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Conjugative and Steric Effects on the Ring-Opening of Substituted Phenylcyclopropanes over Palladium Metal

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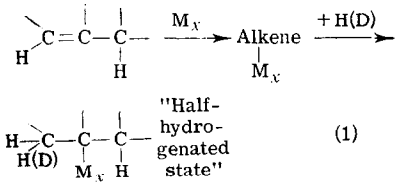
The hydrogenolysis of various phenyl substituted cyclopropanes over palladium metal is considered. The mechanism for this reaction and the conjugative and steric effects associated with the manner of ring-opening are discussed. It is concluded that initial adsorption of phenylcyclopropanes occurs *via* "corner" attack to yield benzyl-adsorbed phenylpropanes and that addition and exchange reactions utilize different catalyst sites. Conjugative effects are concluded to outweigh steric effects in both orienting and facilitating the hydrogenolysis.

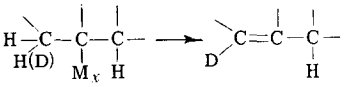
Introduction

The study of the hydrogenation of alkenes has been both enlivened and frustrated by a simultaneous exchange reaction, so that deuterium addition to double bonds is rarely observed as an independent reaction over platinum family heterogeneous catalysts (*1*). The exchange reaction is most pronounced with palladium catalysts (*1–3*). Until recently, this multiplicity of reactions was interpreted as arising from the intermediacy of a species common to all the reactions observed (including isomerization and racemization, as well as hydrogenation and exchange), the "half-hydrogenated state" of the alkene, a monoadsorbed intermediate which had acquired one hydrogen (deuterium) atom from the surface during a two-step addition (*1, 2*).



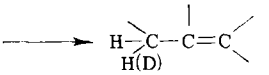
(1)

This intermediate (which must be formed, since hydrogen addition has been shown to be stepwise) has been credited with the ability to 1) revert to the original (or an isomeric) alkene by removal of the first added (or any similar) hydrogen;



(1a)

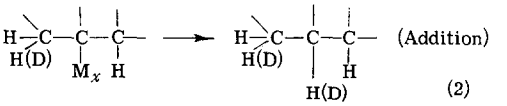
(Exchange)



(1b)

(Exchange–isomerization, and/or racemization)

2) add a second hydrogen (deuterium) atom to yield alkane; or 3) form symmetrically adsorbed alkenes capable of racemization and



(Addition)

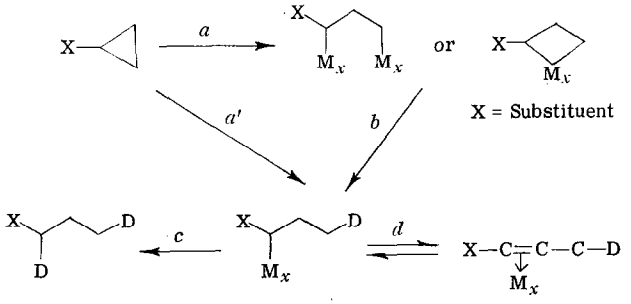
(2)

multiset exchanges of small-ring cyclic hydrocarbons (*4–7*).

If this view is correct, formation of the monoadsorbed species, by any means, should yield the same results.

The hydrogenolysis of cyclopropanes is formally analogous to alkene hydrogenation, with one important exception: ring-

opening is thermodynamically disfavored from reversing and reforming the cyclopropane (*8, 9*). The inability of cyclopropanes to exchange hydrogen for deuterium under hydrogenolysis conditions has been demonstrated (*10–12*). Hydrogen addition



(5)

however, may still be stepwise, as with the alkenes so that once more the monoadsorbed species is formed (*10*). If the "half-hydrogenated state" is truly the common intermediate for hydrogenation and exchange, similar results ought to be obtained from adding deuterium to cyclopropane and propene, for example (*10, 12*).

That substituents exert a pronounced effect upon double bond reduction has been well demonstrated (*3, 12, 15*). The effect of substituents on cyclopropane reactions is also well documented (*3, 8, 10, 11*). Ring opening tends to occur *across* the ring (2,3-opening) from alkyl substituents but always *adjacent* to phenyl (1,3-opening) (*3, 8, 10, 11*). This might be due to bond polarization (*11, 16*), steric effects, intermediate stability, symmetry rules (*10, 17*), or

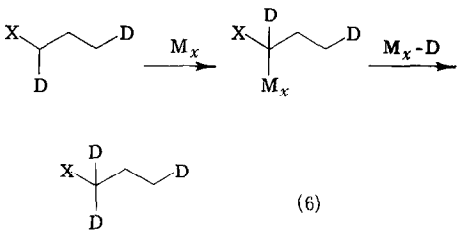
for R = alkyl (3)

for ϕ = phenyl (4)

any combination of these. That the intermediates are not the result of the formation of π-allyl complexes or triadsorbed species has already been reported (*10, 11*).

