ing voltage, an energy resolution of 4000 (V/ΔV) and an analyzer pressure of 1 × 10^{-7} Torr.
(8) Recorded on the MIKE spectrometer (J. H. Beynon, R. G. Cooks, J. W. Amy, W. E. Baitinger, and T. Ridley, *Anal. Chem.*, **45**, 1023A (1973)) at 7.0 keV accelerating voltage, an energy resolution of 3500 ($E/\Delta E$) and an analyzer pressure of 3 × 10^{-7} Torr.
(9) D. H. Williams and R. G. Cooks, *Chem. Commun.*, 663 (1968).
(10) Obtained by a new method[11] at high energy in the Hitachi RMH-2 mass spectrometer.
(11) C. S. Hsu and R. G. Cooks, *Org. Mass Spectrom.*, in press.
(12) Prepared by exchange with D_2O in KOD/dimethoxyethane at 130° for 12 h in a sealed tube.
(13) J. H. Beynon, D. F. Brothers, and R. G. Cooks, *Anal. Chem.*, **46**, 1299 (1974).
(14) Calculated assuming unit isotope effect for both d_1 and for d_2 diisopropyl ketone. The site of deuteration was confirmed by collision-induced dissociation of the mass-selected 115^+, which showed equal loss of d_1 and d_0-propyl radicals.
(15) Primary fragmentation by alkane loss from functionalized molecules is virtually without precedent (D. G. I. Kingston, B. W. Hobrock, M. M. Bursey, and J. T. Bursey, *Chem. Rev.*, **75**, 693 (1975)), but alkane molecular ions have long been known to eliminate neutral alkane fragments; see, for example, M. Vestal and J. H. Futrell, *J. Chem. Phys.*, **52**, 978 (1970).
(16) For a review, see D. G. I. Kingston, J. T. Bursey, and M. M. Bursey, *Chem. Rev.*, **74**, 215 (1974).

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The Photochemical Induced Cyclization of Allyl Grignard Reagents

Sir:

The interconversion of allyl carbanions to cyclopropyl carbanions has been a topic of increasing interest since the formulation of the selection rules by Woodward and Hoffmann.[1] Most of the studies on allyl carbanions have dealt with their thermal transformations, while their photochemical behavior has received only marginal attention.[2,3]

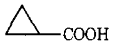
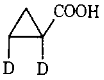
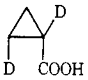
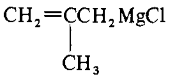
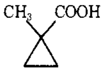
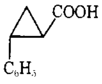
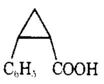
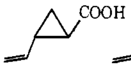
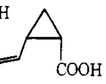
This communication describes the first light-induced cyclization of allylmagnesium halides to cyclopropylmagnesium halides. Allylmagnesium halides have been chosen as model systems for allyl carbanions, since these compounds are known to exist in solution as aggregates of tight anion-cation pairs.[4-6]

Allylmagnesium bromide (**1**) was prepared by dropwise addition of allyl bromide to a large excess of magnesium turnings in peroxide-free, dry ether. After completion of the reaction, the volatile components were evaporated under high vacuum, and the solid residue was redissolved in a new portion of dry ether. The irradiation of the allyl Grignard was carried out in a quartz apparatus for 24 h at 0-5 °C with an external SP 500 Philips high-pressure mercury arc lamp. The irradiated mixture was treated with solid carbon dioxide and hydrolyzed carefully. The acidic reaction products were extracted with base and then separated by either column chromatography (silica gel, Merck 70-230 mesh, methanol-ethyl acetate-benzene 10:10:80), or preparative VPC (10% Carbowax on Chromosorb 30/60, 6 m, ⅜ in., 200 °C). The carboxylic acid mixture was found to contain 45% cyclopropanecarboxylic acid (**2**) as the major photoproduct,[7] 30% of a higher molecular weight compound $C_7H_{10}O_2$,[8] 25% vinylacetic acid, and minor amounts of biallyl and polymeric materials as well. Product **2** was identified by comparison with an authentic sample.

Similarly, irradiation of *cis*-2,3-dideuterioallylmagnesium bromide (**3**) yielded, after carbonation, a 1:1 mixture of *trans*- and *cis*-1,2-dideuteriocyclopropanecarboxylic acid, (**4**) and (**5**), and a mixture of carboxylic acids, $C_7H_7D_3O_2$,[8] each labeled with three deuterium atoms.

