[Contribution from the Department of Chemistry, University of Michigan]

Arylation of Unsaturated Systems by Free Radicals. V. Phenylation of *o*-Xylene, Phenyltrimethylsilane, and Benzotrifluoride. Interpretation of Orientation Phenomena in Arylation of Substituted Benzenes[1]

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1. The ratios of isomeric biphenyls formed by benzoyl peroxide phenylation at 80–100° were determined by infrared spectroscopy to be 63% 2,3-: 37% 3,4- from *o*-xylene; 31% *o*-: 45% *m*-: 24% *p*- from phenyltrimethylsilane; 20% *o*-: 40% *m*-: 40% *p*- from benzotrifluoride. The total rate factors, relative to benzene, were found to be 0.99 for benzotrifluoride, 1.06 for phenyltrimethylsilane, and 1.2 for anisole.

2. A qualitative theory has been proposed to explain the orientations observed in free-radical phenylation of substituted benzenes. It was suggested that primary *ortho-para* substitution was a result of resonance stabilization of the *ortho-* and *para* σ-complexes (Wheland); *ortho-para* substitution decreased as resonance became less important. The usual preponderance of *ortho* substitution was accounted for by a secondary factor, complexing of the incoming radical at the substituent or other site of highest electron density. The theory has been applied to the available data on free-radical phenylation, with generally good agreement.

The predominance of *ortho* substitution when a mono-substituted benzene is arylated by free radicals has been a source of puzzlement. In electrophilic substitution, the *ortho* positions are seldom more reactive than the *para* position. For example, when toluene is attacked by phenyl radicals from decomposing benzoyl peroxide, N-nitrosoacetanilide, or 1-phenyl-3,3-dimethyltriazene, 62%[3] [71%[4]] of 2-methylbiphenyl is produced. *ortho*-Substitution appears to be usual in most other phenylations (see Table I), although it may be reduced by steric hindrance.[3,5–7] A study or the phenylation of *o*-xylene, phenyltrimethylsilane, and benzotrifluoride was undertaken to provide some of the additional information necessary for the construction of a theory of orientation in free-radical aromatic substitution.

TABLE I

Isomer Ratios and Rates in Phenylation of Monosubstituted Benzenes C_6H_5R

R	Total Rate Factor[a]	% *o*	F_o[b]	% *m*	F_m[b]	% *p*	F_p[b]	*m*/*p*	*o*/*p*	Reference[c]
NO_2	4.0	58	7.0	10	1.2	32	7.7	0.3	2.0	24, 17a, 28a
CN	3.7[d]	60	6.7[d]	10	1.1[d]	30	6.7[d]	0.3	2.0	29a
COOMe	—	59	—	15	—	26	—	0.6	2.3	29a, b
SO_3Me	1.5[d]	53	2.4[d]	33	1.5[d]	14	1.3[d]	2.4	3.8	29a
Ph	4.0	48	2.9	23	1.4	28	3.4	0.8	1.7	25
F	1.35	54	2.2	31	1.2	15	1.2	2.1	3.6	26a
Cl	1.44	62	2.7	24	1.0	14	1.2	1.7	3.6	26a, 29a, b
Br	1.75	49	2.6	33	1.8	17	1.8	1.9	2.8	26a, 28b, 29b
I	1.80	52	2.8	32	1.7	17	1.8	1.9	3.1	26a, 29b
OMe	1.2[e]	67	2.4[e]	18	0.7[e]	15	1.1[e]	1.2	4.5	19b, *cf.* 30
Me	1.9	62	3.5	21	1.0	17	1.4	1.2	3.6	3, 4, 6, 27
Et	1.2	50	2.0	25	1.0	25	1.4	1.0	2.0	6, 27
iso-Pr	0.87	26	0.81	53	1.1	21	1 4	2.5	1.2	3, 6, 27
tert-Bu	0.87	18	0.63	62	1.3	22	1.4	2.8	0.8	3, 5
o-Xylene	—	63[f]	—	—	—	37[g]	—	—	1.7	[e]
$SiMe_3$	1.06	31	0.99	45	1.4	24	1.5	1.9	1.3	[e]
CF_3	0.99	20	0.59	40	1.2	40	2.4	1.0	0.5	[e]; 7
CCl_3	—	0	—	60	—	40	—	1.5	0.0	7

[a] Relative to benzene = 1. [b] Partial rate factor. [c] The first reference cited gives the isomer ratio quoted; the other references give slightly different values. [d] Calculated from the data in ref. 29a, using 1.04 as the rate for pyridine. [e] This paper. [f] 2,3-Dimethylbiphenyl. [g] 3,4-Dimethylbiphenyl.

RESULTS

Benzoyl peroxide was decomposed in a large excess of aromatic compound. In one case, N-nitro-

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(1) (a). Paper IV, Rondestvedt and Vogl, *J. Am. Chem. Soc.*, **77**, 3401 (1955); (b) Paper III, Vogl and Rondestvedt, *J. Am. Chem. Soc.*, **77**, 3067 (1955).

(2) Abstracted from the Ph.D. dissertation of H. S. Blanchard, University of Michigan, 1955. Allied Chemical and Dye Corp. Fellow, 1953–1954.

(3) Rondestvedt and Blanchard, *J. Am. Chem. Soc.*, **77**, 1769 (1955). A literature review is given.

(4) Hey, Pengilly, and Williams, *J. Chem. Soc.*, 6 (1955).

(5) Cadogan, Hey, and Williams, *J. Chem. Soc.*, 3352 (1954).

(6) Dannley and Zaremsky, *J. Am. Chem. Soc.*, **77**, 1588 (1955).

(7) Dannley and Sternfeld, *J. Am. Chem. Soc.*, **76**, 4543 (1954).

soacetanilide was the source of phenyl radicals. The biaryl mixture was freed from byproducts, and the isomer ratio was determined by infrared spectroscopy[3] with reference to authentic samples of the pure isomeric biaryls.

o-Xylene. Phenylation of *o*-xylene by benzoyl peroxide (mole ratio 40.1) gave a 34% yield of a mixture containing 2,3-dimethylbiphenyl and 3,4-dimethylbiphenyl in a 63:37 ratio. The reaction also gave 2,2′-dimethylbibenzyl in 36% yield based on benzoyl peroxide. The bibenzyl is derived from side-chain attack by the radical, and other examples have been observed.[3] There was no evidence for the presence of diphenylmethane derivatives[4] although small amounts may have been present.

