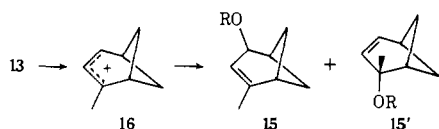


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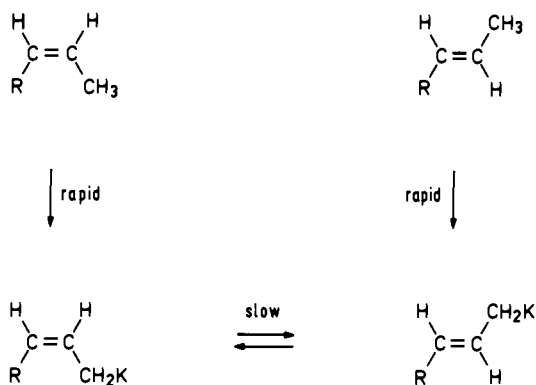
Received April 5, 1976

## 2-Alkenyl Anions and Their Surprising Endo Preference. Facile and Extreme Stereocontrol over Carbon-Carbon Linking Reactions with Organometallics of the Allyl Type

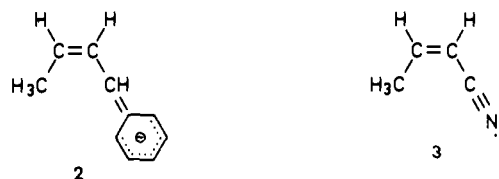
Sir:

Allyl type organometallic compounds merit special attention on account of their potential in the field of organic synthesis.<sup>1</sup> Of particular interest is their stereoselective and regioselective behavior. Organometallic compounds of the allyl type, previously hardly known,<sup>2</sup> became easily available through alkene metalation with butyllithium in the presence of potassium *tert*-butoxide<sup>3–5</sup> or with trimethylsilylmethylpotassium.<sup>6,7</sup>

Spectral<sup>8,9</sup> and chemical<sup>5,10</sup> evidence are in good agreement with a "contact pair" ("contact species") structure<sup>11</sup> and rule out the presence of (solvent-separated) ion pairs or even free carbanions in substantial concentrations. *Z*-Isomers ((*Z*)-**1**) may be converted into the corresponding *E*-isomers ((*E*)-**1**) and vice versa, as was previously established for Grignard<sup>12</sup> and lithium<sup>13</sup> compounds. New and astonishing, however, is the observation<sup>1,4,5,10</sup> that allylpotassium derivatives undergo such configurational changes only very slowly,<sup>14</sup> half-lives of pure isomers falling in the range of hours at normal temperatures in the case of simple hydrocarbon derivatives.



Most surprising was the finding that butenyl-,<sup>5</sup> hexenyl-,<sup>5</sup> 2-methyl-butenyl,<sup>15</sup> and other alkenylpotassium compounds<sup>1,5,16</sup> drastically favor the *Z*-configuration. Although base-catalyzed alkene isomerizations<sup>17</sup> have been known to be highly *cis* selective, this does not necessarily imply an exceptional thermodynamic stability of the intermediary endo-(*cis*)-alkenyl carbanion, since these isomerizations occur under kinetic control and thus may merely reflect differences in the hydrogen transfer mechanisms for *cis*- and *trans*-alkene formation.<sup>18,19</sup> Furthermore the *Z* preference of alkenylpotassium compounds may be, but do not have to be, related to the strong tendency of 1-phenylbutenylpotassium<sup>20</sup> to accommodate the terminal methyl group in an endo(*cis*) position. In liquid ammonia,<sup>20</sup> the phenylbutenylpotassium probably forms a solvent-separated ion pair and it benefits from extensive charge delocalization. Therefore, fundamental dissimilarities with alkenylmetal compounds should still be envisaged. For instance, the electron excess of the 1-phenylbutenyl anion could mainly reside in the aromatic ring and thus make the carbanion (limiting structure **2**) resemble the *Z*-crotonitrile (**3**) which is known to be more stable than the corresponding *E*-isomer.<sup>21</sup> In order to gain deeper insight into the stereochemical behavior of alkenylmetal compounds, we investigated the effects of the organic part, the metal, and the solvent on the equilibrium position.



