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CONCLUSIONS

The molecular structure of dimethylsulfonium cyclopentadienylide was established by the x-ray structure analysis method, and it was shown that the S atom is coplanar with the cyclopentadienyl ring, and that the S-C distance (cyclopentadienyl) is shorter than the S-C distances (methyl).

LITERATURE CITED

1. A. T. Christensen and W. G. Witmore, *Acta Cryst.*, **B25**, 73 (1969).
2. A. T. Christensen and E. Thom, *Acta Cryst.*, **B27**, 581 (1971).
3. L. E. Sutton, *Tables of Interatomic Distances and Configurations of the Molecules and Ions*, The Chemical Society, Special Publication No. 18, London (1965).
4. S. M. Johnson, C. A. Maier, and I. C. Paul, *J. Chem. Soc.*, **B1970**, 1603.
5. A. I. Gusev and Yu. T. Struchkov, *Zh. Strukt. Khim.*, **12**, 1120 (1971).
6. W. Barnes and M. Sundaralingam, *Acta Cryst.*, **B29**, 1868 (1973).
7. H. L. Ammon, C. L. Wheeler, and P. H. Watts, Jr., *J. Am. Chem. Soc.*, **95**, 6158 (1973).

EFFECT OF HIGH PRESSURE ON RADICAL ISOMERIZATION OF 2-ISOPROPYL-1,3-DIOXOLANE

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Rearrangement to the isomeric esters in the presence of free-radical initiators is a general reaction for cyclic acetals [1]. A high pressure noticeably increases the length of the kinetic chain of homolytic processes and gives information regarding the mechanism of the process and its individual steps [2]. In this connection we studied in the present paper the radical liquid-phase isomerization of 2-isopropyl-1,3-dioxolane (DH) to ethyl isobutyrate (EH), initiated by di-tert-butyl peroxide (TBP), at 130°C and pressures up to 10,000 kgf/cm².

EXPERIMENTAL

Freshly distilled 2-isopropyl-1,3-dioxolane, obtained as described in [3], and di-tert-butyl peroxide were used. Using a pure argon stream, the starting solution of TBP and DH was charged into thin-walled teflon ampuls, which were placed in the cylinder of a high pressure press equipped with heating [4]. The reaction products were analyzed as described in [1].

DISCUSSION OF RESULTS

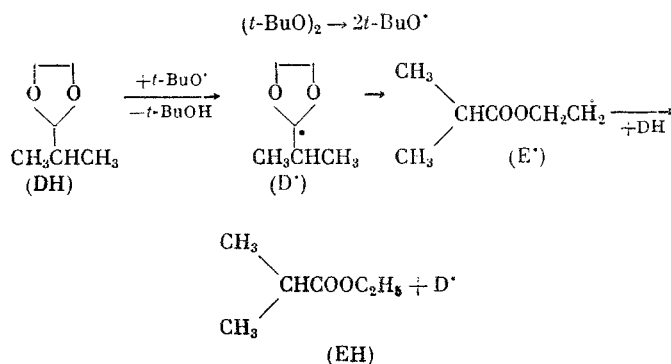
The radical isomerization of 2-isopropyl-1,3-dioxolane can be depicted by scheme [1]; chain termination occurs via recombination involving the (E) and (D) radicals

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TABLE 1. Radical Liquid-Phase Isomerization of 2-Isopropyl-1,3-dioxolane (DH) at High Pressure. 130°C, 2 h, [TBP] = 0.4, and [DH] = 7.6 moles/liter

k_p , kg/cm ²	[EH]	[TMC]	$W_{EH} \cdot 10^5$	$W_{TMC} \cdot 10^5$	ν	$k_p \cdot 10^5$, sec ⁻¹
	mole/liter		mole/liter · sec			
1	0,55	0,11	7,6	1,5	5,0	1,9
2000	0,56	0,062	7,8	0,86	9,0	1,1
5000	0,38	0,031	5,3	0,43	12,2	0,54
10 000	0,22	0,016	3,1	0,22	14,2	0,27



When a cyclic acetal with a substituent in the 2 position is used as the medium the monomolecular decomposition of the tert-butoxyl radicals can be neglected [1, 5], and the rate of accumulating trimethylcarbinol (TMC) determines the initiation rate. The isomeric ester (EH) is formed as a result of the chain process. The ratio of the rates of forming the ester and alcohol determines the length of the kinetic chain (ν).

The experimental results on the isomerization of DH at various pressures are given in Table 1 (it was shown by special experiments that the ester is not formed in the absence of TBP). Using the concentrations of ester (EH) and alcohol (TMC) formed during the time of reaction, we calculated the rates of their formation W_{EH} and W_{TMC} , the chain length ν , and the rate constant for the decomposition of TBP (k_p): $k_p = W_{TMC} / 2[\text{TBP}]$.

