6H_5N(CH_3)_2$	4	15	(218)
$C_6H_5NHCH_2CH_2CH_3$	2	20	(127)	$C_6H_5N(C_2H_5)_2$	4	15	(218)

[a] Based on benzoyl peroxide.

removal of hydrogen from nitrogen is possible. It is here represented in simplified form (218, 219, 221), involving a semiquinone stage.



Para substitution appears to be the rule (169, 218, 219, 221); this also differentiates the process from the benzoyloxylation of phenols and other anilines.

XI. HALOGENATION

Fluorine, chlorine, and bromine atoms, more than other radicals, tend to *add* to aromatic nuclei, yielding hexahalogenated cyclohexanes (and in the case of fluorine, products of polymerization and degradation). When this tendency is associated with the well-known proclivity of chlorine and bromine atoms to enter side chains, it is understandable that few clear-cut atomic halogenations of the ring are known. The one such fluorination is that of pyridine, which yields 2-fluoropyridine and thence a difluoro derivative in a liquid-phase reaction (361). Chlorine atoms from sulfuryl chloride (255) have caused no such substitution, and while *N*-halogenated imides, especially *N*-bromosuccinimide, probably yield halogen atoms, the reaction of these with aromatic nuclei is usually slow and

succeeds only with the more reactive ones, such as phenolic ethers and polynuclear compounds (62, 123). Transfer substitution has been proposed as a chain sequence for such displacements (2). Evidence for both ionic and radical mechanisms of both substitution and addition of bromine in naphthalene has been adduced (286).

The production of brominated phenyl benzoates from silver benzoate and bromine has been interpreted in terms of organic and bromine radicals (189), but the earlier finding that *m*-bromobenzoic acid and *o*- and *p*-bromophenols are the ones formed (46) remains evidence for bromine cations as the active agent (*cf.* silver bromide dibenzoate, page 108). More certainly radical-produced are the chlorobenzoic acids from benzoic acid and aqueous ferric chloride complexes irradiated with ultraviolet light, but these were not further characterized (36).

Irradiation of ethyl bromide and an aromatic substrate with slow neutrons causes substitution by Br^{80} cations and Br^{82} atoms, both arising from the Szilard–Chalmers effect. In toluene, 90 per cent of the bromine goes to the side chain, but the ratio of *o*-, *m*-, and *p*-bromotoluenes (measured by oxidation and separation of the bromobenzoic acids) is about 4:1:2 (154). For other aromatic substrates the ratios are: nitrobenzene, 2.0:0.64:1; methyl benzoate, 20:2.5:1; and ethyl benzoate, 25:2.1:1 (240). From the relative rates of reaction with Br^{82} in competitive brominations, it was concluded (152, 153, 241) that the substitution involves both atoms and cations. The Br^{82} atoms are supposed to dominate the reactions with nitrobenzene and other electron-poor rings, and the Br^{82} cations those with anisole and other rings carrying electron-rich groups.

Another example of a reaction of mixed type is vapor-phase halogenation at 200–700°C. In the chlorination and bromination of monohalogenated benzenes (387, 403, 404, 405), naphthalene (362, 401), pyridine (60, 193, 194, 289, 402), quinoline (244), and thiophene (231), there is a marked dependence of isomer ratio on the temperature of reaction. At about 400°C. (250°C. for the chlorination of pyridine, 700°C. for thiophene) a gradual transition from "normal" to "statistical" orientation occurs. The former is the result of ordinary electrophilic substitution, whereas the latter represents a comparatively indiscriminate attack of radicals on all open positions, complicated somewhat by a steric effect that reduces the accessibility of the ortho positions. The work has been reviewed recently (400).

The polar reaction is favored by electropositivity of the halogen: iodine and pyridine even at 500°C. yield only 3,5-diiodopyridine and some of the pentaiodo derivative (340). It is favored also on surfaces, such as that of graphite, and by metallic halides such as ferric and cupric bromides. Light hinders it. Finally it is favored by electron availability in the aromatic nucleus: naphthalene requires a higher temperature than pyridine or the halogenobenzenes to undergo the same degree of radical halogenation, thiophene a still higher one, and phenol never does give the meta isomer in quantity.

In what appears to be a reaction of this general class, cyanogen and benzene at 740°C. produce not only benzonitrile but also isophthalonitrile and terephthalonitrile (245).

XII. OTHER SUBSTITUTIONS

The high-temperature reactions of sulfur with toluene (222) and ethylbenzene (165) yield exclusively products of side-chain substitution, as would be expected in a homolytic process. Sulfur and benzene, however, at 350°C. give small amounts of thiophenol and phenyl sulfide, and larger ones of diphenyl disulfide, thianthrene, and tars (165). No doubt the substitution would go more smoothly with naphthalene.

The dichlorophosphino radicals, $Cl_2P\bullet$, from phosphorus trichloride and benzoyl peroxide, do not attack benzene (79). A mixture of silicon tetrachloride and benzene subjected to silent electrical discharge yields some phenyltrichlorosilane, but by way of phenyl radicals rather than trichlorosilyl radicals as substituting intermediates (8). Similarly, triphenylsilyl radicals do not substitute on the ring in chlorobenzene (96).

The predominant formation of ortho-substituted derivatives by the mercuration of nitrobenzene, benzoic acid, and benzophenone (242, 399) has long been considered anomalous. To explain this orientation, it has been implied (265) that mercuration by mercuric acetate in nonpolar solvents is a radical-controlled process. The attacking species is indeed not very selective, but its nature remains uncertain (57).

XIII. REFERENCES

(1) ABRAMOVITCH, R. A.: J. Chem. Soc. **1954,** 3839.
(2) ADAM, K., GOSSELAIN, P. A., AND GOLDFINGER, P.: Nature **171,** 704 (1953).
(3) ADAMS, W. J., HEY, D. H., MAMALIS, P., AND PARKER, R. E.: J. Chem. Soc. **1949,** 3181.
(4) ALAMELA, B. S., AND GANAPATHI, K.: Current Sci. **12,** 119 (1943).
(5) ALEXANDER, E. R., AND BURGE, R. E., JR.: J. Am. Chem. Soc. **72,** 3100 (1950).
(6) ALLAN, Z. J., AND MUŽIK, F.: Chem. Listy **48,** 52 (1954); Chem. Abstracts **49,** 1664 (1955).
(7) ANDERSEN, V. S.: Acta Chem. Scand. **4,** 207 (1950); Chem. Abstracts **45,** 7968b (1951).
(8) ANDREV, D. N.: Doklady Akad. Nauk S.S.S.R. **100,** 263 (1955); Chem. Abstracts **49,** 8095 (1955).
(9) ASHLEY, J. N., BUCHANAN, G. L., AND EASON, A. P. T.: J. Chem. Soc. **1947,** 60.
(10) AUGOOD, D. R., CADOGAN, J. I. G., HEY, D. H., AND WILLIAMS, G. H.: J. Chem. Soc. **1953,** 3412.
(11) AUGOOD, D. R., HEY, D. H., NECHVATAL, A., ROBINSON, T. S., AND WILLIAMS, G. H.: Research **4,** 386 (1951).
(12) AUGOOD, D. R., HEY, D. H., NECHVATAL, A., AND WILLIAMS, G. H.: Nature **167,** 725 (1951).
(13) AUGOOD, D. R., HEY, D. H., AND WILLIAMS, G. H.: J. Chem. Soc. **1952,** 2094.
(14) AUGOOD, D. R., HEY, D. H., AND WILLIAMS, G. H.: J. Chem. Soc. **1953,** 44.
(15) AUGOOD, D. R., AND WILLIAMS, G. H.: Chem. Revs. **57,** 123 (1957).
(16) BACHMAN, W. E., AND HOFFMAN, R. A.: *Organic Reactions*, Vol. II, p. 224. John Wiley and Sons, Inc., New York (1944).
(17) BACON, R. G. R., AND BOTT, R. W.: Chemistry & Industry **1953,** 1285.
(18) BACON, R. G. R., BOTT, R. W., DOGGART, J. R., GRIME, R., AND MUNRO, D. J.: Chemistry & Industry **1953,** 897.
(19) BADGER, G. M.: *Structures and Reactions of Aromatic Compounds*, p. 43. Cambridge University Press, London (1954).
(20) Reference 19, p. 323.

