Letters to the Editor

A new method for conjugate nitrosobromination of olefins

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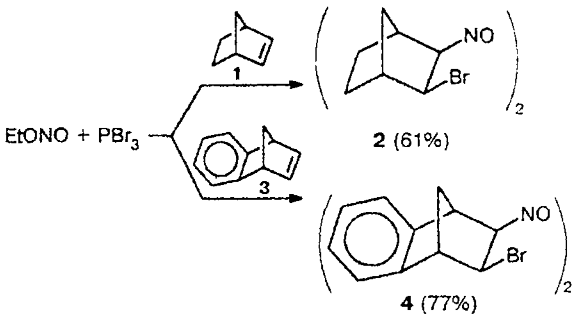
Alkyl nitrites are well known as nitrosating agents. However, carrying out their electrophilic reactions with unsaturated substrates requires additional activation by protic acids (HHal, HCO_2H, *etc.*)[1] or sulfur trioxide.[2] Earlier, we proposed a method for activating low-reactive electrophilic substrates by phosphorus halides and phosphorus oxohalides, which was successfully applied to activation of *N*-chloramines and sulfenamides.[3] For the purpose of extending this method to activation of alkyl nitrites, we studied the reaction of ethyl nitrite with olefins in the presence of PBr_3. It turned out that the action of the EtONO—PBr_3 system gives rise to products resulting from addition of nitrosyl bromide NOBr. The best yields were obtained at a PBr_3/olefin ratio of 1 : 2. Thus, nitrosobromide **2** is formed from norbornene in a high yield and crystallized as a dimer. The reaction is complete at −40 °C in 10 min. A similar result was also obtained for benzonorbornadiene **3**. In the both cases, addition occurs as a *syn-exo*-process, which is typical of reactions of nitrosyl halides with olefins of the bicyclo[2.2.1]heptane series.[4] It should be noted that dibromides and products characteristic of radical addition practically do not form under the conditions mentioned above, as occurs under the action of NOBr itself (either taken in the pure state or generated in an alkyl nitrite—HBr system).[1,5]

The proposed method thus can be used as a simple and convenient approach to nitrosobromination of olefins.



Nitrosobromination of olefins (general procedure). A solution of PBr_3 in $CHCl_3$ was added dropwise to a solution of olefin and ethyl nitrite in $CHCl_3$ with stirring and cooling to −40 °C. The reaction mixture was then heated to 20 °C; the solvent was evaporated *in vacuo* and the crystalline residue washed with a small amount of MeOH and dried in a vacuum desiccator.

***syn-exo*-3-Bromo-2-nitrosobicyclo[2.2.1]heptane (2).** The interaction of norbornene (**1**) (0.47 g, 5 mmol), EtONO (1.13 g, 15 mmol) in 70 mL of $CHCl_3$, and PBr_3 (0.68 g, 2.5 mmol) in 40 mL of $CHCl_3$ afforded compound **2** (0.62 g, 61%, dimer) as colorless crystals, m.p. 122—123 °C (from MeOH). ^1H NMR ($CDCl_3$), δ: 1.30 (m, 2 H, *endo*-C(5)H, C(6)H); 1.41 (dt, 1 H, *syn*-C(7)H, ^2J = −10.5 Hz, ^4J = 1.5 Hz); 1.60—1.75 (m, 2 H, *exo*-C(5)H, C(6)H); 2.2 (dt, 1 H, *anti*-C(7)H, ^2J = −10.5 Hz, ^4J = 1.7 Hz); 2.57 (d, 1 H, C(1)H or C(4)H, ^3J = 4.3 Hz); 2.80 (d, 1 H, C(4)H or C(1)H, ^3J = 2.7 Hz); 4.41 (dd, 1 H, C(3)H, ^3J = 6.9 Hz, ^4J = 1.7 Hz); 4.87 (dd, 1 H, C(2)H, ^3J = 6.9 Hz, ^4J =

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1.7 Hz). Found (%): C, 41.11; H, 4.93; N, 6.80. $C_{14}H_{20}Br_2N_2O_2$. Calculated (%): C, 41.20; H, 4.94; N, 6.86.