As was to be expected, k_p decreases noticeably with the pressure. The volume effect of the activation (ΔV^\ddagger), determined from the correlation equation given in [6], is 11 cm³/mole, and lies within the limits given for TBP in various solvents: 4-13 cm³/mole [7]. A substantial decrease in the initiation rate, which is not compensated by the small increase in the length of the kinetic chain that occurs here, is responsible for the observed decrease in the rate of forming the ester with pressure increase.

The small effect of pressure on the length of the kinetic chain can be explained as follows. It is known that pressure usually retards the rate of isomerization reactions and increases the rate of substitution reactions [2, 8]. This should lead to a relative increase in the concentration of the unrearranged radicals (D[•]) in the system and an increase in the fraction of chain termination involving them, i.e., the possibility appears of the cyclic radicals disappearing before their isomerization without the subsequent formation of the ester and prolongation of the chain.

Another explanation is also possible. If the mechanism of the process does not change substantially with the pressure and chain termination occurs predominantly on the linear E[•] radicals, as is assumed in [1], a decrease in the yield of the ester with pressure can be explained by the low dependence of the recombination rate on the pressure. This means that the rate of the termination reactions in the given case is not determined by the progressive diffusion rate of the radicals, since the latter should decrease with increase in the pressure due to an increase in the viscosity of the medium, which would lead to a substantial increase in the chain length and yield of ester. For this reason it is necessary to assume that the chain termination rate in the given case is determined by the "cage" reaction rate of the radicals, which can be retarded as well as accelerated by pressure [9].

CONCLUSIONS

1. Pressure decreases the rate of forming ethyl isobutyrate during the homolytic liquid-phase isomerization of 2-isopropyl-1,3-dioxolane.
2. The volume effect for the activation of the decomposition of di-tert-butyl peroxide to 2-isopropyl-1,3-dioxolane at 130° is characterized by a substantial value (11 cm³/mole).

LITERATURE CITED

1. D. L. Rakhmankulov, V. S. Martem'yanov, S. S. Zlotskii, and V. I. Isagulyants, *Neftekhimiya*, 14, 275 (1974).
2. M. G. Gonikberg, *Chemical Equilibrium and Reaction Rates at High Pressures* [in Russian], *Khimiya* (1969).
3. C. S. Rondestvidt, *J. Org. Chem.*, 26, 2247 (1961).
4. G. I. Nikishin, S. S. Spektor, G. P. Shakhovskoi, V. G. Glukhovtsev, and V. M. Zhulin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1976, 1664.
5. E. Kh. Kravets, S. S. Zlotskii, V. S. Martem'yanov, and D. L. Rakhmankulov, *Zh. Prikl. Khim.*, 49, 185 (1976).
6. B. S. El'yanov and M. G. Gonikberg, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1969, 1044.
7. C. Walling and G. Metzger, *J. Am. Chem. Soc.*, 81, 5365 (1959).
8. V. M. Zhulin and I. Kh. Milyavskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1974, 1487.
9. V. M. Zhulin and M. G. Gonikberg, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1972, 331.

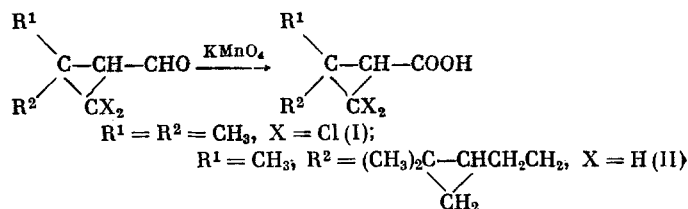
SYNTHESIS OF CYCLOPROPANECARBOXYLIC ACIDS AND THEIR ESTERS

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The synthesis of the esters of cyclopropanecarboxylic and gem-dichlorocyclopropanecarboxylic acids is interesting from the standpoint of obtaining biologically active compounds. We undertook the preparation of some analogs of chrysanthemum acids by starting with the previously synthesized [1-3] cyclopropane aldehydes.

Both the cyclopropane and the gem-dichlorocyclopropane aldehydes are easily oxidized by KMnO₄ to the corresponding carboxylic acids.



The vinyls of the cyclopropanecarboxylic and gem-dichlorocyclopropanecarboxylic acids were obtained from the corresponding aldehydes by the Wittig reaction (Horner modification). The reaction proceeded stereospecifically to give the trans-isomers of the esters of substituted cyclopropyl- or gem-dichlorocyclopropylacrylic acids, but in the case of (III) the yield of the product was a total of 30%, both by the usual method and when the two-phase

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