The nmr spectra of XII-eqOAc in CCl_4 and C_6D_6 are essentially the same except for the signal positions (Figures 4a and 4f). Decoupling experiments similar to the above revealed signal assignments and all J's (Figures 4b–e). These results are consistent with the structure of XII-eqOAc. Long-range J's in these compounds are listed in Table II.

Procedure for the Nmr Spectral Assignments of Benzo[3,4]tricyclo-[3.2.1.0²,⁷]octene Derivaties XI. The spectrum of XI-*exo*-OAc in CCl_4 (Figure 5a) shows complicated signals due to two protons at about τ 7.8 and a broad doublet due to two protons at about τ 8.28, so that the signal assignment was difficult. Moreover, the nmdr spectrum irradiated at τ 7.00 (a broad doublet signal) also gave no insight, as shown in Figure 5b. However, the appearance of only one signal at τ 7.00 assignable to the bridgehead proton can exclude the XV structure. Further, a singlet at τ 5.55 indicates a C_6 *exo*-acetoxyl[21] in the benzo[3,4]tricyclo[3.2.1.0²,⁷]oct-3-ene system. The spectrum in C_6D_6 (Figure 5c) shows all proton signals separated. Double irradiation on a thin triplet at τ 5.35 assignable to H_{6n} (Figure 5d) made each peak of a doublet at τ 7.02 due to the bridgehead H_5 and a multiplet around τ 8.5 fairly sharp, and caused a quartet of triplets at τ 8.38 (J = 7.0, 5.0, and 1.0 Hz) to collapse into a quartet of doublets (J = 7.0, 5.0, and 1.0 Hz). On double irradiation at τ 5.55 (H_5) (Figure 5e), a doublet of quartets at τ 7.85 (J = 11.6, 4.9, and 2.8 Hz), the quartet of triplets at τ 8.38, the multiplet at about τ 8.5, a doublet at τ 9.06 having some broadening (J = 11.6 Hz), and the thin triplet at τ 5.35 due to H_{6n} were changed into a doublet of doublets (J = 11.6 and 2.8 Hz), a quartet of doublets (J = 7.0, 5.0, and 1.0 Hz), a sharper signal, a doublet of doublets (J = 11.6 and 0.6 Hz), and a thin doublet (J = 1.0 Hz), respectively. Triple irradiation on H_5 and H_{6n} (Figure 5f) gave important changes in the two signals at τ 8.38 and 8.5; the former collapsed to a distinct quartet (J = 7.0 and 5.0 Hz), the lowest field peak of which is overlapped with the acetoxyl signal, whereas the latter multiplet collapsed to a doublet of quartets further split into thin doublets (J = 7.0, 5.0, 2.8, and 0.6 Hz). These decoupling experiments confirmed the assignments given in Figure 5 and determined J's in Table II. Dreiding models suggest that several long-range J's should be found in this ring system, besides $J_{1,5}$ and $J_{5,7}$ (1.0 Hz) already obtained, according

to the "W-letter rule."[38] The absence of $J_{8n,8n}$ was indicated by no change in the signal shape of H_{8n} suffered from double irradiation on H_{8n}. Double and triple irradiation on H_7 and H_1 resulted in changes of the signals of H_{6n}, H_5, H_{8x}, and H_{8n} (Figures 5g–i), and showed the presence of $J_{1,6n}$ (0.4 Hz) and the absence of $J_{7,8n}$. Although we failed to determine the magnitudes of $J_{2,8x}$ and $J_{6n,8x}$, they may be up to the extent of 0.2 Hz.

