

## Acyl Iodides in Organic Synthesis: II. Reactions with Acyclic and Cyclic Ethers

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**Abstract**—Reaction of acyl iodides RCOI (R = Me, Ph) was studied with acyclic and cyclic ethers (Et<sub>2</sub>O, MeCHCH<sub>2</sub>(O), ClCH<sub>2</sub>CHCH<sub>2</sub>(O), THF, O(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>O, EtOCH<sub>2</sub>CH<sub>2</sub>OH, EtOCH=CH<sub>2</sub>, PhOEt]. The reaction occurred with the rupture of one or two CO bonds furnishing the corresponding iodides and esters.

In extension of the study on reactivity of acyl iodides RCOI [R = Me (I), Ph (II)] as compared with that of trimethyliodosilane we investigated their reaction with acyclic and cyclic ethers. The reaction of trialkyliodosilanes with ethers is known [1–4] to proceed with a rupture of C–O–C bonds [Scheme (1)].

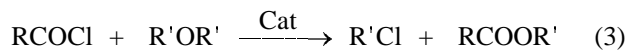


Already in [5, 6] the acyl iodides RCOI were shown to react with ethers along Scheme (2).



These processes were carried out at 80–120°C within 80–240 h. We confirmed that reaction of RCOI (R = Me, Ph) with ethyl ether at 1:1 and 2:1 ratio followed Scheme (2). However unlike previously published data [5, 6] we established that the reaction proceeded already in boiling ether (at 36°C) and completed within 1.5–2 h. Therewith formed ethyl iodide and ethyl acetate or ethyl benzoate respectively.

In contrast the analogous reaction of acyl chlorides or bromides RCOX (X = Cl, Br) with aliphatic ethers occurs cleanly only in the presence of a large quantity of catalyst [ZnCl<sub>2</sub>, FeCl<sub>3</sub>, SnBr<sub>2</sub>, CoCl<sub>2</sub>, Mo(CO)<sub>6</sub>, metallic Zn, Pd complexes and even graphite] [7–9] [Scheme (3)].

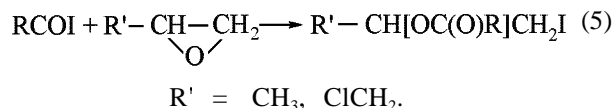


This route to esters is not interesting from the preparative viewpoint for the yields of the target products often are no more than 15–40% due to formation of side products of polymeric and other nature. The attempt to carry out the acetyl chloride reaction with ethers in the presence of elemental

iodine failed [1]. Unlike acyclic ethers the ethylene oxide reacts both with acetyl chloride and acetyl iodide at 25°C within 45 days and 24 days respectively [5] [Scheme (4)].



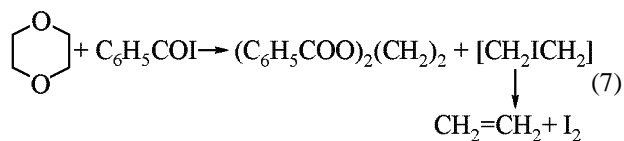
By examples of propylene oxide and epichlorohydrin we established that acyl iodides **I** and **II** readily cleaved the oxirane ring. The process is exothermic, occurs within 1–1.5 h, and same as with Me<sub>3</sub>SiI follows Krasusky rule [10] [Scheme (5)].



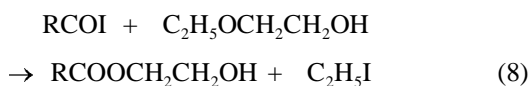
In the same way as trimethyliodosilane [3] the studied acyl iodides reacted also with tetrahydrofuran at 100–110°C in 2 h with the cleavage of C–O bond and formation of 4-iodobutyl acetate [Scheme (6)].



We succeeded in performing reaction between 1,4-dioxane and benzoyl iodide, as in the case of trimethyliodosilane [3], only at the double excess of PhCOI. As a result a crystalline 1,2-dibenzoyloxyethane was isolated [Scheme (7)]. The other reaction product, 1,2-diiodoethane, we failed to isolate due to its instability: it decomposed at distillation into ethylene and elemental iodine.

