ever, places an upper limit to the magnitude of the hyperfine splitting due to such ligands.[22]

The presence of binuclear copper species during the catalytic decomposition of alkylcopper(I) suggests that they play important roles in the mechanism. One such possibility which lies within the framework of the results obtained by Whitesides, *et al.*,[5a] is included in the following scheme (eq 3–5).[23]

$$\mathrm{RCu^I + Cu^0 \longrightarrow [RCu^ICu^0]} \qquad (3)^6$$

$$\mathrm{[RCu^ICu^0] \xrightarrow{fast} R(-H) + Cu^0 + Cu^1H} \qquad (4)$$

$$\mathrm{RCu^1 + Cu^1H \longrightarrow RH + 2Cu^0, etc.} \qquad (5)$$

Finally, we wish to emphasize that the thermal stability of organometals of the transition series depends on the solvent. For example, we find organocopper(I) species are appreciably more stable in THF than in diethyl ether solutions (even with the aid of phosphine ligands).[24] The added stability of organometals in this and related solvents enables kinetic studies to be carried out with greater facility. Furthermore, we were unable to observe the presence of binuclear copper intermediates during the decomposition of organocopper(I) derivatives (with and without tributylphosphine ligands) in diethyl ether.

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(22) Each hyperfine component of the spectrum has a different line width which increases with an increase in m_I, more or less monotonically. It suggests the presence of a small anisotropy of the g and a tensor and a positive $\Delta g/\Delta a$ value. As the temperature is lowered the line widths become broader, but even at −102° (a temperature well below the freezing point of THF) the spectrum retains some of the character of the seven-line splitting. The latter is inconsistent with a copper(II) species.

(23) In this formulation, cluster formation is not explicitly taken into account although it may be important. Our results indicate that only two copper nuclei are coupled to the electron. If other copper nuclei are involved their interaction is much less important.

(24) A property no doubt related to the ability of THF to form more stable complexes with metal ions than diethyl ether. See, *e.g.*, F. W. Walker and E. C. Ashby, *J. Amer. Chem. Soc.*, **91**, 3845 (1969); *Quart. Rev., Chem. Soc.*, **21**, 259 (1967).

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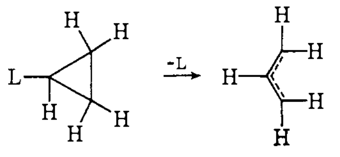
Ring Opening of Cyclopropanes over Palladium Metal

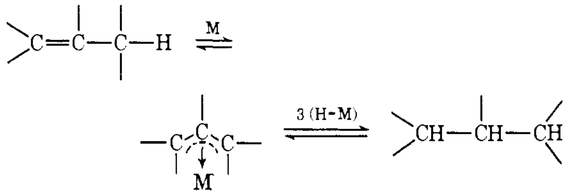
Sir:

The symmetry rules developed for the opening of cyclopropane rings correctly predict the mode of reactions yielding allyl intermediates through either disrotatory or conrotatory processes by removal of a suitable leaving group *across* the ring from the carbon–carbon bond which is broken.[1]



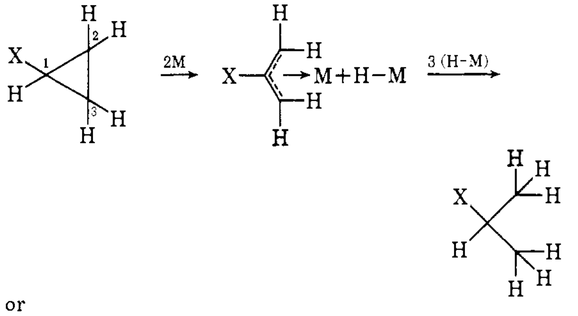
(1)

It has been proposed that heterogeneous catalytic hydrogenation and exchange with deuterium of alkenes over transition metals follow a pathway involving π-allyl adsorbed intermediates.[2] If this view of metal



