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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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SYNTHESIS AND CATALYTIC HYDROGENATION OF DIPHENYLCYCLOPROPANES

The structure of the cyclopropane ring from the standpoint of modern theory has not been fully elucidated. There are a number of works in which the idea is developed that the hybridization of the valences of carbon atoms in a three-membered ring is close to sp^2, i.e., to trigonal hybridization ([1–3]). In other words, the carbon atoms in cyclopropane are, by their nature, close to the carbon atoms in ethylene. If modern theory represents the distribution of valences in the ethylene molecule with sufficient clarity, then the mode of formation of a three-membered ring by three sp^2 carbon atoms is of a much more problematic character. It is easy to imagine that two sp^2-orbitals of each carbon are used to form two C–H bonds, arranged, as in ethylene, at an angle of $\sim 120^\circ$ ([4–6]). Then the third sp^2-orbital and the fourth p-orbital of each carbon must participate in the formation of the C–C bonds of the three-membered ring. Various assumptions have been advanced as to the manner in which these six ($3\,sp^2$ and $3\,p$) orbitals interact to form the three C–C bonds. In different variants it is assumed that one of the valences of each carbon is an almost pure p-orbital and, consequently, in character is close to the orbitals forming a π-bond. From this point of view one may speak of the presence in the cyclopropane ring of a "π-electron cloud," situated, according to the theory, along the perimeter of the triangle in its plane (Fig. 1). Its presence should determine the possibility of conjugation of the three-membered ring with such unsaturated groupings as a carbon-carbon double bond, a carbonyl group, or a phenyl nucleus.

Fig. 1

Since conjugation can take place only when the axes of the π-clouds of the ring and of the substituent are parallel, or close to parallel, it is obvious that the position of several substituents in space should affect the greater or lesser manifes-

tation of conjugation. A work has recently been published on the investigation of the Raman spectra of 1,2-diphenyl- and 1-phenyl-2-cyclopropylcyclopropanes, in which it is shown that steric factors affect the manifestation of conjugation in a definite way ([7,8]). Thus, it was found that the conjugation effect is not the same in two stereoisomers, and in one of them it is manifested considerably more strongly than in the other. Examination of the spatial models of the stereoisomers of these hydrocarbons showed that in the cis-isomers, owing to—

the proximity of two substituent groups, one of them, or both in part, are displaced from the position favorable for conjugation. It is precisely for this reason that the cis configuration was assigned to stereoisomers in which less conjugation is observed. Proceeding from the same considerations, it could be assumed that in 1,1-diphenylcyclopropane there should be no conjugation, since both phenyl groups can occupy in space only such a position in which the axes of their π-clouds are not parallel to the plane of the three-membered ring.

Experimental data confirmed this assumption: conjugation in this hydrocarbon was practically not detected, judging from the combination-scattering spectra*.

In the present work, using the hydrogenation reaction in the presence of palladium black, which we have described repeatedly ([9–12]), as an example, the reactivity of cis- and trans-1,2-diphenylcyclopropane and 1,1-diphenylcyclopropane was studied. The data obtained are in complete agreement with the results of the study of the combination-scattering spectra of these hydrocarbons. Thus, it was found that 1,1-diphenylcyclopropane behaves in this reaction as a non-conjugated hydrocarbon and does not add hydrogen at all, whereas cis- and trans-1,2-diphenylcyclopropanes add hydrogen to the two least hydrogenated carbon atoms of the ring, with formation of 1,3-diphenylpropane

$$\mathrm{Ph{-}CH_2{-}}\overset{\mathrm{CH_2}}{\smile}\mathrm{{-}CH_2{-}Ph} \xrightarrow[20^\circ]{\mathrm{H_2;\ Pd}} \mathrm{Ph{-}CH_2{-}CH_2{-}CH_2{-}Ph.}$$

It is of interest that here also the influence of steric factors is appreciably manifested. Thus, trans-1,2-diphenylcyclopropane is hydrogenated at a considerably higher rate than the cis isomer, whose rate of hydrogenation is lower than that of phenylcyclopropane. Apparently, the proximity of the ortho-hydrogen atoms of the phenyl nuclei in cis-1,2-diphenylcyclopropane disturbs the optimal conditions of conjugation for both phenyl rings. It was thus shown that the reactivity of diphenylcyclopropanes depends on the spatial arrangement of the substituents.

