the uv spectrum and leaving a residual yellow oil. The ir spectrum of this oil showed no absorption at 5.91 μ (C=O in benzaldehyde) but did exhibit absorption at 6.12 μ [(C=N in benzaldimine (**8**)]. The volatile photoproducts were removed *in vacuo* from the reaction mixture at 25° leaving a solid yellow residue and giving as a distillate a clear oil. The ir spectrum of the oil was that of a mixture of benzonitrile and **8** with no benzaldehyde present.[29] Addition of 1.0 ml of water to the distillate, stirring for 10 hr, extraction with ether, and evaporation of the ether gave a second oil whose ir spectrum appeared to be that of a mixture of benzaldehyde and benzonitrile. Treatment of this oil with semicarbazide hydrochloride according to the method of Shriner, Fuson, and Curtin[28] led to the isolation of benzaldehyde semicarbazone, mp 220-222° (lit.[28] mp 222°).

Conversion of Benzaldimine (8) into Benzaldehyde during Chromatography.—Benzaldimine (**8**) (52.1 mg, 0.49 mmol) was chromatographed on a 76 × 2.5 cm column of Florisil slurry packed in 1:9 ether-hexane: 20-ml fractions were collected. The column was eluted as follows: 0.5 l. of hexane; 0.5 l. of 1:99 ether-hexane; 0.5 l. of 1:49 ether-hexane; 1.0 l. of 1:24 ether-hexane; and 0.5 l. of 1:12 ether-hexane.

Fractions 120-140 afforded 45 mg of benzaldehyde, identified by ir spectroscopy and its semicarbazone derivative, mp 218-220° (lit.[28] mp 222°).

Registry No.—**7**, 588-68-1; **8**, 16118-22-2.

Acknowledgment.—This investigation was supported by a research grant from The Cleveland State University. The author is grateful to Professor T. R. Oakes for several valuable discussions of this work.

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[29] The benzaldimine used for comparison was synthesized according to the procedure given in ref 12.

Arylation by Aromatic Nitro Compounds at High Temperatures.
IV. Nitrobenzene with Toluene and Toluene-α-d_3

ELLIS K. FIELDS

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

AND SEYMOUR MEYERSON

Research and Development Department, American Oil Company, Whiting, Indiana 46394

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Nitrobenzene reacts with toluene at 600° to give the arylation product, methylbiphenyl, in addition to biphenyl and the toluene dehydro dimers (bibenzyl, methyldiphenylmethane, and dimethylbiphenyl). Most of the biphenyl contains one benzene ring from toluene and nitrobenzene each; some consists of benzene rings solely from one reactant. Toluene and toluene-α-d_3, pyrolyzed at low conversion, give only the dehydro dimers. The total amount and distribution differ markedly from that resulting in the nitrobenzene reaction. Apparently, in the absence of added free radicals, toluene pyrolyzes largely by a nonradical mechanism.

Earlier papers described the reactions of nitrobenzene with benzene[1] and with its fluorinated derivatives.[2] To extend these studies to compounds containing benzylic hydrogens, we examined the reactions of aromatic nitro compounds with a series of methylated benzenes and naphthalenes. This paper describes the reactions of nitrobenzene with toluene and toluene-α-d_3 and of nitrobenzene-d_5 with toluene, as well as the pyrolysis of toluene-α-d_3 alone.

Experimental Section

Materials. The reagents and standards for gas chromatography, except as noted below, were purchased from Aldrich Chemicals and used as received. Where purity was critical, the reagent was analyzed and, if necessary, purified by distillation, crystallization, and gas chromatography.

Table I shows the source and melting (or boiling) points of the ten $C_{14}H_{14}$ isomers used as gas chromatography standards. Methyldiphenylmethanes were prepared from methylbenzyl bromides rather than the chlorides as Senff described.[3] Reaction with benzene in the presence of ferric chloride was vigorous, and careful addition was necessary to keep the reaction under control.

Dimethylbiphenyls were prepared by stirring and refluxing mixtures of iodotoluenes and copper at atmospheric pressure for 24 hr, instead of in a bomb tube as described by Ullmann.[4] Unsymmetrical dimethylbiphenyls were made from equimolar mixtures of two iodotoluenes. They were not isolated; their retention times were determined by comparison with authentic symmetrical dimethylbiphenyls.

TABLE I

Compound	Synthesized according to	Yield, mol %	Mp (bp), °C	
			Found	Lit.
Bibenzyl	Purchased, Aldrich	...	52	52
2-Methyldiphenylmethane	*a*	54	(279–281)	(279–282)
3-Methyldiphenylmethane	*a*	48	(265–269)	(268–269)
4-Methyldiphenylmethane	*b*	38	(280–282)	(279–280)
2,2′-Dimethylbiphenyl	*c*	33	15–17	17.8
2,3′-Dimethylbiphenyl	*c*	...	...	(265–267)
2,4′-Dimethylbiphenyl	*c*	...	...	(272–260)
3,3′-Dimethylbiphenyl	*c*	38	(285–287)	(286–287)
3,4′-Dimethylbiphenyl	*c*	...	...	(288–289)
4,4′-Dimethylbiphenyl	Purchased, Aldrich	...	120–121	122

[a] See ref 3. [b] A. Behr and N. A. van Dorp, *Ber.*, **7**, 18 (1874). [c] See ref 4.

