1.02 s (3 H). *Anal.* Calcd for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 71.23; H, 7.83.

***cis*-1-Methyl-1-hydroxymethylcyclohexane carboxylic acid γ-lactone** (6) was obtained in 82% yield, bp[22] 51–61° (0.07 mm). The compound solidified in the receiver and in the head during distillation. The analytical sample, from petroleum ether, had mp 49.8–50.6° (lit.[9] mp 43°); infrared ($CHCl_3$) ν_{max} 1770 cm^{-1}; nmr, δ 3.80 t (2 H), 2.18 d (1 H), 2.05–1.80 m (1 H), 1.80–1.30 m (5 H), 1.20 s (3 H). *Anal.* Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.09. Found: C, 70.08; H, 9.20.

***trans*-1-Methyl-1-hydroxymethylcyclohexane carboxylic acid γ-lactone** (8) was obtained as a liquid, which rapidly solidified, in 85% yield, bp[22] 116–125° (5 mm). The analytical sample, from petroleum ether, had mp 38–39°; infrared ($CHCl_3$) ν_{max} 1775 cm^{-1}; nmr, δ 3.90 q (2 H), 2.2–1.2 complex multiplet (7 H), 1.01 s (3 H). *Anal.* Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.09. Found: C, 70.41; H, 8.84.

α and β-Methyl-γ-butyrolactone (16a, b).—Distilled methyl succinic anhydride (an ancient commercial sample of unknown origin) was reduced according to the general procedure to produce a 69% yield of the mixed lactones, bp[22] 80° (9 mm). The nmr spectrum showed two sets of methyl doublets centered at δ 1.18 (minor constituent) and 1.10 (major constituent). Gas–liquid partition chromatography on a 0.25-in., 10-ft column packed with 18% Carbowax 20M and 1% silver nitrate at 165° showed two peaks in the ratio of 1:2.2.

α and β-Phenyl-γ-butyrolactone (17a, b).—Reduction of phenylsuccinic anhydride[32,33] gave a mixture of **17a** and **17b** in 72% yield, bp[22] 113–122° (0.1 mm). Gas–liquid partition chromatography on a 0.25-in., 10-ft 20% Carbowax 20M (containing 1% $CuCl_2$) column at 230° showed two peaks in the ratio of 6:4. The first peak overlapped with one of the peaks produced by a mixture of β- and γ-phenylbutyrolactone,[15,16] indicating that reduction occurred predominately at the more hindered carbonyl.

***cis*-Δ^4-Tetrahydrophthalide** (20) was obtained from **19** in 75% yield: bp[22] 85° (0.1 mm); n^{25}D 1.4998; infrared (smear) 1778 cm^{-1}; nmr, δ 5.75 sextet (2 H), 4.30 q (1 H), 2.95–1.85 very complex multiplet (6 H). *Anal.* Calcd for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 68.98; H, 7.22.

***trans*-Δ^4-Tetrahydrophthalide** (22).—Reduction of **21** produced a crystalline solid, mp 100–102°, in 70.4% yield. Recrystallization from benzene–hexane gave the analytical sample: mp 102.0–102.8°; infrared ($CHCl_3$) ν_{max} 1780 cm^{-1}; nmr, δ 5.75 m (2 H)t 4.68–4.36 m (1 H), 4.15–3.75 m (1 H), 2.75–1.80 br with mos, of area centered at 2.28 (6 H). *Anal.* Calcd for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.40; H, 7.28.

***cis*-Hexahydrophthalide** (24) was produced in 72.8% yield: bp[22] 72–77° (0.5 mm) (lit. bp 134–138 (25 mm),[34] 120° (5 mm)[7]); infrared (smear) ν_{max} 1778 cm^{-1}; nmr, δ 4.18 q (1 H), 3.88 d (1 H), 2.75–2.30 m (2 H), 2.1–1.0 very complex multiplet (8 H).

10-Hydroxymethyl-$\Delta^{2,6}$-hexalin-9-carboxylic Acid γ-Lactone (26).—The anhydride, **25**,[35] was reduced on the 0.1-mole scale described above in 82.7% yield and by the same procedure on a 1.0-mole scale in 79.5% yield. The analytical sample, crystallized from cyclohexane–chloroform, had mp 80.6–81.8°; infrared ($CHCl_3$) ν_{max} 1770 cm^{-1}; δ 5.65 m (4 H), 3.97 s (2 H), 2.8–1.7 complicated ABX multiplet (8 H). *Anal.* Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.71; H, 7.57.

