free of 4-ketopentanoate and sometimes not, generally containing some impurity but not enough to interfere with elemental analysis:[4] NMR ($CDCl_3$) δ 1.11 and 1.25 (d, 3, $CHCH_3$ and t, 3, CH_3CH_2), 1.6–2.2 (m, 3, $CHCH_2$), 2.35 (t, 2, CH_2CH_2CO), 4.10 (q, 2, CH_3CH_2O), 9.60 (d, $J \sim 1$ Hz, CHO). Yields are summarized in Table I.

Our yields of aldehydes are consistently better than those reported for two-step homologations using Wittig reagents, $ROCH{=}PPh_3$; benzaldehyde to phenylacetaldehyde, 55%; 3-pentanone to 2-ethylbutanal 2,4-dinitrophenylhydrazone, 58%; cyclohexanone to cyclohexanecarboxaldehyde 2,4-DNP, 60%.[8] Strong acid hydrolysis of the enol ether intermediate[8] is a limitation. The specificity of $PhSCH{=}PPh_3$ for aldehyde in the presence of unprotected hydroxyl is unique, but enethiol ether hydrolysis is not very efficient.[9] The classical Darzens glycidic ester route usually gives mediocre yields,[10] a notable exception being the 80% reported for homologation of β-ionone in the synthesis of vitamin A.[11] Our route suffers from the inconvenience of preparing tris(dimethoxyboryl)methane, but our current procedure is safe and reproducible.[3]

We have previously reported the condensation of various boron-substituted carbanions with aldehydes and ketones, have briefly explored compatibility with other functional groups, and have isolated a triborylmethide salt.[2,3,12-14] The present work is the first to provide yields consistently high enough for general synthetic use and offers several points of novelty in the preparation of alkeneboronic acids. The boronic esters (**3**) from aldehydes and **2** are 93–100% trans, providing an alternative to hydroboration for synthesizing these compounds, which are already known to be useful sources of cis 1-bromoalkenes,[15] trans 1-iodoalkenes,[16] and potentially, by way of B-alkylation and rearrangement with iodine and alkali, of cis alkenes.[17] Crude β-styreneboronic ester from benzaldehyde showed the NMR $BCH{=}CH$ doublet of the trans isomer, δ 6.0, and none of the cis, reported[18] δ 5.5. Crude *trans*-1-propeneboronic acid from acetaldehyde, probably the least stereoselective case, showed a $BCH{=}$ doublet of quartets, δ 5.56, $J = 18$ and 1.5 Hz, with 7% cis isomer, δ 5.50, $J = 14$ and 1.5 Hz. Other aspects of the structure proof and potential utility of these compounds have recently been outlined elsewhere.[3]

The diborylmethide salt **2** shows the expected selectivity for aldehydes or ketones over unsaturated or carbethoxy functions (Table I). Unexpected selectivity with *p*-nitrobenzaldehyde led to a 34% yield of *p*-nitrostyreneboronic acid, mp 225°, fully characterized as the ethylene glycol ester, mp 175–176°.[4] Potentially more useful selectivity was achieved with 1,3-dichloroacetone, which yielded ~60% of crude 2-(chloromethyl)-3-chloropropene-1-boronic acid, $(ClCH_2)_2C{=}CHB(OH)_2$, recrystallized from moist chloroform with considerable loss: mp 70–72.5°; NMR ($CDCl_3$) δ 4.31 (s, 2, CH_2Cl), 4.59 (broadened s, 2, CH_2Cl), 5.76 (broadened s, 2, $=CH$), with a broad OH band at δ 4–6.[4] Oxidation with hydrogen peroxide in dilute phosphoric acid, though sluggish and incomplete, netted ~30% overall of α-(chloromethyl)acrolein: NMR ($CDCl_3$) δ 4.26 (d, $J \sim 1$, 2 Hz, CH_2Cl), 6.29 (s, 1, $=CHH$), 6.65 (t, $J \sim 1$, 1 Hz, $=CHH$), 9.63 (s, 1, CHO).

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Aluminum Atom–Ethylene Molecular Complex. Matrix Isolation Electron Spin Resonance Study

Sir:

Direct addition reaction of aluminum atoms to olefin molecules to produce aluminum-alkyl bonds has been demonstrated by Skell and Wolf.[1] Organoaluminum compounds were produced when aluminum atoms were cocondensed with excess propene. Based upon the product analysis of the (deuterium oxide) hydrolysis of the resultant organoaluminum compounds, they concluded that the primary reaction between aluminum atoms and olefin is an addition of one aluminum atom to the double bond. The structural feature of this primary product was not elaborated. We report, in this communication, the electron spin resonance (ESR) spectra of Al atom-ethylene adduct generated within a rare-gas matrix at near liquid helium temperature. It is concluded that the Al atom-ethylene complex is formed through the dative bonds resulting from the interaction of the π orbitals of the olefin and the valence orbitals of the Al atom.

