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A New Reaction of Tetrabutylammonium Camphorsulfonate with P_4S_{10}. Synthesis and Crystal Structure of the First Chiral Tetrathiophosphate Derivative

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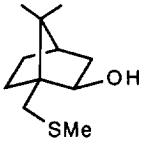
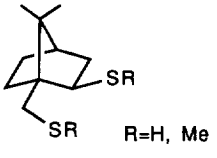
Abstract: Compound **5** has been synthesized in a good yield by reacting tetrabutylammonium camphorsulfonate with P_4S_{10}, and characterized by X ray diffraction. © 1997 Elsevier Science Ltd.

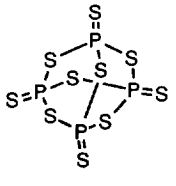
Auxiliary ligands based on the camphorsulfonic backbone have been shown to be highly efficient in asymmetric synthesis.[1] On the other hand, sulfur derivatives such as thiols, sulfides and sulfoxides have been widely used in asymmetric synthesis.[2] So, alkylthioalcohols such as **1** have been successfully used in asymmetric Pauson-Khand reactions.[3] Recently, we have reported the synthesis of new sulfur containing camphor derivatives **2**.[4]



1



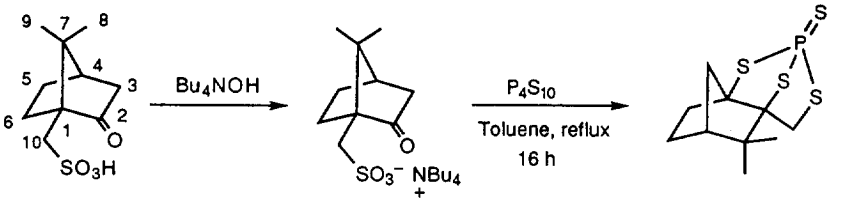
2



P_4S_{10}

While looking for a fast procedure of synthesizing the norbornane dithiol derivative **2** (R=H) we considered the possibility of obtaining the thioketone derived from camphorsulfonic acid **3** by reacting with the Lawesson reagent[5] or with P_4S_{10}.[6] Initially, we tested the reaction of **3** with the Lawesson reagent by heating the mixture to reflux in different solvents (acetonitrile, tetrahydrofuran, dioxane, diglyme, toluene) and in every case a black residue was obtained in which no products could be isolated. Similar results were obtained using P_4S_{10} as reagent.

Scheme 1



3 4 5

Although, these procedures have been used to prepare the thione derived from camphor,[6,7] there are no examples in the literature of a similar reaction with camphor sulfonic acid. So, we decided to test the reaction with the tetrabutyl ammonium salt **4** which was prepared by reacting **3**, a racemic mixture,[8] with tetrabutylammonium hydroxide (Scheme 1). However, when compound **4** was heated in different solvents (benzene, toluene, xylene, diglyme) in the presence of the Lawesson reagent, the starting material was recovered unaltered. Interestingly, when compound **4** was heated to reflux in toluene in the presence of P_4S_{10}, compound **5**[9] was obtained in a good yield (74%).

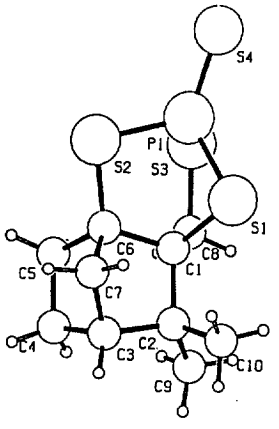
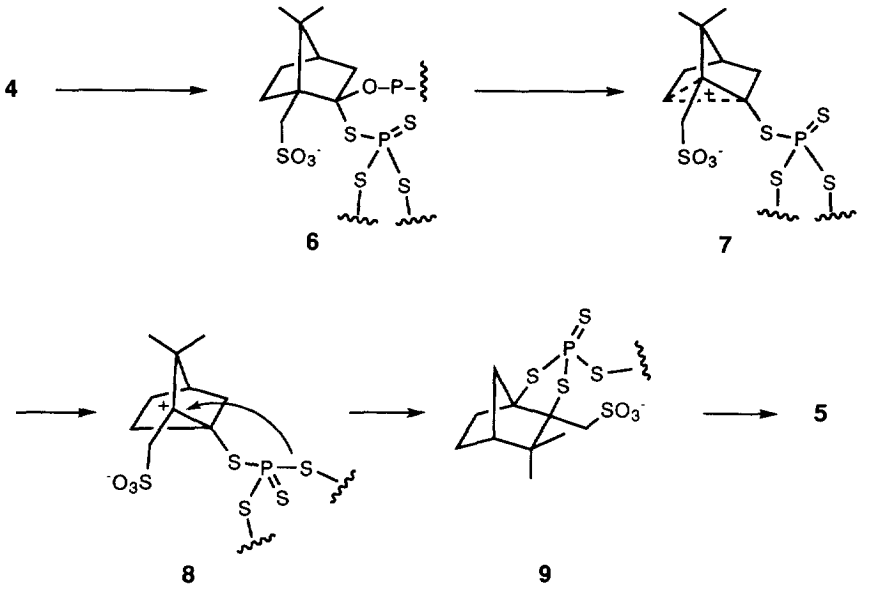


