organomagnesium and organolithium reagents to 5-formyl-4-hydroxy[2.2]paracyclophane.[1] As a result, the hydroxy groups in these diols are in the *endo* orientations.

Compounds **2** and **3** were obtained as white crystalline compounds. Both compounds were characterized by mass spectrometry, ^{1}H NMR spectroscopy, and elemental analysis.

***cis*-4,7-Dibutyl-4,7-dihydroxy-4,7-dihydro[2.2]paracyclophane (2).** M.p. 119.5—120 °C. Found (%): C, 81.56; H, 9.74. $C_{24}H_{34}O_2$. Calculated (%): C, 81.31; H, 9.67. MS (EI, 70 eV), *m/z* (I_{rel} (%)): 354 $[M]^+$ (0.80); 336 $[M - H_2O]^+$ (7.31); 297 $[M - Bu]^+$ (13.61); 104 (100). ^{1}H NMR (400.13 MHz, $CDCl_3$), δ: 0.83 (t, 6 H, 2 $C\underline{H}_3$, ^3J = 7.2 Hz); 1.05—1.50 (m, 12 H, 2 $(CH_2)_3$); 1.90 (s, 2 H, 2 OH); 2.12—2.55 (m, 2 H, bridging $C\underline{H}_2$); 2.65—3.15 (m, 6 H, bridging $C\underline{H}_2$); 4.89 (s, 2 H, H(5), H(8)); 6.96 and 7.05 (both dd, 2 H each, H(12), H(13), H(15), H(16), ^3J = 7.8 Hz, ^4J = 1.8 Hz).

***cis*-4,7-Diallyl-4,7-dihydroxy-4,7-dihydro[2.2]paracyclophane (3).** M.p. 101—101.5 °C. Found (%): C, 81.83; H, 8.00. $C_{22}H_{26}O_2$. Calculated (%) C, 81.95; H 8.13. MS (EI, 70 eV), *m/z* (I_{rel} (%)): 304 $[M - H_2O]^+$ (1.30); 281 $[M - All]^+$ (38.34); 263 $[M - H_2O - All]^+$ (3.70); 240 $[M - 2 All]^+$ (14.21), 104 (100). ^{1}H NMR (400.13 MHz, $CDCl_3$), δ: 2.20 (s, 2 H, 2 OH); 1.95—2.05, 2.15—2.30, 2.62—2.73, and 2.83—3.05 (all m, 12 H, two bridging $-C\underline{H}_2-C\underline{H}_2$, two $-C\underline{H}_2-CH=$); 4.90 (s, 2 H, H(5), H(8)); 5.03 (d, 2 H, two H_a, ^3J = 24.1 Hz); 5.10 (d, 2 H, two H_b, ^3J = 9.7 Hz); 5.76 (m, 2 H, two H_c); 6.92 and 7.06 (both d, 2 H each, H(12), H(13), H(15), H(16), ^3J = 7.8 Hz).

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 97-03-32972a and 96-15-97289) and by the Scientific Training Center of Chemistry of Organometallic Compounds (Grant 234, the Federal Target Program "Integration").

References

1. E. V. Sergeeva, V. I. Rozenberg, E. V. Vorontsov, T. I. Danilova, Z. A. Starikova, A. I. Yanovsky, and Yu. N. Belokon', *Tetrahedron Asymmetry*, 1996, **7**, 3445.
2. N. V. Vorontsova, V. I. Rozenberg, O. L. Tok, and Yu. N. Bubnov, *Izv. Akad. Nauk, Ser. Khim.*, 1997, **12**, 2271 [*Russ. Chem. Bull.*, 1997, **46**, 2271 (Engl. Transl.)].
3. D. J. Cram and A. C. Day, *J. Org. Chem.*, 1966, **31**, 1227.
4. H. M. Crowford, *J. Am. Chem. Soc.*, 1939, **61**, 3310.
5. L. J. Smith and H. H. Hoehn, *J. Am. Chem. Soc.*, 1939, **61**, 2619.
6. B. M. Mikhailov, G. S. Ter-Sarkisyan, and N. A. Nikolaeva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1968, 541 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1968, **17**, 547 (Engl. Transl.)].
7. G. S. Ter-Sarkisyan, N. A. Nikolaeva, V. G. Kiselev, and B. M. Mikhailov, *Zh. Org. Khim.*, 1971, **41**, 152 [*J. Org. Chem. USSR*, 1971, **41** (Engl. Transl.)].

