Reactions of Free Aluminum Atoms. Direct Syntheses of Organoaluminum Compounds

Sir:

We report here some condensed phase chemistry of aluminum atoms.[1,2] There is a recent report of aluminum atom reactions in condensed phase, the only work of which we are aware, by Hinchcliffe, *et al.*,[3] who recognized the presence of $Al_x(CO)_2$ at 20°K by its infrared spectrum in a krypton matrix containing aluminum atoms and carbon monoxide. We have found that aluminum atoms react at $-196°$ with unsaturated compounds by addition to produce aluminum–alkyl bonds.

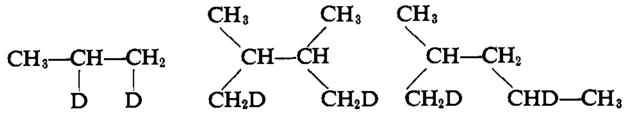
The method developed earlier for the study of carbon atom chemistry[4] is employed, separating by high vacuum the hot aluminum evaporator from the liquid nitrogen cooled reaction zone on the walls. Aluminum vapor produced in this process is monoatomic.[5]

Cocondensation of excess ammonia with atomic aluminum results in release of some hydrogen (10–30% of total) during the codeposition. On slight warming of the matrix the major portion of hydrogen is released, totaling 1.5 mol of H_2 per mole of aluminum. The residue left on warming to room temperature with pumping to pressures below 1 μ releases 1.0 mol of NH_3 per mole of aluminum on hydrolysis. The low-temperature reaction must produce an aluminum triamide which deammonates to aluminum nitride on warming.

Cocondensation of aluminum atoms with a 100-fold excess of propene results in formation of organoaluminum compounds. After completion of the codeposition the excess propene is removed by pumping and warming to room temperature; a light yellow solid remains. The chemical nature of this product is indicated by hydrolysis with deuterium oxide. Dideuterioalkanes (C_3 and C_6) are the major products, indicating that each alkane had been obtained from an organoaluminum product with two attachments to aluminum for each carbon skeleton. Nmr spectra of the major products show the positions of attachment to aluminum. While there is no conclusive evidence to indicate whether these two positions are occupied by a single aluminum atom or two, the high dilution of the aluminum atoms in the substrate and the fact that there is no change of products during warm-up (*vide infra*) suggest that only one aluminum atom is involved. Work in progress may indicate this feature of the product structure. However, the total number of attachments per aluminum atom is 2.7. Thus the main course of the reaction is addition of aluminum(s) to the double bond to make 1,2-dialuminoalkanes. The C_6 products are 1,4-dialuminoalkanes formed, formally, by coupling of 1-alumino-2-propyl radicals, mainly, and 2-alumino-1-propyl radicals to a minor extent.

Table I. Products of Deuterolysis of Organoaluminum Compounds from Propene and Aluminum Atoms (1.43 mmol)

Product	Yield, mmol	% d_0	d_1	d_2	d_3
Propane	1.29	8	4	86	2
Propene	0.141	56	41	3	0
2,3-Dimethylbutane	0.373	1	9	88	2
2-Methylpentane	0.162	1	7	90	2
Hexane	0.0111	11	6	83	0
Hydrogen	0.151	0	28	72	
Methane	0.0016	Not determined			



The major reactions of aluminum atoms with olefins have been described as direct addition, rather than primary formation of Al–H linkages. The final product contains little Al–H (low yield of HD). Had Al–H's been a primary product which then added to propene, a propylaluminum would have been the product, which on deuterolysis would have given a substantial yield of C_3H_7D. The 4% yield of C_3H_7D is attributed to protium inclusion from the glass surfaces, etc.

The process of product formation has been demonstrated to occur prior to warm-up of the cocondensate. The cocondensate on a cesium bromide window cooled to liquid nitrogen temperature shows the same products are present (infrared spectra) prior to warm-up as after warm-up.[6] Thus the reactions go to completion at the low temperature. Further, there is no absorption in the 1900–1700-cm^{-1} region (characteristic of Al–H linkages), but strong absorptions in the 700–600-cm^{-1} region, characteristic of aluminum–alkyl bonds. The absence of Al–H absorption accords with the absence of significant amounts of HD on deuterolysis (3% yield).