The spectra of XI-*endo*-OAc in CCl_4 and C_6D_6 (Figures 6a and 6f) show features similar to that of XI-*exo*-OAc in C_6D_6. However, in XI-*endo*-OAc the signals of H_{6x} and H_5 appear as a quartet having some broadening (J = 5.0 and 3.0 Hz) and as a triplet further split into multiplets (J = 5.0 Hz). Decoupling experiments in CCl_4 (Figures 5b–e) confirmed assignments of the signals and determined the J's in Table II. In this case, the signals of H_1 and H_7 overlapped. However, triple irradiation on H_5 and H_{6x} revealed the H_7 signal. The values of $J_{5,6x}$ (5.0 Hz) and $J_{6x,7}$ (5.0 Hz) indicate an *endo* configuration[21] for the acetoxyl (see the dihedral angles in Table II). Similar nmdr and nmtr experiments in C_6D_6 (Figures 5g–j) also confirmed the assignments and J's. Here, the signals of H_7 and H_{8x} overlapped. Double irradiation on H_2 and on H_7 and H_{8x}, respectively, indicated the presence of $J_{2,6x}$ (0.4 Hz) and $J_{6x,8n}$ ($\leq$0.2 Hz). However, we could not determine the magnitudes of $J_{1,5}$ and $J_{7,8n}$.

Nmr of Benzo[3,4]bicyclo[3.2.1]octene Derivatives in CCl_4. The spectrum of VIII-axOH showed four aromatic H at τ 2.6–3.0 (m), one CHOH at 5.73 (d), two bridgehead H at 6.94 (m) and 7.47 (m), eight H at 7.9–9.1, and $J_{1,2}$ = 2.8 Hz. The spectrum of VIII-eqOH showed four atomatic H at τ 2.7–3.4 (m), one CHOH at 5.24 (d), two bridgehead H at 7.12 (m) and 7.55 (m), eight H at 8.0–8.8, and $J_{1,2}$ = 4.6 Hz. The CHOAc in VIII-axOAc appeared at τ 4.46 ($J_{1,2}$ = 2.5 Hz), and that in VIII-eqOAc appeared at 3.93 ($J_{1,2}$ = 4.6 Hz).

Arylation by Aromatic Nitro Compounds at High Temperatures. II. Nitrobenzene Alone and with Benzene and Benzene-d_6

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Abstract: The nitroarene bond in nitrobenzene and other aromatic nitro compounds breaks above 400°; this provides an easy means of generating phenyl and a great many other aromatic radicals. The decomposition of nitrobenzene alone at 600° seems to parallel rather closely its decomposition under electron impact in the mass spectrometer. With benzene and benzene-d_6, nitrobenzene yields mainly biphenyl and terphenyl and their deuterated analogs, respectively. Higher yields than calculated on the basis of only one radical indicate the involvement of the NO_2 portion of the original nitrobenzene.

Although nitrobenzene has been known for over 130 years[2] and has been the subject of innumerable investigations as well as the source of many useful chemicals, its thermal decomposition products have never been adequately described. Smith[3] studied the kinetics of its decomposition at 455–515° and 17–92 min in Pyrex, and concluded that the reaction was largely homogeneous, between first and second order,

with an activation energy of 51 kcal/mole. Maksimov[4] determined the first-order rate constant for nitrobenzene decomposition at 395–445°, and confirmed Smith's value for the activation energy. Neither author proposed a mechanism or determined any nongaseous products.

The discovery that the nitroarene bond in nitrobenzene and other aromatic nitro compounds breaks above 400° made possible the easy generation of phenyl and

(1) (a) Amoco Chemicals Corp. (b) American Oil Co.
(2) E. A. Mitscherlich, *Ann. Physik*, **31**, 625 (1834).
(3) R. E. Smith, *Trans. Faraday Soc.*, **36**, 985 (1940).

(4) Y. Y. Maksimov, *Teoriya Vzryvchatykh Veshchestv, Sb. Statei*, 338 (1963); *Chem. Abstr.*, **59**, 15137a (1963).

a great many other aromatic radicals.[5] Our first concern was to determine the scope of this new reaction. Accordingly, nitrobenzene was heated in a flow system at 600° alone, and in admixture with a wide variety of aromatic compounds, and the major products were determined by gas chromatography and mass spectrometry. This paper describes the results of thermal decomposition of nitrobenzene alone and with benzene and benzene-d_6.

