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Abstract

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ON THE COMPARATIVE REACTIVITY OF HYDROCARBONS OF THE CYCLOPROPANE SERIES

The nature of the bonds of the three-membered ring, despite a certain analogy with olefins, is distinctive and has not yet been studied sufficiently fully ([1–3]). In studying over a number of years the catalytic transformations in the cyclopropane series (hydrogenation, isomerization), we repeatedly observed that under identical conditions cyclopropane hydrocarbons of different structures react with unequal ease, i.e., possess different reactivities. Especially noticeable in its effect on reactivity is the presence of conjugation of the three-membered ring with unsaturated groupings in the side chain. An increase in reactivity was also observed in those cases where the three-membered ring was bonded to several alkyl substituents ([3]).

Since in reactions of this kind a specific action of the catalyst is possible, we considered it necessary, in order to investigate the dependence of the reactivity of cyclopropane hydrocarbons on structure, to choose a noncatalytic reaction.

Since electrophilic addition reactions are most characteristic of the three-membered ring, the choice had to be limited to this class of reactions. The reaction had to proceed quantitatively in one direction and be sufficiently well studied.

The reaction most consistent with these requirements proved to be the opening of the three-membered ring by salts of mercuric oxide, discovered and studied in detail by R. Ya. Levina ([4]). This reaction proceeds quantitatively under comparatively mild conditions both in an aqueous medium and in absolute alcohol (methyl or ethyl). In this process, as was established in a large number of examples, rupture of the ring occurs at the most polarized bond of the ring with formation, depending on the solvent used, of alcohols mercurated in the γ-position or of the corresponding alkoxy derivatives. As can be judged from

Levina' s work, addition of mercury salts in this reaction proceeds according to Markovnikov' s rule.

$$\mathrm{R{-}CH{-}CH_2} \quad \mathrm{CH_2} \xrightarrow[\mathrm{H_2O}]{\mathrm{Hg(OCOCH_3)_2}} \mathrm{R{-}CH{-}CH_2{-}CH_2}$$

$$\mathrm{OH} \qquad \mathrm{HgOCOCH_3}$$

$$\mathrm{R{-}CH{-}CH_2} \quad \mathrm{CH_2} \xrightarrow[\mathrm{CH_3OH}]{\mathrm{Hg(OCOCH_3)_2}} \mathrm{R{-}CH{-}CH_2{-}CH_2}$$

$$\mathrm{OCH_3} \qquad \mathrm{HgOCOCH_3}$$

On the basis of Levina' s reaction we developed a method for the quantitative determination of the hydrocarbon entering, under standard conditions, into reaction with mercury acetate, which made it possible to evaluate the comparative reactivity of hydrocarbons of the cyclopropane series.

The method of such determination consisted in the following: equimolecular amounts of hydrocarbon and mercury acetate, dissolved in anhydrous methyl alcohol, were introduced into the reaction, and after a definite interval of time, during which the reagents were kept at a specified temperature in a thermostat, the reaction mixture was titrated with ammonium thiocyanate.

in the presence of ferric ions. In doing so it was taken into account that, during the titration, the organomercury compound present in solution, under the action of the thiocyanate salt, may either symmetrize or replace the acetate ion bound to mercury by the thiocyanate ion. In both cases the same stoichiometric amounts of NH_4CNS are required.

$$RHgX + NH_4CNS \rightarrow RHgCNS + NH_4X,$$

$$2RHgX + 2NH_4CNS \rightarrow RHgR + Hg(CNS)_2 + 2NH_4X.$$

Special experiments showed that during the titration period (10 min) the reaction between ammonium thiocyanate and the organomercury compound proceeds to 100%, and thus can readily be taken into account. With the aid of the procedure developed, eight hydrocarbons of the cyclopropane series were investigated. As a representative of this series having an electron-acceptor substituent, methyl cyclopropyl ketone was taken. The structures of the compounds studied and their constants are presented in Table 1.