Toluene-α-d_3 was prepared in 45 mol % yield by reduction of benzotrichloride in D_2O with zinc dust.[5] It had the following isotopic composition: 2.3% d_2, 96.2% d_3, 1.0% d_4, 0.3% d_5, and 0.2% d_6. Nitrobenzene-d_5 was prepared in 50 mol % yield by nitrating benzene-d_6 with nitrogen pentoxide in carbon tetrachloride according to Haines and Adkins.[6] Its isotopic composition was 96.9% d_5 and 3.1% d_4.

Procedure.—Arylations were run in a Vycor tube filled with Vycor beads in an electric furnace maintained at 600 ± 1° under pure dry nitrogen with contact times of 9-12 sec. The vapors were condensed in a bulb at −60°, the condensate was distilled to recover unreacted material, and the residue was analyzed.

In a typical experiment, a solution of 5.011 ml (0.05 mol) of nitrobenzene in 26.6 ml (0.25 mol) of toluene was passed through a Vycor tube at 600° under nitrogen flowing at 20 cc/minute. Contact time was 9.5 sec. The vapors were condensed in a bulb at −60°; the condensate was distilled to recover 20 ml of toluene and give 6.9 g of products, the composition of which is shown in Table II.

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[1] E. K. Fields and S. Meyerson, *J. Amer. Chem. Soc.*, **89**, 3224 (1967).
[2] E. K. Fields and S. Meyerson, *J. Org. Chem.*, **32**, 3114 (1967).
[3] P. Senff, *Ann.*, **220**, 230 (1883).
[4] F. Ullmann and G. H. Meyers, *ibid.*, **332**, 42 (1904).
[5] E. K. Fields and S. Meyerson, forthcoming publication.
[6] L. B. Haines and H. Adkins, *J. Amer. Chem. Soc.*, **47**, 1419 (1925).

TABLE II

PRODUCTS FROM THE REACTION OF NITROBENZENE WITH TOLUENE AND TOLUENE-α-d_3[a]

Product	Relative intensities in low-voltage spectra[b] Toluene	Toluene-α-d_3
Aniline	3	5
Phenol-d_0	22	45[c]
-d_1	...	26[c]
Biphenyl-d_0	42	42
-d_1	...	33
-d_2	...	10
Fluorene-d_0	7	...
-d_2	...	10
Methylbiphenyl-d_0 and diphenylmethane-d_0	100	...
$C_{13}H_{10}D_2$, considered to be diphenylmethane-d_2	...	9
$C_{13}H_9D_3$, considered to be methylbiphenyl-d_3	...	91
$C_{14}(H + D)_{14}$ isomers	61	79

[a] Reaction conditions were 600°, 9.5 sec contact time, and a mole ratio of nitrobenzene to toluene of 0.05:0.25. The weight of products from nitrobenzene + toluene was 6.9 g and that from nitrobenzene + toluene-α-d_3 was 7.0 g. [b] Normalized to a value of 100 for total $C_{13}(H + D)_{12}$. [c] Tentative assignments; shown subsequently (see text) to contain contributions from deuterated anilines as well as phenols.

Table III shows the composition of the dimethylbiphenyls derived from mixtures of two iodotoluenes. The unsymmetrical isomer, as would be expected statistically, was predominant in each case.

TABLE III

Dimethylbiphenyl	Area, %
From *o*- and *p*-Iodotoluenes	
2,2'-	29.5
2,4'-	42.7
4,4'-	19.5
From *o*- and *m*-Iodotoluenes	
2,2'-	25.7
2,3'-	41.5
3,3'-	25.1
From *m*- and *p*-Iodotoluenes	
3,3'- 3,4'- 4,4'-	95.1% of total product[a]

[a] Overlapping peaks for the three constituents.

Best separation of $C_{14}H_{14}$ isomers was achieved on a 20 ft × 0.25 in. column of 10% OV-1 on Chromosorb W. Of the 6 dimethylbiphenyls containing a methyl group in each benzene ring, the 2,2' isomer was cleanly resolved; the 2,3' and 2,4' overlapped somewhat, and the 3,3', 3,4', and 4,4' isomers overlapped considerably.

Gas chromatograms for the $C_{14}H_{14}$ isomers from nitrobenzene and toluene showed identical retention times for 3-methyldiphenylmethane and 2,2'-dimethylbiphenyl, as well as much overlapping of the peaks for 2,4'-dimethylbiphenyl, bibenzyl, 2- and 4-methyldiphenylmethane, and 3,3'-dimethylbiphenyl.

Mass Spectrometry and Gas Chromatography.—Analyses were performed with a Consolidated Model 21-103c mass spectrometer with the inlet system at 250 or 325°; with a directly coupled gas chromatograph–mass spectrometer combination[7] also employing a 21-103c instrument with an electron multiplier in place of the Faraday-cup detector; and by gas chromatography on a column of polyethylene glycol sebacate on Chromosorb W. Mass spectra were measured at the conventional 70 ionizing volts and at low voltage (7.5 V, uncor). For the low-voltage measurements, the repellers were maintained at an average potential of 3 V, the exact values being selected to give maximum sensitivity. Precise mass measurements to distinguish among the overlapping phenol and aniline peaks in the spectrum of the reaction products from nitrobenzene and toluene-α-d_3 were made by peak matching on a Consolidated Model 21-110 double-focusing mass spectrometer.