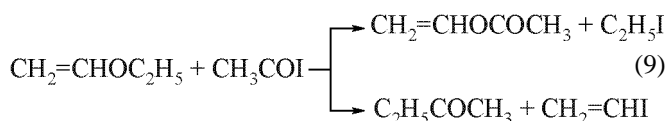


In the acetyl iodide reaction with 2-ethoxyethanol the Et-O bond is subject to rupture resulting in formation of EtI and 2-hydroxyethyl acetate. Interestingly the hydroxy group remained intact [Scheme (8)].



Similarly to reaction with oxiranes this process is exothermal and does not depend on the ratio of the initial reagents (1:1 or 2:1).

Among the product of reaction between acetyl iodide and ethyl vinyl ether vinyl iodide, vinyl acetate, ethyl acetate, and ethyl iodide were identified. This fact evidences the rupture of both ether bonds Et-O and O-CH=CH<sub>2</sub>; the latter process is uncommon [Scheme (9)].

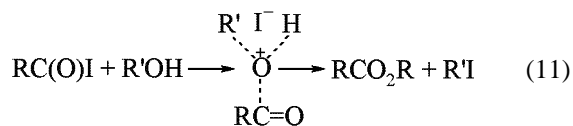


In view of extremely high heat liberation in this reaction and because vinyl ethyl ether is prone to polymerization the reaction has been performed in CH<sub>2</sub>Cl<sub>2</sub> solution. The process occurs virtually at once. The products ratio in the reaction mixture (ethyl iodide: vinyl acetate: ethyl acetate = 1:1.2:1.05; identification and quantitative analysis by GLC) suggests that the reaction occurs with approximately equal probability in both directions.

On the contrary in reaction of acetyl iodide with phenyl ethyl ether only the Et-O bond is ruptured to afford as final products phenyl acetate and ethyl iodide [Scheme (10)].



The similar reactivity exhibited by acyl iodides and trimethyliodosilane with respect to organic compounds containing a C-O-C group suggests that the mechanism of C-O bond cleavage is analogous to that observed for (CH<sub>3</sub>)<sub>3</sub>SiI [3] and consists in formation and decomposition of the corresponding acyloxonium iodides [Scheme(11)].



Thus the studied acyl iodides are as reagents identic to trimethyliodosilane and as such may be used for synthons in the organic synthesis.

## EXPERIMENTAL

IR spectra were recorded on a spectrometer UR-20 from thin films. <sup>1</sup>H NMR spectra were registered on Bruker DPX-400 instrument (400 MHz) in deuteriochloroform, internal reference TMS. The initial acyl iodides were obtained by reaction between the corresponding acyl chlorides with anhydrous sodium iodide by the known procedure [11]. The chromatographic analysis was carried out on LKhM-8M instrument, detector katharometer, carrier gas helium, column 2000 × 4 mm, operation in a programmed mode.

**Acetyl iodide reaction with ethyl ether.** A mixture of 10.6 g of acetyl iodide and 4.6 g of ethyl ether was boiled for 1.5 h. By common distillation 3.21 g (34%) of ethyl iodide, bp 72°C, and 1.22 g (23%) of ethyl acetate, bp 77°C, was isolated. The products were identified by GLC comparison with standards.

**Benzyl iodide reaction with ethyl ether.** A mixture of 11 g of benzyl iodide and 3.5 g of ethyl ether was boiled for 2 h. From the reaction mixture 3.15 g (43%) of ethyl iodide, bp 72°C, was separated and identified by GLC. The residue after distillation of ethyl iodide was distilled in a vacuum to obtain 1.35 g (19%) of ethyl benzoate, bp 90°C (10 mm Hg). Found, %: C 71.86; H 6.92. C<sub>9</sub>H<sub>10</sub>O<sub>2</sub>. Calculated, %: C 72.00; H 6.66.

**Benzyl iodide reaction with propylene oxide.** At mixing of 11 g of benzyl iodide and 2.75 g of propylene oxide the reaction mixture self-heated. The separated dark-brown precipitate was several times washed with ethanol and dried in a vacuum desiccator over P<sub>2</sub>O<sub>5</sub>. 2-Iodoisopropyl benzoate (1,54 g; 11%) was isolated as brown powder, mp 94°C. Found I, %: 43.29. C<sub>10</sub>H<sub>12</sub>IO<sub>2</sub>. Calculated I, %: 43.64.

