HYDROGENATION OF DI-2-CYCLOPENTEN-1-YLACETYLENE OVER

Pd, Pt, AND Ni CATALYSTS

A. F. Plate and V. I. Stanko

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From the investigation of Zal'kind [1], Bourguel [2], and other [3-5], who studied the hydrogenation of phenyl- and diphenyl-acetylenes, it follows that palladium brings about the selective hydrogenation of the triple bond to a double bond. Other authors, who worked with acetylene itself and its derivatives, confirmed this and showed that only after the disappearance of the triple bond does hydrogenation of the double bond begin. Dupont [6] found that Raney nickel also shows selectivity toward an acetylenic bond. Platinum catalysts are less selective. Thus, after the addition of two atomic proportions of hydrogen to phenylacetylene in presence of a palladium catalyst no acetylenic carbon could be detected in the reaction mixture, whereas in presence of a platinum catalyst its presence could still be detected [7].

The hydrogenation of monoethylenic hydrocarbons has been studied in great detail. As a result of an investigation of the rate curves for the addition of hydrogen to numerous aliphatic hydrocarbons Lebedev and co-workers [8] showed that the degree of substitution of the hydrogen atoms at a double bond affects the hydrogenation process. It was shown that monosubstituted ethylene derivatives have the greatest and tetrasubstituted derivatives have the least rates of addition of hydrogen; di- and tri- substituted ethylenic hydrocarbons occupy an intermediate position. The authors advanced the view that this rule is observed also in the hydrogenation of mixtures of hydrocarbons with varying degrees of substitution of carbon atoms linked by a double bond.

Lebedev and Platonov [9], in a study of the hydrogenation of cyclohexenes, extended to these the rule already established for aliphatic compounds; they showed also that on addition of hydrogen to mixtures of unsaturated hydrocarbons in presence of platinum black alicyclic and acyclic ethylene derivatives of identical degree of substitution behave differently, and the difference between them becomes more marked in the case of tri- and tetrasubstituted ethylenes. Disubstituted cyclic ethylenes, i.e. cyclic hydrocarbons having no substituents at the double bond, and disubstituted ethylenes with an open chain are hydrogenated simultaneously, whereas trisubstituted ethylenes with an open chain are hydrogenated before cyclic trisubstituted ethylenes. However, these conclusions of Lebedev and Platonov cannot be regarded as completely proved since no proofs other than rate curves for the absorption of hydrogen were advanced in their favor.

Moreover, in a study of the literature on this question the lack of justification of some of the comparisons becomes obvious, e.g. comparisons of the rate of the addition of hydrogen to olefins, on the one hand, and to unsaturated functional derivatives, on the other. Particularly cautious treatment must be given to conclusions drawn about the direction of the addition of hydrogen to ethylenic hydrocarbons in presence of palladium catalysts, since for a long time due attention was not given to the isomerizing properties of this catalyst. Kazanskii, Lukina, Malyshev, and others [10], in a study of the partial (to the extent of 20%) addition of hydrogen to 2-methyl-1-pentene and 2-methyl-2-pentene in an alcoholic medium at room tempterature and atmospheric pressure, showed that in presence of palladium the isomerization of these hydrocarbons occurred with formation of an equilibrium mixture, whereas in presence of platinum [11] such isomerization did not occur. Gostunskaya, Dobroserdova, and Kazanskii [12], for the case of isoamylenes and 2,5-dimethyl-3-hexene, also observed that in presence of platinum only addition of hydrogen occurred, where as in presence of palladium with partial addition of hydrogen there was simultaneous isomerization with displacement of the double bond. Results obtained on the isomerizing action of palladium under mild conditions of catalytic hydrogenation compels one to make a reexamination of some conclusions reached earlier on the selective action of various catalysts in the addition of hydrogen to unsaturated compounds.

The question of the direction of the addition of hydrogen to di- and poly-olefins, in which the double bonds may be isolated, conjugated, or cumulative, is still more complex. The most detailed study has been given to the hydrogenation of aliphatic hydrocarbons having a system of conjugated double bonds. It was here shown that first one and then the other molecule of hydrogen may add successively at different rates, or both molecules of hydrogen may occur in all possible directions, depending both on the character of the substitution at the doubled-bonded atoms and on the nature of the catalysts and solvents.

