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Abstract

Full Text

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On the Dependence of the Reactivity of Cyclopropane Hydrocarbons on Their Structure

The question of reactivity in the cyclopropane series acquires special significance in connection with modern theoretical concepts concerning the structure of the three-membered ring. At present, the unsaturation of cyclopropane is explained by the fact that the carbon–carbon bonds constituting the three-membered ring have a character different from that of the bonds in paraffins and higher polymethylenes, and more closely resemble an olefinic double bond. It is assumed that in the cyclopropane molecule there exists a certain analogue of a π-electron cloud located in the plane of the ring. As a result of this unsaturation, cyclopropane and its homologues are not inert, but are capable of addition reactions that proceed with opening of the three-membered ring (^{1,2}).

In work (^{3}) we showed that the reactivity of cyclopropane hydrocarbons in interaction with mercury acetate (Levina reaction (^{4})) depends to a considerable extent on the nature of the substituent. It was established that the greatest influence is exerted by those substituents that are capable of donating electrons by the conjugative, rather than by the inductive, mechanism.

The aim of the present work is to determine the influence of the number and position of electron-donating substituents on the reactivity of the three-membered ring. To carry out this investigation, we synthesized four hydrocarbons of the cyclopropane series; their structures and constants are given in Table 1.

Table 1

Structures of the hydrocarbons investigated and their constants

Hydrocarbons	b.p., °C at 760 mm	d_4^{20}	n_D^{20}
$CH_3-C(CH_3)=CH_2-C(CH_3)_2$ [[unclear: cyclopropane structural formula in image]]	76.9	0.7185	1.4004

Hydrocarbons	b.p., °C at 760 mm	d_4^{20}	n_D^{20}
$CH_3-CH-CH_2-C(CH_3)_2$ [[unclear: cyclopropane structural formula in image]]	52.5	0.6948	1.3862
$CH_2-CH_2-C(CH_3)_2$ [[unclear: cyclopropane structural formula in image]]	20.6	0.6586	1.3669
$CH_3-CH-CH_2-CH-CH_3$ (trans) [[unclear: cyclopropane structural formula in image]]	28.2	0.6691	1.3712

The hydrocarbons were introduced into reaction with an equimolecular amount of mercury acetate under standard conditions according to the procedure described earlier (3). After 30 min, the reaction mixture was titrated with ammonium thiocyanate, and from the titration data the amount of reacted hydrocarbon, in percent, was calculated. These values, as well as the relative reactivity of the hydrocarbons investigated—where the amount of 1,2-dimethylcyclopropane that reacted under standard conditions in 30 min was taken as unity—are given in Table 2.

On the basis of the data obtained, the following conclusions may be drawn.

1. Accumulation of methyl groups increases the reactivity of the cyclopropane ring. This is explained by the fact that an increase in the number of electron-donating substituents raises the electron density of the ring, and it is more readily attacked by an electrophilic agent, which in the present case is mercury acetate.
2. The reactivity depends on how the substituents are arranged—

substituents in the ring: the geminal arrangement of substituents sharply increases its reactivity. Examination of Stuart-Briegleb models for gem-substituted methylcyclopropanes shows that in these hydrocarbons the methyl groups are freely arranged at one carbon atom. Thus, the increased reactivity of gem-substituted methylcyclopropanes cannot be attributed to a decrease in the stability of the ring associated with distortion of the valence angles. The high reactivity in this case may be explained by a considerably stronger polarization of the C—C bond of the ring, one of whose carbon atoms bears two electron-donating substituents.

Table 2

Reactivity of hydrocarbons of the cyclopropane series

Hydrocarbon	Amount of hydrocarbon that reacted in 30 min, %	Relative reactivity of hydrocarbons
[structural formula: 1,1,2,2-tetramethylcyclopropane]	100	2.2
[structural formula: trimethylcyclopropane]	87	1.9
[structural formula: dimethylcyclopropane]	79.5	1.8
[structural formula: trans-dimethylcyclopropane] *(trans)*	44.5	1.0

The data obtained by us were compared with Ingold' s data[5] on the electrophilic addition of bromine to olefins of analogous structure. It turned out that, in their reactivity, cyclopropane and olefin hydrocarbons are arranged in one and the same order.