The pure 2,3-dimethylbiphenyl required as an infrared standard was prepared by addition of 2,3-dimethylphenylmagnesium bromide (or iodide) to cyclohexanone. The carbinol was dehydrated, then dehydrogenated over palladium-charcoal. Sulfur dehydrogenation gave a different unidentified product. The nitrosoacetanilide method was not applicable because of indazole formation.[3] 3,4-Dimethylbiphenyl was prepared by the nitrosoacetanilide method in 29% yield from 3,4-dimethylacetanilide.

Phenyltrimethylsilane. Benzoyl peroxide was decomposed in phenyltrimethylsilane (mole ratio 21:1) to give 31% of a mixture of trimethylsilylbiphenyls. The isomer ratio was determined to be 31% *ortho*: 45% *meta*: 24% *para*. The isomeric trimethylsilylbiphenyls were prepared by coupling the appropriate bromobiphenyl with trimethylchlorosilane in the presence of sodium.[8]

Its rate of phenylation relative to pyridine was 1.02, hence the rate relative to benzene was 1.06.

Benzotrifluoride. Benzotrifluoride is reported not to react with 1-phenyl-3,3-dimethyltriazene and acid.[9] However, N-nitrosoacetanilide gave a 30% yield of mixed trifluoromethylbiphenyls; the yield with benzoyl peroxide was 60%. The mixtures from either source had the identical isomer ratio 20% *ortho*: 40% *meta*: 40% *para*.[10] The pure *o*- and *m*-trifluoromethylbiphenyls were prepared from the nitroso derivatives of *o*- and *m*-trifluoromethylacetanilide. The *para* isomer was isolated from the mixture by freezing, and its structure was proved by hydrolysis to *p*-phenylbenzoic acid.[11]

The total rate factor with respect to benzene was shown to be 0.99 by competitive experiments with pyridine. Similar experiments with anisole gave a relative rate of 1.2.

DISCUSSION

A mechanism for homolytic aromatic substitution must explain the following facts. (1). In most cases, the phenyl radical substitutes *ortho* to the group already on the ring. The observed isomer ratio is independent of the source of the phenyl radical[3] and of the reaction temperature[2,12] (in contrast to many electrophilic substitutions). (2). *ortho*-Attack is subject to steric hindrance,[3,5,7] which is less prominent than in electrophilic substitution. (3). Where data are available, it appears that almost any substituent in a monosubstituted benzene is ring-activating, regardless of its electrical nature, except where steric hindrance is prominent.[13] (4). An aryl radical *substitutes*, but methyl radicals appear to *add* to the ring.[14] (5). Side reactions occur, notably attack upon susceptible ring substituents (hydrogen or halogen abstraction), and polyarylation. (6). Substituents in the attacking radical may play an important part in controlling the orientation and rate of arylation.

The substitution process involves phenyl radicals. The strongest support for this hypothesis is the similarity among phenylations by different reagents. Moreover, hydrogen or halogen transfer is a reaction characteristic of radicals. The evidence has been reviewed[15] and need not be discussed further. The three most important sources appear to generate phenyl radicals as follows:

$$(\mathrm{PhCOO})_2 \rightarrow 2\ \mathrm{PhCOO}\cdot \rightarrow \mathrm{Ph}\cdot + \mathrm{CO_2} \quad (1)^{16}$$

$$\begin{aligned}&\mathrm{PhN(NO)Ac} \rightleftharpoons \mathrm{PhN{=}NOAc} \rightarrow \\ &\qquad\qquad \mathrm{Ph}\cdot + \mathrm{N_2} + \mathrm{AcO}\cdot(?) \quad (2)^{17}\end{aligned}$$

$$\begin{aligned}&\mathrm{PhN{=}N{-}NMe_2} + \mathrm{HA} \rightarrow \\ &\qquad \mathrm{PhN{=}NA} \rightarrow \mathrm{Ph}\cdot + \mathrm{N_2} + \mathrm{A}\cdot(?) \quad (3)^{1b,18} \\ &\qquad\qquad \mathrm{Me_2\overset{+}{N}H\cdot HA}\end{aligned}$$

$$\mathrm{A = AcO,\ Cl}$$

The formation of benzoate radicals in the primary decomposition of benzoyl peroxide is indicated by the results of Hammond.[16a,b] Additional evidence for Eqn. 1 is provided by the observation that the very reactive [toward phenylation by N-nitro-

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[8] Clark, Gordon, Young, and Hunter, *J. Am. Chem. Soc.*, **73**, 3798 (1951).

[9] Bradsher and Bond, *J. Am. Chem. Soc.*, **71**, 2659 (1949).

[10] Dannley and Sternfeld[7] report the ratio 18:40:42.

[11] *Cf.* Pettit and Tatlow, *J. Chem. Soc.*, 3459 (1951) and *J. Chem. Soc.*, 1071 (1954).

[12] Hey, Stirling, and Williams, *J. Chem. Soc.*, 2747 (1954).

[13] The available data on activation are incomplete, but no exceptions to this statement have been discovered.

[14] Levy and Szwarc, *J. Am. Chem. Soc.*, **77**, 1949 (1955).

[15] Hey and Waters, *Chem. Revs.*, **21**, 186 (1937). Hey in *Ann. Reports on Progress of Chem.*, **37**, 268 (1940); **41**, 181 (1944).

[16] (a) Hammond, *J. Am. Chem. Soc.*, **72**, 3737 (1950); (b) Hammond and Soffer, *J. Am. Chem. Soc.*, **72**, 4711 (1950); (c) Swain, Stockmayer, and Clarke, *J. Am. Chem. Soc.*, **72**, 5426 (1950); (d) Nozaki and Bartlett, *J. Am. Chem. Soc.*, **68**, 1686 (1945); **69**, 2299 (1946); (e) Dannley and Gippin, *J. Am. Chem. Soc.*, **74**, 332 (1952); (f) Cass, *J. Am. Chem. Soc.*, **68**, 1976 (1946).

[17] (a) DeTar, *J. Am. Chem. Soc.*, **73**, 1442, 1446 (1951); (b) Huisgen, *et al.*, *Ann.*, **562**, 137 (1949); (c) Huisgen, *et al.*, *Ann.*, **573**, 163, 181 (1951); (d) Hey, Stuart-Webb, and Williams, *J. Chem. Soc.*, 4657 (1952).

