hydrogen bonds. To our knowledge no case of a tetrasubstituted diaminosulfene is known with the exception of an unusual sulfene-like salt.[29] It remains to be seen whether the stability of aminosulfenes and similarly substituted cases is largely a consequence of hydrogen bonding or can be supported by the electronic factors outlined in Table I.

Acknowledgments.—We are grateful to the NATO Research Grants Program for partial funding of the work and to Professor David N. Harpp (McGill University) for hospitality and stimulation. Professor Martin Ettlinger (Copenhagen University) kindly drew our attention to the thiourea dioxide literature.

[29] E. Lindner and H. Weber, *Justus Liebigs Ann. Chem.*, **101**, 2832 (1968).

[30] Camille and Henry Dreyfus Teacher-Scholar Grant Recipient, 1971–1976.

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RECEIVED JULY 27, 1973

Photochemistry of Epoxy Olefins. II.[1] The Photosensitized Geometric Isomerization and Rearrangement of the Isomeric 4,5-Epoxy-2-hexenes

Summary: The isomeric monoepoxides of 2,4-hexadiene undergo geometrical isomerization of both the epoxy and olefinic moieties as well as rearrangement to *cis*- and *trans*-4-hexen-2-one when irradiated in acetone solution at 3000 Å.

Sir: In a continuation of our studies of the photochemistry of 3,4-epoxy olefins,[1] we have investigated the acetone-sensitized photolysis of the stereoisomers of 4,5-epoxy-2-hexene. The major results are outlined in Scheme I while representative data are shown in Table I. Photolysis of either **5** or **6** in acetone gives an equilibrium mixture of 55% **5** and 45% **6**. The same equilibrium values are obtained upon prolonged irradiation of **1**, **2**, **3**, or **4**.

SCHEME I
PHOTOCHEMICAL INTERCONVERSIONS

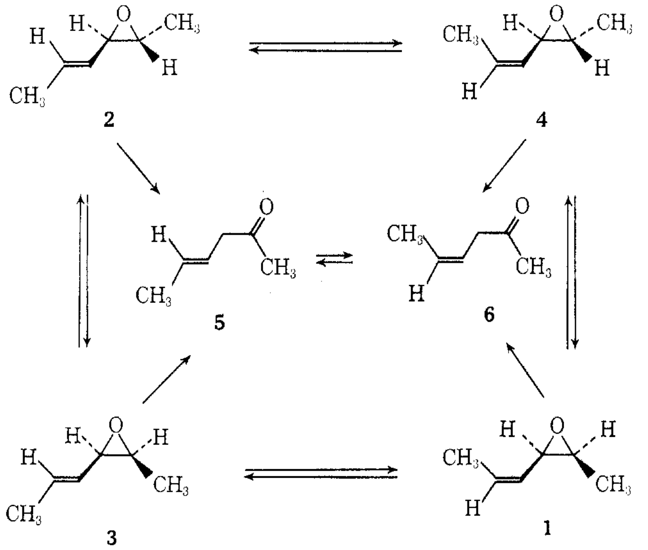

TABLE I

Substrate	Photolysis products,[a] %					
	1	**2**	**3**	**4**	**5**	**6**
1	12	13	6	17	25	27
2	3	12	2	12	37	34

[a] Photolyses were carried out in acetone solutions using a 450-W Hanovia medium-pressure mercury lamp equipped with a Pyrex filter. Values given are per cent of volatile product after irradiation of 0.6 g in 125 ml of acetone for 2.5 hr. The analyses were carried out by gas chromatography on a Carbowax 20M column. The products were identified by direct comparison with authentic samples.

The most striking feature of this work is the very facile geometric isomerization of the epoxide moieties. In their photochemical studies of phenyl-substituted oxiranes, Griffin and Trozzolo[2] did not observe any isomerization of epoxide isomers. Geometric isomerization of epoxides has been observed photochemically only in the case of the α,β-epoxy ketone system.[3]

In Scheme II are shown two possible modes of epoxide geometrical isomerization with the asterisk indicating either ionic or radical centers. Thermal and Lewis acid catalysis of the epoxides was investigated to determine if ground electronic state ionic or radical intermediates would also produce geometrical isomerization of the epoxides. Both thermolysis and Lewis acid catalysis (Table II) gave the same ketones which are ob-

