Table I. Rates and Isotope Effects in Solvolysis of 3-Pentyn-2-yl Compounds

Leaving group	Solvent[a]	k_H, sec^{-1} [b]	$k_H/k_{\alpha\text{-}d}$ [c]	$k_H/k_{\beta\text{-}d_3}$ [c]	$k_H/k_{\gamma\text{-}d_3}$ [c]
OTs[d]	60 E	3.613×10^{-3}	1.213	1.241	1.104
OTs	70 T	8.755×10^{-3}	1.226	1.281	1.109
Br	50 E	1.203×10^{-5}	1.101	1.200	1.081
Br	70 T	8.823×10^{-6}	1.123	1.280	1.108
I	50 E	4.150×10^{-6}	1.087	1.278	
I	70 T	4.666×10^{-6}	1.089	1.283	

[a] 60 E is 60 vol % ethanol–40 vol % water; 70 T is 70% trifluoroethanol–30% water, etc. [b] Errors are of the order of 0.1–0.2%. [c] Errors are in the range of 0.2–0.4%. [d] *p*-Toluenesulfonate.

of ~1.09 made earlier.[2] The reaction of the iodide in 50% ethanol also seems to be limiting since both α-*d* and β-d_3 effects are very similar to those in 70% trifluoroethanol. The lower β-d_3 effects for the bromide (1.200) and toluenesulfonate (1.241) indicate that the reactions for these compounds in the ethanolic solvents are partly nucleophilic.

The products for the solvolysis of these compounds in 70% trifluoroethanol and 50% ethanol are given in Table II. While the amounts of alcohol and ether formed with tosylate and iodide as leaving groups are nearly the same in 70% trifluoroethanol, the products formed with bromide as a leaving group in this solvent are clearly different. Since the tosylate solvolysis is nearly limiting in 60% ethanol, it is possible to compare its solvolysis products in 50% ethanol with those of the limiting reaction with iodide leaving group in this solvent. Again, the amounts of alcohol and ether formed are different with different leaving groups. Since the leaving group should have no influence on products formed from the free carbonium ion,[7-9] it is apparent that the free ion is not an intermediate in all three reactions. Since the large isotope effects indicate little or no covalent attachment in the rate-determining step[2-4,6] the simplest interpretation of these findings is that the rate-determining step is the interconversion of two ion pairs and that the product-forming step is nucleophilic attack on the second-formed ion pair.

Table II. Products of Solvolysis of $CH_3C{\equiv}C{-}CH(X)CH_3$[a]

X	Solvent[b]	% ether	% alcohol
OTs	70 T[c]	20.6 ± 2	79.4 ± 3
Br	70 T[c]	25.4 ± 2	74.6 ± 3
I	70 T[c]	19.2 ± 2	80.8 ± 3
OTs	50 E[d]	22.7 ± 2	77.3 ± 3
Br	50 E[d]	25.8 ± 2	74.2 ± 2
I	50 E[d]	33.2 ± 3	66.8 ± 3

[a] Analyzed by pmr at 100 MHz. [b] 50 E is 50 vol % ethanol–50 vol % water, 70 T is 70% trifluoroethanol–30% water. [c] Trifluoroethyl ether, pmr (70 T) δ 1.42 (d, 3, J = 7 Hz, CH_3CH–), 1.83 (d, 3, J = 2.5 Hz, $CH_3C{\equiv}$); alcohol, pmr (70 T) δ 1.39 (d, 3, J = 7 Hz, CH_3CH), 1.80 (d, 3, J = 2.5 Hz, $CH_3C{\equiv}$). [d] Ethyl ether, pmr (50 E, $CD_3CH_2ODD_2O$) δ 1.37 (d, 3, J = 7 Hz, CH_3CH–), 1.83 (d, 3, J = 2.5 Hz, $CH_3C{\equiv}C$); alcohol, pmr (50 E, $CD_3CH_2ODD_2O$) within 1 Hz of that given in *c*.

It is also interesting to note that the OTs/Br rate ratio observed for the 3-pentyne-2 compounds (994 in 70 T) is in the range of those found for limiting solvolyses[10,11] (466–5126) of such alkyl groups as *tert*-butyl and α-phenylethyl even though it is now understood that this ratio bears no simple direct relationship to mechanism.[12,13] The fact that the bromide solvolyzed faster than the iodide (Br/I, 2.89 in 50 E and 1.89 in 70 T) is at first sight surprising but the same relationship has been observed by Robertson for other alkyl groups.[14]

It is especially important to recognize the dependence of α-deuterium rate effect on leaving group because it allows one to properly compare α-*d* effects of reactions which involve different leaving groups and to identify subtle shifts in mechanism. In practical terms the comparison between chlorides or bromides and arenesulfonates is of particular importance because many solvolyses of secondary arenesulfonates show α-*d* effects of ~1.15. If these values are incorrectly compared with those from the halides the reactions appear to be limiting. However, comparison with the value of 1.23 indicates that these common secondary sulfonate solvolyses involve some nucleophilic attachment to carbon in the transition state. As indicated before[15] in some of these examples the rate-determining step is the formation of the tight ion pair and in others nucleophilic attack on the tight ion pair. SN2 transition states have such strong nucleophilic attachment to carbon that their α-*d* rate effects are near unity.[16]

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Nuclear Quadrupole Resonance Spectra of Some Alkylaluminum Derivatives[1]

Sir:

In a recent communication[2] we reported a study of the nqr spectrum of $Al_2(CH_3)_6$ which confirmed the bridged structure **1** first suggested by Longuet-Higgins,[3]

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(1) This work was supported by the Air Force Office of Scientific Research through Contract No. F44620-70-C-0121.