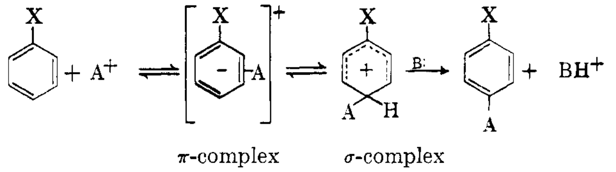
[18] Elks and Hey, *J. Chem. Soc.*, 441 (1943).

soacetanilide[19a]] naphthalene is converted to naphthyl benzoates, rather than phenylnaphthalenes, by benzoyl peroxide.[16e] Phenol is also "benzoated," rather than phenylated.[19b] Coumarin is both phenylated and "benzoated" in the heterocyclic ring by benzoyl peroxide.[1b] In fact, most phenylations by benzoyl peroxide give also detectable quantities of esters. Although the spontaneous thermal decomposition of benzoyl peroxide is accurately first-order[16c] an induced reaction occurs during later stages. The induced decomposition is of least importance in aromatic solvents[16d,f] and at higher temperatures.[16d]

In decompositions of nitrosoacetanilides, Huisgen[17b] and Hey[17d] have shown independently that the rate-controlling step is the rearrangement to the diazo acetate. It is not known whether the subsequent steps may involve an induced decomposition. However, if an acetate radical is produced according to Eqns. 2 and 3, it appears to be very different from the acetate radicals formed from acetyl peroxide. Carbon dioxide cannot be detected during an arylation of an aromatic compound by N-nitrosoacetanilide,[17] although it is plentiful in decompositions of acetyl peroxide in the same solvents.[17a] An alternative hypothesis has been discussed by Allan and Muzhik[20a] and by Huisgen and Horeld.[17b]

Mechanism of homolytic aromatic substitution. In electrophilic substitution, the following path is followed:

(4).



This is pictured on an energy scale in Fig. 1:

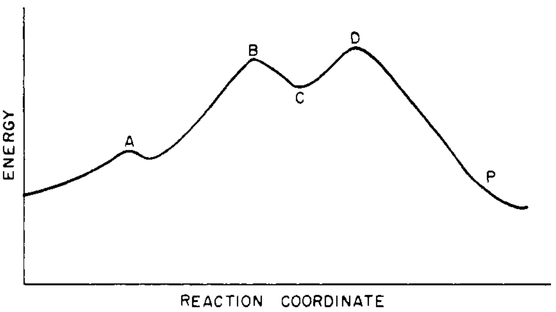


FIG. 1—ENERGY RELATIONSHIPS DURING AROMATIC SUBSTITUTION.

where A = π-complex, B and D imply bond formation and bond breaking, respectively, C = σ-complex, and P = products. No agreement has been reached as to which step is rate-controlling. Dewar[20b] considers that the rate-determining step is formation or decomposition of the π-complex. Brown[21] cites evidence in which the observed rates of electrophilic substitution appear to parallel the stabilities of the σ-complexes. Part of the disagreement may be traced to the differences in the formulation of the π-complex by the two authors.

However, the rate of formation of the σ-complex is proportional to the concentration of the π-complex. Furthermore, the over-all reaction rate is influenced by the relative heights of the barriers at B and D. For example, in aromatic bromination or nitration, there is no detectable hydrogen isotope effect, while in sulfonation, there is a pronounced isotope effect. The problem of the importance of the various steps has been discussed.[22]

Eqn. 4 appears to represent free-radical substitution also, if the positive charge be replaced by an odd electron. The ensuing discussion is based upon this model. The relative importance of the possible rate-controlling steps cannot be determined at present because radical substitution is much less understood than electrophilic substitution. It will be assumed that the stabilities of the various σ-complexes will control the isomer ratios, though in some cases, the case of bond-breaking (hydrogen abstraction) may play some part. The "π-complex" cannot now be formulated precisely because of the dearth of data on complexing of radicals with aromatic rings.[23] It will be termed "preliminary complex" in this paper to avoid implications about its precise structure.

In discussions of orientation during electrophilic aromatic substitution, it is customary to classify groups as *o*-, *p*-directing or *m*-directing depending on whether the amount of *meta* substitution is less or greater than 40%, and as activating or deactivating depending on the total rate of substitution relative to benzene. It is commonly observed with *ortho-para* directing groups that the *o*/*p* ratio is much less than the statistical value of 2, a result usually ascribed to steric hindrance.

The available quantitative data on homolytic aromatic substitution are collected in Table I. It is at once apparent that few groups are *meta*-directing, namely isopropyl, *tert*-butyl, trimethyl-

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[19] (a) Huisgen and Sorge, *Ann.*, **566**, 162 (1950); (b) Suehiro, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **72**, 301 (1951); *Chem. Abstr.*, **46**, 2522 (1952).

[20] (a) Allan and Muzhik, *Coll. Czech. Chem. Comm.*, **19**, 720 (1954); (b) Dewar, *J. Chem. Soc.*, 406, 777 (1946); Dewar, *The Electronic Theory of Organic Chemistry*, Oxford University Press, London, 1949, pp. 168–172.

[21] Brown and Brady, *J. Am. Chem. Soc.*, **74**, 3570 (1952).

[22] Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

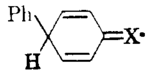
[23] (a) Jaquiss and Szwarc, *Nature*, **170**, 312 (1952); (b) Boozer and Hammond, *J. Am. Chem. Soc.*, **76**, 3861 (1954).

silyl, and trihalomethyl. The remainder are *ortho-para* directing and surprisingly, for most of them, the o/p ratio exceeds 2.

Resonance. An explanation for *ortho-para* direction was proposed by Wheland.[31] On the basis of an approximate model closely resembling the σ-complex, he calculated that the stabilization of the *ortho* and *para* σ-complexes by resonance of the odd electron with the substituent was sufficient to insure *ortho-para* orientation. Table I shows that the unsaturated groups nitro, cyano, carbomethoxy, and phenyl, in which resonance is strong, give a very high proportion of *ortho* and *para* isomers. Hey, Dannley, and DeTar have commented on this parallel. These groups are also the strongest activators, giving total rate factors of about 4.[13] It appears that resonance stabilization in the σ-complex derived from biphenyl is less efficient than with nitrobenzene as shown by the partial rate factors for *ortho* and *para* substitution. This observation is in line with the experiments of Berliner[32] which showed that electrical effects were transmitted less efficiently through a biphenyl nucleus than a benzene nucleus. Furthermore, the small amount of interference among the *ortho*-hydrogens (apparent in models) would impede the coplanarity required for most effective resonance.

A corollary of Wheland's theory is that *ortho-para* orientation should diminish as the ability of the substituent to resonate with the odd electron decreases. This is clearly demonstrated by the alkylbenzenes. The methyl group is a strong *ortho-para* director because of resonance (hyperconjugation).[3] The number of C—H hyperconjugation forms decreases as the α-hydrogens in toluene are replaced by methyl groups, and the proportion of *meta*-substitution rises sharply. The *tert*-butyl group is thus no longer an *ortho-para* director, though part of the effect results from steric hindrance (see below).

