Arylation by Aromatic Nitro Compounds at High Temperatures. V. Reactions of Nitrotoluenes

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

Received May 31, 1968

At 600°, *m*- and *p*-nitrotoluenes arylate benzene and chlorobenzene to give methylbiphenyls and methylchlorobiphenyls, respectively; *o*-nitrotoluene shows a markedly different behavior. It interchanges its oxygen and methyl hydrogen atoms to form anthranilic acid. With methanol, it gives methyl anthranilate; in benzene, it decarboxylates to aniline. Methyl anthranilates and anilines containing *meta* substituents are produced by reaction at high temperature of substituted *o*-nitrotoluenes with methanol and benzene, respectively. With benzene-d_6, *o*-nitrotoluene gives an appreciable amount of aniline-d_6, indicating transfer of the nitro group in a complex where the nitro oxygens and toluene hydrogens react. 2,4-Dinitrotoluene with mixtures of methanol and arenes give aryl-substituted methyl anthranilates.

In the first three papers of this series we described the formation of free radicals from aromatic nitro compounds at high temperatures,[1a] and the reactions of radicals from nitrobenzene with benzene[1b] and fluorinated arenes.[1c]

The fourth paper was concerned with the products of the reaction of nitrobenene with toluene and toluene-α-d_3, as well as of nitrobenzene-d_5 with toluene at 600°.[1d] The results were compared with those obtained in the pyrolyses of toluene and toluene-α-d_3 alone; the comparison gave strong evidence that, in the absence of added free radicals, toluene pyrolyzed largely by a nonradical mechanism.

This paper describes the reactions of the nitro derivatives of toluene at 400–600° with benzene, benzene-d_6, chlorobenzene, and methanol. A marked difference showed for the *ortho* as against the *meta* and *para* isomers; this has led to a one-step synthesis of methyl anthranilates and anilines containing *meta* substituents from substituted *o*-nitrotoluenes.

Experimental Section

Procedure.—Chemicals were reagent grade. 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 indicated in the tables. Solutions of reactants were fed to the Vycor tube by a syringe whose needle fitted through a rubber septum in a glass adapter connected with the Vycor tube by a 24/40 joint; the syringe was pumped by a diffusion pump (Harvard Apparatus Co., Dover, Mass., compact diffusion pump Model 975) at a rate to give the required contact time. Rates were reproducible to 1% or better. The vapors were condensed in a bulb at −60°, the condensate was distilled to recover unreacted material, and the residue was analyzed. Some typical experiments are described.

A. *o*-Nitrotoluene with Benzene.—A solution of 6.14 ml (0.05 mol) of *o*-nitrotoluene in 44.44 ml (0.5 mol) of benzene was passed through a Vycor tube filled with Vycor chips, at 600° under nitrogen flowing at 20 cc/min. Contact time was 20 sec. The vapors were condensed in a bulb at −60°; the condensate was distilled to recover 37 ml of benzene and leave a residue boiling above 165° of 5.3 g, which was analyzed both by 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[2] also employing a Model 21-103c instrument with an electron multiplier in place of the Faraday cup detector; and by gas chromatography, usually on a column of polyethylene glycol sebacate on Chromosorb W. Other types of columns were used in special analyses. 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.

Relative intensities in the low-voltage (7.5 V, uncorrected) 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.[3] For example, in the same sample analyzed by both low-voltage mass spectrometry and gas chromatography, the ratios of peak intensities and areas, respectively, of a series of compounds were those given in Table I. In any case, the use of relative intensities is perfectly valid for intercomparison of concentration ratios of identical components in separate samples,[4] within the limits of reproducibility of the low-voltage data.

Table I

Compounds	Ratios	
	Low-voltage mass spectrometry	Gas chromatograpy
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

Analysis by the two methods of the products from the reaction of *o*-nitrotoluene with benzene are shown in Table II.

B. *o*-Nitrotoluene with Methanol.—A solution of 3.68 ml (0.03 mol) of *o*-nitrotoluene in 12.1 ml (0.3 mol) of methanol was passed through the Vycor tube at 600° with a contact time of 16 sec. The condensate was distilled to recover 8.7 ml of methanol, and the residue boiling above 130° (3.8 g) was analyzed with the results shown in Table III. Considerable care should be taken in the reactions of 2,4-dinitrotoluene and 2,4,6-trinitrotoluene; although no difficulties were encountered in the vapor phase reactions, some explosions occurred during work-up of the liquid products.

Results and Discussion

Nitrotoluene Isomers.—The products of reaction of the three nitrotoluenes with benzene and chlorobenzene are shown in Table IV. At the temperature and con-

---

[1] (a) E. K. Fields and S. Meyerson, *J. Amer. Chem. Soc.*, **89**, 724 (1967); (b) *ibid.*, **89**, 3224 (1967); (c) *J. Org. Chem.*, **32**, 3114 (1967); (d) *ibid.*, **33**, 2315 (1968).

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

[3] G. F. Crable, G. L. Kearns, and M. S. Norris, *Anal. Chem.*, **32**, 13 (1960).