9,10-Bis(hydroxymethyl)-$\Delta^{2,6}$-hexalin (31).—The reduction of the anhydride, **25**,[35] was carried out on 2.1–3.5-mole scale as described above using 100–180 g of $LiAlH_4$ in 2–3 l. of Fisher certified tetrahydrofuran (from a freshly opened bottle) with yields of 85–94%.[36]

***cis*-2-Hydroxymethylcyclobutane Carboxylic Acid γ-Lactone (28).**—Reduction of **27**[37] produced lactone **28** in 70.4% yield: bp[22] 109–113° (15 mm); n^{25}D 1.4687; infrared (smear) ν_{max} 1762 cm^{-1} (with a very weak shoulder at 1848 cm^{-1} which suggested the presence of a small amount of anhydride). The nmr spectrum was very complicated showing multiplets at δ 4.5–4.0 (2 H), 3.5–2.85 (2 H), 2.8–1.8 (4 H). *Anal.* Calcd for $C_6H_8O_2$: C, 64.28; H, 7.36. Found: C, 64.01; H, 7.42.

Registry No.—**2**, 14679-25-5; **4**, 14679-26-6; **5**, 14679-27-7; **6**, 14723-44-5; **8**, 14679-28-8; **9a**, 14679-29-9; **9b**, 14679-30-2; **9c**, 14679-31-3; **9d**, 14679-32-4; **9e**, 14679-33-5; **10**, 14679-34-6; **16a**, 1679-47-6; **16b**, 1679-49-8; **17a**, 6836-98-2; **17b**, 1008-73-7; **20**, 14679-39-1; **21**, 13149-03-6; **22**, 14679-41-5; **24**, 14764-51-3; **26**, 14679-43-7; **28**, 14764-52-4; **29**, 14679-45-9; **30**, 14679-46-0.

---

(32) Prepared by treatment of phenylsuccinic acid[33] with acetyl chloride.

(33) C. F. H. Allen and H. B. Johnson, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 804.

(34) A. Windaus, F. Klänhardt, and G. Reverey, *ibid.*, **55B**, 3981 (1922).

(35) K. Alder and K. H. Backendorf, *ibid.*, **71**, 2199 (1938).

(36) See J. J. Bloomfield and J. R. S. Irelan, *J. Org. Chem.*, **31**, 2017 (1966).

(37) E. R. Buchman, A. O. Reims, T. Skei, and M. J. Schlatter, *J. Am. Chem. Sci.*, **64**, 2696 (1942).

Oxidative Coupling of Alkylbenzenes by Nitric Acid

IMRE PUSKAS AND ELLIS K. FIELDS

Research and Development Department, Amoco Chemicals Corporation, Whiting, Indiana 46394

Received May 5, 1967

o-Xylene, *o*-diethylbenzene, and hemimellitene react with nitric acid to give biphenyls. Reactive intermediates can be preferentially intercepted by a more basic alkylbenzene to produce unsymmetrical alkylbiphenyls. At low temperatures the rate of nitration is slow compared with that of the coupling reaction. Yields are in some cases 30% at about 40% hydrocarbon conversion. The mechanism was investigated by use of deuterionitric acid.

Nitrative coupling and cross coupling of alkylbenzenes to form alkyl homologs of nitrobiphenyl is a preparatively significant side reaction during nitration.[1] The reaction proceeds in two steps;[2] polyalkylbiphenyls are formed by oxidative coupling, and then are nitrated. Nitration of the coupled products is slower at low temperatures than the coupling itself, consequently, it appeared possible to use this procedure as a preparative method for polyalkylbiphenyls. The purpose of the present study was to optimize the reaction conditions, to isolate and identify the polyalkylbiphenyls, and to elucidate the reaction mechanism.

Results

Table I summarizes the experiments aimed at the preparation of polyalkylbiphenyls, which, with one exception, were restricted to methyl compounds. Although *o*-xylene can couple with itself, mixtures of *o*-xylene with more basic methylbenzenes gave predominantly cross coupled products; the small amounts of homo-coupled products were usually nitrated. The cross couplings are the preparatively important reactions.