Experimental Section

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 5–20 sec. The vapors were condensed in a bulb at −10°. The condensate was distilled to recover unreacted material, and the residue was analyzed. Noncondensable gases were caught in a gas bulb for analysis.

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[6] 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 v and at low voltage, 7.5 v, uncorrected. 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.

The reagents and standards for gas chromatography 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.

In a typical experiment, a solution of 5.11 ml (0.05 mole) of nitrobenzene in 22.22 ml (0.25 mole) of benzene was passed through a Vycor tube at 600° under nitrogen flowing at 45 cc/min. Contact time was 9 sec. The vapors were condensed in a bulb at −10°; the condensate was distilled to recover 15.3 ml of benzene and give 8.8 g of products, the composition of which is shown in Table III.

Results and Discussion

Nitrobenzene Alone. After 20 sec at 600°, nitrobenzene was completely decomposed and gave a 30 wt % yield of the products shown in Table I. To help

Table I. Products from Nitrobenzene

| Product	Rel concn,[a]	Product	Rel concn,[a]
Benzene	5.0	Diphenyl ether	0.7
Aniline	1.4	Aminobiphenyl	0.7
Phenol	27.2	Hydroxybiphenyl	3.7
Naphthalene	0.2	Nitrobiphenyl	2.5
Quinoline	2.2	o-Terphenyl	1.6
Biphenyl	20.1	m-Terphenyl	3.0
Carbazole	0.5	p-Terphenyl	3.9
Dibenzofuran	15.1	Quaterphenyl	1.6

[a] Determined by gas chromatography.

explain the formation of these products, we also reexamined the decomposition of nitrobenzene under electron impact in the mass spectrometer.[7a] The major paths in the mass spectrum of nitrobenzene are (solid arrows denote reaction steps supported by metastable peaks)

(5) E. K. Fields and S. Meyerson, *J. Am. Chem. Soc.*, **89**, 724 (1967).

(6) 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).

(7) (a) J. H. Beynon, R. S. Saunders, and A. E. Williams, *Ind. Chim. Belge*, **29**, 311 (1964); (b) S. Meyerson, I. Puskas, and E. K. Fields, "Preprints, Division of Petroleum Chemistry," Vol. 11, No. 3, American Chemical Society, 1966, p 231; *J. Am. Chem. Soc.*, **88**, 4974 (1966).
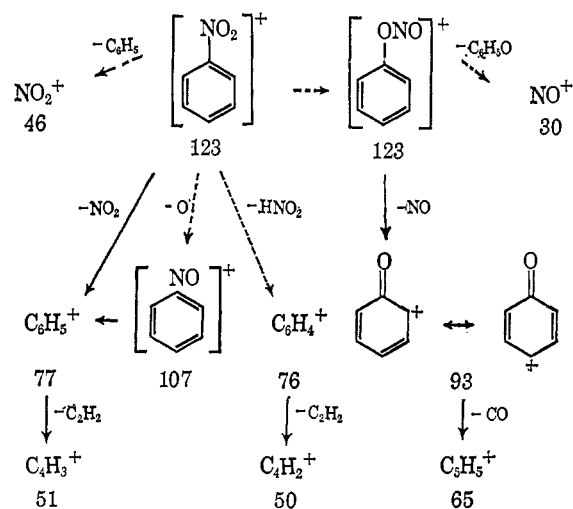
The relative intensities of the different species, expressed as fractions of the total ion yield of mass 29 and higher, are shown in Table II. The major single process thus

Table II. Partial Spectrum of Nitrobenzene

Mass	Species	Rel Inten, %[a]	Mass	Species	Rel Inten, %[a]
123	$C_6H_5NO_2^+$	11.9	65	$C_5H_5^+$	3.8
107	$C_6H_5NO^+$	1.0	51	$C_4H_3^+$	17.9
93	$C_6H_5O^+$	3.5	50	$C_4H_2^+$	7.3
77	$C_6H_5^+$	28.6	46	NO_2^+	0.6
76	$C_6H_4^+$	1.0	30	NO^+	4.5

