Table I. Calculated and Observed Matrix-Isolated Infrared Vibrational Spectral Data for Difluorocyclopropenone

frequencies, cm^{-1}			rel intensities[a]	
calcd	scaled	obsd	calcd	obsd
2169.5	1952	1914.5	11.9	18.2
2004.4	1803	1779.9	48.8	21.8
		1761.2		15.7
1518.3	1366	1285.5	27.7	28.3
1211.7	1090	1071.4	2.8	5.0
974.4	876	860.2	3.7	4.4
800.9	720	699.6	2.2	3.3
788.8	709	656.0	0.7	3.3
715.1	644	*b*	0.7	
694.3	624		0.0	
293	264		0.2	
287	258		0.6	
244	220		0.7	

[a] The intensities are normalized to 100. [b] Band assignment was not possible.

At the MP3/6-31G*//HF/6-31G* level of theory, the relative energies of **2**, **3**, **5**, and **4** plus carbon monoxide are calculated to be 0.0, 25.0, 47.6, and 44.3 kcal/mol, respectively. For the corresponding hydrocarbon derivatives, the relative energies are calculated to be 0.0, 2.1, 35.0, and −4.0 kcal/mol, respectively. It is obvious that fluorine substitution has had a major effect on the relative stabilities of these species. The great electronegativity of fluorine destabilizes difluoroacetylene by about 40 kcal/mol relative to acetylene.[11] A portion of this destabilization is apparently also present in difluorocyclopropenone, which is 20 kcal/mol more strained than the parent hydrocarbon. The relatively small energy change predicted for **3** opening to **5** (22.6 kcal/mol) forewarns of the potential lability of difluorocyclopropenone (see below).

The vibrational spectrum of difluorocyclopropenone was calculated analytically at the HF/6-31G* level of theory, and a comparison of the calculated, scaled (0.9),[12] and experimental values is shown in Table I. The agreement is quite reasonable.[13] In addition, we have calculated (HF/6-31G*) that the observed infrared-active mode for difluoroacetylene will occur at 1331 cm^{-1} (1479 cm^{-1} before scaling by 0.9). This value is consistent with our experimental value but is very different from the value reported in the literature (1149 cm^{-1}).[14] The agreement between our theoretical and experimental infrared spectra give us confidence that both of these structural assignments are correct. Unfortunately, we have so far been unable to remove either species intact from the matrix in order to characterize it more fully.

In conclusion, we have demonstrated that difluoromaleic anhydride is a useful source of matrix-isolated difluoropropadienone, difluorocyclopropenone, and difluoroacetylene.

Acknowledgment. We thank Professor D. M. Lemal for supplying a sample of difluoromaleic acid, and we are grateful to the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (CHE-8822674) for support of this work.

Supplementary Material Available: Ab initio HF/6-31G* optimized geometries and MP2 and MP3 single point energies for compounds **2**–**5** as well as the corresponding hydrocarbon derivatives (2 pages). Ordering information is given on any current masthead page.

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(13) The bands at 1780 and 1761 cm^{-1} have been assigned as one fundamental band split by matrix site defects. In a nitrogen matrix, both of these bands have equal intensities. The disappearance of both bands (as well as the other bands assigned to **3**) occurs at the same rate during irradiation with short-wavelength light.

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Stereochemical Effects in Allylic Rearrangements of Cyclic Phosphates[†,1]

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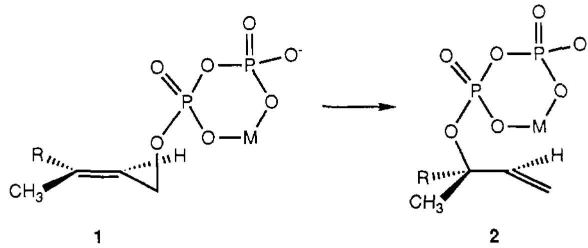
Allylic rearrangements (**1** → **2**) and nucleophilic displacements of prenyl pyrophosphates (prenyl PP) are important initiating steps in the biosynthesis of many mono-, sesqui- and diterpenes.[2,3]



1 **2** (1)

Although the participation of allylic carbocation/PP anion pairs in these processes[2,9] provides a simple means to rationalize the syn (suprafacial) stereochemistry established for several allylic rearrangements,[2a,4–6] the structure (or structures) of the enzyme-bound ion pairs remains uncertain in light of the variable oxygen-18 scrambling observed in two allylic PP rearrangements[10] and the absence of exchange in one PP displacement.[9b] In this communication, we report preliminary results on the allylic rearrangement of isomeric bridged phosphates **5a** and **5b** as chemical models for prenyl PP arrangements. The kinetic data demonstrate that the proximal *P*-oxide group in **5a** facilitates allylic rearrangement, evidently via symmetrical, bidentate ion pair **7A**.