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

TABLE II

Product	Estimated by mass spectrometry Ion %	Analysis by gas chromatography Area %	Analysis by gas chromatography Yield,[b] mol %
Toluene	2.8	3.4	3.9
Aniline	56.4	37.8	43.1
Phenol	5.6	6.2	7.0
o-Cresol	7.9	9.9	9.7
Biphenyl	18.9	19.7	13.6
Fluorene	1.1	1.7	1.1
2-Methylbiphenyl	3.4	4.0[a]	2.5
Stilbene	1.1	1.8	1.1
Bibenzyl and isomers	2.8	3.2[a]	1.9

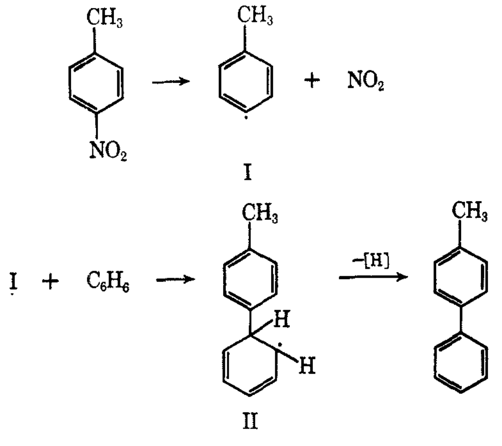
[a] Overlapping peaks, as described in ref 1d. There were additionally eight unknowns of higher boiling point than bibenzyl. [b] Calculated on the basis of 0.05 mol of *o*-nitrotoluene giving 0.05 mol of product if the yield were quantitative.

TABLE III

Product	Estimated by mass spectrometry Ion %	Analyzed by gas chromatography Area %	Analyzed by gas chromatography Yield,[a] mol %
o-Toluidine	10.5	7.4	5.3
Aniline	40.3	26.4	19.4
o-Cresol	7	8.9	7.6
N-Methyl-*o*-toluidine	3.3	1.9	1.8
Methyl anthranilate	38.7	45.2	37.8
Bibenzyl and isomers	0.3	0.6	0.9

[a] Calculated on the *o*-nitrotoluene.

tact times used in this work, no nitrotoluene survived. The products from *m*- and *p*-nitrotoluenes are generally similar, although the relative amounts differ somewhat. Other then biphenyl, which also formed from benzene alone, methylbiphenyl is the major product and this results from arylation of benzene by the tolyl radical



(I). The tolylcyclohexadienyl radical II is presumably restored to aromaticity by NO$_2$, itself a free radical, which goes to HNO$_2$ and its decomposition products, ultimately water, N$_2$, and NO.[1b]

Toluene results from hydrogen abstraction by I; the cresols, from the nitro–nitrite rearrangement observed in the high-temperature reactions of nitrobenzene.[1b]

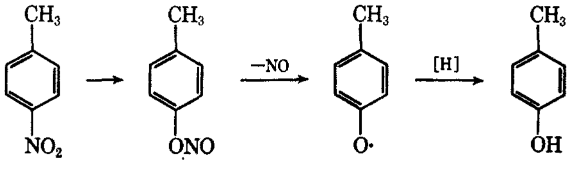


TABLE IV

REACTION PRODUCTS OF NITROTOLUENES WITH BENZENE AND CHLOROBENZENE[a]

Nitrotoluene isomer	None[c]	*ortho*	*meta*	*para*
Total weight of products, g	0.06	5.3	8.0	6.3
	Rel concn[c] with benzene			
Products				
Toluene		15	11	15
Aniline		300		
Phenol		30	12	8
Cresol		42	15	7
Biphenyl	100	100	100	100
Fluorene		6		
Methylbiphenyl		18	49	67
Stilbene		6	2	2
Bibenzyl and isomers		15	6	5
Nitrotoluene isomer	None[d]	*ortho*	*meta*	*para*
Total weight of products, g	0.75	4.25	4.1	6.5
	Rel concn[c] with chlorobenzene			
Products				
Aniline		9		
Cresol		4	28	8
Chlorophenol		28		
Carbazole		22		
Methylbiphenyl		8	31	18
Chlorobiphenyl	23	33	120	64
Methylchlorobiphenyl		20	51	104
Chlorocarbazole		53		
Dichlorobiphenyl	100	100	100	100

[a] Conditions: 600°, 20-sec contact time, nitrogen at 20 cc/min, moles of nitrotoluene:benzene or chlorobenzene 0.05:0.25. [b] Benzene alone (0.25 mol). [c] Relative intensities in the low-voltage (7.5 V nominal) mass spectrum normalized to biphenyl = 100 for the reaction products from benzene, and dichlorobiphenyl = 100 for the reaction products from chlorobenzene. [d] Chlorobenzene alone (0.25 mol).

The products of mass 182 from the three nitrotoluenes, bibenzyl and isomers, may include bitolyls from dimerization of tolyl radicals; however, as shown in the earlier papers of this series,[1] dimerization of aryl radicals at high temperatures, as well as in the liquid phase,[1d,5] is a minor reaction compared with addition to aromatic compounds. The formation of stilbene from all three nitrotoluenes in about the same concentration ratio to "bibenzyl and isomers" may be taken as evidence that bibenzyl is formed in all cases. The other dehydrodimers of toluene are probably also present, as in the reaction of nitrobenzene with toluene.[1d]

o-Nitrotoluene behaved markedly differently from the other two isomers. With benzene it gave only small amounts of *o*-methylbiphenyl and its dehydrogenation product, fluorene. Aniline was the major product, evidently as result of reduction of the nitro and loss of the methyl groups.

To clarify this reaction, we pyrolyzed solutions of the nitrotoluenes in methanol with the results shown in Table V. Methyl anthranilate was formed from the *ortho* isomer in yield about equal to that of aniline. At high temperatures, *o*-nitrotoluene apparently undergoes intramolecular oxidation and reduction to give anthranilic acid; in the absence of methanol to esterify and stabilize it, the carboxyl group is lost to yield

---

(5) J. K. Hambling, D. H. Hey, S. Orman, and G. H. Williams, *J. Chem. Soc.*, 3108 (1961); J. D. Burr, J. M. Scarborough, J. D. Strong, R. I. Akawie, and R. A. Meyer, *Nuclear Sci. Eng.*, **11**, 218 (1961); G. W. Taylor, *Can. J. Chem.*, **35**, 739 (1957); J. E. Bennett, B. Mile, and A. Thomas, *Chem. Commun.*, 265 (1965).