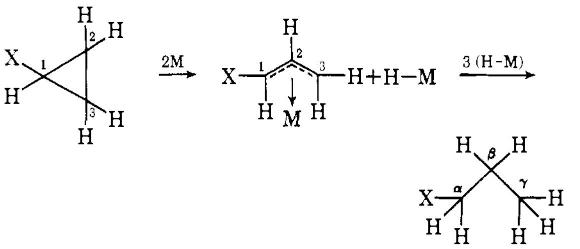
(2)

catalyzed processes is correct, the catalytic ring opening of substituted cyclopropanes might well be expected to occur by a process involving carbon–hydrogen bond cleavage across the ring from carbon–carbon bond breaking in an electrocyclic process[3]



(3a)

or



(3b)

For most substituents (other than alkyl) it has been found that ring opening occurs predominantly at C_1–C_3 (reaction 3b) to yield n-propyl adducts,[4] indicating that if π-allyl intermediates are involved, carbon–hydrogen bond breaking must occur at C_2.

The author wishes to report evidence which indicates that π-allyl intermediates are not so involved in the heterogeneous catalytic ring opening of cyclopropanes. Compounds of the kind shown in sequence 3 above, where X = phenyl, benzyl, and acetyl, were hydrogenolyzed over palladium-on-wide-pore silica with deuterium[5] in the gas phase[6] to produce n-propyl products.[7] The distribution of deuterium found in the products is shown in Table I.[8]

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(1) E. M. Kosower, "An Introduction to Physical Organic Chemistry," Wiley, New York, N. Y., 1968, p 233; R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, 1, 17 (1968).

(2) (a) F. G. Gault, J. J. Rooney, and C. Kemball, *J. Catal.*, 1, 255 (1962); (b) J. J. Rooney, *ibid.*, 2, 53 (1963); J. J. Rooney and G. Webb, *ibid.*, 3, 488 (1964).

(3) F. D. Mango, *Advan. Catal.*, 20, 291 (1969), has suggested a similar process for alkenes; R. Pettit, H. Sugahara, J. Wristers, and W. Merk, *Discuss. Faraday Soc.*, 71 (1969); F. D. Mango and J. H. Schachtschneidner, *J. Amer. Chem. Soc.*, **89**, 2484 (1967).

(4) J. Newham, *Chem. Rev.*, **62**, 123 (1962); J. Newham and R. L. Burwell, Jr., *J. Phys. Chem.*, **66**, 1438 (1962).

(5) J. A. Roth, B. Geller, and R. L. Burwell, Jr., *J. Res. Inst. Catal. Hokkaido Univ.*, **16**, 221 (1968); 0.14% by weight palladium.

(6) A vapor mixture of deuterium and alkane was passed over the palladium catalyst at a rate of 12–15 cm³/min (see also ref 5).

(7) Compounds with X = $-CN$, $-CO_2CH_3$, and $-CH_2$-cyclopropyl did not ring open appreciably below 160° with the same active catalyst. Other products were formed in 1% quantities.

(8) The values reported are the result of integration of the nuclear

Table I. Deuterium Distribution in Products

Compound	Temp, °C	% product	Deuterium distribution[a] C$_1$ (α)	C$_2$ (β)	C$_3$ (γ)	Other
CH_3–CO–C_3H_5	130	20	0.70	0.30	1.00	0.00
C_6H_5–C_3H_5	97	5.5	1.00	0.00	0.91[c]	0.00
C_6H_5–C_3H_5	70	100	2.00	0.00	1.00	0.00
C_6H_5–CH_2–C_3H_5	178	3.5	1.00		1.0[c]	1.42[b]