(21) BAKER, W., AND BROWN, N. C.: J. Chem. Soc. **1948,** 2303.
(22) BAMBERGER, E.: Ber. **28,** 403 (1895).
(23) BAMBERGER, E.: Ber. **29,** 446 (1896).
(24) BAMBERGER, E., AND BRUN, J.: Helv. Chim. Acta **6,** 935 (1923).
(25) BAMBERGER, E., AND CZERKIS, M.: J. prakt. Chem. [2] **68,** 480 (1903).
(26) BAMBERGER, E., AND CZERKIS, M.: J. prakt. Chem. [2] **68,** 486 (1903).
(27) BAMBERGER, E., AND KRAUS, E.: Ber. **29,** 273 (1896).
(28) BAMFORD, W. R., AND STEVENS, T. S.: J. Chem. Soc. **1952,** 4675.
(29) BARLIN, G. B., AND RIGGS, N. J.: J. Chem. Soc. **1954,** 3125.
(30) BARNES, R. A., AND PROCHASKA, R. J.: J. Am. Chem. Soc. **72,** 3188 (1950).
(31) BARROW, H. E., CAVILL, G. W. K., COLE, E. R., GILHAM, P. T., AND SOLOMON, D. H.: Chemistry & Industry **1954,** 76.
(32) BARTLETT, P. D., AND COTMAN, J. D.: J. Am. Chem. Soc. **72,** 3095 (1950).
(33) BARTLETT, P. D., AND LEFFLER, J. E.: J. Am. Chem. Soc. **72,** 3030 (1950).
(34) BATEMAN, L., HUGHES, H., AND NORRIS, A. L.: Discussions Faraday Soc. **14,** 190 (1953).
(35) BATES, H. G. C., EVANS, H. G., AND URI, N.: Nature **166,** 869 (1950).
(36) BATES, H. G. C., AND URI, N.: J. Am. Chem. Soc. **75,** 2754 (1953).
(37) BAUDISCH, O.: Naturwissenschaften **27,** 768 (1939).
(38) BAUDISCH, O.: Science **92,** 336 (1940).
(39) BAUDISCH, O.: J. Am. Chem. Soc. **63,** 622 (1941).
(40) BAUDISCH, O.: Science **108,** 443 (1948).
(40a) BAXENDALE, J. H.: *I. Oxidation of Benzene by Hydrogen Peroxide. II. Reaction of Hydrogen Peroxide with Some Iron Complexes.* University of Notre Dame Press, Notre Dame, Indiana (1955).
(41) BAXENDALE, J. H., AND MAGEE, J.: Discussions Faraday Soc. **14,** 160 (1953).
(42) BAXENDALE, J. H., AND MAGEE, J.: Trans. Faraday Soc. **51,** 205 (1955).
(43) BEILSTEIN: *Handbuch der organischen Chemie,* 4th edition, Vol. 5, p. 185; 2d supplement, p. 139.
(44) BELL, F., AND GIBSON, J. A.: J. Chem. Soc. **1955,** 3560.
(45) BERTHO, A.: Ber. **57,** 1138 (1924).
(46) BOCKEMÜLLER, W., AND HOFFMAN, F. W.: Ann. **519,** 165 (1935).
(47) BÖESEKEN, J., AND GASTER, A.: Rec. trav. chim. **49,** 102 (1930).
(48) BÖESEKEN, J., AND GELISSEN, H.: Rec. trav. chim. **43,** 869 (1924).
(49) BORSCHE, W., AND HAHN, H.: Ber. **82,** 260 (1949).
(50) BOWDEN, S. T., AND JONES, W. J.: J. Chem. Soc. **1928,** 1149.
(51) BOYLAND, E., MANSON, D., AND SIMS, P.: J. Chem. Soc. **1953,** 3623.
(52) BOYLAND, E., AND SIMS, P.: J. Chem. Soc. **1953,** 2967.
(53) BOYLAND, E., AND SIMS, P.: J. Chem. Soc. **1954,** 980.
(54) BROADHEAD, G. D., AND PAUSON, P. L.: J. Chem. Soc. **1955,** 367.
(55) BROCKMAN, C. J.: *Electro-Organic Chemistry,* p. 102. John Wiley and Sons, Inc., New York (1926).
(56) BRODIE, B. B., AXELROD, J., SHORE, P. A., AND UDENFRIEND, S.: J. Biol. Chem. **208,** 741 (1954).
(57) BROWN, H. C., AND MCCRARY, C. W., JR.: J. Am. Chem. Soc. **77,** 2306 (1955).
(58) BRYCE-SMITH, D.: Nature **172,** 863 (1953).
(59) BUCHANAN, G. L., AND LEVINE, R. M.: J. Chem. Soc. **1950,** 2248.
(60) BURSTALL, F. H.: J. Chem. Soc. **1938,** 1662.
(61) BUSCH, M., AND KNOLL, R.: Ber. **60B,** 2243 (1927).
(62) BUU-HOÏ, N. P.: Record Chem. Progr. (Kresge-Hooker Sci. Lib.) **13,** 30 (1952).
(63) BUU-HOÏ, N. P., AND HOAN, N.: Rec. trav. chim. **69,** 1455 (1950).
(64) BUU-HOÏ, N. P., HOAN, N., AND ROGER, R.: Bull. soc. chim. France **17,** 489 (1950).
(65) CADOGAN, J. I. G., HEY, D. H., AND WILLIAMS, G. H.: J. Chem. Soc. **1954,** 794.
(66) CADOGAN, J. I. G., HEY, D. H., AND WILLIAMS, G. H.: J. Chem. Soc. **1954,** 3352.