TABLE V

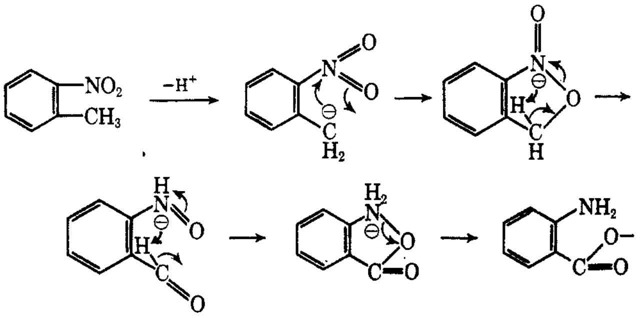
REACTION PRODUCTS OF NITROTOLUENES WITH METHANOL[a]

Nitrotoluene isomer	*Ortho*	*Meta*	*Para*
Total weight of products, g	3.8	1.65	1.7
	Relative concn[b]		
Products			
Toluidine	100	100	100
Aniline	385	6	4
Cresol	67	62	38
N-Methyltoluidine	31	29	17
Methyl aminobenzoate	369		
Bibenzyl and isomers	3	73	17

[a] Conditions: 600°, 16-sec contact time, nitrogen at 20 cc/min, moles of nitrotoluene:methanol 0.03:0.3. [b] Relative intensities in the low-voltage (7.5 V nominal) mass spectrum normalized to toluidine = 100.

aniline.[6] No methyl aminobenzoate was formed from *m*- or *p*-nitrotoluenes.

A complex mixture of products containing *inter alia* anthranil and anthranilic acid has resulted from treatment of *o*-nitrotoluene with concentrated alkali.[7] The mechanism at the high temperature may thus involve formation of a carbanion species followed by a series of hydrogen and oxygen shifts.[8,9] In our work, the proton and carbon or nitrogen anions are presumably never separated to any extent, as the reaction occurs in the gas phase. Evidence has been reported for interchange of hydrogen and oxygen atoms in the sequential loss of OH, CO, and HCN from *o*-nitrotoluene under electron impact in the mass spectrometer;[9] the two processes thus resemble each other closely. Numerous examples of parallel behavior in pyrolysis and under electron impact have been found in other contexts.[4,10a] The high-temperature formation of anthranilic acid also resembles to some extent the thermal elimination of sulfur dioxide from *o*-methyldiarylsulfones to give diarylmethanes.[10b]



Substituted methyl anthranilates result under the same conditions from *o*-nitrotoluenes containing nuclear substituents, as shown in Table VI.[11] The yields, although not high, are sufficient to be of interest for synthetic use, especially as they were obtained in one-step reactions.

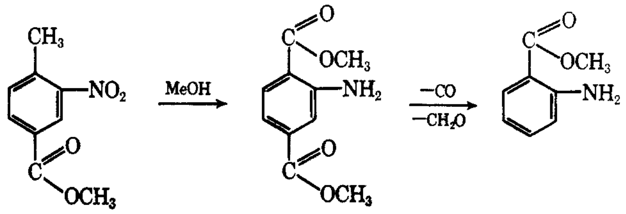
TABLE VI

METHYL ANTHRANILATES FROM *o*-METHYLNITROARENES AND METHANOL[a]

o-Methylnitroarene	Product	Yield, mol %
o-Nitrotoluene	Methyl anthranilate	38[b]
4-Chloro-2-nitrotoluene	Methyl 4-chloroanthranilate	36[b]
4-Fluoro-2-nitrotoluene	Methyl 4-fluoroanthranilate	21[c]
Nitro-*p*-xylene	Methyl 4-methylanthranilate	25[c]
5-Nitropseudocumene	Methyl 3,4-dimethylanthranilate	20[c]
Methyl 3-nitro-4-methylbenzoate	Dimethyl 2-aminoterephthalate	6[c]
	Methyl anthranilate	37[c]
2-Methyl-1-nitronaphthalene	Methyl 1-amino-2-naphthoate	11[c]

[a] Conditions: 600°, 16-sec contact time, mole ratio of *o*-methylnitroarene:methanol 1:10. [b] By gas chromatography. [c] Estimated by low-voltage mass spectrometry.

Methyl 3-nitro-4-methylbenzoate gave only a small amount of dimethyl 2-aminoterephthalate; the major product evidently results by loss of the original CO_2Me group, possibly as CO and CH_2O.



In an attempt to increase the yield of methyl anthranilate, we passed *o*-nitrotoluene with methanol 1:10 at 525° over activated alumina. Only 0.5% methyl anthranilate formed; the major products were N-methylaniline (13%), N,N-dimethylaniline (14%), and N,N-dimethyl-*o*-toluidine (6%). Evidently the alumina promoted decarboxylation of anthranilic acid and catalyzed methylation of the resulting aniline.

Formation of aniline from *o*-nitrotoluene in the absence of methanol suggested that this reaction might be utilized to prepare substituted anilines. *o*-Nitrotoluene was heated at 600°, 11-sec contact time, alone and at a 1:3 mole ratio with various hydrocarbons to determine a set of conditions to be used with substituted *o*-nitrotoluenes. The yields of aniline are given in Table VII. As benzene gave the highest yield of aniline, it was used for the preparation of substituted anilines, with the results shown in Table VIII.

