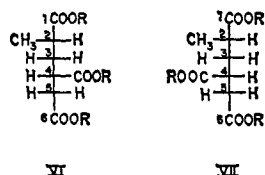that the ester of the optically active acid from degradation does *not* undergo Dieckmann cyclization under conditions which bring about ready conversion of the racemic ester to V. This striking contrast can only be rationalized on the basis that the optically active $C_8H_{12}O_6$ acid initially obtained by degradation is diasteromeric with that resulting from subsequent base-catalyzed equilibration of the corresponding ester, followed by hydrolysis; indeed, consideration of steric factors in the transition states for Dieckmann cyclizations of the diastereomers VI (R = Me) and VII (R

XI   XII

= Me) strongly suggests that serious crowding may impede the formation of a cyclopentanone from VI (R = Me). These considerations permit the tentative assignment of the 2S,4S configuration (VI, R = H) to the optically active acid derived from magnamycin by degradation, and the 2S,4R (2R,4S) configuration (VII, R = H) to the acid obtained from VI by isomerization and by synthesis.

The facts set down above clearly provided occasion for concern with respect to our conclusion *vis-à-vis* the relationship of the C_8 acid, now confirmed as III, and the C_{13} acid IV, based as this conclusion was on our failure to observe cyclopentanone formation from an acid which might be formulated as VI (-CH₂CH₂CH₃ in place of COOR at C-4), and therefore fall in a class, one member of which had now been shown to be very resistant to cyclization. Obviously the alternative (VIII) deserved renewed consideration as the structure

VIII
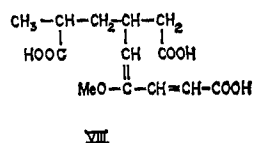
of the C_{13} acid. Examination of the nuclear magnetic resonance spectrum (60 Mc., CCl_4 solution) of the trimethyl ester [b.p. 115–120° (10⁻⁵ mm.); λ_{max} 263 mμ (ϵ 24,300). *Anal.* Calcd.: C, 58.52; H, 7.37; OMe, 37.80. Found: C, 58.65; H, 7.42; OMe, 37.51] of the C_{13} acid revealed at once that structure VIII is correct; sharp bands are present at 420, 405, 359, 344, 312, and 302 c.p.s. downfield from the tetramethylsilane reference band. All these bands are clearly associated with olefinic protons, and the lower field symmetrical quartet must be assigned to the α and β hydrogens of the *trans* -CH=CH- system. Consequently, the remaining *doublet* arises from the hydrogen of the -CH=C(OMe)- group, *which must be adjacent to a methine grouping, as in VIII, and not to a methylene grouping, as in IV.*

The change (IV → VIII) in the structure of the C_{13} acid requires only that the C-9–C-7 bond in the previously proposed structure (I) for magnamycin be replaced by a C-9–C-6 bond, as in II; none of the other elements of the original structural argument is affected by the required modification in the structure of the degradation product. It is of much interest that

the new structure suggests the introduction of a succinic acid unit into the main chain of the macrolide nucleus at C-6 → C-5, in place of the more common acetic acid or propionic acid unit, in the biogenesis of magnamycin, particularly in the light of the observed effective incorporation of succinic acid.[6,7]

R. B. Woodward, Larry S. Weiler, P. C. Dutta
Converse Memorial Laboratory, Harvard University
*Cambridge, Massachusetts 02138*

The Reactions of Carbon Atoms with Saturated Hydrocarbons

Sir:

We have reported[1-3] our studies on the reactions of carbon atoms with olefinic substrates. We now report on the extension of these studies to include reactions with saturated hydrocarbons.

The reaction system used was as described earlier[4]; reactions occur in condensed phase at liquid nitrogen temperature. Analysis was done by vapor phase chromatography, products being identified by isolation and comparison of their infrared and mass spectra with those of known materials.

The reaction of carbon atoms with 2-methylpropane yields two products which have added a carbon atom, 1,1-dimethylcyclopropane and 2-methylbutane.

38% (relative yields)   62%
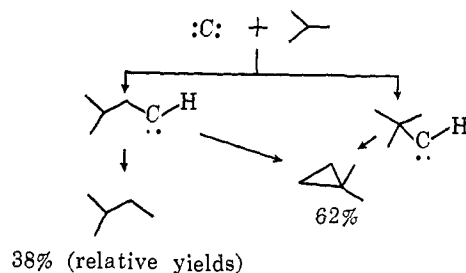
The initial reaction is postulated to be insertion on either the tertiary or a primary carbon–hydrogen bond, giving the intermediate free carbenes shown. Either carbene can undergo intramolecular insertion to give the 1,1-dimethylcyclopropane. The isobutylcarbene can abstract hydrogens from the surrounding 2-methylpropane (~1000-fold molar excess over carbon atoms and molecules) to produce 2-methylbutane. Isomeric octanes resulting from coupling of radicals thus produced were isolated. *Neither 2-methylpropene nor acetylene was formed.*
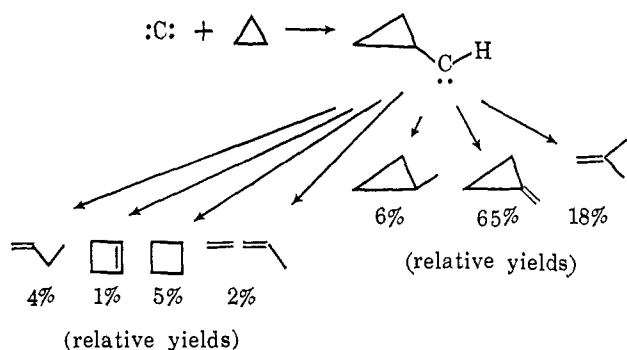
The reaction of carbon atoms with cyclopropane gave as the major product methylenecyclopropane (65%). This can be described as resulting from initial insertion on a carbon–hydrogen bond followed by hydrogen migration. Evidence is not available to define a mechanism for the formation of the hydrogenated products.