The halogens are only weakly *ortho-para* directing. In the σ-complexes derived from the halobenzenes, resonance involving a structure like



requires electronic motion away from the electron-attracting halogen atom. That this is difficult is shown by the ring deactivation exhibited by halogens in electrophilic substitution. The total rate factors increase gradually from F to I, paralleling the decreasing electron affinities of the halogens. The increasing activation is chiefly at the *meta* and *para* positions, however, (as shown by the partial rate factors), indicating perhaps a small amount of steric hindrance by the larger halogens.

The methoxyl group, though electronically similar to the halogens, is a much stronger *ortho-para* director. This effect doubtless results from the smaller electron affinity of oxygen. Surprisingly, the methoxyl group proves to be a much weaker activator than any of the halogens.[33]

Groups in which resonance is unimportant are not *ortho-para* directors. The sulfomethoxy group directs only feebly; the m/p ratio is 2.4. Resonance with the sulfonyl group requires the use of *d*-orbitals. Although *d*-orbital resonance is possible,[34a] it is less important than the *p*-orbital resonance with the carbonyl, nitro, and cyano groups. Thus vinylsulfonyl compounds are reluctant to undergo free-radical vinyl polymerization;[34b] the radical RCH_2-$CHSO_2$- has diminished resonance opportunity and lower stability, hence is harder to form than the carbonyl analog.[35] Furthermore, the arylation of derivatives of 2-phenylethene-1-sulfonic acid by diazonium salts [the Meerwein reaction[36]] could not be accomplished.[37] The total rate factor for methyl benzenesulfonate is considerably lower than

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(24) Augood, Hey, and Williams, *J. Chem. Soc.*, 2094 (1952). *Cf.* Hey, Nechvatal, and Robinson, *J. Chem. Soc.*, 2892 (1951).

(25) Cadogan, Hey, and Williams, *J. Chem. Soc.*, 794 (1954).

(26) (a) Augood, Cadogan, Hey, and Williams, *J. Chem. Soc.*, 3412 (1953); (b) Augood, Hey, and Williams, *J. Chem. Soc.*, 44 (1953); (c) Hey and Williams, *Disc. Faraday Soc.*, **14**, 216 (1953).

(27) Hey, Pengilly, and Williams, *J. Chem. Soc.*, in press (1956).

(28) (a) Simamura, Inukai, and Kanazashi, *Bull. Chem. Soc. Japan*, **23**, 205 (1950); (b) Simamura, Inukai, and Kurata, *Bull. Chem. Soc. Japan*, **25**, 76 (1952); (c) Simamura and Migita, *Bull. Chem. Soc. Japan*, **27**, 228 (1954).

(29) (a) Dannley and Gregg, *J. Am. Chem. Soc.*, **76**, 2998 (1954); (b) Dannley, Gregg, Phelps, and Coleman, *J. Am. Chem. Soc.*, **76**, 445 (1954).

(30) Dunstan and Hughes, *J. Proc. Roy. Soc. N.S.W.*, **80**, 77 (1947).

(31) Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1942).

(32) Berliner and Liu, *J. Am. Chem. Soc.*, **75**, 2417 (1953).

(33) The total rate factor for anisole may be spurious, however. The benzoate radical reacts as such with anisole to a considerable extent, since 147% of the theoretical one mole of benzoic acid was isolated. Therefore, the relative reactivity of only 1.2 (based on phenylanisoles isolated) may actually be much greater if the side reactions are taken into account. The same objection applies in principle to all competitive rate determinations. Although the competitive method is the best available technique for comparing reactivities, great reliance must not be placed on the numerical values of the total and partial rate factors, except when comparing compounds where the side reactions are unimportant.

(34) (a) Doering, *et al.*, *J. Am. Chem. Soc.*, **77**, 509, 514, 521 (1955); (b) For example, Overberger, Baldwin, and Gregor, *J. Am. Chem. Soc.*, **72**, 4864 (1950); Marvel, *et al.*, *J. Polymer Sci.*, **10**, 39 (1953).

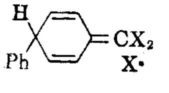
(35) Since the reactivity in polymerization depends both upon "reactivity" of the double bond and the stability of the propagating radical, it cannot be stated with certainty which factor renders the vinylsulfonyl compounds less reactive.

(36) Meerwein, Buchner, and Van Emster, *J. prakt. Chem.*, **152**, 237 (1939); Koelsch, *J. Am. Chem. Soc.*, **65**, 57 (1943); **66**, 412 (1944).

(37) Unpublished experiments in this laboratory with C. D. Ver Nooy and O. Vogl.

that for nitrobenzene or benzonitrile, in line with the relative stabilities of the σ-complexes.

Resonance in phenyltrimethylsilane also requires the use of *d*-orbitals. Although such resonance is possible,[38] it is not strong. In the benzotrihalides, resonance with the odd electron is difficult, requiring structures like



in which the electronic motion is opposed by the electron affinities of the halogen atoms.

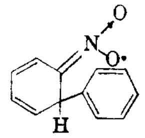
It should be noted that the *ortho-para* directing groups do not cause *meta*-deactivation, insofar as the limited data permit generalization. Most of the partial rate factors for the *meta* positions are slightly greater than 1; anisole appears to be the only exception.[33]

ortho-Activation. The inductive effect. The *primary* factor in orientation control is selective resonance stabilization of the *ortho* and *para* σ-complexes. However, this factor does not explain the high *o/p* ratios usually observed in homolytic substitution, in contrast to the low ratios in the common electrophilic substitutions. This phenomenon suggests that in the non-polar homolytic substitutions there is a subtle *secondary* factor which is masked in electrophilic substitution by the strong electrostatic effects.

We propose that during formation of the preliminary complex, there is a tendency for the incoming radical to become associated (or complexed) with the site of highest electron density, *i.e.*, the phenyl radical is somewhat electron-seeking. In the past, this suggestion has been applied to account for *primary ortho-para* orientation. Although this hypothesis is consistent with the observed orienting of phenyl radicals by groups like alkyl and alkoxyl (*o,p*-directing toward cations), it fails to explain why nitro and cyano (*meta*-directing toward cations) should be strong *o,p*-directors toward phenyl radicals. However, Dannley and Sternfeld[7] found that *meta* substitution in benzotrichloride (highest density at *meta* positions) increased as the attacking radical became more electron-seeking.

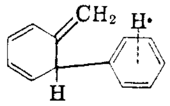
This hypothesis is now revived in altered form to account for selective *ortho*-activation. Although resonance stabilization of the isomeric *ortho* and *para* σ-complexes is identical (steric effects disregarded here), a difference in the energy contents of the isomeric "preliminary complexes" or in the energy barriers to their formation will result in a higher concentration of the more favored preliminary complex. Therefore one of the σ-complexes will be formed more rapidly, and one isomer will predominate among the products. The various modes of selective complex formation will be examined to find correlations with the experimental data.

