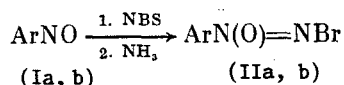


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Aryl azoxybromides have not yet been reported. We propose a simple method for the synthesis of such compounds by the reaction of arylnitroso compounds with NBr_3 in an inert solvent. NBr_3 is generated *in situ* from ammonia and brominating agents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



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^+), 156 (7, $\text{M}^+ - \text{N}_2\text{O}$), 107 (29, $\text{M}^+ - \text{NBr}$), 94 (18), 77 (100, $\text{M}^+ - \text{N}_2\text{OBr}$). 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, $\Delta\nu_{\frac{1}{2}} = 46$ Hz, $\text{N}\rightarrow\text{O}$), -62 ± 5 ($\Delta\nu_{\frac{1}{2}} > 400$ 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^+), 258 (10, $\text{M}^+ - \text{N}_2\text{O}$), 223 (5, $\text{M}^+ - \text{Br}$), 209 (100, $\text{M}^+ - \text{NBr}$), 179 (86, $\text{M}^+ - \text{N}_2\text{OBr}$). 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 ($\Delta\nu_{\frac{1}{2}} = 80$ 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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