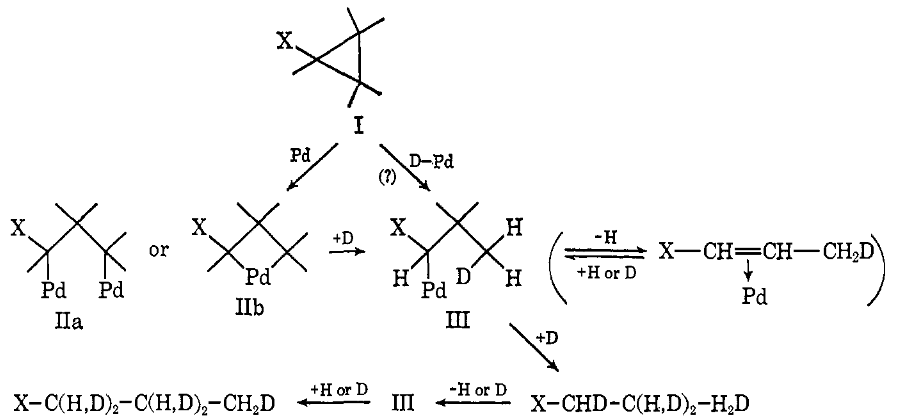
[a] Values are ±0.05. [b] Benzylmethylene group. [c] ±0.12.

Table II. Exchange of Benzylcyclopropane

Temp, °C	% product	Benzylcyclopropane deuterium distribution -CH_2-	-C_3H_5	-C_6H_5
149	1.0	0.18	0.00	0.00
158	1.3	0.45	0.00	0.00
178	3.5	0.65	0.00	0.00

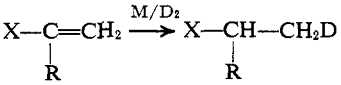
The cyclopropyl group did not exchange for any of the compounds investigated, unlike the analogous alkenes,[9] although the benzyl methylene group of cyclopropylphenylmethane did exchange as indicated in Table II.

If ring opening had occurred *via* π-allyl intermediates, a significant amount of deuterium (near 1.00) should have been found in the β position of the product owing to loss of hydrogen from C-2 and rapid surface H–D equilibration.[10] The amounts actually found were small or near 0.00 (Table I). It is of interest to note the more ready exchange of the open-chain aliphatic (compared to the cyclopropyl) hydrogens.[11,12a] Consequently, the deuterium distributions shown for the products are the result of 1,3 addition only. However, the *n*-propyl product may readsorb dissociatively (see phenylpropane, Table I) or exchange after ring opening while still adsorbed (compare phenylbutane (Table I) with Table II). The results in Tables I and II are also incompatible with intermediates which are triadsorbed[12a] or tetraadsorbed.[12b]



(5)

The γ (3) positions in the products contained one (1.00) deuteron in all the cases studied. This result is directly analogous to those obtained for carbomethoxyl- and phenyl-substituted ethylenes, where the *initial* products of deuterium addition were the β-monodeuterio-substituted ethanes.[13,14] (Subsequent exchange of the alkenes exhibited scrambled deuterium in the alkanes, obscuring the distribution for addition only.[13])



$$X{-}\underset{\displaystyle R}{\underset{|}{C}}{=}CH_2 \xrightarrow{M/D_2} X{-}\underset{\displaystyle R}{\underset{|}{C}H}{-}CH_2D \qquad (4)$$

X = Ph; R = CH_3, H, CO_2CH_3, Ph
X = CO_2CH_3; R = H, CH_3, $CH_2CO_2CH_3$, Ph

These results strongly suggest that cyclopropanes ring open either by initial formation of 1,3-diadsorbed alkanes[10,12] or of 3-monodeuterio-1-monoadsorbed alkane (II or III in eq 5), followed by addition of deuterium to give the 1,3-dideuteriopropanes. That the 1-monoadsorbed species (III) is favored over the 3- may be deduced from the further exchange reactions of the acetyl- and benzylcyclopropanes, after these ring open, at adjacent positions (by formation of the corresponding adsorbed alkene[10]). The deuterium in the β position of the product from the reaction of acetylcyclopropane may be explained by the use of tautomerization of monoadsorbed aliphatic ketones and esters.[9,13-15a] Such species have also been deduced from the deuterogenation of alkenes.[13-15a] The preference for the benzyl monoadsorbed alkanes (III) may also be seen in the lack of exchange of the β (2) position in the phenylpropane and the ready exchange of the α (1) position in the same compound.[15]

Though 1,3-diadsorbed species have been estimated to be difficult to form,[2a,16] several analogous homo-

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magnetic resonance (nmr) multiplets (the average of at least five integrations); deuterium is then determined by difference (see ref 9). The nmr spectra were obtained from Varian A 60A and T 60 spectrometers. The author is indebted to Dr. G. Fred Reynolds of Michigan Technological University for the use of the T 60 instrument.