Relative intensities in the low-voltage (7.5 V, uncor) mass spectra of product mixtures were taken as a first approximation to relative concentrations. Sensitivity, *i.e.*, the proportionality factor between parent-peak intensity and concentration, differs from one compound to another. However, closely related compounds have roughly equal sensitivities at the ionizing voltage employed in our work.[8] For example, the same sample was analyzed by both low-voltage mass spectrometry and gas chromatography, and the ratios of peak intensities and areas, respectively, of a series of compounds are given in Table IV. In any case, the use of relative intensities is perfectly valid for intercomparison of concentration ratios of identical components in separate samples,[9] within the limits of reproducibility of the low-voltage data.

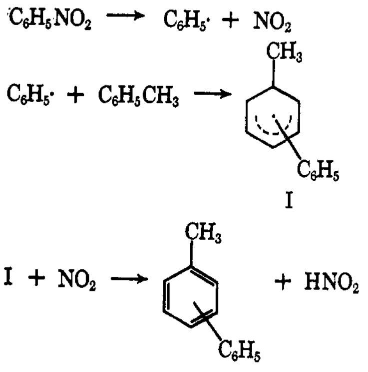
TABLE IV

Compounds	Ratios Low-voltage mass spectrometry	Gas chromatography
Biphenyl/fluorene	6.0	6.16
$C_{14}H_{14}$ isomers/biphenyl	2.39	2.89
Toluene/$C_{14}H_{14}$ isomers	1.37	1.30

Results and Discussion

Nitrobenzene and Toluene.—The major products from the reaction of nitrobenzene with toluene and toluene-α-d_3 are listed in Table II. The product formed in greatest concentration results from arylation by the phenyl radical from nitrobenzene (Scheme I). Distribution (area %) of methylbiphenyl isomers, determined by gas chromatography, was (*meta* and *para* were only partially separated) as follows: *ortho*, 22.5%; *meta* 35.3%; and *para*, 42.2%. This distribution differs considerably from that obtained by Dannley and Zaremsky[10] (% by ir analysis) from phenylation of toluene by benzoyl peroxide at 75°: *ortho*, 65%; *meta*, 19%; and *para*, 16%. Hey and Williams[11] found an even higher proportion of *ortho* phenylation, 71%.

SCHEME I



Our estimate of the methylbiphenyl isomer distribution may differ slightly from the initial product distri-

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[7] R. S. Gohlke, *Anal. Chem.*, **31**, 535 (1959); L. P. Lindeman and J. L. Annis, *ibid.*, **32**, 1742 (1960); J. T. Watson and K. Biemann, *ibid.*, **36**, 1135 (1964).

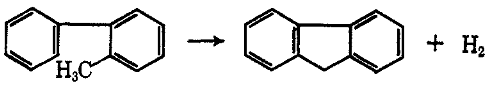
[8] G. F. Crable, G. L. Kearns, and M. S. Norris, *ibid.*, **32**, 13 (1960).

[9] S. Meyerson and E. K. Fields, *Chem. Commun.*, 275 (1966).

[10] R. L. Dannley and B. Zaremsky, *J. Amer. Chem. Soc.*, **77**, 1588 (1955).

[11] D. H. Hey and G. H. Williams, *J. Chem. Phys.*, **23**, 757 (1955).

bution because of thermal intramolecular dehydrogenation of the *ortho* isomer to give fluorene (eq 1). Fluo-



(1)

rene and fluorene-d_2 are formed to about the same extent from toluene and toluene-α-d_3, respectively. Adding the amount of fluorene, determined by gas chromatography, to that of *o*-methyldiphenylmethane gives the distribution: *ortho*, 28.3%; *meta*, 32.7%; and *para*, 39.0%. This isomer distribution still is quite different from those obtained by the authors quoted.

In view of the drastically different conditions involved in our arylation different isomer distributions might be anticipated, especially in light of the induced decomposition of benzoyl peroxide by many reactants. Such decomposition is in fact invoked by Dannley

$$C_6H_5\cdot + C_6H_5CH_3 \longrightarrow C_6H_6 + C_6H_5CH_2\cdot$$

$$C_6H_5CH_2\cdot + (C_6H_5CO_2)_2 \longrightarrow (C_6H_5)_2CH_2 + C_6H_5CO_2\cdot + CO_2$$

and Zaremsky to explain the presence of 15% diphenylmethane among the $C_{13}H_{12}$ products on the basis that the rate of decomposition of benzoyl peroxide in toluene is higher than first order.[12]

Diphenylmethane was also formed, 11.4% of the $C_{14}H_{14}$ isomers estimated by mass spectrometry, 9.6% estimated by gas chromatography. It may result from induced decomposition of nitrobenzene by the benzyl radical. An alternative source may be the

$$C_6H_5CH_2\cdot + C_6H_5NO_2 \longrightarrow C_6H_5CH_2C_6H_5 + NO_2$$

reaction of the relatively stable benzyl radical with a phenyl radical from nitrobenzene, as in the sequence in Scheme II.

