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Abstract

Full Text

Chemistry

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ON THE REACTION OF DICHLOROCARBENES WITH VINYL SULFIDES

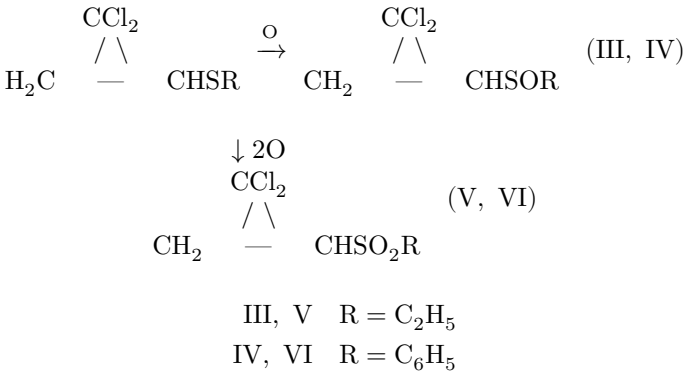
In recent years much attention has been devoted to reactions proceeding through the intermediate formation of carbenes and halocarbenes. One of the characteristic features of these divalent-carbon derivatives is their addition to olefins with the formation of cyclopropane derivatives ([1]). Owing to the electrophilicity of carbenes and halocarbenes, they add especially readily to alkenes whose double bond, as is known, has a nucleophilic character. We have studied the reaction of dichlorocarbene with vinyl sulfides, which, as was shown earlier ([2]), readily interact with other electrophilic reagents. It was to be expected that this reaction would proceed no less readily than in the case of hydrocarbons ([3,4]). This preliminary assumption was confirmed in the reaction of dichlorocarbene with vinylethyl sulfide and vinylphenyl sulfide

$$CH_2{=}CHSR + CCl_2 \rightarrow \begin{array}{l} \quad\quad CCl_2 \\ \quad\quad / \ \backslash \\ CH_2 \quad — \quad CHSR \end{array}$$

$$R = C_2H_5 \text{ (I)}; \quad R = C_6H_5 \text{ (II)}$$

Dichlorocarbene was obtained by the usual method ([3]) from chloroform and potassium tert-butoxide. The reaction with vinylethyl sulfide was carried out in two variants. In one of them a considerable excess of vinyl sulfide was used (5 moles relative to chloroform). In this case the yield of the dichlorocyclopropane compound was 40% (calculated on chloroform). Under comparable conditions the yield for cyclohexene was 59%. In the second variant the reaction was carried out in a solution of anhydrous ether with a small excess of the carbene-forming reagent (1.5 mole per 1 mole of sulfide). Under these conditions the yield was 25% (calculated on vinyl sulfide). Under the same conditions Japanese authors ([4]) obtained 35% of theory of the corresponding dichlorocyclopropane derivative from methyl- and dimethylbutadienes. For vinylphenyl sulfide similar results were obtained, which indicates no very substantial difference in the character of the double bond in these compounds. The actual yield is probably somewhat higher, since dichlorocyclopropane derivatives substituted by SR groups

are unstable and the reaction is always accompanied by the formation of considerable amounts (15-20%) of a resin containing sulfur and chlorine. Naturally, these data on comparative reactivity are not as exact as results obtained by the method of competing reactions, for example, for hydrocarbons ([5]). The synthesized ethylthio- and phenylthiodichlorocyclopropanes were oxidized in good yields to the corresponding sulfinyl and sulfonyl compounds.



Oxidation to sulfoxides was carried out either with hydrogen peroxide in acetone medium, or with one equivalent of concentrated acetyl hydroperoxide in ether solution at a temperature of -10–-12°. Sulfones were obtained by oxidation with an excess of acetyl hydroperoxide in ether medium.

There are very few literature data concerning the formation of sulfides, sulfoxides, and sulfones containing sulfur bonded to a three-membered ring. Only recently has it been possible to synthesize phenylcyclopropanesulfone by dehydrohalogenation of γ-chloropropyl phenyl sulfone ([7]), whereas earlier attempts to obtain substances of this type were unsuccessful ([6]). As for analogous compounds with a chlorinated three-membered ring, in the present work they are described for the first time.

Experimental Part

1-Ethylthio-2,2-dichlorocyclopropane (I). 1) In a stream of dry nitrogen, 4 g of metallic potassium are dissolved in 100 ml of tert-butyl alcohol. The alcohol is distilled off, and the residue is dried for 1.5 h at $170^{\circ}/4$ mm. With cooling to -5° and good stirring, 58 g of vinylethyl sulfide are added, followed by portions of 7 ml of chloroform. The resulting jelly is diluted with 20 ml of isopentane. The mixture is stirred for 0.5 h at room temperature, left overnight, and then poured into water. The upper layer is separated, and the aqueous layer is extracted with isopentane. After drying, evaporation of the solvent and of the excess vinylethyl sulfide, the product is distilled. This gives 6.1 g of substance I (40%, calculated on chloroform). B.p. 72.5–$74.5^{\circ}/16$ mm, $n_d^{20} = 1.5083$, d_4^{20} 1.2183, MR found 41.08; calculated 41.49.

