

SHORT
COMMUNICATIONS

p-Bromo(diacetoxyiodo)benzene, an Efficient Oxidant for Conversion of Oximes into Nitroso Compounds

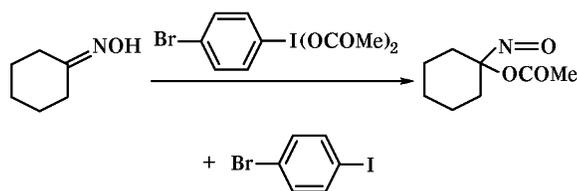
E. V. Zhutov, Yu. V. Skorniyakov, M. V. Proskurina, and N. S. Zefirov

Lomonosov Moscow State University, Moscow, Russia

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Compounds of hypervalence iodine are extensively studied in the recent years in versatile reactions, and many among them became common reagents for organic synthesis. In particular, in 1991 a reaction was investigated between iodobenzene dichloride and aromatic or aromatic-aliphatic oximes of carbonyl compounds in the presence of pyridine [1] which might be regarded as preparative procedure for di-oximation under mild conditions. In 1980 Corey [2] developing a general method for converting oxo compounds into nitro compounds carried out alicyclic oximes oxidation with hypochlorites. He stated basing on quickly arising and rapidly disappearing blue color of the reaction mixture that in this oxidation process intermediately formed chloronitroso compounds.

We demonstrated that reaction of iodo(*p*-bromobenzene) diacetate with oximes of acetone, cyclohexanone, and cyclopentanone afforded in high yields the corresponding 1-nitrosoacetoxy derivatives.



Therewith the *p*-bromoiodobenzene can be quantitatively isolated from the reaction mixture and can serve as initial compound for the synthesis of the corresponding diacetate without losses.

gem-Acetoxy-nitroso compounds. To a stirred mixture of iodo(*p*-bromobenzene) diacetate (0.02 mol) and 10 ml of glacial acetic acid at -15°C was added dropwise within 5 min a solution of ketoxime (0.02 mol) in 5 ml of glacial acetic acid. In 15 min the reaction mixture was diluted with 50 ml

of ether, 50 ml of water was added, ether layer was separated, and the water layer was extracted with ether. The ether solution was washed with water (2×50 ml) and 5% solution of sodium carbonate (2×50 ml). The ether solution of bright blue color was dried over Na_2SO_4 , the solvent was evaporated, and from the semisolid residue the reaction product was distilled in a high vacuum at room temperature (or at slight heating) into a receiver cooled with liquid nitrogen. Thus a crude reaction product was obtained containing as impurities a little of *p*-bromoiodobenzene and of decomposition products of *gem*-acyloxy-nitroso compound. The residue after distillation was recrystallized from ethanol to obtain *p*-bromoiodobenzene in quantitative yield. The crude target product was subjected to repeated distillation in a high vacuum collecting the distillate in a trap cooled with liquid nitrogen. Thus we obtained the *gem*-acyloxy-nitroso compounds of analytical purity as dark-blue liquids (20°C).

2-Acetoxy-2-nitrosopropane. From 8.02 g (0.02 mol) of iodo(*p*-bromobenzene) diacetate and 1.46 g (0.02 mol) of acetone oxime was obtained 2.3 g (88%) of 2-acetoxy-2-nitrosopropane and 5.4 g (95%) of *p*-bromoiodobenzene. IR spectrum, ν , cm^{-1} : 1720 (C=O), 1380 (N=O). ^1H NMR spectrum (DMSO- d_6), δ , ppm: 1.48 s (6H), 2.20 s (3H). ^{13}C NMR spectrum (DMSO- d_6), δ , ppm: 15.034 (2CH_3), 20.123 (1CH_3), 64.921 (C—N), 168.795 (C=O). Published data see in [3].

1-Acetoxy-1-nitrosocyclohexane. From 8.02 g (0.02 mol) of iodo(*p*-bromobenzene) diacetate and 2.26 g (0.02 mol) of cyclohexanone oxime was obtained 3.2 g (94%) of 1-acetoxy-1-nitrosocyclohexane and 5.5 g (97%) of *p*-bromoiodobenzene. IR spectrum, ν , cm^{-1} : 1740 (C=O), 1370 (N=O). ^1H NMR spectrum (DMSO- d_6), δ , ppm: 2.20 s (3H), 1.4–1.9 m (10H). Published data see in [3].

1-Acetoxy-1-nitrosocyclopentane. From 8.02 g (0.02 mol) of iodo(*p*-bromobenzene) diacetate and 1.98 g (0.02 mol) of cyclopentanone oxime was obtained 2.6 g (83%) of 1-acetoxy-1-nitrosocyclopentane and 5.2 g (92%) of *p*-bromiodobenzene. ^1H NMR spectrum (CDCl_3), δ , ppm: 1.70–2.0 m (8H), 2.13 s (3H). ^{13}C NMR spectrum (CDCl_3), δ , ppm: 20.698, 33.591 (4CH_2), 25.103 (CH_3), 130.590 (C–N), 168.791 (C=O). Found, %: C 53.46; H 7.06; N 8.98. $\text{C}_7\text{H}_{11}\text{NO}_3$. Calculated, %: C 53.50; H 7.05; N 8.91.

IR spectra were recorded on spectrophotometer Specord UR-20 from solutions of compounds synthesized in chloroform or mulls in mineral oil. ^1H and ^{13}C NMR spectra were registered on spectrometers Bruker AC-300, Bruker AC-200. Chemical shifts of

^1H and ^{13}C nuclei are given in δ scale measured from chemical shifts of the corresponding solvent peaks or from internal reference TMS.

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