SCHEME II

$$C_6H_5NO_2 \longrightarrow C_6H_5\cdot + NO_2$$

$$NO_2 + C_6H_5CH_3 \longrightarrow HNO_2 + C_6H_5CH_2\cdot$$

$$C_6H_5CH_2\cdot + C_6H_5\cdot \longrightarrow C_6H_5CH_2C_6H_5$$

The apparent proportion of aniline to phenol was about 1:7 and 1:14 in the toluene-d_0 and -d_3 cases, respectively. The discrepancy suggests that the toluene-d_3 reaction probably produced some aniline-d_1 and -d_2, which were obscured by phenol-d_0 and -d_1. This inference was confirmed by precise mass measurements made at low voltage (14 V, uncor) on the high-resolution mass spectrometer, which indicated the isotopic anilines and phenols given in Table V.

TABLE V

	Number of D atoms		Intensity, arbitrary scale division	Isotopic distribution, %
Aniline	0		1.0	42
	1		0.9	37
	2		0.5	21
		Total	2.4	
Phenol	0		7.2	71
	1		3.0	29
		Total	10.2	

The aniline/phenol ratio of 1:4 is *ca.* twice that found in the unlabeled counterpart. The difference may be due, in part at least, to differences in ionizing voltages employed in the high and low resolution measurements. In both cases, however, phenol intensity is substantially greater than that due to aniline.

Phenol probably arises *via* a nitro–nitrite rearrangement[1] (eq 2). The formation of more phenol-d_0

$$\begin{tikzcd} C_6H_5NO_2 \arrow[r] & C_6H_5ONO \arrow[r] & C_6H_5O\cdot + NO \arrow[d, "RH"] \\ & & C_6H_5OH \end{tikzcd} \qquad (2)$$

than phenol-d_1, despite the fivefold excess of trideuterated toluene, would seem to rule out preferential abstraction of benzylic hydrogen atoms. Alternatively, by analogy with the preferred formation of unlabeled phenol in the reaction of nitrobenzene with 5 mol of benzene-d_6,[1] the reaction might involve an intermediate derived from two molecules of nitrobenzene, in which the phenoxy radical as it forms has ready access to a source of hydrogen. The ratios of unlabeled phenol to phenol-d_1 in the reactions of nitrobenzene with toluene-α-d_3 and with benzene-d_6,[1] both present in fivefold excess, were 2.4 and 1.7, respectively. The difference may simply reflect the additional protium atoms and the smaller number of deuterium atoms available in the former reaction.

Biphenyl constituted an appreciable amount of the product. In other reactions involving phenyl radical in the liquid phase, dimerization has been minor or absent in the presence of aromatic systems to which this highly energetic radical can add.[13,14] In the present study, moreover, biphenyl-d_1 from nitrobenzene and toluene-α-d_3 was almost as plentiful as unlabeled biphenyl, and there was an appreciable amount of biphenyl-d_2.

To help identify the source of so much biphenyl, we treated nitrobenzene-d_5 with toluene under the same conditions as nitrobenzene with toluene-α-d_3. The isotopic distribution is shown in Table VI. In the mass region starting at 166, there was so much overlapping of chemical species containing varying numbers of deuterium atoms as to render interpretation extremely difficult. Luckily, the biphenyl region, masses 154–164, was clear of such interference.

The most abundant species is biphenyl-d_5, evidently from arylation of toluene by the phenyl-d_5 radical with subsequent loss of the methyl group (eq 3). However, about half as much biphenyl-d_4 is present; this suggests that either there is intramolecular exchange of protium

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[12] K. Nozaki and P. D. Bartlett, *J. Amer. Chem. Soc.*, **68**, 1680 (1946).

[13] Phenyl radical formed in a variety of ways in the presence of benzene, phenanthrene, and anthracene does not recombine to give biphenyl, but adds to the aromatic systems instead. See J. D. Burr, J. M. Scarborough, J. D. Strong, R. I. Akawie, and R. A. Meyer, *Nucl. Sci. Eng.*, **11**, 218 (1961); G. W. Taylor, *Can. J. Chem.*, **35**, 739 (1957).

[14] The electron spin resonance of phenyl radical at 77°K indicates that the unpaired electron remains in the sp^2 orbital of the carbon atom at which scission occurs. The σ type localized structure can account for the high reactivity of the phenyl radical: J. E. Bennett, B. Mile, and A. Thomas, *Chem. Commun.*, 265 (1965). In a different context, the difference between the ionization potential of the phenyl radical (9.20 eV) and that of benzene (9.50 eV) just barely exceeds the combined uncertainties of the measurements: I. P. Fisher, T. F. Palmer, and F. P. Lossing, *J. Amer. Chem. Soc.*, **86**, 2741 (1964). The near-equality of the two values constitutes further evidence that the odd electron is not coupled into the π system but remains highly localized. In contrast, the ionization potential of the resonance-stabilized benzyl radical (7.76 eV) [J. B. Farmer, I. H. S. Henderson, C. A. McDowell, and F. P. Lossing, *J. Chem. Phys.*, **22**, 1948 (1954)] is considerably lower than that of toluene (9.0 eV) [S. Meyerson, J. D. McCollum, and P. N. Rylander, *J. Amer. Chem. Soc.*, **83**, 1401 (1961)].