Received July 27, 1999;
in revised form December 6, 1999

Synthesis of 4,6-dinitro-2-trihalogenomethyl-2,3-dihydrobenzo[*b*]furans

V. V. Rozhkov,* A. M. Kuvshinov, and S. A. Shevelev

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 117913 Moscow, Russian Federation.
Fax: +7 (095) 135 5328. E-mail: vrozhkov@chat.ru

A method for the synthesis of previously unknown 4,6-dinitro-2-trihalogenomethyl-2,3-dihydrobenzo[*b*]furans has been elaborated. The method is based on condensation of 2,4,6-trinitrotoluene with fluoral or chloral in the presence of K_2CO_3 with subsequent intramolecular cyclization of the resulting 2-picryl-1-(trihalogenomethyl)ethanols.

Key words: 2,4,6-trinitrotoluene, fluoral, chloral, condensation, intramolecular cyclization, 4,6-dinitro-2-trihalogenomethyl-2,3-dihydrobenzo[*b*]furans.

We found that alcohols obtained by the condensation of 2,4,6-trinitrotoluene (TNT) with fluoral or chloral, *viz.*, 2-picryl-1-(trifluoromethyl)ethanol (**1a**) and 2-picryl-1-(trichloromethyl)ethanol (**1b**), undergo, by the action of bases, intramolecular cyclization (with substitution of the *ortho*-nitro group), which leads to 4,6-dinitro-2-trifluoromethyl-2,3-dihydrobenzo[*b*]furan (**2a**) and 4,6-dinitro-2-trichloromethyl-2,3-dihydrobenzo[*b*]furan (**2b**) (Scheme 1).

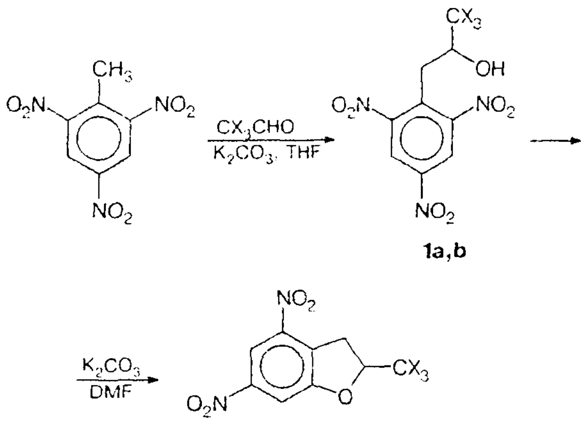
The reaction goes smoothly with specified aldehydes or their hydrates; it may serve as a convenient method for preparation of these previously unknown compounds

---

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 3, pp. 569—570, March, 2000.

1066-5285/00/4903-0573 $25.00

Scheme 1



2a,b

X = F (**a**), Cl (**b**)

from TNT. A few other derivatives of 4,6-dinitro-2,3-dihydrobenzo[*b*]furan were synthesized earlier by a different method.[1]

We should note that the alcohols obtained from condensation of TNT with formaldehyde or acetaldehyde, *viz.*, 2-picrylethanol[2] and 1-methyl-2-picrylethanol,* are not capable of this kind of intramolecular cyclization.

NMR spectra were recorded on a Bruker AC 200 spectrometer with Me_4Si as internal standard. Melting points were measured on a Boetius hot stage. Solvents were purified by standard procedures.

Synthesis of alcohols 1 (general procedure). Anhydrous K_2CO_3 (0.2 mmol) was added at 55 °C to a solution of TNT (3 mmol) and an aldehyde or its hydrate (3.1 mmol) in 25 mL of THF; the mixture began to boil and turned dark brown. The reaction mixture was refluxed for 1 h and then poured into 100 mL of water. The precipitate that formed was filtered off and recrystallized. In the case of fluoral the oil that formed was separated by decantation and chromatographed on silica gel L 5/40 (with toluene as the eluent).

2-Picryl-1-(trifluoromethyl)ethanol (1a). Yield 71%, m.p. 135—137 °C (EtOH). Found (%): C, 33.27; H, 1.91; N, 12.94. $C_9H_6F_3N_3O_7$. Calculated (%): C, 33.23; H, 1.85; N, 12.92. ^1H NMR (DMSO-d_6), δ: 3.46 (m, 2 H, CH_2, ABX spectrum, $\Delta\nu$ = 50 Hz, $^2J_{AB} = -13.8$ Hz, $^3J_{AX} = 10.4$ Hz, $^3J_{BX} = 2.8$ Hz); 4.23 (m, 1 H, C$\underline{H}$OH, $^3J_{HF} = 9.8$ Hz, $^3J_{AX} = 10.4$ Hz, $^3J_{BX} = 2.8$ Hz, $^3J_{HOH} = 6.1$ Hz); 6.80 (d, 1 H, OH, $^3J_{HOH} = 6.1$ Hz); 9.02 (s, 2 H, H_{arom}). ^{19}F NMR (DMSO-d_6), δ relative to $CClF_3$: −77.09 (d, 3 F, CF_3, $^3J = 9.8$ Hz).

