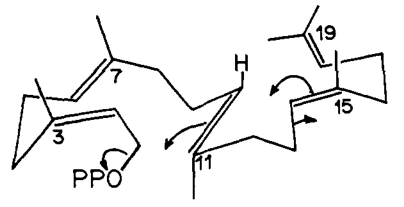
3 is the same as that of 18-OH in **1**, i.e., α.

Floceric acid **4** was obtained as needles, mp 149.5–151 °C (from petroleum ether), $C_{25}H_{38}O_2$ (m/z 370.287, calcd 370.287 M^+), $[\alpha]^{22}_D$ −203° (c 2.3, $CHCl_3$), IR (neat) 1680 and 1635 cm^{-1} (α,β-unsaturated COOH). LAH reduction of the acid yielded flocerol (**3**), and this establishes its structure as **4**.



7

These unprecedented sesterterpenoid skeletons may biogenetically be derived from a head-to-tail cyclization of 2-(Z)-geranylfarnesyl pyrophosphate involving migration as shown in **7**. The biological role of these sesterterpenoids remains to be clarified.

Supplementary Material Available: Physical properties (IR, MS, ^1H and ^{13}C NMR spectra) of the compounds **1–6** and tables of fractional coordinates, thermal parameters, bond distances, and bond angles of compound **5** (42 pages). Ordering information is given on any current masthead page.

Thermal Rearrangement of an Allenic Diazoalkane and Intermolecular Capture of a Diazoethene by a Cyclopropene To Give a Common Dihydropyridazine Product

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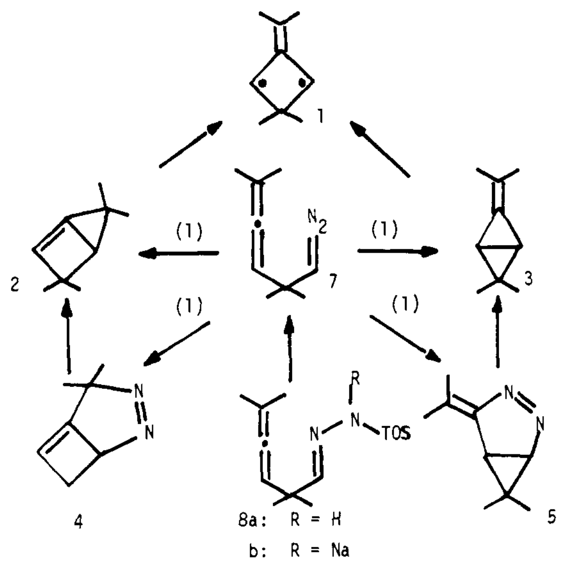
In an exploration of synthetic pathways to a 2-alkylidenecyclobutane-1,3-diyl (**1**) and some of its potential precursors (Scheme I, hydrocarbons **2** and **3**, diazenes **4** and **5**), we have discovered two novel rearrangements which surprisingly give the identical product from two apparently unrelated reactions. The observations bear on the credibility of the previously postulated[2,3] but so far elusive diazoethenes (e.g., **6**).

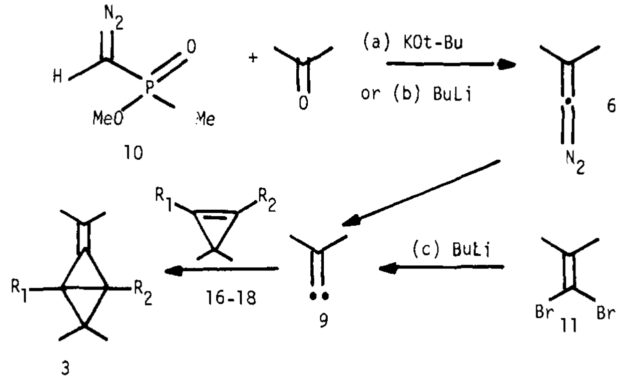
We examined two alternative synthetic approaches: In Scheme I, generation of the allenic diazo compound **7** from the p-toluenesulfonylhydrazonate **8b** followed by intramolecular 1,3-cycloaddition of **7** would give the diazenes **4** and/or **5**, which might serve as sources of **2** and **3**, or deazetation of **7** followed by cyclization of the resulting carbene would give **2** and/or **3** directly. In Scheme II, generation of a dimethylvinylidene equivalent **9** via **6**, formed from the reaction of acetone with the diazophosphonate **10** and (a) KO-t-Bu[2] or (b) BuLi[3] followed by cycloaddition to 3,3-dimethylcyclopropene (**16**), would give **3**. The carbenoid **9** or a closely related species also could be formed by (c) α elimination from 1,1-dibromo-2-methylpropene (**11**) by treatment with BuLi.[4]

Pyrolysis of **8b** in boiling benzene for 3 h (see Scheme I) gives no volatile hydrocarbons but instead gives a 48% yield of 4,4-dimethyl-6-isopropenyl-1,4-dihydropyridazine (**12**, Scheme III), colorless prisms, mp 62–64 °C, from CH_2Cl_2/petroleum ether. The structure of **12** is deduced from its spectroscopic properties,[5] its smooth reduction to the dihydro derivative **13**,[5] and a crystal X-ray diffraction analysis.[5] In boiling CCl_4, the same reaction