TABLE VII

Hydrocarbon	Yield,[a] mol %
None	33
Cyclohexane	35
Toluene	36
Benzene	57

[a] By gas chromatography.

---

(6) W. Lob [*Z. Elektrochem.*, **8**, 715 (1902)] found that *o*-nitrotoluene exploded when passed through a metal tube heated until it glowed light red. By diluting the nitrotoluene with steam, he obtained 8% crude and an unspecified yield of pure anthranilic acid.

(7) I. I. Kukhtenko, *Dokl. Akad. Nauk SSSR*, **132**, 609 (1960); G. A. Russell and E. G. Jansen, *J. Amer. Chem. Soc.*, **89**, 300 (1967), and earlier references cited therein.

(8) When a formally charged species is written in a gas phase reaction, it should be understood, of course, that the counterion is assumed to remain in close association with the charged species. As noted by a referee, a similar mechanism can be written to explain the interchange of O and H atoms *via* a free-radical process, by initial abstraction of H atom and half-arrows to denote 1-electron shifts. The carbanion scheme proposed formally parallels that apparently occurring under electron impact.[9]

(9) S. Meyerson, I. Puskas, and E. K. Fields, *J. Amer. Chem. Soc.*, **88**, 4974 (1966).

(10) (a) For example, E. K. Fields and S. Meyerson, *Chem. Commun.*, 474 (1966); E. K. Fields and S. Meyerson, *J. Amer. Chem. Soc.*, **88**, 2836 (1966). (b) H. Drews, E. K. Fields, and S. Meyerson, *Chem. Ind.* (London), 1403 (1961).

(11) E. K. Fields and S. Meyerson, *Tetrahedron Lett.*, 1201 (1968).

TABLE VIII

AROMATIC AMINES FROM *o*-METHYL NITRO AROMATICS[a]

o-Methyl nitro aromatics	Amine	Yield, mol %
o-Nitrotoluene	Aniline	57[b]
Nitro-*p*-xylene	*m*-Toluidine	59[b]
4-Chloro-2-nitrotoluene	*m*-Chloroaniline	15[b]
4-Fluoro-2-nitrotoluene	*m*-Fluoraniline	27[c]
5-Nitropseudocumene	4-Amino-*o*-xylene	19[c]
Methyl 3-nitro-4-methylbenzoate	Methyl 3-aminobenzoate	32[c]
2-Methyl-1-nitronaphthalene	1-Naphthylamine	70[b]

[a] Conditions: 600°, 20-sec contact time, mole ratio of nitro compound:benzene 1:4. [b] By gas chromatography. [c] Estimated by low-voltage mass spectrometry.

TABLE IX

REACTION PRODUCTS OF NITROTOLUENES WITH BENZENE-d_6[a]

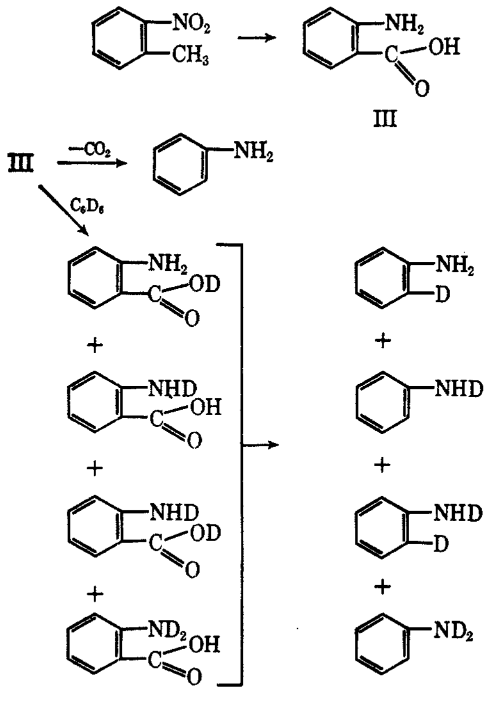
	Relative concn[b]			
	Nitrotoluene isomer			
Products	*ortho*	*meta*	*para*	*e*
Benzene-d_4	1.2		1.8	
-d_5	15.5	15.2	18.5	
-d_6	83.3	84.8	79.7	
Aniline-d_0	100			
-d_1	90			
-d_2	40			
-d_3	13			
-d_4	6			
-d_5	9			
-d_6	16			
Phenol-d_0	*c*	10	10	
-d_1	*c*	10	8	
-d_2	*c*	4	4	
-d_3	*c*	2	3	
-d_4	*c*	5	6	
-d_5	*c*	18	7	
Cresol-d_0	*d*	30	14	
-d_1	*d*	19	7	
-d_2	*d*	17	3	
Biphenyl-d_0	0.4	1	1	490
-d_1	0.4	2	3	50
-d_2	0.4	2	4	25
-d_3	0.4	2	4	75
-d_4	3	7	11	450
-d_5	13	34	48	850
-d_6	10	35	48	50
-d_7	3	15	27	25
-d_8	5	10	14	125
-d_9	33	37	47	278
-d_{10}	100	100	100	100
Methylbiphenyl-d_0	5	3	6	
-d_1	7	6	10	
-d_2	14[f]	7	10	
-d_3	29[f]	6	9	
-d_4	19[f]	16	24	
-d_5	19[f]	75	92	
-d_6	24[f]	50	57	
-d_7	15[f]	20	21	
Bibenzyl + isomers	5	6	5	
Terphenyl-d_4			1	
-d_5			4	
-d_6	0.7		4	
-d_7	1		4	
-d_8	9		3	
-d_9	9	6	9	
-d_{10}	6	11	17	
-d_{11}	1	6	10	
-d_{12}	0.8		4	
-d_{13}	0.8		3	
-d_{14}	4		5	

[a] Conditions: 600°, 8.5-sec contact time, mole ratio of nitrotoluene: benzene-d_6 1:5; isotopic composition of initial benzene, 96.4% d_6, 3.6% d_5. [b] Relative intensities in the low-voltage (7.5 V, uncorrected) mass spectra normalized to biphenyl-d_{10} = 100. [c] Overlapping peaks with aniline. [d] Overlapping peaks with *o*-toluidine. [e] From nitrobenzene-d_5 with toluene.[1d] [f] Mainly deuterated carbazole and diphenylamine (see text).