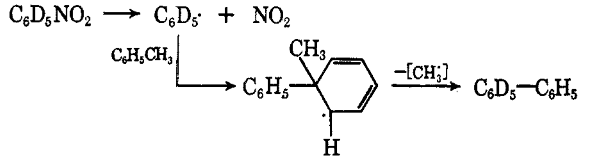
TABLE VI

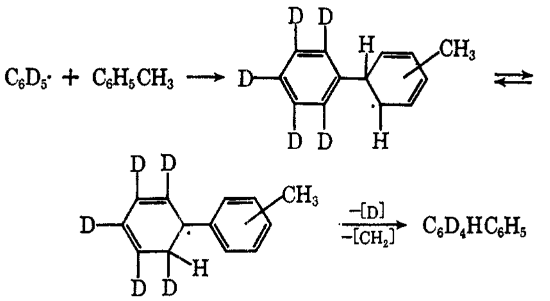
ISOTOPIC COMPOSITION OF BIPHENYL FROM NITROBENZENE-d_5 AND TOLUENE[a]

Mol wt	Number of D atoms	Rel concn, %[b]
154	0	19
155	1	2
156	2	1
157	3	3
158	4	18
159	5	34
160	6	2
161	7	1
162	8	5
163	9	11
164	10	4

[a] Reaction conditions were a mole ratio of nitrobenzene-d_5 to toluene of 1:5, 600°, and 9 sec contact time. [b] From relative intensity in the low-voltage (7.5 V, uncor) mass spectrum.

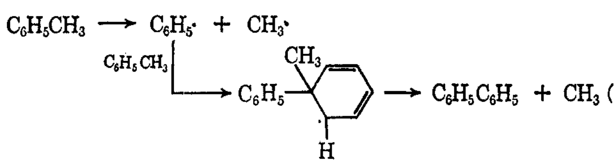
and deuterium in the intermediate cyclohexadienyl radical with subsequent loss of a methyl radical or CH_2 group (eq 4), or that biphenyl-d_4 arises by way of a phenyl radical derived from toluene (eq 5). There is


(3)


(4)

$$C_6H_5CH_3 \longrightarrow C_6H_5\cdot + CH_3\cdot$$
$$\xrightarrow[-[D]]{C_6D_5NO_2} C_6H_5C_6D_4NO_2 \xrightarrow[+[H]]{-NO_2} C_6H_5C_6D_4H \quad (5)$$

evidence for both eq 4 and 5. Product of molecular weight 172 was formed in relative concentration 35 on the scale of Table VI; this is attributed chiefly to methylbiphenyl-d_4. Intramolecular interchange of deuterium and protium has been demonstrated in the reaction of nitrobenzene with benzene-d_6,[1] in which biphenyl-d_6 formed in about equal amount to the normal arylation product, biphenyl-d_5. Biphenyl-d_0 in Table II, about the same concentration as biphenyl-d_4, must be derived solely from toluene, and is most readily explained by phenylation of toluene by phenyl radical derived from toluene, followed by loss of methyl radical (eq 6).


(6)

The formation of three times as much biphenyl-d_9 as -d_{10}, the expected product of dimerization of C_6D_5 radical, strongly suggests its formation by eq 7.

$$C_6D_5\cdot + C_6D_5NO_2 \xrightarrow{-[D]} C_6D_5C_6D_4NO_2 \xrightarrow{-NO_2} C_6D_5C_6D_4\cdot \xrightarrow{C_6H_5CH_3} C_6D_5C_6D_4H + C_6H_5CH_2\cdot (\text{or } CH_3C_6H_4\cdot) \quad (7)$$

Toluene Alone.—To determine whether the products in Tables II and VI may be derived from toluene alone or require reaction with nitrobenzene, we pyrolyzed toluene and toluene-α-d_3 alone under the identical conditions used in the nitrobenzene reaction. Pyrolysis of toluene is a well-documented reaction, and it would appear unnecessary to repeat it. However, there are discrepancies in the literature.

In 1867 Berthelot passed toluene through a glowing red porcelain tube and obtained hydrogen, methane, acetylene, benzene, and bibenzyl, as well as aromatic hydrocarbons with condensed rings.[15] The possibility that isomers of bibenzyl were present was posed both by Berthelot and by the editors of Beilstein who abstracted his work.[16]

Since that time, some investigators have found bibenzyl as the only $C_{14}H_{14}$ isomer;[17] others have evidence for the formation of dimethylbiphenyls as well.[18] Blades, Blades, and Steacie identified a dimethylbiphenyl among the products from toluene at 722°, and assumed it was a secondary product derived from bibenzyl.[19] Blades and Steacie[20] pyrolyzed impure toluene-α-d_3 at 722° and 0.45-sec contact time and obtained H_2, HD, and D_2. They suggested that hydrogen atoms were being abstracted from the ring. Cleavage of ring (in competition with side chain) carbon-hydrogen bonds, which could most simply lead to dimethylbiphenyl formation, has been suggested to account for anomalous kinetic data[18] and for labeling results in pyrolysis of toluenes-3-d and -4-d.[21] Badger and Spotswood[22] pyrolyzed toluene at 700° for an unspecified contact time and identified 23 products, among which was 4,4′-dimethylbiphenyl.

