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Acyl Iodides in Organic Synthesis. Reaction of Acetyl Iodide with Dialkyl Sulfides and Disulfides

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Abstract—Reactions of acetyl iodide with dialkyl and dialkenyl sulfides RSR (R = Et, Bu, CH_2=CH, CH_2=$CHCH_2$) and with disulfides RSSR (R = Pr, C_6H_{13}, $PhCH_2$) were studied. Dialkyl sulfides reacted with MeCOI to give the corresponding alkyl ethanethioates and alkyl iodides as a result of cleavage of the S–C bond. The reactions of acetyl iodide with divinyl and diallyl sulfides involved addition across the double bond and subsequent polymerization of 1-alkenylsulfanyl-2(3)-iodoalkyl methyl ketones. Dialkyl disulfides RSSR (R = Pr, C_6H_{13}) and dibenzyl disulfide reacted with acetyl iodide via cleavage of the S–S bond to produce the corresponding ethanethioates and organylsulfenyl iodides. The latter underwent disproportionation to form the initial disulfide and molecular iodine.

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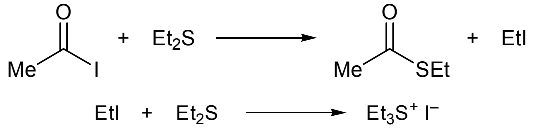
We previously found that reactions of acyl iodides RCOI (R = Me, Ph, etc.) with acyclic and cyclic ethers involve cleavage of one or both C–O bonds under very mild conditions, at room temperature or in boiling ether within 1.5–2 h [1], with formation of the corresponding esters and alkyl iodides. Likewise, acyl iodides readily reacted with alkyl vinyl ethers via cleavage of O–C_{sp^3} and O–C_{sp^2} bonds [2]. In continuation of our studies on acyl iodides as synthons and reagents in organic and organometallic synthesis, in the present work we examined reactions of acetyl iodides with sulfur analogs of ethers, dialkyl sulfides, and compounds containing a disulfide moiety.

The early assumption [3] that acyl iodides could not react with dialkyl sulfides [3] was disproved in 1930s [4]. When a mixture of diethyl sulfide with acetyl iodide was allowed to stand over a period of 20 days, the formation of *S*-ethyl ethanethioate and ethyl iodide was observed as a result of cleavage of the sulfide C–S bond. The reaction was accompanied by addition of liberated ethyl iodide to initial diethyl sulfide with formation of crystalline triethylsulfonium iodide [4].

We found that, in fact, acetyl iodide reacts with dialkyl sulfides RSR (R = Et, Bu) under more severe conditions than with their oxygen analogs. The reactions were complete in 7 days at 70–80°C, and triethylsulfonium iodide was isolated in the reaction with diethyl sulfide (Scheme 1).

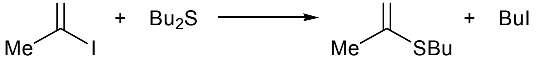
Scheme 1.



As shown in [4], the primary product is *S*-ethyl ethanethioate which forms an azeotrope with residual acetyl iodide. The presence of *S*-ethyl ethanethioate in the azeotrope was confirmed by GLC and IR spectroscopy [ν(S–C=O) 1690 cm^{-1}].

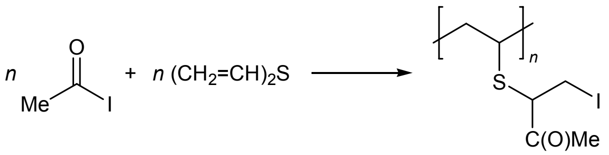
No tributylsulfonium iodide was detected in the reaction of acetyl iodide with dibutyl sulfide under analogous conditions. In this case, a difficultly separable mixture of *S*-butyl ethanethioate and butyl iodide at a ratio of 1 : 1 (GLC) was obtained (Scheme 2).

Scheme 2.



