## GENERATION OF CYCLOHEXENE-S-PHENYLEPISULFONIUM FLUOBORATE AND ITS REACTION WITH NUCLEOPHILIC REAGENTS

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The reaction of methylsulfenyl fluoborate (I) with cyclohexene (II), which leads to a stabilized cationoid intermediate of hypothetical structure ( $K_1$ ), was reported previously [1]. As a continuation of this research we studied the possibility of generating an analogous intermediate, which contains the S-phenyl group instead of the S-methyl group. The reagent needed for this, namely  $C_6H_5BF_4$  (III), was obtained in the same manner as (I) by the following exchange reaction.

$$C_6H_5SHal + AgBF_4 \rightarrow C_6H_5SBF_4 + AgHal$$
(III)

Reagent (III) can be obtained either in advance, since it is stable in  $C_2H_4Cl_2$  solution at  $-40^{\circ}C$  for at least several hours, or directly at the time of reaction with the olefin.

The reaction of (III) with (II) was run at  $-40^{\circ}$  in  $C_2H_4Cl_2$  solution. Even under these conditions the reaction is exceedingly fast and is ended in less than 5 min. The question of the structure of the reaction complex that is formed here is quite complex and for its rigorous solution requires a detailed study of the properties of the complex by spectral methods. However, the data obtained by us regarding its chemical properties make it possible to assume that it is an intermediate of the episulfonium fluoborate type (K<sub>2</sub>). Such a concept is supported both by the stability of this intermediate\* and by the fact that its reactions with various "external" nucleophilic reagents proceed with exceeding ease and smoothly even at low temperature and lead to adducts of general formula  $C_6H_5SC_6H_{10} \cdot Z$  ((IVa-d), where Z is the nucleophilic group of the added base). The structure of these adducts as being 1,2-cyclohexane derivatives is unequivocally proved by the elemental analysis, IR, NMR, and mass spectral data, and is also confirmed by conversion to compounds of known structure.



 $\label{eq:constraint} Z = \text{OCOCH}_3 \, (a), \quad \text{OCH}_3 \, (b), \quad \text{Cl} \, (c), \quad \text{CH}(\text{COOC}_2\text{H}_5)_2(d)$ 

We assume that all of the obtained adducts have a trans-configuration, which does not contradict the existing data on the character of the signals of the H-C-Z protons in the NMR spectra, but the final solution to this problem requires the preparation of the corresponding deuterated analogs from 3,3,6,6-tetradeuterocyclohexene.

\* In particular, the relative stability of this complex is confirmed by the fact that the yield of adduct (IVb) remains practically constant if the time of holding the  $K_2$  complex at -40° is increased from 5 to 60 min (before the methanol is added).

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The cationoid electrophile  $C_6H_5SBF_4$  behaves the same as  $CH_3SBF_4$  in the reactions with olefins, and makes it possible to realize the scheme of a two-step addition to the double bond, in which the steps of adding the electrophile,  $C_6H_5S$ , and the "external" nucleophile Z are separated in time and are independent It could be expected that the intermediates, obtained in the reactions with  $CH_3SBF_4$  and  $C_6H_5SBF_4$  (respectively  $K_1$  and  $K_2$ ), will differ noticeably both in stability and in the direction of their reactions with nucleophilic reagents, since the phenyl group on the sulfur atom in  $K_2$  should stabilize the episulfonium ring and reduce the ease of adding the "external" nucleophile to the C atom. The data obtained by us show that if this difference does exist, then it is extremely slight.

## EXPERIMENTAL METHOD

The NMR spectra were taken on a DA-60-IL spectrometer in CCl<sub>4</sub> solution, and the chemical shifts  $(\delta)$  are given relative to HMDS. The IR spectra were recorded on a UR-10 instrument, while the mass spectra were taken on a Varian CH-6 instrument. The GLC was run on an instrument equipped with a flame-ionization detector, using a 200 × 3.5 mm column packed with 5% XE-60 deposited on Chromatone N-AW-DMDC, at 150°, and 50 ml/min of N<sub>2</sub>. Diphenyl disulfide was obtained by the oxidation of thiophenol with DMSO [2]. Phenylsulfenyl chloride was prepared as described in [3]. 2-(Phenylthio)cyclohexyl acetate was obtained the same as 2-(methylthio)cyclohexyl acetate [4], while 1-chloro-2-(phenylthio)cyclohexane was obtained as described in [5].

Addition of Phenylsulfenyl Fluoborate to Cyclohexene. The reaction was run by the general method used to obtain all of the adducts (IVa-d). With stirring, to a solution of 0.61 g of  $C_6H_5SC1$  in 4 ml of absolute  $CH_2Cl_2$ , cooled to -40 to -45°, was added 5 ml of a solution of 0.34 g of (II) and 0.98 g of AgBF<sub>4</sub> in a 3:2  $CH_3NO_2-CH_2Cl_2$  mixture in 1-2 min. The precipitation of AgCl was observed here and the formation of a colored solution of the complex ( $K_2$ ), which was kept at the same temperature for another 5 min and then treated with the necessary base. The further isolation of the (IV) adducts was effected by neutralization with aqueous NaHCO<sub>3</sub> solution, extraction with CHCl<sub>3</sub>, washing the extract with water, and drying over Na<sub>2</sub>SO<sub>4</sub>.