Above the optimal temperature ranges the coupled products nitrated fast to nitropolyalkylbiphenyls.[2] With *o*-xylene–pseudocumene and *o*-xylene–prehnitene

---

(1) I. Puskas and E. K. Fields, *J. Org. Chem.*, **31**, 4204 (1966).

(2) I. Puskas and E. K. Fields, *ibid.*, **32**, 589 (1967).

TABLE I

YIELD AND CONVERSION OF THE OXIDATIVE COUPLING REACTION OF ALKYLBENZENES

Hydrocarbon components 1	Hydrocarbon components 2	Reaction time, min	Temp, °C	Averaged hydrocarbon conversion, %	Yield of polyalkylbiphenyls[a] Major isomer mole %	Yield of polyalkylbiphenyls[a] Total mole %
o-Xylene[b]		30	−23 → −42	23	4	6
Hemimellitene		55	−26 ± 3	41	10	15
Toluene	Mesitylene	45	−44 ± 4		No coupling	
o-Xylene	*m*-Xylene	45	−46 ± 4	34	13	13
o-Xylene	Hemimellitene	60	−44 ± 3	34	17	21
o-Xylene	Pseudocumene	75	−46 ± 2	32	25	26
o-Xylene	Mesitylene	210	−40 ± 2	42	29	30
o-Xylene	Prehnitene	65	−21 ± 2	51	27	27
o-Xylene	Isodurene	140	−38 ± 2	40	25	25
m-Xylene	Mesitylene	80	−33 ± 2		No coupling	
Hemimellitene	Mesitylene	70	−37 ± 2	36	3[c]	3[c]
o-Diethylbenzene	Mesitylene	60	−38 ± 4	49	9	9.5

[a] Results are based on gas chromatographic analyses. Isomeric impurities in trace quantities are not indicated. [b] Freezing of part of the *o*-xylene could not be avoided. This might be responsible for the low conversion and low coupling yield. [c] This product is assumed to be a hexamethylbiphenyl on the basis of its gas chromatographic retention time.

pairs, the rate of nitration of the coupled products increased so abruptly with increasing temperature within a narrow temperature range (−44 to −38 and −20 to −14°, respectively) that the alkylbiphenyls nearly disappeared from the products. At very low temperatures, however, (*e.g.*, at −55° with the *o*-xylene–mesitylene pair) the hydrocarbons were nearly quantitatively recovered from their mixture with nitric acid; neither coupling nor nitration occurred.

To understand the coupling mechanism, it would be important to learn whether the nitration of the starting hydrocarbons and the coupling are entirely independent reactions or interrelated by some common intermediate or common dependence on a particular reagent. In the latter cases, during the course of the reaction the changes in the reaction variable (*e.g.*, concentration of the reactants, of the acid reagent) would have a similar effect on both reactions. Therefore, the course of the reaction was studied at −40° with the *o*-xylene–mesitylene pair by analyzing samples withdrawn during and after addition of the nitric acid. Quantitative rate studies under the conditions of the experiments would be extremely difficult and were beyond the scope of this work. The results shown in Figure 1 are semiquantitative only. Nitration and coupling evidently are influenced by the reaction variables in similar ways and appear to stop at the same time.

Isolation and Characterization of the Polyalkylbiphenyls.—Although the nitration mixtures contained many components such as the starting hydrocarbons, nitrated hydrocarbons, polyalkylbiphenyls, and nitrated polyalkylbiphenyls, the polyalkylbiphenyls were easily isolated by fractionation. Seven new polymethylbiphenyls and a diethyltrimethylbiphenyl were separated and characterized by melting points, elemental analyses, and mass spectrometric molecular weights (Table II). Alternative isomeric diarylmethane structures were ruled out by the presence of biphenyl absorption bands[3] in the ultraviolet spectra, by the absence of $-CH_2-$ protons in the nmr spectra, and by the absence of the mass spectroscopic fragmentation pattern characteristic for *ortho*-substituted diarylmethanes.[4] The positions of the methyl substituents

