New molecular rearrangement of tricyclic spirofuranoid into the α,α-disubstituted *p*-semiquinoid system

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A new acid-catalyzed molecular rearrangement of *Z*-2,3,4,5,6,7-hexahydro-3-methoxycarbonyl-4′-trichloromethyl-4′,6,6-trimethylspiro[benzofuran-2,1′-[2,5]cyclohexadien]-4-one into 4-methyl-4-trichloromethyl-1-[(4,4-dimethyl-2-hydroxy-6-oxocyclo-1-hexenyl)(methoxycarbonyl)methylene]-2,5-cyclohexadiene was found. The structure of the latter compound was confirmed analytically, by spectral data, and by X-ray diffraction study.

Key words: cyclohexadienones, alkylidenecyclohexadienes, spirofuranoids; molecular rearrangements.

Studies of the semiquinoid systems (cyclohexadienones and alkylidenecyclohexadienes[1,2]) demonstrated that trienedione **1** (see Ref. 3) may be converted to stereoisomeric tricyclic spirofuranoids **2** (see Ref. 4). In this work, it was established that the representative of this class of compounds *Z*-**2a** readily undergoes cleavage of the heterocycle with rearrangement of the exocyclic fragment of the molecule upon keeping in $CHCl_3$ (Scheme 1).

The product isolated from this rearrangement is stable only upon storage in the solid state at −70 °C. In solutions, this compound undergoes further chemical conversions. Conventional spectral methods (IR and mass spectra) are not characteristic for the compound obtained, whereas the ^1H NMR spectra are characterized by a complex dynamic behavior indicative of prototropic equilibria. Therefore, we used X-ray structural analysis for establishing the structure of this compound. Based on these data, the product is 4-methyl-4-trichloromethyl-1-[(4,4-dimethyl-2-hydroxy-6-oxocyclo-1-hexenyl)(methoxycarbonyl)methylene]-2,5-cyclohexadiene (**6**) (Fig. 1, Table 1).

The most probable mechanism of the rearrangement found involves the initial protonation of any one (see Scheme 1, intermediates **3** and **4**) of the electron-donating oxygen atoms of **2a** followed by the cleavage of the five-membered heterocycle and the formation of Weland's σ-complex **5**; β-elimination of the proton from the tertiary carbon atom of **5** yielded triene **6**.

If the structures of product **6** and its semiquinoid precursor **1** are compared, the sequence of conversions **1** → **2** → **6**, which was reported previously[4] and described in this work, may be of interest in modern molecular design as a new strategy of exo-homologization of *p*-semiquinoid systems, which involves the attachment of the formally carbene equivalent =C(H)COOMe to the inter-ring π-bond of molecule **1**.

Experimental

The reaction was monitored by TLC on Silufol UV-254 plates; development was carried out using UV light and I_2 vapor. ^1H NMR spectra were recorded on a Bruker WP-200

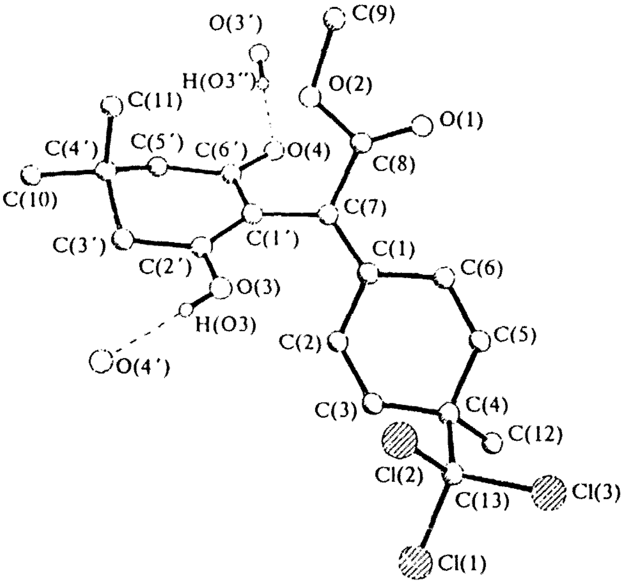

Fig. 1. Structure of molecule **6** in the crystal. The dihedral angle of the bend along the C(3′)—C(5′) line is 45.6°. In the crystal, molecules **6** are linked in infinite chains through H-bonds O(3)—H(03)...O(4) (−1−*x*, 1/2+*y*, 1/2−*z*) (O—H 0.79(4), H...O 1.78(4), O...O 2.577(4) Å, O—H...O 176(4)°).