Previous evidence suggests that cyclopropanes ring-open through 1,3-addition of hydrogen in a two-step addition process (sequence 5), without prior cyclopropyl exchange, even when other alkyl groups do exchange by an independent process (*10*) (sequence 6).

The simplicity of the exchange patterns found in products from the addition to cyclopropanes, however, raises some fundamental questions



(6)

with respect to the nature of the bonding, mode of formation, and kinds of catalytic sites involved in the α,β process (*1*).

The compounds cyclopropylbenzene (I), cyclopropylphenylmethane (II), 1-methyl-1-phenylcyclopropane (III), *trans*-1-phenyl-2-methylcyclopropane (IV), *cis*-1-phenyl-2-methylcyclopropane (V), methyl-*trans*-2-phenyl-cyclopropane carboxylate (VI), 1,1-diphenylcyclopropane (VII), *trans*-1,2-diphenylcyclopropane (VIII), *cis*-diphenylcyclopropane (IX), and methylcyclopropyl ketone (X) were hydrogenolyzed with deuterium over palladium metal in a gas phase flow system (*4–6*) at temperatures between 90°–170°C. Compound *trans*-1-phenylpropene (Ia) was also hydrogenated in the same way for comparison to I. These compounds were selected for study to examine the orienta-

tion of ring opening, the deuterium distribution due to addition, the degree and position of exchange with deuterium, and the steric effects associated with these reactions. The phenyl substituted compounds are especially valuable in these respects since phenyl does not itself exchange under the reaction conditions and it has been shown that the *alpha*-monoadsorbed species is greatly preferred in the "half-hydrogenated state" (*13–15*).

Experimental

Compounds. Both hydrogen and deuterium (Matheson Co., 98% isotopic purity) were prepurified by diffusion through a silver–palladium alloy tube (*4*). II and X were obtained from the Aldrich Chemical Co., Inc. I (98%) was purchased from the Chemical Samples Co. These three were used without further purification. VI was prepared from the corresponding acid (Aldrich Chemical Co.) via the diazomethane method, followed by solvent ether evaporation and distillation at 92°/1 Torr to yield chromatographically pure methyl ester. VIII was prepared by the method of Kishner from benzalacetophenone, using the Huang–Minlon modification (*18*); after distillation and preparative gas chromatography, it was 100% pure. III, IV, V, VII, and IX were prepared from α-methylstyrene (J. T. Baker), *trans*-propenylbenzene (Aldrich) (Ia), *cis*-propenylbenzene (Chemical Samples), 1,1-diphenylethylene (Chemical Samples), and *cis*-stilbene (Aldrich), respectively, by the LeGoff modification (*19*) of the Simmons–Smith cyclopropanation reaction (*20*); all were purified by preparative gas chromatography before use.

The catalysts were prepared by impregnating wide-pore silica gel (60–80 mesh, Filtros Corp. (*4*)) with 4.5×10^{-3} *M* $Pd(NH_3)_2(NO_2)_2$ (*21*). After drying at 100°C for one day in air, one gram of this mixture was sealed, in a U-tube, to the flow system and heated to 400°C in flowing hydrogen (10 cc/min) for 4 hr, producing an active 0.14% palladium catalyst. All catalysts were prepared in the same way and no catalyst was used for more than three experiments. Catalysts, if not freshly prepared, were preactivated at 400°C in flowing hydrogen immediately before use.

Reactions. Hydrogenolyses were performed in a gas phase flow system (*4*, *5*) by flowing the prepurified hydrogen (deuterium) through a thermostatted U-tube containing wide-pore silica gel impregnated with the compound of interest; in this way, the hydrogen (deuterium) swept out the vapor of the compound and this mixture then passed on to the thermostatted catalyst. The flow rate was 10–15 cc/min and the hydrogen (deuterium) to compound ratio of the gas mixture was 75:1 for I–V, 150:1 for VI, 800:1 for VII–IX, and 30:1 for X. After passing through the catalyst bed, the reaction mixture was collected in a dry ice/acetone cooled trap.

