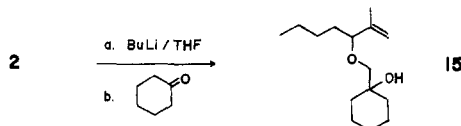
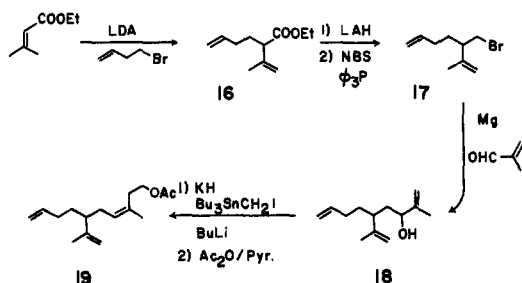


addition of *n*-butyllithium to **2** at  $-78\text{ }^\circ\text{C}$  (THF, 30 s) followed by immediate quenching with cyclohexanone produced **15**: 73% yield; IR (neat)  $3400\text{ cm}^{-1}$ ; NMR ( $\text{CCl}_4$ )  $\delta$  6.84 ( $=\text{CH}_2$ , br s), 3.55 ( $>\text{CHO}-$ , m), 3.03 ( $-\text{OCH}_2-$ , AB q,  $\Delta\nu_{\text{AB}} = 20\text{ Hz}$ ,  $J = 9\text{ Hz}$ ), 1.62 ( $=\text{CMe}-$ , s).



At this time the most useful aspect of the reaction seems to be its high stereoselectivity for *Z*-trisubstituted olefins. While a variety of natural products incorporate double bonds of this type, most trisubstituted olefin syntheses produce *E* isomers as the major products (see exceptions<sup>13</sup>).

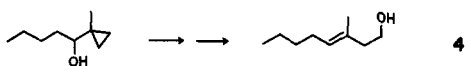
The trienyl acetate **19** is an active component in the sex attractant of a major citrus pest, the California red scale.<sup>14</sup> We have prepared this compound from the ethyl ester of  $\beta,\beta$ -dimethylacrylic acid as summarized in Scheme I. Alkylation



(LDA, THF/HMPA,  $-78\text{ }^\circ\text{C}$ ) with 4-bromobutene gave the  $\beta,\gamma$ -unsaturated ester **16** in 80% yield. Hydride reduction and NBS-phosphine bromination<sup>15</sup> then gave **17** (93% yield). Conversion to the Grignard reagent and reaction ( $\text{Et}_2\text{O}$ ,  $-20\text{ }^\circ\text{C}$ ) with methacrolein proceeded in 52% yield and led to a mixture of diastereomeric allylic alcohols **18** which was suitable for the [2,3]-sigmatropic rearrangement described above. Alkylation with iodomethyltributyltin and butyllithium-induced rearrangement (30 min,  $-78\text{ }^\circ\text{C}$ ) proceeded as usual. The product was chromatographed and acetylated ( $\text{Ac}_2\text{O}/\text{pyr}$ ) to yield the racemic red scale triene **19** in 83% yield. VPC and NMR comparison with authentic material<sup>16</sup> showed our product to consist of 95–96% of the desired *Z* isomer.<sup>17</sup>

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- (17) This work was generously supported by grants from Research Corporation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and Grant Number CA 23084, awarded by the National Cancer Institute, DHEW.

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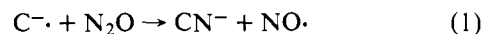
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## Concerning $\text{CH}_2=\text{C}^-$ and Its Reaction with $^{14}\text{N}^{15}\text{NO}$

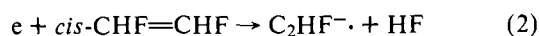
Sir:

In their paper entitled "Gaseous Anion Chemistry",<sup>1</sup> Smit and Field report that an ion of  $m/e$  26 is always present in the negative ion CI spectrum of the bath gas which they used ( $\text{N}_2\text{O}/\text{CH}_4$  1:1). Their work with  $\text{CD}_4$ , measurements of natural isotope abundance ratios of the ion, and their observation that the relative intensity of the ion was dependent on the temperature of the source filament all suggest that the ion is  $\text{CN}^-$  rather than  $\text{C}_2\text{H}_2^-$ . We would point out that further evidence to support this view comes from the absence of a peak at  $m/e$  40, most significantly with the sample 1-octyne where the  $m/e$  26 intensity was enhanced. It is known that  $m/e$  40,  $\text{CH}_2\text{CN}^-$ , is formed by the reaction of  $\text{C}_2\text{H}_2^-$  with  $\text{N}_2\text{O}$ .<sup>2</sup> The route which was suggested to these authors to explain the formation of  $\text{CN}^-$ , namely:



seems extremely attractive until it is recalled that Fehsenfeld and Ferguson<sup>3</sup> specifically did not observe the reaction under flowing afterglow conditions. Instead, they record that these collisions led to a rapid associative electron detachment reaction, but it was not known if the products of the reaction were  $\text{CN}^- + \text{NO} + e$  or  $\text{N}_2 + \text{CO} + e$  or something else.

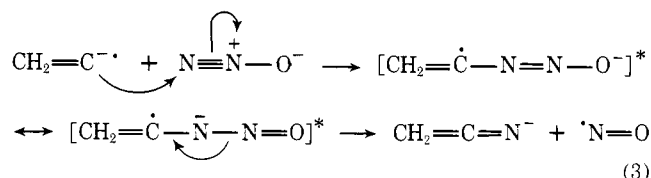
The alternative composition for  $m/e$  26, viz.  $\text{C}_2\text{H}_2^-$ , has been observed in a number of independent laboratories.<sup>4-7</sup> MINDO/3 calculations<sup>8</sup> which have now been performed in our laboratory<sup>9</sup> predict electron affinities of 0 eV for  $\text{CH}_2=\text{C}^-$ : and  $-1.8\text{ eV}$  for  $\text{HC}\equiv\text{CH}$  (in their ground states), so that acetylenic molecular anions should not be stable with respect to electron detachment. Furthermore, we have recently discovered that at near-zero electron energy *cis*-1,2-difluoroethylene undergoes a resonant dissociative electron attachment process giving in good yield ions of  $m/e$  44:



However, we have so far been unable to find any ionization of the isomeric 1,1-difluoroethylene. This divergence of behavior

may readily be explained if one imagines that the stable  $C_2HF^-$  ions observed have the structure  $CHF=C^-$ , which can be derived with ease only from the 1,2 isomer. (In the absence of a sample of the trans compound we imagine that it will behave similarly to the cis isomer.) Thus there are now five pieces of evidence<sup>10</sup> all pointing to the conclusion that stable  $C_2H_2^-$  has the structure  $CH_2=C^-$ .

Smit and Field also discuss the reactions of a number of anions with neutral nitrous oxide which has the two main resonance structures  $^-N=N^+=O$  and  $N\equiv N^+ - O^-$ .<sup>11</sup> Since the central atom in both resonance structures is positively charged, it is tempting to imagine (as do Smit and Field) that anionic attack will take place there. However, very detailed <sup>15</sup>N and <sup>18</sup>O labeling studies have been carried out on the  $O^-/N_2O$  system itself,<sup>12</sup> and in that case it was the considered opinion of the authors that the intermediate in the well-known reaction forming  $NO^-$  was of the form  $(\cdot ON=NO^-)^*$ . In previously unpublished work we have carried this matter a little further forward by studying again the related reaction of  $CH_2=C^-$  with  $N_2O$ . Using specifically labeled <sup>14</sup>N<sup>15</sup>N<sup>13</sup>O in standard ion cyclotron resonance drift cell experiments,<sup>14</sup> we find that there is no incorporation of the <sup>15</sup>N label into the  $CH_2CN^-$  product ions. Thus notwithstanding any initial electrostatic attraction to the central atom in nitrous oxide it seems that in the cases for which labeling results are available reaction actually takes place at the terminal nitrogen; in the case of  $CH_2=C^-$  as shown in eq 3. The transitory gas-phase



reaction intermediate proposed in reaction 3 is expected to be favorable both because it is an unbranched odd-atom system and because of its analogy to the commonly observed conjugated alkoxide anions.<sup>15</sup>