[a] Not corrected for contributions of species containing naturally occurring heavy isotopes.

is loss of NO_2, directly and to some extent by a two-step sequence, to give $C_6H_5^+$, accompanied by the complementary loss of C_6H_5 to give NO_2^+. The $C_6H_5^+$ ion splits out acetylene and goes to $C_4H_3^+$. A significant fraction of the nitrobenzene parent ions forms phenoxy ions by loss of NO or NO^+ by loss of a phenoxy radical, presumably through an intermediate nitro–nitrite rearrangement;[7] summing the intensities for $C_6H_5O^+$, $C_5H_5^+$, $C_3H_3^+$, which most likely arises chiefly by loss of acetylene from $C_5H_5^+$,[8] and NO^+ leads to an estimate of 14.8% for the fraction of nitrobenzene ions that react by this pair of complementary paths.

The thermolysis products can be rationalized in similar fashion. Phenyl radical, formed by breaking of the phenyl–nitro bond, can abstract hydrogen from another molecule of nitrobenzene and give benzene; this is, however, only a minor reaction. It prefers to dimerize to biphenyl or to add to the aromatic system, as in solution chemistry,[9] to give nitrobiphenyls.

At 600° little nitrobiphenyl survives; it undergoes decomposition just as nitrobenzene, and gives biphenyl by hydrogen abstraction, quaterphenyl by dimerization, and hydroxybiphenyl by rearrangement as well as by alkylating the nitrobenzene and nitrobiphenyl.

(8) S. Meyerson, J. D. McCollum, and P. N. Rylander, *ibid.*, **83**, 1401 (1961); S. Meyerson, *ibid.*, **85**, 3340 (1963).

(9) D. H. Hey, A. Nechvatal, and T. S. Robinson, *J. Chem. Soc.*, 2892 (1951); T. Inukai, K. Kobayashi, and O. Simamura, *Bull. Chem. Soc. Japan*, **35**, 1576 (1962); *Chem. Abstr.*, **58**, 5552f (1962).
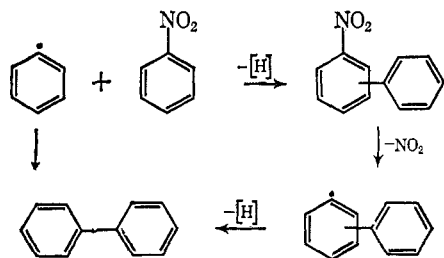
Phenol, and probably some of the hydroxybiphenyl, arises by a nitro–nitrite rearrangement paralleling the process under electron impact.
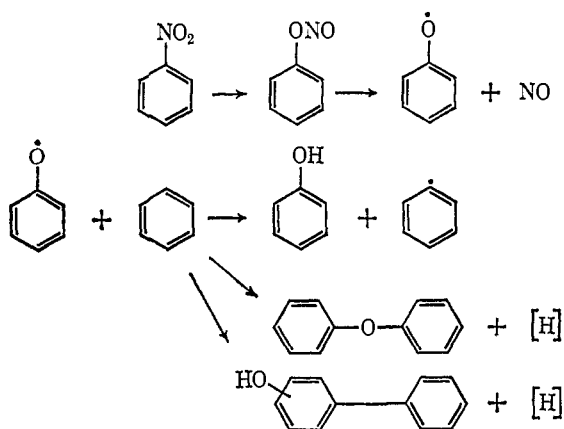
Dibenzofuran forms from diphenyl ether, *o*-hydroxybiphenyl, or both, by intramolecular loss of hydrogen. It does not come directly from phenol itself, as phenol alone under identical conditions is converted in only 0.5% yield to a mixture of diphenyl ether, hydroxybiphenyls, and dibenzofuran.

