Notes A department for short papers of immediate interest.

Reaction of β-Bromostyrene and Dinitrogen Tetroxide. A Radical Displacement

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Addition of free radical reagents to halogenated olefins has been known to lead to adducts that have lost a halogen atom.[1] For instance, various alkyl radicals and 1,2-dichloroethylene interacted to produce 1-chloro-2-alkylethylenes,[2] and the dinitrogen tetroxide–allyl iodide reaction yielded 3-nitropropene.[3]

The addition of dinitrogen tetroxide to β-bromostyrene now has been found to give β-nitrostyrene as the major product, apparently by a radical path as outlined.[4] Slow addition of dinitrogen tetroxide to an ether solution of the bromostyrene produced the nitrostyrene (67%) and

$$NO_2 + C_6H_5\text{—}CH\text{=}CHBr \longrightarrow$$
$$[C_6H_5\text{—}\underset{\cdot}{C}H\text{—}CHBrNO_2] \longrightarrow C_6H_5\text{—}CH\text{=}CHNO_2 + Br\cdot$$

even inverse addition of the styrene to the tetroxide in ether yielded β-nitrostyrene (47%). Formation of the relatively stable intermediate radical which may reversibly eliminate the NO_2 radical or which may eliminate a bromine atom to give the unreactive β-nitrostyrene makes this a favorable case for the observation of such a radical displacement reaction.

The other products of this β-bromostyrene reaction undoubtedly were the saturated compounds derived from the addition of bromine and dinitrogen tetroxide to β-bromostyrene. Only one of the possible adducts, a dibromonitrophenylethane, m.p. 73–74°, was isolated. The nitro group absorption at 1540 cm.$^{-1}$ in the infrared spectrum of this adduct indicated it was 1,1-dibromo-2-nitro-2-phenylethane; absorption at higher wave length would be expected for the isomeric 1,2-dibromo-1-nitro-2-phenylethane.[5]

EXPERIMENTAL

Addition of dinitrogen tetroxide to β-bromostyrene. A solution of 4.3 g. (23.5 mmoles) of β-bromostyrene in 100 ml. of ether was stirred at 10° while 25 mmoles of dinitrogen tetroxide[6] was swept into the ether solution in a nitrogen stream over a 1-hr. period. The mixture was stirred for an additional hour at 15°. Water (100 ml.) then was added, and the ether layer was separated and washed with water and 10% sodium bicarbonate solution. Evaporation of the ether left 4.72 g. of residue. The residue was dissolved in methylene chloride–pentane and chromatographed on a silica gel column as described previously.[4] The first fraction eluted, 1.60 g., contained almost no β-nitrostyrene as evidenced by infrared spectra of the cuts. A 0.83-g. portion of this, probably 1,1-dibromo-2-nitro-2-phenylethane, solidified, and was recrystallized from hexane, m.p. 73–74°.

Anal. Calcd. for $C_8H_7Br_2NO_2$: C, 31.10; H, 2.28; N, 4.53. Found: C, 31.31; H, 2.39; N, 4.38.

The next fraction eluted was β-nitrostyrene, 2.36 g., (67%), m.p. 56–57°; the mixed melting point with an authentic sample of the same melting point was not depressed. The infrared spectrum was identical with that of an authentic specimen.

The last fractions eluted from the column, a total of 0.71 g. of oily material showing hydroxyl absorption in the infrared spectrum, were not characterized.

Addition of β-bromostyrene to dinitrogen tetroxide. A solution of 28 mmoles of dinitrogen tetroxide in 100 ml. of ether was stirred at 10° while 23.5 mmoles of β-bromostyrene in 15 ml. of ether was added over 20 min. The reaction mixture was stirred in a nitrogen atmosphere during this addition and for an additional hour at 15°. The reaction mixture then was worked up as described above. From 4.40 g. of crude residue was obtained 1.55 g. of material eluted prior to β-nitrostyrene; a 0.73-g. portion of this solidified and melted at 74° after hexane recrystallization. The β-nitrostyrene fraction weighed 1.66 g. (47%), m.p. 56–57°, identified as described above.

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(1) Several examples are given in C. Walling, *Free Radicals in Solution,* Wiley and Sons, New York, 1957, pp. 268–271.

(2) L. P. Schmerling and J. P. West, *J. Am. Chem. Soc.,* **71,** 2015 (1949); **75,** 6216 (1953).

(3) J. F. Brown, Jr., General Electric Company, personal communication.

(4) The homolytic nature of the dinitrogen tetroxide–olefin reaction appears to be well established; see H. Shechter, J. J. Gardikes, and A. H. Pagano, *J. Am. Chem. Soc.,* **81,** 5421 (1959) and T. E. Stevens, *J. Am. Chem. Soc.,* **81,** 3593 (1959).

(5) J. F. Brown, Jr., *J. Am. Chem. Soc.,* **77,** 6341 (1955).

(6) Obtained from the Matheson Co. and distilled before use.

The Hydrogenation of Nitriles to Primary Amines

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The catalytic hydrogenation of nitriles to primary amines is a reaction of considerable importance in organic synthesis and has been the subject of many investigations because good yields of primary amines are frequently difficult to obtain. The difficulty apparently arises because the re-