

Formation of Benzyne by the Decomposition of *N*-Nitrosoacetanilide and *N*-(2-Iodophenyl)-*N*-nitrosobenzamide

By B. H. KLANDERMAN and D. P. MAIER

(Research Laboratories, Eastman Kodak Company, Rochester, New York 14650)

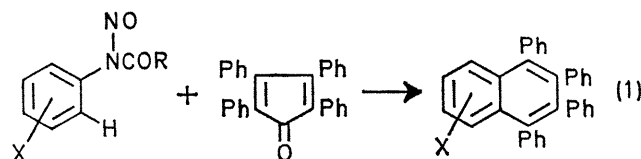
and G. W. CLARK and J. A. KAMPMEIER*

(Department of Chemistry, University of Rochester, Rochester, New York 14627)

Summary Decomposition of *N*-nitrosoacetanilide and *N*-(2-iodophenyl)-*N*-nitrosobenzamide in benzene in the presence of 1,4-dimethoxyanthracene gives B- and A-ring adducts in ratios which are consistent with those reported for other benzyne precursors.

EXPERIMENTAL evidence on the formation of arynes by the thermal decompositions of *N*-nitrosoacylanilides is confusing. The decompositions of various substituted nitrosoacylanilides in benzene or carbon tetrachloride in the presence of tetraphenylcyclopentadienone (TPCP) give the apparent aryne adducts,^{1,2} in yields which depend upon solvent and substitution, but the pattern of yields does not lead to any simple mechanistic conclusion.² Although the TCPCP adducts are usually formed by the formal loss of an ortho-hydrogen [equation (1)], one case involves loss of an *ortho*-iodine.³ Some nitrosoacylanilides give adducts with TCPCP, but fail other classical aryne tests such as *cine*-substitution and cycloaddition with furan.² The latter observation, and other aspects of these decompositions, led to the proposal that non-aryne species reacted with TCPCP.^{1,2} Cadogan recently showed^{1,4} that the precursor of the TCPCP adduct in the decomposition of 4-*t*-butyl-*N*-nitrosoacetanilide is bidentate, thereby ruling out the 4-*t*-butyl carbonium ion, carbanion, or radical as the reactive species. In addition,⁴

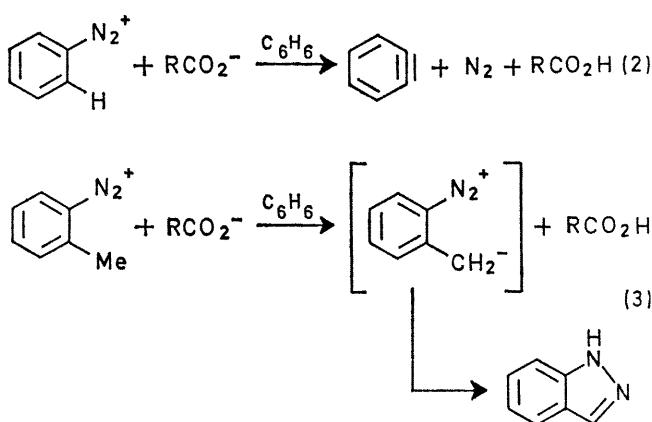
the reactive species from *N*-nitrosoacetanilide (NNA) competes for substituted TCPCP's and anthracenes according to rate ratios observed with anthranilic acid and pentyl nitrite as the benzyne source. We report here independent experiments which lead to the same conclusion.



Previous work established 1,4-dimethoxyanthracene (DMA) as a useful probe for the intermediacy of benzyne. Both A- and B-ring addition occurs; the B/A values are 2.1—3.5 : 1 for a series of six benzyne precursors.⁵ We have applied this test to the decompositions of NNA and *N*-(2-iodophenyl)-*N*-nitrosobenzamide (INB). Each nitroso-compound† was decomposed in benzene at 60—65° in the presence of DMA, using both the nitroso-compound and DMA in excess in separate experiments. The ratios of B/A-ring adducts in the four experiments were determined gas-chromatographically to be: NNA, 2.4 : 1, 2.9 : 1; INB,

† Nitroso-compounds, prepared by nitrosation⁶ of the corresponding amines, were washed with large quantities of cold water and dried at 0.05 mm; NNA, m.p. 52—53° (decomp) (E. Bamberger, *Ber.*, 1894, **27**, 914); INB, m.p. 85° (decomp.).³

2:6:1, 3:4:1. Gas chromatography-mass spectrometry of the same reaction mixtures permitted positive identification of the B- and A-ring adducts, and other components of the mixtures were characterized. Mass spectral patterns were compared with those of authentic materials when possible. The following components of the NNA mixtures were observed: biphenyl (a major product), *p*-quaterphenyl, 1,4-dimethoxy-9-phenylanthracene (a major product), a 1,4-dimethoxyphenylanthracene, a 1,4-dimethoxyphenyldihydroanthracene, 1,4-dimethoxy-9-phenyltritycene or a 1,4-dimethoxydiphenylanthracene, B-ring adduct, and A-ring adduct. In addition to the DMA-benzene adducts, the following components of the INB mixtures were observed: 1,2-di-iodobenzene, 2-iodobiphenyl (the major product), *o*-terphenyl, 2-iodophenyl benzoate, 2'-iodobenzanilide, 1,4-dimethoxy-9-(2-iodophenyl)anthracene, a biphenylbenzoate, and other 1,4-dimethoxy-(2-iodophenyl)anthracenes.



