THE SYNTHESIS OF 1-ARYL-2-BROMODIAZENE 1-OXIDES

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UDC 542.91:547.545:546.173'141

Aryl azoxybromides have not yet been reported. We propose a simple method for the synthesis of such compounds by the reaction of arylnitroso compounds with NBr_3 in an inert solvent. NBr_3 is generated *in situ* from ammonia and brominating agents such as N-bromosuccinimide (NBS) or dibromoisocyanurate (DBI) [1].

$$\underset{\text{(Ia, b)}}{ArNO} \xrightarrow[2.\ NH_3]{1.\ NBS} \underset{\text{(IIa, b)}}{ArN(O)=NBr}$$

Synthesis of (II). A sample of 300 ml (13.3 mmoles) gaseous ammonia was introduced using a syringe with stirring into a suspension of 10 mmoles (I) and 40 mmoles NBS in 1:1 CH_2Cl_2–CH_3CN at from −60 to −70°C and then let warm to 0°C. The mixture was maintained for 1 h at 0°C. The solvent was distilled off in vacuum and (II) was extracted with pentane from the solid residue.

DBI, which permits the use of CH_2Cl_2 for the extraction, is conveniently employed for the preparation of (IIb), which has poor solubility in pentane.

The yield of (IIa) was 90%, mp 46-47°C (from pentane). Mass spectrum (for ^{79}Br and ^{35}Cl isotopes), *m/z* (relative intensity, %): 200 (11, $M^{+\cdot}$), 156 (7, $M^{+\cdot} - N_2O$), 107 (29, $M^{+\cdot} - NBr$), 94 (18), 77 (100, $M^{+\cdot} - N_2OBr$). IR spectrum in KBr (ν, cm^{-1}): 1470 (N(O)N). PMR spectrum in $CDCl_3$ (δ, ppm from TMS): 7.47 (*m*-H), 7.56 (*p*-H), 8.05 (*o*-H). ^{13}C NMR spectrum in $CDCl_3$ (δ, ppm from TMS): 122.51 (*o*-C), 129.21 (*m*-C), 132.48 (*p*-C), 145.13 (*ipso*-C). ^{14}N NMR spectrum (δ, ppm from $MeNO_2$): −38.3 (width at half-height, $\Delta\nu_{1/2}$ = 46 Hz, N→O), −62±5 ($\Delta\nu_{1/2}$ > 400 Hz, NBr).

The yield of (IIb) was 85%, mp 76-77°C (from pentane). Mass spectrum (for ^{79}Br and ^{35}Cl isotopes), *m/z* (relative intensity, %): 302 (22, $M^{+\cdot}$), 258 (10, $M^{+\cdot} - N_2O$), 223 (5, $M^{+\cdot} - Br$), 209 (100, $M^{+\cdot} - NBr$), 179 (86, $M^{+\cdot} - N_2OBr$). IR spectrum in KBr (ν, cm^{-1}): 1446 (N(O)N). PMR spectrum in $CDCl_3$ (δ, ppm from TMS): 7.36. ^{13}C NMR spectrum in $CDCl_3$ (δ, ppm from TMS): 126.95 (*m*-C), 129.69 (*o*-C), 137.23 (*p*-C), 140.45 (*ipso*-C). ^{14}N NMR spectrum (δ, ppm from $MeNO_2$): −41.9 ($\Delta\nu_{1/2}$ = 80 Hz).

The elemental analysis data for (IIa) and (IIb) correspond to the calculated values.

We should note that the chemistry of aryl azoxyhalides has not been studied extensively [2-4]. The chemical properties of (II) differ significantly from those for the corresponding fluorides and chlorides.

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N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii SSSR, Seriya Khimicheskaya, No. 4, p. 953, April, 1990. Original article submitted November 20, 1989.

 0568-5230/90/3904-0858$12.50