The source of quinoline is not apparent. Quinoline results from the reaction of benzyne with pyridine,[10] and benzyne may well form from nitrobenzene at 600° by elimination of HNO_2, as under electron impact, and indeed may account for all the naphthalene and some of the biphenyl listed in Table I. But whether pyridine forms at all here is uncertain. Intramolecular loss of oxygen at high temperatures has been observed for dibenzothiophene 5,5-dioxide,[11] and could conceivably occur in aromatic nitro compounds to give nitrenes; nitrene precursors form pyridine from benzene by insertion.[12] However, the lack of evidence for both pyridine and phenylpyridines among nitrobenzene decomposition products renders this mechanism unlikely. A 3-carbon atom fragment seems called for, to react with aniline in a Skraup-type synthesis, but none of the other products (except benzo-, dibenzo-, and tribenzoquinolines in trace amounts) gives evidence for such fragments. The formation of quinoline, and the detailed steps in nitrobenzene reduction to aniline, remain to be clarified.

Nitrobenzene with Benzene and Benzene-d_6. Nitrobenzene with benzene gave the products shown in Table III. Phenol is a minor product, suggesting that the decomposition of nitrobenzene to phenyl radical and nitrogen dioxide is faster than the nitro–nitrite

(10) E. K. Fields and S. Meyerson, *Chem. Commun.*, 474 (1965); *J. Org. Chem.*, **31**, 3307 (1966).
(11) E. K. Fields and S. Meyerson, *J. Am. Chem. Soc.*, **88**, 2836 (1966).
(12) K. F. Schmidt, *Ber.*, **58**, 2409 (1925); T. Curtius and A. Bertho, *ibid.*, **59**, 565 (1926).
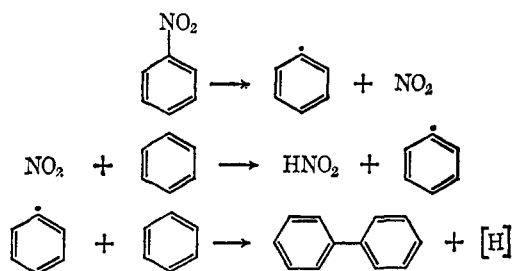
Table III. Reaction of Nitrobenzene with Benzene[a]

Product	Rel concn,[b] mole ratio, nitrobenzene:benzene 1:5	1:25
Phenol	1.8	1
Naphthalene	0.3	...
Biphenyl	100.0	100
Dibenzofuran	11.5	1
Diphenyl ether, hydroxybiphenyl	3.4	3
Terphenyl	44.4	23
Phenyldibenzofuran	7.3	...
Phenyldiphenyl ether	1.0	...
Quaterphenyl	8.2	2
Diphenyldibenzofuran	1.8	...
Bisbiphenyl ether	0.3	...
Quinquephenyl	0.9	...
Triphenyldibenzofuran	0.3	...

[a] At 600°, contact time 9 sec. [b] Relative intensities of the parent peaks of components in the mass spectrum measured at reduced ionizing voltage (7.5 v, uncorrected), normalized to biphenyl = 100 and 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 [G. F. Crable, G. L. Kearns, and M. S. Norris, *Anal. Chem.*, **32**, 13 (1960)]. For example, in the same sample analyzed by both low-voltage mass spectrometry and gas chromatography, the ratios of the concentrations of phenol and biphenyl were 1.37 and 1.35, respectively. In any case, the use of relative intensities is perfectly valid for intercomparison of concentration ratios of identical components in separate samples [S. Meyerson and E. K. Fields, *Chem. Commun.*, 275 (1966)] within the limits of reproducibility of the low-voltage data.

rearrangement. Most of the biphenyl arises by reaction of benzene with the nitrobenzene rather than dimerization of the phenyl radical from nitrobenzene decomposition, as shown by the increasing proportion of biphenyl with decreasing concentration of the nitrobenzene. The yields of products are considerably different in the reactions at the two different concentration ratios, and thus give a clue to the mechanism of biphenyl formation.