These intramolecular competitions (B-ring/A-ring) agree with the intermolecular results reported by Cadogan,⁴ and we conclude that benzyne is formed in the decomposition of NNA and INB. The same conclusion was reached from other evidence on the decomposition of INB.³ Many of the other products of these decompositions are from normal radical pathways. The decompositions of acylnitrosoanilides are recognized as sources of both radicals and ions.⁶⁻⁸

A route from NNA to phenyl radicals to benzyne is unattractive,^{1,4} but an acid-base reaction of the diazonium acrylate ion pair [equation (2)], provides a convenient pathway.^{1,8} This route has analogy in the formation of indazole^{6,8-10} by the decomposition of acylnitroso-*o*-toluidides [equation (3)].

Rüchardt¹¹ and Cadogan¹² recently described alternative routes to diazonium-acrylate ion pairs. We have made similar, independent observations. For example, decomposition of *N*-nitroso-*N*-acetyl-*o*-toluidine (NAT) in benzene gives indazole⁹ in yields as high as 85%, presumably *via* the *o*-tolyl diazonium-acetate ion pairs [equation (3)].[‡] Diazotization of *o*-toluidine (mole ratio amine: acetic acid: isopentyl nitrite 1:2:1) in benzene provides a different approach to the same ion pair; isolated indazole yields, however, are only 20–25%. The marked difference in indazole yields by these alternative routes is attributed¹³ to the water formed in the diazotization. Indazole is not formed (<1% yield) by the reaction of *o*-toluidine with 1 equiv. of isopentyl nitrite in benzene in the absence of added acid. In a related experiment, toluene-*o*-diazonium chloride was treated with anhydrous sodium acetate in ether-acetic acid to give indazole (38–65%). Use of sodium acetate trihydrate gives only traces of indazole. Because of the hazard, samples of toluene-*o*-diazonium chloride were not rigorously dried and the erratic yields of indazole are ascribed to the presence of varying amounts of water. Benzyne is obtained by the reaction of 2-iodobenzenediazonium chloride with anhydrous sodium acetate in diglyme-acetic acid containing TPCP, as shown by the formation of tetraphenylnaphthalene¹⁴ (7–12%).

The diazonium-acrylate ion pair from nitrosoacylanilides clearly has competitive ionic and radical chain options. For example, the DMA experiments described herein reveal both ionic (benzyne) and homolytic (biphenyls) products. The sensitivity of these nitrosoacylanilide decompositions to solvent changes,^{1-3,10} the nature of the gegenion,^{2,15} structural features,^{2,6,10} and the presence of water^{2,12,13} is probably not surprising in view of the complex equilibria and competitions involved.¹⁶

This work was supported, in part, by the National Science Foundation.

(Received, April 22nd, 1971; Com. 620.)

[‡] Thermal decomposition of *o*-tolylazotriphenylmethane in benzene does not give indazole (<1% detectability); S. Rosenbaum and J. A. Kampmeier, unpublished observations.

¹ D. L. Brydon, J. I. G. Cadogan, D. M. Smith, and J. B. Thomson, *Chem. Comm.*, 1967, 727.

² J. I. G. Cadogan, M. J. P. Harger, and J. T. Sharp, Preprints of the Division of Petroleum Chemistry, Inc., American Chemical Society, 1969, Vol. 14, No. 2, p. C19.

³ J. A. Kampmeier and A. B. Rubin, *Tetrahedron Letters*, 1966, 2853; cf. D. L. Brydon and J. I. F. Cadogan, *J. Chem. Soc. (C)*, 1968, 819; G. W. Clark and J. A. Kampmeier, *Chem. Comm.*, 1970, 996.

⁴ J. I. G. Cadogan, J. Cook, M. J. P. Harger, and J. T. Sharp, *Chem. Comm.*, 1970, 299.

⁵ B. H. Klanderma and T. R. Criswell, *J. Amer. Chem. Soc.*, 1969, 91, 510; Preprints of the Division of Petroleum Chemistry, Inc. American Chemical Society, 1969, Vol. 14, No. 2, p. C36.

⁶ P. Miles and H. Suschitzky, *Tetrahedron*, 1962, 18, 1369; H. Suschitzky, *Angew. Chem.*, 1967, 79, (636).

⁷ 'Homolytic Aromatic Substitution,' G. H. Williams, Pergamon, London, 1960, pp. 29, 57; R. Huisgen and G. Horeld, *Annalen*, 1949, 562, 137.

⁸ C. Rüchardt and C. C. Tan, *Chem. Ber.*, 1970, 103, 1774 and references cited therein.

⁹ P. Jacobson and L. Huber, *Ber.*, 1908, 41, 660.

¹⁰ R. Huisgen and H. Nakaten, *Annalen*, 1951, 573, 181; 1954, 586, 84.

¹¹ C. Rüchardt and C. C. Tan, *Angew. Chem.*, 1970, 82, 547; *Angew. Chem. Internat. Edn.*, 1970, 9, 522.

¹² J. I. G. Cadogan, J. R. Mitchell, and J. T. Sharp, *Chem. Comm.*, 1971, 1.

¹³ G. W. Clark, Ph.D. Thesis, University of Rochester, 1970.

¹⁴ L. F. Fieser and A. Haddadin, *Canad. J. Chem.*, 1965, 43, 1604.

¹⁵ R. W. Franck and K. Yanagi, *Tetrahedron Letters*, 1966, 2905.

¹⁶ This subject was recently reviewed; J. I. G. Cadogan, *Accounts Chem. Res.*, 1971, 4, 186.