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- The authors greatly acknowledge the cooperation of H. Dits in performing the MINDO/3 calculations.
- (i) The absence of any report of long-lived acetylene molecular anions; (ii) the discovery<sup>6</sup> that  $C_2H_2^-$  and  $C_2D_2^-$ , but not  $C_2HD^-$ , are the products of the reaction of  $O^-$  with  $CH_2=CD_2$ ; (iii) the observation<sup>2</sup> of the reaction  $C_2H_2^- + N_2O \rightarrow C_2H_2N^- + NO$ ; (iv) the calculations presented herein; (v) analogy with the difluoroethylene data presented here.
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## Solid-State High Resolution NMR Spectroscopy of Spin $1/2$ Nuclei (<sup>13</sup>C, <sup>29</sup>Si, <sup>119</sup>Sn) in Organic Compounds

Sir:

Proton-enhanced nuclear induction spectroscopy, which combines spin decoupling with polarization transfer in the rotating frame from the abundant protons to the isotopically rare or chemically dilute spins, provides a useful new technique for the study of the NMR spectra of solids.<sup>1</sup> In amorphous solids or microcrystalline powders, the presence of numerous anisotropy-broadened lines destroys the resolution achieved by dipolar decoupling, and high resolution can only be achieved by additional magic-angle sample spinning, which reduces the anisotropic chemical shifts to their isotropic averages.<sup>2</sup> This combination of techniques was first applied to polymers<sup>3</sup> and shortly thereafter to powder samples.<sup>4</sup>

We have carried out preliminary experiments with some representative groups of organic compounds in order to establish the possibilities and limitations of this new technique. Several rather general conclusions about the solid-state <sup>13</sup>C chemical shifts can be drawn from the data for some selected compounds,<sup>5</sup> presented in Table I. (1) In the absence of specific solid-state effects, differences between the isotropic shift values measured in the neat liquid and a microcrystalline powder are small and do not exceed the usual solvent effects (see also Table II). (2) If the molecular structure has inversion symmetry in the liquid state, this is usually retained in the solid-state NMR spectrum. Other types of symmetry (such as reflection, etc.) are generally lost and additional line splittings appear. (3) The freezing of free rotation of bulky substituents leads to the formation of fixed conformations with the appearance of different chemical shifts for different geometrical arrangements of the interacting groups (see Table II). (4) Intramolecular nonbonded interactions predominate over the intermolecular ones. In *p*-dimethoxybenzene, the 1,4-nonbonded interactions between the substituent and the aromatic ring lead to unequal chemical shifts of the ortho carbons<sup>6,7</sup> in a  $\xi$ -shaped conformation with the methyl groups located in the plane of the ring.<sup>8</sup> (5) Intramolecular hydrogen bond formation leads to loss of molecular symmetry and to splitting of the spectral lines.<sup>9</sup> (6) Large Knight shifts<sup>10</sup> and the corresponding line splittings<sup>7</sup> appear in the <sup>13</sup>C spectra of charge-transfer complexes with one-dimensional metallic conductivity ( $-250$  and  $-400$  ppm in the tetrathiofulvalene-tetracyanoquinodimethane (TTF-TCNQ) complex).

As a general rule, in all solid silicon and tin compounds, where the proton  $T_1$  is short enough for the <sup>13</sup>C spectra to be obtained, the <sup>29</sup>Si and <sup>119</sup>Sn NMR spectra can be measured as well. However, excessive complexation in the oxygenated and halogenated derivatives can lead to a very limited lattice mobility and very long proton  $T_1$  values.