to distinguish antipodes by mass spectrometry. There are indications that it is not necessary that the spectra of the unknown and those of the reference compounds are recorded using exactly the same mass spectrometer. Correct identifications have been obtained for spectra recorded by other mass spectrometers of the same design as the one used for the reference compounds.[14]

The potential of this new method for unequivocal identification of microgram amounts of stereoisomeric monosaccharides, which form part of the set of reference compounds, is demonstrated in these experiments. The method turned out to be reasonably fast: the total time for analysis is mainly determined by the necessary purification of the TMS derivatives and by memory effects in the mass spectrometer.

Although mixtures of TMS derivatives of monosaccharides can be fairly well separated by gas–liquid chromatography (glc), a straightforward glc identification of monosaccharides may sometimes meet with difficulties, particularly when the mixtures are composed of a large number of different monosaccharides with extreme variations in concentration. Experiments are in progress to test the value of an on-line operating glc–mass spectral computer system for analyses of monosaccharide mixtures.

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[14] We processed, for instance, the literature[7] spectrum of TMS-α-D-glucose (recorded with an AEI MS 902) as well as spectra recorded with our AEI MS 9; in both cases correct identifications have been obtained. The applicability of the identification method under different instrumental conditions and using other types of mass spectrometers will be further investigated.

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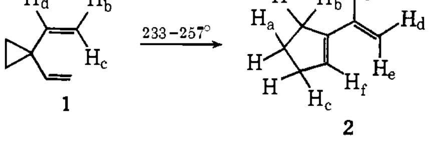
## Thermal Reorganization of 1,1-Divinylcyclopropane

*Sir:*

1,1-Divinylcyclopropane was synthesized from cyclopropane-1,1-diacetic acid[1] *via* sequential (1) reduction by $LiAlH_4$, (2) tosylation, and (3) elimination using potassium *tert*-butoxide in DMSO at 26°. The overall yield for the process was ~45%. The structure of **1**

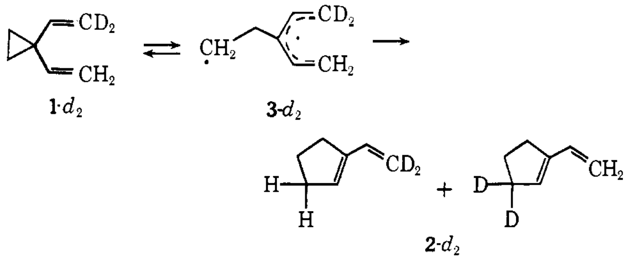


was verified by its nmr, ir, and mass spectra and analysis. The nmr ($CCl_4$) showed a sharp singlet at δ 0.79 ppm (4 H) as well as doublets at 4.89 ($J_{bd} = 9.5$, $J_{bc} = 1.7$ Hz, 2 H), 4.91 ($J_{cd} = 18$, $J_{bc} = 1.7$ Hz, 2 H), and 5.78 ppm ($J_{bd} = 9.5$, $J_{cd} = 18$ Hz, 2 H); the ir spectrum showed strong peaks at 1670, 1000, and 808 $cm^{-1}$ and the mass spectrum at *m/e* 94 (P), 79 (base), 77, and 39.

**1** could be converted quantitatively at temperatures above 230° to 1-vinylcyclopentene:[2,3] nmr, a broad doublet at δ 1.93 (2 H), a broad multiplet at 2.30–2.50 (4 H), doublets at 4.94 ($J_{dg} = 9.5$, $J_{de} < 2$ Hz, 1 H) and 4.96 ($J_{eg} = 18$, $J_{de} < 2$ Hz, 1 H), a broad singlet at 5.62 (1 H), and a doublet of doublets at 6.48 ppm ($J_{dg} = 9.5$, $J_{eg} = 18$ Hz, 1 H); ir, strong peaks at 2980, 990, and 902 $cm^{-1}$; uv, $\lambda_{max}$ 233 $m\mu$ (ε 22,400).