At a nitrobenzene:benzene mole ratio of 1:5, the yield of biphenyl and terphenyl combined, as measured by gas chromatography, was 85 mole % based on 1 mole of phenyl radical produced per mole of nitrobenzene decomposed. At a mole ratio of 1:25, the yield on the same basis jumped to 170%. Both the phenyl radical and the nitrogen dioxide from the nitrobenzene must have been involved. The sequence of reactions is probably

Benzene in nitrogen dioxide at 600° gave a 12% yield of biphenyl plus terphenyl.

The gases from the reaction of nitrobenzene with benzene at 1:5 mole ratio at 600° run under helium

Table IV. Reaction of Nitrobenzene with Benzene-d_6[a]

Product	Isotopic distribution[b]		Total concn[c]
Benzene	d_0	0.9	
	d_1	2.4	
	d_2	1.7	
	d_3	0.8	100
	d_4	2.2	
	d_5	17.3	
	d_6	74.7	
Phenol	d_0	29.1	
	d_1	19.8	
	d_2	9.9	
	d_3	10.6	4.4
	d_4	11.2	
	d_5	5.2	
	d_6	0.8	
Biphenyl	d_0	0.7	
	d_1	1.3	
	d_2	1.6	
	d_3	1.6	
	d_4	4.4	
	d_5	18.2	20.6
	d_6	16.4	
	d_7	8.5	
	d_8	5.8	
	d_9	14.4	
	d_{10}	27.1	
Terphenyl	d_0	0.3	
	d_1	0.6	
	d_2	0.9	
	d_3	1.4	
	d_4	2.4	
	d_5	5.6	
	d_6	7.7	
	d_7	7.5	4.2
	d_8	8.0	
	d_9	12.8	
	d_{10}	16.5	
	d_{11}	11.8	
	d_{12}	7.0	
	d_{13}	7.9	
	d_{14}	9.7	

[a] At 600°, contact time 9.3 sec; mole ratio nitrobenzene:benzene = 1:5; isotopic composition of benzene, 0.2% d_4, 5.7% d_5, 94.1% d_6. [b] Estimated from low-voltage (7.5 ionizing v, uncorrected) mass spectrum. [c] Relative intensities in the low-voltage spectrum, normalized to benzene = 100.

had the percentage composition:[13] CO_2, 0.3; CO, 2.4; N_2O, 0.9; NO, 9.8; N_2, 0.7; H_2, 1.4; He, 84.5. The NO_2 fragment of the nitrobenzene molecule apparently ends up chiefly as nitric oxide, either by direct reduction or via a series of free radical hydrogen abstractions and decompositions.[14]

$$NO_2 + RH \longrightarrow HNO_2 + R \cdot$$

$$2HNO_2 \longrightarrow H_2O + NO + NO_2$$
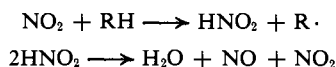
To observe more clearly the interaction of nitrobenzene fragments, nitrobenzene was decomposed at 600° in benzene-d_6 and the isotopic distribution of the products determined, as shown in Table IV. Despite some inevitable scrambling of protium and deuterium,[15,16] the results are revealing.

(13) Small amounts of NO_2 might have been present and been removed by inadvertent chemical reaction with surface deposits in the mass spectrometer. See R. A. Friedel, A. G. Sharkey, J. L. Shultz, and C. R. Humbert, *Anal. Chem.*, **25**, 1314 (1953).

(14) For the structure of nitrous acid in the gas phase and its dissociation products, see A. P. Cox and R. L. Kuczowski, *J. Am. Chem. Soc.*, **88**, 5071 (1966), and references cited therein.

