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Abstract

Full Text

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COMPARISON OF THE REACTIVITY OF ALKYLCYCLOPROPANES OF DIFFERENT STRUCTURE BY THE BROMOMETRIC METHOD

Continuing the study of the dependence of the reactivity of cyclopropane hydrocarbons on their structure ([1,2]), we decided to use for this purpose the bromination reaction, proceeding with cleavage of the three-membered ring. There are many papers in the literature on the addition of bromine to cyclopropane hydrocarbons, and chiefly the behavior of cyclopropane itself in this reaction has been studied ([3–7]). In these works, both pure bromine and its solutions in acetic acid, chloroform, and other solvents were used for bromination. The influence of light, temperature, and oxygen on this reaction was investigated ([5]). Depending on the experimental conditions, the addition of bromine was or was not accompanied by a substitution reaction. There are few data on the direction of cleavage of the three-membered ring during bromination, and in all cases addition occurred at the least hydrogenated carbon atoms of the ring:

$$\text{ethylcyclopropane} \xrightarrow{Br_2} CH_2Br{-}CH_2{-}CHBr{-}CH_2{-}CH_3 \qquad (6)$$

$$\text{1,1,2-trimethylcyclopropane} \xrightarrow{Br_2} (CH_3)_2CBr{-}CH_2{-}CHBr{-}CH_3 \qquad (7)$$

Judging from the literature data, for addition of bromine at the C–C bond of the three-membered ring considerably harsher conditions are required than for addition at a double bond. This difference is evident even in the qualitative test with bromine water, which is instantly decolorized in the presence of olefins and only with difficulty upon prolonged standing in the presence of saturated hydrocarbons of the cyclopropane series.

As in the case of the reaction with mercury acetate ([1,2]), we had to find an analytical procedure that would permit a quantitative comparison of the reactivity of hydrocarbons of different structure.

An analytical procedure of practical application for the addition of bromine to olefins is the determination of bromine numbers by the Kaufmann-Halpern

method ([8,9]). In this procedure, a 0.1 N solution of bromine in methanol, previously saturated with sodium bromide, is used. In such a solution, owing to complex formation,

$$Br_2 + NaBr \rightleftharpoons NaBr_3$$

the concentration of free bromine is lowered, and in this way especially mild bromination conditions are created. This analytical method has been applied to a large number of unsaturated hydrocarbons of different structure, and it was found that in those cases where the double bond of the olefin is branched, bromine, in addition to adding at the double bond, is consumed in a substitution reaction. In these cases elevated bromine numbers are obtained ([10,11]). The mechanism of the interaction of bromine with olefins under the conditions of the analysis is rather complex and has been discussed repeatedly ([9,10]).

In using this procedure for the analysis of alkylcyclopropanes, we did not set ourselves the task of studying the reaction mechanism as applied to this class of compounds and did not attempt to identify the products of interaction with bromine. We were interested in the dependence of the reactivity of the hydrocarbon on its structure under the experimental conditions and in analogies in the behavior of alkylcyclopropanes and olefins of similar structure. Taking into account the lower reactivity of the three-membered ring in the reaction with bromine in comparison ···

···with a double bond, we lengthened the contact time, keeping the reagents in the thermostat for a more or less prolonged period. In doing so, one might have feared that prolonged contact of the hydrocarbon with bromine could lead to substitution reactions, irrespective of the presence in the molecule of a double bond or of a three-membered ring. A special experiment established that this does not occur in the case of a paraffinic hydrocarbon: 2,2,3-trimethylpentane did not react at all with bromine after five hours of contact at a temperature of 20°.

The hydrocarbons used in the work are given in Table 1.

Table 1

Name of hydrocarbon	b.p., °C	n_D^{20}	d_4^{20}
Ethylcyclopropane	35.8	1.3783	0.6835
Isopropylcyclopropane	58.2	1.3864	0.6981
cis-1-Methyl-2-ethylcyclopropane	67.2	1.3938	0.7104
trans-1-Methyl-2-ethylcyclopropane	58.9	1.3848	0.6933
cis-1,2-Dimethylcyclopropane	37.1	1.3820	0.6940
trans-1,2-Dimethylcyclopropane	28.2	1.3712	0.6691
1,1,2-Trimethylcyclopropane	52.5	1.3862	0.6948
1,1,2,2-Tetramethylcyclopropane	76.9	1.4004	0.7185
2,2,3-Trimethylpentane	109.6	1.4030	0.7162

structural formulas showing relative reactivities 1.3, 1.5, 2.6, and 76.9

Figure 1: structural formulas showing relative reactivities 1.3, 1.5, 2.6, and 76.9

reaction schemes for bromine approach to ethylene and tetramethylethylene; v = 1.0 and v = 14.0, "approach facilitated"