With rings substituted by unsaturated, strongly electron-withdrawing groups (nitro, cyano, carbomethoxy, phenyl, sulfomethoxy), the greatest electron density is at the substituent itself. Association of the incoming radical with the substituent sets up a preliminary complex which can most readily rearrange to the *ortho* σ-complex. This association may involve only a temporary loose coordination of the radical with the mobile unsaturation electrons, or the association may continue into the σ-complex. For example, structures of the type



are possible, as indicated by Fisher-Hirschfelder models, if the substituent is a two-atom group. They do not appear likely when the group is a single atom, like halogen. With halogen and methoxyl, the coordination is doubtless at the unshared electrons. Such coordination has been suggested in discussions of electrophilic substitution to account for the large amount of *ortho* substitution given by reagents like benzoyl nitrate.

The methyl group is one of the stronger *ortho* activators, as shown by the data for *o*-xylene and toluene.[39] However, it is difficult to visualize how a phenyl radical could coordinate with a methyl group. Perhaps structures like



are involved, with the H atom serving as the bridge. On the other hand, we may consider that the inductive effect of the methyl group acts most strongly at the *ortho* position, making this position more electron-rich than the *para*, and more susceptible to attack by the electron-seeking radical. At first glance, this suggestion appears to be refuted by the data for the alkylbenzenes, since the inductive effect increases from methyl to *tert*-butyl but the percentage of *ortho* substitution falls. Actually, the data support the interpretation in terms of the inductive effect. The decreasing *ortho* substitution is doubtless a result of steric hindrance. If the radicals diverted from the *ortho* position by steric repulsion seek the site of next higher electron density (the *meta* position), *meta* substitution would become increasingly activated along the series from toluene to *tert*-butylbenzene. The partial rate factors for the

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(38) Roberts, McElhill, and Armstrong, *J. Am. Chem. Soc.*, 71, 2923 (1949).

(39) In *o*-xylene, all of the positions are *meta* to a methyl group. Since $F_m^{PhCH_3} = 1.0$ (no *meta* activation), it is justifiable to consider the 3-position as "*ortho*" and the 4-position as "*para*." Thus *o*-xylene shows an "*o/p*" ratio of 1.7 on phenylation, signifying strong *ortho*-activation.

alkylbenzenes show a monotonic increase of F_m from toluene to *tert*-butylbenzene, while F_p is precisely constant for the series.

The secondary inductive effect may explain in part the data for the benzotrihalides, where resonance is deemed unimportant. The inductive effect of the trihalomethyl group causes the electron densities to decrease in the order $p > m > o$, and it will be seen from Table I that the trihalomethyl groups give rise to the highest percentage of *para* substitution of any of the groups in the Table. Substantial *ortho* deactivation is evident in benzotrifluoride and benzotrichloride; steric hindrance cannot be responsible in the former case, since trifluoromethyl is the same size as methyl.

Steric hindrance. The reality of steric hindrance to radical substitution has been discussed above. However, it is less than hindrance to electrophilic substitution. For example, mixed-acid nitration of toluene, ethylbenzene, cumene, and *tert*-butylbenzene gives o/p ratios of 1.57, 0.93, 0.48, and 0.22, respectively.[40] Free-radical phenylation of the same alkylbenzenes gives o/p ratios of 3.64, 2.00, 1.24, and 0.82.[3]

It is significant that a substituent on the ring undergoing attack does not greatly impede arylation *ortho* to itself. A bulky substituent in the free radical *ortho* to the odd electron exerts much greater hindrance. For example, the *o-tert*-butylphenyl radical substitutes benzene only with great difficulty and in very low yield.[3,5]

The covalent radius of silicon (1.17 Å) is much greater than that of carbon (0.97 Å), with the result that the methyl groups are held further from the ring and exert less steric influence upon the *ortho* positions; *ortho* phenylation is observed to increase from 18% to 31% when the *tert*-butyl group is replaced by trimethylsilyl. Phenylation of trimethylsilylbenzene resembles nitration in giving approximately the statistical isomer ratio. If it were assumed that 9% of the phenyl radicals are diverted from the *ortho* position by steric hindrance, the corrected statistical distribution would be 31% *ortho*: 46% *meta*: 23% *para;* these values agree with the experimental phenylation data.[41]

It would be desirable to have data on the entropies and enthalpies of activation for the phenylation of alkylbenzenes. Unfortunately, such data are very difficult to obtain, since the measurable step in phenylation is the decomposition of the radical generator, not the attack on the ring.

Abstraction of hydrogen. The reaction is completed by loss of a hydrogen atom from the σ-complex. In some cases it may be lost as a free atom, since Wieland and others have observed in the phenylation of nitrobenzene the production of small amounts of aniline and azoxybenzene which they attribute to reduction of nitrobenzene by the free hydrogen atom.[42] Furthermore, quinhydrone is isolated from phenylations carried out in the presence of benzoquinone.[17b] These experiments do not, however, *prove* that hydrogen *atoms* are formed, since other ingredients of the reaction mixture could function as reducing agents.

It should be energetically easier to remove the hydrogen by reaction with another radical. If the decomposition of the radical generator and the subsequent arylation process took place within a solvent cage,[43] the second radical (acetate, benzoate, chlorine) would be available in a position for easy hydrogen abstraction from the σ-complex. This picture permits rationalization of the failure of the acetate radical from nitrosoacetanilide to decarboxylate during arylation of aromatic compounds.

The preceding discussion has been based on the assumption that orientation is governed by the ease of formation and the stabilities of the isomeric σ-complexes. It is probable that there exist examples of homolytic substitution where hydrogen abstraction (bond-breaking) is rate-controlling.[44] As noted earlier, different rate-controlling processes have been observed with electrophilic substitutions.

If this is so, a partial explanation for the anomalous orientation of benzotrifluoride is at hand. As noted by Kooyman, *et al.*,[45] nuclear substituents strongly affect the rate of abstraction by radicals of hydrogen from alkylbenzene side-chains. Electron-releasing groups facilitate, electron-withdrawing groups retard this hydrogen transfer. In the phenylation σ-complex, removal of an *ortho* hydrogen might likewise be impeded by an electron-withdrawing group like trifluoromethyl more than removal of a more distant hydrogen. This would increase the probability that the *ortho* σ-complex would decompose to a product other than a biaryl. This effect is probably unimportant except in those cases where resonance is minimal.