Analyses. After collection, reaction mixtures were analyzed with a Varian-Aerograph Model 1720 dual column, thermal conductivity detector gas chromatograph. The instrument was operated with 15 ft 8% Carbowax 20M, 8 ft 10% QF-1, and 6 ft 10% SF-96 columns at temperatures near the boiling points of the compounds in the mixtures. Preparative separation of these mixtures were effected similarly, trapping components in dry ice/acetone cooled collector tubes.

The compounds thus collected were analyzed for deuterium content (by position) by nuclear magnetic resonance (NMR) methods. Varian A-60A or T-60 instruments were employed. Integration of NMR multiplets yielded the average hydrogen content by alkyl group (except where chemical shifts were too similar for resolution) in the reaction products, and therefore (by difference) the deuterium content by alkyl group position (since deuterium does not exhibit resonance at 60 MHz and 14,100 G) (*4*, *13*). The average of at least three integrations are those reported in Tables 1 and 2.

Mass spectra were also obtained with chromatographically pure compounds. Spectra were recorded of the parent and associated peaks at 15 eV ionizing voltage with a Consolidated CEC 21-130 instrument.

TABLE 1
DEUTERIUM DISTRIBUTION IN RING-OPENED PRODUCTS OVER PALLADIUM

Temp. (°C)	Reactant	Products	%	C_1[a]	C_2	C_3	Other	D_{avg}[b]	M[c]
97	I	Ph—C—C—C	5.5	1.00	0.00	0.91[d]	—	1.91	—
99.5	I	Ph—C—C—C	100	2.00	0.00	0.99	—	3.00	3.00
102	Ia	Ph—C—C—C	100	1.14[e]	1.02	0.13	—	2.29	—
159	II	Ph—C—C—C—C	3.5	1.00	1.00[f]		1.42[g]	3.42	3.41
129	III	Ph—C(C)—C—C	99	1.00	0.23	0.80[h]	0.63[i]	2.66	—
130	III	Ph—C(C)—C—C	95	1.00	0.20	1.00	0.78[i]	2.98	—
142	III	Ph—C(C)—C—C	91	1.00	0.39	1.00	1.14[i]	3.53	—
126	IV	Ph—C—C(C)—C	88	2.00	0.08[d]	0.84[h]	—	2.92	3.22
		and Ph—C—C—C—C	5.9						
170	IV	Ph—C—C(C)—C	81	1.00	0.07	1.10[d]	—	2.27	—
		and Ph—C—C—C—C	5.3						
103	V	Ph—C—C(C)—C	76	2.00	0.00	0.89[d]	—	2.89	2.98
		and Ph—C—C—C—C	22	2.00	1.1[d,f]			3.1	—
132	VI	Ph—C—C—C—CO_2Me	35						
		and Ph—C—C(C)—CO_2Me	10.5						
137	VII	$(Ph)_2$C—C—C	100	1.00	0.00	1.00	—	2.00	—
124	VIII	Ph—C—C—C—Ph	66	1.00	0.00	1.00	—	2.00	—
		and Ph—C—C(C)—Ph	23	1.00	0.00	1.00	—	2.00	—
116	IX	Ph—C—C—C—Ph	18	1.00	0.00	0.98	—	1.98	—
		and VIII	27						
125	X	C—CO—C—C—C	19	0.70	0.30	1.00	0.00	2.00	—

[a] C_1, C_2, and C_3 refer to the carbon atom positions in the product relative to 1,3-ring-opening of the corresponding cyclopropane; ±0.05 deuterium atoms except as indicated (see footnotes *d* and *h*).
[b] The sum of the NMR integration determinations.
[c] $\Sigma_i d_i$ from the mass spectral determinations (4,13); these should equal D_{avg}.
[d] ±0.10 deuterium atoms.
[e] Relative to phenyl in 1-phenylpropane; values are ±0.02.
[f] C_2 and C_3 could not be resolved for separate integration at 60 MHz.
[g] The benzyl methylene group.
[h] ±0.15.
[i] The *alpha* methyl group.

