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SYNTHESIS OF TRISHOMOCUBANE AND DIHOMOBASKETANE DERIVATIVES VIA THE SKELETAL REARRANGEMENT UNDER THE ACTION OF CHLOROSULPHONIC ACID

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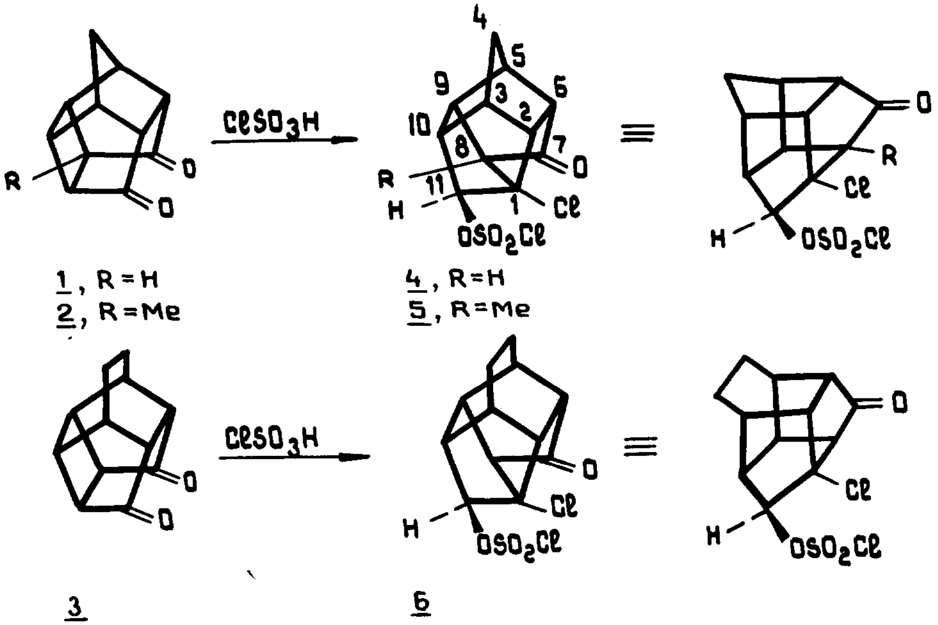
Trishomocubane (pentacyclo[$6.3.0.0^{2,6}.0^{3,10}.0^{5,9}$]undecane) recently attracted attention as the most stable structure isomer among the series of pentacycloundecanes. Its derivatives have been prepared by skeletal isomerization of some pentacyclo[$6.2.1.0^{2,7}.0^{4,10}.0^{5,9}$]undecanes or by cyclization of tetracyclo[$6.3.0.0^{4,11}.0^{5,9}$]undecanes [1]. In all these syntheses the compounds transformed into the substituted trishomocubanes have been obtained from the known diketone 1. We wish to report here a direct route to trishomocubane derivatives via interaction between diketone 1 and chlorosulphonic acid. The reaction proceeds selectively with the participation of one keto group to give exo-11-chlorosulphate of 1-chloropentacyclo[$6.3.0.0^{2,6}.0^{3,10}.0^{5,9}$]undecan-7-one 4 in 64% yield; m.p. 135-136°; m/e 308 (M^+); ν 1766 (C=O), 1410 (OSO_2Cl); δ (CF_3COOH) 1.43 (s, CH_2), 1.91-3.00 (m, 7 CH), 4.75 (s, $CHOSO_2Cl$).

The methyl substituted diketone 2 was obtained quantitatively by photocyclization (pyrex, 10% ethyl acetate solution, 5 h) of the cyclopentadiene - toluquinone Diels-Alder adduct, m.p. 51-54°(subl.); m/e 188 (M^+); ν 1725,1745 (C=O); δ (CCl_4) 1.08 (s, CH_3), 1.88 (q, J=11 Hz, CH_2), 2.16-3.29 (m, 7 CH). Reaction of diketone 2 with $ClSO_3H$ leads, in a yield of 57%, to the trishomocubane derivative 5 as a viscous oil; m/e 322 (M^+); ν 1750,1780 (C=O); 1410 (OSO_2Cl); δ (CF_3COOH) 0.74 (s, CH_3), 1.41 (s, CH_2), 1.88-3.00 (m, 6 CH), 4.72 (d, J=2 Hz, $CHOSO_2Cl$); 2,4-dinitrophenylhydrazone, m.p. 201-202°. Diketone 3 reacts with $ClSO_3H$ to give the dihomobasketane derivative 6 in the yield of



1, R=H
2, R=Me

4, R=H
5, R=Me

3

6

ca. 90%; m.p. 94-95°; m/e 322 (M^+); ν 1775 (C=O), 1410 (OSO_2Cl); δ (CF_3COOH) 1.31 (s, CH_2CH_2), 1.60-2.58 (m, 7 CH), 4.69 (d, J=2 Hz, $CHOSO_2Cl$).