If the second radical (benzoate, acetate) escaped from the solvent cage or reacted with the solvent before reacting with the σ-complex, the latter would then donate the hydrogen to a solvent molecule. The new radical would then decompose to other products, explaining in part the complex tarry materials usually formed as by products in free radical arylations.

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[40] Jones and Russell, *J. Chem. Soc.*, 921 (1947); Brown and Bonner, *J. Am. Chem. Soc.*, **76**, 605 (1954); Nelson and Brown, *J. Am. Chem. Soc.*, **73**, 5605 (1951).

[41] Benkeser and Brumfield, *J. Am. Chem. Soc.*, **73**, 4770 (1951), observed the ratio 30:40:30 by semi-quantitative analysis of the mixture obtained by nitrating phenyltrimethylsilane with copper nitrate in acetic anhydride. *Cf.* Spier, *J. Am. Chem. Soc.*, **75**, 2930 (1953).

[42] Wieland, *et al.*, *Ann.*, **514**, 145 (1934); Cohen, *J. Polymer Sci.*, **2**, 511 (1947).

[43] Hammond, Rudesill, and Modic, *J. Am. Chem. Soc.*, **73**, 3929 (1951).

[44] Deuterium tracer experiments are now in progress with P. A. McVeigh of this laboratory.

[45] Kooyman, Van Helden, and Bickel, *Proc. Koninkl, Ned. Akad. Wetenschap.*, **B56**, 75 (1953); Van Helden and Kooyman, *Rec. trav. chim.*, **73**, 269 (1954).

Substituents in the attacking radicals. The effect of a substituent in the attacking radical is not clear, because the available data are limited and discordant. Hey [24,46] studied the arylation of nitrobenzene by *p*-tolyl, phenyl, *p*-bromophenyl, and *p*-nitrophenyl radicals. He observed 9, 10, 13, and 15% *meta*-substitution, respectively, and the *ortho* and *para* percentages were likewise substantially constant (the variations are practically within experimental error). On the other hand, Hey very recently[47] found that *p*-chlorophenyl radicals arylated chlorobenzene and nitrobenzene less rapidly than did phenyl radicals. Dannley[7] observed 60, 83, and 100% *meta* substitution of benzotrichloride by phenyl, *p*-chlorophenyl, and *p*-nitrophenyl radicals, respectively. Simamura[28c] noted that a *p*-anisyl radical did not give any *meta* substitution in nitrobenzene, though possibly a small amount of the *meta* isomer escaped detection; the *o/p* ratio was unaffected by the methoxyl group. These limited data suggest the tentative hypothesis that the arylation of a benzene substituted by a strongly resonating group will show little variation in isomer ratio as the substituent in the radical is changed. The reactivities may be altered somewhat, however. Only when the substituted benzene is almost incapable of resonance will the isomer ratio be strongly affected. Obviously, further data are needed to test this proposal.

Alkylation by radicals. Alkyl radicals will attack aromatic compounds. An aromatic ring can be incorporated into growing polymer molecules.[48] However, bromobenzene acts as a chain-transfer agent in styrene polymerization without entering the polymer.[49] Szwarc has obtained evidence for the addition of methyl radicals to benzene.[14,50] Methylation of trinitrotoluene by acetyl peroxide or lead tetraacetate and alkylation of quinones by diacyl peroxides have been reported by Fieser and coworkers.[51]

Alkyl radicals appear to *add*, rather than substitute like aryl radicals. The apparent *substitution* in trinitrotoluene and quinones is not necessarily an exception, since the addition products would readily be oxidized during the reaction. The difference between alkyl and aryl radicals probably arises from the lesser ability of the alkyl radical to interact with the electrons of the aromatic ring. Possible forms of interaction have been suggested by Mayo[52] and Allan and Muzhik.[20a] A definitive interpretation is not now available.

EXPERIMENTAL[53]

Materials. Phenyltrimethylsilane was prepared by coupling bromobenzene and trimethylchlorosilane with molten sodium under toluene (66%) or by condensation of phenylmagnesium bromide with trimethylchlorosilane (60% yield); b.p. 167–167.5°, n^{25}_D 1.4881, reported[54] b.p. 170–173°, n^{25}_D 1.4880. Benzotrifluoride was obtained from the Hooker Electrochemical Co. and used directly, since it boiled constantly at 101.6°, n^{25}_D 1.4147; recovered material was washed with conc'd sulfuric acid and water, dried, and distilled before re-use. *o*-Xylene (Eastman Kodak Co.) was dried with sodium and fractionated through an efficient column. The main fraction, b.p. 141.5–141.8° (740 mm.), was shown by the method of Young[55] to be free from isomers. Benzoyl peroxide and N-nitrosoacetanilide were obtained as previously described.[3]

Phenylation of phenyltrimethylsilane. The general procedure for phenylation has been described.[3] The excess phenyltrimethylsilane was distilled from the reaction mixture of 0.042 mole of benzoyl peroxide and 0.88 mole of phenyltrimethylsilane. Benzoic acid was isolated in 48% (42%) yield from two runs. The residue was distilled to give 3.0 g. (2.9 g.) of crude biaryl, b.p. 87–100° (0.1 mm.) or 80–135° (1.0 mm.). The product in petroleum ether was passed through an alumina column; after the trimethylsilylbiphenyls had passed through, continued elution with petroleum ether gave a small amount of a white waxy solid which fluoresced under ultraviolet light. It softened and liquefied gradually above 100°. Since it distils in the same range as the biaryl, it is believed to be 1,2-*bis*(phenyldimethylsilyl)ethane. It could not readily be purified, and it was not investigated further.

The relative rate of phenylation was determined by heating a mixture of 437 g. (2.92 moles) of phenyltrimethylsilane, 230 g. (2.92 moles) of pyridine, and 36.3 g. (0.15 mole) of benzoyl peroxide at 83–85° for 16 hrs. The bulk of the solvent was removed by vacuum distillation. The residue was dissolved in benzene and washed with sodium bicarbonate solution. The extracts were acidified and extracted with chloroform. Evaporation of the chloroform gave 13.8 g. (75%) of benzoic acid. The benzene solution was washed with 500 ml. of ice-cold 1:1 hydrochloric acid in four portions. The acid extract was basified and extracted with benzene; the organic layer was dried and distilled, giving 4.5 g. (0.0290 mole, 19%) of mixed phenylpyridines, b.p. 129–131° (11 mm.) and 0.3 g. of tarry residue. The benzene solution containing the neutral materials was distilled, giving 10.7 g. of crude trimethylsilylbiphenyls, b.p. 135–180° (10 mm.) and 8 g. of residue, part of which could be distilled. The crude material exhibited strong infrared bands characteristic of aryl benzoates. It was dissolved in petroleum ether and passed through a 2.5 × 30 cm. column of alumina. The product in the first 400 ml. of eluate was distilled, giving 6.7 g. (0.0296 mole, 20%) of mixed trimethylsilylbiphenyls, b.p. 135–160° (10 mm.). Continued elution with an additional 600 ml. of petroleum ether and 250 ml. of benzene gave only a little material, part of which resembled the white waxy solid. The total rate factor 0.0296/0.0290 = 1.02 with respect to pyridine was multiplied by 1.04 to give the total rate factor with respect to benzene.[55a]

Phenylation of o-xylene. The reaction of 0.062 mole of benzoyl peroxide with 2.48 moles of *o*-xylene gave 73% (79%) yield of benzoic acid in two runs. The crude distillates [4.17 g., b.p. 170–185° (40 mm.), and 4.50 g., b.p.

