

The Reaction of Nitromethane with Benzene at 500°

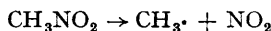
By ELLIS K. FIELDS*

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

and SEYMOUR MEYERSON

(Research and Development Department, American Oil Company, Whiting, Indiana)

THERMAL decomposition of nitromethane at 5–400 mm,¹ as well as at 12–40 atmospheres,² has been thoroughly investigated, and the first-order kinetics have been derived by analysis of the gaseous products. The initial step in the decomposition is postulated as



We have found that the $\text{C}_6\text{H}_5\text{--NO}_2$ bond in nitrobenzene breaks above 400° to give a phenyl radical and NO_2 .³ In the presence of benzene, the major products arise by arylation of benzene by the phenyl radicals derived from nitrobenzene, as well as by those formed from benzene *via* hydrogen-abstraction by NO_2 , as shown by the products of reaction of nitrobenzene with perdeuterobenzene.⁴

To find if nitromethane behaves similarly, a solution of 0.05 mole of nitromethane in 0.25 mole of benzene was passed through a Vycor tube filled with Vycor beads at 500° in a stream of dry nitrogen, flowing at 50 c.c./min., and the liquid products were condensed in a bulb chilled at –20°. Distillation gave 0.194 mole of benzene, 0.0046 mole of nitromethane, 0.0018 mole of methanol, and 1.9 g. of products boiling above 100°. These were analyzed by mass spectrometry and gas chromatography and are listed in the Table.

TABLE

Product	Relative concentration ^a
Toluene	1
Aniline	5
Phenol	6
<i>N</i> -Methylenedianiline	16
<i>N</i> -Methylaniline	21
Nitrobenzene	0.4
Biphenyl	100
Aminobiphenyl	10
<i>N</i> -Benzylideneaniline	3

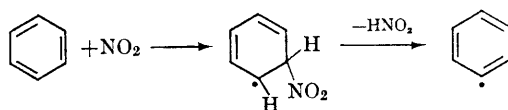
^a Relative intensities in the low-voltage (7.5 v, uncorrected) mass spectrum, normalized to biphenyl = 100.

Under identical conditions, benzene alone (0.25 mole) gave 0.024 g. of product, of which 92% was biphenyl and 8% terphenyl.

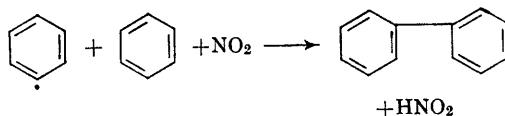
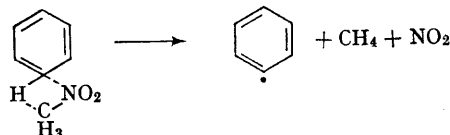
With the exception of toluene, *N*-methylaniline, *N*-methylenedianiline, and *N*-benzylideneaniline,

the products in the Table also resulted from the reaction of nitrobenzene with benzene, although not in the identical ratios.⁴ This would suggest the formation of nitrobenzene or other common intermediates in the reaction of nitromethane with benzene.

Although nitrobenzene was among the products, the small concentration and the large amount of biphenyl suggest that phenyl radicals are formed directly:



The fate of HNO_2 at high temperatures has been described.⁵ A concerted reaction of benzene with nitromethane to produce phenyl radicals is at best



only minor; nitromethane with C_6D_6 gave CH_4 and CH_3D in approximately a 6 : 1 ratio.

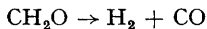
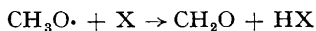
The major portion of phenyl radical adds to the aromatic system and gives biphenyl. By contrast, the major portion of methyl radicals from nitromethane gave carbon monoxide and methane; very little toluene was formed. Methyl radicals generated in a variety of ways add to benzene and other aromatic compounds in about 10% yields;⁶ methyl-radical affinities of benzene derivatives roughly parallel the relative rates of attack on the same compounds by phenyl radicals.⁷ Methylations are not as clear-cut as arylations, because the primary products contain benzylic hydrogens which are readily abstracted by free radicals.⁸

Nonetheless, if formed, an appreciable amount of toluene and dibenzyl should have survived.