TABLE 2
DEUTERIUM DISTRIBUTION IN REACTANTS[a]

Temp. (°C)	Reactant	% Conversion	Ph	C_3H_5	CH_2	CH_3	D_{avg}	M
97	I	5.5	0.00	0.00	—	—	0.00	0.00
149	II	1.0	0.00	0.00	0.18	—	0.18	—
158	II	1.3	0.00	0.00	0.45	—	0.45	—
178	II	3.5	0.00	0.00	0.65	—	0.65	0.65
105	III	1.0	0.00	0.00	—	0.00	0.00	0.00
116	IX	48	0.00	0.00	—	—	0.00	0.00
137	VII	83	0.00	0.00	—	—	0.00	—
124	VIII	89	0.00	0.00	—	—	0.00	—
125	X	11.2	—	—	—	—	—	0.17
125	X	19	—	0.18[b]	—	0.00	0.18	0.18

[a] Values are ±0.05, except as indicated.
[b] For the C_1 position of cyclopropyl; value is ±0.08.

Deuteriospecies were determined through iterative corrections for natural fragments and naturally abundant isotopes (*4*).

RESULTS

Addition to phenylcyclopropanes was found in most cases to be largely 1,3-addition; in every instance, exactly one (within experimental limits) deuterium atom was found in the propyl group at the position corresponding to the third carbon from the substituent (usually phenyl). The first carbon (bearing the substituent) also acquired one deuterium atom during addition, but with active catalysts (reflected by high conversion to propanes) or higher temperatures, an additional independent exchange occurred here also to further introduce deuterium, if possible (see Table 1, compound I). This exchange occurred *after* ring-opening, since the reactant was found *not* to exchange significantly in the cyclopropyl group (Tables 2 and 3). These results contrast with compound Ia, where the exchange which occurred did so at the allyl position in agreement with other evidence (*13, 15, 22, 23*). This also differs from the hydrogenation of styrenes, where rapid exchange occurs at the *beta*-vinyl positions (*13, 14*). That cyclopropyl did not exchange, even when other aliphatic groups did, may be seen in the reactions of II, wherein the benzyl methylene exchanged readily, though cyclopropyl conversion was low; both reactions increased proportionally with temperature. Compounds VII, VIII, and IX ring-opened as expected, (*3, 8, 10, 11, 23*) selectively breaking the bond between the phenyl-bearing carbons to yield mainly dideuteriodiphenylpropanes (Table 1 and 2). Interestingly IX isomerized extensively to VIII (Table 1), and VIII yielded a significant amount of product from ring-opening across from one phenyl group.

Direct competition between phenyl and methyl for orienting the mode of ring-opening may be seen in the series III, IV, V, where phenyl always dominated. Compound IV and V are of interest, since there are three distinguishable modes of opening; that found was largely adjacent to phenyl but across from methyl. Some ring-opening with IV adjacent to methyl also occurred (5–6% relative to 80–90% of the former mode), illustrating methyl's poorer selectivity. With IV and V no exchange occurred in the methyl group. It is of interest to observe that ring-opening was much less selective with V (the *cis* isomer) where bond breaking adjacent to methyl accounted for one-third that of opening across from methyl. Also of interest with respect to methyl's directing influence is the product from the reaction of III; here methyl and phenyl are directly opposed in orienting influence: the product (90–99% 2-phenylbutane, 0% *t*-butyl benzene) illustrates the relatively strong influence of phenyl. Also worthy of note is

TABLE 3
MASS SPECTRAL DEUTERIUM DISTRIBUTIONS

Compound	% Conversion	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9	M
Ph—C—C—C[a]	100	0.00	0.27	8.0	84.6	6.0	1.0	0.17	0.04	—	—	3.00
I	5.5	100	—	—	—	—	—	—	—	—	—	0.00
Ph—C—C[b]	50.9	9.5	26.4	32.9	19.4	10.0	1.71	—	—	—	—	2.0
Ph—C—C—C—C[c]	3.5	9.9	5.7	11.6	21.0	29.4	13.0	5.3	2.3	1.5	—	3.41
II	3.5	62.5	10.2	26.8	0.11	0.10	0.07	0.06	0.02	—	—	0.65
Ph—C—C(C)$_2$[d]	88	0.00	0.00	2.34	81.4	12.7	1.80	0.83	0.51	0.34	0.21	3.22
Ph—C—C(C)$_2$[e]	76	0.00	0.18	5.02	93.1	0.85	0.46	0.16	0.08	0.04	0.07	2.98
X	19	83.8	14.9	1.40	0.06	—	—	—	—	—	—	0.18
X	11.2	84.2	14.3	1.19	0.20	—	—	—	—	—	—	0.17

[a] From cyclopropylbenzene (I). [b] From styrene; taken from Ref *13*. [c] From cyclopropylphenylmethane (II). [d] From IV. [e] From V.

that ring-opening was as fast (large conversions at similar temperatures) with this compound as with IV or V.