Table 1

Structures and constants of the compounds studied

Substance	B.p., °C (at 760 mm)	n_D^{20}	d_4^{20}
Cyclopropyl-$CH(CH_3)_2$	58.2	1.3864	0.6967
Cyclopropyl-CH_2CH_3	35.8	1.3783	0.6835
trans-CH_3-cyclopropyl-CH_2CH_3	58.7	1.3848	0.6932
trans-CH_3-cyclopropyl-CH_3	28.2	1.3712	0.6691
Cyclopropylbenzene	91.5 (52 mm)	1.5337	0.9420
trans-1,2-Diphenylcyclopropane	144.1 (5.2 mm)	1.5997	1.0346
cis-1,2-Diphenylcyclopropane	131.6 (4.8 mm)	1.5887	1.0290
[[unclear: cyclopropane derivative with fused aromatic substituent, structure shown in table]]	136.2 (6.5 mm)	1.5882	1.0323
Methyl cyclopropyl ketone, cyclopropyl-$COCH_3$	111.8–112.1	1.4248	0.8993

From the titration data for the reaction mixture, the amount of hydrocarbon that had reacted was calculated in percent. These values, found for the eight hydrocarbons studied, are given in Table 2.

The experiments carried out show that the reactivity of the cyclopropane ring changes greatly depending on the nature of the substituents. As was to be expected, the presence of electron-donor substituents increases the reactivity of the cyclopropane ring toward an electrophilic agent (which in the present case is mercury acetate), whereas the presence of electron-acceptor substituents lowers

this ability. Evidence for this is the experiment with methyl cyclopropyl ketone, in which it was found that, under the adopted conditions, this compound does not react with mercury acetate.

Electron-donor substituents differ sharply among themselves in the strength of their effect on the three-membered ring. The greatest influence is exerted by substituents capable of donating electrons by a conjugative mechanism (conjugation of the ring with unsaturated groupings and hyperconjugation), rather than by an inductive mechanism.

This is well illustrated by the data on the relative reactivity of the hydrocarbons, where the reactivity of isopropylcyclopropane, corresponding to the amount of hydrocarbon that reacted in 3 hours, is taken as unity.

cyclopropyl-$CH(CH_3)_2$	cyclopropyl-CH_2CH_3	cyclopropyl-$CH_2CH_2CH_3$	dimethylcyclopropane	cyclop
1	2.2	12	32	

Ethylcyclopropane is twice as reactive as isopropylcyclopropane. Meanwhile, if the inductive effect, and not the hyperconjugation effect, had a greater influence on the three-membered ring, the picture would be the reverse. The strong increase in the reactivity of the ring of 1,2-methylethylcyclopropane in comparison with ethylcyclopropane speaks to the same point: the appearance of one methyl group, possessing a comparatively small inductive effect but having three C—H bonds capable of hyperconjugation, increases the reactivity of the ring approximately 5-fold. Two methyl groups increase the reactivity of the ring to 32 conventional units.

Table 2

Substance	Amount of unreacted hydrocarbon, %after 3 hours	Amount of unreacted hydrocarbon, %after 21 hours
Phenylcyclopropane	71	
1,2-Dimethylcyclopropane (trans)	48.5	
1-Methyl-2-ethylcyclopropane (trans)	18.5	
Ethylcyclopropane	3.5	
Isopropylcyclopropane	1.5	3
trans-1,2-Diphenylcyclopropane		3.8
cis-1,2-Diphenylcyclopropane		3.5

Substance	Amount of unreacted hydrocarbon, %after 3 hours	Amount of unreacted hydrocarbon, %after 21 hours
1,1-Diphenylcyclopropane		2.5
Methyl cyclopropyl ketone	under the adopted conditions did not react	under the adopted conditions did not react

The greatest substituent effect in the series of hydrocarbons studied was observed in the case of conjugation of the three-membered ring with an unsaturated group. In phenylcyclopropane the reactivity reaches 47 conventional units.

