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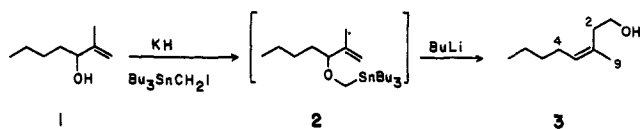*F. 38041 Grenoble Cedex, France*

A Highly Stereoselective Synthesis of Z-Trisubstituted Olefins via [2,3]-Sigmatropic Rearrangement. Preference for a Pseudoaxially Substituted Transition State

Sir:

Sigmatropic rearrangements of the [2,3] and [3,3] type are some of the most widely used reactions for the stereoselective preparation of di- and trisubstituted olefins.[1] Previous examples[2] of these reactions have led mainly to *E* olefins via cyclic transition states having the greatest possible number of pseudoequatorial substitutents. We have found, however, that this preference for transition states having pseudoequatorial substitution may not be as general as previously assumed. We report here a convenient and efficient [2,3]-sigmatropic Wittig rearrangement which produces *Z*-trisubstituted homoallylic alcohols in high yields and with ≥95% stereoselectivity. To the best of our knowledge this reaction is the first example of a [2,3]-sigmatropic rearrangement having a transition state which prefers pseudoaxial substitution.[3]

As outlined below, when the allylic alcohol **1** was deproto-

nated (KH, THF) and alkylated with iodomethyltributyltin[4] (30 min, 25 °C), the allyl stannylmethyl ether **2** (NMR (CCl₄) δ 4.80 (=CH₂, m), 3.45 (-OCH₂Sn, ABq, $\Delta\nu_{AB}$ = 27 Hz, J = 10 Hz), 3.30 (>CHO-, m)) was formed quantitatively.[5] Although this material could be isolated, direct treatment of the chilled reaction mixture with excess *n*-butyllithium resulted in tin/lithium exchange and smooth [2,3]-sigmatropic rearrangement (30 min, −78 °C) to the homoallylic alcohol **3** (>95% yield; NMR (CCl₄) δ 5.22 (=CH-, br t, J = 8 Hz), 3.56 (-CH₂OH, t, J = 8 Hz), 2.24 (=C(Me) CH₂-, t, J = 8 Hz), 1.69 (=CMe-, br s)). VPC (Carbowax) analysis showed **3** to be 96–97% one isomer and an examination by ¹³C NMR strongly suggested this isomer to be the *Z* one shown. This tentative assignment followed from the upfield[6] value (δ 34.4) of carbon 2 and a normal value (δ 21.6) for the relatively unhindered carbon 9.[7] Conformation was obtained by comparison with authentic *E* isomer **4** prepared by the method of Johnson.[8] Coinjection VPC and ¹H NMR showed that the minor isomer in **4** was identical with the major isomer in **3** and vice versa. Furthermore the ¹³C NMR of **4** showed a shielding pattern for

C-2 (δ 43.0) and C-9 (δ 16.0) which was opposite to that observed in the [2,3]-sigmatropic rearrangement product **3**. Thus the olefinic stereochemistry of our product may be unambiguously assigned as *Z*.

Aside from the obvious synthetic potential of this reaction, the transition-state geometry is of special interest. It is clear from the stereochemistry of **3** that transition state A having a pseudoaxial butyl substituent is strongly preferred over transition state B.[9] Since the stereoelectronics of the two
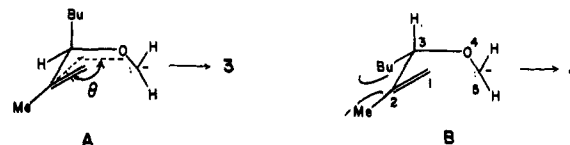

transition states are virtually identical, the observed preference for A implies that the steric interaction of the butyl substituent with the C-1 methylene is much less severe than the alternative butyl/vinyl methyl interaction in B. This state of affairs is understandable given the two reasonable assumptions that the transition state is very early[10] (C-1 is sp² and C-3 is sp³) and that the planes defined by C-1-C-2-C-3 and C-1-C-3-O-4-C-5 are not quite perpendicular (θ > 90°). A careful examination of the geometry of A reveals that, while the pseudoequatorial substituent (hydrogen in A) almost eclipses the methyl attached to C-2, the pseudoaxial substituent (butyl in A) is in fact rather far removed from the C-1 methylene.

Further support for our postulated transition-state geometry came from a study of the [2,3]-sigmatropic rearrangement of allylic ethers having different substitution patterns. If for example the vinyl methyl in **2** was replaced by hydrogen then the model above would predict a marked decrease in the selectivity for transition state A and thus for the *Z* product. When the allylic alcohol **5** was rearranged as above, a 40:60 mixture of homoallylic alcohols **6** and **7** (>95% yield) was obtained.[11,12]
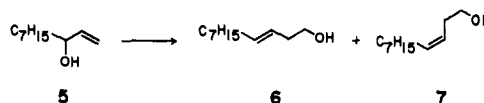
A similar result was found with the trans allylic alcohol **8**; a roughly 35:65 mixture of compounds **9** and **10** (96% yield) was produced. The cis allylic alcohol **11** on the other hand would be expected to strongly destabilize transition state A relative to B, and in fact rearrangement of **11** led exclusively to **9**: 91% yield; IR (neat) 965 cm⁻¹; NMR (CCl₄) δ 5.35 (-CH=CH-, J = 15 Hz).
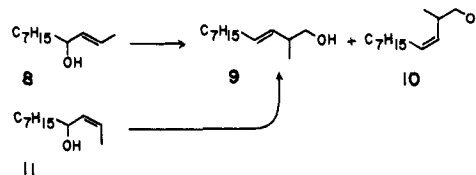