Experimental Part

The hydrocarbons used in the present work were obtained by decomposition of the corresponding pyrazoline bases: **phenylcyclopropane**—in 70% yield from 5-phenyl-2-pyrazoline, synthesized by the action of hydrazine hydrate on cinnamaldehyde ([13]); **1,2-diphenylcyclopropane**—in 70% yield from

3,5-diphenylpyrazoline, synthesized by the action of hydrazine hydrate on benzylideneacetophenone ([14]); **1,1-diphenylcyclopropane**—in 83% yield from 3,3-diphenylpyrazoline, obtained by the action of diazomethane on 1,1-diphenylethylene ([15]).

The hydrocarbons were distilled under reduced pressure on a column of 30 theoretical plates efficiency. Separation of 1,2-diphenylcyclopropane into stereoisomers was carried out by continuous distillation of 100 g of hydrocarbon on a column of 100 theoretical plates efficiency. The degree of purity of the stereoisomers, determined from the freezing point, was 99.8%.

The properties of the hydrocarbons are given in Table 1.

Hydrogenation of the hydrocarbons was carried out in a duck-shaped vessel at a temperature of 20° in the presence of palladium black of one and the same preparation, with a high stirring rate (900 oscillations per minute). In attempts to hyd—

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* The combination-scattering spectrum of 1,1-diphenylcyclopropane will be published in the near future.

ration of 1,1-diphenylcyclopropane, no addition of hydrogen was observed in four experiments.

Hydrogenation of 1,2-diphenylcyclopropane.
Experiment 1. 24.6 g (0.127 mole) of 1,2-diphenylcyclopropane was taken in the form of a mixture of isomers, 0.32 g of Pd black and 40 ml of alcohol.

Table 1

Hydrocarbon	B.p., °C/mm	n_D^{20}	d_4^{20}	M.p., °C
Phenylcyclopropane	91.4–91.5°/52	1.5337	0.9415	–
cis-1,2-Diphenylcyclopropane	131.6–131.7°/4.8	1.5887	1.0290	+36.7
trans-1,2-Diphenylcyclopropane	144.1–144.2°/5.2	1.5997	1.0346	+15.3
1,1-Diphenylcyclopropane	135.0°/6.5	1.5878	1.0330	–

2758 ml of hydrogen was absorbed*. The amount of hydrogen corresponding to one mole is 2840 ml. After isolation and drying, the catalyzate was distilled on a column with an efficiency of 30 theoretical plates. Six fractions were collected, boiling from 154.0 to 157.0° (8–9 mm), having similar constants: n_D^{20} 1.5598–1.5601 and d_4^{20} 0.9800–0.9803. On distillation under atmospheric pressure the substance boiled at 298.2° (760 mm) and had n_D^{20} 1.5598 and d_4^{20} 0.9801. The constants of hydrocarbons that could have formed in this process are given in Table 2.