The last-named authors obviously employed such severe conditions as to cause many secondary reactions. In our pyrolyses of toluene and toluene-α-d_3 we used 600° and a contact time of 6 sec, which gave about 0.1% conversion into the dehydro dimers, $C_{14}H_{14}$, and no other products. The parent ions from toluene-α-d_3 had the following isotopic composition: mass (D atoms, relative abundance, %), 186 (4, 80.3%), 187 (5, 6.8%), and 188 (6, 12.9%). If deuterium atoms are only in benzylic or α positions and undergo no exchange during pyrolysis, and if species derived from isotopic impurities in the toluene-α-d_3 are ignored, the dimers containing four, five, and six deuterium atoms must represent bibenzyl (I), methyldiphenylmethanes (II), and dimethylbiphenyls (III), respectively. Any ex-

(15) M. Berthelot, *Ann.*, **142**, 254 (1867).

(16) F. K. Beilstein, "Handbuch der organische Chemie," Vol. 5, Springer-Verlag, Berlin, 1922, p 283.

(17) C. Graebe, *Ber.*, **7**, 48 (1874); P. Ferko, *ibid.*, **20**, 622 (1887); H. Meyer and A. Hofmann, *Monatsh.*, **37**, 684 (1916); L. R. Herndon and E. E. Reid, *J. Amer. Chem. Soc.*, **50**, 3069 (1928); M. Szwarc, *J. Chem. Phys.*, **16**, 128 (1948); *Chem. Rev.*, **47**, 75 (1950); M. Szwarc and J. S. Roberts, *J. Chem. Phys.*, **16**, 609 (1948); F. Hein and H. J. Mesee, *Ber.*, **76**, 430 (1943); K. U. Ingold and F. P. Lossing, *Can. J. Chem.*, **31**, 30 (1953); L. A. Errede and J. P. Cassidy, *J. Org. Chem.*, **24**, 1890 (1959).

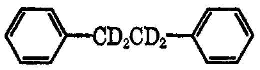
(18) M. Takahashi, *Bull. Chem. Soc. Jap.*, **33**, 801 (1960).

(19) H. Blades, A. T. Blades, and E. W. R. Steacie, *Can. J. Chem.*, **32**, 298 (1954).

(20) H. Blades and E. W. R. Steacie, *ibid.*, **32**, 1142 (1954).

(21) M. Takahashi, *Bull. Chem. Soc. Jap.*, **33**, 808 (1960).

(22) G. B. Badger and T. M. Spotswood, *J. Chem. Soc.*, 4420 (1960).



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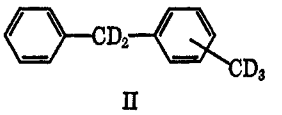
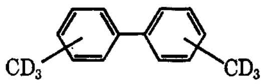


II



III

tensive exchange is ruled out by the close agreement in isotopic composition of the recovered toluene (0.3% d_1, 2.5% d_2, 95.9% d_3, 0.9% d_4, 0.3% d_5, 0.1% d_6) with that of the starting material (2.3% d_2, 96.2% d_3, 1.0% d_4, 0.3% d_5, 0.2% d_6).[23] The dimer isotopic distribution found corresponds to the approximate isomer distribution (mol %): I, 87; II, 5; and III, 8.[24]

The question raised by Berthelot, whether dimethylbiphenyls result from the pyrolysis of toluene, thus appears to have been answered. We tried to determine bibenzyl, the three methyldiphenylmethanes, and six dimethylbiphenyls by gas chromatography, but overlapping was so extensive that the value of this type of analysis was limited.

By contrast, the breakdown of isomers into the three groups, bibenzyl, methyldiphenylmethanes, and dimethylbiphenyls, by the number of deuterium atoms, as shown in Table VII, is clean and unambiguous. This analytical method is of considerable value when (a) extensive scrambling has not occurred and (b) position isomers within each group need not be determined.

TABLE VII

C_{14} ISOMERS FROM TOLUENE-α-d_3 ALONE AND WITH NITROBENZENE[a,b]

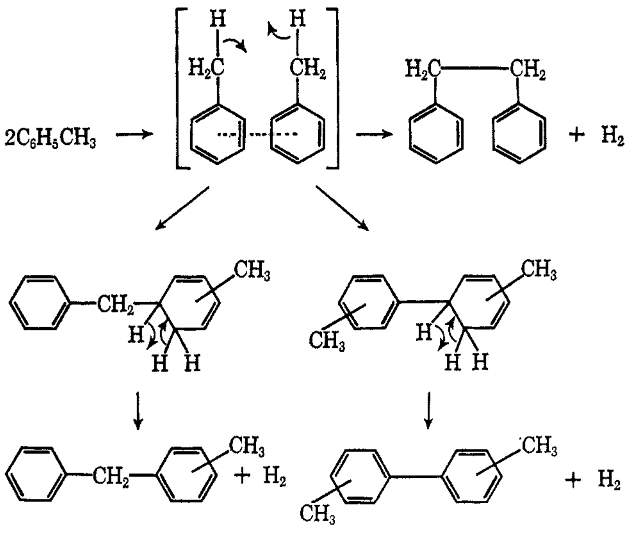
		% of total ^{14}C fraction			
		Alone		With nitrobenzene	
Mass	Probable structure	Rel intensity	Ratio	Rel intensity	Ratio
186	$C_6H_5CD_2CD_2C_6H_5$	80.3	11.8	44	2.4
187	$C_6H_5CD_2C_6H_4CD_3$	6.8	1	18	1
188	$CD_3C_6H_4$–$C_6H_4CD_3$	12.9	1.9	38	2.1

[a] Reaction conditions were toluene, 0.25 mol; nitrobenzene 0.05 mol; 600°; and 9.5-sec contact time. [b] The weight of the C_{14} fraction alone was 0.015 g and with nitrobenzene it was 1.15 g.