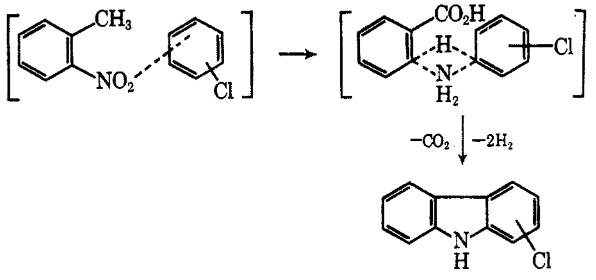
No attempt was made to find optimum conditions; the large variation in yields suggests that these probably differ considerably among the nitro compounds. Our novel preparation gives amines in one step, in most cases with a *meta* substituent. These are usually the most difficult to synthesize by other methods.

To determine the mode of formation of the products with benzene shown in Table IV, nitrotoluene isomers were allowed to react separately with benzene-d_6 at 600°. The products and their isotopic compositions are listed in Table IX.

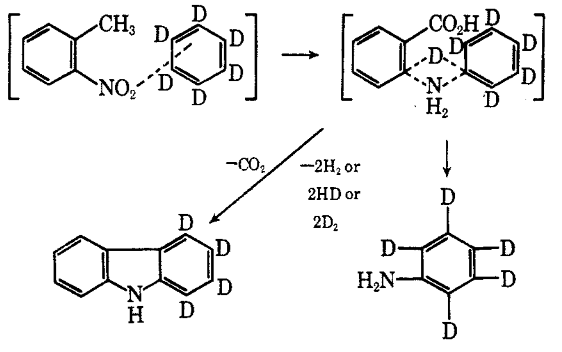
The major aniline species from *o*-nitrotoluene were d_0, d_1, and d_2. Aniline-d_1 and -d_2 may arise by a rapid exchange of the reactive carboxyl and amino hydrogens with benzene-d_6. The high reactivity of amino and carboxyl hydrogens in solution presumably carries over to the gas phase provided that the pressure is high enough to permit solvation. The exchange may be by way of the anthranilic acid zwitterion before it loses carbon dioxide.



Aniline-d_3 could be similarly rationalized, but the d_4, d_5, and d_6 species, which almost certainly came from benzene-d_6, are not so easily explained. The formation of these aniline species parallels the formation of chlorocarbazole from *o*-nitrotoluene and chlorobenzene shown in Table IV. Likewise, aniline formed in only trace amounts in the reaction of nitrobenzene and nitrobenzene-d_5 with toluene, as well as that of nitrobenzene with toluene-α-d_3.[1d] Transfer of the nitro group from *o*-nitrotoluene to chlorobenzene or benzene-d_6 seems thus to occur in a complex involving a concerted reaction with the methyl group (eq 1 and 2). The 167–169 mass region of the products from *o*-nitrotoluene with unlabeled benzene shows relative intensities of 19, 5, and 13 for carbazole, methylbiphenyl, and diphenylamine, respectively. Therefore, the region of masses 168–175, shown in Table IX under the methylbiphenyl species, probably involves for *o*-nitrotoluene mainly deuterated species of carbazole and diphenylamine, with only a minor contribution from *o*-methylbiphenyl. Thus the major isotopic species of carbazole is d_4 and that of diphenylamine is d_5, which fit neatly into the proposed scheme (eq 1 and 2).



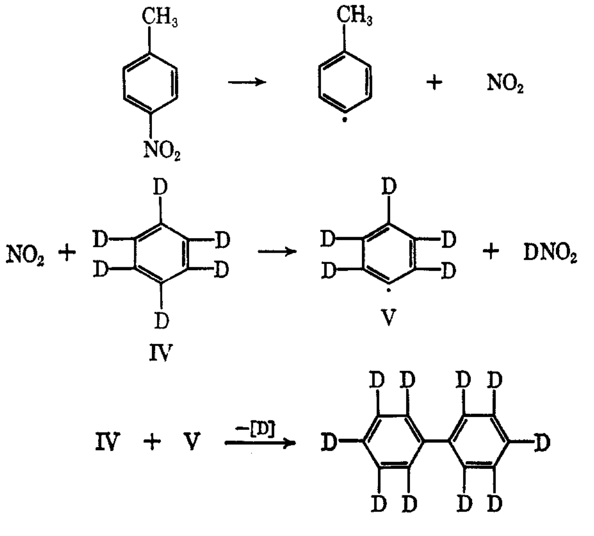
(1)



(2)

The analysis of reaction products from *o*-nitrotoluene with benzene-d_6, because of overlapping peaks in the 167–177 region, is not perhaps so clear-cut as one would like; however, taken together with analysis of the same reaction with unlabeled benzene and chlorobenzene, it enables us to derive a fairly coherent reaction pattern.

The biphenyl region is free from overlapping species of other products and is therefore relatively uncomplicated. Almost no biphenyl arises from two benzene rings derived solely from nitrotoluenes. The main component, biphenyl-d_{10}, comes from benzene-d_6, presumably by abstraction of a deuterium by NO_2 (eq 3).