The design of the liquid helium cryostat and an x-band ESR spectrometer assembly that would permit trapping of high temperature vapor phase species in a rare-gas matrix and observation by ESR of the resulting matrix has been described previously.[2] In the present experiment, Al atoms were vaporized from a resistively heated tantalum cell and trapped in a neon matrix together with ethylene molecules introduced through a separate gaseous sample inlet. The composition of the matrix was roughly 1000:10:1 for neon atoms, ethylene molecules, and Al atoms, respectively. The frequency of the spectrometer locked to the sample cavity was 9.420 GHz.

A neon matrix containing Al atoms ($3s^2\ 3p^1$) alone appeared white and showed no ESR spectrum. The absence of ESR signal attributable to Al atoms is ascribed to the extreme broadening caused by the degeneracy of the p orbitals.[3] When Al atoms were trapped together with ethylene, the matrix appeared green, and a strong ESR signal possessing a unique pattern appeared centered about the posi-

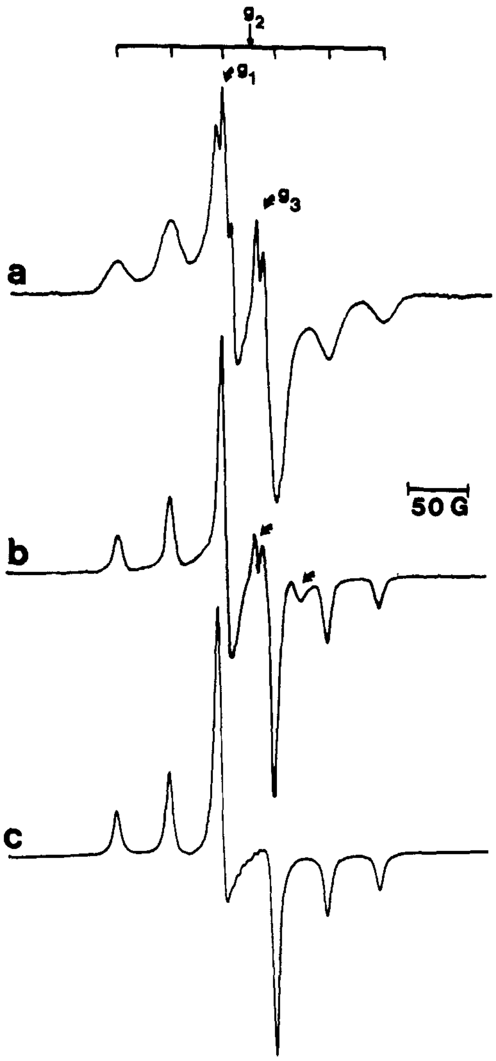


Figure 1. ESR spectra of (a) Al atom-ethylene (C_2H_4) molecular complexes, (b) Al atom-ethylene (C_2D_4) molecular complexes, and (c) that computer-simulated based upon the parameters given in the text.

tion corresponding to $g = 2.00$. Shown in Figures 1a and 1b are such spectra obtained when normal ethylene (C_2H_4) and perdeuterioethylene (C_2D_4) were used, respectively. We propose to assign these spectra to Al atom-ethylene molecular complexes randomly oriented within the matrix.

The sharpening of the spectrum upon deuteration is quite conspicuous. It is clear, however, that the prominent sextet feature indicated in the figure must be attributed to the hyperfine interaction with the ^{27}Al nucleus (natural abundance = 100%, $I = \frac{5}{2}$). The unique intensity pattern of the sextet reflects an extremely uniaxial nature of the hyperfine coupling tensor ($|A_{\parallel}| \gg |A_{\perp}| \simeq 0$). The following g tensor and the hyperfine coupling tensor to Al were assessed from the spectrum of the deuterated species (Figure 1b).

$$g_1 = 2.014 \pm 0.002$$

$$g_2 = 2.002 \pm 0.002$$

$$g_3 = 1.996 \pm 0.002$$

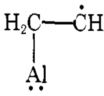
$$|A_1|_{\text{Al}} = 0 \pm 2\text{ G}$$

$$|A_2|_{\text{Al}} = 44 \pm 1\text{ G}$$

$$|A_3|_{\text{Al}} = 0 \pm 2\text{ G}$$

The computer-simulated spectrum[4] (Figure 1c) based upon these parameters and a Lorentzian line shape with the line width of 7 G is in excellent agreement with the observed spectrum. The two small signals indicated by arrows in Figure 1b are believed to be caused by some minor (most likely secondary) reaction product(s).