Figure 2: reaction schemes for bromine approach to ethylene and tetramethylethylene; v = 1.0 and v = 14.0, "approach facilitated"

Name of hydrocarbon	b.p., °C	n_D^{20}	d_4^{20}

All the hydrocarbons presented here, judging from their constants and chromatograms, are pure substances. The exception is cis-1-methyl-2-ethylcyclopropane, which contains an admixture of *n*-hexane and 3-methylpentane. Owing to the closeness of their boiling points, these could not be separated by distillation on a 100-theoretical-plate column. Since paraffinic hydrocarbons do not react with bromine, this impurity should not substantially affect the results of the analysis, which made it possible for us to use the hydrocarbon.

The results of the analysis of alkylcyclopropanes are presented in Table 2. On the basis of these data one may conclude that, under the adopted conditions, isopropylcyclopropane, and also ethylcyclopropane, react only slightly with bromine. The reactivity of alkylcyclopropanes increases when a methyl group appears as a substituent, and rises sharply with the accumulation of methyl substituents in the ring. The relative reactivity of alkylcyclopropanes, taking as unity the reactivity of isopropylcyclopropane, corresponding to the amount of hydrocarbon that reacted in 5 hr, is as follows:

Here, as in the reaction of alkylcyclopropanes with mercuric acetate, the hyperconjugation effect exerts a greater influence on the three-membered ring than the inductive effect. The reactivity increases especially strongly when the methyl substituents are geminally arranged.

Ingold [12], who studied the relative rates of bromine addition to olefins in a solution of CH_2Cl_2 at −78°, found that in the case of $(CH_3)_2C{=}C(CH_3)_2$ the reaction proceeds 14 times faster than in the case of ethylene. This is explained by the fact that the first stage of the reaction, consisting in attack of the olefin by the halogen, is facilitated if the electron density of the double bond is increased by electron-donating substituents, which leads to an increase in the overall rate of addition.

A similar argument is applicable also to the case of alkylcyclopropanes,

since here too the methyl substituents exert a distinctly pronounced influence, facilitating attack of the three-membered ring by the halogen. As an illustra-

tion of this effect one may cite 1,1,2-trimethylcyclopropane and, in particular, 1,1,2,2-tetramethylcyclopropane, which react very actively with bromine under the conditions of the analysis. In these hydrocarbons, whose three-membered ring possesses, owing to the substituents, increased electron density and strongly polarized bonds, the analogies with olefins extend still further.

Table 2

Hydrocarbon	Amount of hydrocarbon that reacted with bromine, %	Amount of hydrocarbon that reacted with bromine, %	Amount of hydrocarbon that reacted with bromine, %	Amount of hydrocarbon that reacted with bromine, %
	in 5 min	in 1 hour	in 5 hours	in 10 hours
[[structural formula: cyclo-propane derivative, skeletal formula shown]]	–	–	1.3	–
[[structural formula: cyclo-propane derivative, skeletal formula shown]]	–	–	1.7	2.5
[[structural formula: trans-cyclopropane derivative, skeletal formula shown]]	–	–	1.9	5.5
trans-				

Hydrocarbon	Amount of hydrocarbon that reacted with bromine, %	Amount of hydrocarbon that reacted with bromine, %	Amount of hydrocarbon that reacted with bromine, %	Amount of hydrocarbon that reacted with bromine, %
[[structural formula: trans-cyclopropane derivative, skeletal formula shown]] trans-	–	–	3.4	7.2
[[structural formula: cyclo-propane derivative, skeletal formula shown]]	–	52.4	100	–
[[structural formula: tetram-ethylcyclo-propane, skeletal formula shown]]	62.0	98.4	–	–

Thus, we found that in experiments in which deliberately excessive amounts of bromine were taken for the reaction, with a sufficiently long time of interaction of the reagents, bromine was consumed in excess of the amount required for addition at the C–C bond of the ring. In these cases, as also for olefins with branching near the double bond ([10], [11]), inflated bromine numbers were obtained (see Table 3).

Apparently, the methyl groups located at the quaternary carbon atom forming the three-membered ring,

$$\begin{array}{c} CH_3 \\ | \ C \\ CH_3 \end{array}$$

as well as in the case of the carbon at a double bond

$$-\mathrm{C}=\mathrm{C}\quad\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix},$$

are capable, under the conditions of the analysis, of replacing hydrogen atoms by bromine.

