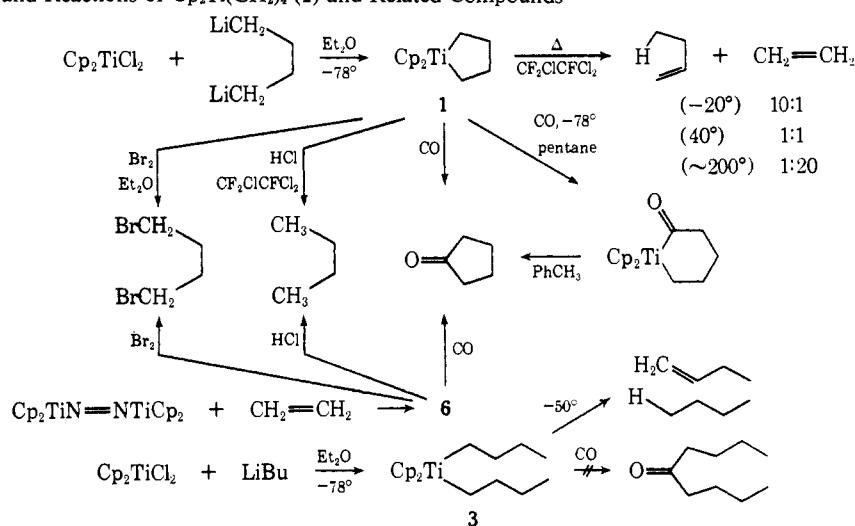


Scheme I. Formation and Reactions of  $\text{Cp}_2\text{Ti}(\text{CH}_2)_4$  (**1**) and Related Compounds

First, metallocycle **1** is much more stable than **3**; **1** decomposes slowly at  $-30^\circ$  and has a half-life of several minutes at  $+25^\circ$ ; **3** decomposes rapidly at  $-50^\circ$ . Second, certain of the products of thermal decomposition of **1** must be produced by a different mechanism than those of **3**. Compound **3** yields butane and 1-butene on decomposition, presumably by a mechanism broadly analogous to that established for di-*n*-butylbis(triphenylphosphine)platinum(II).<sup>5</sup> In contrast, **1** yields both the analogous 1-butene and ethylene. Although the mechanism of formation of the latter compound has not been established, it probably involves a carbon-carbon bond cleavage encouraged by the  $\sim 0^\circ$  Ti-C-C-C dihedral angle.<sup>6,7</sup> Finally, **3** decom-

unsuccessful; nonetheless, the similarity in reactivity and properties of **6** and **1** suggests that they are identical.

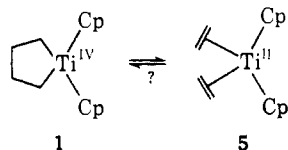
The chemistry of **1** and **3** provides a concrete demonstration of the proposition that metallocycle formation may encourage unusual reactions of transition metal alkyls by suppressing metal hydride elimination. The formation of a metallocycle (**6**) from ethylene indicates that it should be possible to prepare representative metallocycles directly from olefinic precursors. Together, these observations suggest that it may prove practical to devise new synthetic reactions—using olefins as starting materials and metallocycles as intermediates—that differ in useful ways from those involving intermediate metal hydrides.

(10) John A. Lyons Fellow, 1972–1974.

Joseph X. McDermott,<sup>10</sup> George M. Whitesides\*

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Received November 5, 1973



poses rather than carbonylating under conditions that transform **1** to cyclopentanone.

The observation that ethylene is formed by carbon-carbon bond cleavage on thermal decomposition of **1** prompted us to try to detect the reverse reaction (**5** → **1**); related reactions have been observed previously with strained olefins.<sup>8</sup> Reaction of  $\text{Cp}_2\text{TiN}_2\text{TiCp}_2$ <sup>9</sup> with excess ethylene in toluene or ether below  $-30^\circ$  afforded reaction mixtures whose properties strongly suggest the presence of titanium metallocycles (Scheme I). Thus, reaction of the crude mixtures with bromine, HCl, or carbon monoxide yielded products containing the tetramethylene moiety in yields up to 15%, based on  $\text{Cp}_2\text{TiN}_2\text{TiCp}_2$ . The structure of the precursor of these products, designated **6** in Scheme I, has not been determined, and efforts to isolate **6** have so far been

(5) G. M. Whitesides, J. F. Gaasch, and E. R. Stedronsky, *J. Amer. Chem. Soc.*, **94**, 5258 (1972).

