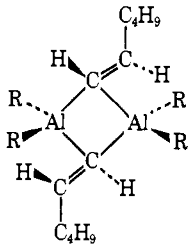
Table I. Nmr Data (60 MHz) for Alkenyl–Hydride-[a] and Dialkenyl-Bridged Alkylaluminum Dimers in *n*-Hexane

	Proton resonance positions (δ) and coupling constants (Hz)				
	α-Alkenyl		β-Alkenyl		
Alkenylalane derived from[b]	Complex I[c]	Complex II[d]	Complex I[c]	Complex II[d]	Hydride[d]
n-$C_4H_9C{\equiv}CH$	5.75 $J_{\alpha,\beta} = 20$ $J_{\alpha,\gamma} = 1$	5.49 $J_{\alpha,\beta} = 20$ $J_{\alpha,\gamma} = 1$	7.42 $J_{\beta,\gamma} = 6$	7.55 $J_{\beta,\gamma} = 6$	3.75
tert-$C_4H_9C{\equiv}CH$	5.78 $J_{\alpha,\beta} = 20$	5.58 $J_{\alpha,\beta} = 20$	7.39	7.51	3.80
$C_6H_5{-}C{\equiv}CH$[e]	6.57 $J_{\alpha,\beta} = 21$	6.28	8.12	8.10	3.92
$C_2H_5C{\equiv}CC_2H_5$			7.14 $J_{\beta,\gamma} = 6$	7.24 $J_{\beta,\gamma} = 6$	3.74

[a] No attempt has been made to isolate the mixed alkenyl–hydride-bridged dimers. [b] 1.0–1.5 *M* solutions in *n*-hexane. [c] Complex I = dialkenyl-bridged compound. [d] Complex II = mixed alkenyl–hydride-bridged compound. [e] The hydroalumination of phenylacetylene affords vinylalane, alkynylalane (*via* metalation), and styrene (by exchange reactions): J. R. Surtees, *Aust. J. Chem.*, **18**, 14 (1965); R. L. Miller, unpublished results.

dimer, and the mixed-bridged structure II for the complex between diisobutylaluminum hydride and the dialkylalkenylalane.[7]



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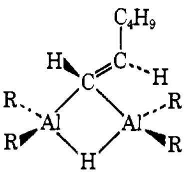

II

Structure I is similar to that proposed by Visser and Oliver[9] for vinyl-bridged alkylgallium dimers. The driving force for the formation of an alkenyl bridge may be due to stabilization obtained by overlap of the double-bond π orbitals with the vacant nonbonding three-center orbital of the aluminum atom. The formation of the alkenyl–hydride-bridged species II can be accounted for in terms of a diminished steric interaction when hydride serves as a bridge between the aluminum atoms. Supporting evidence for this view stems from the observation that the more sterically hindered diisobutyl(1-ethyl-*trans*-1-buten-1-yl)alane, derived from the monohydroalumination of 3-hexyne, has a greater tendency to form the mixed-bridge complex than does diisobutyl(*trans*-1-hexen-1-yl)alane. Finally, the equilibrium constant for the formation of the mixed dimeric complex II is 4.3 × 10³ in hexane

$$2(R_2AlH)_3 + 3(R_2AlCH{=}CHC_4H_9)_2 \rightleftarrows 6R_2AlH{\cdot}R_2AlCH{=}CHC_4H_9$$

at 37°, indicating that formation of the mixed bridge compound is favored over reversal to the component species.[10]

Investigation of the hydroalumination of other alkynes with diisobutylaluminum hydride revealed that formation of the mixed-bridge complexes is a general phenomenon. A summary of the nmr spectral properties of compounds resulting from the hydroalumination of various alkynes is shown in Table I.

From the results obtained in this study, it is apparent that elucidation of the mechanism of the hydroalumination reaction involving alkynes must take into account mixed-bridged alkenyl–hydride species as reactive intermediates.

[7] Additional evidence for the formation of mixed-bridged species was obtained by taking the ir spectra during the hydroalumination reaction. The intense Al–H stretching band[8] at 1760 cm⁻¹ disappeared rapidly as the hydroalumination of 1-hexyne and 3-hexyne progressed and was replaced by an intense band in the 1300–1400-cm⁻¹ region. After 50% reaction, the 1760-cm⁻¹ band disappeared, and the 1300–1400-cm⁻¹ band reached its maximum intensity. As the reaction progressed further, the intensity of the latter band decreased.

[8] G. Schomburg and E. G. Hoffmann, *Z. Elektrochem.*, **61**, 1110 (1957).

[9] H. D. Visser and J. P. Oliver, *J. Amer. Chem. Soc.*, **90**, 3579 (1968).