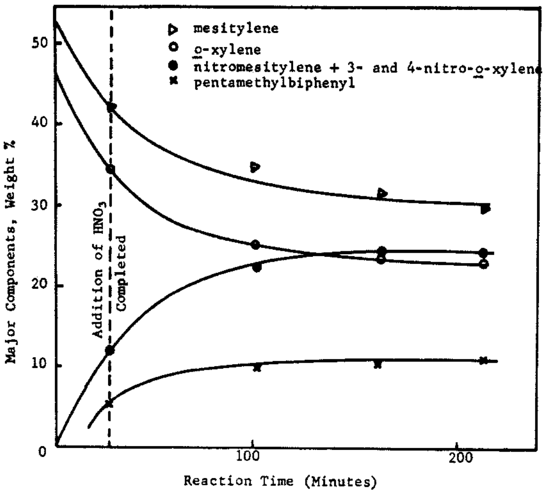
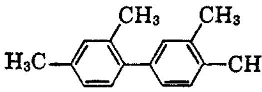


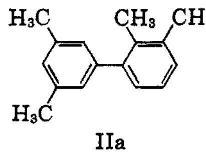
Figure 1.—Nitration of *o*-xylene–mesitylene mixture (1:1) at −40 ± 2°.

were inferred from the ultraviolet spectra (Table III) and in some cases from the nmr spectra (Table III). Five of the compounds were identified by their ultraviolet spectra as biphenyls with one methyl and three hydrogens occupying the *ortho* positions;[3] the other two biphenyls must be *ortho,ortho* or *ortho,ortho'* disubstituted.

The coupled product from hemimellitene, I is 2,3,3',4,4',5'-hexamethylbiphenyl, since the nmr spectrum clearly indicated an unsymmetrically substituted biphenyl. The isolated product of cross coupling from *o*- and *m*-xylenes might be either II or IIa; both satisfy the ultraviolet data. Formula II is our choice since its nitration (but not of IIa) would be expected to give



II



IIa

a product distribution similar to that encountered in nitrative cross coupling.[2] For the same reason, formula III, and not IIIa, is assigned tentatively to the

---

(3) G. H. Beaven and E. A. Johnson, *Spectrochim. Acta*, **14**, 72 (1958).

(4) S. Meyerson, H. Drews, and E. K. Fields, *J. Am. Chem. Soc.*, **86**, 4964 (1964).

TABLE II

PHYSICAL CONSTANTS AND ELEMENTAL ANALYSES OF NEW POLYALKYLBIPHENYLS

No.	Compd	Mp, °C	Molecular formula[a]	Calcd, % C	Calcd, % H	Found, % C	Found, % H
I	2,3,3′,4,4′,5′-Hexamethylbiphenyl	63–65[b]	$C_{18}H_{22}$	90.7	9.3	90.6	9.2
II	2,3′,4,4′-Tetramethylbiphenyl	Liquid[b]	$C_{16}H_{18}$	91.4	8.6	89.6	8.6
III	2,3,3′,4,4′-Pentamethylbiphenyl	50	$C_{17}H_{20}$	91.0	9.0	91.6	8.6
IV	2,3′,4,4′,5-Pentamethylbiphenyl	Liquid[c]	$C_{17}H_{20}$	91.0	9.0	90.8	9.1
V	2,3′,4,4′,6-Pentamethylbiphenyl	49	$C_{17}H_{20}$	91.0	9.0	91.0	8.9
VI	2,3,3′,4,4′,5-Hexamethylbiphenyl	58–59	$C_{18}H_{22}$	90.7	9.3	90.5	9.3
VII	2,3,3′,4,4′,6-Hexamethylbiphenyl	57	$C_{18}H_{22}$	90.7	9.3	90.5	9.2
VIII	2,4,6-Trimethyl-3′,4′-diethylbiphenyl	Liquid	$C_{19}H_{24}$	90.4	9.6	90.2	9.5

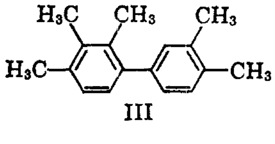
[a] By mass spectrometry. [b] This compound was 92% pure according to gas chromatography. [c] Gas chromatography revealed the presence of impurities which might have prevented crystallization.