2-Picryl-1-(trichloromethyl)ethanol (1b). Yield 70%, m.p. 145—146 °C (Pr^iOH). Found (%): C, 28.88; H, 1.58; N, 11.25. $C_9H_6Cl_3N_3O_7$. Calculated (%): C, 28.84; H, 1.60; N, 11.21. ^1H NMR (acetone-d_6), δ: 3.87 (m, 2 H, CH_2, ABX spectrum, $\Delta\nu$ = 50 Hz, $^2J_{AB} = -13.4$ Hz, $^3J_{AX} = 10.2$ Hz, $^3J_{BX} = 2.7$ Hz, $^4J_{BCCOH} = 1.6$ Hz); 4.57 (m, 1 H, C$\underline{H}$OH, $^3J_{AX} = 10.2$ Hz, $^3J_{BX} = 2.7$ Hz, $^3J_{HOH} = 5.4$ Hz); 6.40 (dd, 1 H, OH, $^3J_{CHO\underline{H}} = 5.4$ Hz, $^4J_{BOH} = 1.6$ Hz); 9.00 (s, 2 H, H_{arom}).

Synthesis of benzodihydrofurans 2 (general procedure). A mixture of alcohol **1** (3 mmol) and anhydrous K_2CO_3 (3 mmol) in 20 mL of DMF was stirred at ~20 °C until the starting alcohol was consumed (~2 h, TLC monitoring). The mixture was poured into 100 mL of water; precipitate was filtered off and recrystallized from an appropriate solvent.

4,6-Dinitro-2-trifluoromethyl-2,3-dihydrobenzo[*b*]furan (2a). Yield 59%, m.p. 79—80 °C (EtOH). Found (%): C, 38.89; H, 1.83; N, 10.12. $C_9H_5F_3N_2O_5$. Calculated (%): C, 38.85; H, 1.80; N, 10.07. ^1H NMR (DMSO-d_6), δ: 4.02 (m, 2 H, CH_2, ABX spectrum, $\Delta\nu$ = 90 Hz, $^2J_{AB} = -19.3$ Hz, $^3J_{AX} = 9.9$ Hz, $^3J_{BX} = 5.5$ Hz); 5.84 (m, 1 H, C$\underline{H}$O, $^3J_{HF} = 11.1$ Hz, $^3J_{AX} = 9.9$ Hz, $^3J_{BX} = 5.5$ Hz); 8.21 (d, 1 H, H_{arom}, $^4J_{HH} = 1.7$ Hz); 8.45 (d, 1 H, H_{arom}, $^4J_{HH} = 1.7$ Hz). ^{19}F NMR (DMSO-d_6), δ relative to $CClF_3$: − 78.14 (d, 3 F, CF_3, $^3J = 11.1$ Hz).

4,6-Dinitro-2-trichloromethyl-2,3-dihydrobenzo[*b*]furan (2b). Yield 63%, m.p. 94—96 °C (Pr^iOH). Found (%): C, 32.98; H, 1.53; N, 8.55. $C_9H_5Cl_3N_2O_5$. Calculated (%): C, 33.01; H, 1.55; N, 8.55. ^1H NMR (DMSO-d_6), δ: 4.06 (m, 2 H, CH_2, ABX spectrum, $\Delta\nu$ = 80 Hz, $^2J_{AB} = -19.6$ Hz, $^3J_{AX} = 9.9$ Hz, $^3J_{BX} = 5.6$ Hz); 5.9 (dd, 1 H, C$\underline{H}$O, $^3J_{AX} = 9.9$ Hz, $^3J_{BX} = 5.6$ Hz); 8.26 (d, 1 H, H_{arom}, $^4J_{HH} = 2.0$ Hz); 8.45 (d, 1 H, H_{arom}, $^4J_{HH} = 2.0$ Hz).

This work was financially supported by the International Center of Science and Technology (Project No. 419).

References

1. T. Severin, R. Schmitz, and H.-L. Temme, *Chem. Ber.*, 1964, **97**, 467.
2. E. E. Gilbert, *J. Energetic Mater.*, 1984, **2**, 215.

Received October 4, 1999;
in revised form November 24, 1999

---

* Synthesis of this compound will be published later.