Discussion

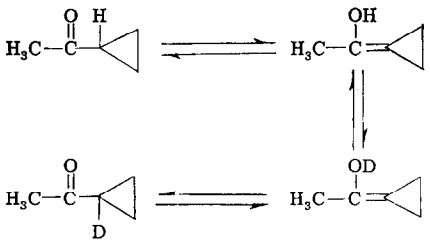
Addition. Table 1 clearly demonstrates the simplicity of the addition reaction, uncomplicated by rapid exchange or isomerization. All compounds contained (within measuring error) 1.0 deuterium atom in the 3-position and all contained 1.0 deuterium atom in the 1-position, except those which had been hydrogenolyzed to high conversions and X, which redistributed deuterium between positions 1 and 2, probably by enolization of the intermediate or product (*10, 14*). It is quite clear that the first step in hydrogenolysis of cyclopropanes is the irreversible addition of at least one deuterium atom to give a 1-monoadsorbed species (*10*).

That the proximity of a phenyl substituent to cyclopropane not only orients but facilitates ring-opening may be seen in Table 1 by comparing the conversions and reaction temperatures for compounds I and II; the intervention of a methylene group (II) drastically reduced the ease of reaction suggesting that the orienting power of phenyl is due to a conjugation effect upon the reaction, through intermediate stabilization. A similar free radical intermediate has been found in the peroxide initiated ring-opening of phenyl-substituted cyclopropanes (*25*). The mixed products from IV and V, the nearly equal ease of ring-opening of III–V, and the singularity of product from III all indicate the weak orienting power of a methyl substituent relative to phenyl. The effect produced by methyl is probably due to a rather small steric effect (see below), which becomes important only in the absence of strong conjugative effects. The effect of conjugation may also be seen in compounds VI-IX, where large phenyl and carbomethoxyl groups might be expected to hinder ring-opening, these instead directed the reaction to occur at bonds between substituent-bearing carbons, the most sterically hindered position for attack. Carbomethoxyl, while a better orienting group (adjacent-opening) than methyl, is similar to phenyl, since opening across from this group was observed to be minor (Table 1).

Exchange. Tables 2 and 3 reveal again the relatively low degree of exchange of the compounds studied. The data for compound I demonstrate the independent nature of the exchange reaction; at low conversion, no detectable exchange occurred; at high conversion selective exchange at benzyl occurred, in keeping with previous information concerning the preference for benzyl monoadsorbed species in the exchange of phenyl substituted hydrocarbons by dissociative adsorption (*10, 13–15, 26*); thus *n*-propylbenzene from I, *n*-butylbenzene from II, and isobutylbenzene from IV and V exchanged a benzyl hydrogen over freshly prepared catalysts at high conversions (Table 1 and Scheme 6). The benzyl group may be seen to have exchanged independently of ring-opening with II (Table 2). The *n*-butylbenzene contained much more deuterium there than can be accounted for by the exchange of II above, however (compare Table 1 and 2); this may merely indicate that the product's benzyl group exchanged more easily (after ring-opening) than before.

The only phenyl-substituted cyclopropane which exchanged extensively at any position other than benzyl was III, which indicated extensive exchange at the *alpha*-methyl group, contrasting with IV and V which exchanged there not at all. This is, however, in keeping with formation of the benzyl monoadsorbed species, which more readily forms diadsorbed intermediates *via* the α,β-process with adjacent chain termini (methyl groups) than with longer chains (see ethyl benzene in Table 3 and scheme 5d (*13–15*).

The only compound to exchange in the cyclopropyl group was X; this may occur through enolization of X, though



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the same might be said for the methyl group, which did not exchange (*13, 14*).

Steric effect. As mentioned above, conjugative stabilization of ring-opened intermediates is the main orienting and activating influence on the hydrogenolysis and exchange reactions. The steric effects are also significant, however, and provide an insight into the mode of adsorption of the cyclopropane rings.