TABLE III

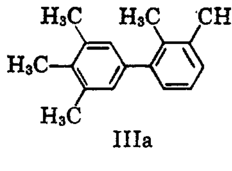
NMR AND ULTRAVIOLET ABSORPTIONS OF THE NEW POLYMETHYLBIPHENYLS

	Nmr τ values			
	In deuteriochloroform		In benzene	
Compd	Aromatic protons[a]	Methyl protons	Methyl protons	Ultraviolet absorption in isooctane[b]
I	3.02 3.07	7.68 (9) 7.79 (9)	7.85 (6) 7.90 (6) 7.99 (3) 8.05 (3)	λ_{max} 242 mμ (ϵ_{max} 12000)
II	3.04	7.74 (3) 7.81 (9)	7.81 (6) 7.96 (6)	λ_{max} 241 mμ (ϵ_{max} 13900)
III	2.96 3.04	7.72 (6) 7.74 (6) 7.81 (3)	7.88 (6) 7.94 (6) 8.01 (3)	λ_{max} 240 mμ (ϵ_{max} 14200)
IV	3.03 3.11	7.88 (15)	7.96 (15)	λ_{max} 242.5 mμ (ϵ_{max} 9900)
V	3.10	7.70 (3) 7.73 (6) 7.98 (6)	7.81 (3) 7.96 (9) 7.99 (3)	End absorption only (ϵ_{240} 6400)
VI	2.97 (3) 3.10 (1)	7.75 (12) 7.80 (3) 7.85 (3)	7.87 (6) 7.94 (12)	λ_{max} 242 mμ (ϵ_{max} 12400)
VII	2.93[c] 3.11[c]	7.71 (9) 7.83 (3) 8.03 (6)	7.88 (3) 7.92 (12) 8.01 (3)	End absorption only (ϵ_{240} 5900)

[a] Numbers in brackets indicate the number of protons. Where the number of protons is not given τ values correspond to the main peaks of partially resolved multiplets. [b] Only the conjugation bands are indicated; minor, low intensity inflections in the region of long wave bands are somewhat unreliable in our case because of lack of extreme purity. [c] For interpretation see Figure 2.

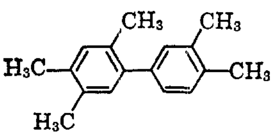


III

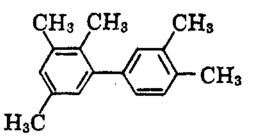


IIIa

cross-coupled product from *o*-xylene and hemimellitene and IV to that from *o*-xylene and pseudocumene.



IV



IVa

For compounds V, VI, and VII there is only one possible formula which agrees with the ultraviolet spectra.

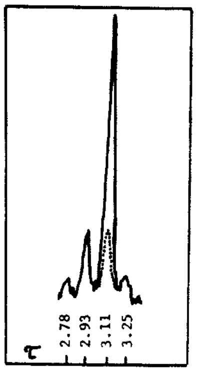


Figure 2.—Nmr spectrum of 2,3,3′,4,4′,6-hexamethylbiphenyl (VII) in the aromatic proton range (in deuteriochloroform).

The identification of VII as 2,3,3′,4,4′,6-hexamethylbiphenyl was confirmed by the nmr spectrum in the aromatic proton region (Figure 2). We interpret the absorption pattern as arising from the superposition of a slightly perturbed doublet (line is dotted in the location of superposition in Figure 2) and of two singlets, appearing at the same frequency. The coupling constant, 7.7 cps, indicates coupling by two *ortho* protons.[5]

o-Diethylbenzene probably reacts with mesitylene as does *o*-xylene. On this basis the product must be 2,4,6-trimethyl-3′,4′-diethylbiphenyl (VIII).

Discussion

Formation of coupled products unsubstituted by a nitro group showed that nitroaronium ion intermediates could not be responsible for the coupling. Additionally, coupling without nitration explained why coupling occurred only with nitric acid but not with acid mixtures. At low temperature, absolute nitric acid is dissociated to ionic species only to an extent of 3–4%[6,7] (eq 1), whereas the nitric–sulfuric acid mixture is nearly 100% ionic species[8] (eq 2). Nitric and acetic acids are

$$2HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O \qquad (1)$$

$$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^- \qquad (2)$$

also known to interact.[9] The species required to initiate coupling evidently is present in nitric acid but is practically absent in acid mixtures. This species might be the free nitric acid molecule (HNO_3). As a corollary of this, we wonder if the nitroaronium ion is

---

[5] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 193.

[6] R. J. Gillespie, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 2552 (1950).

[7] C. K. Ingold and D. J. Millen, *ibid.*, 2612 (1950).