SCHEME II

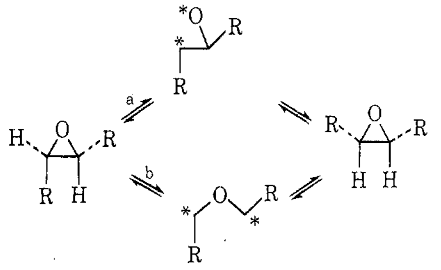

TABLE II
LEWIS ACID AND THERMAL CATALYZED REARRANGEMENTS

Substrate	Temp, °C	Products (%)		
1[a]	25	**1** (0)	**5** (98)	**6** (2)
2[a]	25	**2** (0)	**5** (40)	**6** (60)
1[b]	200	**1** (89)	**5** (trace)	**6** (5)
1[b]	250	**1** (68)	**5** (2)	**6** (26)
1[b]	300[c]	**1** (9)	**5** (20)	**6** (64)
2[b]	200	**2** (88)	**5** (9)	**6** (0)
2[b]	250	**2** (64)	**5** (32)	**6** (0)
2[b]	300[c]	**2** (4)	**5** (47)	**6** (21)

[a] Rearrangement induced by treating substrate with MgI_2 in ether as described by N. Heap, G. E. Green, and G. H. Whitham, *J. Chem. Soc. C*, 1525 (1969). [b] The pyrolyses were carried out (15 min) in sealed Pyrex ampoules using 20 mg of substrate. Less than 1% of the epoxide isomers could have been detected if present. [c] At 300° and above several unidentified products were obtained.

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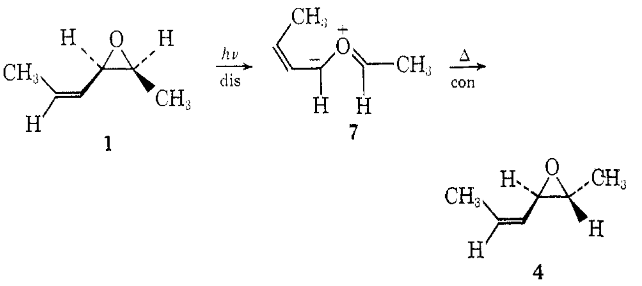
[1] For the previous paper in this series, see D. R. Paulson, G. Korngold, and G. Jones, *Tetrahedron Lett.*, 1723 (1972).

[2] T. Do-Minh, A. M. Trozzolo, and G. W. Griffin, *J. Amer. Chem. Soc.*, **92**, 1402 (1970), and references contained therein.

[3] C. K. Johnson, B. Dominy, and W. Reusch, *J. Amer. Chem. Soc.*, **85**, 3894 (1963).

tained photochemically. However, we failed to observe any geometrical isomerization of the epoxides under either conditions. The thermal rearrangements could be occuring by a radical path or by an ionic catalyzed wall reaction. In the photolysis these ketones are generated by a 1,2-hydrogen atom shift. Radical 1,2 shifts occur rarely, if at all, and they are symmetry forbidden.[4] However, 1,2-radical migrations might indeed be quite favorable starting from a 1,3 diradical since the energy gained from concurrent formation of the carbonyl group may overcome the orbital symmetry considerations.

In view of the failure of C–O bond opening by both ionic or thermal (Table II) conditions to produce any epoxide isomerization and the demonstrated formation of carbonyl ylides in the photochemistry of aryl-substituted epoxides,[5] it is tempting to assign the intermediate in pathway "b" (Scheme II) to a carbonyl ylide. Similar carbonyl ylides have also been generated thermally.[6] In the present case isomerization could be explained by a photochemically allowed disrotatory ring opening followed by a thermally allowed conrotatory ring closure as shown below for the conversion of 1 to 4. However, a carbonyl ylide intermediate (*i.e.*, 7) seems unlikely for several reasons. Photolysis of 1 in acetone solutions containing various amounts of dimethyl acetylenedicarboxylate (an efficient carbonyl ylide trapping agent[6]) at 25 or at −78° failed to produce any adduct of a carbonyl ylide. The only effect of the trapping agent was to slightly decrease the rate of product formation. Secondly, if 7 were generated in the photolysis of 1, it seems highly likely that ring closure to a 4,5-dihydrofuran would occur. We could find no evidence for any dihydrofuran formation at 25 or at −78°. The only effect of low temperature was to slow the rate of reaction. For example, the formation of 5 and 6 was ~1.5 times as slow at −78° as at 25°. However, the overall results were identical. Thermolysis of epoxide 1 in the presence of dimethyl acetylenedicarboxylate also failed to trap any carbonyl ylide intermediate.