The C_{14} isomers from toluene-α-d_3 pyrolyzed alone and with nitrobenzene are compared in Table VII. In addition to the 80-fold greater weight of product in the nitrobenzene reaction, the proportions of the three groups are so markedly different as to demand different dominant mechanisms in the two reactions.

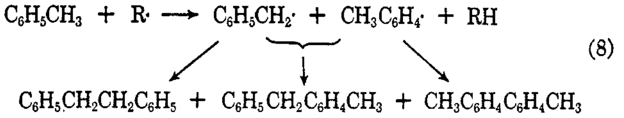
A free-radical mechanism for the pyrolysis of toluene has been generally accepted (ref 22, and references cited therein). We propose, instead, that in the absence of added free-radical precursors, toluene decomposes largely by way of a bimolecular complex (see Scheme III) which can either lose hydrogen intramolecularly to give bibenzyl, or collapse to a benzyl- or tolylmethylcyclohexadiene. The cyclohexadiene in turn loses hydrogen intramolecularly to give methyldiphenylmethane or dimethylbiphenyl. A similar mechanism

SCHEME III



involving a phenylcyclohexadiene intermediate was invoked to explain the scrambling of protium and deuterium in benzene-*d* at 690° and 21-sec contact time.[23]

In the presence of other free radicals, as in our nitrobenzene reaction, toluene pyrolysis indeed seems to go by a free-radical mechanism involving benzyl and tolyl radicals (eq 8).



$$C_6H_5CH_3 + R\cdot \longrightarrow C_6H_5CH_2\cdot + CH_3C_6H_4\cdot + RH \qquad (8)$$
$$C_6H_5CH_2CH_2C_6H_5 + C_6H_5CH_2C_6H_4CH_3 + CH_3C_6H_4C_6H_4CH_3$$

The large difference in bond strengths of aromatic and benzylic carbon–hydrogen bonds (bond, D (kcal/mol): C_6H_5–H, 112;[25] $C_6H_5CH_2$–H, 85[26]) would seem to render hydrogen abstraction from the benzene ring unlikely in the presence of available benzylic hydrogen. However, abstraction of hydrogen from aromatic rings by various radicals occurs *via* addition to give cyclohexadienyl radicals;[27] the reported parameters are therefore not applicable,[28] and the formation of almost as much dimethylbiphenyl as bibenzyl in Table VII seems reasonable.

Effect of Benzylic Substituents.—To see if benzylic substituents influence the composition of the product in the reaction with nitrobenzene, we compared the major products from benzotrifluoride and toluene under identical conditions, as shown in Table VIII. Toluene was somewhat more reactive, as the total yield of products was about 50% greater than from benzotrifluoride, and no nitro compound survived. This may be added evidence for induced decomposition. The product distributions were generally similar. However, in several groups of isomers the nature of products differed sharply.

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(23) E. K. Fields and S. Meyerson, *J. Amer. Chem. Soc.*, **88**, 21 (1966).

(24) Relative parent-peak sensitivities, measured at the low-voltage conditions employed here, of some of the isomers, taken as representative of the three isomer groups, are bibenzyl, 0.565; 2-methyldiphenylmethane, 0.825; 3,3'- and 4,4'-dimethylbiphenyls, 1.00.

(25) T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd ed, Butterworth and Co. Ltd., London, 1958, pp 270–289.

(26) R. Walsh, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, **88**, 650 (1966), and references cited therein.

(27) R. D. Giles and E. Whittle, *Trans. Faraday Soc.*, **62**, 128 (1966), and earlier references therein; M. Levy and M. Szwarc, *J. Amer. Chem. Soc.*, **77**, 1949 (1955); A. P. Stefani, L. Herk, and M. Szwarc, *ibid.*, **83**, 4732 (1961); A. P. Stefani and M. Szwarc, *ibid.*, **84**, 3661 (1962).

(28) A. S. Rodgers, D. M. Golden, and S. W. Benson, *ibid.*, **89**, 4578 (1967).

TABLE VIII
COMPARISON OF PRODUCTS FROM TOLUENE AND BENZOTRIFLUORIDE WITH NITROBENZENE[a,b]

Products, X = F or H	Rel concn[c] Benzotrifluoride	Rel concn[c] Toluene
Phenol	7	22
Biphenyl	25	42
Nitrobiphenyl	12	...
Trifluoromethylbiphenyl, $C_{13}H_{14}$	100	100
$X_3CC_6H_4C_6H_4CX_3$ and isomers	42	61
Terphenyl	5	5
X_3C-Terphenyl and isomers	21	8
$(X_3C)_2$-Terphenyl and isomers	21	7

[a] Reaction conditions were 600°; contact time, 9.5 sec; and a mole ratio of nitrobenzene to $X_3C-C_6H_5$ of 1:5. [b] The total weight of products from benzotrifluoride was 4.4 g and that from toluene was 6.9 g. [c] From relative intensities in the low-voltage (7.5 V, uncor) mass spectrum, normalized to X_3C–biphenyl = 100.