A special place in this series is occupied by the three diphenylcyclopropanes. As the experiment showed, in the reaction with mercuric acetate they possess very low reactivity, differing little among the three hydrocarbons.

trans

cis

1 1.3 1.1 0.8

At the same time, as we showed earlier ([5]), in 1,2-diphenylcyclopropanes significant conjugation is observed, differing somewhat for the cis and trans isomers, while in 1,1-diphenylcyclopropane conjugation is practically absent. Examination of Stuart–Briegleb models showed that in all diphenylcyclopropanes the phenyl groups, which occupy a large volume, prevent the mercuric acetate molecule from approaching the three-membered ring, which hinders the course of the reaction. In the case of phenylcyclopropane and all the alkylcyclopropanes studied, steric hindrance, judging from the models, is absent.

The experimental data obtained by us agree well with the concepts of the presence in the three-membered ring of a sort of π-electron cloud capable of conjugation and hyperconjugation, i.e., resembling in character the π-electron cloud of an olefinic double bond.

Experimental Part

1. Hydrocarbons. The hydrocarbons used were synthesized by known methods. The diphenylcyclopropanes were supplied by I. L. Safonova, and 1-methyl-2-ethylcyclopropane by G. A. Khotimskaya, to whom the authors express their gratitude.

Their constants, as well as the constants of methyl cyclopropyl ketone, are given in Table 1.

2. Solutions. a) **Ammonium thiocyanate.** In the experiments a 0.1 molar solution of ammonium thiocyanate in distilled water was used (7 g of ammonium

thiocyanate in 1 liter of solution). The titer was established with a solution of mercuric nitrate of known concentration. b) **Mercuric acetate.** In the experiments was used—

was a freshly prepared 0.075 M solution of mercuric acetate in anhydrous methyl alcohol (25 g of mercuric acetate in 1 l of solution). The titer was established with ammonium thiocyanate. c) Hydrocarbon solution. An accurately weighed portion of the hydrocarbon was dissolved in a volumetric flask in anhydrous methyl alcohol. The weighed amount was calculated so that the molarity of the resulting solution would be exactly twice the molarity of the mercuric acetate solution.

3. Procedure for carrying out the experiments. A mixture of 20 ml of mercuric acetate solution and 10 ml of hydrocarbon solution in a dark-glass bottle with a ground-glass stopper was placed in a thermostat at 20°; after the required time had elapsed, the reaction mixture was poured into 100 ml of distilled water cooled to 0–5°, and titrated at 15° for 10 min with a solution of ammonium thiocyanate until a faint brownish-pink coloration appeared. An acidified aqueous solution of ammonium ferric alum served as the indicator.

The discrepancy between parallel experiments did not exceed 1%. The mean results of parallel experiments are given in Table 2.

4. Calculation of the amount of hydrocarbon that had reacted. In the titration, ammonium thiocyanate is consumed, first, by the unreacted mercuric acetate (2 moles of ammonium thiocyanate per 1 mole of mercuric acetate) and, second, by the organomercury compound (1 mole of ammonium thiocyanate per 1 mole of organomercury compound). From the titration data it is known: a is the amount of ammonium thiocyanate consumed by all the mercuric acetate taken into the reaction (in ml); b is the amount of ammonium thiocyanate consumed in the titration (in ml); $a-b$ corresponds to the amount of ammonium thiocyanate consumed by the organomercury compound. Then $2(a-b)$ is the amount of ammonium thiocyanate corresponding to the mercuric acetate that entered into the reaction; $\frac{2(a-b)}{a} \cdot 100$ will express the amount of hydrocarbon that reacted, in percent.

5. Proof of the quantitative course of the reaction between the organomercury compound formed and ammonium thiocyanate. Two bottles were placed in a thermostat at 25°; each contained 1.000 g of phenylcyclopropane and 1.350 g of mercuric acetate in 20 ml of anhydrous methyl alcohol. After 18 h had elapsed, a test for mercury ion taken from one bottle was negative. This indicated that during this time the reaction proceeds to completion. The contents of the second bottle were transferred to a volumetric flask, made up with alcohol to 50 ml, and titrated under the usual conditions with a 0.0649 M solution of ammonium thiocyanate. The titration time was 10 min. It was found that for 10 ml of a solution of the organomercury compound (calculated as 0.0185 M), 12.6 and 12.5 ml of ammonium thiocyanate solution were

required in two parallel experiments. If the reaction proceeds quantitatively, 12.57 ml of ammonium thiocyanate should be required.

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