[†] Deceased.

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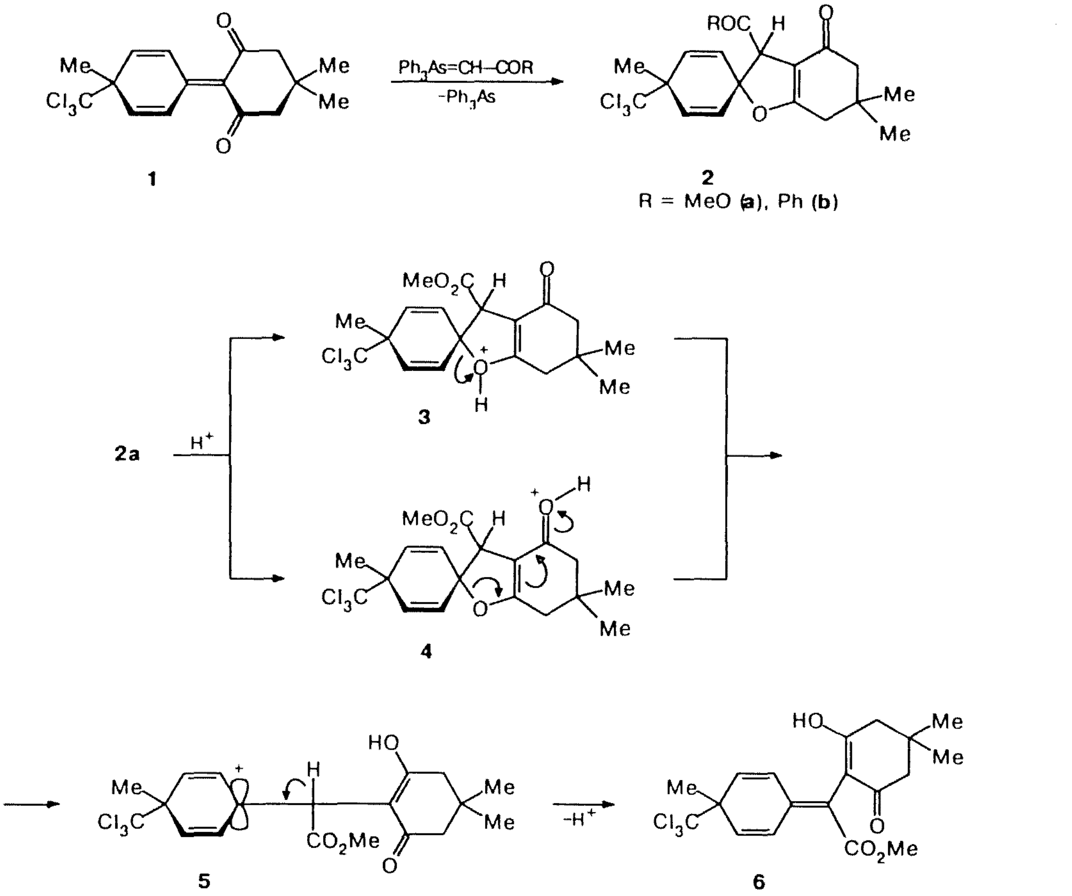
Scheme 1



SY spectrometer (200.13 MHz) relative to TMS; the IR spectra were obtained on a UR-20 spectrophotometer (Karl Zeiss); the Raman spectra of solid samples were measured on a Romanos HG-2S spectrometer (the argon laser excitation line was 5145 Å); the mass spectra (EI) were obtained on a Kratos MS 30 spectrometer (70 eV).