(6) The crystal structure of  $\text{L}_2\text{Pt}(\text{CH}_2)_4$  has been reported by C. G. Biefield, H. A. Eick, and R. H. Grubbs, *Inorg. Chem.*, **12**, 2166 (1973).

(7) Related fragmentation reactions have been invoked in transition metal catalyzed rearrangements of strained rings [L. Cassar, P. E. Eaton, and J. Halpern, *J. Amer. Chem. Soc.*, **92**, 3515 (1970)] and in olefin metathesis [R. H. Grubbs and T. K. Brunck, *ibid.*, **94**, 2538 (1972)].

(8) A. R. Fraser, P. H. Bird, S. A. Bezman, J. R. Shapley, R. White, and J. A. Osborn, *J. Amer. Chem. Soc.*, **95**, 597 (1973); R. Noyori, T. Ishigami, N. Hayashi, and H. Takaya, *ibid.*, **95**, 1675 (1973).

(9) J. E. Bercau, R. H. Marvich, L. G. Bell, and H. H. Brintzinger, *J. Amer. Chem. Soc.*, **94**, 1219 (1972).

### Stereochemistry of the Electrophilic Ring Opening of Cyclopropanes by $\text{D}^+$ . Evidence for an Unsymmetrical, Nonrotating, Corner-Protonated Cyclopropane

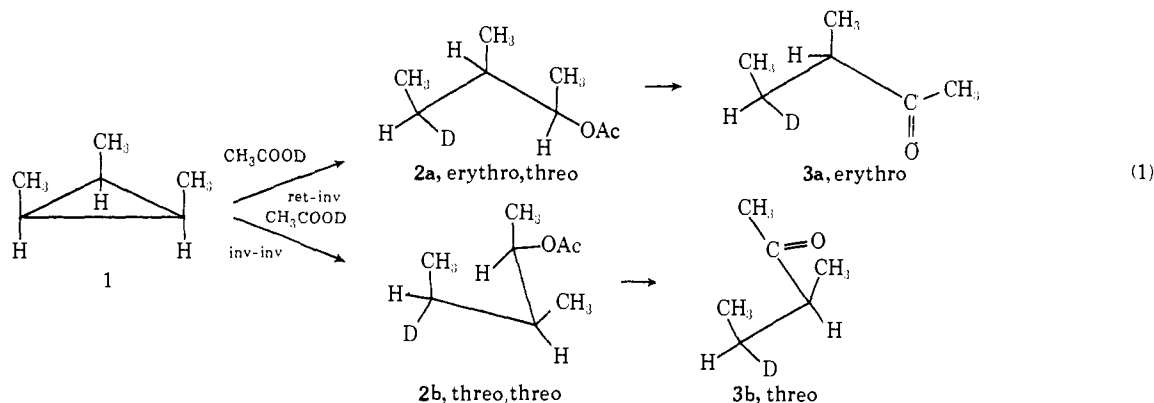
Sir:

Although a number of studies have been carried out on the stereochemistry of the opening of cyclopropanes by a proton, none has examined the stereochemistry alone, uncomplicated by the question of which bond in the molecule is most susceptible to attack.<sup>1</sup> We have recently shown, for example, that except in completely symmetrical systems the stereochemistry of electrophilic opening of cyclopropanes by mercuric acetate is controlled by the nature and stereochemistry of the ring substituents.<sup>2</sup> We now wish to report two stereochemical studies on cyclopropanes in which the direction of attack by the electrophile,  $\text{D}^+$ , does not effect the results, so that the true, intrinsic reaction stereochemistry is revealed.