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(46) Hey, private communication.

(47) Cadogan, Hey, and Williams, *J. Chem. Soc.*, 1425 (1955).

(48) Stockmayer and Peebles, *J. Am. Chem. Soc.*, **75**, 2278 (1953).

(49) Mayo, *J. Am. Chem. Soc.*, **75**, 6133 (1953).

(50) Levy, Steinberg, and Szwarc, *J. Am. Chem. Soc.*, **76**, 3439 (1954).

(51) For example, Fieser, *et al.*, *J. Am. Chem. Soc.*, **64**, 2053, 2060 (1942).

(52) Mayo, *Disc. Faraday Soc.*, **2**, 372 (1947).

(53) Melting points are uncorrected. Microanalyses are by Anna Griffin in this laboratory. The infrared spectra taken during this work are reproduced in the thesis of H. S. B., available from the University of Michigan Library.

(54) Eaborn, *J. Chem. Soc.*, 3077 (1950).

(55) Young, DuVall, and Wright, *Anal. Chem.*, **23**, 709 (1951).

(55a) Hey, Stirling, and Williams, *J. Chem. Soc.*, 3963 (1955).

125–190° (2 mm.)] were decolorized on an alumina column, then diluted with a small amount of 30–40° petroleum ether and chilled. Repetition of this process gave 35% (37%) of 2,2′-dimethylbibenzyl, m.p. and mixture m.p. 66–67°, whose infrared spectrum was identical with that of an authentic sample.[56]

Phenylation of benzotrifluoride. Damp N-nitrosoacetanilide was dissolved in 3.5 l. of benzotrifluoride; the water was separated and measured, so that 95 g. (0.578 mole) of reagent was present. The excess benzotrifluoride was removed by flash distillation, and the residue was distilled to give 40.8 g. of crude product. The solution of the crude product in petroleum ether was chromatographed on alumina to give 37.8 g. (29%) of mixed trifluoromethylbiphenyls, b.p. 110–122° (8 mm.), mostly 112–117°. Continued elution of the column with more polar solvents eluted small amounts of material which appeared to be nitrobenzene (odor), azobenzene (m.p.), and aniline (tribromoaniline). In other experiments, the yields of mixed trifluoromethylbiphenyls ranged from 24–32%.

In a check experiment benzoyl peroxide was heated at 80–100° in benzotrifluoride (mole ratio 33:1). The yield of twice-distilled product was 60%. Dannley and Sternfeld[7] obtained a 49% yield using a 16:1 ratio at 75°. The isomer ratios were identical in the mixtures from either radical generator.

Attempts were made to hydrolyze the mixed biaryls by various methods.[57] Dilute (50%) sulfuric acid was ineffective and conc'd acid caused simultaneous sulfonation. Phosphoric acid (85%) did not react at 180° in 3 hrs. Partial success was achieved by heating the mixture with equal parts of 48% aqueous hydrobromic acid and 30% hydrogen bromide in acetic acid in the presence of powdered silica at 155° for 20 hrs., or by boiling the mixture (120°) for 68 hrs. A small amount of fluorenone (from cyclization of the *ortho* acid) could be isolated, together with *m*- and *p*-phenylbenzoic acids, but hydrolysis was never quantitative.

The pure *o*- and *m*-trifluoromethylbiphenyls were synthesized by the nitrosoacetanilide method from the *o*- and *m*-aminobenzotrifluorides[58] in 50% and 35% yields; the physical properties agreed with literature values.[7,11] The pure *p*-trifluoromethylbiphenyl was isolated by chilling the mixed biaryl fraction. The recovery was substantially lower than the total amount present. It was purified by crystallization from aqueous methanol, m.p. 71.0–71.5°,[7,11] and by sublimation at 70° (10 mm.). A sample was hydrolyzed in 55% yield by hydrogen bromide in aqueous acetic acid to *p*-phenylbenzoic acid identified by its m.p. and conversion to the methyl ester with diazomethane.

The reactivity was determined with respect to pyridine by heating 475 g. (6.0 moles) of pyridine, 877 g. (6.0 moles) of benzotrifluoride, and 36.3 g. (0.15 mole) of benzoyl peroxide at 80–88° for 16 hrs. The bulk of the solvent was distilled at atmospheric pressure and most of the remainder at reduced pressure. The residue then was boiled with 24 g. (0.6 mole) of sodium hydroxide in 550 ml. of water for 22 hrs. Benzene was added, and the aqueous solution was acidified with carbon dioxide. Phenolic material was extracted with chloroform, and the aqueous solution was acidified and extracted with chloroform to give 17.9 g. (98%) of benzoic acid, m.p. 110–117°. The benzene solution was extracted with 500 ml. of 1:1 hydrochloric acid. Basification, extraction with benzene, and distillation gave 7.8 g. (0.0503 mole, 34%) of mixed phenylpyridines, b.p. 138° (14 mm.) and a trace of tarry residue. The neutral material was distilled, giving 11.1 g. (0.0500 mole, 33%) of mixed trifluoromethylbiphenyls, b.p. 115–128° (12 mm.), and 4.8 g. of tarry residue. $\frac{0.0500}{0.0503} \times 1.04 = 1.03$ for the rate relative to benzene. In a duplicate experiment, 100% of benzoic acid was recovered, together with 0.0482 mole of trifluoromethylbiphenyls and 0.0535 mole of phenylpyridines. The rate with respect to benzene is thus 0.94. The average value is 0.99.

In preliminary experiments with benzotrichloride, we confirmed Dannley's[7] isolation of 1,1,2,2-tetrachlorobibenzyl, but the investigation was not pursued.

