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Abstract

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VINYL COMPOUNDS IN THE DIENE SYNTHESIS

ON THE DIENE SYNTHESIS OF THIOVINYL ETHERS WITH CYCLOPENTADIENE AND HEXACHLOROCYCLOPENTADIENE

(Presented by Academician A. V. Topchiev, 25 VII 1957)

It was shown earlier (1) that simple vinyl ethers of the formula $CH_2{=}CH{-}OR$, where R is an alkyl, aryl, or saturated hydroaromatic radical, are capable of participating in the diene synthesis with cyclopentadiene and hexachlorocyclopentadiene as the philodiene component:

$$CH_2{=}CH{-}OR + \text{ cyclopentadiene } \longrightarrow \text{ adduct } \longrightarrow \text{ isomeric adduct} \quad (1)$$

The facts known up to that time concerned individual representatives of simple vinyl ethers, and the investigations were episodic in character. Thus, Platz and Meierovich (2) obtained an adduct of cyclopentadiene and vinyl butyl ether. Abramov et al. (3) demonstrated the possibility of diene synthesis on the basis of vinyl butyl and vinyl phenyl ethers and cyclones.

In continuation of a systematic study of the diene-synthesis reaction involving vinyl compounds, we investigated the possibility of participation in it by thiovinyl ethers. These compounds, individual representatives of which had been obtained earlier (4,5), became accessible thanks to a method for their preparation developed by one of us and Prilezhaeva (6). The aim of the present investigation was to study the conditions of the diene-synthesis reaction of vinyl ethyl sulfide and vinyl phenyl sulfide with cyclopentadiene and hexachlorocyclopentadiene.

The question of the participation of thiovinyl ethers in the diene synthesis has been covered in the literature only for one example, n-tolyl thiovinyl ether (7). In the condensation of this compound with cyclopentadiene, Alder isolated one adduct containing one molecule of diene in the molecule. We had previously noted ([8]) that vinyl aryl ethers show a greater tendency toward reactions by a radical mechanism than vinyl alkyl ethers, while observations of the behavior of both in the diene synthesis revealed that vinyl aryl ethers also enter this reaction more readily ([1]). As for vinyl sulfides, they too have been noted ([6]) to show a greater tendency toward free-radical transformations in comparison with their oxygen analogs. On the basis of the observed similarity in the behavior of these compounds, one could expect the diene-synthesis reactions with thiovinyl ethers to proceed more readily than with vinyl alkyl ethers, which was confirmed experimentally. The diene synthesis of cyclopentadiene and hexachlorocyclopentadiene with thiovinyl ethers proceeds at lower temperatures than with vinyl alkyl ethers, and at equal ratios of the starting components the yields of thiovinyl-ether derivatives are higher. The synthesis is accompanied by the formation of thioethers of bicycloheptene and the corresponding derivatives of octahydronaphthalene.

$$\mathrm{CH_2{=}CH{-}SR} + \text{ cyclopentadiene } \longrightarrow \text{ bicycloheptene derivative }, \quad R = \mathrm{C_2H_5}\ (I);\ \mathrm{C_6H_5}\ (II) \tag{2}$$

$$\text{[scheme]} \quad , \quad R = \mathrm{C_2H_5}\ \text{(III)};\ \mathrm{C_6H_5}\ \text{(IV)} \tag{3}$$

With hexachlorocyclopentadiene, thiovinyl ethers form thioethyl- and thiophenylhexachlorobicycloheptenes:

$$\mathrm{CH_2{=}CH{-}SR} + \text{[hexachlorocyclopentadiene]} \longrightarrow \text{[hexachlorobicycloheptene derivative]}, \quad R = \mathrm{C_2H_5}\ \text{(V)};\ \mathrm{C_6H_5} \tag{4}$$

The stepwise character of the reaction is also evident from the fact that the isolated thioethers of bicycloheptene (I and II) condense with hexachlorocyclopentadiene to form thioethers of dihydroaldrin (VII and VIII):

$$\text{[bicycloheptene thioether]} + \text{[hexachlorocyclopentadiene]} \longrightarrow \text{[dihydroaldrin thioether]}, \quad R = \mathrm{C_2H_5}\ \text{(VII)};\ \mathrm{C_6H} \tag{5}$$

Thus, conditions have been found for the diene synthesis based on vinylethyl and vinylphenyl sulfides with cyclopentadiene and hexachlorocyclopentadiene. The corresponding thioethyl- and thiophenylbicycloheptenes, hexachlorobicycloheptenes, octahydronaphthalene derivatives, and thioethers of dihydroaldrin have been isolated. A certain commonality was also established in the behavior of vinylaromatic ethers and thiovinyl ethers in diene-synthesis reactions with cyclopentadiene and hexachlorocyclopentadiene.

Reaction of vinylethyl sulfide with cyclopentadiene*. 6.6 g (0.05 mole) of dicyclopentadiene and 9.7 g (0.11 mole) of vinylethyl sulfide were heated in an autoclave (150 ml) to 160° for 14 hours. After cooling and distilling off the excess vinylethyl sulfide, two products were isolated by fractionation:

1) 2-Thioethylbicyclo-(2,2,1)heptene-5 (I), 4.5 g (42.7% of theory), b.p. 53.5-54°/2 mm; n_D^{20} 1.5160; d_4^{20} 0.9957; MR_D 46.81; $C_9H_{14}S$ F; calculated MR_D 46.87.

