

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 benzonorbomadiene **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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References

1. J. Meinwald, Y. C. Meinwald, and T. N. Baker, *J. Am. Chem. Soc.*, 1963, **85**, 2513.
2. N. S. Zefirov, N. V. Zyk, Yu. A. Lapin, E. E. Nesterov, and B. I. Ugrak, *J. Org. Chem.*, 1995, **60**, 6771.
3. E. K. Beloglazkina, V. S. Tyurin, I. D. Titanyuk, N. V. Zyk, and N. S. Zefirov, *Dokl. Akad. Nauk*, 1995, **344**, 487 [*Dokl. Chem.*, 1995 (Engl. Transl.)].
4. R. C. Fahey, *Top. Stereochem.*, 1968, **3**, 237.
5. S. V. Vasil'ev, O. T. Burdelev, V. N. Kopranenkov, and L. M. Zakharova, *Zh. Org. Khim.*, 1971, **7**, 1622 [*J. Org. Chem. (USSR)*, 1971, **7** (Engl. Transl.)].

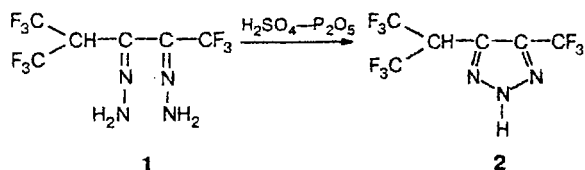
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Formation of 4-(1,1,1,3,3,3-hexafluoroisopropyl)-5-trifluoromethyl-2H-1,2,3-triazole by the oxidation of dihydrazone of 1,1,1,5,5,5-hexafluoro-4-trifluoromethylpentane-2,3-dione

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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-2H-1,2,3-triazole (**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 2H-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-2H-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.

References

I. M. D. Bargamova and L. S. German, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 1463 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, 40, 1302 (Engl. Transl.)].

2. M. D. Bargamova, M. Yu. Antipin, L. S. German, and Yu. T. Struchkov, *Dokl. Akad. Nauk*, 1993, 329, 44 [*Dokl. Chem.*, 1993 (Engl. Transl.)].

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A mild synthesis of the $[B_{12}H_{11}CO]^-$ anion

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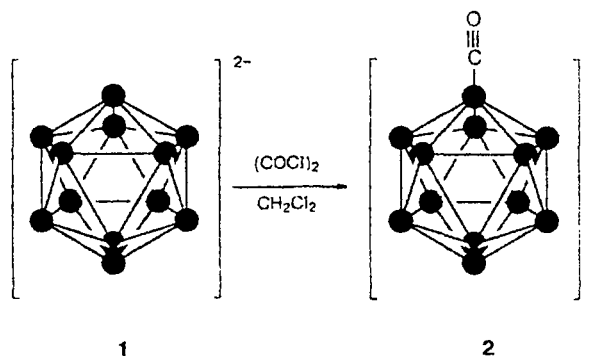
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Key derivatives in the chemistry of the dodecahydro-*closo*-dodecaborate anion $[B_{12}H_{12}]^{2-}$ (**1**) are its carbonyl derivatives $[B_{12}H_{11}CO]^-$ (**2**), 1,7- and 1,12- $[B_{12}H_{10}(CO)_2]$, which possess high reactivity and can be used for the synthesis of a variety of anion $[B_{12}H_{12}]^{2-}$ derivatives (acids, ethers, esters, amides, alcohols, amines, isocyanates, etc.).¹ In connection with this, it seems to be promising to use monocarbonyl derivative **2** for the synthesis of biologically active boron-containing compounds, which could be used in boron neutron capture therapy of malignant tumors.² Chemical properties of anion **2** remain almost unstudied, because the only reported method for preparation of $[B_{12}H_{11}CO]^-$ is an inconvenient, for laboratory practice, synthesis from acid $(H_3O)_2[B_{12}H_{12}] \cdot nH_2O$ and CO at 1000 atm in the presence of $Co_2(CO)_8$ as the catalyst.³ Only transformation of $[B_{12}H_{11}CO]^-$ to $[B_{12}H_{11}NCO]^{2-}$, when it reacts with sodium azide has been reported.⁴ It is also known⁵ that reaction of decahydro-*closo*-decaborate anion $[B_{10}H_{10}]^{2-}$ with oxalyl chloride results in formation of monocarbonyl derivative $[2-B_{10}H_9CO]^-$.

We found that reaction of tetrabutylammonium salt of $[B_{12}H_{12}]^{2-}$ with oxalyl chloride in CH_2Cl_2 , carried out under mild conditions at 20 °C and atmospheric pressure, results in quantitative conversion of anion **1** to monocarbonyl derivative $[B_{12}H_{11}CO]^-$.

In the IR spectrum of product **2**, there are intensive absorption bands at 2507 and 2172 cm^{-1} that are as-



signed to the stretching vibrations of the B—H bonds of the boron skeleton (2480 cm^{-1} for $[B_{12}H_{12}]^{2-}$) and the $[-C\equiv O]^+$ group, respectively. The ^{11}B NMR spectrum of product **2** consists of three doublets at $\delta -3.0$ ($J = 142$ Hz), -12.1 ($J = 129$ Hz), and -12.1 ($J = 135$ Hz) and a singlet at $\delta -33.5$ (with the integral intensity ratio of 1 : 5 : 5 : 1).

Anion **2** is also formed when oxalyl chloride reacts either with triethylammonium salt $[B_{12}H_{12}]^{2-}$ in MeCN or with tetrabutylammonium salt $[B_{12}H_{12}]^{2-}$ in THF.

Carbonyl derivative **2** is readily hydrated to form the corresponding carboxy derivative $[B_{12}H_{11}COOH]^{2-}$ (**3**) as indicated by disappearance of the band at 2172 cm^{-1} and appearance of the absorption band of the carbonyl group at 1660 cm^{-1} in the IR spectrum. In this case, the