The chemical reactions of various allylic phosphates,[11–13]

[†] Dedicated to the late Roger Adams on the occasion of the 100th anniversary of his birth in January 1889.

(1) Presented at the Great Lakes Regional American Chemical Society meeting in Duluth, MN, May 31, 1989.

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Table I. First-Order Rate Constants (10^5 s^{-1})[a] for Loss of Optical Activity (k_α) and Either Solvolysis (k_s) or Isomerization (k_i) of Bridged Phosphate Isomers **5a** and **5b** in Aqueous Acetone or Nitrobenzene

A. 30/70 D_2O–Acetone-d_6, 25 °C[b]

phosphate	k_α	k_s	k_α/k_s	k_{rac}[c]
5a	5.68	3.38	1.7	2.30
5b	9.27	9.38	1.0	0.0

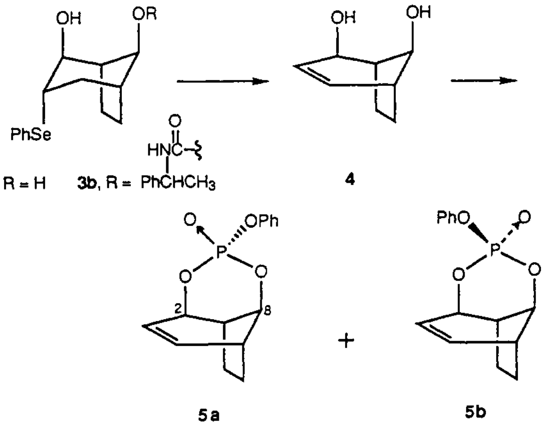
B. $C_6D_5NO_2$, 145 °C[d]

phosphate	k_α	k_i[e]	k_α/k_i	k_{rac}
5a	2.33	0.78	299	232
5b	5.60	2.30	2.4	3.30

[a] Average of two or three runs followed over at least 1.5–2 half-lives. Deviations from the average were typically ±5% or less. [b] Solvolysis rates (measured in the presence or absence of 5 equiv of pyridine. [c] $k_{rac} = k_\alpha - k_s$ (or $k_\alpha - k_i$). [d] Three equivalents of 2,6-lutidine present. [e] Initial rates.

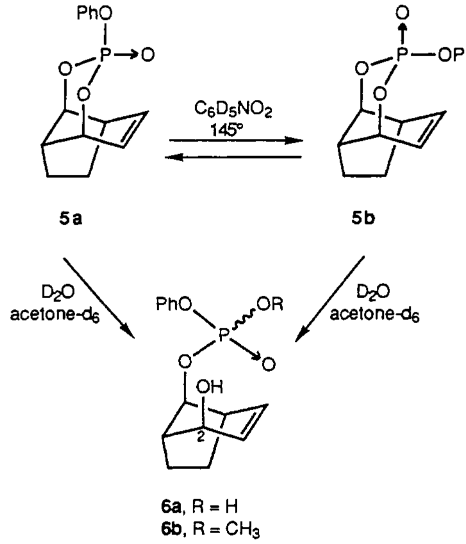
thiophosphates,[14] phosphonates,[15] and pyrophosphates[12,16,17] have been investigated as models for enzyme-catalyzed PP reactions in isoprenoid biosyntheses. Although the possibility of ion-pair intermediates has been considered,[11b,12b,c] products presumably formed by ion-pair return have been observed only in nonnucleophilic solvents.[14,15,18]

Racemic diol **4** (mp 131 °C)[19] was prepared from *syn*-bicyclo[3.2.1]oct-2-en-8-ol[20] by epoxidation, selenophenoxide opening of the epoxide to **3a**, and selenoxide elimination.[21] Resolution of **4** was accomplished by chromatographic separation of diastereomeric (S)-α-phenethylcarbamates **3b**, selenoxide elimination, and carbamate cleavage with $LiAlH_4$. Reaction of racemic and optically pure **4** with phenyl phosphorodichloridate (CH_2Cl_2, iPr_2NH, 25 °C) afforded chromatographically separable mixtures of bridged tricyclic phosphates **5a** and **5b**.[22] The relative stereochemistry of the less polar isomer **5a** was established by an X-ray crystallographic analysis, which shows that C–O–P–O–C atoms of the cyclic phosphate ring are approximately planar.[23]



(2)

Solvolysis of **5a** and **5b** in 30% D_2O–70% acetone-d_6 (v/v) at 25 °C afforded phospho diester **6a**, which was characterized as a diastereomeric mixture of methyl esters **6b**. A C–O bond cleavage mechanism is indicated by solvolysis in 30% H_2O–70% MeOH to a mixture of **6a** and its C(2) methyl ether. Furthermore, the dihydro derivatives of **5a** and **5b** were completely stable to the solvolysis conditions.