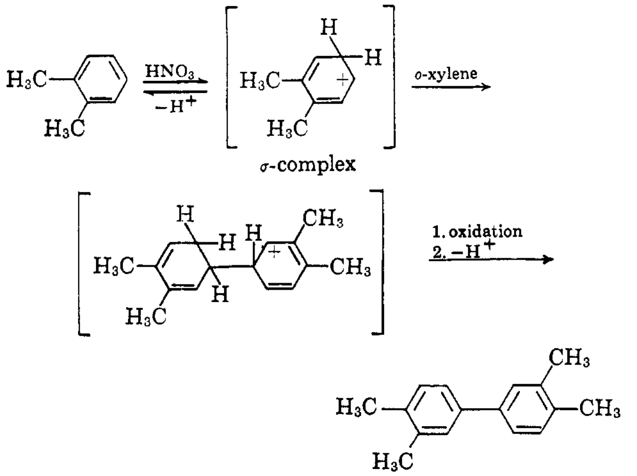
[8] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp 269–288, and references cited.

[9] A. Pictet and P. Genequand, *Ber.*, **35**, 2526 (1902).

an intermediate, or at least the first intermediate, in nitrations with nitric acid at low temperatures.

Although in nitration mixtures there is copious formation of nitrogen oxides having free-radical character, a free-radical mechanism is unlikely. This would require the formation of aryl radicals which generally are formed from unstable precursors like peroxides and diazonium salts.[10] The role of the nitrous fumes is probably limited to the oxidation of the dihydrobiphenyls which are very likely intermediates, no matter what the mechanism of the coupling step might be.

SCHEME I



Since protonation of the aromatic hydrocarbon might be considered as an intermediate step during coupling according to Scheme I, experiments were designed to test this. *o*-Xylene was treated with 100% DNO_3 at −23° and the products were analyzed by mass spectrometry. Deuteration of the aromatic ring to a σ complex in an activation step would require that after coupling either a protium or a deuterium is lost. The chance for losing a deuterium would be 50% (neglecting any kinetic isotope effect) which would mean that 50% of the coupled products should contain a deuterium label. Since none of the products contained any deuterium (see Experimental Section) the coupling could not be initiated by protonation.

In the cross-coupling reactions in combination with *o*-xylene we also used mesitylene and isodurene; these are 930 and 1860 times more basic, respectively, than *o*-xylene itself.[11] They are readily protonated, and, consequently, these cross-coupling reactions might differ in mechanism from the coupling of *o*-xylene. Therefore, we treated mixtures of *o*-xylene and mesitylene separately with trifluoroacetic and methanesulfonic acid in the presence of oxygen and catalytic quantities of perchloric acid. Under these experiments conditions mesitylene is probably protonated; however, no coupling took place. Coupling was not achieved either when nitro–sulfuric acid mixture was added to a mixture of *o*-xylene and mesitylene. The absence of a general acid catalysis appears to indicate that not even in cross coupling can protonation play an important role.

The formation of stable, unsymmetrical charge-transfer complex intermediates similar to those postulated by R. D. Brown[12] may account for all the features of electrophilic aromatic substitution and coupling. In a generalization of Brown's theory, the acceptor can also be a neutral molecule and not necessarily an ionic species. However, we were unable to provide proof for such a mechanism. The usual methods of complex characterization[13] could not be used for these reasons: (1) if the charge-transfer complexes are reactive intermediates as assumed, their concentration must be low and very sensitive methods are required for their detection; (2) since in the nitration mixtures a great number of products are produced, all of which might form complexes, the identification of a specific charge-transfer complex would be extremely difficult; (3) the nitration mixtures are not clear solutions and are unsuitable for ultraviolet and visible spectroscopic studies. Nevertheless, the dark color of the nitration mixture might be due to the assumed charge-transfer complex intermediate. Most of this color is discharged upon quenching the reaction.

Charge-transfer complexes may be common intermediates to both nitration and coupling. Alkylbenzenes which give reactive intermediates for coupling are relatively strong π bases[13] but are weak σ bases.[11] These might be the conditions when the activation energy requirements for the coupling step (going from IX to XI in Scheme II) are comparable with that of the inner complex (X) formation: both nitration and coupling occur. On this basis alone *p*-xylene would also be expected to couple. In this case probably the unfavorably situated methyl groups cause steric hindrance to coupling. Steric hindrance might also account for the fact that coupling essentially stops at the dimer, although oligomers have also been observed in trace quantities.