Initial compound *Z*-**2a** was prepared according to the procedure described previously.[4]

4-Methyl-4-trichloromethyl-1-[(4,4-dimethyl-2-hydroxy-6-oxocyclo-1-hexenyl)(methoxycarbonyl)methylene]-2,5-cyclohexadiene (6). A solution of *Z*-**2a** (0.035 g, 0.08 mmol) in 1 mL of $CHCl_3$ was kept at 20 °C for 8 days, then the solvent was distilled off, and C_6H_6 (1 mL) was added to a yellow residue. The solution obtained was kept at 0 °C for 1 h. The white precipitate formed was filtered off, washed with benzene (1 mL), and dried *in vacuo* for 4 h (1 Torr). The compound **6** was obtained in a yield of 15 mg (42 %). Found (%): C, 55.34; H, 5.24; Cl, 24.33. $6(C_{19}H_{21}O_4Cl_3) \cdot 1(C_6H_6)$. Calculated (%): C, 55.51; H, 5.12; Cl, 24.57. IR (Vaseline oil), ν/cm^{-1}: 1600 v.s (O=C—C=C—OH); 1710 v.s (C(O)OMe); 3000 br (OH). Raman spectrum, ν/cm^{-1}: 1636 and 1653 (C=C); 1712 (C(O)OMe). The mass spectrum, m/z (I_{rel}(%)): 346 [M^+–2HCl] (0.3), 316 [M^+–2HCl–CH_2O] (6.4), 302 [M^+–2HCl–CO_2] (2.4), 287 [M^+–2HCl–C(O)OMe] (3.37), 268 (53), 253 (72), 143 (100). ^1H NMR (DMSO-d_6), δ: 1.15 (s, 6 H, 2 Me); 1.58 (s, 3 H, Me); 2.35 (br.s, 2 H, CH_2); 2.48 (br.s, 2 H, CH_2); 3.64 (s, 3 H, MeO); 6.35 (m, 3 H, 3 CH); 7.15 (s, 1/6 C_6H_6); 7.58 (br.d, 1 H, CH, ^3J = 10.0 Hz).

The single crystal of compound **6** was obtained from a saturated solution in acetone kept in pentane vapor. X-ray structural study: single crystals of **6** are monoclinic, at –70 °C a = 6.384(3) Å, b = 13.221(6) Å, c = 24.017(10) Å, β = 95.53(3)°, V = 2017.7(6) Å^3, d_{calc} = 1.382 g cm^{-3}, Z = 4, M = 419.7 [$C_{19}H_{21}O_4Cl_3$], space group $P2_1/c$. The unit-cell parameters and intensities of 2043 independent reflections with $I \geq 3\sigma(I)$ were measured on a Siemens P3/PC diffractometer (Mo-Kα radiation, graphite monochromator, $\theta/2\theta$ scanning technique, $\theta \leq 26°$). The structure was solved and refined by the least-squares method with anisotropic-isotropic thermal parameters for nonhydrogen atoms. The final values of the R factors are as follows: R = 0.037, R_w = 0.041. All calculations were carried out on an IBM PC/AT computer using the

Table 1. Principal bond lengths (d) and torsion angles (φ) in molecule **6**

Bond	d/Å	Angle	φ/deg
C(6′)—O(4)	1.248(4)	C(6)—C(1)—C(7)—C(1′)	–170.4
C(6′)—C(1′)	1.441(5)	C(2)—C(1)—C(7)—C(8)	–174.6
C(1′)—C(2′)	1.366(5)	C(1)—C(7)—C(1′)—C(6′)	–123.9
C(2′)—O(3)	1.325(4)	C(1)—C(7)—C(1′)—C(2′)	60.9
C(1′)—C(7)	1.477(5)		
C(1)—C(7)	1.365(5)		
C(1)—C(2)	1.453(5)		
C(1)—C(6)	1.454(5)		
C(2)—C(3)	1.318(6)		
C(5)—C(6)	1.330(5)		

SHELXTL PC program package.[5] Atomic coordinates are deposited at the Cambridge Crystallographic Data Centre.*