The first example studied was *cis*-1,2,3-trimethylcyclopropane (**1**), which was allowed to react for 1 hr

(1) For a review see C. H. DePuy, *Fortschr. Chem. Forsch.*, **40**, 74 (1973).

(2) C. H. DePuy and R. J. McGirk, *J. Amer. Chem. Soc.*, **95**, 2366 (1973).



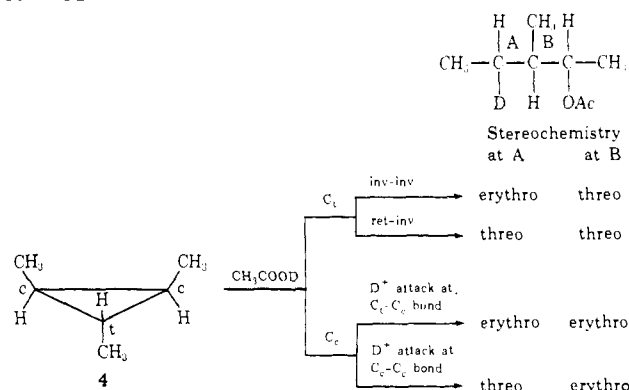
at 90° in acetic acid-*O-d* containing a trace of  $D_2SO_4$  (eq 1). The acetate formed, in 50% yield (isolated product), was shown (gc and nmr) to be 95% *threo*-3-methyl-2-pentyl-4-*d* acetate (**2**) (and 5% the erythro isomer) by comparison with an authentic sample.<sup>3</sup> This acetate, which contained a single deuterium atom as shown by mass spectral analysis, was hydrolyzed and oxidized to 3-methyl-2-pentanone-4-*d* (**3**) by  $Na_2Cr_2O_7-H_2SO_4$  in ether, a procedure which has been shown<sup>4</sup> (and which we have confirmed for this particular case) not to epimerize an adjacent chiral center.

Ketone **3** has diastereotopic<sup>5</sup> hydrogens at C-4, and in the presence of shift reagent,  $Eu(FOD)_3$ , these are clearly separated from one another in the nmr spectrum. Direct quantitative analysis of the deuterium content in the *threo* and *erythro* positions of **3** from the proton spectrum is inaccurate because one of the proton peaks is partially obscured by a methyl resonance and because of the presence of  $d_0$  species under some conditions. Both of these problems are eliminated in the deuterium resonance spectrum (dmr). The two deuterium resonances are well separated and mixtures of authentic samples of the diastereoisomers of **3** can be analyzed to within  $\pm 2\%$ . Peak assignments were confirmed by Baeyer-Villiger oxidation and hydrolysis of **3** to 3-deuterio-2-butanol and comparison with authentic samples prepared by reaction of *cis*- and *trans*-2-butene oxide with  $LiAlD_4$ .

In two separate experiments the stereochemical results were the same; attack by the  $D^+$  on **1** occurs 68% with retention and 32% with inversion of configuration (68% *erythro* and 32% *threo* deuterium observed). The nucleophile reacts with at least 95% inversion of configuration. Essentially the same stereochemical results for both electrophile and nucleophile were found for ring opening in  $CF_3COOD$  (room temperature) and  $DBr$  in  $CH_2Cl_2$  (room temperature).

Stereochemical analysis of the ring opening of the *trans* isomer, **4**, is more complicated, but the finding of nearly complete inversion by the nucleophile in the reactions of **1** simplifies the problem. Deuterium attack can occur at the carbon which holds the *trans* methyl group, labeled  $C_t$  in Scheme I, or at either of the other two carbons,  $C_c$ . The bonds joining  $C_t$  to the other two carbons of the ring are identically substituted, so that the stereochemistry of attack at  $C_t$  is a true mea-

Scheme I



sure of the intrinsic stereochemistry of the reaction at that carbon. Attack at  $C_t$  and ring opening with inversion by the nucleophile can give only *threo* acetate.