[10] The equilibrium constant for the formation of II was obtained by integration of the vinyl proton region of spectra resulting from solutions of known amounts of I and diisobutylaluminum hydride. Owing to the small amount of dissociation of the mixed-bridged species derived from 3-hexyne, its equilibrium constant could not be determined by this method.

[11] National Defense Education Act Fellow (Title IV) at the University of California, Davis, 1968–1970.

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The Configurational Stability of Phosphorus in Five-Membered Ring Phosphorochloridites

Sir:

Although previous nmr investigations[1,2] have established the configurational stability of phosphorus in five-membered ring phosphite esters, analogous phosphorochloridites I allegedly undergo rapid inversion of configuration at phosphorus *via* a bimolecular chlorine exchange mechanism.[2] Thus, in pinacol phosphorochloridite (Ia), rapid inversion at phosphorus results in equivalence of the methyl nmr signals.[2] Similar studies[3,4] of ethylene phosphorochloridite (Ib) also indicate that exchange of chlorine occurs in the neat liquid at room temperature. We wish to report our initial investigations of the nmr spectra of isobutylene phosphorochloridite (Ic), which show that the configurational lability at phosphorus in five-membered ring phosphorochloridites is solely a matter of the purity of the sample.

[1] H. Goldwhite, *Chem. Ind. (London)*, 494 (1964).

[2] B. Fontal and H. Goldwhite, *Tetrahedron*, **22**, 3275 (1966).

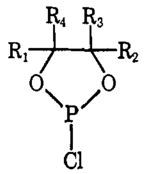
[3] D. Gagnaire, J. B. Robert, and J. Verrier, *Bull. Soc. Chim. Fr.*, 3719 (1966).

[4] P. Haake, J. P. McNeal, and E. J. Goldsmith, *J. Amer. Chem. Soc.*, **90**, 715 (1968).

Table I. Nmr Parameters for Two Five-Membered Ring Phosphorochloridites[a]

Compd (solvent)	ν_1[b]	ν_2	ν_3	ν_4	J_{23}[c]	J_{25}	J_{35}	J_{13}	J_{14}
Ic (neat)	1.545	4.379	4.350	1.814	−8.85	1.30	14.52	0.7[d]	0.6[d]
Ic (10% benzene)	0.842	3.839	3.499	1.210	−8.87	1.12	14.69	0.7[d]	0.6[d]
Ib[e] (10% benzene)	3.77	3.77	3.38	3.38	−8.79	1.62	10.0	6.96	−8.79

[a] The numbering of nuclei follows the system of ref 4. [b] In parts per million downfield from tetramethylsilane. [c] In hertz. [d] From a first-order analysis. [e] Data taken from ref 4, J_{12} = 8.1 Hz.



Ia, $R_1, R_2, R_3, R_4 = -CH_3$
b, $R_1, R_2, R_3, R_4 = -H$
c, $R_1, R_4 = -CH_3; R_2, R_3 = -H$

The nmr spectrum[5] of a neat sample of Ic from initial preparations[6] exhibited a singlet for the methyl protons at 1.679 ppm and a complex pattern for the methylene protons. Upon cooling the sample, the methyl singlet split into two singlets with a separation of 0.27 ppm at −40°. When this sample was diluted with methylene chloride, the spectrum was similar to that of the neat solution of −40°. This behavior is identical with that reported for Ia[2] and Ib.[3,4] Attempts to measure the rate of chloride exchange and the kinetic parameters associated with the exchange were frustrated by the nonreproducibility of results obtained from different preparations of Ic. This behavior suggested that an impurity was catalyzing the exchange of chlorine.

An nmr spectrum of a later sample of neat Ic prepared on a smaller scale[6] (Figure 1) displayed distinct nonequivalent protons. The separation between the methyl peaks was unchanged over the temperature range −40 to +150°. We conclude that there is no detectable exchange of chlorine occurring over this temperature range. Small-scale preparations of pinacol phosphorochloridite[6] (Ia) resulted in an nmr spectrum for the neat liquid in which the methyl protons were nonequivalent with a separation between the singlets of 0.17 ppm. This sample did undergo chlorine exchange at higher temperature. However, the coalescence temperature was much higher than previously reported (+73 *vs.* −23°). This observation is also consistent with the idea that an impurity is responsible for exchange in these compounds.

Addition of a trace water to neat Ic effected complete coalescence of the nmr methyl proton signals. This observation led us to believe that a reaction product of water and Ic was responsible for the equilibration of the methyl protons. However, addition of HCl–benzene solution to a solution of Ic in benzene had no effect on the separation of the two methyl singlets. Addition of dry HCl gas directly to neat Ic caused partial decomposition of the sample. It seems clear from these experiments that HCl in benzene does not effect exchange in Ic and related compounds. We have not investigated the effect of isobutylene hydrogen phosphonate, the other principal reaction product, on Ic. Addition of a trace of pyridine to Ic caused complete coalescence of the methyl protons; we cannot be entirely sure, however, that the pyridine used was completely dry.