Figure 1. Molecular structure with atom numbering of compound **5**.

The ^{31}P NMR spectrum shows the presence of phosphorus coupled with one proton from an isolated CH_2 group. Elemental analysis shows that there are four sulfur atoms in the molecule, and in the HRMS the molecular ion perfectly matches the proposed molecular formula. The crystal structure[10] fully confirms molecule **5** as a tetrathiophosphate (Figure 1). Only one enantiomeric pair is present in the crystal showing that the reaction is steroespecific. The tetrathiophosphate moiety is bonded to the norbornane skeleton in such a way that two bicyclic systems, one with a methylene bridge and the other with a sulfur bridge, are bonded by a carbon-carbon bond.

Although it has been suggested that the SPS_2^- anion is the reagent in the conversion of ketones into thioketones using P_4S_{10},[6] in this case a full tetrathiophosphate unit has been transferred. The mechanism of the reaction has not been elucidated, but some conclusions can be drawn from the analysis of the molecular structure (Scheme 2). The presence of a sulfur bonded to a bridged carbon atom as well as a methylene bridge suggeststhat an intermediate such as **6** must have been formed and that a Wagner-Meerwein rearrangement[11] has been produced through a non classical carbocation **7**. Moreover, the fact that a

Scheme 2



sulfur is bonded to the C-1 (starting material numbering), together with the *trans* disposition between the methylene bridge and the CH_2–S group, indicates that a sulfur has attacked C-1, as shown in intermediate **8**, to give intermediate **9**. An additional removal of the SO_3 group and the formation of a new carbon-sulfur bond completes the formation of **5**. This is, to the best of our knowledge, the first reported example of a chiral tetrathiophosphate derivative.

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8. Draw as (+)-camphor-10-sulfonic acid.

9. *Selected characterization data* for **5**: MP: 181-183°C. ^{1}H RMN ($CDCl_3$, 300 MHz) δ 4.05 (dd, 1H, J=16.5, 11.5), 3.84 (d, 1H, J=11.5), 2.67 (m, 1H), 2.20-1.65 (m, 6H), 1.44 (s, 3H), 1.23 (s, 3H). ^{13}C RMN ($CDCl_3$, 75.4 MHz) δ 48.6, 46,1, 46.0 (d, J=2.9 Hz), 44.7, 32.3, 29.5, 29.4, 24.8, 22.2 (2C). ^{31}P RMN ($CDCl_3$, 121 MHz) δ 103.6 (d, J=16.5). EM: 293.979426 (6.1 ppm). Elemental Analysis: Calc. for $C_{10}H_{15}PS_4$ C, 40.81; H, 5.10; S, 43.54; Found, C, 41.05, H, 5.16, S, 43,55.

10. *Crystal structure data* for **5**: $C_{10}H_{15}PS_4$, monoclinic, space group $P2_1/c$ (no 14), a=6.651(5), b=14.716(2), c=13.442(4)Å, β=99.63(4)°, U=1297(1)Å^3, Z=4, D_c=1.508g.cm^{-3}, F(000)=616, crystal size 0.50x0.36x0.11mm, μ=0.82 mm^{-1} (Mo-Kα), T=293K. An Enraf-Nonius CAD4 diffractometer with graphite monochromated Mo Kα (λ=0.71069Å) was used to collect 2273 independent reflections in the range 2<2θ<50°. The structure was solved by direct methods (SHELXS86) and refined on F^2 (SHELXL-93). All reflections were used in the refinement. The final R(F) value was 0.0487 (Rw(F^2)=0.1036) for all observed reflections. H-atoms were included in riding mode.

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