Chemistry

E. N. Prilezhaeva, L. V. Tsymbal

1961

SovietRxiv

Abstract

Full Text

Chemistry

E. N. Prilezhaeva, L. V. Tsymbal
and Corresponding Member of the Academy of Sciences of the USSR
M. F. Shostakovskii

On the Comparative Dienophilic Reactivity in the Series: Vinyl Sulfide–Vinyl Sulfoxide–Vinyl Sulfone

Our previous work has shown that, in the series of sulfur-containing vinyl compounds, the electrophilicity of the double bond increases from vinyl sulfide through vinyl sulfoxide to vinyl sulfone. Vinyl alkyl sulfides, under ionic conditions, add reagents only according to Markovnikov' s rule in the presence of acidic catalysts (^{1}). It follows from this that the sulfur atom acts in their molecule as an electron donor:

$$\mathrm{CH_2{=}CH{-}S{-}R}$$

and the double bond therefore has, as in oxygen-containing vinyl ethers, a nucleophilic character. Vinyl sulfoxides and sulfones add HX reagents only under the influence of alkaline catalysts ($^{2-4}$) and only with the formation of compounds $\mathrm{RSOCH_2CH_2X}$, or $\mathrm{RSO_2CH_2CH_2X}$, while the activity of addition of the nucleophilic reagent (and, consequently, the electrophilicity of the double bond) increases from the sulfoxide to the sulfone (^{4}). This indicates a considerably higher electron-acceptor tendency of the sulfonyl group in comparison with the sulfinyl group.

It was of interest to trace how the reactivity of this series of compounds changes if they are used as dienophiles in reaction with one and the same diene. Cyclopentadiene (CP) and hexachlorocyclopentadiene (HCCP) were chosen as the dienes. It was already known earlier that vinyl ethyl sulfide reacts on heating with CP and HCCP (^{5}), while vinyl ethyl sulfone enters into an exothermic reaction with CP and reacts on heating with HCCP (^{3}). Nothing was known about the reactivity of vinyl ethyl sulfoxide in these reactions, nor, indeed, generally about diene-synthesis reactions involving α, β-unsaturated sulfinyl compounds.*

We carried out the reactions between, respectively, vinyl ethyl sulfide, sulfoxide, and sulfone and CP or HCCP, as far as possible under comparable conditions. Table 1 gives our results together with the literature data cited above. Examination of Table 1 leads to the conclusion that the dienophiles studied by us, with respect to CP and HCCP, are arranged in series opposite to one another. Indeed, CP, which has electropositive H atoms next to the diene system, reacts exothermically with vinyl ethyl sulfone, whereas with vinyl ethyl sulfide it requires prolonged heating; i.e., for $CH_2{=}CHX$ the activity increases in the series: $X = RS < RSO \ll RSO_2$. With respect to HCCP, which has electronegative chlorine at the double bond, the opposite relationship is observed: $X = RS > RSO > RSO_2$, and vinyl ethyl sulfide is the most reactive. The reactive cap—

* The only work found by us in the literature concerns the reaction of CP with disulfoxides ArSOCH=CHSOAr (^{6}).

Table 1

Conditions and yields of products in diene condensation of $CH_2{=}CHX$ ($X = C_2H_5S, C_2H_5SO, C_2H_5SO_2$)

X	Cyclopentadiene: procedure*	Cyclopentadiene: temp., °C	Cyclopentadiene: duration, h	Cyclopentadiene: yield, % of dienophile taken — monoadduct	Cyclopentadiene: yield, % of dienophile taken —diadduct	Hexachlorocyclopentadiene: procedure*	Hexachlorocyclopentadiene: temp., °C	Hexachlorocyclopentadiene: duration, h	Hexachlorocyclopentadiene: yield, % of dienophile taken	Source
C_2H_5S	a	room temp.	840	–	–	a	room temp.	840	71	Present work
C_2H_5S	b	100–110	25	–	–	a	room temp.	840	71	Present work
C_2H_5S	v	room temp.	96	–	–	a	room temp.	840	71	Present work
C_2H_5S	v	160	14	29.3**	21.2**	g	100–105	3.5	64.8**	(^{5})
C_2H_5SO	a	room temp.	840	–	–	a	room temp.	840	–	Present work
C_2H_5SO	a	75–80	29	34–35	–	a	90–95	35	19	Present work
C_2H_5SO	b	room temp.	108	–	–	a	room temp.	840	–	Present work
C_2H_5SO	b	100–110	25	33–38	–	a	room temp.	840	–	Present work
C_2H_5SO	b	room temp.	96	–	–	a	room temp.	840	–	Present work
$C_2H_5SO_2$	g	room temp.***	48	90	–	a	room temp.	840	–	Present work
$C_2H_5SO_2$	g	room temp.***	48	90	–	g	140–150	16	82	(^{3})

* Methods of carrying out the reaction: **a**—in a sealed ampoule with monomeric

diene without solvent; **b**—in a sealed ampoule with monomeric diene in dioxane medium (20 ml per 0.1-0.05 mole of reagents); **v**—in an autoclave with dimeric CP; **g**—in a flask with a reflux condenser.

