Polysubstituted derivatives of Pentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane

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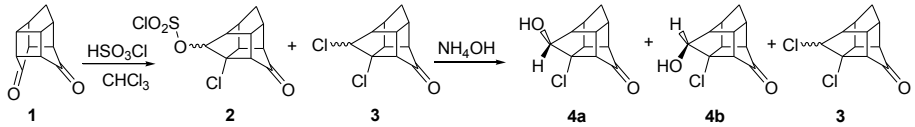
Synthesis of polysubstituted derivatives of pentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (D_3-trishomocubane) is an interesting task for both fundamental and applied research. For this purpose we have used reaction of Cookson diketone **1** (PCUD-8,11-dione) with chlorosulfonic acid. This reaction suggested more than 30 years ago[1] and practically has not been studied.

We have performed this reaction in chloroform solution at room temperature, which led to the increase of yield from 64 to 75%.

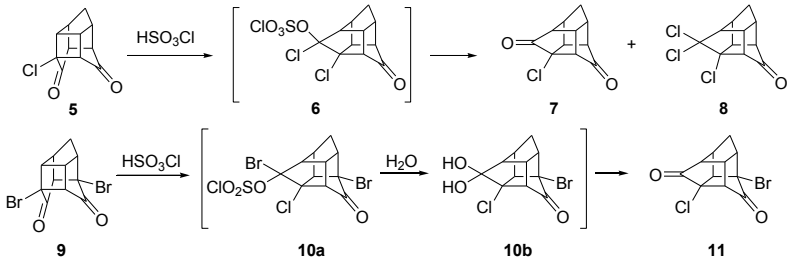


1 **2** **3** **4a** **4b** **3**

Scheme 1. The syntheses of chloroketoalkohols of D_3-trishomocubane.

Reaction mixture after chlorosulfation contains 11% the impurities dichloroketone **3** that can be easily separated by chromatography on aluminum oxide. Chlorketoalcohol **4** contains two stereoisomers **4a** and **4b** with the ratio of 9:1. This mixture can be purified by recrystallization.

The interaction of other derivatives of Cookson diketone – monochlorine and dibromine show that the replacement of the halogen atom by chlorine of chlorosulfonic acid takes place.



5 **6** **7** **8**

9 **10a** **10b** **11**

Scheme 2. The rearrangement of halosubstituted PCUD derivatives.

The structures of compounds are confirmed by GC/MS, NMR, ^{1}H and ^{13}C spectra, possible reaction mechanism was proposed based on B3PW91/6–31G(d,p) and MP2/cc–pVDZ calculations.[2] Selectivity of the chlorosulfation gives hope that this reaction may be used for obtaining derivatives of D_3-trishomocubane substituted at the C_3 axis. Such substitution is extremely interesting, hardly obtained and not well investigated. [3]

[1] Tolstikov G.A. Lerman B.M., *Tetrahedron Lett.*, **1978,** *43,* 4145-4148.

[2] D.I. Sharapa, A.V. Gayday, A.G. Mitlenko, I.A. Levandovskiy, T.E. Shubina, *EJOC*, **2011**, *ASAP*.

[3] I. A. Levandovsky, D. I. Sharapa, O. A. Cherenkova, A. V. Gaidai, T. E. Shubina, *Russ Chem Rev* **2010**, *79*, 1089.