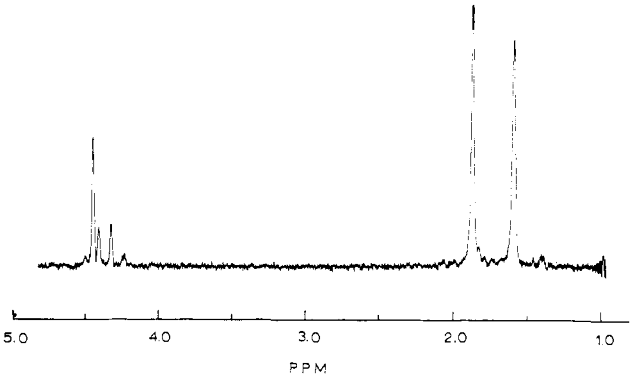


Figure 1. A 100-MHz nmr spectrum of neat isobutylene phosphorochloridite (Ic) at room temperature.

Although the experiments described are partial and inconclusive in establishing the identity of the impurity which causes the chlorine exchange, the results clearly show that pure samples of Ic do not exchange and that exchange can be induced by the addition of traces of water. Only a short exposure of pure Ic to a humid atmosphere is necessary to effect coalescence of the methyl protons.

The nmr parameters observed for the methylene protons of Ic are interesting and deserve comment. The spectrum[5] of pure, neat Ic exhibits a complex seven-line spectrum at room temperature as a result of the protons being nonequivalent and spin coupled to phosphorus (Figure 1). Analysis of the spectrum yields the parameters given in Table I. The protons were assigned by comparison of nmr parameters of similar compounds[3,4] and from considerations of a model of Ic. The proton cis to the lone pair on phosphorus has a larger POCH coupling constant than that observed for Ib (Table I) while the proton trans to the lone pair has a smaller POCH coupling constant than that observed for Ib.

Two explanations have been offered for the different POCH coupling constants in five-membered ring phosphites: (1) the five-membered ring exists in an envelope conformation and the protons overlap to different extents with the lone pair on phosphorus[2] and (2)

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(5) All spectra were obtained on a Varian Associates HA-100 spectrometer. Data for the methyl protons were obtained from a first-order analysis of the spectra while data for the methylene protons were obtained with the aid of the computer program LAOCN3 (A. A. Bothner-By and S. Castellano, Carnegie-Mellon University, Pittsburgh, Pa.). The temperatures were calibrated using the standard methanol and ethylene glycol samples.

(6) Ia and Ic were prepared by the Arbuzov procedure (A. E. Arbuzov and M. M. Azanovskaya, *Izv. Akad. Nauk. SSSR, Otd. Khim. Nauk*, 473 (1949)). In early preparations of Ic, the reaction was conducted on a 0.5-mol scale. These samples exhibited chlorine exchange. The sample of Ic that showed no exchange was prepared on a 0.078-mol scale. Similarly, the sample of Ia was prepared on a 0.060-mol scale.

the five-membered ring exists in a twist-envelope conformation resulting in different POCH dihedral angles for the two protons.[4] We favor the latter explanation since it is difficult to explain the larger POCH coupling constant in Ic compared to Ib on the basis of overlap with the lone pair on phosphorus. Examination of a model of Ic indicates that the POCH dihedral angle approaches 180° with increasing twist of the ring. The methyl group in Ic should cause some steric interactions, compared to Ib, resulting in a larger twist in the five-membered ring. Furthermore, the chemical shifts and coupling constants for Ic and analogous phosphite esters are temperature dependent with $J_{\mathrm{P-H}_{13}}$ changing by as much as 1.0 Hz over a temperature range of 150°.[7] This observation indicates rapid equilibration of Ic between two or more twist envelope conformations. Further work is in progress on the nmr spectra and will be reported in the future.

(7) R. H. Cox, M. G. Newton, and B. Campbell, unpublished results.