Table 3 presents data on the relative reactivity of hydrocarbons of the cyclopropane and olefin series. In the olefin series, the reactivity of styrene was taken as the conventional unit; in the cyclopropane series, that of phenylcyclopropane.*

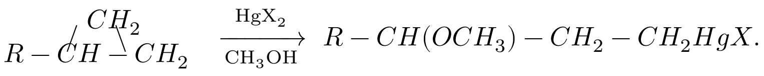
Table 3

Relative reactivity in the olefin and cyclopropane series in electrophilic addition reactions

Olefin hydrocarbons	Relative reactivity	Cyclopropane hydrocarbons	Relative reactivity
$(CH_3)_2C = C(CH_3)_2$	5	[structural formula: tetramethylcyclopropane]	2.5

Olefin hydrocarbons	Relative reactivity	Cyclopropane hydrocarbons	Relative reactivity
$CH_3CH = C(CH_3)_2$	3.3	[structural formula: trimethylcyclopropane]	2.2
$H_2C = C(CH_3)_2$	1.7	[structural formula: dimethylcyclopropane]	2
$H_2C = CHC_6H_5$	1	[structural formula: phenylcyclopropane]	1

The work carried out makes it possible to establish a relationship between the number and arrangement of electron-donating substituents and the reactivity of cyclopropane hydrocarbons, and also once again emphasizes the analogy in the behavior of cyclopropane and olefin hydrocarbons, which may serve as confirmation of the closeness of their structures. The similarity of their structures and the presence of a π-electron cloud in cyclopropane compounds is also indicated by the fact that the addition of mercury acetate, as may be concluded from the work of Levina[4], who investigated the reaction products in all cases, proceeds according to Markovnikov' s rule. Indeed, under the influence of the substituent, just as is observed for olefins, a shift of the π-electron cloud occurs, and mercury acetate attacks not the carbon atom bearing the electron-donating substituent, but the neighboring one. As a result, the cation adds to the more highly hydrogenated carbon atom of the ring, and the anion to the least hydrogenated one:



$$R - \overset{CH_2}{CH - CH_2} \xrightarrow[\mathrm{CH_3OH}]{\mathrm{HgX_2}} R - CH(OCH_3) - CH_2 - CH_2HgX.$$

* We specifically established that in 30 min phenylcyclopropane reacts by 40%. The reactivity of phenylcyclopropane is discussed in detail in work [3].

Experimental Part

Synthesis of hydrocarbons. The hydrocarbons were synthesized by the methods described in the literature. During purification, special attention was paid to removing olefin impurities. All the hydrocarbons obtained were repeatedly washed with an aqueous solution of potassium permanganate until its decolorization completely ceased. After drying, the hydrocarbons were distilled on efficient columns.

The hydrocarbons used in the work and their constants are presented in Table 1.

1. 1,1,2,2-Tetramethylcyclopropane was obtained by the action of zinc dust on 2,4-dimethyl-2,4-dibromopentane and was distilled on a column of 100 theoretical plates ([6]).
2. 1,1,2-Trimethylcyclopropane was synthesized by a somewhat modified Kishner procedure ([7]) and was distilled on a column of 30 theoretical plates.
3. gem-Dimethylcyclopropane was obtained by the action of zinc dust on 2,2-dimethyl-1,3-dibromopropane according to the method of Borde ([8]) and was distilled on a column of 30 theoretical plates.
4. A mixture of the cis- and trans-isomers of 1,2-dimethylcyclopropane was obtained by the action of zinc dust on 2,4-dibromopentane ([9]). Separation of the stereoisomers was carried out by distillation on a column of 100 theoretical plates. The trans-isomer was used for studying the reactivity.

Experimental procedure. Determination of the relative reactivity of the hydrocarbons was carried out by the same procedure as in work ([3]). The average results of the experiments, representing the amount of hydrocarbon that had entered into reaction in 30 min, are presented in Table 2.

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