The product from benzotrifluoride containing two rings and one methyl group was apparently, in view of the retention of all three fluorine atoms, solely trifluoromethylbiphenyl, whereas that from toluene contained a substantial contribution from the isomeric diphenylmethanes. In the product containing two rings and two methyl groups, benzotrifluoride gave only bis(trifluoromethyl)biphenyl; toluene gave bibenzyl and dimethylbiphenyl in almost equal amounts, as well as an appreciable amount of methyldiphenylmethane (Table VI). This difference apparently follows as a consequence of the difference in bond dissociation energies of C_6H_5C-F and C_6H_5C-H,[29] which makes fluorine abstraction unlikely when hydrogen is available in the same molecule. Only in the absence of hydrogen is fluorine abstracted, as in the reaction of nitrobenzene with hexafluorobenzene.[2] Even in the latter case the fluorine was retained to a considerable extent through intramolecular exchange with hydrogen, and hexafluorobiphenyl was formed in about the same concentration as pentafluorobiphenyl.

Registry No.—Nitrobenzene, 98-95-3; toluene, 108-88-3; toluene-α-d_3, 1124-18-1; nitrobenzene-d_5, 4165-60-0.

Acknowledgment.—The authors are greatly indebted to D. K. Albert of the American Oil Co. for his assistance in the gas chromatographic analyses.

[29] C_6H_5C-F, D = 120 kcal/mol;[25] C_6H_5C-H, D = 85 kcal/mol.[26]

Kinetics of the Reversible Reaction of Piperidine with 2,4-Dinitroanisole in Methanol Solution[1]

J. F. BUNNETT[2] AND ROGER H. GARST

Department of Chemistry, Brown University, Providence, Rhode Island 02912

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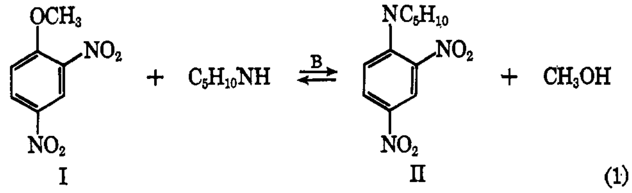
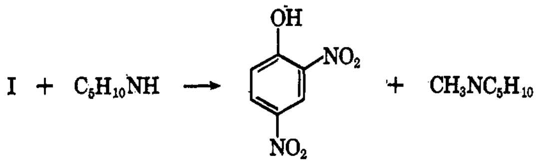
2,4-Dinitroanisole reacts with piperidine in methanol to form 2,4-dinitrophenylpiperidine (eq 1). The reaction is reversible, and the equilibrium constant at 67.9° is about 100 l. mol^{-1}. The reaction rate has been determined in both directions as a function of $NaOCH_3$ concentration. Catalysis by methoxide ion is strong, and the second-order rate coefficient (k_A) for the forward reaction is related to [$NaOCH_3$] in a nearly linear fashion. The forward reaction in the absence of $NaOCH_3$ is catalyzed by methoxide ion generated by the basic dissociation of piperidine in methanol, and probably also by piperidine. A side reaction which produces 2,4-dinitrophenol, *via* S_N2 displacement by piperidine at methyl carbon (eq 2), is important in the absence of $NaOCH_3$; its rate has been estimated.

The reaction of 2,4-dinitrodiphenyl ether with piperidine to form 2,4-dinitrophenylpiperidine is strongly catalyzed by bases.[3,4] The formally similar reaction of ethyl formate with *n*-butylamine to form *n*-butylformamide is also very responsive to base catalysis.[5] We therefore expected that bases would catalyze the reaction of 2,4-dinitroanisole (I) with piperidine to form 2,4-dinitrophenylpiperidine (II). Accordingly, a kinetic investigation of this reaction in methanol solution was undertaken.

Subsequent to our work, the same reaction in 10% dioxane–90% water was investigated by Bunnett and Bernasconi[4] and by Bernasconi.[6]



(1)



(2)

Years ago, Cahn[7] examined the reactions of several nitroanisoles with refluxing neat piperidine. He reported that 2,4-dinitroanisole gave 2,4-dinitrophenylpiperidine quantitatively within 15 min on the water bath. This indicates piperidinodemethoxylation at aromatic carbon, since 2,4-dinitrophenylpiperidine was not formed by heating 2,4-dinitrophenol with piperidine at reflux. In contrast, 2,4,6-trinitroanisole was quantitatively converted to picric acid within 1 min under the same conditions. Also, 2-methyl-4-nitroanisole gave almost 100% of 2-methyl-4-nitrophenol within 1 hr at reflux. The latter two examples suggest that nucleophilic displacement at methyl carbon occurred, although Cahn recognized hydrolysis due to traces of water to be

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[1] (a) Supported, in part, by the National Science Foundation. (b) Based on the Ph.D. Thesis of R. H. Garst, Brown University, June, 1964; *Dissertation Abstr.*, **25**, 4404 (1965).

[2] University of California at Santa Cruz, Santa Cruz, Calif.

[3] J. F. Bunnett and R. H. Garst, *J. Amer. Chem. Soc.*, **87**, 3879 (1965).

[4] J. F. Bunnett and C. Bernasconi, *ibid.*, **87**, 5209 (1965).

[5] J. F. Bunnett and G. T. Davis, *ibid.*, **82**, 665 (1960).

[6] C. F. Bernasconi, *J. Org. Chem.*, **32**, 2947 (1967).

[7] R. S. Cahn, *J. Chem. Soc.*, 1121 (1931).