

Acyl Iodides in Organic Synthesis: VI.* Reactions with Vinyl Ethers

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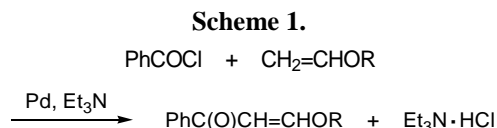
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Received June 27, 2003

Abstract—Reactions of acetyl iodide with butyl vinyl ether, 1,2-divinyloxyethane, phenyl vinyl ether, 1,4-divinyloxybenzene, and divinyl ether were studied. Vinyl ethers derived from aliphatic alcohols (butyl vinyl ether and 1,2-divinyloxyethane) react with acetyl iodide in a way similar to ethyl vinyl ether, i.e., with cleavage of both O–C_{sp²} and Alk–O ether bonds. From butyl vinyl ether, a mixture of vinyl iodide, butyl acetate, vinyl acetate, and butyl iodide is formed, while 1,2-divinyloxyethane gives rise to vinyl iodide, vinyl acetate, and 2-iodoethyl acetate. The reaction of acetyl iodide with divinyl ether involves cleavage of only one O–C_{sp²} bond, yielding vinyl acetate and vinyl iodide. In the reactions of acetyl iodide with phenyl vinyl ether and 1,4-divinyloxybenzene, only the O–C_{Vin} bond is cleaved, whereas the O–C_{Ar} bond remains intact.

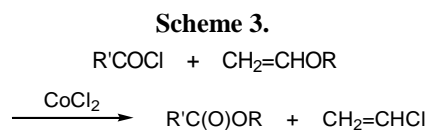
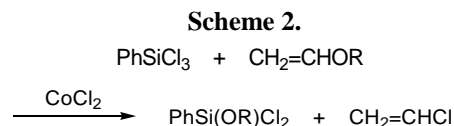
We previously studied reactions of acyl iodides with acyclic and cyclic ethers [1] and found that in the reaction of acetyl iodide with ethyl vinyl ether both ether bonds, Et–O and O–CH=CH₂ are cleaved. Later on, an analogous cleavage of the O–C_{sp²} bond was observed in the reaction of acetyl iodide with vinyl acetate [2]. Both these reactions occurred under mild conditions in the absence of a catalyst.

It is known that in most reactions of vinyl ethers R–O–CH=CH₂ with electrophilic reagents the latter adds to the β-carbon of the vinyl group with subsequent cleavage of only the O–R bond [3, 4]. Likewise, the reaction of benzoyl chloride with alkyl vinyl ethers in the presence of palladium catalyst and triethylamine results in benzylation exclusively of the β-carbon atom [5] (Scheme 1).



Prior to our studies, only two examples of cleavage of the O–C_{sp²} bond in vinyl alkyl ethers have been reported. These are (1) the reaction of alkyl vinyl ethers with trichloro(phenyl)silane [6] (Scheme 2) and

(2) the reaction of acyl chlorides with alkyl vinyl ethers in acetonitrile, catalyzed by CoCl₂ [7] (Scheme 3). In the presence of (Ph₃P)₂CoCl₂ as catalyst, only addition of acyl chlorides at the double C=C bond occurs [7].

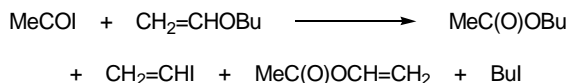


In continuation of our studies on cleavage of acyclic and cyclic ethers [1], we examined reactions of acetyl iodide with butyl vinyl ether, 1,2-divinyloxyethane, phenyl vinyl ether, 1,4-divinyloxybenzene, and divinyl ether. The reactions were carried out in methylene chloride at 10°C, and in all cases the process was accompanied by heat evolution. Vinyl ethers derived from aliphatic alcohols, namely butyl vinyl ether and 1,2-divinyloxyethane, reacted with acetyl iodide in a way similar to the reaction with ethyl vinyl ether. As a result, both ether bonds, O–C_{sp²} and Alk–O were cleaved. In the two cases, the products

* For communication V, see [1].