(9) G. V. Smith and J. A. Roth, *Proc. Int. Congr. Catal., 3rd*, 379 (1964).

(10) R. L. Burwell, Jr., *Accounts Chem. Res.*, **2**, 289 (1969).

(11) No exchange could be detected for any of the compounds studied, including those in ref 7, within the limits of the method (see ref 8).

(12) (a) J. R. Anderson and N. R. Avery, *J. Catal.*, **8**, 48 (1968); (b) J. C. Prud'homme and F. G. Gault, *Bull. Soc. Chim. Fr.*, 827 (1966).

(13) J. A. Roth, Ph.D. Thesis, Illinois Institute of Technology, Chicago, Ill., 1966, pp 56–57.

(14) G. V. Smith and J. A. Roth, *Proc. Int. Congr. Catal., 4th*, 813 (1968).

(15) (a) G. V. Smith and J. A. Roth, *J. Amer. Chem. Soc.*, **88**, 3879 (1966); *J. Catal.*, **4**, 406 (1965); (b) E. Crawford and C. Kemball, *Trans. Faraday Soc.*, **58**, 2452 (1962).

(16) C. Kemball, *ibid.*, **50**, 1344 (1954), but see ref 10; J. R. Anderson and N. R. Avery, *J. Catal.*, 7, 315 (1967); M. Boudart and L. D. Ptak, *ibid.*, 16, 90 (1970).

geneous rhodium compounds (intermediates) have been identified which are thought to contain two carbon–metal bonds at the 1 and 3 positions of propanes from the reactions of cyclopropyl compounds.[17]

Acknowledgment. The major portion of this research was supported by the Petroleum Research Fund, administered by the American Chemical Society.

[17] H. C. Volger, H. Hogeveen, and M. M. P. Gasbeek, *J. Amer. Chem. Soc.*, 91, 218, 2137 (1969); H. Hogeveen and H. C. Volger, *ibid.*, 89, 2486 (1967); *Chem. Commun.*, 1133 (1967); D. M. Roundhill, D. N. Lawson, and G. Wilkinson, *J. Chem. Soc. A*, 845 (1968); L. Cassar, P. E. Eaton, and J. Halpern, *J. Amer. Chem. Soc.*, **92**, 3515 (1970); T. J. Katz and S. A. Cerefice, *ibid.*, **91**, 2405, 6519 (1969).

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The Base-Induced Reaction of Organoboranes with Bromine. A Convenient Procedure for the Anti-Markovnikov Hydrobromination of Terminal Olefins *via* Hydroboration–Bromination

Sir:

Organoboranes from terminal olefins react rapidly with bromine at 0° in the presence of sodium methoxide in methanol to give the corresponding primary alkyl bromides with utilization of all three alkyl groups of the organoborane. Consequently, this reaction provides a convenient procedure for the anti-Markovnikov hydrobromination of terminal olefins *via* hydroboration–bromination.

The dark reaction of trialkylboranes with bromine in various inert solvents at 25° gives a maximum conversion of only one alkyl group into the corresponding bromide.[1] Consequently, the reaction is of limited synthetic value for the preparation of alkyl bromides.

Previous work had revealed that organoboranes obtained by the hydroboration of terminal olefins undergo a very rapid reaction with iodine under the influence of sodium hydroxide.[2] The conversion of two of the three alkyl groups of a trialkylborane into the alkyl iodide occurred in less than 5 min at 25°. Consequently, the hydroboration–iodination procedure has made possible a simple synthetic route from terminal olefins to primary iodides.

Since the reaction of organoboranes with iodine was greatly facilitated by the addition of sodium hydroxide, the present study was undertaken to determine what effect sodium hydroxide or other bases would have on the reaction of organoboranes with bromine in THF. Direct adaptation of the iodination procedure resulted in the conversion of less than two of the three alkyl groups into the corresponding alkyl bromide. Bromination in the presence of sodium hydroxide was further complicated by concurrent oxidation of the organoborane to give the alcohols as a major by-product.