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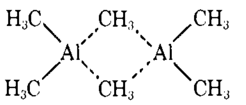
Table I

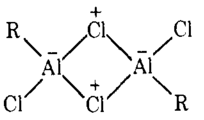
Compd	T, °K	^{27}Al resonances, MHz	^{35}Cl resonances, MHz	^{27}Al e^2Qq, MHz	η
Me_3Al	77	5.382, 6.507		23.71	0.78
	196	5.372, 6.454		23.55	0.79
Et_3Al	196	5.622, 6.278		23.23	0.87
i-Bu_3Al	77	6.155, 6.870		25.42	0.87
Me_2AlCl	77	6.57, 10.54		36.44	0.45
Et_2AlCl	77	6.68, 11.03	9.85	37.82	0.42
n-Pr_2AlCl	77	6.59, 10.79	9.97	37.18	0.43
i-Bu_2AlCl	77	6.67, 10.56	10.08	36.60	0.47
	196	6.57, 10.44	9.86	36.15	0.47
Me_2AlBr	77	6.46, 10.65		36.66	0.42
	196	6.42, 10.58		36.41	0.42
Et_2AlBr	77	6.525, 10.960[a] 11.345[a]		38.20	0.37
Et_2AlI	77	6.39, 11.16		38.02	0.34
$EtAlCl_2$	77	4.74,[a] 7.20[a] 4.81,[a] 7.43[a]	10.46, 11.35[a] 11.50[a]	25.50	0.51
i-$BuAlCl_2$	77	4.825, 7.702	10.824, 11.723	26.66	0.46
$PhAlCl_2$	196	4.66, 7.00	10.48, 11.47	36.41	0.54
	Room temp	4.66, 6.94	11.325	24.32	0.54
$AlBr_3$[b]	77	3.034, 3.833		13.86	0.73

[a] Crystal-field doublets. [b] P. A. Casabella, P. J. Bray, and R. G. Barnes, *J. Chem. Phys.*, **30**, 1393 (1959).

in contrast to some recent suggestions. Since this result suggested that useful information could be obtained concerning the structure and bonding of other compounds of this type, and since analogous bridged aluminum derivatives are of current interest as homogenous catalysts, we have examined the nqr spectra of a number of compounds AlR_nX_{3-n} where R is an alkyl or aryl group and X a halogen. Since ^{27}Al has a spin of $^5/_2$, two resonances are observed in cases where the asymmetry parameter (η) differs from unity; from these one can calculate both η and the coupling constant e^2Qq.[4] The measurements were made at 77 or 196°K, or room temperature, using a modified superregenerative spectrometer of the type described by Peterson and Bridenbaugh;[2,5] the measured resonance frequencies and derived quantities are listed in Table I, together with published data for $AlBr_3$.



1



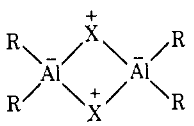
2

The similarity between the nqr spectra of Me_3Al, Et_3Al, and i-Bu_3Al indicates that all three must have analogous dimeric bridged structures. All three have high asymmetry parameters (*ca.* 0.8) and similar coupling constants (*ca.* 24 MHz). The conclusion that i-Bu_3Al is dimeric in the solid phase is in accord with a recent report that this compound, long thought to be monomeric, is 40% dimerized as a liquid at 10°.[6] i-$BuAlCl_2$ and $PhAlCl_2$ showed two distinct chlorine resonances. Since the separation of these (*ca.* 1 MHz) is rather large to be attributed to crystal-field effects, the compounds probably contain two chemically nonequivalent chlorine atoms. If so, they presumably must exist as the chlorine-bridged dimers **2** (R = i-Bu or Ph). The fact that the terminal chlorine resonances (higher frequency) are unsplit by crystal-field effects further indicates, by comparison with the case of $GaCl_3$,[7] that they are in the trans configuration, which is in accord with the X-ray results for $MeAlCl_2$.[8]

The spectrum of $EtAlCl_2$ is similar, the only difference being that each resonance, except the lower chlorine frequency, is split, presumably by crystal-field effects. The asymmetry parameters (0.46, 0.54, and 0.51) are also much less than for the trialkyl derivatives; according to the treatment of Casabella, Bray, and Barnes,[9] η depends only on the angle (α) between the aluminum orbitals used to bond the bridging groups, being given by

$$\eta = -3 \cos \alpha \qquad (1)$$

One would certainly expect a change in the nature of the bridge bonds, and so in α, in passing from alkyl, which can form only three-center bonds, to chlorine, which can form separate two-center bonds to each aluminum (*cf.* **1** with **2**). The chlorine resonances are both very low implying a high degree of ionic character;[10] analogy with gallium trichloride[7] makes it likely that the lower frequency corresponds to the bridging chlorine.