The skeleton, the position of substituents and the exo-configuration of the C^{11}-O bond in compound 4 follows from the X-ray analysis data.

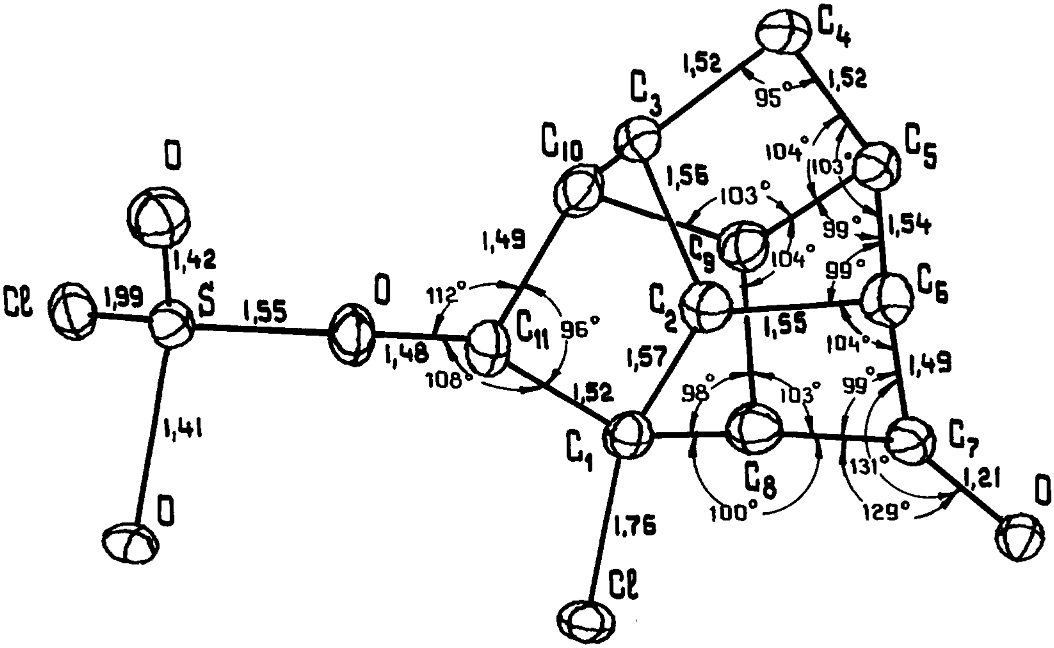
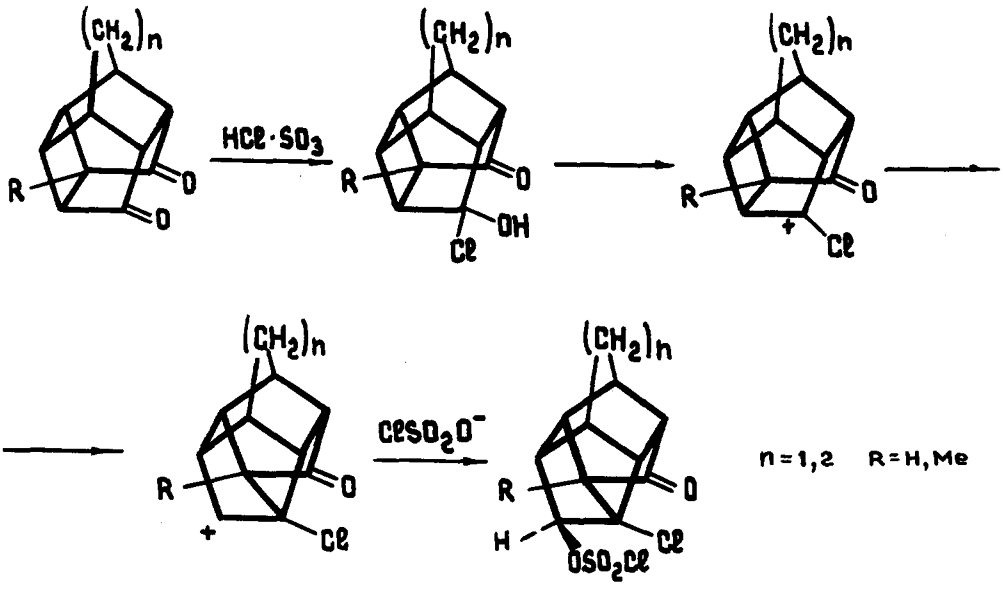