Biphenyl consisted mainly of four species: d_5, d_6, d_9, and d_{10}. Only 0.7% was unlabeled; this measures roughly the extent of dimerization of the phenyl radical derived from nitrobenzene. Almost 40 times as much was biphenyl-d_{10}, formed presumably by abstraction of a deuterium atom from the benzene-d_6 by either fragment of the decomposed nitrobenzene, followed by dimerization of the phenyl-d_5 radical or arylation of benzene-d_6 by the phenyl-d_5 radical. The appreciable amount of biphenyl-d_9 probably forms in part, at least, by arylation of benzene-d_5 by the phenyl-d_5 radical. Arylation of benzene-d_6 by unlabeled phenyl radical should give biphenyl-d_5; the formation of almost as much biphenyl-d_6 suggests that in the reaction
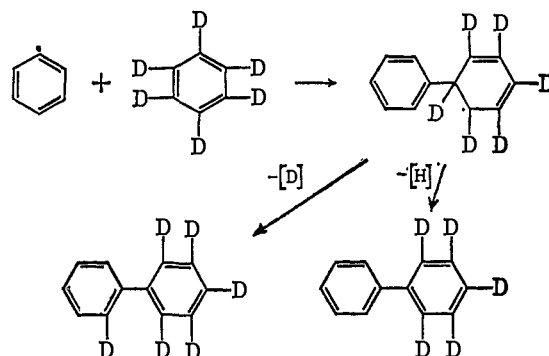
the intermediate phenylcyclohexadienyl radical has a lifetime sufficiently long to exchange protium and deuterium intramolecularly before it is restored to full aromaticity. This is perhaps not too surprising, in view of the evidence for a phenylcyclohexadienyl intermediate in scrambling of protium and deuterium in the pyrolysis of benzene-d.[15a]

Isotopic composition of the terphenyl indicates that the bulk of the terphenyl consists of two rings originally derived from benzene-d_6 and one from nitrobenzene. This suggests either of two processes: phenylation of biphenyl-d_9 and -d_{10} by unlabeled phenyl radical, or attack by phenylcyclohexadienyl radical on benzene-d_6, followed by rearomatization. That the concentration of terphenyl-d_4 is less than half that of terphenyl-d_5, if these small numbers are significant, may be accounted for by an isotope effect, directing the incoming phenyl radical to the unlabeled, rather than to the deuterated, benzene ring.

Isotopic composition of the phenol is unexpected. Such a reactive aromatic system should exchange ring hydrogens with benzene-d_6 more readily than an unsubstituted benzene, which from the isotopic spread seems to be the case. However, phenol-d would be predicted far to exceed in amount the unlabeled phenol, if abstraction by the phenoxy radical occurred with equal ease from benzene-d_6 or nitrobenzene. Formation of more unlabeled than monodeuterated phenol suggests a reaction involving an intermediate derived from two molecules of nitrobenzene, in which the phenoxy radical site has ready access to a source of hydrogen.

(15) (a) E. K. Fields and S. Meyerson, *ibid.*, **88**, 21 (1966); (b) *ibid.*, **88**, 3388 (1966).

(16) To estimate the extent of scrambling to be expected, an equimolar mixture of benzene and benzene-d_6 was heated at 600° for 9 sec. The percentage isotopic composition of the recovered benzene was: d_0, 46.2; d_1, 4.0; d_2, 0.4; d_3, 0.1; d_4, 0.7; d_5, 6.8; d_6, 41.8. The scrambling is low enough to justify conclusions drawn from the reaction of nitrobenzene with benzene-d_6.

Subsequent articles will describe the phenylation of additional aromatic and heterocyclic compounds by nitrobenzene at elevated temperatures.

The Participation of Solvent and General Acids in Acetal Hydrolysis. The Hydrolysis of 2-(*para*-Substituted Phenyl)-4,4,5,5-tetramethyl-1,3-dioxolanes