Nitric acid provides a powerful oxidizing medium which makes it the only known π acid to produce coupling, as shown in Scheme II.

Experimental Section

Melting points are corrected. The spectroscopic and gas chromatographic analyses were performed as described previously.[1,2]

Coupling with Nitric Acid. General Procedure.—The reaction vessel was a round-bottomed, three-necked flask equipped with a mechanical stirrer, a thermometer, and a dropping funnel. The flask, containing 0.2 moles of *o*-xylene or hemimellitene in homo-coupling experiments, or 0.1 mole of each hydrocarbon in cross-coupling experiments, was immersed in a thermostated bath and brought to the lower limit of the temperature range specified in Table I. Then 28.2 ml of 90% nitric acid (about 0.6 mole) was added dropwise, slowly enough to control the exothermic reaction. After all the acid had been added (20–35 min), the mixture was stirred an additional 20–40 min and immediately poured on a mixture of ethanol-free ether and ice to quench the reaction. Products were extracted into the ether layer, which was washed with a 10% solution of sodium hydroxide and with water and dried with saturated sodium chloride solution. The ether was removed in a Rotavapor at room temperature. The residues were analyzed by gas chromatography.

In the preparative-scale experiments, larger amounts of reactants (up to 1.0 mole each of the hydrocarbons) were used with correspondingly longer reaction times. With *o*-xylene–pseudocumene and *o*-xylene–prehnitene the yield of biphenyls was lower than in the small-scale experiments owing to nitration of the product. The reaction mixtures obtained after ether extraction were vacuum fractionated through a Vigreux column. The

---

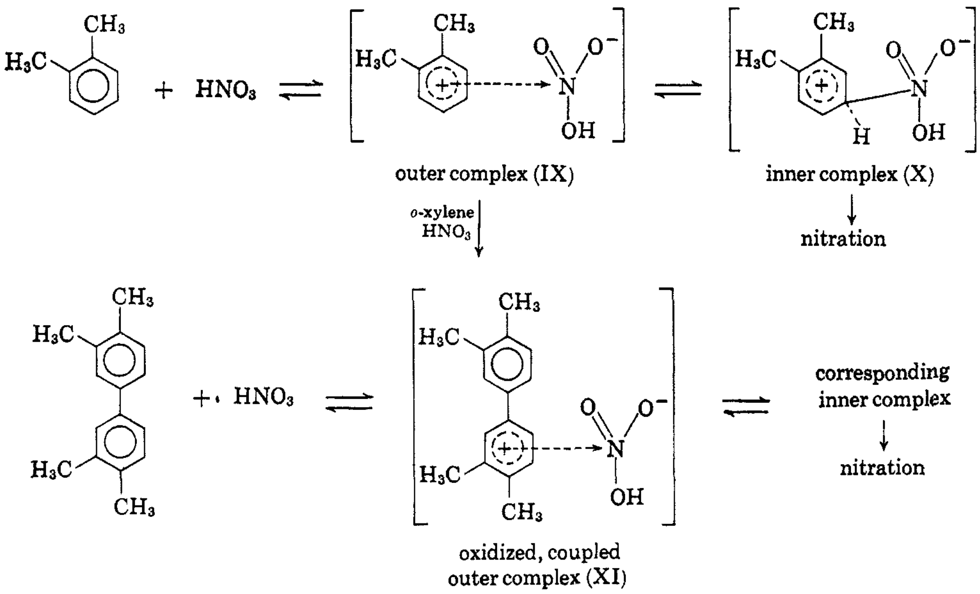
[10] For review, see W. A. Waters, Ed., "Vistas in Free-Radical Chemistry," Pergamon Press Ltd, London, 1959, pp 209–223.

[11] D. A. McCaulay and A. P. Lien, *J. Am. Chem. Soc.*, **73**, 2013 (1951).

[12] R. D. Brown, *J. Chem. Soc.*, 2224, 2232 (1959).

[13] L. J. Andrews, *Chem. Rev.*, **54**, 753 (1954).

SCHEME II



methylbiphenyls distilled in the 102–145° range at 0.1 Torr (the boiling range was much narrower for the individual cases). They were crystallized from methanol containing a little ethyl acetate. The details and the ease of purification for the individual compounds are briefly outlined below.