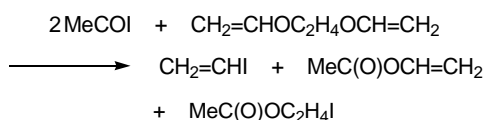
were vinyl iodide and vinyl acetate. In the reaction with butyl vinyl ether, butyl acetate (39.8%) and butyl iodide (12.5%) were also isolated (Scheme 4). Thus, unlike ethyl vinyl ether [1], cleavage of the O–C_{sp²} bond predominates over cleavage of the O–C_{sp³} bond.

Scheme 4.



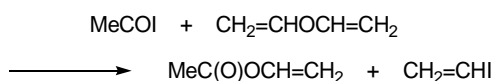
Acetyl iodide reacted with 1,2-divinyloxyethane to afford approximately equal amounts of vinyl iodide and vinyl acetate (40.5 and 42.8%, respectively) together with 2-iodoethyl acetate (Scheme 5). These results indicate that the probabilities for cleavage of the O–C_{sp²} and O–C_{sp³} bonds in 1,2-divinyloxyethane are almost equal.

Scheme 5.



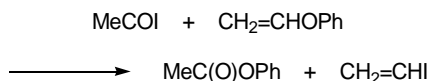
According to early data [8], the reaction of acetyl iodide with divinyl ether resulted in explosion. Under our conditions, the reaction occurred smoothly and involved cleavage of only one ether bond even in the presence of excess acetyl iodide (Scheme 6). The yield of vinyl iodide and vinyl acetate was greater than 80% (GLC).

Scheme 6.

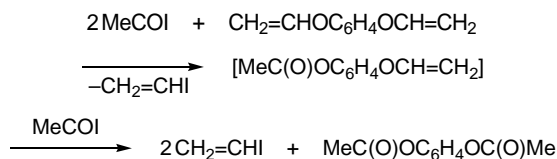


The formation of vinyl acetate (which is readily cleaved by acetyl iodide [2]) in the presence of excess acetyl iodide may be explained by very mild reaction conditions and the presence of vinyl iodide in the mixture. The reactions of acetyl iodide with phenyl vinyl ether and 1,4-divinyloxybenzene involve only the O–C_{Vin} bond, while the O–C_{Ar} bond remains intact. In the first case, the products are vinyl iodide and phenyl acetate (Scheme 7), and in the second, vinyl

Scheme 7.



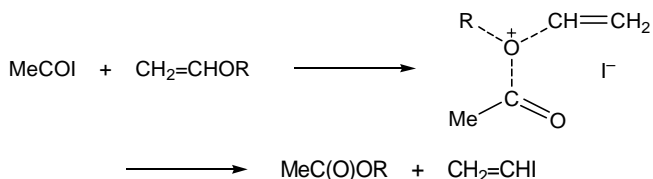
Scheme 8.



iodide and 1,4-diacetoxybenzene (Scheme 8; a possible intermediate product, 4-vinyloxyphenyl acetate, was not detected).

Despite very low basicity and nucleophilicity of the oxygen atom in alkyl vinyl ethers (which was noted for the first time as early as 1947 [9]), their reaction with strongly electrophilic acetyl iodide possessing a readily departing iodine atom (as iodide ion) begins with electrophilic attack on the oxygen atom with formation of intermediate oxonium complex, i.e., according to the mechanism proposed by us previously and substantiated by theoretical calculations [2, 10] (Scheme 9).

Scheme 9.



We previously found that the reaction of acetyl iodide with phenyl acetate leads to cleavage of only the ester O–C=O bond [2]. Likewise, acetyl iodide reacts with aryl vinyl ethers selectively at the O–CH=CH₂ bond [2]. This is explained by very high stability of the O–C_{Ar} bond due to *n*– π conjugation between the oxygen lone electron pair and aromatic π -electron system. The same factor is responsible for our failure to effect cleavage of diphenyl ether and dibenzofuran by the action of acetyl iodide (contrary to published data [11] which were not confirmed subsequently).