Synthetically the reaction has a number of interesting features. The rearrangement proceeds smoothly in cyclic systems so long as the β carbon is relatively unhindered. 2-Cyclohexenol for example was converted to the hydroxymethylcyclohexene **12** in 93% yield. The more hindered octalols **13** and **14** reacted


only sluggishly to yield mixtures of [1,2] and [2,3] rearranged products in low yield. It is also possible to trap the intermediate alkoxymethyllithium intermediates with reactive electrophiles prior to rearrangement. For that reaction the stannylmethyl ether (e.g., **2**) is first isolated and then transmetalated in a second step in the absence of strong chelating agents. Thus

addition of *n*-butyllithium to **2** at −78 °C (THF, 30 s) followed by immediate quenching with cyclohexanone produced **15**: 73% yield; IR (neat) 3400 cm^{-1}; NMR (CCl$_4$) δ 6.84 (=CH$_2$, br s), 3.55 (>CHO−, m), 3.03 (−OCH$_2$−, AB q, $\Delta\nu_{AB}$ = 20 Hz, J = 9 Hz), 1.62 (=CMe−, s).
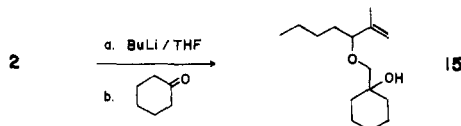
At this time the most useful aspect of the reaction seems to be its high stereoselectivity for Z-trisubstituted olefins. While a variety of natural products incorporate double bonds of this type, most trisubstituted olefin syntheses produce E isomers as the major products (see exceptions[13]).

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

Scheme I
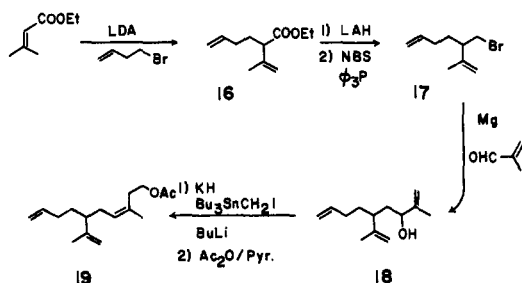
(LDA, THF/HMPA, −78 °C) with 4-bromobutene gave the β,γ-unsaturated ester **16** in 80% yield. Hydride reduction and NBS–phosphine bromination[15] then gave **17** (93% yield). Conversion to the Grignard reagent and reaction (Et$_2$O, −20 °C) with methacrolein proceeded in 52% yield and led to a mixture 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 °C) proceeded as usual. The product was chromatographed and acetylated (Ac$_2$O/pyr) to yield the racemic red scale triene **19** in 83% yield. VPC and NMR comparison with authentic material[16] showed our product to consist of 95–96% of the desired Z isomer.[17]

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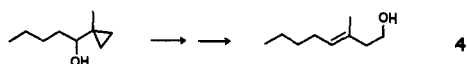
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## Concerning CH$_2$=C$^-$· and Its Reaction with ^{14}N^{15}NO

Sir:

In their paper entitled "Gaseous Anion Chemistry",[1] Smit and Field report than an ion of *m/e* 26 is always present in the negative ion CI spectrum of the bath gas which they used (N$_2$O/CH$_4$ 1:1). Their work with 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 CN$^-$ rather than C$_2$H$_2$$^-$·. We would point out that further evidence to support this view comes from the absence of a peak at *m/e* 40, most significantly with the sample 1-octyne where the *m/e* 26 intensity was enhanced. It is known that *m/e* 40, CH$_2$CN$^-$, is formed by the reaction of C$_2$H$_2$$^-$· with N$_2$O.[2] The route which was suggested to these authors to explain the formation of CN$^-$, namely:

$$C^-\cdot + N_2O \rightarrow CN^- + NO\cdot \qquad (1)$$
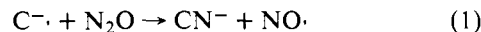
seems extremely attractive until it is recalled that Fehsenfeld and Ferguson[3] specifically did not observe the reaction under flowing afterglow conditions. Instead, they record that these collisions led to a rapid associative electron detachment reaction, but it was not known if the products of the reaction were CN· + NO· + e or N$_2$ + CO + e or something else.

The alternative composition for *m/e* 26, viz. C$_2$H$_2$$^-$·, has been observed in a number of independent laboratories.[4-7] MINDO/3 calculations[8] which have now been performed in our laboratory[9] predict electron affinities of 0 eV for CH$_2$=C: and −1.8 eV for HC≡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:

$$e + cis\text{-}CHF=CHF \rightarrow C_2HF^-\cdot + HF \qquad (2)$$
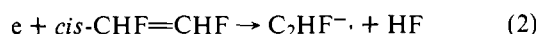
However, we have so far been unable to find any ionization of the isomeric 1,1-difluoroethylene. This divergence of behavior