Table 2

Hydrocarbon	B.p., °C (760 mm)	n_D^{20}	d_4^{20}
1,2-Diphenylpropane ([16])	283.66	1.5585	0.97739
1,3-Diphenylpropane ([16])	298.7	1.5594	0.97996

Table 3

Hydrocarbon	Hydrocarbon taken into reaction, g	Hydrocarbon taken into reaction, moles	Pd, g	Alcohol, ml	Amount of H_2 absorbed, ml	Amount of H_2 required by calculation, ml	Average rate of hydrogenation, ml/min
Phenylcyclopropane	0.57	0.0048	0.06	20	120	108	5
cis-1,2-Diphenylcyclopropane	0.93	0.0048	0.06	20	100	107	3
Same	6.63	0.0342	0.2	85	809	766	6
trans-1,2-Diphenylcyclopropane	0.93	0.0048	0.06	20	108	107	8
Same	6.63	0.0342	0.2	85	776	766	13

Comparison of the constants of the hydrocarbon obtained by hydrogenation with the data in Table 2 shows that hydrogenation of 1,2-diphenylcyclopropane gives 1,3-diphenylpropane.

Experiment 2. 6.63 g (0.0342 mole) of cis-1,2-diphenylcyclopropane, 0.2 g of Pd black and 85 ml of alcohol were taken. 809 ml of hydrogen was absorbed (theoretical amount 766 ml).

The catalyzate (5.4 g) had the following constants. B.p. 138–140° (5–6 mm), n_D^{20} 1.5598, d_4^{20} 0.9802, i.e., it was 1,3-diphenylpropane. Comparative hydrogenation of phenylcyclopropane and of the stereoisomers of 1,2-diphenylcyclopropane was carried out under the same conditions, with allowance for the rate of hydrogenation. The results are given in Table 3.

The data of Table 3 show that the rate of hydrogenation of trans-1,2-diphenylcyclopropane is more than twice the rate of hydrogenation–

* The volume of hydrogen in all cases is reduced to normal conditions.

of the cis isomer. The magnitude of the hydrogenation rate of phenylcyclopropane occupies an intermediate position between the hydrogenation rates of cis- and trans-1,2-diphenylcyclopropanes.

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REFERENCES

1. A. D. Walsh, *Trans. Farad. Soc.*, **45**, 179 (1949).
2. C. A. Coulson, W. E. Moffitt, *Phill. Mag.*, **40**, 1 (1949).
3. M. E. Dyatkina, Ya. K. Syrkin, DAN, **122**, 837 (1958).
4. H. A. Skinner, *Nature*, **160**, 902 (1947).
5. O. Bastiansen, O. Hassel, C. A., **40**, 6059 (1946).
6. L. Pauling, L. O. Brockway, *J. Am. Chem. Soc.*, **59**, 1223 (1937).
7. V. T. Aleksanyan, Kh. E. Sterin, M. Yu. Lukina, I. L. Safonova, B. A. Kazanskii, *Optics and Spectroscopy*, **7**, 178 (1959).
8. B. A. Kazanskii, M. Yu. Lukina, I. L. Safonova, V. T. Aleksanyan, Kh. E. Sterin, *Izv. AN SSSR, OKhN*, 1958, No. 10, 1280.
9. B. A. Kazanskii, M. Yu. Lukina, A. I. Malyshev, V. T. Aleksanyan, Kh. E. Sterin, *Izv. AN SSSR, OKhN*, 1956, No. 1, 36.
10. B. A. Kazanskii, M. Yu. Lukina, L. G. Sal' nikov, DAN, **115**, 301 (1957).
11. B. A. Kazanskii, M. Yu. Lukina, L. G. Sal' nikova, *Izv. AN SSSR, OKhN*, 1957, No. 11, 1401.
12. B. A. Kazanskii, M. Yu. Lukina, I. L. Safonova, *Izv. AN SSSR, OKhN*, 1958, No. 1, 102.
13. N. M. Kizhner, *ZhRKhO*, **45**, 949 (1913).
14. N. M. Kizhner, *ZhRKhO*, **47**, 1102 (1915).
15. R. Ya. Levina, Yu. S. Shabarov, K. S. Shanazarov, E. G. Treshchova, *Vestn. Mosk. Univ.*, No. 5, 145 (1957).

16. K. T. Serijan, P. H. Wise, *J. Am. Chem. Soc.*, **73**, 4766 (1951).

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