

SHORT
COMMUNICATIONS

Reaction of Benzoylium Hexachloroantimonate(VI) with 2-Methyloxetane

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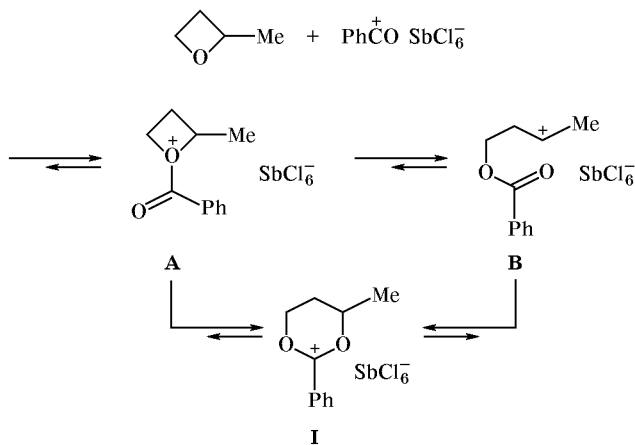
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We previously found that acylation of 1,3-dioxanes with acylium ions leads to formation of 1,3-dioxanium salts [1]. It was presumed that an analogous reaction can occur between acylium ions and cyclic ethers derived from 1,2- and 1,3-diols [1]. Acid-catalyzed reactions of oxetanes are known to give 1,3-substituted propanes when opening of the ring is preceded by electrophilic attack on the ring oxygen atom [2]. Treatment of oxetane with carboxylic acid chlorides yields 3-haloalkyl carboxylates [3].

The reaction of 2-methyloxetane with benzoylium hexachloroantimonate(VI) $\text{PhCO}^+\text{SbCl}_6^-$ gave 1,3-dioxanium hexachloroantimonate (**I**) in high yield. Initial attack by the acylium ion on the ring oxygen atom leads to formation of oxonium ion **A** which undergoes rearrangement into more stable 1,3-dioxanium ion through intermediate **B** (Scheme 1).

Scheme 1.



The formation of salt **I** from 2-methyloxetane can be regarded as a convincing proof for the existence

of intermediate oxetane-like cation, which was previously discussed by Searles [3] while studying the reaction mechanism of 2-methyloxetane with acetyl chloride. Bartok and co-workers [4] believe that such a structure can actually be formed and that it should readily rearrange into a more stable acyloxonium ion due to more favorable steric conditions, greater electron density on the carbonyl oxygen atom, and higher stability of the six-membered ring.

The physical constants and spectral parameters of compound **I** were consistent with those reported in [1]. The IR spectrum of **I** contains absorption bands at 1585–1540 and 1525–1490 cm^{-1} , which were assigned to vibrations of the $\text{O}-\overset{+}{\text{C}}-\text{O}$ fragment. The 2-phenyl group in the cation gives rise to a group of bands belonging to vibrations of the aromatic $\text{C}=\text{C}$ bonds (3080, 1610–1580, 1550–1530, and 1520–1500 cm^{-1} [1]). In the ^1H NMR spectrum of **I** signals from protons of the carbocyclic moiety were the same as those found in [5] for solution in $\text{C}_6\text{D}_5\text{NO}_2$.

2-Methyloxetane was synthesized by the procedure reported in [3].

4-Methyl-2-phenyl-1,3-dioxanium hexachloroantimonate (I). A mixture of 0.72 g (0.01 mol) of 2-methyloxetane, 1.27 ml (0.01 mol) of SbCl_5 , and 1.3 ml (0.01 mol) of benzoyl chloride in 5 ml of methylene chloride was refluxed for 3–5 min. It was then cooled and diluted with 25 ml of ether. The precipitate was filtered off, washed with 10 ml of 1:3 ethyl acetate–ether and with dry ether. Yield 3.85 g (80%), mp 140–141°C. IR spectrum, ν , cm^{-1} : 1540, 1510 ($\text{O}-\overset{+}{\text{C}}-\text{O}$); 3080, 1595 (Ph) [1]. ^1H NMR spectrum ($\text{C}_6\text{H}_5\text{NO}_2$), δ , ppm: 1.95 d (3H, 4-Me), 3.01 m (2H, C^5H_2), 5.5 m and 5.8 m (3H, 4-H and C^6H_2) [5]. Found, %: C 25.94; H 2.88; Cl 42.96. $\text{C}_{11}\text{H}_{13}\text{Cl}_6\text{O}_2\text{Sb}$. Calculated, %: C 25.80; H 2.50; Cl 42.68.

The IR spectra were recorded in the range from 400 to 4000 cm^{-1} on a Specord 71 instrument in mineral oil. The ^1H NMR spectra were measured on a Tesla BS-467A instrument (60 MHz) relative to HMDS as internal reference.

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