The photochemical reactions described here are most likely triplet sensitized processes resulting from energy transfer from triplet state acetone. Supporting evidence for this is found in that the reactions are efficiently quenched by piperylene. The cis–trans isomerization of the olefinic functionality of the epoxides and the β,γ-unsaturated ketones are most likely analogous to the well-studied triplet sensitized isomerizations of alkenes. A very inefficient photoisomerization of 5 and 6 by direct irradiation has been observed.[7] More recently Engel has reported an example of acetone sensitized cis–trans isomerization of a β,γ-unsaturated ketone.[8] Thus the formation of 5 in the photolysis of 1 and 4 and the formation of 6 in the photolysis of 2 and 3 are due in part to photoisomerization of the enones.

From the results presented here it is clear that, whether the epoxide isomerization occurs *via* a carbonyl ylide which is too short lived to be trapped or *via* an initial C–O bond cleavage, the intermediate is able to undergo reversible ring closure. We currently favor pathway "a" in Scheme II with homolytic bond cleavage, but any of several ionic pathways can not be ruled out at this time. The mode of formation of the β,γ-unsaturated ketones was discussed in a previous paper.[1]

We are currently investigating the nature of the intermediate responsible for the epoxide isomerization as well as extending our studies to nonconjugated epoxy olefins.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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[4] M. J. Perkins in "Organic Reaction Mechanisms, 1968," B. Capon and C. W. Rees, Ed, Interscience Publishers, London, 1969, p 293.

[5] D. R. Arnold and L. A. Karnischky, *J. Amer. Chem. Soc.*, 1404 (1970); see also ref 2.

[6] H. Hamberger and R. Huisgen, *Chem Commun.*, 1190 (1971); A. Dakmen, H. Hamberger, R. Huisgen, and V. Markowski, *ibid.*, 1192 (1971).

[7] H. Morrison, *Tetrahedron Lett.*, 3653 (1964).

[8] P. S. Engel and M. A. Schnexnayder, *J. Amer. Chem. Soc.*, **94**, 9252 (1972).

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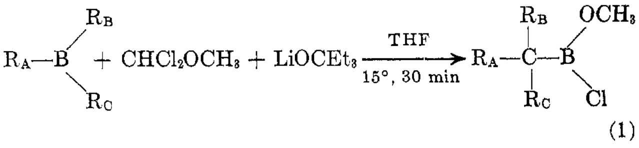
RECEIVED JULY 31, 1973

The Facile Transfer of Tertiary Alkyl Groups from Boron to Carbon in the Base-Induced Reaction of α,α-Dichloromethyl Methyl Ether with Organoboranes Containing Tertiary Alkyl Groups. A Novel Route to Highly Hindered Trialkylcarbinols Involving Exceptionally Mild Conditions

Summary: Trialkylboranes containing tertiary alkyl groups, such as *tert*-butyl and thexyl (2,3-dimethyl-2-butyl), undergo rapid reaction with α,α-dichloromethyl methyl ether and lithium triethylcarboxide at 25° to give the corresponding highly branched trialkylcarbinols after oxidation. B–C migration of the tertiary group occurs under exceedingly mild conditions without isomerization.

Sir: Treatment of relatively hindered trialkylboranes containing a tertiary alkyl group with α,α-dichloromethyl methyl ether (DCME) and lithium triethylcarboxide under mild conditions (25°) results in the transfer of all three groups from boron to carbon without rearrangement (eq 1). The product can then be



$$R_A{-}\overset{R_B}{\underset{R_C}{B}} + CHCl_2OCH_3 + LiOCEt_3 \xrightarrow[15°,\ 30\ \text{min}]{\text{THF}} R_A{-}\overset{R_B}{\underset{R_C}{C}}{-}\overset{OCH_3}{\underset{Cl}{B}} \qquad (1)$$

R_A = *tert*-butyl, thexyl (2,3-dimethyl-2-butyl)