Scheme I

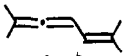
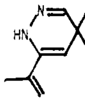
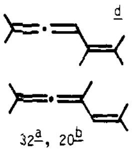


Scheme II



16: R_1,R_2 = H
17: R_1 = H; R_2 = CH_3
18: R_1,R_2 = CH_3

Table I. Products from the Reactions of Dimethyl Diazomethylphosphonate (**10**), Acetone, and Cyclopropenes

	products, % yield[c]	
cyclopropene	allenes	nitrogenous compd
 16	 16[a],16[b]	 5[a],10[b]
 17	[d]  32[a], 20[b]	none
 18	none[e]	none

[a] Method a, Scheme II. [b] Method b, Scheme II. [c] Isolated by GC. [d] Unstable. Not obtained pure but identified spectroscopically (see supplementary material) in the reaction mixture from method c, Scheme II. [e] Major hydrocarbon products are 2,5-dimethylhexa-2,3,4-triene (carbene dimer) and 1-isopropylidene-3,4,4-trimethylspiro[2.2]pentane from method c.

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[1] National Science Foundation Graduate Fellow, 1979–1981.

[2] (a) Gilbert, J. C.; Weerasooriya, U.; Giamalva, D. *Tetrahedron Lett.* **1979**, 4619; (b) Gilbert, J. C.; Weerasooriya, U. *J. Org. Chem.* **1979**, *44*, 4997.

[3] Colvin, E. W.; Hamill, B. J. *J. Chem. Soc., Perkin Trans. 1* **1977**, 869.

[4] Hartzler, H. D. *J. Am. Chem. Soc.* **1964**, *86*, 526.

[5] Described in supplementary material.

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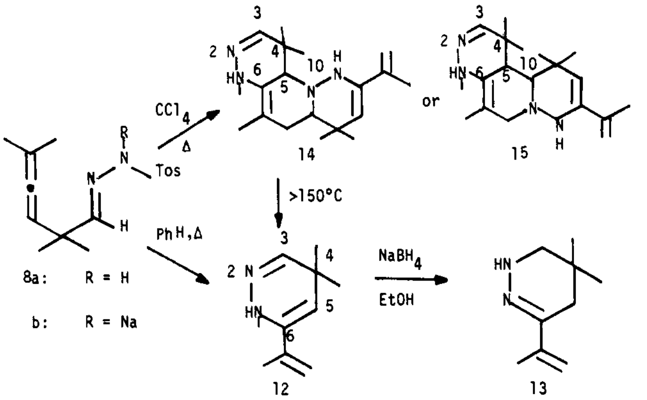
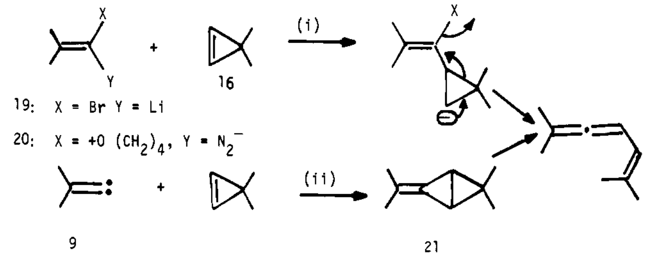
Scheme III



gives a 38% yield of a dimer of **12**, with spectroscopic properties[5] in accord with the structure **14** or, less satisfactorily, structure **15**.[6] The dimer decomposes to the monomer **12** upon gas chromatography (GC) on an OV-101 column (injector at 250 °C, column temperature 150 °C).[7]

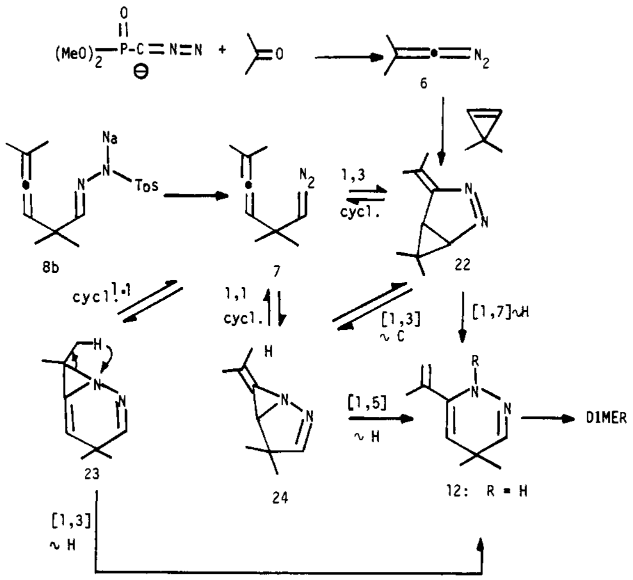
In the reactions of Scheme II 3,3-dimethylcyclopropene (**16**), 1,3,3-trimethylcyclopropene (**17**), and 1,2,3,3-tetramethylcyclopropene (**18**) give rise to the products shown in Table I. The two most likely pathways for allene formation are illustrated for the product from **16**: (i) addition of the α-bromoalkenyllithium **19** or the THF-derived diazo-oxonium zwitterion-**20**[2] to the cyclopropene followed by fragmentation or (ii) addition of a carbenoid **9** to give an isopropylidenebicyclo[1.1.0]butane (**21**) followed by a thermal decomposition analogous to the bicyclo[1.1.0]butane → 1,3-butadiene reaction.[8] Further work will be required to establish the mechanism of this reaction.



