

was produced rapidly. After 1 hr at -70° , 1.40 g (0.01 mole) of VIII⁹ was added, and the orange solution was allowed to warm over 3 hr to -20° and then stored at that temperature for 12 hr. Addition of water, extraction with pentane, and distillation afforded 1.32 g (72.5%) of pure methyl *trans*-chrysanthemate, bp $90-92^{\circ}$ (12 mm), infrared absorption at 1720 cm^{-1} (C=O), nmr peaks at 1.11 and 1.25 ppm due to *gem*-dimethyl groups attached to the cyclopropane ring, 1.69 and 1.71 ppm (6 H) due to the isopropylidene protons, 1.38 (doublet, $J = 5$ cps) and 2.05 ppm (multiplet) (1 H each) due respectively to the protons α and β to the carbomethoxy group, 3.65 ppm (COOCH₃), and 4.89 ppm (1 H, olefinic proton). Hydrolysis of the methyl ester with alkali afforded (\pm)-*trans*-chrysanthemic acid, mp $46-47^{\circ}$ (lit.^{10a} $46-48^{\circ}$).

The synthetic method described herein provides a simple route to many substances hitherto accessible only by lengthy or complicated syntheses. It should be especially useful in the field of isoprenoid synthesis; for example, it provides a simple approach to the structure proposed for the sesquiterpenoid ketone aristolone (X).¹² The other known direct approaches to *gem*-dimethylcyclopropane structures appear to be complementary to the route *via* I; these include the use of the reagent from chromous salts and 2,2-dibromopropane¹³ and the replacement of bromine in *gem*-dibromocyclopropanes by methyl using lithium dimethylcopper complex.¹⁴

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1,3 Eliminations. I. Stereochemical Considerations and Terminology¹

Sir:

Three-membered rings are formed by net 1,3 eliminations under a variety of circumstances.² In a five-atom

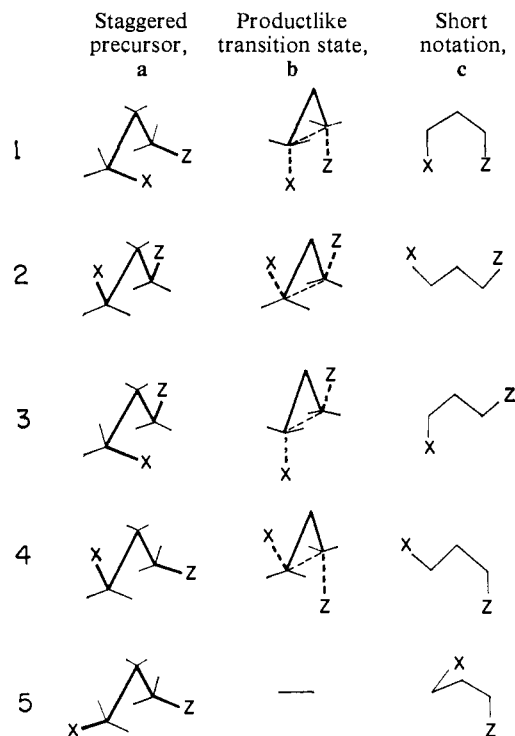
(1) Supported by the National Science Foundation and the Petroleum Research Fund (administered by the American Chemical Society).

(2) (a) Solvolyses: S. Winstein, E. Clippinger, R. Howe, and E. Vogelfanger, *J. Am. Chem. Soc.*, **87**, 376 (1965); (b) deaminations: G. J. Karabatsos, R. A. Mount, D. O. Rickter, and S. Meyerson, *ibid.*, **88**, 5651 (1966); A. T. Jurewicz and L. Friedman, *ibid.*, **89**, 149 (1967); A. A. Aboderin and R. L. Baird, *ibid.*, **86**, 2300 (1964); P. S. Skell and I. Starer, *ibid.*, **82**, 2971 (1960); M. S. Silver, *ibid.*, **82**, 2971 (1960); (c) Bamford-Stevens reactions: F. Cook, H. Schechter, J. Bayless, L. Friedman, R. L. Folz, and R. Randall, *ibid.*, **88**, 3870 (1966); A. Nickon and N. H. Werstiuk, *ibid.*, **88**, 4543 (1966); K. B. Wiberg and J. M. Lavanish, *ibid.*, **88**, 5272 (1966); (d) deoxidations: P. S. Skell and I. Starer, *ibid.*, **81**, 4117 (1959); P. S. Skell and R. J. Maxwell, *ibid.*, **84**, 3963 (1962); (e) pyrolyses: R. C. Bicknell and A. Maccoll, *Chem. Ind. (London)*, 1912 (1961); W. Huckel and H.-J. Kern, *Ann.*, **687**, 40 (1965); G. Komppa and R. H. Roschier, *ibid.*, **429**, 175 (1922); J. McKenna and J. B. Slinger, *J. Chem. Soc.*, 2759 (1958); F. M. Sonnenberg and J. K. Stille, *J. Org. Chem.*, **31**, 3441 (1966); (f) Favorskii reactions: G. Stork and I. J. Borowitz, *J. Am. Chem. Soc.*, **82**, 4307 (1960); H. O. House and W. F. Gilmore, *ibid.*, **83**, 3980 (1961); H. O. House and H. W. Thompson, *ibid.*, **28**, 164 (1963); H. O. House and G. A. Frank, *J. Org. Chem.*, **30**, 2948 (1965); N. J. Turro and W. B. Hammond, *J. Am. Chem. Soc.*, **87**, 3258, (1965); E. E. Smitsman, T. L. Lemke, and O. Kristiansen, *ibid.*, **88**, 334 (1966); (g) Ramberg-Bäck-