Three types of bonding schemes, I, II, and III, are possible for the addition product of Al and ethylene.



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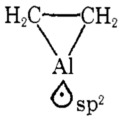

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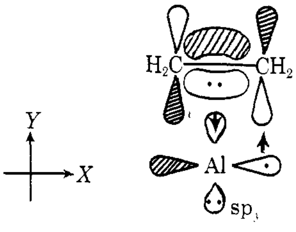

III

The scheme I is self-explanatory. The scheme II invokes a sp^2 hybridization of the Al atom and the formation of σ bonds between the Al and carbon atoms. The scheme III invokes a s-p$_y$ hybridization of Al, and the formation of two dative bonds, one resulting from migration of electrons from the bonding π orbital of the olefin into the vacant s-p$_y$ orbital of Al, and the other resulting from back-donation into the vacant antibonding π orbital from the semifilled p$_x$ orbital of the Al atom.

In scheme I the unpaired electron is localized on the terminal carbon. The observed large, anisotropic coupling tensor to the Al nucleus rules out this scheme immediately.

In the bonding schemes II and III, the distribution of the unpaired electron in the vicinity of the Al nucleus is axially symmetric. The Al hyperfine coupling tensor is then expected to take the form of $A_{\parallel} = A_{\text{iso}} + 2A_{\text{dip}}$ and $A_{\perp} = A_{\text{iso}} - A_{\text{dip}}$, where A_{iso} represents the isotropic interaction arising from the spin density in the Al 3s orbital, and A_{dip} represents the anisotropic interaction related to the spin density in the 3p orbital.[5] The observed Al coupling tensor indeed possesses an axial symmetry and yields

$$|A_{\text{iso}}| \simeq |A_{\text{dip}}| = 14.7 \pm 2\text{ G}$$

The values of A_{iso} and A_{dip} calculated for the "pure" 3s and 3p Al orbitals are 985 and 21 G, respectively.[5] The spin densities in the 3s and 3p Al orbitals in the complex are thus determined to be 0.015 and 0.70. The extremely small s character and the dominance of the p character of the semifilled orbital are most compatible with the bonding scheme III. An isotropic coupling interaction of the observed magnitude is often induced by an unpaired electron in a p orbital through polarization of the filled s orbitals.

The partially resolved structure in the g_1 region of Figure 1a must surely be caused by the hyperfine interaction with the protons. Its intensity pattern strongly suggests that the four protons are structurally equivalent in the complex. From the difference in the apparent line widths of the signals of the deuterated and nondeuterated species, the isotropic coupling constant to the protons was estimated to be 4 ± 1 G. The proton coupling constant of such magnitude cannot be expected from the bonding scheme II where the unpaired electron resides in the nonbonding sp^2 orbital pointing away from the ethylene moiety. The LCAO description of the semifilled orbital in the bonding scheme III is:

$$\Phi = a\text{p}_x(\text{Al}) + b[\text{p}_y(\text{C}_1) - \text{p}_y(\text{C}_2)]$$

If $a^2 = 0.70$ as determined from the Al coupling tensor, b^2 would be ~0.15. The McConnell relation[6] then predicts the isotropic interaction with the protons of ~3.5 G in close agreement with the value estimated above.

We have also succeeded in generating and observing the

ESR spectra of Ga-ethylene and In-ethylene complexes. More detailed analyses of the spectra presented here and those of Ga- and In-ethylene complexes will be reported shortly.

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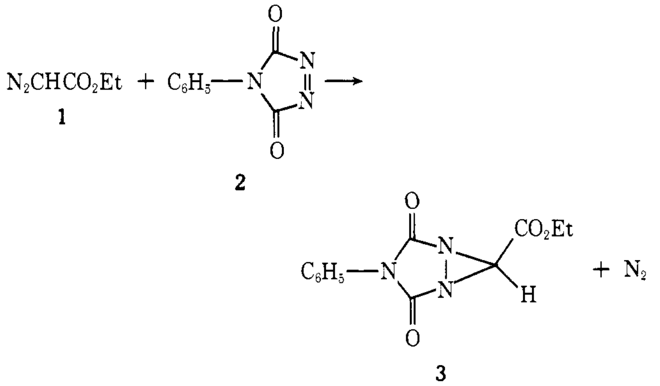
1,2-Addition Reaction of Ethyl Diazoacetate and 4-Phenyl-1,2,4-triazoline-3,5-dione

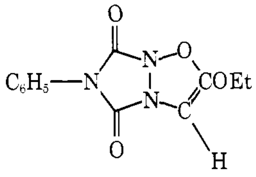
Sir:

The formation of three-membered carbocyclic ring systems by the reaction of carbene intermediates with olefinic and acetylenic sites has been well documented. However, the analogous reaction of these intermediates with azo compounds to give diaziridine derivatives has not been reported. Carbene sources such as ethyl diazoacetate have been found to react with *trans*-diacyldiimides by 1,4- rather than 1,2-addition.[1] When the groupings about the azo linkage are forced to occupy a cis configuration, 1,4-addition is no longer possible. Instead 1,2-addition is likely to occur. We wish to present evidence of the first known example of this latter type of addition.