Trialkylboranes have been shown to undergo oxidation by sodium hypochlorite to give the corresponding alcohols.[3] Therefore, in the present study the alcohol is presumably formed *via* an oxidation of the organoborane with sodium hypobromite. Only 1-hexanol and a trace of 2-hexanol were formed when a THF solution of tri-*n*-hexylborane was added to a colorless solution of bromine in methanolic sodium hydroxide at 0°.[4] The oxidation is probably occurring *via* a reaction sequence analogous to the mechanism proposed by Kuivila and coworkers for the hypohalite oxidation of areneboronic acids.[5]

The procedure reported[2] for the iodination reaction was to add the iodine to the organoborane in THF, followed by the dropwise addition of methanolic sodium hydroxide. By changing to a simultaneous dropwise addition of bromine and base to the organoborane in THF, the yield of primary bromide derived from a terminal olefin could be increased to around 67%. If enough sodium hydroxide was added to completely decolorize all of the bromine, then a quantitative recovery of all three alkyl groups was obtained (eq 1).

$$R_3B + 3Br_2 + 4NaOH \longrightarrow 2RBr + ROH + B(OH)_3 + 4NaBr \qquad (1)$$

We now wish to report that this undesirable oxidation side reaction proved to be easily circumvented by using sodium methoxide in methanol as the base, presumably because the reaction of bromine with sodium methoxide does not result in the formation of sodium hypobromite.[6] Table I gives a summary of the results that were obtained when sodium methoxide was used to induce the bromination of various representative trialkylboranes.

Study of the reaction resulted in the development of two different procedures. Procedure A involves the addition of bromine (33% excess) to the organoborane in THF, followed by a solution of sodium methoxide (67% excess) in methanol, all at 0°. Procedure B involves the simultaneous addition of bromine and base (10% excess) at 25°. Procedure A provided essentially quantitative conversions of monosubstituted olefins into primary bromides. Unfortunately, the yield dropped with the secondary and the more hindered primary alkyl groups. Procedure B provides more satisfactory yields for these derivatives.

The hydroboration–bromination of methyl 10-undecenoate is representative of procedure A. A dry 300-ml flask equipped with septum inlet, thermometer well, pressure-equalizing dropping funnel, and magnetic stirrer was flushed with nitrogen and then maintained under a positive nitrogen pressure. The flask was charged with 75 ml of dry THF and 33.5 ml (150 mmol) of dry methyl 10-undecenoate and cooled to ∼0° with an ice–water bath. Hydroboration was achieved by the dropwise addition of 19.5 ml of a 2.58 *M* solution of borane (151 mmol of hydride) in THF. The solution was stirred for 30 min at 0° and 30 min at 20°. Then 1 ml of methanol was added to destroy excess

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[1] C. F. Lane and H. C. Brown, manuscript in preparation.

[2] H. C. Brown, M. W. Rathke, and M. M. Rogić, *J. Amer. Chem. Soc.*, **90**, 5038 (1968).

[3] H. C. Brown and W. R. Heydkamp, unpublished results.

[4] The reactive oxidizing agent is assumed to be the hypobromite ion, $Br_2 + 2OH^- \rightarrow Br^- + BrO^- + H_2O$.

[5] H. G. Kuivila, L. E. Benjamin, C. J. Murphy, A. D. Price, and J. H. Polevy, *J. Org. Chem.*, **27**, 825 (1962).

[6] The reaction of bromine with sodium methoxide presumably gives extremely unstable methyl hypobromite which does not react under these conditions with trialkylboranes. For example, when bromine (30 mmol) was added to sodium methoxide (60 mmol) in methanol at 0°, a clear solution and a white precipitate resulted. This slurry was then passed into a THF solution of tri-*n*-hexylborane (30 mmol) *via* a stream of dry nitrogen. Glpc analysis of the resulting mixture indicated that neither 1-hexanol nor 1-bromohexane was formed in any detectable amount.