(67) CADOGAN, J. I. G., HEY, D. H., AND WILLIAMS, G. H.: J. Chem. Soc. **1955,** 1425.
(68) CAMPBELL, I. G. M., AND MORRILL, D. H.: J. Chem. Soc. **1955,** 1662.
(69) CAMPBELL, N.: Ann. Repts. on Progr. Chem. (Chem. Soc. London) **50,** 197 (1953) (pub. 1954).
(70) CARLIN, R. B., AND SWAKON, E. A.: J. Am. Chem. Soc. **77,** 966 (1955).
(71) CAVILL, G. W. K., COLE, E. R., GILHAM, P. T., AND MCHUGH, D. J.: J. Chem. Soc. **1954,** 2785.
(72) CAVILL, G. W. K., AND SOLOMON, D. H.: J. Chem. Soc. **1955,** 1404.
(73) CHASE, B. H., AND HEY, D. H.: J. Chem. Soc. **1952,** 553.
(74) CHATTERJEE, N.: J. Indian Chem. Soc. **12,** 410 (1935).
(75) CHICHIBABIN, A. E.: J. Russ. Phys.-Chem. Soc. **50,** 502 (1918); Chem. Abstracts **18,** 1495 (1924).
(76) CHICHIBABIN, A. E., AND SCHEMYAKINA, E. M.: J. Russ. Phys.-Chem. Soc. **53,** 217 (1921); Chem. Abstracts **18,** 2342 (1924).
(77) CHU, J. C., AI, H. C., AND OTHMER, D. F.: Ind. Eng. Chem. **45,** 1266 (1953).
(78) CHWALA, A., AND PAILER, M.: J. prakt. Chem. **152,** 45 (1939).
(79) CLAYTON, J. O., AND JENSEN, W. L.: J. Am. Chem. Soc. **70,** 3880 (1948).
(80) CLIFTON, P. V., AND PLANT, S. G.: J. Chem. Soc. **1951,** 461.
(81) COATES, H., COOK, A. H., HEILBRON, I. M., HEY, D. H., LAMBERT, A., AND LEWIS, F. B.: J. Chem. Soc. **1943,** 401.
(82) COATES, H., COOK, A. H., HEILBRON, I. M., HEY, D. H., LAMBERT, A., AND LEWIS, F. B.: J. Chem. Soc. **1943,** 406.
(83) COATES, H., HEILBRON, I. M., HEY, D. H., LAMBERT, A., AND IMPERIAL CHEMICAL INDUSTRIES, LTD.: British patent 558,009 (December 15, 1943); Chem. Abstracts **40,** 1888 (1946).
(84) COHEN, S. G., AND SPARROW, D. B.: J. Am. Chem. Soc. **72,** 611 (1950).
(85) COOK, A. H., HEILBRON, I. M., HEY, D. H., LAMBERT, A., AND SPINKS, A.: J. Chem. Soc. **1943,** 404.
(86) COOK, A. H., HEILBRON, I. M., AND SPINKS, A.: J. Chem. Soc. **1943,** 417.
(87) COOK, A. H., HEILBRON, I. M., AND STEGER, L.: J. Chem. Soc. **1943,** 413.
(88) COOK, J. W., AND SCHOENTAL, R.: J. Chem. Soc. **1950,** 47.
(89) CORNFORTH, J. W., AND COOKSON, E. J.: J. Chem. Soc. **1952,** 1085.
(90) COSGROVE, S. L., AND WATERS, W. A.: J. Chem. Soc. **1949,** 3189.
(91) COSGROVE, S. L., AND WATERS, W. A.: J. Chem. Soc. **1951,** 388.
(92) COSGROVE, S. L., AND WATERS, W. A.: J. Chem. Soc. **1951,** 1726.
(93) CRAMER, P. L.: J. Am. Chem. Soc. **60,** 1406 (1938).
(94) CRONHEIM, G.: J. Org. Chem. **12,** 7 (1947).
(95) CROSS, C. F., BEVAN, E. J., AND HEIBERG, T.: Ber. **33,** 2015 (1900).
(96) CURTICE, J. S.: Iowa State Coll. J. Sci. **29,** 399 (1955).
(97) CURTIUS, T.: J. prakt. Chem. **125,** 303 (1930).
(98) CURTIUS, T., AND HAAS, F.: J. prakt. Chem. **102,** 85 (1921).
(99) CURTIUS, T., AND SCHMIDT, F.: Ber. **55,** 1571 (1922).
(100) DAINTON, F. S.: J. Chem. Soc. **1952,** 1533.
(101) DANNLEY, R. L. AND COLEMAN, C. B.: Abstracts of papers presented at the 119th Meeting of the American Chemical Society, Cleveland, Ohio, April, 1951, p. 81M.
(102) DANNLEY, R. L., AND GIPPIN, M. J.: J. Am. Chem. Soc. **74,** 332 (1952).
(103) DANNLEY, R. L., AND GREGG, E. C.: Abstracts of papers presented at the 121st meeting of the American Chemical Society, Buffalo, New York, April, 1952, p. 1K.
(104) DANNLEY, R. L., AND GREGG, E. C., JR.: J. Am. Chem. Soc. **76,** 2997 (1954).
(105) DANNLEY, R. L., GREGG, E. C., JR., PHELPS, R. E., AND COLEMAN, C. B.: J. Am. Chem. Soc. **76,** 445 (1954).
(106) DANNLEY, R. L., AND STERNFELD, M.: J. Am. Chem. Soc. **76,** 4543 (1954).
(107) DANNLEY, R. L., AND ZAREMSKY, B.: J. Am. Chem. Soc. **77,** 1588 (1955).
(108) DATTA, P.: J. Indian Chem. Soc. **24,** 109 (1947).

(109) DAUBEN, W. G., AND TILLES, H.: J. Am. Chem. Soc. **72,** 3185 (1950).
(110) DAVIS, P., EVANS, M. G., AND HIGGINSON, W. C.: J. Chem. Soc. **1951,** 2563.
(111) DAY, M. J., AND STEIN, G.: Nature **164,** 671 (1949).
(112) DENTON, W. I., DOHERTY, H. G., AND KRIEBLE, R. H.: Ind. Eng. Chem. **42,** 777 (1950).
(113) DERMER, O. C., AND EDMISON, M. T.: J. Am. Chem. Soc. **77,** 70 (1955).
(114) DE TAR, D. F.: J. Am. Chem. Soc. **72,** 1028 (1950).
(115) DE TAR, D. F., AND HOWARD, J. C.: J. Am. Chem. Soc. **77,** 4393 (1955).
(116) DE TAR, D. F., AND KAZIMI, A. A.: J. Am. Chem. Soc. **77,** 3842 (1955).
(117) DE TAR, D. F., AND SAGMANLI, S. V.: J. Am. Chem. Soc. **72,** 965 (1950).
(118) DE TAR, D. F., AND SAVAT, C. S.: J. Am. Chem. Soc. **75,** 5117 (1953).
(119) DE TAR, D. F., AND SCHEIFELE, J. H.: J. Am. Chem. Soc. **73,** 1442 (1951).
(120) DE TAR, D. F., AND TURETSKY, M. N.: J. Am. Chem. Soc. **77,** 1745 (1955).
(121) DEWAR, M. J. S.: *The Electronic Theory of Organic Chemistry*, p. 278. The Clarendon Press, Oxford (1949).
(122) DIETRICH, W.: Helv. Chim. Acta **8,** 149 (1925).
(123) DJERASSI, C.: Chem. Revs. **43,** 271 (1948).
(124) DOBRES, R. M., AND SELWOOD, P. W.: J. Am. Chem. Soc. **72,** 5731 (1950).
(125) DUNLOP, H. G., AND TUCKER, S. H.: J. Chem. Soc. **1939,** 1945.
(126) DUNSTAN, W. J., AND HUGHES, G. K.: J. Proc. Roy. Soc. N. S. Wales **80,** 77 (1947); Chem. Abstracts **42,** 4160 (1948).
(127) EDWARD, J. T.: J. Chem. Soc. **1954,** 1464.
(128) EGLOFF, G.: *The Reactions of Pure Hydrocarbons*, p. 478. Reinhold Publishing Corporation, New York (1937).
(129) EISTERT, B.: *Chemismus und Konstitution*, p. 284. F. Enke, Stuttgart (1948).
(130) ELKS, J., HAWORTH, J. W., AND HEY, D. H.: J. Chem. Soc. **1940,** 1284.
(131) ELKS, J., AND HEY, D. H.: J. Chem. Soc. **1943,** 441.
(132) FARMER, E. H., AND MOORE, C. G.: J. Chem. Soc. **1951,** 131.
(133) FICHTER, F.: *Organische Elektrochemie*, p. 75. T. Steinkopff, Dresden and Leipzig (1942).
(134) FICHTER, F., AND STOCKER, R.: Ber. **47,** 2003 (1914).
(135) FIESER, L. F.: In *Organic Chemistry*, edited by Henry Gilman, 2nd edition, Vol. I, p. 120. John Wiley and Sons, Inc., New York (1943).
(136) FIESER, L. F., CLAPP, R., AND DAUDT, W.: J. Am. Chem. Soc. **64,** 2052 (1942).
(137) FIESER, L. F., AND HERSHBERG, E. B.: J. Am. Chem. Soc. **60,** 1893 (1938).
(138) FIESER, L. F., AND HERSHBERG, E. B.: J. Am. Chem. Soc. **60,** 2542 (1938).
(139) FIESER, L. F., AND HERSHBERG, E. B.: J. Am. Chem. Soc. **61,** 1565 (1939).
(140) FIESER, L. F., AND PUTNAM, S. T.: J. Am. Chem. Soc. **69,** 1038 (1947).
(141) FORD, M. C., AND WATERS, W. A.: J. Chem. Soc. **1951,** 824.
(142) FORD, M. C., WATERS, W. A., AND YOUNG, A. T.: J. Chem. Soc. **1950,** 833.
(143) FORSYTH, H., AND PYMAN, F.: J. Chem. Soc. **1926,** 2912.
(144) FRANCE, H., HEILBRON, I. M., AND HEY, D. H.: J. Chem. Soc. **1938,** 1364.
(145) FRANCE, H., HEILBRON, I. M., AND HEY, D. H.: J. Chem. Soc. **1939,** 1283.
(146) FRANCE, H., HEILBRON, I. M., AND HEY, D. H.: J. Chem. Soc. **1939,** 1288.
(147) FREEMAN, G. R., VAN CLEAVE, A. B., AND SPINKS, J. W. T.: Can. J. Chem. **31,** 448 (1953).
(148) FRYE, C. F., KRETSCHMER, C. B., AND WIEBE, R.: Ind. Eng. Chem. **46,** 1517 (1954).
(149) GAERTNER, R.: Chem. Revs. **45,** 493 (1949).
(150) GAERTNER, R.: J. Am. Chem. Soc. **74,** 4950 (1952).
(151) GAMBARJAN, S.: Ber. **42,** 4003 (1909).
(152) GAVORET, G.: J. chim. phys. **50,** 183 (1953).
(153) GAVORET, G.: J. chim. phys. **50,** 434 (1953).
(154) GAVORET, G., AND IVANOFF, N.: Bull. soc. chim. France **1952,** 166.
(155) GELISSEN, H., AND HERMANS, P. H.: Ber. **58,** 285 (1925).