***syn-exo*-10-Bromo-9-nitrosotricyclo[6.2.1.0^{2,7}]undeca-2(7),3,5-triene (4).** The interaction of benzonorbornadiene 3 (0.57 g, 4 mmol), EtONO (0.9 g, 12 mmol) in 70 mL of $CHCl_3$, and PBr_3 (0.54 g, 2 mmol) in 40 mL of $CHCl_3$ afforded compound **4** (0.78 g, 77%, dimer) as colorless crystals, m.p. 140—141 °C (from MeOH). ^1H NMR ($CDCl_3$), δ: 2.15 (d, 1 H, *anti*-C(11)H, $^2J = -9.9$ Hz); 2.67 (dt, 1 H, *syn*-C(11)H, $^2J = -9.9$ Hz, $^4J = 1.5$ Hz); 3.62 (s, 1 H, C(1)H or C(8)H); 3.76 (s, 1 H, C(8)H or C(1)H); 4.44 (dd, 1 H, C(10)H, $^3J = 6.7$ Hz, $^4J = 1.5$ Hz); 4.96 (dd, 1 H, C(9)H, $^3J = 6.7$ Hz, $^4J = 1.5$ Hz); 7.15 (m, 2 H, CH arom.); 7.23 (m, 2 H, CH arom.). ^{13}C NMR ($CDCl_3$), δ: 46.7, 47.1, 50.0 (C(1), C(8), C(11)); 53.0 (C—Br); 71.0 (C—N); 122.2, 122.4, 127.5, 127.7, 144.0, 145.0 (C arom.). Found (%): C, 51.91; H, 3.87; N, 5.32. $C_{22}H_{20}Br_2N_2O_2$. Calculated (%): C, 52.40; H, 3.99; N, 5.55.

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Formation of 4-(1,1,1,3,3,3-hexafluoroisopropyl)-5-trifluoromethyl-2*H*-1,2,3-triazole by the oxidation of dihydrazone of 1,1,1,5,5,5-hexafluoro-4-trifluoromethylpentane-2,3-dione

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Dihydrazone of 1,1,1,5,5,5-hexafluoro-4-trifluoromethylpentane-2,3-dione (**1**) (for the synthesis, see Ref. 1) in the presence of the H_2SO_4—P_2O_5 mixture (molar ratio 3 : 1) at 100—120 °C is oxidized to 4-(1,1,1,3,3,3-hexafluoroisopropyl)-5-trifluoromethyl-2*H*-1,2,3-triazole (**2**).

1 **2**

The H_2SO_4—P_2O_5 mixture has not been previously used for the oxidation of *N,N*-unsubstituted hydrazones of aliphatic α-diketones. No formation of 2*H*-1,2,3-triazoles during their oxidation by other reagents was observed. It is noteworthy that α-dihydrazone **1**, similarly to other nonfluorinated analogs, is readily hydrolyzed in the presence of concentrated H_2SO_4 to α-ketohydrazone.[2]

4-(1,1,1,3,3,3-Hexafluoroisopropyl)-5-trifluoromethyl-2*H*-1,2,3-triazole (2): b.p. 75—77 °C (3 Torr). Found (%): N, 14.24. $C_6H_2F_9N_3$. Calculated (%): N, 14.69. ^{19}F NMR, δ: —14.5 (s, 3 F, CF_3); —9.33 (d, 6 F, $(CF_3)_2CH$, $J = 8$ Hz). ^1H NMR, δ: 13.0 (br.s, 1 H, NH); 4.5 (hept, 1 H, $H(CF_3)_2$, $J = 8$ Hz). IR, ν/cm^{-1}: 1460 m, 1560 m (unsaturated bonds); 3000 w (CH); 3270 br (NH). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 287 [M^+] (64.81); 268 $[M-F]^+$ (38.95); 248 $[M-F, HF]^+$ (17.99); 218 $[M-CF_3]^+$ (100.00); 199 $[M-CF_3, F]^+$ (7.34); 198 $[M-CF_3, HF]^+$ (2.08); 168 $[M-CF_3, 2 HF]^+$ (56.40); 69 $[CF_3]^+$ (60.17).

The MS-GLC method confirmed that compound 2 exists in the form of a single isomer. Based on the ^{19}F and ^1H NMR and IR spectroscopic data, structure 2 was assigned to the product obtained.

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