** Yields recalculated by us from the experimental data of the authors.

*** The reaction is exothermic; the temperature rises to 70-80°.

the reactivity of vinylethyl sulfoxide in all cases lies in the middle. Thus, the activity of the diene synthesis depends not so much on the nature of the polarization of the double bond of the dienophile as on the relationship between the polarizations of the double bonds of the diene and the dienophile, which agrees with views on the mechanism of this reaction through the formation of a diene–dienophile complex (^{7}). Thus, HCCP should be active toward dienophiles with electron-donor substituents, and CP toward those with electron-acceptor substituents. It has recently been shown, for example (^{8}), that simple vinyl ethers and HCCP give adducts at room temperature in high yield. On the other hand, it is known that CP reacts exothermically with vinyl ketones (^{9}), acrylonitrile (^{10}), etc.

In our experiments, vinylethyl sulfoxide gave only monoadducts (I, II) both with HCCP and with CP:

$$\begin{tikzcd} & CH_2{=}CH{-}SOC_2H_5 & \\ \text{cyclopentadiene} \arrow[d] \arrow[rr] & & \text{hexachlorocyclopentadiene} \arrow[d] \\ \text{adduct (I), } -SOC_2H_5 & & \text{adduct (II), } -SOC_2H_5 \end{tikzcd}$$

In the reaction with CP, a mixture of crystalline and liquid (I) is formed in a ratio of ~3 : 1; the higher-melting product apparently has the endo configuration, and the Alder rule is obeyed in this reaction.

In the reaction with HCCP, (II) is formed, having a narrow melting point that does not change upon recrystallization, which indicates its steric homogeneity. At the same time, the adducts obtained by us from HCCP and vinylethyl sulfide (III) and sulfoxide (II), upon oxidation with acetyl hydroperoxide under mild conditions excluding isomerization, give the same

2-Ethylsulfonyl-1,4,5,6,7,7-hexachlorobicyclo-(2,2,1)-heptene-5 (IV), which is formed from HCHP and vinylethyl sulfone (^{3}).

[reaction scheme: (II) (IV) (III); reagents CH_3COOOH and $2CH_3COOOH$ at −5 to +5°; melting points/liquid notes shown under structures]

Recently, two of us, together with Azovskaya et al. (^{11}), showed that for divinyl sulfone the main product of the reaction with HCHP is the adduct of exo structure. This apparent deviation from the Alder rule was explained by the experimentally demonstrated facile thermal isomerization of the corresponding endo monoadduct into the exo form. In the present case, apparently, the same regularity is observed. Thus the adduct with vinylethyl sulfide (III), synthesized by us at room temperature, evidently undergoes complete isomerization during distillation of the reaction mixture.

Experimental Part

Endo- and exo-2-ethylsulfinylbicyclo-(2,2,1)-heptene-5 (I). 20.8 g (0.2 mole) of vinylethyl sulfoxide, 13.2 g (0.2 mole) of freshly prepared CP, and 60 ml of dioxane, sealed in an ampoule purged with nitrogen in the presence of several milligrams of hydroquinone, were heated at 95-99° for 34 h. After distillation of the unreacted starting materials and the CP dimer formed, 11.0 g (32.3%) were obtained [b.p. 74-75° at 0.05 mm; n_D^{20} 1.5300], a highly hygroscopic substance beginning to crystallize at room temperature.

Found, %: C 63.16; 63.20; H 8.10; 8.26; S 18.84; 18.97

$C_9H_{14}SO$. Calculated, %: C 63.30; H 8.26; S 18.77.

To separate the stereoisomeric (I), ether was added to 9.1 g of the adduct in the amount calculated as 0.7 ml/g; the mixture was cooled with stirring in ice water, and the unfrozen portion was filtered off with pressing ([4]). The crystalline portion, endo-(?) I, weighed 6.8 g (~73%), had b.p. 71-72° at 0.035 mm and freezing point 33-34°; after repeated freezing out, b.p. 72-73° at 0.025 mm, freezing point 36.5-37°, m.p. 36-37°. Found, %: C 62.78; H 8.30; S 18.70.

From the portion dissolved in ether the solvent was distilled off; after distillation, exo-(?) I was obtained, b.p. 62-63° at 0.025 mm (yield 2 g–22%), n_D^{20}1.5300; d_4^{20}1.1132; MR_D found 47.48; $C_9H_{14}SO$, calculated 47.24.