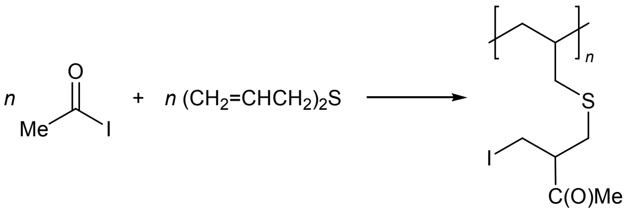
When an equimolar mixture of divinyl sulfide and MeCOI was heated to 45°C, it spontaneously warmed up, finally leading to explosion. Likewise, a mixture of acetyl iodide with divinyl ether blew up in 6 h without external heating [5]. Nevertheless, we succeeded in reacting acetyl iodide with divinyl sulfide without explosion at room temperature in 5 h. As a result, we isolated a dark infusible polymer with the composition C_6H_9OSI, which was insoluble in common organic solvents. Its IR spectrum contained an absorption band at 1753 cm^{-1} assignable to carbonyl stretching vibrations. The elemental composition and IR data suggest that the first step of the reaction is addition of acetyl iodide to one double bond in divinyl sulfide with formation of 4-iodo-3-vinylsulfanylbutan-2-one which then undergoes polymerization at the second vinyl group, catalyzed by traces of acetyl iodide (Scheme 3).

Scheme 3.



The reaction of acetyl iodide with diallyl sulfide was also accompanied by polymerization, but the process was not so vigorous as the reaction with divinyl sulfide. The resulting black infusible polymer was also insoluble in common organic solvents. Its elemental composition corresponded to the formula $C_8H_{12}OSI$, and carbonyl stretching vibration band was observed in the IR spectrum at 1748 cm^{-1}. Presumably, the reaction pattern is analogous to that proposed for the reaction with divinyl sulfide, and the process involves polymerization of intermediate 4-allylsulfanyl-3-iodomethylbutan-2-one (Scheme 4).

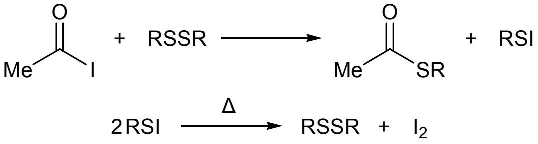
Scheme 4.



Addition reactions of acyl iodides with unsaturated compounds have been poorly studied. Among numerous examined unsaturated compounds, only the additions of acetyl iodide to 2-methylbut-2-ene and cyclohexene were reported [5].

Acetyl iodide reacted with diorganyl disulfides RSSR (R = Pr, C_6H_{13}, $PhCH_2$) at 60–70°C to give *S*-organyl ethanethioates as a result of cleavage of the S–S bond. Unlike *S*-organyl ethanethioates which were isolated from the reaction mixtures, the other products, the corresponding sulfenyl iodides RSI, underwent disproportionation into molecular iodine and initial disulfide [6]. Therefore, just the latter were isolated as the second product.

Scheme 5.



R = Pr, C_6H_{13}, $PhCH_2$.

EXPERIMENTAL

The IR spectra were recorded from films on a UR-20 spectrometer. The reaction mixtures were analyzed by GLC on an LKhM-8MDII chromatograph equipped with a thermal conductivity detector and a 1000×4-mm column packed with 5% SE-30 on Chromaton N-AW-HMDS (0.2–0.25 mm); carrier gas helium. Initial diethyl, dibutyl, divinyl, and diallyl sulfides were commercial products; initial dialkyl disulfides were synthesized as described in [7].

Reaction of diethyl sulfide with acetyl iodide. A mixture of 5.1 g (56 mmol) of diethyl sulfide and 9.6 g (56 mmol) of acetyl iodide was stirred first for 30 min at room temperature and then for 10 h at 65–70°C. Yellowish crystals of triethylsulfonium iodide were separated from the mixture. The product was insoluble in diethyl ether and soluble in water, mp 110–115°C; published data [4]: mp 119°C. Found, %: C 29.08; H 5.98; I 47.66; S 12.47. $C_6H_{15}IS$. Calculated, %: C 29.27; H 6.09; I 48.85; S 13.00.

Distillation of the reaction mixture gave a fraction boiling in a broad range, bp 104–115°C. According to the GLC data, it was a mixture of *S*-ethyl ethanethioate and unreacted acetyl iodide. IR spectrum, ν, cm^{-1}: 1796 (C=O in MeCOI), 1711 (S–C=O), 626 (S–C), 540 (C–I).