The hydrogenation of hydrocarbons containing several isolated double bonds has received relatively little study. It is known that in individual cases such hydrocarbons may undergo selective hydrogenation, and in some cases Lebedev's rule has been confirmed. Vavon [13] was the first to observe that in the hydrogenation of limonene in presence of platinum black the two molecules of hydrogen add at different rates: the first more rapidly than the second. Here the isopropenyl group (disubstituted ethylene) is hydrogenated first, and only after the addition of one molecule of hydrogen does the second double bond (trisubstituted bond in the ring) begin to be hydrogenated:



Such selectivity in the addition of hydrogen to limonene was observed also by Ipat'ev [14] in hydrogenation over copper catalysts under pressure and by Armstrong and Hilditch [15] over nickel. On the other hand, in the hydrogenation of 1,5-dimethyl-1,5-hexadiene [8] in presence of platinum no selectivity was observed: the two molecules of hydrogen added at equal and constant speeds.

We considered it to be of interest to study the order of the addition of hydrogen to multiple bonds in the case of a compound in which the degree of substitution at the double-bonded carbon atoms was the same in every case, but the bonds differed in that two were present in five-membered rings and one in an aliphatic chain. With this object we studied the hydrogenation of a compound containing two double bonds in five-membered rings and one triple bond between the rings, namely di-2-cyclopenten-1-ylacetylene $\boxed{-C = C - \langle - \langle - \rangle}$ (I), in presence of various catalysts; on partial selective addition of hydrogen this compound should give, in the first place, a hydrocarbon with three isolated double bonds $\boxed{-C = C - \langle - \rangle}$, which is the compound in which we were interested from the point of view of the study of the character of its hydrogenation.

DISCUSSION OF EXPERIMENTAL RESULTS

The rate curves for the addition of hydrogen to di-2-cyclopenten-1-ylacetylene in presence of various catalysts are given in Fig. 1. It will be seen that in presence of platinum the rate of addition of hydrogen remains constant until 75 -78% of the hydrogen theoretically required for the complete saturation of the multiple bonds has added. We studied the incomplete-hydrogenation product obtained after the addition of 75% of the hydrogen. It was found that it did not contain compounds with a triple bond and was mainly cis-1,2-dicyclopentylethylene(II)



This conclusion was reached with reasonable certainty on the basis of the Raman spectrum of the catalyzate; in the region of the valence vibrations of the double bond in this spectrum there was only one line, 1651 cm^{-1} , which is characteristic of a cis-disubstituted double bond [16][•]. This line might correspond also to 1-(1-cyclo-

*Here we assume that the frequency of the line does not change on replacement of alkyl groups at the double bond by cyclopentyl groups.

penten-1-yl)-2-cyclopentylethane (III) but, as under the given hydrogenation conditions platinum has no isomerizing action on unsaturated hydrocarbons [11] and compound (III) could not be formed by the direct addition of hydrogen to (I), we reject this possibility. An analysis of the Raman spectra leads to the same conclusion, for in the spectrum of a compound having the structure (III) the presence of lines in the region 800-900 cm⁻¹ would be expected (apart from the lines for the pulsation vibration of the five-membered ring), but such lines are not found in the spectrum of the catalyzate.

Hence, in the partial addition of hydrogen to di-2-cyclopenten-1-yl-acetylene in presence of platinum black the double bonds in the five-membered rings appear to be saturated in preference to the aliphatic double bond formed as a result of the partial selective hydrogenation of the triple bond; hence, the addition of hydrogen proceeds in accordance with the scheme:



Since, in the given example in presence of platinum, hydrogen added preferentially to the double bonds in five-membered rings, we considered it to be of interest to study the partial addition of hydrogen to a mixture of two unsaturated hydrocarbons, namely an aliphatic olefin and a cyclopentene homolog in which the degree of substitution at the carbon atoms of the double bond was the same in each case. For this purpose we took an equimolecular mixture of 3-methylcyclopentene and 2-octene. A study of the catalyzate obtained after the addition of 50% of the hydrogen required for the complete saturation of the double bonds in presence of platinum black showed that in this case also there was preferential hydrogenation of the double bond in the five-membered ring: the first hydrocarbon was hydrogenated to the extent of 75%, but the second only to the extent of 22-24%.



ylacetylene.

In the presence of palladium black the addition of hydrogen to di-2-cyclopenten-1-ylacetylene proceeded differently. The relevant curve (Fig. 1) shows that the rate of addition of hydrogen at first increases continuously and then, after a maximum is reached (at the absorption of 56-57% of the theoretically required hydrogen), it gradually falls.