system X-A-B-C-Z, independent rotation about the A-B and B-C bonds gives rise to numerous conformations, and for concerted loss of X and Z to form a three-membered ring it has not been established whether any of these conformations are favored over others.³

If we consider only staggered conformations for the precursor (or for a transition state that resembles precursor) five distinct arrangements (1a-5a, Chart I) of X and Z exist, whereas four arrangements (1b-4b) are possible for a transition state that resembles the cyclopropyl ring. The simple nonperspective notation 1c-5c delineates adequately the five relevant atoms of the precursor or of its corresponding transition state. We propose the following terminology for concerted 1,3 eliminations, to be used whether the transition state resembles staggered precursor or cyclopropyl product: 1 = U; 2 = W; 3 = *exo*-Sickle; 4 = *endo*-Sickle; 5 = *apo*-Sickle.⁴ The same nomenclature can be used for cyclopropyl ring cleavages that are the microscopic reverse of 1,3 eliminations. In the present context *exo* and *endo* refer to Z, which is defined to be of greater electronegativity than X. Commonly X is hydrogen,

Chart I. Concerted 1,3 Eliminations and Cyclopropane Ring Cleavages



land reaction: N. P. Neureiter and F. G. Bordwell, *ibid.*, **85**, 1209 (1963); (h) reactions of sulfoxides: R. Baker and M. J. Spillett, *Chem. Commun.*, 757 (1966); (i) heterogeneous reactions: H. Pines and C. N. Pillai, *J. Am. Chem. Soc.*, **82**, 2921 (1960); (j) quaternary ammonium compounds: C. L. Bumgardner, *J. Org. Chem.*, **29**, 767 (1964); ref 3a; (k) α -lactams: H. E. Baumgartner, J. F. Fuerholzer, R. D. Clark, and R. D. Thompson, *J. Am. Chem. Soc.*, **85**, 3303 (1963).

(3) For E1cB processes see: (a) C. L. Bumgardner and H. Iwerks, *ibid.*, **88**, 5518 (1966); (b) S. J. Cristol and B. B. Jarvis, *ibid.*, **89**, 401 (1967); S. J. Cristol, J. K. Harrington, and M. S. Singer, *ibid.*, **88**, 1529 (1966); S. J. Cristol and B. B. Jarvis, *ibid.*, **88**, 3095 (1966); (c) J. Meinwald, C. Swithenbank, and A. Lewis, *ibid.*, **85**, 1880 (1963); J. Meinwald and J. K. Crandall, *ibid.*, **88**, 1292 (1966); (d) H. O. House and co-workers.^{2f}

(4) This nomenclature preserves terms (U, W, Sickle) and their geometric significance already used in the chemical literature in various connections: R. B. Bates, R. H. Carnighan, and C. E. Stables, *J. Am. Chem. Soc.*, **85**, 3031 (1963); R. B. Bates, D. W. Gosselink, and J. A. Kaczynski, *Tetrahedron Letters*, 199, 205 (1967); A. Rassat, C. W. Jefford, J. M. Lehn, and B. Waegell, *ibid.*, 233 (1964); R. Hoffman, *Trans. N. Y. Acad. Sci.*, [II], **28**, 475 (1966).

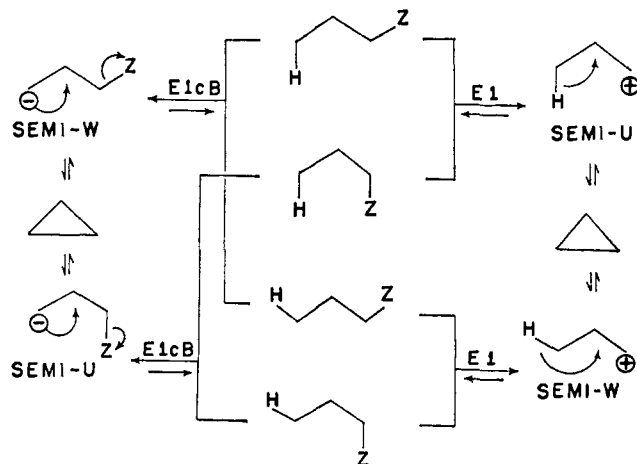
and Z is the departing group. The electronegativity distinction may be necessary when both X and Z can serve as leaving groups (e.g., when X and Z are different halogens). In the special case where X = Z, structures 3 and 4 are geometrically equivalent, and the *exo-endo* prefixes are dropped. The *apo-S* form 5 refers only to the staggered precursor because it must twist to one of the other four transition states 1b-4b for ring closure. Arrangement 2a is the only one that can go to product without conformational rotation (viz., 2a → 2b), and arrangement 1 is the only one in which X and Z can partake in cyclic transition states.

