Reports of the Academy of Sciences of the USSR

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1964

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1964. Vol. 158, No. 1

CHEMISTRY

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SELENIUM-CONTAINING DERIVATIVES OF ACRYLIC AND METHACRYLIC ACIDS

(Presented by Academician B. A. Arbuzov, March 7, 1964)

At the present time, a large number of various esters of acrylic and methacrylic acids have been obtained that contain tin, lead, mercury, phosphorus, and other elements. In a number of studies, thio esters of acrylic and methacrylic acids have been investigated in considerable detail. Marvel and co-workers (1) synthesized a series of alkyl thioacrylates as a result of the interaction of the acid chloride of α, β-dibromopropionic acid with mercaptans in the presence of alkali, followed by elimination of bromine from the resulting thio esters of α, β-dibromopropionic acid. Koton, Kiseleva, and Podgorskaya obtained thiophenyl and thiobenzyl esters of methacrylic acid from methacryloyl chloride, thiophenol, and benzyl mercaptan in alkaline solution (2). Both thio esters polymerize upon heating both in the absence and in the presence of radical-polymerization initiators. Studies (3–5) are devoted to the polymerization of thioacrylates and thiomethacrylates. Despite the very broad and intensive study of derivatives of acrylic and methacrylic acids, the literature contains no information on selenium-containing derivatives of these acids. To fill this gap, we studied the reaction of selenophenol with methacryloyl chloride. The reaction was carried out in ethereal solution in the presence of triethylamine with equimolecular amounts of the reagents. As a result of the reaction, two products were obtained. The lower-boiling product, according to analytical data and IR spectra, is the selenophenyl ester of methacrylic acid (I). In its IR spectrum there is absorption in the region of 1630 cm^{-1}, characteristic of a double bond, and an absorption band in the region of 1680 cm^{-1}, characteristic of a CO group attached to a selenophenyl group and conjugated with a double bond. I is a mobile yellow liquid with a characteristic odor and is soluble in acetone, ether, and alcohol.

Investigation of the higher-boiling product showed that it is the product of addition of selenophenol to the selenophenyl ester of methacrylic acid formed in the first phase of the reaction—the selenophenyl ester of α-methyl-β-selenophenylpropionic acid (II). The structure of II is confirmed by the results of analysis for selenium content, determination of molecular refraction and molecular weight, and the IR spectrum. In the IR spectrum of II there is an intense absorption band at 1713 cm^{-1}, characteristic of the carbonyl group; the frequency is lowered due to conjugation with the phenyl ring, transmitted through selenium; absorption frequencies characteristic of a double bond are absent.

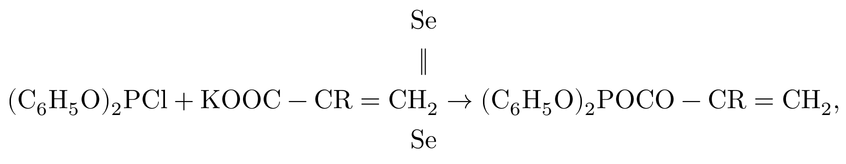
$$C_6H_5SeH + ClCO{-}C(CH_3){=}CH_2 \rightarrow C_6H_5SeC(=O){-}C(CH_3){=}CH_2 \tag{I}$$

$$C_6H_5SeH \longrightarrow C_6H_5SeC(=O){-}CH(CH_3){-}CH_2SeC_6H_5 \tag{II}$$

Under the adopted experimental conditions, I is formed in approximately three times greater amount than II. II is a viscous liquid, soluble in alcohol, ether, and acetone.

For a more convincing demonstration of the proposed course of the reaction, its second stage was carried out separately. As a result of the interaction of selenophenol and selenophenyl methacrylate, an addition product was obtained in 54% yield, identical with II according to its constants and IR spectra. The literature contains data on the formation of compounds of type II also in reactions of mercaptans with acid chlorides of α,β-unsaturated acids. Preliminary experiments on the polymerization of I showed that, in the presence of 0.5 mole % benzoyl peroxide at 80° and heating for sixty hours, a rubber-like polymer is formed. In the presence of 1.5 mole % azobisisobutyronitrile and heating for forty hours at 80°, a hard brittle polymer is obtained, soluble in dimethylformamide, swelling in carbon tetrachloride and benzene, and insoluble in water, alcohol, and acetone. On heating it softens and at 120–125° melts to a viscous liquid. In the presence of 0.5 mole % azobisisobutyronitrile and heating for forty hours at 100°, hard polymers with m.p. 60–64° are also formed; they are soluble in benzene, chloroform, carbon tetrachloride, acetone, and dimethylformamide. All the polymers are yellow in color and have very high adhesion to glass.