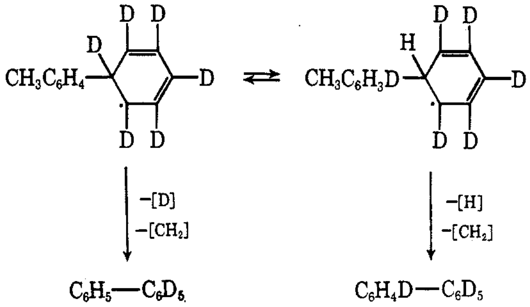


(3)

From total weights of products and relative proportions of biphenyl shown in Table IV, appreciably more biphenyl is formed in the reaction with benzene from the *m*- and *p*-nitrotoluenes than from the *ortho* isomer, as would be expected. The nitro group in the *ortho* isomer is involved in the intramolecular reaction with the methyl group rather than in cleavage of the aryl-nitro bond. Much biphenyl is formed from a benzene ring derived from both benzene-d_6 and nitrotoluene; the nearly equal amounts of d_5 and d_6 species indicate reactions 4 and 5. The almost complete absence of

$$CH_3C_6H_4NO_2 \longrightarrow CH_3C_6H_4\cdot + NO_2 \qquad (4)$$

$$IV + C_6D_6 \longrightarrow$$



(5)

biphenyl-d_0 and -d_1 in this work contrasts with the considerable amount from the reaction of nitrobenzene-d_5 with toluene,[1d] shown under column *e* in Table IX. This indicates that loss of a methyl or CH_2 group from toluene or its derivatives probably occurs from the intermediates of radical addition or abstraction, rather than as a primary process in pyrolysis as postulated by previous workers (see ref 12 and references cited therein). Similarly, we have reported evidence

$$C_6H_5{-}CH_3 \longrightarrow C_6H_5\cdot + \cdot CH_3$$

for different dominant mechanisms in thermal decomposition of toluene alone and in the presence of free radicals.[1d]

Some of the products in Table IV and Table IX may be derived by transfer of a nitro group from nitrotoluene to benzene (reaction 6). At first glance the widely

$$CH_3C_6H_4NO_2 + C_6D_6 \longrightarrow CH_3C_6H_4D + C_6D_5NO_2 \qquad (6)$$

differing concentrations of biphenyl species in Table IX under column *e* and the other columns would seem to render this reaction unlikely. However, reactant ratios were considerably different in the two studies; furthermore, phenol-d_4 and -d_5 shown in Table IX appear to demand a nitro–nitrite rearrangement of nitrobenzene-d_5 from reaction 6.

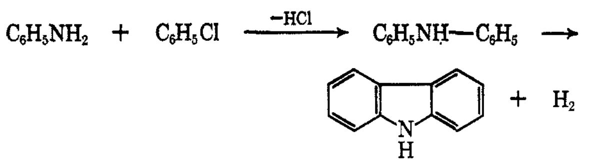
The main terphenyl species are d_9 and d_{10}, with as much d_8 as d_9 in the *o*-nitrotoluene reaction. These evidently arise from the combination of biphenyl-d_8, -d_9, and -d_{10} with a molecule of nitrotoluene as shown in the scheme for biphenyl formation. Terphenyl-d_{11} may be the result of deuterium–protium scrambling, although somewhat more formed from *m*- and *p*-nitrotoluenes than might be anticipated from the complete absence of other species in the *m*- and much lower amounts in the *p*-nitrotoluene reactions. Some or most terphenyl-d_{11} might be the result of nitrobenzene-

---

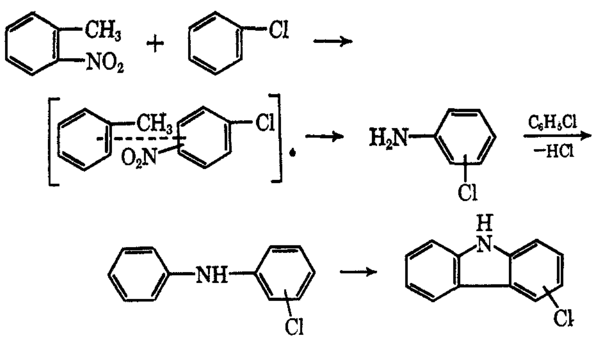
(12) G. B. Badger and T. M. Spotswood, *J. Chem. Soc.*, 4420 (1960).

d_5 attack on methylbiphenyl-d_6 with subsequent or concerted loss of the methyl group.

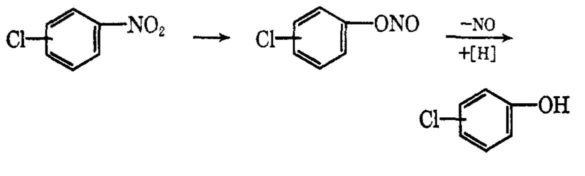
Carbazole shown in Table IV probably arises by reaction of aniline from *o*-nitrotoluene with chlorobenzene (reaction 7). Carbazole results both from diphenylamine[13] and 2-aminobiphenyl[14] at high temperatures. Chlorocarbazole, however, indicates transfer of a nitro group from *o*-nitrotoluene to chlorobenzene reduction to chloroaniline, and reaction with another molecule of chlorobenzene (reaction 8). Additional evidence for formation of nitrochlorobenzene is chlorophenol, about half as much as chlorocarbazole, most readily accounted for by a nitro–nitrite rearrangement (reaction 9). With benzene, *o*-nitrotoluene gave an appreciable amount of phenol, presumably also by transfer of its nitro group to benzene.