3

The dialkylhaloaluminums all have asymmetry parameters close to 0.4; comparison with R_3Al and $RAlCl_2$ implies that they must have the halogen-

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(9) See Table I, footnote *b*.

(10) A neutral covalent chlorine should resonate at the same frequency as Cl_2 (54.25 MHz); this implies *ca.* 75% ionic character in the Al–Cl bonds.

bridged structure **3**.[11] Further confirmation is provided by the observed coupling constants. According to the Casabella–Bray–Barnes treatment,[9] the coupling constant for a bridged aluminum compound Al_2X_6 should be given approximately by

$$e^2Qq = 37.52(b - a)(1 + \eta/3)^{-1} \qquad (2)$$

where a and b are the electron densities in a bridging Al orbital and a terminal orbital, respectively. Thus, replacement of a bridging alkyl group by an electronegative group, *e.g.*, halogen, should reduce a and so increase the coupling constant, while analogous replacement of a terminal alkyl group should reduce b and so decrease the coupling constant. In agreement with this we see a rapid increase in e^2Qq along the series $AlBr_3$ (14 MHz), $RAlCl_2$ (26 MHz), R_2AlX (37 MHz); each replacement of one terminal halogen per aluminum in the dimer by alkyl increases e^2Qq by *ca.* 12 MHz. Conversely, replacement of the final halogen leads to a decrease from 37 MHz for R_2AlX to 24 MHz for R_3Al, *i.e.*, a change of 6 MHz for each Al for each bridging group. Since the three-center bond linking the bridging group X can be regarded as a covalent bond from X to an Al_2 unit, changes in X should alter the orbital density in each aluminum by about half the amount for a corresponding change in a normal Al–X bond; replacement of bridging halogen by alkyl should therefore lower the coupling constant by about one-half the amount that corresponding replacement of terminal halogen raises it.

These preliminary studies therefore seem to emphasize the potential utility of nqr as a tool for studying the structure of compounds of this type and also the bonding involved in them. It is true that most of the structures deduced here agree with current intuition; however, there has been as yet little direct evidence for them. The measurement of nqr spectra is also much less time consuming than structure determination by X-ray or electron diffraction while deductions from nmr are usually complicated by the possibility of rapid interchange of terminal and bridging groups.

Acknowledgment. We are grateful to Texas Alkyls, Inc., Pasadena, Tex., for donating many of the compounds used in this study.

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External Heavy-Atom-Induced Spin–Orbital Coupling. Spectroscopic Study of Naphthonorbornanes[1]

Sir:

According to present theory,[2] spin–orbital coupling provides the crucial mechanism which allows the otherwise "forbidden" interconversion of the singlet and triplet states of organic molecules. By studying the factors which affect spin–orbital coupling, we can hope to better understand the nature of forbidden radiationless and radiative electronic transitions. The magnitude of spin–orbital coupling in most organic molecules is strongly dependent on the atomic number of nuclei in the vicinity of the optical (orbitally decoupled) electrons. The effect of directly affixed internal[3] heavy (third row of the periodic table and beyond) atoms and external[4] (solvent) heavy atoms on the singlet–triplet interconversions of organic molecules has been the focus of much theoretical[5] and experimental work.[4a,d,e,6] Although spin–orbital coupling induced by external heavy-atom perturbation has been shown in some cases[2,5] to be quite significant, hardly any data exist on how the heavy-atom effect varies as a function of geometry and distance between a chromophore and a nonconjugated perturber.[7] It has been assumed that a collision complex[2] or its equivalent is required for effective spin–orbital perturbation of a chromophore (*e.g.*, naphthalene or its derivatives) and an external heavy atom (*e.g.*, an alkyl halide).[5] Whether charge transfer[2c,8] or electron exchange[2c,9] would be a predominant mechanism of spin–orbital interaction in such a complex, although a matter of considerable interest, is still a matter of controversy. The external heavy-atom effect has been used[5] (a) as a probe for the mechanism of molecular electronic state mixing, (b) to enhance sensitivity in phosphorimetry, and (c) to enhance intersystem crossing in photochemical studies.

We have prepared and investigated the emission spectroscopy of a series of monobromonaphthonorbornanes (II–VII) in which the position of the halogen atom is systematically varied among all of the unique positions of the norbornane framework. The rigidity of the bicyclic [2.2.1]heptene system allows us to precisely estimate the position[10] in space of the bromine atom relative to the naphthalene chromophore.

The results of our investigation are quite striking and are summarized in Table I. Of considerable interest is the observation that there is no obvious general relationship between the distance of the bromine atom from the naphthalene nucleus and the magnitude of spin–orbital coupling as measured by the values of k_{IS} ($S_1 \rightarrow T_1$), k_P ($T_1 \rightarrow S_0 + h\nu$), and k_D ($T_1 \rightarrow S_0 + \Delta$).[11]

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