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References

1. V. A. Nikanorov, V. I. Rozenberg, and O. A. Reutov, *Proc. Indian Natl. Sci. Acad.*, 1989, **55**, A, 363.
2. V. A. Nikanorov, G. V. Gavrilova, S. V. Sergeev, V. I. Rozenberg, and O. A. Reutov, *Metalloorg. Khim.*, 1989, **2**, 102 [*Organomet. Chem. USSR*, 1989, **2**, 51 (Engl. Transl.)].
3. V. A. Nikanorov, S. V. Sergeev, V. I. Rozenberg, and O. A. Reutov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 925 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1988, **37**, 804 (Engl. Transl.)].
4. V. G. Kharitonov, V. A. Nikanorov, S. V. Sergeev, M. V. Galakhov, S. O. Yakushin, V. V. Mikul'shina, V. I. Rozenberg, and O. A. Reutov, *Dokl. Akad. Nauk SSSR*, 1991, **319**, 177 [*Dokl. Chem.*, 1991, **319** (Engl. Transl.)].
5. W. Robinson and G. M. Sheldrick, SHELX, in *Crystallographic Techniques and New Technologies*, Eds N. W. Isaac and M. R. Taylor, Oxford Univ. Press, Oxford, England, 1988, 366.

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Synthesis of 1,1-dihydroperfluorooxaalkan-1-ols and their interaction with terephthaloyl chloride

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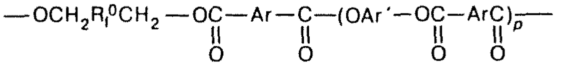
A series of 1,1-dihydroperfluorooxaalkan-1-ols and α,α,ω,ω-tetrahydroperfluorooxaalkanediols has been synthesized. Some terephthalates were synthesized by the reaction of these alcohols and diols with terephthaloyl chloride.

Key words: 1,1-dihydro-3,6,9-trioxaperfluorodecan-1-ol, 1,1-dihydro-3,6,9,12,15-pentaoxaperfluorohexadecan-1-ol, 1,1-dihydro-3,6,9,12,15,18-hexaoxaperfluorononadecan-1-ol, 1,1-dihydro-2,5-perfluorodimethyl-3,6-dioxaperfluorononan-1-ol, 1,1,3-trihydro-2,2,3,3-tetrafluoropropan-1-ol, terephthaloyl chloride, terephthalates of fluorinated alcohols.

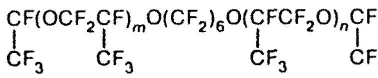
Block-copolymers consisting of macromolecular fragments of different chemical natures make it possible to create materials possessing valuable properties. Block-copolymers of simple perfluoropolyesters (flexible blocks) with polyarylates and polyarylsulfones (rigid blocks) have not been much studied. In the present work, the synthesis of fluorine-containing alcohols and diols is performed, and their reaction with terephthaloyl chloride is studied. This interaction is a model of one of the pathways of the formation of block-copolymers of the following structure:



$$-\mathrm{OCH_2R_f^0CH_2}-\mathrm{O}\underset{\substack{\|\\ \mathrm{O}}}{\mathrm{C}}-\mathrm{Ar}-\underset{\substack{\|\\ \mathrm{O}}}{\mathrm{C}}-(\mathrm{OAr'}-\mathrm{O}\underset{\substack{\|\\ \mathrm{O}}}{\mathrm{C}}-\mathrm{Ar}\underset{\substack{\|\\ \mathrm{O}}}{\mathrm{C}})_p-$$

Ar = C_6H_4 *etc.*; Ar′ = $C_6H_4{-}C(CH_3)_2{-}C_6H_4$ *etc.*;

$R_f^0 = (CF_2CF_2O)_k(CF_2O)_lCF_2$;



$$\underset{\substack{|\\ \mathrm{CF_3}}}{\mathrm{C}}\mathrm{F(OCF_2}\underset{\substack{|\\ \mathrm{CF_3}}}{\mathrm{C}}\mathrm{F)}_m\mathrm{O(CF_2)_6O(}\underset{\substack{|\\ \mathrm{CF_3}}}{\mathrm{C}}\mathrm{FCF_2O)}_n\underset{\substack{|\\ \mathrm{CF_3}}}{\mathrm{C}}\mathrm{F}$$

The vitrification temperature (T_g) of perfluoropolyesters depends primarily on the structure of the monomer

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