(156) GELISSEN, H., AND HERMANS, P. H.: Ber. **58,** 476 (1925).
(157) GELISSEN, H., AND HERMANS, P. H.: Ber. **58,** 764 (1925).
(158) GELISSEN, H., AND HERMANS, P. H.: Ber. **58,** 765 (1925).
(159) GELISSEN, H., AND HERMANS, P. H.: Ber. **58,** 770 (1925).
(160) GELISSEN, H., AND HERMANS, P. H.: Ber. **59,** 662 (1926).
(161) GERNGROS, O., AND DUNKEL, M.: Ber. **57,** 739 (1924).
(162) GERNGROS, O., SCHACHNOW, C., AND JONES, R.: Ber. **57,** 747 (1924).
(163) GINGRAS, B. A., AND WATERS, W. A.: J. Chem. Soc. **1954,** 1920.
(164) GLADSTONE, M. T.: J. Am. Chem. Soc. **76,** 1581 (1954).
(165) GLASS, H. B., AND REID, E. E.: J. Am. Chem. Soc. **51,** 3428 (1929).
(166) GOLDHAMMER, H.: Biochem. Z. **189,** 81 (1927).
(167) GOLDSCHMIDT, S., AND DACHS, K.: Chem. Ber. **88,** 583 (1955).
(168) GOLDSCHMIDT, S., AND MINSINGER, M.: Chem. Ber. **87,** 956 (1954).
(169) GOODE, W. E., AND GRATCH, S.: Abstracts of Papers Presented at the 126th Meeting of the American Chemical Society, New York City, September, 1954, p. 7-S.
(170) DE GRAAF, G. B. R., VAN DIJCK-ROTHUS, J. H., AND VAN DE KOLK, G.: Rec. trav. chim. **74,** 143 (1955).
(171) GRAEBE, C., AND SCHESTAKOW, P.: Ann. **284,** 306 (1895).
(172) GREENE, F. D.: Abstracts of Papers Presented at the 128th Meeting of the American Chemical Society, Minneapolis, Minnesota, September, 1955, p. 16-O.
(173) GRIESS, P.: Ber. **21,** 978 (1888).
(174) GRIEVE, W. S., AND HEY, D. H.: J. Chem. Soc. **1934,** 1797.
(175) HADDOCK, N. H., AND IMPERIAL CHEMICAL INDUSTRIES, LTD.: British patent 530,881 (December 24, 1940); Chem. Abstracts **36,** 279 (1942).
(176) HALFPENNY, E., AND ROBINSON, P. L.: J. Chem. Soc. **1952,** 928.
(177) HALFPENNY, E., AND ROBINSON, P. L.: J. Chem. Soc. **1952,** 939.
(178) HAMMOND, G. S., AND RAVVE, A.: J. Am. Chem. Soc. **73,** 1891 (1951).
(179) HAMMOND, G. S., RUDESILL, J. T., AND MODIC, F. J.: J. Am. Chem. Soc. **73,** 3929 (1951).
(180) HAMMOND, G. S., AND TODD, R. W.: J. Am. Chem. Soc. **76,** 4081 (1954).
(181) HARLEY-MASON, J., AND MANN, F. G.: J. Chem. Soc. **1940,** 1379.
(182) HASTINGS, S. H., AND MATSEN, E. A.: J. Am. Chem. Soc. **70,** 3514 (1948).
(183) HAWORTH, J. W., HEILBRON, I. M., AND HEY, D. H.: J. Chem. Soc. **1940,** 349.
(184) HAWORTH, J. W., HEILBRON, I. M., HEY, D. H., WILKINSON, R., AND BRADBOOK, E. F.: J. Chem. Soc. **1945,** 409.
(185) HAYASHI, T., AND WILSON, C. L.: Abstracts of Papers Presented at the 126th Meeting of the American Chemical Society, New York City, September, 1954, p. 78-O.
(186) HEACOCK, R. A., AND HEY, D. H.: J. Chem. Soc. **1952,** 1508.
(187) HEACOCK, R. A., AND HEY, D. H.: J. Chem. Soc. **1952,** 4059.
(188) HEACOCK, R. A., AND HEY, D. H.: J. Chem. Soc. **1953,** 3.
(189) HEINTZLER, M.: Ann. **569,** 102 (1950).
(190) HENDERSON, G. G., AND BOYD, R.: J. Chem. Soc. **97,** 1660 (1910).
(191) HEPP, P.: Ann. **215,** 344 (1882).
(192) HERMANS, P. H., AND VAN EYK, J.: J. Polymer Sci. **1,** 407 (1946).
(193) HERTOG, H. J., AND WIBAUT, J. P.: Rec. trav. chim. **51,** 381 (1932).
(194) HERTOG, H. J., AND WIBAUT, J. P.: Rec. trav. chim. **51,** 940 (1932).
(195) HESLOP, R. B.: Chemistry & Industry **1954,** 1487.
(196) HESLOP, R. B., AND ROBINSON, P. L.: J. Chem. Soc. **1954,** 1271.
(197) HEUSLER, F.: Ann. **260,** 227 (1890).
(198) HEY, D. H.: J. Chem. Soc. **1934,** 1966.
(199) HEY, D. H.: J. Chem. Soc. **1952,** 1974.
(200) HEY, D. H.: Progress in Organic Chemistry **1,** 219 (1952).
(201) HEY, D. H.: *Reactions of Free Radicals in Solution.* University of Notre Dame Press, Notre Dame, Indiana (1954).