Deuterium attack on either of the other two carbons of **4** ( $C_c$ ) can occur from two different directions, through the *trans*-substituted bond ( $C_t-C_c$  bond) or through the *cis*-substituted bond ( $C_c-C_c$  bond). No matter from which direction the deuterium comes, attack at  $C_c$  and ring opening with inversion by the nucleophile can give only *erythro* acetate. Separation of the reaction products into *threo* and *erythro* acetates, which can be accomplished by preparative scale gas chromatography, allows the reaction stereochemistry at  $C_t$  and  $C_c$  to be examined separately. Ring opening of **4** at 90° by acetic acid-*O-d* containing a trace of  $D^+$  gives a 35–65% mixture of *threo* and *erythro* acetates, showing that attack on each carbon is approximately statistical.

Within the *threo* acetate, the deuterium configuration reveals the stereochemistry of electrophilic attack at  $C_t$ , *erythro* deuterium arising from inversion and *threo* deuterium arising from retention. The results are the same as for **1**, 68% retention and 32% inversion of configuration (68% *threo* and 32% *erythro* deuterium). Within the *erythro* acetate, the deuterium configuration reveals the relative amount of attack on  $C_c$  from the two directions, since attack through the  $C_c-C_t$  bond with either retention or inversion gives *erythro* deuterium and attack through the  $C_c-C_c$  bond gives only *threo* deuterium. The *erythro* acetate contains 75% *threo* and 25% *erythro* deuterium, showing that attack from the *cis*-substituted side is three times more favorable than attack from the *trans*-substituted side.

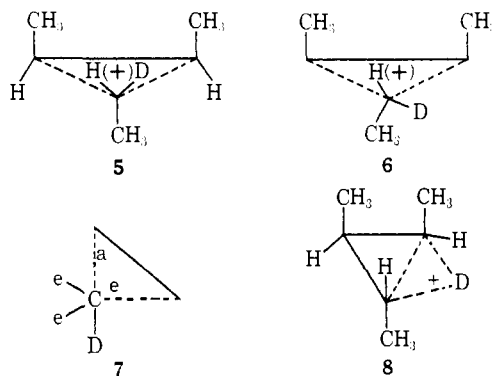
Since **1** and **4** give different amounts of the two deuterated products, there cannot be a freely rotating corner-protonated cyclopropane intermediate, and a symmetrical, nonrotating structure (**5**) is also ruled out

(3) Synthesized by hydroboration of *trans*-3-methyl-2-pentene and acetylation. C. H. DePuy and R. H. McGirk, *J. Amer. Chem. Soc.*, in press.

(4) H. C. Brown, C. P. Garg, and K. T. Liu, *J. Org. Chem.*, **36**, 387 (1971).

(5) D. Arigoni and E. L. Eliel, *Top. Stereochem.*, **4**, 127 (1969).

by the finding of a 68–32% mixture of inversion and retention. We believe our data are best accounted for if opening occurs by way of an unsymmetrical corner-protonated cyclopropane (**6**) in which the attacking  $D^+$  is in the plane of the ring. In such an intermediate the ring-carbon would resemble a trigonal bipyramid (**7**) making the two ring-bonds slightly different and leading naturally to a non 50–50% mixture of threo and erythro deuterium products. We reject an edge-protonated



structure (**8**) as the intermediate giving rise directly to products<sup>6</sup> since its structure as usually written does not reveal why inversion and retention reactions have nearly the same activation energy. Of course **6** and **8** differ only slightly in the position of the proton and **8** may be a transition state on the way to **6** or an intermediate which leads to **6**. We hope that further experiments now underway will shed further light on these possibilities.

**Acknowledgment.** The authors wish to thank the National Science Foundation for support of this research by Grant GP 13783X.

(6) It could be argued that opening occurs both from corner- and edge-protonated species, with perhaps the 5% erythro acetate found in the opening of **1** (the product of nucleophilic retention) arising from the latter intermediate *via* an open carbonium ion. We think it unlikely that if opening were occurring competitively from both **6** and **8**, the stereochemical results would remain constant over such a wide range of solvents and reaction conditions.

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Received September 13, 1973

## Book Reviews\*

**Aromatic and Heteroaromatic Chemistry. Volume I.** Edited by C. W. BIRD and G. W. H. CHEESEMAN (University of London). The Chemical Society, London, 1973. xvi + 445 pp. £11.00.