The activation parameters for this reaction were determined in benzene solution using a temperature range of from 233 to 257°:[4] $E_a = 39.6 \pm 1$ kcal/mol; $\log A = 12.57$; $\Delta H^{\ddagger} = 38.6 \pm 1$ kcal/mol and $\Delta S^{\ddagger} = -2.8 \pm 4$ cal/deg. These results indicate that the addition of a *second* vinyl groups lowers the activation energy for the vinylcyclopropane → cyclopentene rearrangement by ~11–12 kcal/mol. The fact that one observes an activation energy lowering almost equal to that due to the presence of the first vinyl group (~14 kcal/mol)[5,6] could be construed as being consistent with either a concerted process or the intermediacy of a diradical species in the reaction.

Our earlier work on the (2 + 2) cycloadditions of 1,1-dideuterioallene[9] indicated that the product-forming cyclization process of an intermediate diradical can give rise to a significant normal secondary deuterium isotope effect. In a similar manner, the intermediacy of a diradical **3** in the conversion of **1** → **2** was probed utilizing the dideuterated and tetradeuterated species **1**-$d_2$ and **1**-$d_4$. Using quantitative integrations of **2**-$d_2$, the value of the *intramolecular* isotope effect for the reaction was determined to be: $(k_H/k_D)_{intra} = 1.07 \pm 0.02$.[10] The intermolecular



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[1] B. Chamboub, Y. Etienne, and R. Pallond, *C. R. Acad. Sci.*, 536 (1962).

[2] S. F. Birch, R. A. Dean, N. J. Hunter, and E. W. Whitehead, *J. Org. Chem.*, 20, 1178 (1955).

[3] The reaction was carried out in sealed tubes, both in the gas phase and as a dilute benzene or pentane solution.

[4] Rate constants were determined by glpc using benzene as solvent and pentane as internal standard. Least-squares analyses were performed to obtain the best fit of the data.

[5] For a review of the vinylcyclopropane rearrangement, see: C. D. Gutsche and D. Redmore, "Carbocyclic Ring Expansion Reactions," Academic Press, New York, N.Y., 1968, p 163.

[6] These values may be compared with the values of $E_a = 42.7$ and $\log A = 14.76$ for the geometrical isomerization of spiroheptadiene (4).[7,8]

4 4′

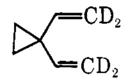
[7] R. G. Bergman, as quoted in M. R. Willcott, R. L. Cargill, and A. B. Sears, *Progr. Phys. Org. Chem.*, 9, 50 (1972).

[8] J. M. E. Krekels, J. W. de Haan, and H. Kloosterziel, *Tetrahedron Lett.*, 275 (1970).

[9] W. R. Dolbier, Jr., and S. H. Dai, *J. Amer. Chem. Soc.*, 90, 5028 (1968).

[10] This value is an average derived from five independent determinations, with the error being expressed as standard deviation.

isotope effect was taken as the rate ratio of **1**/**1**-$d_4$ at 242°:[4] $(k_H/k_D)_{inter} = 1.08 \pm 0.07$.



1-$d_4$

While the identity of the two secondary isotope effects *could* be interpreted as deriving from a common transition state for the rate-determining and the product-forming steps, and this may be equated with the process being concerted, we do *not* favor this explanation. Most importantly, the preponderant weight of analogy insists that a rate-determining process, in which an sp$^2$ carbon is transformed into an sp$^3$ carbon, should be associated with an *inverse* kinetic secondary deuterium isotope effect.[9,11] It is difficult to conceive a single transition-state process which can simply account for the nature of the observed isotope effect. Nevertheless, due to a general paucity of isotope effect data for similar reactions, it is presently not possible to definitively rule out a concerted mechanism.

Presently, in light of all past analogy, we tend to favor the interpretation of the results as indicating a multistep process. In this case, there are two possible pathways, rate-determining diradical formation or rate-determining diradical destruction.

In the former situation, there is some analogy that a normal intermolecular isotope effect is to be expected for the conversion, sp$^2$ → radical,[13-15] in which case our observed intermolecular effect could derive from rate-determining formation of diradical **3**, and our observed intramolecular effect, while being relatively small,[9,15] can be understood as deriving from the product-forming destruction.