In general, the *Z/E* equilibrium for each system was established by the metalation of each of the pure olefin isomers. The resulting reaction mixture was stirred until the equilibrium point was reached (at least 24 h in tetrahydrofuran<sup>22</sup>), oxirane was then added and the derived isomeric alcohols were analyzed by gas phase chromatography.<sup>23</sup> The *Z/E* ratios of the product mixtures should be equal to the *Z/E* ratios of the organometallic precursors provided that product yields are high and  $\alpha/\gamma$ -ratios (oxirane attack at the vinylogous vs. the terminal position of the allylic system) observed for both confi-

**Table I.** *Z/E* Equilibrium Composition of 2-Alkenylmetallic compounds RCH=CHCH<sub>2</sub>M in Hexane Solution or Suspension (in parentheses: in tetrahydrofuran), as Reflected by the *Z/E* Isomeric Composition of Derivatives Obtained by Quenching with Oxirane

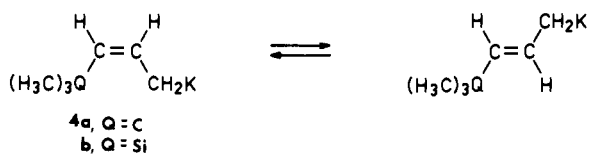
	M = H	M = MgBr <sup>a</sup>	M = Li <sup>b</sup>	M = Na <sup>c</sup>	M = K <sup>c</sup>	M = Cs <sup>c</sup>
R = CH <sub>3</sub>	23:77 <sup>d</sup>	54:46	67:33 (85:15) <sup>e</sup>	93:7	96:4 (99.2:0.8)	99.9:0.1 <sup>f</sup>
R = CH <sub>2</sub> CH <sub>3</sub> <sup>g</sup>	29.71 <sup>d</sup>	39:61	24:76 (80:20) <sup>e</sup>	61:39 (85:15)	94:6	90:10
R = CH(CH <sub>3</sub> ) <sub>2</sub>	26:74 <sup>d</sup>	23:77	14:86	38:62	56:44 (78:22) <sup>h</sup>	66:34
R = C(CH <sub>3</sub> ) <sub>3</sub>	0.1:99.9 <sup>i</sup>	0.2:99.8	3:97 (4:96) <sup>e</sup>	7:93 (8:92)	8:92 (13:87)	9:91 (12:88)

<sup>a</sup> Data taken from ref 25a; experimental details (temperature, e.g.) unknown. <sup>b</sup> Equilibrium established at 0° and in ether rather than in petroleum ether. <sup>c</sup> Equilibrium established at -48°. <sup>d</sup> Ratio computed from thermochemical data published in "Handbook of Chemistry and Physics", 52d ed, Chemical Rubber Company, Cleveland, Ohio, 1971, p D-76. <sup>e</sup> In tetrahydrofuran solvent-separated ion pairs might be present to a certain extent. <sup>f</sup> No products with trans configuration were detected. <sup>g</sup> R = CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> instead of R = CH<sub>2</sub>CH<sub>3</sub> for M = Li, Na, K, and Cs. <sup>h</sup> Equilibrium established at -30°. <sup>i</sup> Ratio estimated on the basis of known heats of hydrogenation<sup>26</sup> and typical entropy differences between *Z*- and *E*-alkenes.<sup>d</sup>

gurationally isomeric alkenylmetal compounds are either small or identical. Normally this happens to be the case<sup>24</sup> and under such favorable circumstances chemical derivatization seems to give more accurate and less ambiguous information about the *Z/E*-isomeric composition of organometallics than spectroscopic methods.<sup>25</sup>