(202) HEY, D. H., AND LAWTON, S. E.: J. Chem. Soc. **1940,** 374.
(203) HEY, D. H., AND MULLEY, R. D.: J. Chem. Soc. **1952,** 2276.
(204) HEY, D. H., NECHVATAL, A., AND ROBINSON, T. S.: J. Chem. Soc. **1951,** 2892.
(205) HEY, D. H., AND OSBOND, J. M.: J. Chem. Soc. **1949,** 3164.
(206) HEY, D. H., AND OSBOND, J. M.: J. Chem. Soc. **1949,** 3172.
(207) HEY, D. H., PENGILLY, B. W., AND WILLIAMS, G. H.: J. Chem. Soc. **1955,** 6.
(208) HEY, D. H., STIRLING, C. J. M., AND WILLIAMS, G. H.: J. Chem. Soc. **1954,** 2747.
(208a) HEY, D. H., STIRLING, C. J. M., AND WILLIAMS, G. H.: J. Chem. Soc. **1955,** 3963.
(209) HEY, D. H., AND WALKER, E. W.: J. Chem. Soc. **1948,** 2213.
(210) HEY, D. H., AND WILLIAMS, J. M.: J. Chem. Soc. **1950,** 1678.
(211) HEY, D. H., AND WILLIAMS, G. H.: Discussions Faraday Soc. **14,** 216 (1953).
(212) HICKINBOTTOM, W. J.: Nature **142,** 830 (1938).
(213) HICKINBOTTOM, W. J.: Nature **143,** 520 (1939).
(214) HIRSCH, R.: Ber. **23,** 3705 (1890).
(215) HIRSCH, R.: Ber. **25,** 1973 (1892).
(216) HODGSON, H. H., AND FOSTER, C. K.: J. Chem. Soc. **1954,** 581.
(217) HOLT, P. F., AND HOPSON-HILL, B. I.: J. Chem. Soc. **1952,** 4251.
(218) HORNER, L., AND BETZEL, C.: Ann. **579,** 175 (1953).
(219) HORNER, L., AND JUNKERMANN, H.: Ann. **591,** 53 (1955).
(220) HORNER, L., AND NAUMANN, W.: Ann. **587,** 93 (1954).
(221) HORNER, L., AND SCHWENK, E.: Ann. **566,** 69 (1950).
(222) HORTON, A. W.: J. Org. Chem. **14,** 761 (1949).
(223) HOSAKA, Y.: J. Chem. Soc. Japan, Ind. Chem. Sect. **57,** 197 (1954); Chem. Abstracts **49,** 11578 (1955).
(224) HOSAKA, Y., NAITO, T., AND URANO, Y.: J. Chem. Soc. Japan, Ind. Chem. Sect. **57,** 282 (1954); Chem. Abstracts **49,** 13132 (1955).
(224a) HOSAKA, Y., URANO, Y., AND YASUMOTO, M.: J. Chem. Soc. Japan, Ind. Chem. Sect. **57,** 375–6 (1954); Chem. Abstracts **49,** 15774 (1955).
(225) HOWTON, D. R.: J. Am. Chem. Soc. **69,** 2060 (1947).
(226) HUISGEN, R., AND NAKATEN, H.: Ann. **586,** 70 (1954).
(227) HUISGEN, R., AND SORGE, G.: Ann. **566,** 162 (1950).
(228) HUNTRESS, E. H., ATKINSON, E. R., HAN, E. A., AND TIBBETTS, M. S.: J. Am. Chem. Soc. **75,** 743 (1953).
(229) HUNTRESS, E. H., AND SEIKEL, M. K.: J. Am. Chem. Soc. **61,** 1066 (1939).
(230) HURD, C. D.: *The Pyrolysis of Carbon Compounds.* The Chemical Catalog Co., Inc., New York (1929).
(231) HURD, C. D., AND ANDERSON, H. J.: J. Am. Chem. Soc. **75,** 3517 (1953).
(232) HURD, C. D., AND POLLACK, M. A.: J. Org. Chem. **3,** 550 (1939).
(233) I. G. FARBENINDUSTRIE A.-G.: British patent 513,846 (October 24, 1939); Chem. Abstracts **35,** 2156 (1941).
(234) IKEDA, Y., AND WAKITA, M.: Bull. Liberal Arts Coll., Wakayama Univ. (Nat. Sci.) **5,** 12 (1955); Chem. Abstracts **49,** 10240 (1955).
(234a) IMOTO, M.: Kakagu (Chemistry) **7,** 358–66 (1952); Chem. Abstracts **49,** 15805 (1955).
(235) INGOLD, C. K., AND SHAW, F. R.: J. Chem. Soc. **1949,** 575.
(236) INOUE, E.: J. Soc. Org. Synthetic Chem. (Japan) **11,** 256 (1953); Chem. Abstracts **47,** 12048 (1953).
(237) IOFFE, I. I.: Zhur. Fiz. Khim. **28,** 772 (1954); Chem. Abstracts **49,** 6697 (1955).
(237a) IOFFE, I. I.: Zhur. Fiz. Khim. **28,** 1555 (1954); Chem. Abstracts **50,** 36 (1956).
(238) IOFFE, I. I., LEVIN, Y. S., AND KRONICH, I. G.: Zhur. Fiz. Khim. **28,** 1395 (1954); Chem. Abstracts **49,** 8674 (1955).
(239) IOFFE, I. I., SOLOKOVA, E. V., KRONICH, I. G., AND SHIROKOVA, N. I.: Zhur. Fiz. Khim. **28,** 1386 (1954); Chem. Abstracts **49,** 8674 (1955).
(240) IVANOFF, N.: Bull. soc. chim. France **1953,** 266.
(241) IVANOFF, N.. AND GAVORET, G.: J. chim. phys. **50,** 524 (1953).