In conclusion, having at our disposal samples of cis- and trans-disubstituted alkylcyclopropanes, we studied their comparative reactivity. In all cases the cis isomers proved to be more reactive than the trans forms (see Table 4).

Table 3

Hydrocarbon	Amount of hydrocarbon that reacted with one-and-a-half amount of bromine, %	Amount of hydrocarbon that reacted with one-and-a-half amount of bromine, %	Amount of hydrocarbon that reacted with one-and-a-half amount of bromine, %	Amount of hydrocarbon that reacted with one-and-a-half amount of bromine, %	Amount of hydrocarbon that reacted with one-and-a-half amount of bromine, %
	in 30 min	in 1 1/2 hours	in 3 hours	in 5 hours	in 8 hours
[[structural formula: cyclopropane derivative, skeletal formula shown]]	–	–	–	111.7	121.1
[[structural formula: tetramethylcyclopropane, skeletal formula shown]]	108.9	125.6	125.4	–	–

Table 4

Hydrocarbon	Amount of hydrocarbon that reacted, %	Amount of hydrocarbon that reacted, %	Amount of hydrocarbon that reacted, %
	in 3 hours	in 5 hours	in 10 hours
[[structural formula: disubstituted cyclopropane, skeletal formula shown]] cis-	1.3	2.8	7.6
[[structural formula: disubstituted cyclopropane, skeletal formula shown]] trans-	0.4	1.9	5.5
[[structural formula: disubstituted cyclopropane, skeletal formula shown]] cis-	3.6	5.4	9.9
[[structural formula: disubstituted cyclopropane, skeletal formula shown]] trans-	2.3	3.4	7.2

A similar observation was made earlier ([13], [14]) in the mercuration of stereoisomeric olefins: the rate of addition for cis isomers of ethylene derivatives exceeded the rate of mercuration of the corresponding trans isomers.

Summing up, it should be noted that the experimental data obtained in the present work once again emphasize the profound analogy in the reactivity of the three-membered ring and the double bond, arising···

···arising from features of the electronic structure of cyclopropane. These data are in good agreement with the experimental material obtained by us in studying the interaction of alkylcyclopropanes with mercury acetate (1, 2). The fact that in both electrophilic-addition reactions the cyclopropane hydrocarbons studied

are arranged, in terms of their reactivity, in one and the same series allows us to assess with greater confidence the influence of structure on their behavior in chemical reactions.

Experimental Part

Hydrocarbons. The syntheses of ethylcyclopropane (15), isopropylcyclopropane (16), 1,2-dimethylcyclopropanes (2), 1,1,2-trimethylcyclopropane (17), and 1,1,2,2-tetramethylcyclopropane (2) have been described by us previously.

1-Methyl-2-ethylcyclopropane was obtained by the action of zinc dust on 2,4-dibromohexane (18). The hydrocarbon was purified from impurities of unsaturated compounds by titration with bromine solution (19), after which it was separated into stereoisomers by fractionation on a column of 100 theoretical plates. The cis isomer differed in its constants from those reported in the literature. Gas-liquid chromatography established that it contained about 2% 3-methylpentane and 8% *n*-hexane. The trans isomer contained no impurities. Literature constants (18): trans isomer—b.p. 58.66°/760 mm, n_D^{20} 1.3846, d_4^{20} 0.6935; cis isomer—b.p. 67.01°/760 mm, n_D^{20} 1.3953, d_4^{20} 0.7146.

2,2,3-Trimethylpentane was synthesized by dehydration, with the aid of β-naphthalenesulfonic acid, of 2,2,3-trimethylpentanol (from pinacoline and ethyl bromide), followed by hydrogenation of the olefin (20). The hydrocarbon was purified by chromatography on silica gel and distilled on a column of 100 theoretical plates. Lit. (21): b.p. 109.847°/760 mm, n_D^{20} 1.40280, d_4^{20} 0.71608.

Solutions were prepared according to the procedure (22). The bromine solution was prepared in a large quantity; its titer was checked and, as it changed, adjusted to the initial value in order to maintain standard conditions in all experiments. The experiments were carried out according to the method (22), with the difference that for analysis either equimolecular amounts of hydrocarbon and bromine were taken (Tables 2 and 4), or one mole of hydrocarbon and one and a half equivalents of bromine (Table 3). In addition, the contact time of the reagents was lengthened; for this purpose they were kept for the specified time in a thermostat in the dark at 20°. Parallel experiments showed good agreement. The results of the analyses are given in Tables 2, 3, and 4.

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