2,3,3′,4,4′,5′-Hexamethylbiphenyl (I). From Hemimellitene).—The fraction boiling at 143–147° at 0.25 Torr was a complex mixture containing dinitrohemimellitenes and nitrobihemimellityls. Repeated recrystallization from methanol and hexane gave I in 92% purity.

2,3′,4,4′-Tetramethylbiphenyl (II). From *o*-Xylene–*m*-Xylene.—The fraction boiling at 102–103° at 0.1 Torr failed to crystallize from different solvents. After refractionation, the center cut was 94.6% pure II according to gas chromatography.

2,3,3′,4,4′-Pentamethylbiphenyl (III). From *o*-Xylene–Hemimellitene.—The fraction boiling at 118–126° (0.1 Torr) was 85% pure and was very difficult to purify from impurities such as hexamethylbiphenyl by crystallization from a variety of solvents. Small amounts of high purity (99.3%) product were obtained in the third crop from methanol.

2,3′,4,4′,5-Pentamethylbiphenyl (IV). From *o*-Xylene–Pseudocumene.—The syrupy fraction boiling at 113–123° (0.1 Torr) was 94% pure IV according to gas chromatography. The low-voltage mass spectrum suggested approximately 77% purity; the major impurity was hexamethylbiphenyl. Attempts to crystallize from different solvents failed. Refractionation did not raise the purity.

2,3′,4,4′,6-Pentamethylbiphenyl (V). From *o*-Xylene–Mesitylene.—The fraction distilling at 120–122° (0.3 Torr) solidified on cooling, and was recrystallized from methanol. Twenty grams of pure V was isolated from 1 mole of *o*-xylene and 1 mole of mesitylene.

2,3,3′,4,4′,5-Hexamethylbiphenyl (VI). From *o*-Xylene–prehnitene.—The fraction distilling at 132–134° (0.1 Torr) was crystallized at 0° from methanol containing very little ethyl acetate. One gram of pure VI was obtained from 0.1 mole each of *o*-xylene and prehnitene.

2,3,3′,4,4′,6-Hexamethylbiphenyl (VII). From *o*-Xylene–Isodurene.—The fraction boiling at 128–136° (0.1 Torr) was refractionated and crystallized from methanol–ethyl acetate (5:1). Nine and one-half grams of VII was isolated from 0.5 mole each of *o*-xylene and isodurene.

2,4,6-Trimethyl-3′,4′-diethylbiphenyl (VIII). From *o*-Diethylbenzene–Mesitylene.—The fraction boiling at 127–130° (0.2 Torr) was 70% pure VIII. Pure VIII was isolated by preparative gas chromatography ($n^{19.4}\text{D}$ 1.5580).

Experiments with Deuterionitric Acid.—Deuterionitric acid was prepared from anhydrous potassium nitrate and deuteriosulfuric acid.[14]

Reaction of Deuterionitric Acid with *o*-Xylene.—Under anhydrous conditions, 4.5 ml of deuterionitric acid was added to 6.0 ml of *o*-xylene at −22 ± 2° with stirring over 12 min. The mixture was stirred for an additional 7 min, then quenched in ice and ether. After the usual work-up, the components were separated by gas chromatography and trapped out for mass spectrometric analysis. Only the major isomers were analyzed. *o*-Xylene and 4-nitro-*o*-xylene contained no deuterium; 3,3′,4,4′-tetramethylbiphenyl and 2-nitro-3′,4,4′,5-tetramethylbiphenyl contained 0% up to a maximum of 1% singly deuterated material.

Reaction of Deuterionitric Acid with *o*-Xylene–Mesitylene Mixture.—Under anhydrous conditions, 4.5 ml of deuterionitric acid was added to a mixture of 3.0 ml of *o*-xylene and 3.5 ml of mesitylene at −43 ± 3° over 11 min; the mixture was stirred for an additional 9 min, then was quenched. After the usual work-up, gas-chromatographic trap-outs were analyzed by mass spectrometry; results are given in Table IV.

TABLE IV

	d_0%	d_1%	d_2%
Mesitylene	67.0	28.3	4.7
2,3′,4,4′,6-Pentamethylbiphenyl	69	27	4

Acknowledgment.—The authors are indebted to S. Meyerson, E. M. Banas, and R. D. Hites, of the American Oil Co., for the spectroscopic analyses.

---

[14] D. J. Millen and I. R. Morton, *J. Chem. Soc.*, 1523 (1960).