(7)



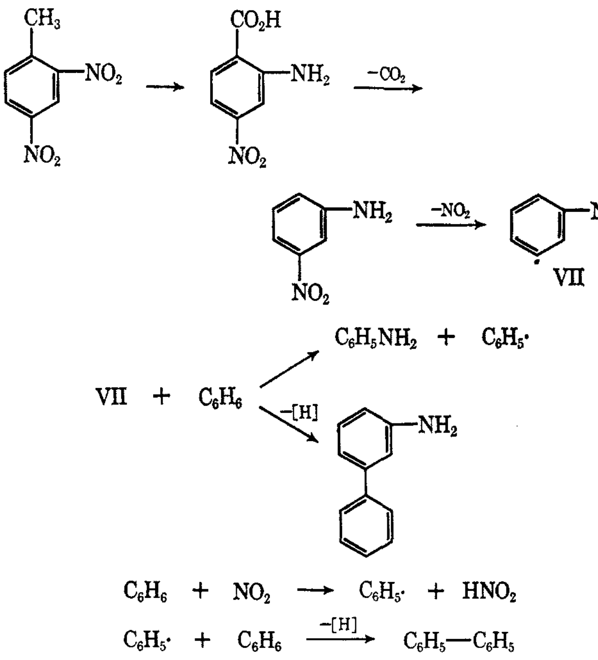
(8)



(9)

2,4-Dinitrotoluene with benzene both at 500 and 550° gave mainly biphenyl, and about one-fourth as much each of aniline and aminobiphenyl. The *m*-aminophenyl radical (VII) evidently abstracts hydrogen almost as readily as it adds to aromatic systems (Scheme I).

SCHEME I



$$C_6H_6 + NO_2 \longrightarrow C_6H_5\cdot + HNO_2$$

$$C_6H_5\cdot + C_6H_6 \xrightarrow{-[H]} C_6H_5{-}C_6H_5$$

The reaction products of 2,4-dinitrotoluene with methanol alone, with methanol plus benzene, and with methanol plus fluorobenzene are shown in Table X. Methyl anthranilate and aniline were major products from the anthranilic acid rearrangement followed by esterification or loss of carbon dioxide. The aryl radical formed by cleavage of the second nitro group evidently abstracts hydrogen more readily than it adds to benzene or fluorobenzene, at least at 600°. The ratio of methyl anthranilate to aniline from the methanol reaction is much higher than in the same reaction of *o*-nitrotoluene; apparently, 4-nitroanthranilic acid esterifies faster than anthranilic acid. The ratio of abstraction to addition products might change appreciably at lower temperatures to give more arylated methyl anthranilates.

TABLE X

REACTIONS OF 2,4-DINITROTOLUENE[a]

Reactant, mol	Methanol, 1.2	Methanol, 0.625; benzene, 0.5	Methanol, 0.625; fluorobenzene, 0.5
Total weight of products, g	2.75	5.25	2.5
	Relative concn[b]		
Products			
Aniline	20	93	45
Biphenyl		185	
Difluorobiphenyl			4
Methylbiphenyl		133	
Fluoromethylbiphenyl			15
Methyl anthranilate	100	100	100
Methyl phenylanthranilate		25	
Methyl fluorophenylanthranilate			8

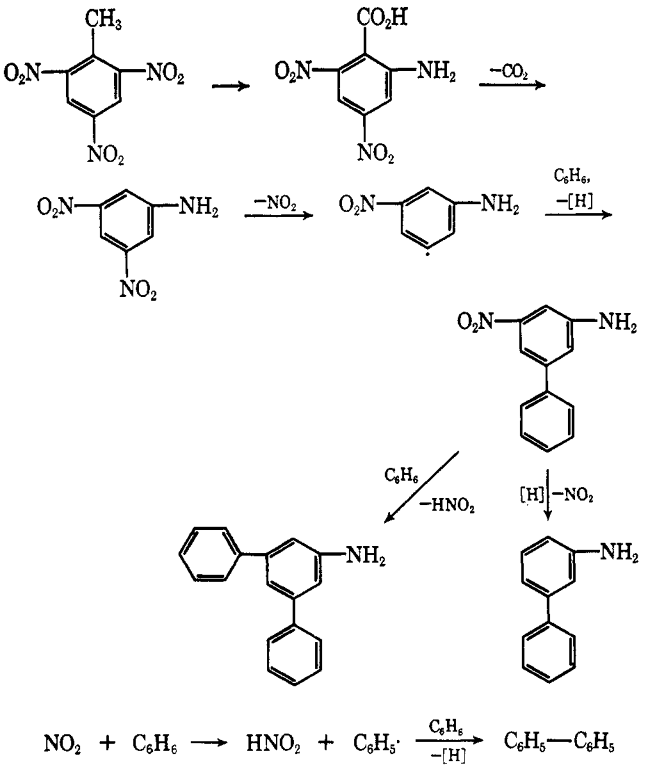
[a] Conditions: 600°, 10-sec contact time, N_2 at 20 cc/min, moles of dinitrotoluene 0.05. [b] Relative intensities in the low-voltage (7.5 V, uncorrected) mass spectrum normalized to methyl anthranilate = 100.

2,4,6-Trinitrotoluene.—The products from the reaction of 2,4,6-trinitrotoluene (TNT) with benzene at various temperatures are listed in Table XI. The predominant product in all cases was biphenyl. Benzene alone under these conditions gives only a trace of biphenyl; therefore, the relatively large amounts from the TNT reactions probably arise from phenyl radicals by way of hydrogen abstraction. The products in the table indicate the series of reactions in Scheme II. Interchange of oxygen and hydrogen atoms probably occurs before or at the same time as loss of nitro groups; were it to take place appreciably more slowly, we would anticipate finding some products that retain the methyl group (or at least the corresponding fluorene by dehydrogenation), which is not the case.