(3)

The solvolytic and polarimetric rates (k_s and k_α)[24] for the isomeric phosphates in D_2O–acetone-d_6 (Table I) were determined by ^1H NMR spectroscopy and polarimetry. When heated in $C_6D_5NO_2$ at 145 °C, phosphates **5a** and **5b** underwent thermal equilibration, K_e = [**5b**]/[**5a**] = 0.34. The initial isomerization and polarimetric rates (k_i and k_α) for this process were measured in a similar manner (Table I).

The higher polarimetric rate for **5a** (k_α/k_s = 1.7) indicates that ion-pair return competes with dissociation and nucleophilic capture in D_2O–acetone. In contrast, the equality of the polarimetric and solvolytic rates for **5b** demonstrates the absence of ion-pair return to (±)-**5b**.[25]

The observation that **5a** and **5b** both undergo racemization faster than isomerization in $C_6D_5NO_2$ at 145 °C requires that the isomers racemize predominantly by independent mechanisms. Although kinetic data for carbonium ion pair reactions in nonnucleophilic solvents are limited,[26] solvent effects on the rearrangements of **5a** and **5b**[27a] and substituent effects on the rearrangement kinetics of the related *P*-methyl phosphonates[27b] are consistent with the assumption of heterolytic mechanisms via allylic carbocation/phosphate anion zwitterions in $C_6D_5NO_2$.[28] Thus, the existence of two discrete ion pairs from **5a** and **5b** is implicated.

The high k_α/k_i ratio (298) for **5a** reveals a particularly facile mechanism for allylic rearrangement of this phosphate stereo-

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(19) All new compounds gave IR and ^1H NMR spectra as well as microanalytical data in accord with the structures shown. Appropriate ^{13}C and ^{31}P NMR spectra were obtained on selected compounds.

(20) Le Bel, N. A.; Spurlock, L. A. *Tetrahedron* **1964**, *20*, 215–229.

(21) Conditions as follows: (a) *m*-$ClC_6H_4CO_3H$, CH_2Cl_2, 0 °C (90%); (b) NaSePh, EtOH, 45–50 °C (92%); (c) *m*-$ClC_6H_4CO_3H$, CH_2Cl_2, −78 °C; Et_3N, −78 to 25 °C (81%).

(22) **5a**: mp 155–156 °C; $[\alpha]^{25}_D$ +(or −)95.6° (*c* 0.745, CH_2Cl_2). **5b**: mp 108–109 °C; $[\alpha]^{25}_D$ −(or +)151.2° (*c* 0.510, CH_2Cl_2). The absolute configurations of **3b**, **4**, **5a**, and **5b** are unknown.

(23) The crystal structure shows that the cyclic phosphate ring is considerably flattened compared to the drawings (torsion angles: C2–O1–P–O2 = 11.9°; C8–O2–P–O1 = −37.2°). The *P*-oxide to C(4) distance is 4.5 Å. We are grateful to Charlotte Stern for carrying out the crystallographic determination.

(24) The racemization rate is given by $k_{rac} = k_\alpha - k_s$ (or $k_\alpha - k_i$); see: Goering, H. L.; Vlazny, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 1801–1805.

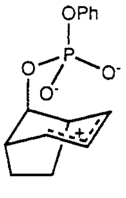
(25) A small amount (5–10% of remaining phosphate) of **5a** could be observed in the ^1H NMR spectra after ca. 1.5 half-lives.

(26) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*; VCH: Weinheim, 1988.