β-Methylallylmagnesium chloride (**6**), cinnamylmagnesium bromide (**8**), and γ-vinylallylmagnesium chloride (**11**) were found to undergo analogous cyclization reactions. Thus irradiation of (**6**) yielded after carbonation 1-methylcyclopropanecarboxylic acid (**7**) as the major product and trace amounts of a higher molecular weight material $C_8H_{12}O_2$,[8] while irradiation of (**8**) furnished a mixture of *cis*- and *trans*-2-phenylcyclopropanecarboxylic acid, (**9**) and (**10**). The trans isomer **10** was found to be the predominant one; (trans/cis ratio 49:1, determined by analytical VPC). Similar results were obtained on irradiation of γ-vinylallyl Grignard (**11**). Thus, a mixture of *trans*- and *cis*-2-vinylcyclopropanecarboxylic acid (**12**) and (**13**), was obtained (trans/cis ratio 6:1). The yields of the various prod-

Table I

Irradiated allyl Grignard	Uv spectrum	Cyclic photoproducts	% yield[7]	Trans/cis ratio
$CH_2{=}CHCH_2MgBr$ **1**	246 (ϵ 4 300)[a]	 **2**	45	–
$CHD{=}CDCH_2MgBr$ **3**		  **4** **5**	45	1:1
 $CH_2{=}C(CH_3)CH_2MgCl$ **6**	251 (ϵ 4 100)[a]	 **7**	70	–
$C_6H_5CH{=}CHCH_2MgBr$ **8**	252 (ϵ 20 000)[12]	  **10** **9**	75	49:1
$CH_2{=}CHCH_2{=}CHCH_2MgCl$ **11**		  **12** **13**	50	6:1

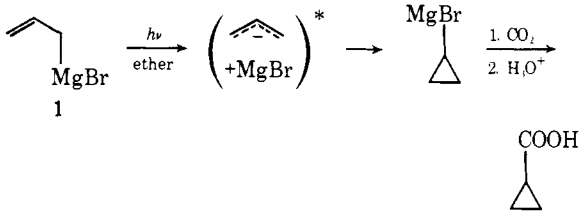
[a] The UV spectrum was measured in ether solutions after filtration. With addition of water, the absorption band of the Grignard reagent disappeare ' The resultant spectrum was due to the superposition absorption of the magnesium salts and the olefinic coupling products which were formed during the preparation of the Grignard reagent.

ucts are summarized in Table I. The cyclopropane derivatives were identified by comparison with authentic samples.[9-11]

These allyl Grignard compounds did not undergo cyclization upon heating, but gave polymeric materials. Thus, several experiments were made in sealed evacuated tubes at 200 °C for different periods of time, 0.5–24 h, or upon heating in diglyme solution under reflux (165 °C).

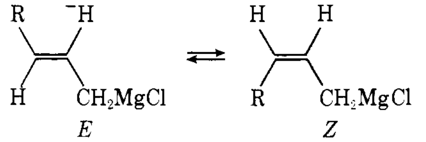
We have measured the uv absorption spectra of allylmagnesium bromide (**1**) and of β-methylallylmagnesium chloride (**6**) in ether solutions (Table I). These, along with the known uv spectra of cinnamylmagnesium bromide,[12] show absorption maxima at longer wavelengths than the hydrocarbons from which they are derived. The uv spectra as well as other spectroscopic data (mainly NMR) indicate that the organomagnesium bonds in these systems are highly polarized, and exhibit ionic character with partial delocalization of the metal–carbon bond electron pair into the Π electron system.[4-6]

The observed light-induced transformation may thus be visualized as ring closure of the electronically excited allyl anion to the cyclopropyl anion (eq 1).



1 **2** (1)

Theoretical considerations suggest the disrotatory course[1] for such cyclization; however, the degree of stereoselectivity could not be established for these systems since the geometry of the anionic intermediates is not retained during the reactions. This behavior is likely to be due to: (a) inversion of the cyclopropylic anion to the preferred trans geometry and (b) the rapid rotation around the C–C bonds of the allyl anion.[13] NMR studies established that allyl Grignard compounds exist in ether solutions as a rapidly equilibrating mixture of two isomers *E* and *Z* (2), the relative amounts of each isomer being determined by the nature of the substituent R.[14] The *E* form is favored when R is bulky. The 1:1 formation of *trans*- and *cis*-1,2-dideuteriocyclopropane carboxylic acids and the predominant formation of the thermodynamically more stable trans cyclopropyl isomers **10** and **12** might be the result of these two phenomena.