Ethyl diazoacetate (**1**) reacted vigorously in a mildly exothermic manner with 4-phenyl-1,2,4-triazoline-3,5-dione (**2**)[2] in either methylene chloride or benzene solution at 0° to form a one-to-one adduct, mp 175-177° dec, *m/e* 261, in near quantitative yield.[3,4] The structure of the product was assigned as 6-carbethoxy-3-phenyl-1,3,5-triazabicyclo[3.1.0]hexane-2,4-dione (**3**) rather than that of the bicyclic compound **4** or the triazolinium-*N*-ylide **5**. There is literature analogy for compounds of type **4** and **5**.[5-7] Generally, however, compounds of type **4** which have three adjacent saturated heteroatoms are unstable and readily rearrange to ylide structures.[6,7] The adduct is a white solid whereas ylides are colored and give a visible spectrum. The ir spectrum shows the carbonyl absorptions centered at 1745 cm^{-1}. Ylides containing the $-N{=}N^{+-}CHCO_2Et$ grouping have their carbonyl absorption at 1645-1660 cm^{-1} [5,6] owing to the delocalization of the negative charge on to the carbonyl oxygen. The behavior of the product in the presence of either acid or base was inconsistent with both **4** and **5**. It was recovered unchanged when treated with 15% hydrochloric acid for 48 hr but decomposed immediately in 5% sodium hydroxide. It failed to react with excess acetic acid (60:1) and acetic anhydride in methylene chloride solution at room temperature over a 3-week period. However, when the reaction was repeated and a small excess (2:1) of either lead diacetate or sodium acetate was added to the reaction mixture, the diacetoxytriazole **6** was recovered in high yield.[8] This reaction can best be rationalized as a double nucleophilic displacement by acetate anion at C-6 of **3** to give 4-phenylurazole followed by diacetylation of the urazole ring with acetic anhydride.[9] Thus the above results strongly support **3** as the structure of the product.



1 **2** **3**



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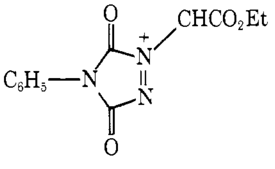

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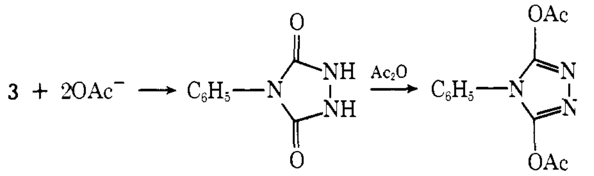
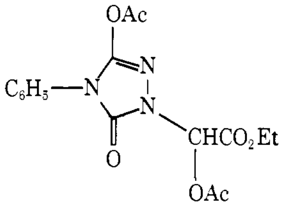


6

The in situ reaction of **2**, prepared by the lead tetraacetate oxidation of 4-phenylurazole,[2] with **1** also gave **3** (30-40%). In addition a small quantity (1-3%) of 1-(acetoxycarbethoxymethyl)-3-acetoxy-4-phenyl-1,2,4-triazoline-5-one (**7**)[10] was isolated which was possibly formed by ring-opening of **3** under the reaction conditions.



7

The ^1H NMR spectrum of **3** showed two complex and broad multiplets for the ethoxy protons. Only slight changes in the appearance of the multiplets were observed as the temperature was varied between −78 and 80°. A 10^{-3} *M* solution of **3** in chloroform did not give an ESR spectrum. The proton decoupled ^{13}C NMR spectrum[11] showed signals at 13.8 (CH_3), 63.4, and 64.7 ($O{-}CH_2$ and C-H) ppm downfield from internal TMS in addition to the carbonyl and aromatic absorptions. All of the signals were considerably broadened. The presence of a single set of ethoxy absorptions indicates that only one isomer, presumably the exo isomer, was formed in high yield. The cause of the broadening of both the ^1H and ^{13}C NMR signals is most likely due to either the presence of a low concentration of a paramagnetic species that was not detected by ESR spectroscopy or to an effect of slow inversion of the phenyl group about the nitrogen atom and/or slow rotation of the carbethoxy group about the C—C=O bond.[12]

The diaziridine compound **3** is thermally unstable. Heat-