A study of the catalyzate obtained after the addition of 25% of the hydrogen necessary for the complete saturation of the multiple bonds showed that it boiled over a narrow temperature range, contained none of the original compound, and in the region of the valence vibrations of the double bond in the Raman spectrum had two lines at 1611 and 1649 cm⁻¹ of approximately equal intensity. The first corresponded to the double bond in a five-membered ring (having no substituents on the double-bonded carbons), and the second could correspond to a cis-disubstituted ethylenic bond in an aliphatic chain (see above). In this case the product had the structure of 1,2-di-2-cyclopenten-1-ylethylene (IV), in which there is a system of three isolated double bonds. As isomerization with displacement of double bonds is possible in presence of palladium, we must take into consideration also that the frequency 1649 cm⁻¹ may belong to a double bond in a five-membered ring such that there is a substituent on one of the carbon atoms of the double bond. A bond of this kind is present in compounds (V) and (VI), in which, however, the double bonds are conjugated, and it is known that conjugation leads to a considerable increase in the intensity of the frequencies corresponding to the double bonds, which is not observed in the case of the cata-lyzate under investigation. We may therefore conclude that the addition of 25% of hydrogen proceeds according to the scheme



and that isomerization with displacement of the double bonds proceeds only to a slight extent, if at all:



Hence, while the mixture still contains some of the original compound with a triple bond the isomerizing action of palladium scarcely shows itself because of the preferential absorption of molecules on the catalyst at the $C \equiv C$ bond.

However, with the further addition of hydrogen (hydrogenation to the extent of 75%) in presence of palladium the picture becomes complicated and there appears to occur considerable isomerization with displacement of double bonds. In the spectrum of the resulting catalyzate in the region of the valence vibrations of the double bond there are three lines: 1617 (1), 1652 (9), and 1678 (3) cm⁻¹. The first (the weakest) appears to correspond to 1-(2-cyclopenten-1-yl)-2-cyclopentylethane (VII)



and the second, the most intense, may be attributed, with equal justification, to cis-1,2-dicyclopentylethylene (II) and 1-(1-cyclopenten-1-yl)-2-cyclopentylethane (III). We succeeded in proving the presence of these two compounds experimentally by a study of the products of the oxidation of the catalyzate with potassium permanganate, as a result of which we isolated cyclopentanecarboxylic acid



and 7-cyclopentyl-5-oxoheptanoic acid



No other oxidation products were detected.

The line 1678 cm⁻¹ may belong to trans-1,2-dicyclopentylethylene (II), for according to Goubeau [16] transdisubstituted ethylenes in the aliphatic series correspond to a frequency of 1670-1673 cm⁻¹; this frequency may correspond also to 1-cyclopentyl-2-cyclopentylideneethane (VIII)



for it has been shown recently [17] that the double-bond frequency in the spectra of ethylidene-, propylideneand butylidene-cyclopentanes is 1680-1681 cm⁻¹. However, on oxidation of (VIII) with potassium permanganate cyclopentanone should be formed, and we could not detect this in the oxidation products of the catalyzate. Hence, while not rejecting finally the possibility that such a compound is present in the catalyzate in small amounts, we are more inclined to attribute the frequency of 1678 cm⁻¹ to trans-1,2- dicyclopentylethylene (II), by the oxidation of which cyclopentanecarboxylic acid is again formed^{*}.

Hence, in the 75% hydrogenation of di-2-cyclopenten-1-ylacetylene in presence of palladium, the mixture formed is more complex than that formed in presence of platinum and its main components are dicyclopentylethylene (II) and 1-(1-cyclopenten-1-yl)-2-cyclopentylethane (VII). The formation of these and other hydrocarbons may be the result of several reactions: the hydrogenation and isomerization of substances formed at different stages of the hydrogenation (addition of the first, second, and third molecule of hydrogen):



As regards the addition of hydrogen to di-2-cyclopenten-1-ylacetylene in presence of Raney nickel, as ca be seen from Fig. 1 in this process there first occurs absorption of hydrogen at a uniform rate and, after the absorption of two molecular proportion of hydrogen, the rate of hydrogenation slowly falls. On fractional distillation of the catalyzate obtained as a result of the addition of 75% of the total hydrogen required, it was found that no single component was present in predominant amount and that the mixture formed boiled over a wide temperature range. We did not study this mixture in greater detail.