Exo-2-ethylsulfinyl-1,4,5,6,7,7a-hexachlorobicyclo-(2,2,1)-heptene-5 (II). 5.2 g (0.05 mole) of vinylethyl sulfoxide and 27.6 g (0.1 mole) of HCHP were heated in a sealed ampoule (nitrogen, hydroquinone) for 35 h at 90-95°.* The unreacted products were distilled off; the viscous residue was diluted with benzene and the solution passed through a column of Al_2O_3. After removal of the benzene in vacuo, 3.65 g (19%) of exo-II were obtained with m.p. 122-122.5° (from heptane), not changing its melting point after repeated recrystallizations.

Found, %: Cl 56.95

$C_9H_8Cl_6OS$. Calculated, %: Cl 56.45

* In attempts to carry out the reaction at temperatures above 100°, resinification of the products occurred, accompanied by rupture of the ampoule; with an equimolar ratio of the reagents the yield decreased.

2-Ethylthio-1,4,5,6,7,7a-hexachlorobicyclo-(2,2,1)-heptene-5 (III). 4.4 g (0.05 mole) of vinyl ethyl sulfide and 13.7 g (0.05 mole) of HCCP were sealed in an ampoule (nitrogen, hydroquinone) and left for 40 days. Distillation gave 13.8 g (71%) of adduct III with b.p. 84-85° at 0.05 mm, 124-125° at 3 mm, n_D^{20} 1.5672 (literature [5]: b.p. 122-123° at 3 mm, n_D^{20} 1.5668).

Oxidation II → IV. 1.0 g of exo-II was dissolved, with stirring, in 36 ml of ether, and 0.26 g of 79% CH_3COOOH was added to the solution with cooling by ice and salt. On the following day the ether layer was washed with water to remove acetic acid, dried over Na_2SO_4, and the ether was distilled off. This gave 0.9 g (64%) of crude exo-IV, which after recrystallization from aqueous ethanol had m.p. 71-72.2° and showed no depression of the melting point with IV obtained from vinyl ethyl sulfone [3].

Oxidation III → IV. From 2.8 g of III, on oxidation under the same conditions with 1.4 g of 79% CH_3COOOH in 30 ml of dry ether, 3.22 g (97%) of crude exo-IV was obtained; after recrystallization it melted at 70-73° and showed no depression of the melting point with IV from vinyl ethyl sulfone.

Institute of Organic Chemistry
named after N. D. Zelinsky
Academy of Sciences of the USSR

Received
14 II 1961

REFERENCES

1. M. F. Shostakovskii, E. N. Prilezhaeva, N. I. Uvarova, *Izv. AN SSSR, OKhN*, **1955**, 154; *Synthesis and certain properties of thiovinyl ethers*, N. I. Uvarova, Candidate' s dissertation, IOC AS USSR, 1953.
2. W. Reppe, *Ann.*, **601**, 81 (1956).
3. M. F. Shostakovskii, E. N. Prilezhaeva, V. A. Azovskaya, G. I. Dmitrieva, *ZhOKh*, **30**, 1123 (1960); *ZhOKh*, **31**, No. 6 (1961); M. F. Shostakovskii, E. N. Prilezhaeva, V. A. Azovskaya, L. V. Tsymbal, N. I. Starova, *Izv. AN SSSR, OKhN*, **1959**, 2239.
4. M. F. Shostakovskii, E. N. Prilezhaeva, L. V. Tsymbal, N. I. Starova, R. Ya. Tolchinskaya, *ZhOKh*, **31**, No. 8 (1961).
5. M. F. Shostakovskii, A. V. Bogdanova, T. M. Ushakova, *DAN*, **118**, 520 (1958).
6. E. Bertotti, G. Luciani, F. Montanari, *Gazz. chem. Ital.*, **89**, 1564 (1959).
7. K. Alder, XIV Intern. Congr. of Pure and Applied Chemistry, 1955.
8. M. F. Shostakovskii, F. P. Sidilkovskaya, M. T. Zelenskaya, *Izv. AN SSSR, OKhN*, **1961**, 128.
9. I. N. Nazarov, *Usp. khim.*, **18**, 377, 390 (1949); Allen, *J. Am. Chem.*

Soc., **62**, 656 (1940); A. A. Petrov, *ZhOKh*, **11**, 309, 665 (1941).

10. J. Gillois-Doucet, *Ann. Chim.* (Paris), **10**, 497 (1955).
11. M. F. Shostakovskii, E. N. Prilezhaeva, V. A. Azovskaya et al., *ZhOKh*, **31**, No. 6 (1961).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.