(242) JACKSON, G. R., JR., AND FRANT, M. S.: J. Am. Chem. Soc. **77,** 5625 (1955).
(243) JACOBSON, P., AND LOEB, A.: Ber. **36,** 4082 (1903).
(244) JANSEN, H. E., AND WIBAUT, J. P.: Rec. trav. chim. **56,** 699 (1937).
(245) JANZ, G. J.: J. Am. Chem. Soc. **74,** 4529 (1952).
(246) JOHNSON, A. W.: J. Chem. Soc. **1946,** 895.
(247) JOHNSON, A. W.: J. Chem. Soc. **1954,** 1331.
(248) JOHNSON, G. R. A., STEIN, G., AND WEISS, J.: J. Chem. Soc. **1951,** 3275.
(249) JORIS, G. G.: U. S. patents 2,546,639 and 2,546,640 (1951); Chem. Abstracts **45,** 9561 (1951).
(250) KAILAN, A.: Sitzber. Akad. Wiss. Wien, Abt. IIa, **135,** 611; Chem. Zentr. **1927, II,** 2147.
(251) KAMBARA, S., AND FUTSU, T.: J. Chem. Soc. Japan, Ind. Chem. Sect. **51,** 113 (1948); Chem. Abstracts **44,** 9717 (1950).
(252) KASLOW, C. E., AND SUMMERS, R. M.: Org. Syntheses **33,** 56 (1953).
(253) KEHRMANN, F., OULEVAY, A., AND REGIS, F.: Ber. **46,** 3712 (1913).
(254) KELLAR, R. N., AND SMITH, P. A. S.: J. Am. Chem. Soc. **66,** 1122 (1944).
(255) KHARASCH, M. S., AND BROWN, H. C.: J. Am. Chem. Soc. **61,** 2142 (1939).
(256) KHARASCH, M. S., AND DANNLEY, R. L.: J. Org. Chem. **10,** 406 (1945).
(257) KHARASCH, M. S., AND FIELDS, E. K.: J. Am. Chem. Soc. **63,** 2316 (1941).
(258) KHARASCH, M. S., GOLDBERG, W., AND MAYO, F. R.: J. Am. Chem. Soc. **60,** 2004 (1938).
(259) KHARASCH, M. S., MCBAY, H. C., AND URRY, W. H.: J. Org. Chem. **10,** 401 (1945).
(260) KHARASCH, M. S., AND REINMUTH, O.: *Grignard Reactions of Nonmetallic Substances,* p. 116. Prentice-Hall, Inc., New York (1954).
(261) KHARASCH, M. S., ROWE, J. L., AND URRY, W. H.: J. Org. Chem. **16,** 905 (1951).
(262) KHARASCH, M. S., SAYLES, D. C., AND FIELDS, E. K.: J. Am. Chem. Soc. **66,** 481 (1944).
(263) KHARASCH, M. S., SCHWARTZ, D., ZIMMERMAN, M., AND NUDENBERG, W.: J. Org. Chem. **18,** 1051 (1953).
(264) KHARASCH, M. S., STAMPA, G., AND NUDENBERG, W.: Science **116,** 309 (1952).
(265) KLAPPROTH, W. J., AND WESTHEIMER, F. H.: J. Am. Chem. Soc. **72,** 4461 (1950).
(266) KOENIGS, E., AND RUPPELT, E.: Ann. **509,** 142 (1934).
(267) KOLB, K. E.: "Bromination and Alkoxylation of Furan Compounds," Ph.D. Dissertation, The Ohio State University (1953).
(268) KONECNY, J. O.: J. Am. Chem. Soc. **76,** 4993 (1954).
(269) KONECNY, J. O.: J. Am. Chem. Soc. **77,** 5748 (1955).
(270) KÜHLING, O.: Ber. **28,** 41 (1895).
(271) KÜHLING, O.: Ber. **28,** 523 (1895).
(272) KÜHLING, O.: Ber. **29,** 165 (1896).
(273) KUMAGAI, T., AND WOLFFENSTEIN, R.: Ber. **41,** 247 (1908).
(274) LAVILLE, J. R., AND WATERS, W. A.: J. Chem. Soc. **1954,** 400.
(275) LEFFLER, J. E.: J. Am. Chem. Soc. **72,** 67 (1950).
(276) LETSINGER, R. L., COLLAT, R., AND MAGNUSSON, M.: J. Am. Chem. Soc. **76,** 4185 (1954).
(276a) LEWIS, B., AND VON ELBE, G.: *Combustions, Flames and Explosions of Gases,* p. 187. Academic Press, Inc., New York (1951).
(277) LINSTEAD, R. P., SHEPHARD, B. R., AND WEEDON, C. L.: J. Chem. Soc. **1952,** 3624.
(278) LOEBL, H., STEIN, G., AND WEISS, J.: J. Chem. Soc. **1949,** 2074.
(279) LOEBL, H., STEIN, G., AND WEISS, J.: J. Chem. Soc. **1950,** 2704.
(280) LOEBL, H., STEIN, G., AND WEISS, J.: J. Chem. Soc. **1951,** 405.
(281) LYTHGOE, B., AND RAYNER, L. S.: J. Chem. Soc. **1951,** 2323.
(282) MACKENZIE, C. A., AND CHUCHANI, G.: J. Org. Chem. **20,** 336 (1955).
(283) MAGIDSON, O. Y., POROZOVSKA, E. Y., AND SELIGSOHN: Trans. Sci. Chem. Pharm. Inst. (Moscow), No. **6,** 23 (1923); Chem. Abstracts **22,** 3884 (1928).

(284) MAGIDSON, O. Y., AND PREOBRAZHENSKIĬ, N. A.: Trans. Sci. Chem. Pharm. Inst (Moscow), No. **16,** 65 (1926); Chem. Abstracts **23,** 1630 (1929).
(285) MARTINON: Bull. soc. chim. [2] **43,** 155 (1885).
(286) MAYS, F. R., AND HARDY, W. B.: J. Am. Chem. Soc. **74,** 911 (1952).
(287) McBAY, H. C., AND TUCKER, A. J.: J. Org. Chem. **19,** 869 (1954).
(288) McCANTS, J. F.: "The Vapor-Phase Oxidation of Nitrobenzene," M.S. Thesis, Oklahoma A. & M. College (1943).
(289) McELVAIN, S. M., AND GOESE, M. A.: J. Am. Chem. Soc. **65,** 2227 (1943).
(290) MERZ, J. H., AND WATERS, W. A.: J. Chem. Soc. **1949,** 515.
(291) MERZ, J. H., AND WATERS, W. A.: J. Chem. Soc. **1949,** 2427.
(292) MEYER, K. H.: Ann. **379,** 73 (1911).
(293) MEYER, H., AND HOFMANN, A.: Monatsh. **38,** 343 (1917).
(294) MILAS, N. A.: J. Am. Chem. Soc. **59,** 2342 (1937).
(295) MILAS, N. A., AND SUSSMAN, S.: J. Am. Chem. Soc. **59,** 2345 (1937).
(296) MIZUGUCHI, J., AND MATSUMOTO, S.: J. Pharm. Soc. Japan **71,** 737 (1951); Chem. Abstracts **45,** 10099 (1951).
(297) MOHLAU, R., AND BERGER, R.: Ber. **26,** 1196 (1893).
(298) MOHLAU, R., AND BERGER, R.: Ber. **26,** 1994 (1893).
(299) MORGAN, G. T., AND WALLS, L. P.: J. Chem. Soc. **1930,** 1502.
(300) MOSHER, W. A., AND KEHR, C. L.: J. Am. Chem. Soc. **75,** 3172 (1953).
(301) MÜLLER, E.: Angew. Chem. **64,** 233 (1952).
(302) MÜLLER, E.: In Houben-Weyl's *Methoden der organischen Chemie*, 4th edition, **4,** II, 482–3 (1955).
(303) MUMM, O., AND DIEDERICHSEN, J.: Ber. **72,** 1523 (1939).
(304) MURAYAMA, K., AND DANNOURA, T.: Ann. Rept. Takamine Lab. **3,** 34 (1953); Chem. Abstracts **49,** 7522 (1955).
(305) NAGASAKA, A., ODA, R., AND NUKINA, S.: J. Chem. Soc. Japan, Ind. Chem. Sect. **57,** 227 (1954); Chem. Abstracts **49,** 11626 (1955).
(306) NAGASE, Y., AND MATSUMOTO, U.: J. Pharm. Soc. Japan **74,** 9 (1954); Chem. Abstracts **49,** 1681 (1955).
(306a) NELSON, P. F.: J. Chem. Educ. **32,** 606 (1955).
(306b) NESMAYANOV, A. N., PEREVALOVA, E. G., AND GOLOVNYA, R. V.: Doklady Akad. Nauk S.S.S.R. **99,** 539 (1954); Chem. Abstracts **49,** 15918 (1955).
(307) NESMAYANOV, A. N., AND REUTOV, O. A.: Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk **1949,** 611; Chem. Abstracts **44,** 7791 (1950).
(308) NEWITT, D. M., AND SZEGO, P.: Chemistry & Industry **52,** 645 (1933).
(309) NORRIS, J. F., MACINTIRE, B. G., AND CORSE, W. M.: Am. Chem. J. **29,** 120 (1903).
(310) OGATA, Y., KOMETANI, R., AND ODA, R.: Bull. Inst. Phys. Chem. Research (Tokyo) **22,** 583 (1943); Chem. Abstracts **43,** 7797 (1949).
(311) ONO, K., OYAMADA, T., AND KATSURAGI, H.: J. Soc. Chem. Ind. Japan **41,** Suppl. binding 209 (1938); Chem. Abstracts **32,** 7429 (1938).
(312) OVERHOFF, J., AND TILMAN, G.: Rec. trav. chim. **48,** 993 (1929).
(312a) PAUSON, P. L.: Quart. Revs. **9,** 391 (1955).
(313) PAUSON, P. L., AND SMITH, B. C.: J. Org. Chem. **18,** 1403 (1953).
(314) PETTIT, M. R., AND TATLOW, J. C.: J. Chem. Soc. **1951,** 3459.
(315) PETTIT, M. R., AND TATLOW, J. C.: J. Chem. Soc. **1954,** 1941.
(316) POWELL, G.: J. Am. Chem. Soc. **51,** 2436 (1929).
(317) PRELOG, V., AND SCHNEIDER, R.: Helv. Chim. Acta **32,** 1632 (1949).
(318) PRESTON, R. W. G., AND TUCKER, S. H.: J. Chem. Soc. **1943,** 659.
(319) PUMMERER, R., AND CHERBULIEZ, E.: Ber. **52B,** 1414 (1919).
(320) RAFIKOV, S. R., AND KUDINOVA, V. S.: Doklady Akad. Nauk S.S.S.R. **87,** 987 (1952); Chem. Abstracts **47,** 10499 (1953).
(321) RAFIKOV, S. R., AND KUDINOVA, V. S.: Izvest. Akad. Nauk Kazakh. S.S.R. No. **123,** Ser. Khim. No. **7,** 54 (1953); Chem. Abstracts **49,** 2422 (1955).