From the present investigation it may be concluded that the presence in a molecule of not only a triple bond, but also double bonds in five-membered rings, does not hinder the selective hydrogenation of the triple bond in presence of palladium, because the molecule appears to be preferentially absorbed on the catalyst at the triple bond. To Lebedev's rules on the relation of the rate of addition of hydrogen to double bonds in presence of platinum to the number of substituents at the double bond we can make this supplement: for a given degree of substitution at a double bond in presence of platinum the double bond in a five-membered ring is hydrogenated preferentially to a double bond in an open chain. However, on hydrogenation in presence of palladium the isomerizing action of the latter results in the formation of a mixture of products; a similar picture, with the formation of a still more complex mixture, is observed also in presence of nickel.

EXPERIMENTAL

Di-2-cyclopenten-1-ylacetylene (I) was prepared by the reaction of the Iotsich complex with 2-cyclopen-*A frequency of 1678 cm⁻¹ might be attributed also to a cyclopentene in which there is a substituent on each of the double bonded atoms: However, it can scarcely be imagined that skeletal isomerization of this kind could occur in hydrogenation in the cold in the presence of palladium.

	Amt. taken for reaction			Consumption of hydrogen			
Expt.	Dicyclo-	A1-		(moles)	(ml of STP)		Notes
	pentenyl- acetylene (g)	cohol (ml)	Catalyst (g)		Theo- retical	Exptl.	Notes
1	0,4003	40	Pt 0,20	4	227	229	Bend after addition of 75% H ₂
2	0,2387	30	Pt 0,087	4	163	164	Bend after addition of 78% H ₂
3	25.1	100	Pt 1,2	3	10670		-
4	0,3298	30	Pd 0,067	4	187	181	Maximum after addition of 57% H ₂
.5	0,3378	30	Pd 0,067	4	191	186	Maximum after addition of 56% Ha
6	12.33	50	Pd 0.51	1	1750	1760	
7	17.2	50	Pd 0.60	3	7310	7330	
8	0.30	30	Ni 0,30	4	170	173	
9	10,0	50	Ni 3,0	3	4250	4280	

Hydrogenation of Di-2-cyclopenten-1-ylacetylene

ten-1-yl chloride [18]; it has: b.p. 106° (9-9.5 mm); n_D^{20} 1.5172; d_4^{20} 0.9596. The hydrogenation was carried out in glass hydrogenation flasks at room temperature and atmospheric pressure; agitation was effected by means of a shaker giving 150-180 double shakes per minute. The rate of absorption of hydrogen was determined every 30 seconds with the aid of a gas buret having 1-ml graduations. A fresh portion of catalyst was taken for each experiment. Platinum and palladium blacks were prepared by Zelinskii's method [19] and Raney nickel by Adkin's method [20]. The experimental results are given in the table; curves were constructed from the results of Experiments 1, 2, 4, and 8 (Fig. 1).

In the investigation of the reaction products alcohol was washed from the catalyzate with water, and the catalyzate was then dried with calcium chloride and distilled through a column of 40-plate efficiency. Catalyzate of Expt. 3: Fraction I, head fraction up to $90.2^{\circ}(7 \text{ mm})$, $1 g (n_D^{20}1.4804)$; Fraction II, b.p. $90.2-90.4^{\circ}(7-7.5 \text{ mm})$, $14.8 g (n_D^{20}1.4822)$; Fraction III, residue from distillation, $5 g (n_D^{20}1.4864)$.

In the Raman spectrum of Fraction II $(d_4^{20} \ 0.8746)$ only one line, 1651 cm⁻¹, was found in the region of the valence vibrations of the double bond.

<u>Catalyst of Expt. 6.</u> After fractionation we obtained 9.8g; b.p. 99-99.5° (15 mm); nD^{20} 1.5112; d_4^{20} 0.9061. In the spectrum of this fraction we found bright lines of approximately equal intensity at 1611 and 1649 cm⁻¹.

Catalyst of Expt. 7. Fractionation gave 14.6 g (91% of amount taken in fractionation) of a fraction having b.p. $108-108.5^{\circ}$ (13 mm); n_{D}^{20} 1.4781; d_{4}^{20} 0.8771. In the spectrum of this fraction we found the lines : 1617(1), 1652(9), and 1678(3) cm⁻¹ (the figures in parentheses are visual intensities on a ten-grade scale). On oxidation of the catalyzate of Expt. 7 (3 g) with potassium permanganate (7.5 g) in aqueous solution (120 ml) at 0-5° we obtained about 0.5 g of cyclopentanecarboxylic acid, the amide of which had m.p. 176.5-177° (the literature [21] gives m.p. 179°), and 7-cyclopentyl-5-oxoheptanoic acid, the semicarbazone of which had m.p. 150-151°. Analysis of semicarbazone : Found C 58.10, 58.07; H 8.51; 8.59; N 15.02; 15.10%. C₁₃H₂₃O₃N₃. Calculated : C 57.98; H 8.58; N 15.61%.