 $\frac{2-(\text{Phenylthio})\text{cyclohexyl Acetate (IVa)}. \text{ The reaction complex (K_2) was treated with glacial CH_3COOH at -50° for 10 min. By preparative TLC (SiO<sub>2</sub>, 5:3 petroleum ether-benzene) we isolated 0.72 g (70%) of (IVa), which was identical with an authentic specimen. Infrared spectrum: 1735 cm<sup>-1</sup> (OCOCH<sub>3</sub>). NMR spectrum*: 1.77 s (3H, OCOCH<sub>3</sub>), 3.00 m (1H, HCSC<sub>6</sub>H<sub>5</sub>), 4.67 m (1H, HCOAc, J<sub>1,2</sub> = 9 Hz†), 7.17 m (5H, SC<sub>6</sub>H<sub>5</sub>). Found: C 67.32; H 7.40; S 12.42%. C<sub>14</sub>H<sub>18</sub>O<sub>2</sub>S. Calculated: C 67.20; H 7.20; S 12.80%.$ 

<u>1-Methoxy-2-(phenylthio)cyclohexane (IVb)</u>. The complex (K<sub>2</sub>) was treated with 15 ml of absolute methanol at  $-30^{\circ}$  for 5 min. Based on the GLC data, the obtained product was mainly (IVb). Distillation in a narrow-necked flask gave 0.87 g (97%) of (IVb), nD<sup>22</sup> 1.5572. Found: C 69.85; H 7.96; S 14.42%. C<sub>13</sub>H<sub>18</sub>OS. Calculated: C 70.27; H 8,11; 14.41%. NMR spectrum: 3.07 m (2H, HCS, HCO), 3.25 s (3H, OCH<sub>3</sub>), 7.16 m (5H, SC<sub>6</sub>H<sub>5</sub>).

 $\frac{1-\text{Chloro-2-(phenylthio)cyclohexane (IVc).}}{(C_2H_5)_4\text{NCl in 9 ml of CH_3NO_2 at -40° for 10 min.}} \text{ Vacuum-distillation gave 0.8 g (88\%) of (IVc), bp 120-122° (1 mm); nD<sup>17</sup> 1.5840.} Based on the GLC data, (IVc) is identical with an authentic specimen. Found: C 63.71; H 7.01\%. C_{12}H_{15}\text{SCl.} Calculated: C 63.30; H 6.64\%.} \text{ NMR spectrum: 3.18 m (1H, H-C-S-), 3.90 m (1H, HCCl), 7.18 s (5H, SC_6H_5).}$ 

 $\frac{2-(\text{Phenylthio})\text{ cyclohexanemalonic Acid, Diethyl Ester (IVd). Starting with 2.24 g of C<sub>6</sub>H<sub>5</sub>SCl, 3.90 g of AgBF<sub>4</sub>, and 1.36 g of (I) we obtained the complex (K<sub>2</sub>) by the above described method, which was treated with sodium malonate (from 3.5 g of Na and 50 ml of malonic ester) at -40° for 10 min, and at ~20° for 1 h. The excess malonic ester was removed in vacuo. From the residue by preparative TLC (Al<sub>2</sub>O<sub>3</sub>, 10:1 hexane-ethyl acetate) we isolated 0.97 g (20.9%) of (IVd). Found: C 65.37; H 7.64; S 8.48%. C<sub>19</sub>H<sub>26</sub>O<sub>4</sub>S. Calculated: C 65.14; H 7.45; S 9.14%. NMR spectrum: 1.13 and 1.18 t(two CH<sub>3</sub>--CH<sub>2</sub>--), 3.05 m (1H, H-C-S-), 3.97 and 4.05 Hz), 4.20 d(1H, CH(COOR)<sub>2</sub>, J = 4Hz), 7.18 m (5H, SC<sub>6</sub>H<sub>5</sub>). Mass spectrum: M<sup>+</sup> with m/e 350, and intense fragments with m/e 305, 259, 241, 190, 167, 149, 82.$ 

\* Besides the given signals in the 1.10-2.10 ppm region, all of the NMR spectra have a group of signals of the four  $CH_2$  groups of the cyclohexane ring.

<sup>†</sup> This value of the coupling constants of the protons (obtained by the double resonance method) at  $C_1$  and  $C_2$  is characteristic for 1, 2-trans-disubstituted cyclohexanes (cf. [6]).

## CONCLUSIONS

It was shown that a stable intermediate of the episulfonium ion type can be generated by the reaction of cyclohexene with phenylsulfenyl fluoborate, and its reactions with nucleophilic reagents were studied.

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