(322) RALEY, J. R., RUST, F. F., AND VAUGHN, W. E.: J. Am. Chem. Soc. **70,** 88 (1948).
(323) RAPOPORT, H., LOOK, M., AND KELLY, G. J.: J. Am. Chem. Soc. **74,** 6293 (1952).
(324) RAPSON, W. S., AND SHUTTLEWORTH, R. G.: Nature **147,** 675 (1941).
(325) RAZUVAEV, G. A., AND FEDOTOVA, E. I.: Zhur. Obshcheĭ Khim. **21,** 1118 (1951); Chem. Abstracts **46,** 5006 (1952).
(326) RAZUVAEV, G. A., MORYGANOV, B. N., AND STEPUSHKINA, V. A.: Zhur. Obshcheĭ Khim. **23,** 1379 (1953); Chem. Abstracts **48,** 9962 (1954).
(327) RAZUVAEV, G. A., AND OL'DEKOP, Y. A.: Zhur. Obshcheĭ Khim. **21,** 1122 (1951); Chem. Abstracts **46,** 1479 (1952).
(328) RAZUVAEV, G. A., AND OL'DEKOP, Y. A.: Sbornik Statei Obshcheĭ Khim. **2,** 981 (1953); Chem. Abstracts **49,** 6822 (1955).
(329) RAZUVAEV, G. A., OL'DEKOP, Y. A., AND BAGAEV, I. F.: Doklady Akad. Nauk S.S.S.R. **74,** 73 (1950); Chem. Abstracts **45,** 3320 (1951).
(330) RAZUVAEV, G. A., AND PETUKHOV, G. G.: Zhur. Obshcheĭ Khim. **21,** 646 (1951); Chem. Abstracts **45,** 6495 (1951).
(331) REEDER, W. H.: U. S. patent 2,662,923 (1953); Chem. Abstracts **49,** 1793 (1955).
(332) RELYEA, D. I., AND DETAR, D. F.: J. Am. Chem. Soc. **76,** 1202 (1954).
(333) REMICK, A. E.: *Electronic Interpretations of Organic Chemistry*, 2nd edition, p. 491. John Wiley and Sons, Inc., New York (1943).
(334) REUTOV, O. A.: Vestnik Moskov. Univ. **8,** No. 3, Ser. Fiz.-Mat. i Estestven. Nauk No. **2,** 119 (1953); Chem. Abstracts **49,** 3867 (1955).
(335) RICE, F. O., AND FREAMO, M.: J. Am. Chem. Soc. **73,** 5529 (1951).
(336) RINKES, I. J.: Rec. trav. chim. **62,** 116 (1943).
(337) RITCHIE, E.: J. Proc. Roy. Soc. N. S. Wales **78,** 169 (1945); Chem. Abstracts **40,** 880 (1946).
(338) ROBERTSON, A., AND WATERS, W. A.: J. Chem. Soc. **1948,** 1578.
(339) ROBINSON, D., SMITH, J. N., AND WILLIAMS, R. T.: Biochem. J. **50,** 228 (1951).
(340) RODEWALD, Z., AND PLAZEK, E.: Ber. **70,** 1159 (1937).
(341) ROITT, I. M., AND WATERS, W. A.: J. Chem. Soc. **1952,** 2695.
(342) RONDESTVEDT, C. S., JR., AND BLANCHARD, H. S.: J. Am. Chem. Soc. **77,** 1769 (1955).
(343) RUSSELL, K. E.: J. Am. Chem. Soc. **77,** 3487 (1955).
(344) SANDIN, R. B., AND BROWN, R. K.: J. Am. Chem. Soc. **69,** 2253 (1947).
(345) SANDIN, R. B., AND MCCORMACK, W. B.: J. Am. Chem. Soc. **67,** 2051 (1945).
(346) SAUNDERS, K. H.: *The Aromatic Diazo Compounds and Their Technical Applications*, 2nd edition, p. 112. Edward Arnold and Co., London (1947).
(347) Reference 346, p. 254.
(348) Reference 346, p. 263.
(349) SCHMID, H., AND LEUTENEGGER, W. E.: Helv. Chim. Acta **30,** 1965 (1947).
(350) SCHMIDLIN, J.: Ber. **45,** 3171 (1912).
(351) SCHMIDLIN, J., AND GARCIA-BANUS, A.: Ber. **45,** 1344 (1912).
(352) SCHMIDT, F.: Ber. **55,** 1581 (1922).
(353) SCHMIDT, F.: Ber. **58,** 2409 (1925).
(354) SCHÖNBERG, A., SCHÜTZ, O., AND PETER, J.: Ber. **62B,** 440 (1929).
(355) SCHOFIELD, K., AND THEOBALD, R. S.: J. Chem. Soc. **1951,** 2992.
(356) SCHORIGIN, P.: Ber. **59B,** 2502 (1926).
(357) SEAMAN, H., TAYLOR, P. J., AND WATERS, W. A.: J. Chem. Soc. **1954,** 4690.
(358) SETHNA, S. M.: Chem. Revs. **49,** 91 (1951).
(359) SIMAMURA, O., INUKAI, T., AND KANAZASHI, M.: Bull. Chem. Soc. Japan **23,** 205 (1950); Chem. Abstracts **46,** 6623 (1952).
(360) SIMAMURA, O., INUKAI, T., AND KURATA, M.: Bull. Chem. Soc. Japan **25,** 76 (1952); Chem. Abstracts **47,** 9945 (1953).
(360a) SIMAMURA, O., AND MIGITA, T.: Bull. Chem. Soc. Japan **27,** 228–31 (1954); Chem. Abstracts **49,** 15720 (1955).
(361) SIMONS, J. H., AND HERMAN, D. F., Abstracts of Papers Presented at the 112th Meeting of the American Chemical Society, New York City, September, 1947, p. 13J.