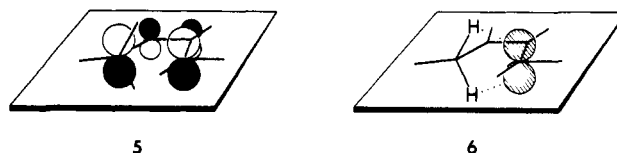
From the tabulated results two major conclusions can be drawn. First, in each alkenyl series (same R) the *Z/E* ratio increase with increasing electropositivity of the metal (Li < Na < K < Cs). In our opinion this trend provides convincing evidence for the hypothesis that cis stereoselectivity of alkenylmetallic compounds does not have its origin in special binding features of the metal<sup>27</sup> but is due to inherent properties of the underlying allyl carbanion. As chemical reactivity<sup>9,28</sup> as well as electronic excitation<sup>29</sup> clearly demonstrated, the properties of resonance-stabilized organometallic contact pairs approach closer and closer to those of true (= free) carbanions as the metal is varied from the less electropositive (magnesium, lithium) to the more electropositive (rubidium, cesium). As one would expect, enhanced peripheral<sup>9</sup> solvation of the metal has the same effect.

Secondly, the endo preference is not particularly dependent on the electronic capacity or the bulk of the alkyl group R. At configurational equilibrium, all alkenylpotassium mixtures contain significantly more *Z*-form than do the corresponding alkenes. A "bonus" ( $\Delta\Delta G_{Z/E}^{M=K/M=H}$ ) of 3.0, 1.7, 1.8, and 3.1 kcal/mol for the enhanced thermodynamic stability of the organometallic *Z*-isomer (in tetrahydrofuran solution) was computed on the basis of comparison between the configurational stabilities of the alkenylpotassium compounds ( $\Delta G_{Z/E}^{M=K}$ ) with those ( $\Delta G_{Z/E}^{M=H}$ ) of the hydrocarbons from which they were derived (2-butene, 2-pentene, 4-methyl-2-pentene, and 4,4-dimethyl-2-pentene, respectively). Moreover, trimethylsilylallylpotassium<sup>30</sup> (**4b**) showed a quite similar stereochemical behavior as the isologous 4,4-dimethyl-2-pentenylpotassium (**4a**): *Z/E* = 5:95 and 10:90 in hexane and tetrahydrofuran, respectively.



The observed "endo preference" must mainly be attributed to attractive forces working between the alkyl groups and the negatively charged methylene terminus.<sup>31</sup> At first sight their origin seems to be most satisfactorily explained by a symmetry-allowed hyperconjugative  $\pi$ -interaction (**5**; indicated is the highest occupied molecular orbital of a delocalized 6 $\pi$ -system). We favor, however, another description<sup>32</sup> which is based on the assumption of hydrogen bonds between the alkyl groups and the electron-rich terminal carbon atom (as in **6**). Consistent with this view is the relative insensitivity of the endo

preference to the individual nature of the alkyl group. This fact argues against the hyperconjugative model which would predict more pronounced variations in the series butenyl-, 4,4-dimethylpentenyl-, and trimethylsilylallyl anion because of the differences in CH-, CC-,<sup>33</sup> and SiC<sup>34</sup>-hyperconjugative efficiency.



Intramolecular hydrogen bonding has been invoked in order to take into account the unusual properties of 2-methylpyridine *N*-oxide<sup>35</sup> and 2-chlorophenol.<sup>36</sup> Moreover this concept could help to rationalize the exceptional gas phase acidities of 2-methylphenol and 2-*tert*-butylphenol.<sup>37</sup>

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### Crossed Molecular Beam Measurement of the Intrinsic Activation Barrier for the Endoergic Reaction $\text{Hg} + \text{I}_2 \rightarrow \text{HgI} + \text{I}$

Sir:

We report an accurate experimental determination of the threshold energy for a neutral atom-diatomic molecule exchange reaction. From this measurement and the known endoergicity of the reaction the intrinsic activation barrier is directly obtained.<sup>1</sup>

We have studied the endoergic reaction of ground state Hg atoms with  $\text{I}_2$  in the vicinity of the reaction threshold via the crossed molecular beam technique. Based on the experimental threshold energy the intrinsic activation barrier has been determined to be essentially zero (within 1 kcal mol<sup>-1</sup>). This experimental result is to be contrasted with the substantial barrier energies (usually tens of kilocalories) inferred for many gas phase reactions from bulk kinetic studies.