Reactivity of anisole. A mixture of 6 moles of pyridine, 6 moles of anisole, and 0.15 mole of benzoyl peroxide was heated for 18 hrs. at 83–85°. The solvent was stripped at reduced pressure, the residue was boiled with 24 g. of sodium hydroxide in 500 ml. of water for 18 hrs., and the mixture was separated as above. There was obtained 0.221 mole (147%) of benzoic acid, 0.0374 mole (25%) of phenylpyridines, [b.p. 139–142° (14 mm.)], and 0.0434 mole (29%) of methoxybiphenyls [b.p. 148–160° (14 mm.)]. The rate ratio is 1.16, or 1.20 relative to benzene.

In a duplicate run, using instead 0.20 mole of benzoyl peroxide, the yield of phenylpyridines was 0.0452 mole (23%), and of methoxybiphenyls 0.0511 mole (26%). The rate ratio is 1.13, or 1.18 relative to benzene.

2,3-Dimethylbiphenyl. 2,3-Dimethylbromobenzene[59] (15.2 g., 0.082 mole) was converted to its Grignard reagent in tetrahydrofuran solution. Even after refluxing overnight, the reaction was not complete. A solution of 8.1 g. (0.0825 mole) of cyclohexanone in tetrahydrofuran was added dropwise at 0–5°. The mixture was refluxed briefly, then hydrolyzed with 12 ml. of saturated ammonium chloride solution. The ether layer was decanted and evaporated, leaving 9 g. (58%) of crude, reddish 1-(2,3-dimethylphenyl)cyclohexanol. With the Grignard reagent from 2,3-dimethyliodobenzene, the yield of crude carbinol was 80%. The crude carbinol was boiled with 90% formic acid, and the 1-(2,3-dimethylphenyl)cyclohexene was washed and distilled. Dehydrogenation was accomplished by heating a mixture of 5.1 g. (0.0274 mole) of the olefin with 2 g. of 5% palladium-charcoal at 190–200° for 2 hrs., then at 290° for 4 hrs. The evolved hydrogen was swept out with dry carbon dioxide. The residue was extracted with benzene and distilled, giving 1.38 g. (36%) of 2,3-dimethylbiphenyl, b.p. 98–100° (2 mm.), n^{23}_{D} 1.5845.

Anal. Calc'd for $C_{14}H_{14}$: C, 92.25; H, 7.74. Found: C, 92.03; H, 7.92.

Dehydrogenation of 15.5 g. (0.0833 mole) of undistilled 1-(2,3-dimethylphenyl)cyclohexene with 5.5 g. (0.172 g.-atom) of sulfur at 200–250° for 4.5 hrs. (a pinch of zinc dust was added during the last 10 min. of heating) gave 6.4 g. of a yellow semi-solid, b.p. 160–170° (40 mm.). Recrystallization from methanol (Norit) gave 4.0 g. of white plates, m.p. 115.5–116.5°. After recrystallization from methanol and again from ether, it melted at 120–121°; it depressed to 104° the m.p. of 4,4′-dimethylbiphenyl. Qualitative tests showed the absence of sulfur and unsaturation. Its analysis corresponds with a dihydrodimethylbiphenyl, but this structure is highly unlikely.[60] It was not further investigated.

Anal. Calc'd for $C_{14}H_{16}$: C, 91.30; H, 8.72. Found: C, 91.05; H, 8.63.

Evaporation of the original methanol mother liquors gave 0.8 g. of a pale green liquid, presumably 2,3-dimethylbiphenyl. Repetition of the experiment for a shorter time

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[56] Moritz and Wolffenstein, *Ber.*, **32**, 2531 (1899).

[57] See footnote 21 of reference 7.

[58] *o*-Aminobenzotrifluoride, Jones, *J. Am. Chem. Soc.*, **69**, 2346 (1947); *m*-Aminobenzotrifluoride, Hooker Electrochemical Co.

[59] Fieser and Hershberg, *J. Am. Chem. Soc.*, **59**, 497 (1937).

[60] Sulfur dehydrogenation of *p*-xylene gives 4,4′-dimethylstilbene.[61] It is possible that this unknown material is 2,2′-dimethyl-3,3′-dicyclohexenylstilbene, or a position isomer, although the negative unsaturation tests argue against it. Evidently the hydroaromatic rings escaped complete dehydrogenation because of the limited amount of sulfur used.

gave a small amount of liquid product containing sulfur. After several purification attempts, the sulfur-free material did not analyze correctly, and its infrared spectrum indicated the probable presence of 3,4-dimethylbiphenyl as an impurity.

3,4-Dimethylbiphenyl. 3,4-Dimethylaniline was acetylated and crystallized to constant m.p. to insure isomeric purity. The acetyl derivative (32.6 g., 0.2 mole) was nitrosated with nitrosyl chloride, giving 70% of crude air-dried nitroso derivative. It was dissolved in 500 ml. of benzene and allowed to stand for 2 hrs.; the temperature rose to 47°. After 6 hrs. of reflux, the solvent was stripped and the residue distilled, yielding a red liquid, b.p. 110–120° (1.7 mm.). Redistillation from sodium gave an orange liquid (10.5 g., 29%) which was dissolved in petroleum ether (40–60°) and passed through an alumina column. This treatment removed carbonyl compounds (infrared) and the orange color, but a narrow yellow-green band was eluated at the same rate as the hydrocarbon, so that the redistilled 3,4-dimethylbiphenyl was pale green; b.p. 112–113° (0.7 mm.), n^{23}_{D} 1.6008.[62] The infrared spectrum indicated high purity.

Anal. Calc'd for $C_{14}H_{14}$: C, 92.24; H, 7.74. Found: C, 92.33; H, 7.89.

Attempted preparation of 2,4-dimethylbiphenyl. 5-Methylindazole. 2,4-Dimethylacetanilide (26.3 g., 0.161 mole) was nitrosated in 80% yield (crude, air-dry). When the nitroso derivative was dissolved in benzene and allowed to stand at room temperature, nitrogen evolution was barely perceptible and no heat developed. After several hours of reflux, the solution darkened. The benzene was stripped and the residue was distilled, giving 12.5 g. (60%) of 5-methylindazole, b.p. 165–190° (1–2 mm.), m.p. 115–117°; *picrate,* m.p. 167–168°.[63]

Determination of isomer ratios. The *o*:*m*:*p*-ratios were determined by infrared spectroscopy as previously described.[3]

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[61] Aronstein and Van Nierop, *Rec. trav. chim.*, **21**, 452 (1902).

[62] Ghigi, *Ber.*, **71**, 687 (1938), reported b.p. 281–283°.

[63] Heilbron, *Dictionary of Organic Compounds,* Vol. III, Oxford University Press, New York, N. Y., 1953, p. 432.