Found, %:	C 70.13; 70.00;	H 9.11; 9.16;	S 19.85; 20.06
$C_9H_{14}S$. Calculated, %:	C 69.88;	H 9.19;	S 20.75

2) 1,4,5,8-Dienomethylene-2-thioethyl-(1,2,3,4,4a,5,8,8a)-octahydronaphthalene (III), 5.1 g (23.3% of theory). B.p. 122-123°/2 mm; n_D^{20} 1.5464; d_4^{20} 1.0652; MR_D 65.55; $C_{14}H_{20}S$ F; calculated MR_D 65.55.

Found, %:	C 76.17; 76.41;	H 9.28; 9.32;	S 14.34; 14.51
$C_{14}H_{20}S$. Calculated, %:	C 76.28;	H 9.15;	S 14.55

Reaction of vinylethyl sulfide with hexachlorocyclopentadiene. A mixture of 2.25 g (0.025 mole) of vinylethyl sulfide and 6.75 g (0.025 mole) of hexachlorocyclopentadiene was heated in a flask with a reflux condenser on a Wood' s-metal bath to 100-105° for 3.5 hours. Fractionation of the mixture gave 5.9 g (83% of theory, based on the diene that had entered into the reaction) of 2-thioethyl-1,4,5,6,7,7a-hexachlorobicyclo-(2,2,1)heptene-5 (V), in the form of a viscous light-yellow liquid. B.p. 127-128°/2 mm; n_D^{20} 1.5668; d_4^{20} 1.5482; MR_D 76.15; $C_9H_8Cl_6S$ F; calculated MR_D 76.07.

Found, %:	C 30.37; 30.48;	H 2.35; 2.29;	S + Cl 68.34; 67.90
$C_9H_8Cl_6S$. Calculated, %:	C 29.94;	H 2.23;	S + Cl 67.80

* For convenience, dicyclopentadiene was used in the reaction; under the reaction conditions it depolymerizes to the monomer. With monomeric cyclopentadiene, the reaction with thiovinyl ethers can be carried out at a lower temperature.

Reaction of 2-thioethylbicycloheptene-5 (I) with hexachlorocyclopentadiene. A mixture of 3.75 g (0.025 mole) of adduct (I) with 6.75 g (0.025 mole) of hexachlorocyclopentadiene was heated to 120-130°, as described above, for 4 h. Fractionation of the mixture gave 1,4,5,8-diendoethylene-2-thioethyl-5,6,7,8,9,9a-hexachloro-1,2,3,4,4a,5,8,8a-octahydronaphthalene (VII) in an amount of 7 g (89.0% of theory, based on (I) entering into the reaction). B.p. 192-193°/2 mm.

Found, %:	C 39.57; 39.64;	H 3.50; 3.57;	S + Cl 56.50; 56.45
$C_{14}H_{14}Cl_6S$. Calculated, %:	C 39.34;	H 3.31;	S + Cl 57.33

Reaction of vinyl phenyl sulfide with cyclopentadiene. 13 g (about 0.1 mole) of vinyl phenyl sulfide and 6.6 g (0.05 mole) of dicyclopentadiene were heated in an autoclave to 160–170° for 13 h. Fractionation gave 2-thiophenylbicyclo(2,2,1)heptene-5 (II), 8.5 g (42.0% of theory), a colorless product with a faint odor. B.p. 107–108°/1 mm; n_D^{20} 1.5925; d_4^{20} 1.0982; MR_D 62.38; $C_{13}H_{14}S_4F$; calculated MR_D 61.74.

Found, %:	C 76.97; 77.03;	H 7.14; 7.00;	S 15.53; 15.89
$C_{13}H_{14}S$. Calculated, %:	C 77.20;	H 6.98;	S 15.82

A resinous product of pale-yellow color was also isolated, which proved to be 1,4,5,8-diendoethylene-2-thiophenyl-(1,2,3,4,4a,5,8,8a)-octahydronaphthalene (IV). B.p. 200–201°/4 mm. M.p. 67–68°.

Found, %:	C 80.18; 80.42;	H 7.50; 7.76;	S 11.84; 11.92
$C_{15}H_{20}S$. Calculated, %:	C 80.56;	H 7.51;	S 11.93

Yield 6.9 g, 26.2% of theory.

Reaction of vinyl phenyl sulfide with hexachlorocyclopentadiene. A mixture of 5.4 g (0.02 mole) of hexachlorocyclopentadiene and 2.8 g (0.02 mole) of vinyl phenyl sulfide was heated in a flask to 110–120° for 3 h. Vacuum distillation gave 0.5 g of unreacted diene and 5.9 g of yellow oily, rapidly crystallizing 2-thiophenyl-1,4,5,6,7,7a-hexachlorobicyclo-(2,2,1)-heptene-5 (VI). B.p. 190–191°/2 mm. M.p. 41–42°.

Found, %:	C 38.31; 38.22;	H 1.95; 2.03;	S + Cl 60.02; 60.42
$C_{18}H_8Cl_6S$. Calculated, %:	C 38.17;	H 1.97;	S + Cl 59.86

Yield 71.5% of theory.

Reaction of 2-thiophenylbicyclo-(2,2,1)heptene-5 (II) with hexachlorocyclopentadiene. A mixture of 1 g (0.005 mole) of bicycloheptene (II) and 1.4 g (0.005 mole) of hexachlorocyclopentadiene was heated to 120–130° for 4 h. 0.5 g of starting products and 0.9 g of adduct were isolated; the latter was a glassy mass of yellowish color. The isolated 1,4,5,8-diendoethylene-2-thiophenyl-5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydronaphthalene (VII) had b.p. 257–258°/3 mm.

Found, %:	C 45.76; 45.97;	H 2.69; 2.78
$C_{18}H_{14}Cl_6S$. Calculated, %:	C 45.64;	H 2.96

Yield 36.0% of theory.

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