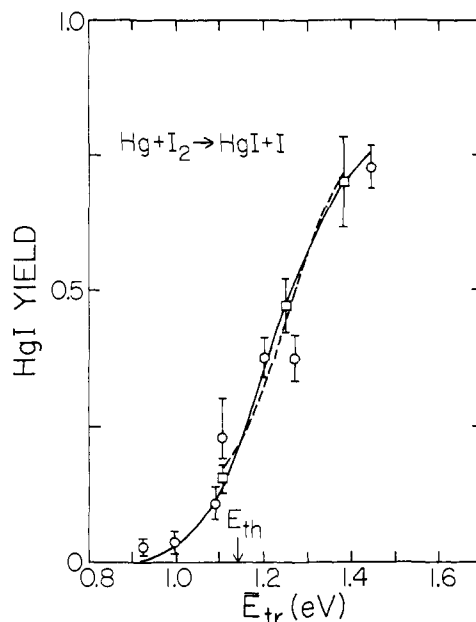


Figure 1. Translational energy dependence of the yield of HgI. Circles and squares denote data sets with different distributions of reactants' translational energy. The solid and dashed curves are the calculated fits (see text) to the circles and squares, respectively, using the "best" experimental (translational) threshold  $E_{th} = 1.14$  eV, indicated by the arrow.

The HgI product from the reactive scattering of a seeded supersonic nozzle beam of Hg by a beam of  $\text{I}_2$  was measured. The yield of scattered HgI was determined at ten values of the average collision energy,  $\bar{E}_{tr}$ , from 0.9 to 1.5 eV, and was found to increase monotonically with translational energy over this range.<sup>2</sup> The reaction threshold energy was then determined through comparison of the experimental reactive yield with that calculated by convoluting an Arrhenius (line-of-centers) cross section functionality with the known distribution of reactants' relative kinetic energy (at each  $\bar{E}_{tr}$ ). The results of two separate series of experiments are displayed in Figure 1. This procedure leads to a total energy threshold for reaction of  $1.18 \pm 0.03$  eV. Since the endoergicity of the reaction is  $\Delta E_0^\circ = 1.15 \pm 0.01$  eV (using the recently reevaluated  $D_0(\text{HgI}) = 0.39 \pm 0.01$  eV<sup>3</sup>), this result implies an intrinsic activation barrier of  $0.03 \pm 0.03$  eV.

This study of the reactive scattering of Hg by  $\text{I}_2$  is an extension of previous work<sup>4</sup> in this laboratory, in which the elastic scattering of the same system was investigated. The apparatus is essentially unchanged. Briefly, it consists of a supersonic nozzle beam of Hg (1 Torr) seeded in a variable excess (70–150 Torr) of  $\text{H}_2$ , a crossed beam of iodine from a multichannel array source (363 K), and a rotatable (in-plane) detector, which includes a high efficiency electron bombardment ionizer, quadrupole mass filter, and a channel electron multiplier operated in the pulse-counting mode. The mercury atoms are accelerated to hyperthermal velocities (most-probable speed,  $v_{m.p.}$ , in the range 1200–1600 m s<sup>-1</sup>). The velocity distribution of each of the ten mercury beams was measured via the time-of-flight (TOF) technique with a beam monitor consisting of an electron bombardment ionizer and a quadrupole mass filter mounted opposite the nozzle beyond the main scattering chamber. The velocity distribution of the  $\text{I}_2$  ( $v_{m.p.} = 245$  m s<sup>-1</sup>) was measured with this monitor placed opposite the array. The distribution of relative kinetic energy is thereby experimentally determined for each value of  $\bar{E}_{tr}$  at which scattering is observed.

The angular distribution of the HgI scattered in the plane of the incident beams is measured at each experimental energy. The distributions are essentially isomorphic, exhibiting peaks at lab angles of about  $10^\circ$  with respect to the Hg beam. An-