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer from samples prepared as thin films. GLC analysis was performed on an LKhM-8M chromatograph equipped with a thermal conductivity detector; carrier gas helium; 2-m \times 4-mm column; oven temperature programming mode. Initial acetyl iodide was synthesized by reaction of acetyl chloride with anhydrous sodium iodide following the known procedure [7].

Reaction of butyl vinyl ether with acetyl iodide.

Acetyl iodide, 5.3 g, was added dropwise to a solution of 3.1 g of butyl vinyl ether in 15 ml of methylene chloride, cooled to 10°C. Immediately after mixing the reactants, GLC analysis of the reaction mixture (using authentic samples) showed the presence of vinyl iodide (35.8%), vinyl acetate (11.8%), butyl iodide (12.8%), and butyl acetate (39.8%).

Reaction of acetyl iodide with 1,2-divinyloxyethane.

Acetyl iodide, 10.6 g, was slowly added to a solution of 3.6 g of 1,2-divinyloxyethane in 30 ml of methylene chloride, cooled to 10°C. Distillation of the mixture gave 1.95 g (40.5%) of vinyl iodide, bp 54–55°C, $n_D^{23} = 1.537$ (published data [12]: bp 56–56.5°C, $n_D^{20} = 1.5385$); 1.15 g (42.8%) of vinyl acetate, bp 75–80°C, $n_D^{23} = 1.391$ (published data [12]: bp 73°C, $n_D^{20} = 1.3958$); and 5.15 g (54.9%) of 2-iodoethyl acetate, bp 80°C (20 mm). IR spectrum, ν , cm^{-1} : 2962 s (C–H_{asym}), 2872 s (C–H_{sym}), 1745 s (C=O), 1050 s (C–O–C), 510 m (C–I). Found, %: C 22.41; H 3.39; I 62.75. C₄H₇O₂. Calculated, %: C 22.42; H 3.27; I 59.34.

Reaction of acetyl iodide with divinyl ether.

Divinyl ether, 2.2 g, was added dropwise to a solution of 5.31 g of acetyl iodide in 15 ml of methylene chloride, cooled to 10°C. The solvent was distilled off, and the residue was analyzed by GLC. Only vinyl iodide and vinyl acetate were identified (using authentic samples). Likewise, GLC analysis of the reaction mixture obtained from 10.6 g of acetyl iodide and 2.2 g of divinyl ether showed the presence of vinyl iodide, vinyl acetate, and unreacted acetyl iodide.

Reaction of acetyl iodide with phenyl vinyl ether.

Phenyl vinyl ether, 3.75 g, was added dropwise to a solution of 5.31 g of acetyl iodide in 15 ml of dry methylene chloride, cooled to 10°C. Distillation of the mixture gave 1.54 g (32%) of vinyl iodide, bp 53–56°C, which was identified by GLC using an authentic sample. The residue was distilled under reduced pressure to isolate 2.53 g (59.5%) of phenyl acetate, bp 90–92°C (20 mm), $n_D^{20} = 1.4990$. IR spectrum, ν , cm^{-1} : 1760 s (C=O); 1580, 1450 (C=C_{arom}); 1210 v.s.,

br (C–O–C). Found, %: C 71.81; H 6.15. C₈H₈O₂. Calculated, %: C 70.58; H 5.88.

Reaction of acetyl iodide with 1,4-divinyloxybenzene.

Following a similar procedure, distillation of the reaction mixture obtained from 5.06 g of 1,4-divinyloxybenzene and 10.6 g of acetyl iodide in 30 ml of methylene chloride gave 3.78 g (78.6%) of vinyl iodide. By recrystallization of the residue from ethanol we isolated 1.12 g (19.4%) of 1,4-diacetoxybenzene with mp 121°C; published data [12]: mp 121°C, 123–124°C. Found, %: C 61.04; H 4.8. C₁₀H₁₀O₄. Calculated, %: C 61.85; H 5.15.

This study was performed under financial support by the Council for Grants of the President of the Russian Federation (project no. NSH-1129.2003.3).

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