A blank reaction was carried out to learn if clean-surface condensed forms of aluminum would also react with propene. Aluminum atoms (2.0 mmol) were cocondensed with propane, a hydrocarbon with essentially the same melting point as propene. After shutting off the supply of aluminum vapor, propene was condensed on the matrix. In contrast to the work described above, the matrix was black as a result of self-condensation of aluminum. The residue left after pumping off unreacted hydrocarbon was deuterolyzed with D_2O. The major product is D_2, 25% yield. Propane and propene are obtained in 5 and 4% yields, respectively, the latter being 100% d_0, the propane 35% d_1 and 13% d_2. Hexanes, if present, were formed in yields less than 0.05%, the detection limit. It is clear that the reactions of free aluminum atoms are not those of the bulk metal, regardless of the state of subdivision.

The 1- and 2-butenes show analogous behavior from which one learns the additional ambiguous feature that either of the 2-butenes gives nearly the same mixture of *meso*- and *d,l*-2,3-dideuteriobutanes.

Addition of aluminum atoms to 1,3-butadiene produces 3,4-dideuterio-1-butene as the major product on deuteriolysis.

The reactions of platinum[7] or nickel[8] with propene

---

[1] P. S. Skell, *Proc. Int. Union Pure Appl. Chem., XXIIIrd*, **4**, 215 (1971).

[2] B. Siegel and P. Breisacher (*J. Amer. Chem. Soc.*, **86**, 5053 (1964)) have reported mass spectrometric recognition of aluminum hydrides when aluminum is evaporated in a hydrogen atmosphere.

[3] A. J. Hinchcliffe, J. S. Ogden, and D. D. Oswald, *J. Chem. Soc., Chem. Commun.*, 338 (1972).

[4] P. S. Skell, L. D. Wescott, Jr., J.-P. Goldstein, and R. R. Engel, *J. Amer. Chem. Soc.*, **87**, 2829 (1965).

[5] R. F. Porter, *et. al.*, *J. Chem. Phys.*, **23**, 339 (1955).

[6] Work done in cooperation with Professor I. C. Hisatsune, The Pennsylvania State University.

[7] P. S. Skell and J. J. Havel, *J. Amer. Chem. Soc.*, **93**, 6687 (1971).

[8] P. S. Skell, M. J. McGlinchey, J. J. Havel, and D. L. Williams-Smith, *J. Chem. Soc., Chem. Commun.*, in press.

produce organometallics which yield mainly unlabeled hydrocarbons on deuterolysis; this suggests that π-type complexes are formed. In contrast, the high deuterium incorporation in the hydrocarbons from the deuterolysis of the organoaluminum compounds indicates σ-type carbon–metal bonds.

Aluminum atoms react similarly with propyne and 2-butyne, mainly by addition to make 1,2-dialuminoalkenes. Partial protolysis of this product by unreacted propyne accounts for the deuteration pattern of the propyne and allene on deuterolysis with deuterium oxide. A combination of mass spectral cracking patterns and infrared data show that the propene product has vinyl but no methyl deuterium. The propyne has some deuterium at the methyl and some at the ethynyl positions. This labeling and the formation of allene-d_1 can be explained if $AlCH_2C{\equiv}CH$ is present in addition to the $CH_3C{\equiv}CAl$.

Table II. Products of Deuterolysis of Organoaluminum Compounds from Propyne and Aluminum Atoms (1.25 mmol)

Product	Yield, mmol	%					
		d_0	d_1	d_2	d_3	d_4	d_6
Propene	1.07	3	43	53	1	0	0
Propyne	0.63	35	61	4	0	0	
Allene	0.075	1	83	16	0	0	
Propane	0.030	2	5	33	36	20	4
Hydrogen	0.034	0	11	89			
Methane	0.055			Not determined			

The reaction of 2-butyne is cleaner, the only products being *cis*- and *trans*-2-butenes in a 2:1 ratio.

Benzene does not appear to react with aluminum atoms; a negligible amount of volatile product is recovered on hydrolysis of the residue. The small amount of benzene recovered (20%) is d_0.

Reactions of aluminum atoms with other substrates will be reported later.