As a result of the reaction of diphenyl selenophosphoric acid chloride with the potassium salt of acrylic and methacrylic acids, mixed anhydrides of diphenylselenophosphoric acid and acrylic and methacrylic acids were obtained in yields of about 50%:



$$(C_6H_5O)_2PCl + KOOC - CR = \underset{\mathrm{Se}}{\overset{\overset{\mathrm{Se}}{\|}}{CH_2}} \rightarrow (C_6H_5O)_2POCO - CR = CH_2,$$

where $R = \mathrm{H},\ CH_3$.

The unsaturated anhydrides obtained are crystalline substances with m.p. 58–59° and 74–75°, respectively, soluble in most organic solvents. They polymerize in the presence of 1.5 mole % azobisisobutyronitrile at a temperature of 90° very slowly.

Experimental Part

Interaction of selenophenol with methacrylic acid chloride. In a three-necked round-bottomed flask equipped with a stirrer, reflux condenser, and dropping funnel were placed 15.6 g (0.1 mole) of selenophenol, 10.1 g (0.1 mole) of triethylamine, and absolute ether, and 10.4 g (0.1 mole) of methacrylic acid chloride was added dropwise. The mixture was stirred for about six hours; the precipitate of triethylamine hydrochloride was filtered off, and the ether was distilled off in vacuo. Distillation of the residue in vacuo gave: I selenophenyl methacrylate –9.2 g (40.8%), b.p. 104°/1 mm, n_D^{20} 1.5980, d_4^{20} 1.3545, MR found 56.66, calculated 55.23.

Found, %: Se 34.87, 35.12
$C_{10}H_{10}OSe$. Calculated, %: Se 35.11

II selenophenyl ester of α-methyl-β-selenphenylpropionic acid –3.5 g, b.p. 180–181°/1 mm, n_D^{20} 1.6455, d_4^{20} 1.5039; MR found 92.19, calculated 90.72.

Found, %: Se 41.35, 41.52
$C_{16}H_{16}OSe_2$. Calculated, %: Se 41.34

Molecular weight found 376, calculated 382.

Addition of selenophenol to selenophenyl methacrylate. To 7.9 g of selenophenyl methacrylate was added 5.9 g

selenophenol. The temperature rose from 15 to 27°. The mixture was then heated for 10 h under a reflux condenser at 120–130°. After distillation in vacuo, 8.2 g of the selenophenyl ester of α-methyl-β-selenophenylpropionic acid was obtained. B.p. 180°/1 mm, n_D^{20} 1.6447, d_4^{20} 1.4980; MR found 92.23, calculated 90.72.

Reaction of diphenyl selenophosphoric acid chloride with the potassium salt of acrylic acid. To 6 g (0.05 mole) of the potassium salt of acrylic acid in absolute ether, 16 g (0.05 mole) of diphenyl selenophosphoric acid chloride was added with stirring. As a result of the reaction, the mixed anhydride of diphenyl selenophosphoric and acrylic acids was obtained, m.p. 58–59°.

Found, %: Se 21.42; P 8.76, 8.63
$C_{15}H_{13}O_4SeP$. Calculated, %: Se 21.51; P 8.44

Reaction of diphenyl selenophosphoric acid chloride with the potassium salt of methacrylic acid. To 6.2 g (0.05 mole) of the potassium salt of methacrylic acid in absolute ether, 16 g (0.05 mole) of diphenyl selenophosphoric acid chloride was added with stirring. After removal of the ether and distillation of the residue in vacuo, 8.4 g of the mixed anhydride of diphenyl selenophosphoric and methacrylic acids was obtained. B.p. 191°/1 mm, m.p. 74–75° (from alcohol).

Found, %: Se 21.27, 20.87; P 8.31, 8.19
$C_{16}H_{15}O_4SeP$. Calculated, %: Se 20.70; P 8.13

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Received
29 II 1964

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Note: Figure translations are in progress. See original paper for figures.