With respect to the atoms bearing X and Z, it is relevant to note that in the U path both centers undergo formal retention of configuration, and in the W path both undergo inversion. In the *exo-S* path there is retention at X and inversion at Z, and *vice versa* for the *endo-S* path. The over-all stereochemical outcome from the *apo-S* array will depend on which of the four transition states the *apo-S* form adopts during reaction.

Arrangements 1-4 are clearly defined in a chair cyclohexane ring where the U forms utilizes 1,3-diaxial bonds, the W form utilizes 1,3-diequatorial bonds, and each of the two S forms involves one axial and one equatorial bond. Other common instances of U, W, *exo-S*, and *endo-S* geometries, or slight distortions thereof, include various boat-type molecules like bicyclo[2.2.1]heptanes, as well as puckered cyclobutanes,⁵ bicyclo[n.1.1] systems, and appropriate conformations of cyclopropylmethanes that are precursors of bicyclo[1.1.0]butanes. *apo-S* units exist in these cyclic systems but involve endocyclic ring bonds, which must rupture during formation of a new three-membered ring.

With slight adaptation this terminology readily accommodates stepwise 1,3 eliminations in which stereochemistry at one center is lost prior to the ring closure. Since U and W are associated, respectively, with retention and with inversion at both centers, stepwise 1,3 eliminations (and the reverse ring cleavages) are termed semi-U and semi-W according to whether formal retention or inversion of configuration, respectively, occurs at the remaining center in the ring-forming step. Common situations are those that involve loss

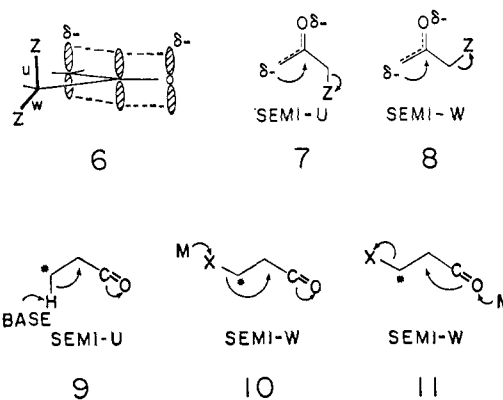
Scheme I. Stepwise 1,3 Eliminations and Cyclopropane Ring Cleavages



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of HZ *via* cationic (E1 type) and anionic (E1cB type) intermediates (see Scheme I), but the nomenclature serves equally well for ions and radicals derived other ways (e.g., by addition to various multiply bonded systems).

Delocalization of electrons can affect the geometry of nearby centers. However, even when the mesomerism implicates a pair of adjacent atoms in the A-B-C unit, only two extreme cyclopropyl transition states appear attainable, closely akin to semi-U and semi-W, and so no additional names are necessary. Structure 6 depicts an enolate ion as a precursor to a cyclopropanone (as in a Favorskii reaction). In the semi-U array the C-Z bond is initially more nearly



parallel to the p orbitals of the enolate system, and in the semi-W form the orientation is more nearly orthogonal. The corresponding abbreviated notations are 7 and 8, but it must be kept in mind that any single structure cannot accurately portray the dynamic situation, which demands appreciable conformational change from start to finish. For a half-chair cyclohexanone enolate, semi-U corresponds to Z initially quasi-axial and semi-W corresponds to Z initially quasi-equatorial. Similar considerations apply to allylic cations or radicals that lose a hydrogen to form methylenecyclopropane systems.

Finally, we illustrate uses of semi-U and semi-W for neutral molecules with trigonal centers. Thus, the abstraction of homoenolic hydrogens by alkali⁶ as in 9 and the generation of homoenolate ions by metal (M) reductions (e.g., 10 or 11) would be classed as shown in accord with the retention or inversion criterion at the relevant center (*).

(6) A. Nickon, J. L. Lambert, R. O. Williams, and N. H. Werstiuk, *J. Am. Chem. Soc.*, **88**, 3354 (1966).

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1,3 Eliminations. II. Behavior of *exo*-Norbornyl Tosylate in Alkaline Media and Preference for *exo-S* over W Geometry¹

Sir:

We present evidence that the *exo-S* arrangement is favored over the W arrangement when *exo*-norbornyl

(1) Supported by the National Science Foundation and the Petroleum Research Fund (administered by the American Chemical Society). Part I: A. Nickon and N. H. Werstiuk, *J. Am. Chem. Soc.*, **89**, 3914 (1967).