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Photochemistry of 8-Methyl-1-hydrindanones and 9-Methyl-1-decalones

Sir:

In the photochemistry of aliphatic ketones in solution, nonradiative decay always plays a substantial role among the behaviors of excited states. Ketones which do not undergo type II and related processes undergo the type I process in the gas phase with a quantum efficiency approaching unity.[1] However, ketones such as *tert*-butyl ketones may also undergo the type I process in solution, but the combined quantum efficiencies for all modes of ketone decomposition fall short of unity.[2,3] It has been suggested by Franck and Rabinowitsch that cage recombination of dissociated radicals in solution may account for the decrease in quantum efficiency,[4] but such a process has not been demonstrated in a definitive and quantitative manner. The current communication deals with the photochemistry of both cis and trans isomers of 8-methyl-1-hydrindanones (**1a** and **1b**) and 9-methyl-1-decalones (**2a** and **2b**) and its implication on the nature of nonradiative decay processes of their excited states. The systems were chosen because (1) the cage recombination of biradicals initially generated in the photolysis may lead to cis–trans isomerization of the starting ketone;[5] (2) the intersystem crossing efficiency of these ketones may be estimated by the method of Lamola and Hammond,[6] which is not applicable to acyclic *tert*-alkyl ketones, owing to the high concentration of radicals generated; and (3) the photochemistry of these ketones may provide interesting information concerning conformational effects on photochemistry.

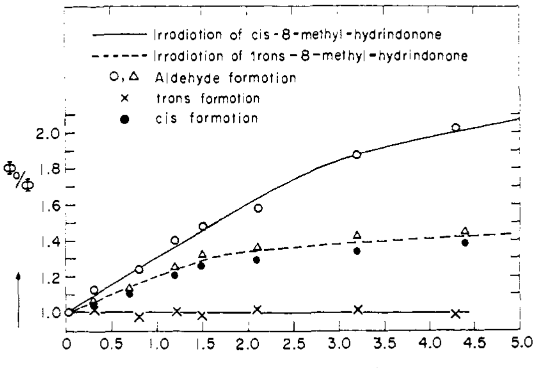


Figure 1.

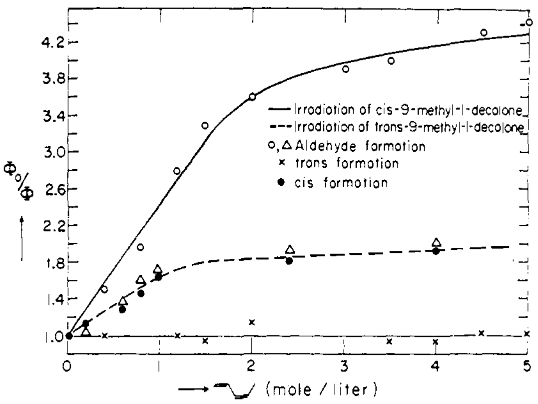
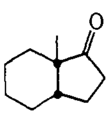
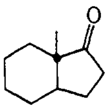


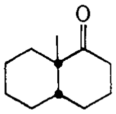
Figure 2.



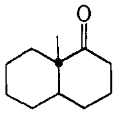
1a



1b



2a



2b

Isomeric 8-methyl-1-hydrindanones were prepared according to the method of Johnson,[7] and isomeric 9-methyl-1-decalones were prepared as a mixture following the procedure of Ireland and Marshall[8] and separated by preparative vpc. Irradiation of these compounds in hexane yielded the corresponding isomer and an unsaturated aldehyde (**3**) as the only detectable products by vpc. The unsaturated aldehydes were isolated by preparative vpc and characterized.[9] When the irradiation of these compounds in hexane (*ca.* 0.3 *M*) at 313 nm was followed quantitatively in an apparatus previously described[10] using ferrioxalate actinometry and 2-hexanone as the secondary standard, the decomposition of these ketones followed zero-order kinetics up to 15% conversion. The irradiations of these ketones were then carried out in the presence

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(1) For a review on photochemistry of aliphatic carbonyl compounds, see J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, pp 377–399.

(2) N. C. Yang and E. D. Feit, *J. Amer. Chem. Soc.*, **90**, 504 (1968).

(3) N. C. Yang, E. D. Feit, M. H. Hui, N. J. Turro, and J. C. Dalton, *ibid.*, **92**, 6974 (1970).

(4) J. Franck and E. Rabinowitsch, *Trans. Faraday Soc.*, 30, 120 (1934).

(5) The cis–trans isomerization of 2,6-dimethylcyclohexanone in the gas phase has been reported, but no quantum yields were given and the nature of reactive states was not analyzed: R. L. Alumbaugh, G. O. Pritchard, and B. Rickborn, *J. Phys. Chem.*, **69**, 3225 (1965).

(6) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

(7) W. S. Johnson, *J. Amer. Chem. Soc.*, **66**, 215 (1944).

(8) R. E. Ireland and J. A. Marshall, *J. Org. Chem.*, **27**, 1615 (1962).

(9) All compounds reported have been characterized by elemental analysis, crystalline derivative, and uv, ir, and nmr spectra.

(10) D. R. Coulson and N. C. Yang, *J. Amer. Chem. Soc.*, **88**, 4511 (1966).