Found, %: C 35.13, 35.20; H 4.71, 4.78; S 18.73, 18.92; Cl 41.64, 41.45
$C_5H_8SCl_2$. Calculated, %: C 35.04; H 4.71; S 18.72; Cl 41.45

2) From 36 g of metallic potassium and 600 g of tert-butyl alcohol, potassium tert-butoxide is prepared as described above. With good stirring, 0.4 mole of vinylethyl sulfide in 300 ml of abs. ether is added. Then, over 3 h, 72 g of chloroform (0.6 mole), diluted with an equal volume of abs. ether, are added. The reaction is conducted at 5–7°. The solution is stirred for 2 h at room temperature and left overnight. On the following day, 7 g of chloroform are added, and the mixture is stirred for 1 h. Water acidified with phosphoric acid is added, and the ether layer is separated. The aqueous layer is extracted with ether. After evaporation of the solvent the product is distilled, giving 18.2 g of substance I (25.6%, calculated on vinyl sulfide). B.p. 86–89°/20 mm, $n_d^{20} = 1.5080$.

1-Phenylthio-2,2-dichlorocyclopropane (II). Obtained by method 2 from 9.4 g of metallic potassium, 150 g of tert-butyl alcohol, 15 g of vinyl phenyl sulfide, and 18 g of chloroform in a solution of 100 ml of abs. ether. This gave 7.6 g of substance II (25.9%, calculated on vinyl sulfide). B.p. 65–68°/$4 \cdot 10^{-2}$ mm, $n_d^{20} = 1.5892$, d_4^{20} 1.2983, MR found 56.89; calculated 56.96.

Found, %: C 49.44, 49.60; H 3.86, 3.86; S 14.49, 14.43; Cl 32.74, 32.69
$C_9H_8SCl_2$. Calculated, %: C 49.33; H 3.68; S 14.63; Cl 32.40

1-Ethylsulfinyl-2,2-dichlorocyclopropane (III). To 8 g of substance I (0.047 mole) in 8 ml of abs. acetone, cooled with a salt-snow mixture, with stirring, 1.62 g of hydrogen peroxide in the form of a 91% solution (0.047 mole) was added dropwise at such a rate that the temperature of the reaction mixture did not exceed −10°. The reaction mixture was stirred for 6 h at 0–5°. Oxidation was carried out for 7 days. A qualitative test showed the absence of H_2O_2. The acetone was evaporated in vacuo, and the residue was extracted with chloroform and dried over Na_2SO_4. After evaporation of the chloroform in vacuo and distillation, 5.6 g (66.3%) of substance III was obtained, with b.p. 65–67°/$3.8 \cdot 10^{-2}$ mm, m.p. 27–29°.

Found, %: C 32.21, 31.97; H 4.66, 4.66; Cl 37.98, 37.97
$C_5H_8OSCl_2$. Calculated, %: C 32.09; H 4.31; Cl 37.90

1-Phenylsulfinyl-2,2-dichlorocyclopropane (IV). To 2 g of substance II (0.009 mole) in 6 ml of abs. ether, cooled to −10°, there was added dropwise 0.9 g (0.009 mole) of acetyl hydroperoxide diluted with an equal volume of abs. ether. The oxidation was carried out for 2 days. The mixture was diluted with abs. ether and washed with water. After drying and evaporation of the solvent in vacuo, 1.9 g (90.5%) of (IV) was obtained, m.p. 55.5-56.5°.

Found, %: C 46.21; H 3.53; S 13.94, 13.91
$C_9H_8O_2SCl_2$. Calculated, %: C 45.97; H 3.43; S 13.64

1-Ethylsulfonyl-2,2-dichlorocyclopropane (V). Obtained from 8 g of substance I (0.047 mole) and 8.6 g (0.097 mole) of 83% acetyl hydroperoxide in 15

ml of abs. ether. Yield 5.6 g (55.6%). M.p. 55–56°.

Found, %: C 29.67, 29.63; H 4.27, 4.16; S 15.73, 15.85; Cl 35.00, 34.77
$C_5H_8O_2SCl_2$. Calculated, %: C 29.52; H 3.98; S 15.74; Cl 34.92

1-Phenylsulfonyl-2,2-dichlorocyclopropane (VI). Obtained from 2.4 g of substance II (0.0094 mole) and 2.2 g (0.019 mole) of 83% acetyl hydroperoxide in 6 ml of abs. ether. Obtained 1.7 g of VI (65.38%). M.p. 88.5–89.5°.

Found, %: S 12.85, 12.87; Cl 28.14, 28.03
$C_9H_8O_2SCl_2$. Calculated, %: S 12.74; Cl 28.23

It has been shown that dichlorocarbenes add to α,β-unsaturated sulfides no less actively than to alkenes, which confirms the nucleophilic character of their double bond.

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