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Abstract: The hydrolysis of 2-phenyl-4,4,5,5-tetramethyl-1,3-dioxolane in 0.100 M HCl is characterized by a ΔS^* of -14.2 eu and a D_2O solvent isotope effect of $k_D/k_H = 2.4$. The value of ρ for hydrolysis of a series of 2-(*para*-substituted phenyl)-4,4,5,5-tetramethyl-1,3-dioxolanes in 0.100 M HCl at 30° was found to be -2.0. The values of ΔS^* and k_D/k_H are considerably less than normally found in acetal hydrolysis while the ρ value is much more positive than found previously for hydrolysis of the diethyl acetals of *meta*- and *para*-substituted benzaldehydes. The rate constants for hydrolysis of 2-(*p*-nitrophenyl)-4,4,5,5-tetramethyl-1,3-dioxolane in moderately concentrated HCl solutions are proportional to the stoichiometric acid concentration while a plot of log k_{obsd} *vs.* $-H_0$ shows a pronounced downward curvature. The slope w of a plot of log $k_{obsd} + H_0$ *vs.* the logarithms of the activity of water is $+1.9$. Thus the evidence supports the incursion of an A2 mechanism involving attack of water on the protonated substrate. The rate of hydrolysis of 2-(*p*-methoxyphenyl)-4,4,5,5-tetramethyl-1,3-dioxolane is subject to catalysis by increasing concentrations of formic acid at constant pH and ionic strength.

The generally accepted mechanism for the acid-catalyzed hydrolysis of acetals involves a fast preequilibrium protonation of the substrate followed by a unimolecular rate-determining decomposition to an alcohol and a resonance-stabilized carbonium ion.[1] The hydrolysis of fully protonated 2-(substituted phenyl)-3-ethyloxazolidines, carbonyl derivatives similar to acetals (1,3-dioxolanes) in which an oxygen has been replaced by an N-ethyl group, is marked however by solvent participation and general catalysis in the ring-opening step.[2]

It was thought that similar mechanisms might be observable in the hydrolysis of acetals if the A1 transition state could be made sterically unfavorable. Intramolecular participation by various functional groups in acetal hydrolysis has been postulated in several instances.[3-6] The mechanism of such participation, however, has not been established. The clearly unambiguous finding of buffer catalysis and solvent participation in an acetal hydrolysis could lead to insight into the mechanistic possibilities by which glycosidic enzymes effect catalysis since it is likely that functional groups at the active sites of these enzymes are involved in the bond-breaking process.

In preliminary work it was found that the hydronium ion catalyzed hydrolysis of 2-(p-methoxyphenyl)-4,4,-5,5-tetramethyl-1,3-dioxolane proceeded in water at 30° with a second-order rate constant approximately

1030-fold less than that of the corresponding ethylene glycol derivative. There is little doubt that this large observed effect is steric in origin resulting from substitution at the 4 and 5 positions in the 1,3-dioxolane ring system. While this rate effect could be reflecting differences in the dissociation constants for the conjugate acids it is also quite likely that the bond-breaking process is strongly hindered with the tetramethylethylene glycol derivative due to greater steric interactions in the A1 transition state than in the ground state. Since the 1,3-dioxolane ring is normally puckered by carbon–oxygen bond angles of less than 109°,[7] a substantial dihedral angle should exist between the methyl groups on adjoining carbons so that ground-state interactions would not be unusually large. A detailed study of the hydrolysis of a series of 2-(substituted phenyl)-4,4,5,5-tetramethyl-1,3-dioxolanes has therefore been made. It has indeed been found that the hydrolysis reactions of these acetals proceed by an A2 mechanism with general acid catalysis by formic acid being detectable.

Experimental Section

Materials. 2-(*para*-Substituted phenyl)-4,4,5,5-tetramethyl-1,3-dioxolanes were prepared by refluxing in benzene or toluene equivalent amounts of the appropriately substituted benzaldehyde and tetramethylethylene glycol. A trace of *p*-toluenesulfonic acid was added as a catalyst. Water was continuously removed from the reaction by azeotropic distillation with the solvent. After collection of a theoretical amount of water the reaction mixture was washed with 1 M KOH solution. The benzene or toluene extract was then dried over anhydrous sodium sulfate. The solvent was removed by flash evaporation, and the residue was either distilled or recrystallized from an ether–hexane mixture.

(1) For the evidence which has led to this mechanism and the pertinent references see T. H. Fife and L. K. Jao, *J. Org. Chem.*, **30**, 1492 (1965).
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