Reaction of dibutyl sulfide with acetyl iodide. A mixture of 7.2 g (49 mmol) of dibutyl sulfide and 8.3 g (49 mmol) of acetyl iodide was stirred for 7 h on heating at 90–110°C. Distillation gave a fraction with bp 162–171°C which was a mixture of *S*-butyl ethanethioate and butyl iodide at a ratio of ~1 : 1 (according to the GLC data). IR spectrum, ν, cm^{-1}: 1693 (S–C=O), 627 (S–C), 529 (C–I).

Reaction of divinyl sulfide with acetyl iodide. Acetyl iodide, 2.0 g (10 mmol), was slowly added under stirring at room temperature to 1.0 g (10 mmol) of divinyl sulfide. The mixture spontaneously warmed up. It was stirred for 5 h at room temperature, and the initially viscous mixture solidified to form a black polymeric material which was difficultly soluble in diethyl ether and chloroform and soluble in acetone. Yield 2.6 g (86%). IR spectrum, ν, cm^{-1}: 1751 (C=O), 1693 (S–C=O), 627 (S–C), 539 (C–I). Found, %: C 28.49; H 3.63; I 51.42; S 12.18. C_6H_9IOS. Calculated, %: C 28.13; H 3.52; I 49.61; S 12.50.

Reaction of diallyl sulfide with acetyl iodide. Diallyl sulfide, 4.3 g (38 mmol), and acetyl iodide, 6.4 g (38 mmol), were mixed together at room temperature. The mixture slightly warmed up and was stirred for 6 h at 100–110°C. The initially viscous mixture gradually solidified to form a black polymeric material which was poorly soluble in diethyl ether, insoluble in chloroform, and soluble in acetone. Yield 7.3 g (68%). IR spectrum, ν, cm^{-1}: 1751 (C=O), 1693 (S–C=O), 627 (S–C), 539 (C–I). Found, %: C 27.06; H 3.87; I 51.41; S 13.37. C_6H_9IS. Calculated, %: C 28.13; H 3.52; I 49.61; S 12.50.

Reaction of dipropyl disulfide with acetyl iodide. Acetyl iodide, 7.7 g (45 mmol), was slowly added under stirring at room temperature to 6.8 g (45 mmol) of dipropyl disulfide. The mixture slightly warmed up and was stirred for 6 h at 60–65°C. Distillation gave 2.4 g (35%) of *S*-propyl ethanethioate, bp 143°C, n_D^{20} = 1.4638. IR spectrum: ν 1694 cm^{-1} (S–C=O). Found, %: C 50.36; H 8.70; S 29.89. $C_5H_{10}OS$. Calculated, %: C 50.76; H 8.46; S 27.07.

Reaction of dihexyl disulfide with acetyl iodide. Acetyl iodide, 7.1 g (42 mmol), was added under stirring at room temperature to 9.8 g (42 mmol) of dihexyl disulfide, and the mixture was heated for 6 h at 65–70°C. The liquid product was separated from liberated molecular iodine by extraction with diethyl ether. The extract was kept for 6 h over metallic copper to remove residual iodine. The solvent was distilled off, and the residue was distilled under reduced pressure to isolate 3.2 (19%) of *S*-hexyl ethanethioate, bp 92–94°C (14 mm), n_D^{20} = 1.4620. IR spectrum: ν 1695 cm^{-1} (S–C=O). Found, %: C 59.08; H 9.29; S 21.74. $C_8H_{16}OS$. Calculated, %: C 59.89; H 9.98; S 19.96.

Reaction of dibenzyl disulfide with acetyl iodide. Acetyl iodide, 6.4 g (38 mmol), was slowly added under stirring at room temperature to 9.3 (38 mmol) of dibenzyl disulfide in 40 ml of heptane. The mixture was heated for 6 h, crystals of iodine were filtered off, the solvent was distilled off from the filtrate, and the residue was distilled under reduced pressure to isolate 3.9 g (25%) of *S*-benzyl ethanethioate as a red oily substance, bp 94–95°C (3 mm). IR spectrum: ν 1691 cm^{-1} (S–C=O). Found, %: C 65.25; H 6.05; S 21.11. $C_9H_{10}OS$. Calculated, %: C 64.97; H 6.02; S 19.25.

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