In the latter situation, a preequilibrium formation of diradical **3** would result in the rate-determining and product-forming transition states being one and the same, and thus the two isotope effects should be near identical and resembling in value those ordinarily observed for diradical cyclizations.[9,15]

Secondary deuterium isotope effects have not generally been applied to mechanistic studies of thermal rearrangements. It is our feeling that they may indeed be useful in probing the intricacies of the energy surfaces of such reactions and may provide insight as to the relationships between diradicals generated from cycloaddition processes and these generated in thermal rearrangements. We are presently involved in further studies which we hope will increase our understanding of secondary deuterium isotope effects and enhance their viability as a probe in distinguishing one- and two-step mechanisms.

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[11] The only possible exception to this general observation is the as-yet anomalous ketene–styrene [2 + 2] study of Baldwin.[12] It is difficult to relate his results to our work at present.

[12] J. E. Baldwin and J. A. Kapecki, *J. Amer. Chem. Soc.*, **91**, 3106 (1969).

[13] J. E. Baldwin and R. Fleming, *Fortsch. Chem. Fortsch.*, **15**, 281 (1970).

[14] W. A. Pryor and R. W. Henderson, *Int. J. Chem. Kinet.*, in press; we thank Professor Pryor for allowing us to read his manuscript prior to publication.

[15] S. H. Dai and W. R. Dolbier, *Jr.*, *J. Amer. Chem. Soc.*, in press.

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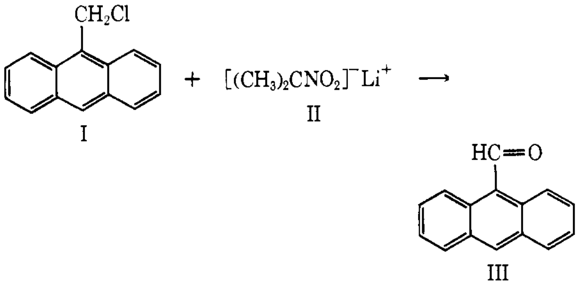
## A New Type of Substitution at a Saturated Carbon Atom

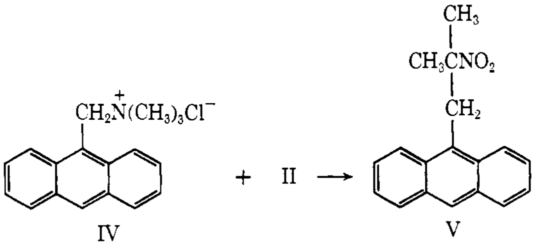
*Sir:*

We describe a new type of substitution which occurs at a saturated carbon atom attached to the anthracene nucleus and which, presumably, will be observed with other polycyclic derivatives and related heterocycles.

Nitroparaffin salts ordinarily undergo oxygen alkylation on treatment with benzylic halides;[1] it is not surprising, then, that when 9-chloromethylanthracene (I) is treated with the lithium salt of 2-nitropropane (II) in hexamethylphosphoramide (HMPA) at 25° an 85% yield of 9-anthraldehyde (III) is obtained (eq 1). In sharp contrast, when the quaternary ammonium salt IV reacts with the lithium salt of 2-nitropropane (II) a 90% yield of the pure carbon alkylate V is produced (eq 2).



(1)



(2)

If the reaction of eq 2 is carried out using less than a stoichiometric amount of the nitroparaffin salt a new compound VI, isomeric with the carbon alkylate V, can be isolated;[2] this new compound is rapidly and quantitatively isomerized to V on treatment with the lithium salt of 2-nitropropane (eq 3) and clearly is an intermediate in the carbon alkylation reaction.

The isomerization process described by eq 3 is not intramolecular; for, if instead of II, the salt of 2-nitrobutane is used, then the alkylated 2-nitrobutane VII is obtained in 89% yield (eq 4). Thus, carbon alkylation (eq 2) occurs in stages: in the first the intermediate VI

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[1] L. Weisler and R. W. Helmkamp, *J. Amer. Chem. Soc.*, 67, 1167 (1945); H. B. Hass and M. L. Bender, *ibid.*, 71, 3482 (1949).

[2] Satisfactory elemental analyses and nmr and ir spectra were obtained for all new compounds.