(2)

References and Notes

(1) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, New York, N.Y. 1970.
(2) M. Newcomb and W. T. Ford, *J. Am. Chem. Soc.*, **96**, 2968 (1974).
(3) E. E. van Tamelem, J. Schwartz, and J. I. Brauman, *J. Am. Chem. Soc.*, **92**, 5798 (1970).
(4) L. A. Fedorov, *Usp. Khim.*, **39**, 1389 (1970); *Russ. Chem. Rev. (Engl. Transl.)*, **39**, 655 (1970).
(5) D. Leibritz, B. O. Wagner, and J. O. Roberts, *Justus Liebigs Ann. Chem.*, **763**, 173 (1972).
(6) E. A. Hill, *J. Organomet. Chem.*, **91**, 123 (1975).
(7) Yields are given relative to the total amount of carboxylic acids obtained after irradiation and carbonation.
(8) The structure of these compounds is under investigation and will be described in a forthcoming publication.
(9) S. Siegal and C. G. Bergstrom, *J. Am. Chem. Soc.*, **72**, 3815 (1950).
(10) A. Burger and W. L. Yost, *J. Am. Chem. Soc.*, **70**, 2198 (1948).
(11) J. A. Landgrebe and L. W. Becker, *J. Org. Chem.*, **33**, 1173 (1968).
(12) R. H. DeWolf, D. L. Hagmann, and W. G. Young, *J. Am. Chem. Soc.*, **79**, 4795 (1957).
(13) J. E. Nordlander and J. D. Roberts, *J. Am. Chem. Soc.*, **81**, 1769 (1959).
(14) D. A. Hutchison, K. R. Beck, R. A. Benkeser, and J. B. Grutzner, *J. Am. Chem. Soc.*, **95**, 7075 (1973).

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A Novel Tridentate Ligand Formed by the Condensation and Rearrangement of Three Ethoxycarbonyl Isothiocyanate Molecules in the Presence of $RhCl(PPh_3)_3$

Sir:

We wish to describe the preparation and characterization of a complex of Rh(III) in which a new tridentate ligand, formed by the condensation and rearrangement of three molecules of ethoxycarbonyl isothiocyanate in the presence of tris(triphenylphosphine)chlororhodium(I), is attached to the metal atom through two S linkages and one carbene C linkage.

A benzene solution of $RhCl(PPh_3)_3$ (0.432 mmol) and excess EtOCONCS = L (3.66 mmol) was stirred at room temperature for 30 min and was then refluxed under Ar for an additional 2 h. After removal of the solvent under reduced pressure the residue was washed with *n*-hexane to yield a reddish orange powder. This crude product was redissolved in a minimal amount of acetone. Diethyl ether was added dropwise until crystals appeared. The mixture was kept at 5° overnight to yield reddish orange prisms. Analysis of the material is consistent with its formulation as $RhCl(PPh_3)_2L_3\cdot(CH_3)_2CO$. Anal. Calcd: C, 54.96; H, 4.61; N, 3.77. Found: C, 54.94; H, 4.69; N, 3.78. The NMR spectrum of this complex dissolved in $CDCl_3$ shows two equivalent ethyl groups at τ 8.76 (t, 6 H, CH_3; J = 7.5 Hz) and 5.87 (q, 4 H, CH_2; J = 7.5 Hz) as well as a different ethyl group at τ 8.79 (t, 3 H, CH_3; J = 6.8 Hz) and 6.04 (q, 2 H, CH_2; J = 6.8 Hz). The acetone resonance at τ 7.95 (s, 6 H) is found to be consistent with one acetone molecule per molecule of complex. The ir (KBr disk) shows $\nu(C{=}O)$ absorptions at 1785 (s), 1765 (s), and 1711 cm^{-1} (s) (acetone). A similar spectroscopic analysis indicates that when the material is recrystallized from a 1:1 acetone–diethyl ether solution the hemietherate is formed.

Previously we reported[1,2] the unexpected product $RhCl(PPh_3)_2L'_2$, formed by the condensation of two molecules of L′ = PhCONCS with $RhCl(PPh_3)_3$. Even with a knowledge of the tridentate ligand in that complex we could not arrive at a satisfactory, unambiguous formulation for the present complex, $RhCl(PPh_3)_2L_3$. Accordingly, an x-ray diffraction study was undertaken.

The compound $RhCl(PPh_3)_2(EtOCONCS)_3\cdot(CH_3)_2CO$ crystallizes with four formula units in the triclinic space group C_i^1-$P\bar{1}$ in a cell of the following dimensions: a = 15.214 (6), b = 27.571 (9), c 12.857 (6) Å; α = 103.12 (2), β = 90.24 (2), γ = 100.03 (2)°; V = 5166 Å^3; d_{calcd} = 1.432, d_{obsd} = 1.35 (3) g cm^{-3}; μ (Cu Kα) = 53.56 cm^{-1}. Data were collected on a Picker x-ray diffractometer using Ni-filtered Cu Kα radiation out to 2θ (Cu Kα_1) of 94°.[3] A total of 7375 unique reflections having $F_o^2 > 3\sigma(F_o^2)$ was used in the ensuing calculations. The fact that the cell is indeed triclinic was established through extensive photographs, through a cell reduction, and by comparison of F_o^2 values of low-order planes. The presence of two formula units per asymmetric unit necessitates the location of 64 individual atoms and 12 rigid phenyl groups. Refinement of