(1) P. S. Skell and R. R. Engel, *J. Am. Chem. Soc.*, **87**, 1135 (1965).
(2) P. S. Skell and R. R. Engel, *ibid.*, **87**, 1135 (1965).
(3) P. S. Skell and R. R. Engel, *ibid.*, **87**, 2493 (1965).
(4) P. S. Skell, L. D. Wescott, Jr., J-P. Golstein, and R. R. Engel, *ibid.*, **87**, 2829 (1965).

$$:C: + \triangle \longrightarrow \triangle\!\!\!-C\substack{H \\ \cdot\cdot}$$

6%   65%   18%

(relative yields)

4%   1%   5%   2%

(relative yields)

There were also isomeric C_6 materials, presumably radical coupling products, but *no* acetylene was formed. This is unlike the reactions of 2-methylpropane and cyclopropane with carbon atoms produced by nuclear processes where acetylene is formed to the extent of 21.2 and 42.7%, respectively, in oxygen-scavenged systems.[5]

Using the time-delay technique as previously described,[3] it was determined that all products were resulting from reactions of the ^1S state of carbon. In studies where ^1D and ^3P species only were present no products were formed. This conclusion is also supported by the low absolute yields obtained in these reactions, being $\sim35\%$ of the yields in the reactions with olefins. It was previously determined[2] that $\sim40\%$ of the carbon species generated with these arc conditions were in the ^1S state.

The insertion of singlet carbon atoms into C–H bonds of paraffin hydrocarbons produces monoalkyl-

(5) A. P. Wolf, *Advan. Phys. Org. Chem.*, 2, 202 (1964).

carbenes as intermediates. These carbenes are generated in a dilute paraffin hydrocarbon matrix and are thus subject to minimum solvation and efficient relaxation of vibrational excitation. It will be interesting to compare the behavior of these "free carbenes" with the "carbenes" produced by other procedures, photolyses of diazo compounds, α-eliminations of HX by bases, etc., where solvation of the vacant orbital sites by good Lewis bases may be important. Cyclopropyl- and *t*-butylcarbenes have been generated,[6,7] and the product compositions differ significantly from those obtained in carbon atom insertions. Because the comparisons are made with data from widely different temperatures, caution should be used in their interpretation. Further work may cast light on this problem.

Conservation of spin during ^1S insertions implicates singlet-state alkylcarbene intermediates, probably with higher energies than those obtained from photolyses of diazo compounds.

(6) L. Friedman, H. Shechter, J. Smith, and J. Bayless, *J. Am. Chem. Soc.*, 87, 659 (1965).

(7) W. Kirmse and B. von Wedel, *Ann.*, 666, 1 (1963).

(8) National Science Foundation Cooperative Graduate Fellow, 1963–1966.

R. R. Engel,[8] P. S. Skell

Department of Chemistry, The Pennsylvania State University
University Park, Pennsylvania

Book Reviews

Silicate Science. Volume 1. Silicate Structures. By WILHELM EITEL, Institute for Silicate Research, University of Toledo, Toledo, Ohio. Academic Press Inc., 111 Fifth Ave., New York, N. Y. 1964. xii + 666 pp. 17.5 × 25 cm. $21.00, subscription; $24.00, regular.

Professor Eitel has compiled a comprehensive set of correlated abstracts of the literature related to silicates from 1954 to 1964. The subject matter is meticulously classified and is keyed to his "The Physical Chemistry of Silicates" of 1954 by selected references to older work.

About one-third of the work is devoted to silicate crystal structures, a separate section treats clay minerals, and about half is devoted to colloidal aspects of silicate dispersoids. Something near 2000 references are cited, and more than 2000 authors appear in the author index. About 400 illustrations are excerpted from the original sources.

The crystal structure references are arranged according to the Bragg and the Belov schemes. Frequent cross references and multiple citations provide continuity, and the reader is frequently aided by critical annotations. Less frequently, somewhat unorthodox contributions are merely abstracted without comment. The separated sectioning for clay minerals reflects the lesser degree of authenticity inherent in interpretations often necessarily based on inadequate or incomplete data.

The achievement of continuity in the more highly diversified catalog of the colloid chemical literature has obviously been the greater problem. It seems true in many instances that the information cited only calls attention to the nature of the work cited, and the conclusion. It will be required that the reader refer to the original work for full understanding of the formulas and the selected illustrations of data presented.

The greatest value of the book will be that it collects under one cover keys to ten prolific years of literature which could otherwise be surveyed by interested research personnel only by prohibitively intensive library searches. Volume 1 will be followed by four more volumes covering glasses, enamels, and slags; phase-rule phenomena; hydrothermal silicate systems; and ceramics and Portland cements.

W. F. Bradley

Department of Chemical Engineering
University of Texas, Austin, Texas