This volume represents still further expansion of the Specialist Periodical Reports. It covers the literature between July, 1971, and June, 1972. Future volumes are planned yearly. There are fifteen contributed chapters that cover such subjects as synthesis by intramolecular cyclizations, condensation reactions, and cycloaddition reactions; ring interconversions; substitution of various types; ring cleavages; reactions of substituents, and various important naturally occurring systems, such as porphyrins.

**Electronic Structure and Magnetism of Inorganic Compounds. Volume 2.** Edited by P. DAY (University of Oxford). The Chemical Society, London, 1973. ix + 372 pp. £8.00.

This volume of the Specialist Periodical Reports reviews the literature of 1971 and early 1972. The contributed chapters are: Photoelectron Spectroscopy, Electronic Spectra, Optical Activity, Magnetic Susceptibility Measurements, and Molecular Calculations.

**Electron Spin Resonance. Volume I.** Edited by R. O. C. NORMAN (University of York). The Chemical Society, London, 1973. x + 273 pp. £7.00.

This is a volume in the Specialist Periodical Reports, successors to the former Annual Reports. It is a group of ten contributed chapters in which the literature published between January, 1971, and May, 1972, is reviewed comprehensively. Future volumes are planned to cover 18-month intervals. The subject is treated from various standpoints, including the theory and phenomenon of esr, endor and eldor, free radicals in the solid state and in solution, and inorganic and organometallic radicals; biochemical applications will be treated in a future volume.

**Molecular Spectroscopy. Volume 1.** Edited by R. F. BARROW, D. A. LONG, and D. J. MILLEN. The Chemical Society, London, 1973. xv + 622 pp. £12.00.

This part of the expanded Specialist Periodical Reports series covers the "recent" literature up to December, 1971, and in some chapters "additionally into 1972". Future volumes are planned at

yearly intervals. The emphasis is on the principles and practice of spectroscopy, as applied to microwave, electronic, infrared (near and far), and Raman spectra. Special chapters are devoted to macromolecules and to matrix isolation.

**Statistical Mechanics. Volume I.** Edited by K. SINGER (University of London). The Chemical Society, London, 1973. viii + 256 pp. £6.50.

The expansion of the series of Specialist Periodical Reports now embraces statistical mechanics. This volume reviews "the recent literature published up to July, 1972"; future volumes are planned to appear every other year. The four chapters cover Integral Equation Approximations in the Theory of Fluids, Equilibrium Theory of Liquid Mixtures, Perturbation Theory in Classical Statistical Mechanics of Fluids, and Thermal Transport of Coefficients for Dense Fluids. As in other volumes of the series, there is an author index (very useful in such reviews), but a subject index has been dispensed with.

**Dielectric and Related Molecular Processes. Volume 1.** Edited by M. DAVIES (The University College of Wales, Aberystwyth). The Chemical Society, London, 1972. xv + 394 pp. £8.00.

This is the first volume in what is intended to be a biennial series; it covers the literature in the period 1966–1971. The chapters are intended not to presume "too much previous knowledge of their subjects." There are seven of them, of which the last, entitled "General Molecular Theory and Electric Field Effects in Isotropic Dielectrics," constitutes half the book. There is no subject index, but the table of contents is very detailed.

**Advances in Free-Radical Chemistry.** Edited by G. H. WILLIAMS (Bedford College, London). Academic Press, New York, N. Y. 1972. ix + 307 pp. \$19.50.

There are four reviews in this volume, each covering the material published up to mid-1970: Homolytic Substitution Reactions of Heteroaromatic Compounds in Solution (K. C. Bass and P. Nababing); Absolute Rate Constants for Reactions of Oxy Radicals (J. A. Howard); Allylic Halogenation (A. Nechtaval); Free-Radical Reactions in the Presence of Metal Ions (G. Sosnovsky and D. J. Rawlinson). The last chapter is subtitled "Reactions of Nitrogen Compounds" and covers both uncharged radicals and cation-

\* Unsigned book reviews are by the Book Review Editor.