---

(13) C. Graebe, *Ber.*, **5**, 377 (1872); *Ann.*, **167**, 128 (1873); **174**, 180 (1874).
(14) A. Blank, *Ber.*, **24**, 306 (1891).

SCHEME II



Aminobiphenyl is present in appreciably greater amount than aniline. This may be because the radical from dinitroaniline must participate in two hydrogen abstractions rather than one as in the case of the aminobiphenyl radical.

With increasing temperature the products still containing nitro groups, dinitroaniline and nitroaminobiphenyl, decreased, as would be anticipated. Even at the lowest temperature, 400°, no trinitrotoluene apparently survived; it is therefore considerably less stable than *o*-nitrotoluene, 50% of which was recovered after 20 sec at 500°.

TABLE XI

PRODUCTS FROM 2,4,6-TRINITROTOLUENE WITH BENZENE AT VARIOUS TEMPERATURES[a]

Total weight of products, g	2.75	3.7	3.92	4.0
Temperature, °C	400°	450°	500°	550°
	Relative concn[b]			
Products				
Aniline	5	7	20	19
Biphenyl	100	100	100	100
Aminobiphenyl	13	29	29	27
Dinitroaniline	8	3	1	1
Nitroaminobiphenyl	2	3	0.4	0.3
Aminoterphenyl		3	5	6

[a] Conditions: 20-sec contact time, N_2 at 20 cc/min, moles of TNT:benzene 0.05:0.5. [b] Relative intensities in the low-voltage (7.5 V, uncorrected) mass spectrum normalized to biphenyl = 100.

The present work has shown a striking difference in the reactions of *o*-nitrotoluene and substituted *o*-nitrotoluenes from those of the *meta* and *para* isomers. We are pursuing this study further by examining the behavior of labeled and unlabeled *o*-nitroethylbenzene, *o*-nitrocumene, and *o*-nitro-*t*-butylbenzene at 600°.

Registry No.—Benzene, 71-43-2; benzene-d_6, 1076-43-3; chlorobenzene, 108-90-7; methanol, 67-56-1; *o*-nitrotoluene, 88-72-2; *m*-nitrotoluene, 99-08-1; *p*-nitrotoluene, 99-99-0; 2,4-dinitrotoluene, 121-14-2; 2,4,6-trinitrotoluene, 118-96-7.

Acid-Catalyzed Cleavage of 1-Methylnortricyclene[1]

JAMES H. HAMMONS, ELIZABETH K. PROBASCO, LEE A. SANDERS, AND E. JOYCE WHALEN

Department of Chemistry, Swarthmore College, Swarthmore, Pennsylvania 19081

Received January 22, 1968

The preparation of 1-methylnortricyclene (**7**) was accomplished in good yield from 1-methyl-2-norbornanone *p*-toluenesulfonylhydrazone (**6**). The kinetic product from reaction of **7** with acetic acid was 2-*endo*-methyl-2-*exo*-norbornyl acetate (**9**), which was slowly converted into 1-methyl-2-*exo*-norbornyl acetate (**3**), and 2-*exo*-methyl-2-*endo*-norbornyl acetate (**10**) under the reaction conditions. Cleavage with acetic acid-O-*d* gave a mixture of **3**, **9**, and **10** containing up to five deuteriums per molecule. Treatment of the acetates with alumina, ozonolysis, and washing with aqueous alkali gave monodeuterated 2-norbornanone (**1**). The infrared spectrum of this material showed that the deuterium was 62 ± 3% 6-*endo* and 38 ± 3% 6-*exo*, demonstrating that cleavage of the cyclopropyl C–C bond by the electrophile, D^+, occurs with predominating retention of configuration. The results are accounted for in terms of a carbonium ion intermediate which can react by any of five paths; qualitative conclusions are presented on the way in which the intermediate partitions among these paths.

Studies of cleavage of the cyclopropane ring in tricyclo[2.2.1.$0^{2,6}$]heptanes with acetic acid have been concerned for the most part with the question of product distribution. In the case of unsymmetrically substituted tricyclo[2.2.1.$0^{2,6}$]heptanes, any one of three bonds may cleave, and each can add an unsymmetrical reagent like acetic acid with either of two modes of orientation. Thus, as many as six different products can be formed, neglecting stereochemistry. Compounds such as apocyclene[2] (3,3-dimethyltricyclo-[2.2.1.$0^{2,6}$]heptane) and epicyclene[3] (3,3,4-trimethyltricyclo[2.2.1.$0^{2,6}$]heptane), which have hydrogens on all three cyclopropyl carbons, give mixtures of isomeric acetates on reaction with acetic acid. In contrast, derivatives of 1-methylnortricyclene (**7**) have been reported to be converted cleanly into substituted 1-methyl-2-norbornyl acetates;[4] 1-methylnortricy-

---

[1] This research was supported in part by a National Science Foundation Undergraduate Research Participation grant to the Department of Chemistry, Swarthmore College.

[2] S. S. Nametkin and Z. Alexandrova, *J. Russ. Phys. Chem. Soc.*, **57**, 395 (1926); S. S. Nametkin and Z. Alexandrova, *Ann.*, **467**, 191 (1928).

[3] S. S. Nametkin and L. Bryusova, *J. Russ. Phys. Chem. Soc.*, **62**, 333 (1930).

[4] S. Moycho and F. Zienkowski, *Ann.*, **340**, 17 (1905).