

Pyrolytic Decomposition of *N*-Aryl-*N'*-tosyloxydi-imide *N*-Oxides

By ERNEST A. DORKO

(*U.S. Army Missile Command, Redstone Arsenal, Alabama*)

and TRAVIS E. STEVENS

(*Rohm and Haas Company, Huntsville, Alabama*)

AN unexpected result occurred when *N*-aryl-*N'*-tosyloxydi-imide *N*-oxides (I)¹ were pyrolyzed at temperatures above 80°. Nitrogen was the chief gaseous product formed. The only related reaction reported in the literature involved an *N*-alkyl-*N*-acetoxidi-imide *N*-oxide system, which on

pyrolysis gave nitrous oxide.² The Table summarizes the results of the present work.

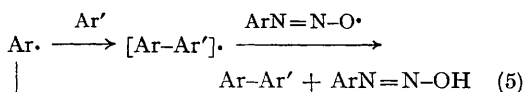
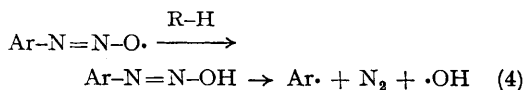
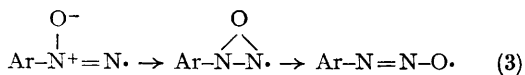
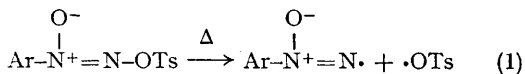
Decomposition started at 80° and became rapid in the region 90—100°. A large amount of tar was formed during the reaction. The formation of the biphenyl derivatives from aromatic solvents

TABLE

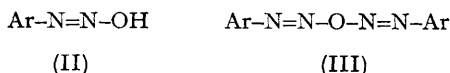
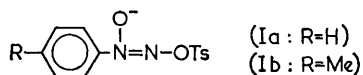
Substrate	Percent of substrate reacted	Solvent	Maximum temp. (°C)	Gaseous products ^a	Condensable products
(Ia)	85	Toluene	104	98% N ₂ 2% NO	Phenyl tosylate (25%) <i>p</i> - and <i>o</i> -Methylbiphenyl (21%)
(Ib)	100	Toluene	108	96% N ₂ 3% NO 1% N ₂ O	Tolyl tosylate (45%) <i>pp'</i> - and <i>op'</i> -Dimethylbiphenyl (19%)
(Ia)	—	Chlorobenzene	93	100% N ₂	Phenyl tosylate (47%) <i>p</i> - and <i>o</i> -Chlorobiphenyl (—)
(Ia)	100	Propan-2-ol	82	100% N ₂	Benzene (12%) Toluene- <i>p</i> -sulphonic acid (52%) Acetone

^a Composition determined by mass-spectral analysis

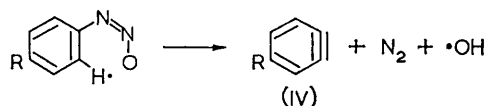
and of acetone from propan-2-ol indicates that the solvent takes part in the reaction. A mechanism consistent with these results is presented below.



From an analysis of products resulting from reaction in aromatic and nonaromatic solvents, a similarity to the Gomberg-Bachmann^{3,4} reaction and *N*-nitrosoacetanilide decomposition⁵ is immediately noted. However, under pyrolytic conditions the direct decomposition of the diazoate



(II) is more likely than prior formation of the diazo-anhydride (III) since the formation of (III) in the Gomberg-Bachmann reaction is postulated to involve an ionic species⁴ which occurrence is highly unlikely in the nonaqueous systems employed. It is also possible to conceive of a reaction step involving intramolecular hydrogen abstraction to give a benzyne (IV). However, when (Ib) was decomposed there was no occurrence of scrambling of the position of the methyl group in the tolyl tosylate produced.



While there is no direct experimental evidence⁶ to eliminate the alternative, step (3) postulates that the oxygen atom migrates rather than the aryl group.

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¹ T. E. Stevens, *J. Org. Chem.*, 1964, **29**, 311.

² E. H. White and D. W. Grisley, Jr., *J. Amer. Chem. Soc.*, 1961, **83**, 1191.

³ D. H. Hey and W. A. Waters, *Chem. Rev.*, 1937, **21**, 169.

⁴ C. Rüchardt and E. Merz, *Tetrahedron Letters*, 1964, 2431; C. Rüchardt and B. Freudenberg, *ibid.*, p. 3623; G. Binsch and C. Rüchardt, *J. Amer. Chem. Soc.*, 1966, **88**, 173.

⁵ E. L. Eliel, J. G. Saha, and S. Meyerson, *J. Org. Chem.*, 1965, **30**, 2451.

⁶ The work involving coupling reactions with [α -¹⁵N]phenyl *n*- and iso-diazotate (P. F. Holt and B. I. Bullock, *J. Chem. Soc.*, 1950, 2310; G. A. Swan and P. Kelly, *ibid.*, 1954, 416) which would have some bearing on the present results involves an aqueous system and further the work does not unambiguously demonstrate oxygen attachment to the α -nitrogen in the iso-diazotate.