The catalyzate of Expt. 9 boiled in the range 92.5-98° (9.5 mm) and was not investigated more closely.

Hydrogenation of an Equimolecular Mixture of 2-Octene and 3-Methylcyclopentene over Platinum Black. 2-Octene was isolated by fractionation through a column of 100-plate efficiency from a mixture of octenes obtained by the dehydration of octanol with 2.85% phosphoric acid [22]; it had: b. p. 126.0° (752 mm); nD^{20} 1.4150. The literature [23] gives: cis-2-octene, b. p. 125.64°, nD^{20} 1.4150; trans-2-octene, b.p. 125.0°, nD^{20} 1.4132. 3--Methylcyclopentene was isolated by fractionation through a column of 60-plate efficiency from the mixture of methylcyclopentenes obtained by the isomerization of cyclohexene over alumina; it had: b.p. 64.9° (760 mm) nD^{20} 1.4219; d_4^{20} 0.7647. The literature [23] gives: b.p. 65.0°; nD^{20} 1.4207; d_4^{20} 0.7622. In presence of 0.3 g of platinum black, 2.44 liters (at 19° and 745 mm) of hydrogen (50% of the amount required to saturate the multiple bonds completely) was caused to add to a mixture of 11.2 g (0.1 mole) of 2-octene and 8.2 g (0.1 mole) of 3-methylcyclopentene in 50 ml of alcohol. After suitable treatment the catalyzate was fractionated through a column of 40-plate efficiency.

Fraction I; b.p. 67.7-71.0°; n_D^{20} 1.4162; d_4^{20} 0.7566; 2.1 g; Fraction II; b.p. 71.0°, n_D^{20} 1.4101; d_4^{20} 0.7502; 4.2 g; Fraction III; b.p. 71.0-122°; 1.1 g; Fraction IV; b.p. 122-122.5°; n_D^{20} 1.4112; d_4^{20} 0.7160; 7.2 g; Residue; n_D^{20} 1.4102; 2.0 g.

Fraction I was a mixture of 3-methylcyclopentene and methylcyclopentanes (compostion of mixture, calculated from the additivity of refractive indices and specific volumes: 59% and 41%); Fraction II was almost pure methylcyclopentane; Fraction III was an intermediate fraction; Fraction IV was a mixture of octenes and octane [bromine value 108 (duplicate 111), according to which the octene content of this fraction was 76-77.5%]. Hence, from the results obtained it follows that 3-methylcyclopentene was hydrogenated to the extent of 75%, but 2-octene only to the extent of 22.5-24%.

The spectrum investigations on the catalyzates were carried out in the laboratory of the Spectroscopy Commission of the Academy of Sciences of the USSR by V. T. Aleksanyan and Kh. E. Sterin and in the P. N. Lebedev Physics Institute of the Academy of Sciences of the USSR by M. M. Sushinskii; we express our deep gratitude to these workers.

SUMMARY

1. The presence of palladium the triple $C \equiv C$ bond in di-2-cyclopenten-1-ylacetylene is selectively hydrogenated to a double bond.

2. In presence of platinum, after the addition of three molecular proportions of hydrogen to di-2-cyclopenten-1-ylacetylene 1,2-dicyclopentylethylene is formed, i.e., the double bonds in the five-membered rings are preferentially hydrogenated.

3. In presence of palladium, as a result of the isomerizing action of this catalyst, the addition of three molecular proportions of hydrogen to di-2-cyclopenten-1-ylacetylene results in the formation of a mixture of unsaturated hydrocarbons, in which 1,2-dicyclopentylethylene and 1-(1-cyclopenten-1-yl)-2-cyclopentylethane predominate.

4. The preferential addition of hydrogen at the double bond in the five-membered ring rather than at the double bond in the open chain is observed also in the partial hydrogenation (to the extent of 50%) of an equimo-lecular mixture of 3-methylcyclopentene and 2- octene over platinum black.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-tocover English translations appears at the back of this issue.

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