**Acetyl iodide reaction with epichlorohydrin.** At room temperature 10.6 g of acetyl iodide was mixed with 5.8 g of epichlorohydrin. The vacuum distillation afforded 9.54 g (61%) of 1-iodo-3-chloroisopropyl acetate, bp 100–110°C (10 mm Hg). Found, %: C 22.84; H 3.36; Cl + I 60.65. C<sub>5</sub>H<sub>8</sub>ClIO<sub>2</sub>. Calculated, %: C 22.85; H 3.04; Cl + I 61.9.

**Acetyl iodide reaction with tetrahydrofuran.** A mixture of 10.6 g of acetyl iodide and 4.5 g of tetrahydrofuran was heated to boiling for 2 h. By vacuum distillation was separated 10.55 g (73%) of 4-iodobutyl acetate, bp 110°C (10 mm Hg). IR spectrum, ν, cm<sup>-1</sup>: 2900–2850s (CH), 1745s (C=O), 1275, 1050, ν.s (COC), 500 m (C-I). <sup>1</sup>H NMR spectrum, δ, ppm: 4.1 (2H, CCH<sub>2</sub>O), 3.2 (2H, CCH<sub>2</sub>I),

2.1 s (CH<sub>3</sub>COO). Found, %: C 30.34; H 4.57; I 52.76. C<sub>6</sub>H<sub>11</sub>IO<sub>2</sub>. Calculated, %: C 29.75; H 4.54; I 52.47.

**Benzyl iodide reaction with 1,4-dioxane.** At mixing of 11 g of benzyl iodide and 2.05 g of 1,4-dioxane a precipitate immediately separated. The latter was filtered off, dissolved in ethanol, reprecipitated with water, and dried in a vacuum desiccator over P<sub>2</sub>O<sub>5</sub>. Thus was isolated 1.43 g (23%) of 1,2-dibenzoyloxyethane, bp 73°C (publ. [12]: bp 73–74°C). Found, %: C 70.66; H 5.27. C<sub>16</sub>H<sub>14</sub>O<sub>4</sub>. Calculated, %: C 71.1; H 5.18.

**Acetyl iodide reaction with 2-ethoxyethanol.** At mixing of 10.6 g of acetyl iodide and 5.6 g of 2-ethoxyethanol the reaction mixture self-heated. By distillation of the reaction mixture at the atmospheric pressure we separated 4.21 g of ethyl iodide, bp 67–72°C,  $n_D^{25}$  1.5011 (publ. [12]: bp 72°C,  $n_D^{20}$  1.5137), and 4.92 g (79%) of 2-hydroxy ethyl acetate, bp 80–85°C (25 mm Hg.) {publ. [12]: bp 182°C (760 mm Hg.)}. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 3450 (OH), 2962 s, 2872 s (CH), 1750 s (C=O), 1275, 1050 s (COC). Found, %: C 46.86; H 8.31. C<sub>4</sub>H<sub>8</sub>O<sub>3</sub>. Calculated, %: C 46.15; H 7.69.

**Acetyl iodide reaction with vinyl ethyl ether.** To a solution of 5.3 g of acetyl iodide in 20 ml of dichloromethane at 10°C was added 2.25 g of vinyl ethyl ether. After mixing by a common distillation of the reaction mixture was isolated 0.45 g (10%) of vinyl iodide, bp 56°C,  $n_D^{18}$  1.541 (publ. [12]: bp 56–56.5°C,  $n_D^{20}$  1.5385). In the second fraction ethyl iodide, vinyl acetate, and ethyl acetate were identified by GLC.

**Acetyl iodide reaction with phenyl ethyl ether.** At room temperature 5.31 g of acetyl iodide was

mixed with 5.8 g of phenyl ethyl ether. From the mixture was separated by distillation 2.5 g (53%) of ethyl iodide, bp 70–72°C,  $n_D^{27}$  1.5022 (publ. [12]: bp 72°C,  $n_D^{20}$  1.5137), and 2.3 g (71%) of phenyl acetate, bp 75°C (10 mm Hg) {publ. [12]: bp 195.5°C (760 mm Hg.)}. Found, %: C 70.1; H 5.52. C<sub>8</sub>H<sub>8</sub>O<sub>2</sub>. Calculated, %: C 70.58; H 5.92.

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