Figure. Atom numbering, bond lengths and bond angles for 4 .

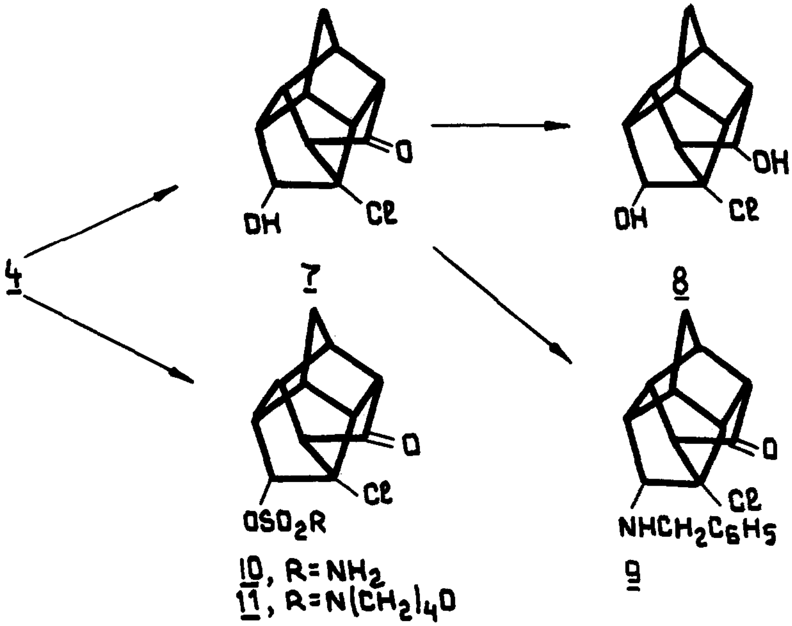
Crystals are monoclinic, a=6.146(2), b=15.373(5), c=12.845(2) Å, β=97.85(2)°, Z=4, space group $P2_1/c$. The structure was solved by direct method and refined by anisotropic (isotropic for H atoms) least squares procedure, R=0.098.

The molecular structure with bond lengths is shown in the Figure. Despite the different hybridization of C(7) a trishomocubane framework has the almost ideal D_3 symmetry (the three-fold axis connecting C(2) and C(9)). In this framework six five-membered and three six-membered rings have severely distorted half-chair and boat conformations respectively. Distortions are caused by incorporation of these rings in a rigid framework built of norbornane units. Bond lengths are unexeptional [2]. As in other saturated polycyclic cage sistems [3] the endocyclic bond angles are decreased to 94.5-106.2°.

It seems possible to picture the scheme of the skeletal isomerization as occuring through the addition of HCl to C=O bond, with the further 1,2-shift and subsequent trapping of the rearranged cation with $ClSO_3$ nucleophile.



The following examples show some possibilities for synthesis of various 1,7,11-trisubstituted trishomocubane derivatives. Hydrolysis of compound 4 with NH_4OH gives rise to ketol 7, m.p. 183-185° (aq. EtOH), which in turn is converted to diol 8, m.p. 170-172° and to N-benzilic derivative 9, m.p. 174-178° (EtOH).



The reaction of 4 with gaseous NH$_3$ in dry THF results in sulphamide 10, m.p. 123-125°, and that with morpholine leads to morpholinosulphate 11, m.p. 140-141° (CCl$_4$) [4].

REFERENCES AND NOTES

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2. Tables of interatomic distances and configuration in molecules and ions. Supplement 1956-1959. Ed.L.E.Sutton. The Chemical Society. Special Publication No 18, London, 1965.

3. G.A.Sim, J. Chem. Soc., 5974 (1965).

4. The structure of compounds 7-11 follows from IR-, PMR- and mass spectra, satisfactory data from elemental analysis have obtained for all the compounds involved.

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