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CATALYTIC HYDROGENATION OF CYCLOPROPYL ALKENES. I. EFFECT OF ALKYL SUBSTITUTION ON THE HETEROGENEOUS HYDROGENOLYSIS REACTION

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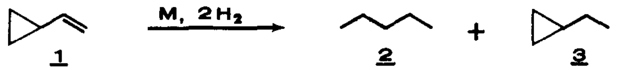
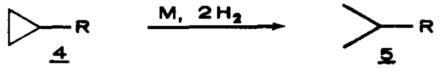
Catalytic reduction of conjugated cyclopropyl alkenes is accompanied by hydrogenolysis of the allylic cyclopropyl ring bonds (i.e., eq. 1), under conditions which do not affect isolated cyclopropane rings (3,4). Under more drastic conditions, isolated cyclopropane rings suffer hydrogenolysis (4,5), mainly at the bond opposite the position of substitution (eq. 2) (5,6,7).



(1)



(2)

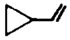
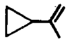
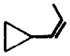
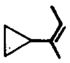
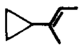
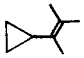
We have initiated a systematic study of the hydrogenation of various substituted cyclopropyl alkenes in the presence of several catalysts. One aspect of this investigation has been an examination of the effect of methyl substitution on the degree of simple double bond reduction (eq. 1, 1 → 3) and conjugate hydrogenolysis (eq. 1, 1 → 2). We now wish to communicate the preliminary results of this aspect of our study. The question of the intermediates involved in the latter reaction will be dealt with separately.

Table I summarizes the results of the reduction of a series of double-bond alkylated vinylcyclopropanes over Pd-C, Pt-C, and Rh-C. As will be seen from the table, reductions over palladium lead to almost complete ring hydrogenolysis, and this course is not significantly altered by the degree of double bond substitution. Since the alkyl cyclopropanes were shown to be stable under the conditions of the reaction, ring hydrogenolysis must precede or occur concomitantly with double bond saturation.

On the other hand, reactions over platinum or rhodium give mostly double bond reduction. The small amounts of "non-conjugate" hydrogenolysis observed in the case of platinum probably arise by a secondary reduction of initially formed alkyl cyclopropane, since control runs showed that these compounds are slowly attacked under the conditions employed. It will also be noted that, over

TABLE I

Degree of Hydrogenolysis as a Function of Double Bond Substitution[a]

		5% Pd-C		5% Pt-C		5% Rh-C	
Olefin		Alkyl Cyclopropane	Alkane	Alkyl Cyclopropane[b]	Alkane	Alkyl Cyclopropane	Alkane
	6	5	95	74	26	78	22
	7	1	99	72	28	77	23
	8	—		63	37	72	28
 	9	1	99	47	53	64	36
	10	4	96	47	53	—	

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[a] Reductions were carried out on 100 μℓ of olefin with 10 mg of the catalyst in 1 ml of isopropanol at atmospheric pressure and room temperature. All catalysts used were aged for more than one year and the results are believed to be reproducible within 2-3% for the same catalyst batch.

[b] Figures given include 1-5% "non-conjugate" ring opening, probably from over reduction of initially formed alkyl cyclopropane.

platinum and rhodium, the degree of ring hydrogenolysis gradually increases as additional methyl groups are added to the double bond. A similar trend has been noticed in the reduction of certain cyclopropylalkenes in the presence of barium promoted copper chromite (8).

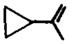
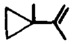
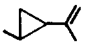
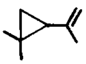
Table II summarizes the results obtained from three ring-methylated isopropenylcyclopropanes. Again, almost total hydrogenolysis is observed with palladium, while platinum and rhodium give mostly simple double bond reduction. The effect of the C-1 methyl group in 11 is interesting. Over platinum and rhodium, this methyl group almost completely inhibits the hydrogenolysis reaction. With all three catalysts, the C-2 alkylated compounds 12 and 13 undergo preferential opening of the less substituted conjugate ring bond.

In Table III is listed the amount of ring hydrogenolysis over Pt-C as a function of the size of the group at C-1 of the double bond. It will be noted that a steric effect operates, the larger alkyl substituents causing relatively less conjugate hydrogenolysis.

Finally, we have examined the reduction of methyl cis- and trans-3-cyclo-

TABLE II

Degree of Hydrogenolysis as a Function of Ring Substitution[a]

Olefin		5% Pd-C[b]			5% Pt-C[b]			5% Rh-C[b]		
		A	B	C	A	B	C	A	B	C
	7	1	48.5	48.5	71	14.5	14.5	77	11.5	11.5
	11		—		91[c]	4.5	4.5	95	2	2
	12	2.4	90.4	7.2	73[d]	25	2	83	17	0
	13	0	99	1	59	40	1	79	21	0

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[a] For conditions, see footnote a, Table I.

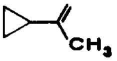
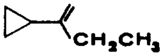
[b] A = % Alkylcyclopropane product; B = % opening of the 1-3 cyclopropane bond; C = % opening of the 1-2 cyclopropane bond.

[c] Includes 9% of product from opening of the 2-3 cyclopropane bond, probably from secondary hydrogenolysis of initially-formed alkylcyclopropane. A longer reaction time was necessary in order to assure complete saturation of the intermediate alkenes.

[d] Includes 2% of product from opening of the 2-3 cyclopropane bond.

TABLE III

Degree of Hydrogenolysis as a Function of the Double Bond Alkyl Substituent[a]

Olefin		Product		
		Alkylcyclopropane	Conjugate Opening	Nonconjugate Opening
	7	67	28	5
	14	76	20	4
	15	79	14	7

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[a] Over 5% platinum on carbon.

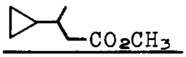
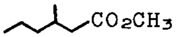
propylcrotonate (16). The results, summarized in Table IV, closely parallel

16  (cis and trans)

the results obtained from 2-cyclopropyl-2-butene (Table I). These results seem to invalidate the hypothesis (9) that ring opening occurs through the addition of hydride, with subsequent ring opening of a cyclopropylcarbinyl anion. Such a

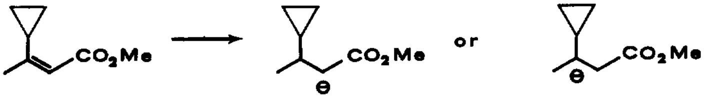
TABLE IV

Degree of Hydrogenolysis of Methyl 3-Cyclopropyl Crotonates[a]

	Product	
Catalyst		
5% Pd-C	0%	100%
5% Pt-C	44	56
5% Rh-C	60	40

[a] A mixture containing 80% cis- and 20% trans-.

mechanism would give predominately the more stable anion 17, which cannot undergo ring opening (eq. 3).



16 **17** **18** (3)

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2. Fellow of the Alfred P. Sloan Foundation.
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