(362) SIXMA, F. L., AND WIBAUT, J. P.: Rec. trav. chim. **69,** 577 (1950).
(363) SMITH, J. N.: Biochem. Soc. Symposia (Cambridge, Engl.) No. **5,** 15 (1950).
(364) SMITH, P. A. S., AND BOYER, J. H.: J. Am. Chem. Soc. **73,** 2626 (1951).
(365) SMITH, P. A. S., AND BROWN, B. D.: J. Am. Chem. Soc. **73,** 2435 (1951).
(366) SMITH, P. A. S., BROWN, B., PUTNEY, R. K., AND REINISCH, R. F.: J. Am. Chem. Soc. **75,** 6335 (1953).
(367) STEIN, G., AND WEISS, J.: Nature **161,** 650 (1948).
(368) STEIN, G., AND WEISS, J.: J. Chem. Soc. **1949,** 3245.
(369) STEIN, G., AND WEISS, J.: J. Chem. Soc. **1949,** 3254.
(370) STEIN, G., AND WEISS, J.: J. Chem. Soc. **1951,** 3265.
(371) STEPHENSON, O., AND WATERS, W. A.: J. Chem. Soc. **1939,** 1796.
(372) STIEGLITZ, J., AND BROWN, R. L.: J. Am. Chem. Soc. **44,** 1270 (1922).
(373) STORRIE, F. R., AND TUCKER, S. H.: J. Chem. Soc. **1931,** 2255.
(374) SUEHIRO, T.: J. Chem. Soc. Japan, Pure Chem. Sect. **72,** 301 (1951); Chem. Abstracts **46,** 2522 (1952).
(375) SUEHIRO, T.: J. Chem. Soc. Japan, Pure Chem. Sect. **72,** 1070 (1951); Chem. Abstracts **47,** 3268 (1953).
(376) SUGINO, K., AND INOUE, E.: J. Soc. Org. Synthetic Chem. (Japan) **7,** 198 (1949); Chem. Abstracts **47,** 6884 (1953).
(377) SUGINO, K., AND INOUE, E.: J. Chem. Soc. Japan, Pure Chem. Sect. **71,** 518 (1950); Chem. Abstracts **45,** 9499 (1951).
(378) SUGINO, K., AND INOUE, E.: Japanese patent 2468 (1951); Chem. Abstracts **47,** 426 (1953).
(379) SUGINO, K., AND INOUE, E.: Japanese patent 2670 (1951); Chem. Abstracts **47,** 426 (1953).
(380) SUGINO, K., AND INOUE, E.: Japanese patent 3264 (1951); Chem. Abstracts **47,** 1510 (1953).
(381) SUGINO, K., AND INOUE, E.: Bull. Chem. Soc. Japan **24,** 93 (1951); Chem. Abstracts **47,** 7918 (1953).
(382) SWORSKI, T. J.: J. Chem. Phys. **20,** 1817 (1952).
(383) TARBELL, D. S.: *Organic Reactions*, Vol. II, p. 1. John Wiley and Sons, Inc., New York (1944).
(384) ULLMAN, F.: Ann. **332,** 82 (1904).
(385) URI, H.: Chem. Revs. **50,** 375 (1952).
(386) URRY, W. H., AND AMIR, E. M.: Abstracts of Papers Presented at the 118th Meeting of the American Chemical Society, Chicago, Illinois, September, 1950, p. 16N.
(387) VAN LOON, M., AND WIBAUT, J. P.: Rec. trav. chim. **56,** 815 (1937).
(388) VDOVTSOVA, E. A., AND TSUKERVANIK, I. P.: Doklady Akad. Nauk S.S.S.R. **80,** 61 (1951); Chem. Abstracts **49,** 7506 (1955).
(389) VDOVTSOVA, E. A., AND TSUKERVANIK, I. P.: Sbornik Statei Obschei Khim. **2,** 1027 (1953); Chem. Abstracts **49,** 7506 (1955).
(390) VDOVTSOVA, E. A., AND TSUKERVANIK, I. P.: Zhur. Obshchei Khim. **24,** 558 (1954); Chem. Abstracts **49,** 6189 (1955).
(391) WALTERS, L. A., AND MCELVAIN, S. M.: J. Am. Chem. Soc. **55,** 4625 (1933).
(392) WATERS, W. A.: *Chemistry of Free Radicals*. The Clarendon Press, Oxford (1946).
(393) WEINMAYR, V.: J. Am. Chem. Soc. **77,** 3012 (1955).
(394) WESSELY, F., KOTLAN, J., AND METLESICS, W.: Monatsh. **85,** 69 (1954).
(395) WESSELY, F., AND SCHINZEL, E.: Monatsh. **84,** 425 (1953).
(396) WESSELY, F., AND SCHINZEL, E.: Monatsh. **84,** 969 (1953).
(397) WESSELY, F., AND SINWEL, F.: Monatsh. **81,** 1055 (1950).
(398) WHELAND, G. W.: *Advanced Organic Chemistry*, 2nd edition, p. 663. John Wiley and Sons, Inc., New York (1949).
(399) WHITMORE, F. C.: *Organic Compounds of Mercury*. The Chemical Catalog Co., Inc., New York (1921).
(400) WIBAUT, J. P.: Experentia **5,** 337 (1949).

(401) WIBAUT, J. P., AND BLOOM, G. P.: Rec. trav. chim. **69,** 586 (1950).
(402) WIBAUT, J. P., AND NICOLAI, J. R.: Rec. trav. chim. **58,** 709 (1939).
(403) WIBAUT, J. P., SIXMA, F. L., AND LIPS, H.: Rec. trav. chim. **69,** 1031 (1950).
(404) WIBAUT, J. P., VAN DE LANDE, L. M., AND WALLACH, G.: Rec. trav. chim. **52,** 794 (1933).
(405) WIBAUT, J. P., VAN DE LANDE, L. M., AND WALLACH, G.: Rec. trav. chim. **56,** 65 (1937).
(406) WIELAND, H.: Ann. **381,** 290 (1911).
(407) WIELAND, H.: Ber. **44,** 2550 (1911).
(408) WIELAND, H.: Ann. **514,** 145 (1934).
(409) WIELAND, H., HEYMAN, K., TSATSAS, T., JUCHUM, D., VARVOGLIS, G., LABRIOLA, G., DABBELSTEIN, G., AND BOYD-BARRETT, H. S.: Ann. **514,** 145 (1935).
(410) WIELAND, H., AND MEYER, A.: Ann. **551,** 249 (1942).
(411) WIELAND, H., AND MÜLLER, C.: Ann. **401,** 233 (1913).
(412) WIELAND, H., PLOETZ, T., AND INDEST, H.: Ann. **532,** 166 (1937).
(413) WIELAND, H., AND RAZUVAEV, G.: Ann. **480,** 165 (1930).
(414) WIELAND, H., AND ROTH, K.: Ber. **53,** 210 (1920).
(415) WILSON, R. H.: J. Applied Chem. **3,** 37 (1953).
(416) WITTIG, G., AND GEISSLER, G.: Ann. **580,** 44 (1953).
(417) ZONIS, S. A.: Sbornik Statei Obshchei Khim. **2,** 1091 (1953); Chem. Abstracts **49,** 5414 (1955).