Consider the reactions of I, III, IV, and V; that the methyl groups directed ring-opening at nonadjacent positions in IV and V has been mentioned. The same influence must govern the reaction of III, therefore; yet III reacted *adjacent* to methyl as easily as IV and V did *across* from methyl. The orientation is governed by phenyl, but some reduction in ease of *initial* attack (before the benzyl intermediate is formed) might well be expected (if the critical step in determining the orientation of the product involves close proximity of the cyclopropane ring with at least one palladium atom of the catalyst site). This would be true if initial catalyst hydrogen attack or hydrocarbon adsorption were to occur adjacent to methyl, but is quite consistent if attack occurs β to methyl, in which case III could react as easily as IV or V (and perhaps more easily, since there are two such unhindered positions). That a steric effect is caused by phenyl may be seen in the products from VIII (Table 1), the minor product arising from ring-opening across from at least one phenyl group. With VIII, there is no way for the catalyst to adsorb or catalyst hydrogen to attack without a significant steric effect caused by the *trans* orientation of the phenyl groups. Even so, this mode of attack leads mainly to 1,3-diphenyl-1-mono-adsorbed-propane.

Yet another related fundamental question is the initial relative arrangement of the cyclopropyl ring with respect to the surface. There are three different manners in which the ring might approach the catalyst site: "face"-oriented (coplanar with the catalyst site atoms), "edge"-oriented, or "corner"-oriented. A "face"-oriented mode of approach may be quickly ruled out, since *gem*-disubstituted and *trans*-disubstituted compounds could not be readily adsorbed. "Edge"-orientation would also be very difficult for *gem*-disubstituted compounds, yet III reacted as easily as IV and V, and VII as well as VIII and IX. "Corner" attack is feasible with all the compounds studied; therefore initial attack must occur on the cyclopropyl *carbon atom*, and not on the ring itself or any of its bonds. With VIII, corner attack at the 2 position relative to one phenyl group

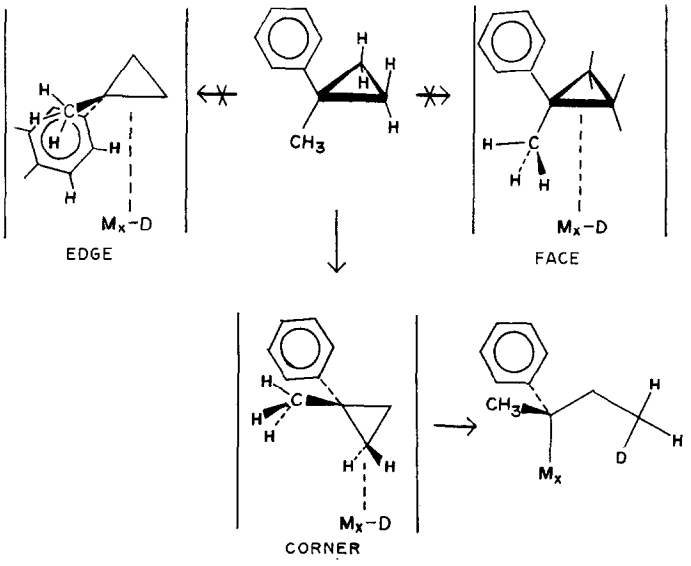

FIG. 1. Orientations of cyclopropanes during adsorption.

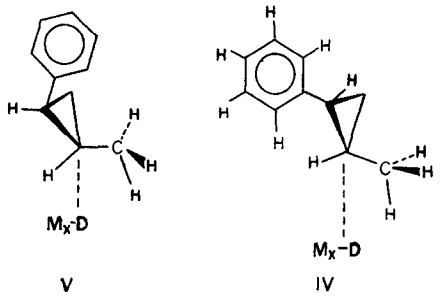

FIG. 2. "Tilted" corner adsorption for *cis*-1,2-disubstituted cyclopropanes.

may be severely hindered by the second phenyl, forcing some opening at the 3 position (Fig. 1).

The steric effect of methyl in IV and V can be more easily understood in these terms (Fig. 2). For any adjacent-to-methyl opening (minor in IV and V) attack on the methyl-bearing corner must occur by a "tilted" ring. Such a modification would be more difficult with *trans*-(IV) than with *cis*-(V) substitutents [assuming that the catalyst site is as large as the hydrocarbon compounds (a few palladium atoms)]. Hence V yielded much more *n*-butylbenzene than IV.

Catalyst sites. The 1-mono-adsorbed-1-phenylpropane is the principal species for both hydrogenolysis and exchange. Yet the two reactions appear to occur independently. For low conversions, where molecules are likely to reside only once on the surface (*4–6*), no exchange could be found for the compounds studied. At high conversion where most of the molecules are adsorbed a number of times, exchange occurred readily, though quite selectively at the benzyl position, apparently through dissociative adsorption. Since the organic moiety is essentially the same in both cases, and since associative exchange is possible (Compound Ia, Table 1) the difference may lie in a multiplicity of catalyst site types which perform different functions (*27, 28*).

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