Methanol was formed in a small amount, probably by rearrangement of nitromethane similar to that of nitrobenzene, both under electron impact in the mass spectrometer to give the $C_6H_5O^+$ ion⁹ and at high temperatures to give phenol:^{3,4}



Either the nitro-nitrite rearrangement is not as extensive for nitromethane as for nitrobenzene, or the methoxy-radical prefers to lose a hydrogen to some abstracting species such as NO or NO₂ and go to formaldehyde:†



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† The reaction $CH_3O \cdot + CH_3 \cdot \rightarrow CH_2O + CH_4$; $E = -1.5$ kcal./mole has been established in the photolysis of methyl acetate over the temperature range of 29–217°; M. H. J. Wijnen, *J. Chem. Phys.*, 1957, **27**, 710.

‡ A mixture of *N*-benzylideneaniline and aminobiphenyl was not cleanly resolved by gas chromatography on a column of diethylene glycol sebacate on Chromosorb W. However, the presence among the reaction products of incompletely resolved components of the identical retention times, together with the low-voltage mass-spectral analysis, suggested the identities of these products.

¹ H. A. Taylor and V. V. Vesselovsky, *J. Phys. Chem.*, 1935, **39**, 1095; C. Fréjacques, *Compt. rend.*, 1950, **231**, 1061; T. L. Cottrell, T. E. Graham, and T. J. Reid, *Trans. Faraday Soc.*, 1951, **47**, 584; P. Gray, A. D. Yoffe, and L. Roselaar, *ibid.*, 1955, **51**, 1489; L. J. Hillenbrand and M. L. Kilpatrick, *J. Chem. Phys.*, 1953, **21**, 525.

² K. H. Mueller, *J. Amer. Chem. Soc.*, 1955, **77**, 3459; A. Makovsky and T. B. Gruenwald, *Trans. Faraday Soc.*, 1959, **55**, 1952.

³ E. K. Fields and S. Meyerson, *J. Amer. Chem. Soc.*, 1967, **89**, 724.

⁴ E. K. Fields and S. Meyerson, "Arylation by Aromatic Nitro-compounds at High Temperatures. Part 2. Reactions of Nitrobenzene Alone and With Benzene and Benzene-*d*₆," in the press.

⁵ A. P. Cox and R. L. Kuczowski, *J. Amer. Chem. Soc.*, 1966, **88**, 5071, and references cited therein.

⁶ E. L. Eliel, K. Rabindran, and S. H. Wilen, *J. Org. Chem.*, 1957, **22**, 5731; L. F. Fieser, R. Clapp, and W. Daudt, *J. Amer. Chem. Soc.*, 1942, **64**, 2052.

⁷ D. H. Hey and G. H. Williams, *J. Chem. Phys.*, 1955, **23**, 757.

⁸ G. H. Williams, "Homolytic Aromatic Substitutions," Pergamon Press, New York, 1960, ch. 6.

⁹ J. H. Beynon, R. A. Saunders, and A. E. Williams, *Ind. chim. belge*, 1964, **29**, 311; S. Meyerson, I. Puskas, and E. K. Fields, *A.C.S. Petroleum Preprints*, 1966, **11**, No. 3, 231; *J. Amer. Chem. Soc.*, 1966, **88**, 4974.

Traces of formaldehyde were found, as well as considerable amounts of hydrogen and carbon monoxide, much of which could have come from decomposition of formaldehyde.

Three products listed in the Table apparently arose by retention of the carbon-nitrogen bond in nitromethane: methylaniline, methyleneaniline, and benzylideneaniline.‡ From the diversity of products formed in its reaction with benzene, nitromethane evidently decomposes at elevated temperatures according to a scheme far more complex than hitherto described. To elucidate the mechanism of this decomposition, we are presently studying in detail the reactions of nitromethane at 500°, alone and with C₆D₆ as well as with other aromatic and heterocyclic compounds.