Acknowledgment. The financial support of the Air Force Office of Scientific Research (1983) is acknowledged with gratitude. L. R. Wolf thanks the National Science Foundation for a Graduate Fellowship.

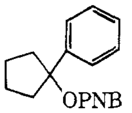
P. S. Skell,* L. R. Wolf
Department of Chemistry, The Pennsylvania State University
University Park, Pennsylvania 16802
Received July 24, 1971

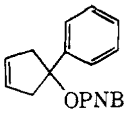
Effect of a Homoallylic Double Bond on the Rates of Solvolysis of 1-Phenylcyclopentyl and 2-Phenyl-2-norbornanyl *p*-Nitrobenzoates. Evidence for the Absence of π Participation as a Factor in the High Exo:Endo Rate Ratio in the 2-Phenyl-2-norbornenyl System

Sir:

The introduction of a homoallylic double bond into 1-phenylcyclopentyl and *exo*- and *endo*-2-phenyl-2-norbornanyl *p*-nitrobenzoates causes modest rate retardations of comparable magnitudes. It is considered that π participation cannot be significant in the rate of solvolysis of 2-phenyl-2-*exo*-norbornenyl *p*-nitrobenzoate, so that the observed high exo:endo rate ratio must arise from other factors, presumably steric hindrance to ionization in the endo isomer.[1]

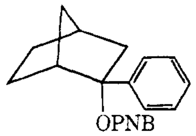
The rate of solvolysis in 80% acetone of 1-phenylcyclopentyl *p*-nitrobenzoate (I) is retarded by a factor of 3.3 by the introduction of a homoallylic double bond (II). Clearly, participation by the homoallylic double bond in II cannot be significant.[2] The small rate retardation which is observed is in the direction anticipated for the inductive effect of the double bond on the rate of solvolysis.[3]

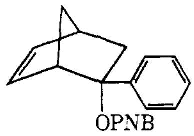

I


II

$k_{\text{rel}}^{25°}$ 1.0 1.0/3.3

This conclusion is supported by the behavior of the 2-phenyl-2-*endo*-norbornenyl *p*-nitrobenzoate (IV). This derivative solvolyzes 8.8 times slower than the saturated analog, 2-phenyl-2-*endo*-norbornyl *p*-nitrobenzoate (III). Participation is believed not to be a significant factor in the solvolysis of *endo*-norbornyl derivatives. Consequently, here also the modest rate retardation is presumably a reflection of the unfavorable inductive influence of the double bond.

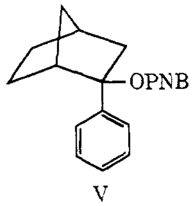

III

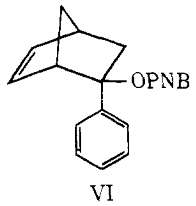

IV

$k_{\text{rel}}^{25°}$ 1.0 1.0/8.8

In the corresponding exo isomers, the possibility of participation must be considered. However, in the saturated derivative, 2-phenyl-2-*exo*-norbornyl *p*-nitrobenzoate (V), evidence has been offered that it must solvolyze without significant σ participation.[4] Indeed, a detailed nmr study of the 2-phenyl-2-norbornyl cation led to the conclusion that the data supported a classical formulation.[5]

Consequently, the observation that the rate of solvolysis of 2-phenyl-2-*exo*-norbornenyl *p*-nitrobenzoate (VI) solvolyzes at a rate 6.2 times slower than the saturated derivative V reveals that the effect of the double bond on the exo isomer is almost identical with the effect of the double bond on the endo isomer. Clearly,


V


VI

$k_{\text{rel}}^{25°}$ 1.0 1.0/6.2

---

[1] E. N. Peters and H. C. Brown, *J. Amer. Chem. Soc.*, **94**, 5899 (1972).

[2] It has been concluded that the cyclopentyl system has an unfavorable planar geometry for π participation: P. D. Bartlett and M. R. Rice, *J. Org. Chem.*, **28**, 3351 (1963).

[3] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1969, Chapter II.

[4] K. Takeuchi and H. C. Brown, *J. Amer. Chem. Soc.*, **90**, 2693 (1968).

[5] D. G. Farnum and G. Mehta, *ibid.*, **91**, 3256 (1969).