The key observation of Table I is the formation of the dihydropyridazine **12**, the same substance obtained earlier from the p-toluenesulfonylhydrazonate **8b** (Scheme III). A plausible rationale (Scheme IV) would involve capture of the diazoethene intermediate **6**, previously postulated[2] to be formed in the acetone–diazomethyl phosphonate reaction, to give the 1,3-addition product **22**. The latter species can intersect the pathway which originates in the hydrazonate **8b** by any of several reactions (Scheme IV).

The present results suggest that the normally reversible 1,1-addition of diazoalkanes[9,10] can be driven to completion if a suitable trapping process (e.g., hydrogen shift) is available (see Scheme IV, **22**–**24** → **12**). They also provide the first example of the dipolarophilic interception of a nitrogenous intermediate in the

Scheme IV



diazomethyl phosphonate–ketone–olefin reaction. The observation that this same adduct is obtained from the phosphorus-free precursor **8b** constitutes strong presumptive evidence in support of the proposed[2,3] free diazoethene intermediate.

Acknowledgment. We are grateful to the National Science Foundation (CHE-8011399) and the National Institute of General Medical Sciences (GM-23375) for partial support of this research. We also thank the National Science Foundation (CHE-7916210) for its support of the NSF Regional NMR Facility at Yale University and Professor Richard D. Adams for the X-ray structure determination.

Supplementary Material Available: Spectroscopic data characterizing compounds **12** and **14**. Details of X-ray crystallographic analysis of compound **12**, diagrams of bond angles and distances, and a listing of atomic positional and thermal parameters (5 pages). Ordering information is given on any current masthead page.

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[6] Although the choice is not crucial here, we favor structure **14** for the dimer on the basis of both the ^{1}H and the ^{13}C NMR spectra.[5]

[7] Heating monomer **12** in pure CCl$_4$ does not produce dimer **14**, whose formation from the salt **8b** in that solvent therefore presumably involves a catalytic mechanism in which **12** is formed but does not survive the (basic) conditions of the hydrazonate decomposition.

[8] (a) Srinivasan, R. *J. Am. Chem. Soc.* **1963**, *85*, 4045. (b) Closs, G. L.; Pfeffer, P. E. *Ibid.* **1968**, *90*, 2452. (c) Wiberg, K. B.; Lavanish, J. M. *Ibid.* **1966**, *88*, 5272. (d) Wiberg, K. B.; Szeimies, G. *Tetrahedron Lett.* **1968**, 1235. (e) Frey, H. M.; Stevens, I. D. R. *Trans. Faraday Soc.* **1965**, *61*, 90. (f) Srinivasan, R.; Levi, A. A.; Haller, I. *J. Phys. Chem.* **1965**, *69*, 1775.

[9] (a) Padwa, A.; Ku, H. *Tetrahedron Lett.* **1980**, 1009. (b) Padwa, A.; Rodriguez, A. *Ibid.* **1981**, 187.

[10] Miyashi, T.; Nishizawa, Y.; Sugiyama, T.; Mukai, T. *J. Am. Chem. Soc.* **1977**, *99*, 6109; (b) Nishizawa, Y.; Miyashi, T.; Mukai, T. *Ibid.* **1980**, *102*, 1176; (c) Miyashi, T.; Fujii, Y.; Nishizawa, Y.; Mukai, T. *Ibid.* **1981**, *103*, 725.

Kinetic Bistability in the Permanganate Oxidation of Oxalate

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A chemical reaction carried out in a continuous flow stirred tank reactor (CSTR) may exhibit more than one stationary state at a particular pumping rate, provided the kinetics of the reaction are appropriately nonlinear. Steady-state multiplicity is a phenomenon of considerable intrinsic interest and is important to our understanding of chemical dynamics in systems far removed from equilibrium. Of the few isothermal chemical systems known to exhibit kinetic bistability, only the acidic bromate oxidation of cerium(III) is understood in detail.[1] Bistability has been recently discovered in the iodate oxidation of arsenous acid and significant progress has been made toward explaining the behavior in terms of elementary chemical reactions.[2,3] In this communication, we

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[1] (a) Geiseler, H.; Föllner, H. H. *Biophys. Chem.* **1977**, *6*, 107–115. (b) Bar-Eli, K.; Noyes, R. M. *J. Phys. Chem.* **1978**, *82*, 1352–1359.

[2] Papsin, G. A.; Hanna, A.; Showalter, K. *J. Phys. Chem.* **1981**, *85*, 2575–2582.

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