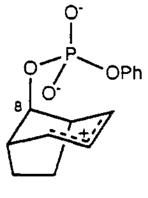
(27) (a) Similar kinetic measurements were conducted in C_6D_5Br and mesitylene at 145 °C. For example, **5a** exhibits $k_\alpha = 65$ and 37×10^{-5} s^{-1} in these two solvents, respectively. The solvent effect on k_α (k_{PhNO_2}/k_{PhBr} = 3.6) is similar to that reported for the camphanyl chloride/bornyl chloride rearrangement (k_{PhNO_2}/k_{PhCl} = 3.2): Meerwein, H.; van Emster, K. *Chem. Ber.* **1922**, *55*, 2500–2528. (b) The CH_3/H rate ratio for allylic rearrangement of *P*-methyl phosphonates corresponding to **5a** bearing CH_3 and H at C(2) is $k_{CH_3}/k_H = 2k_i/k_\alpha$ = 240 at 145 °C in $C_6D_5NO_2$.

(28) The possibility of a concerted [3,3]-sigmatropic rearrangement of **5a** occurring concurrently with the heterolytic processes cannot be excluded. However, in the absence of compelling evidence, this more complex scenario seems unnecessary.

isomer presumably via symmetric zwitterion **7A**. In contrast, the slower racemization of **5b** evidently reflects the relatively large torsional motion (120° rotation about the P–OC(8) bond) and charge separation necessary to effect allylic rearrangement to its enantiomer.[29] Since the kinetic data for **5b** represent the combined barriers to both ionization and rotation, the structure and relative stability of the ion pair(s) from this isomer remain obscure. Heterolysis of **5b** to asymmetric ion pair **7B** followed by collapse back to **5b** without 120° rotation about the P–OC(8) bond would not be detected.



7A



7B

Although the rigid tricyclic structures of **5a** and **5b** allow access to a limited array of allyl carbocation/phosphate anion configurations, it is clear that the proximity of the *P*-oxide group to the double bond in **5a** leads to an enhanced rate of allylic rearrangement.

Acknowledgment. We thank Professor Ronald M. Magid for helpful discussions and the National Institutes of Health for financial support (GM-13956).

Supplementary Material Available: Physical and spectral properties for **3a,b**, **4**, **5a,b**, **6b**, and synthetic intermediates (5 pages). Ordering information is given on any current masthead page.

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[29] An alternative mechanism involves inversion of the cyclic phosphate ring to a boat conformation followed by heterolysis and both C–O and O–P bond rotations to attain an open or anti zwitterion with C_s symmetry.

Free-Radical Arylation of Cubane Using Cubyl Lead Acylates

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Two methods have been applied recently for functionalization of the cubyl ring system. The first is hypervalent iodine oxidative displacement of the iodo group in a cubyl iodide to yield the derived (*m*-chlorobenzyl)oxy,[1] chloro,[1] acetoxy,[1] tosyloxy,[2] mesyloxy,[2] trifluoroacetoxy,[2] or fluoro[2] analogues. The second involves the elegant ortho-metalation procedure of Eaton et al. upon a cubylcarboxamido precursor and subsequent electrophilic addition.[3]

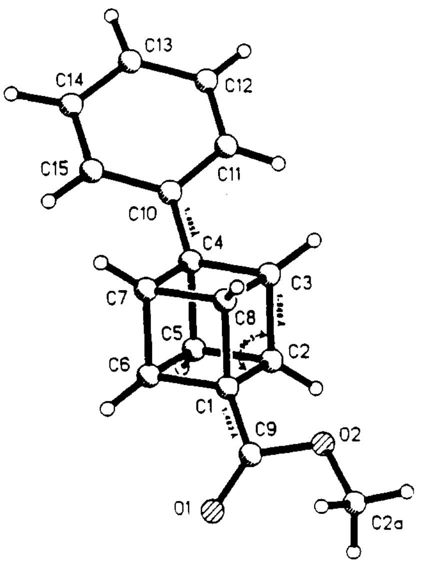
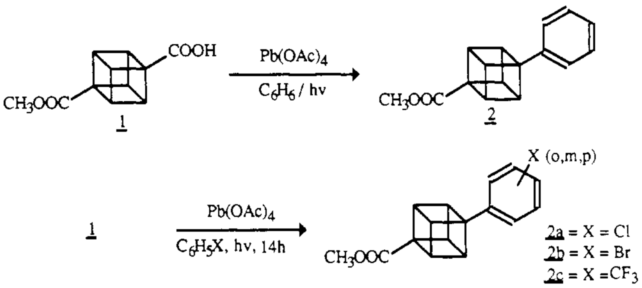


Figure 1. X-ray structure of methyl 1-phenylcubane-4-carboxylate (**2**).

These procedures correspond formally to carbocationic and carbanionic reactions, respectively. To date, radical reactions have not been applied to cubane functionalization in a systematic way, although the generation, stability, and selectivity of the cubyl radical was first studied 10 years ago.[4,5] Furthermore, regardless of the method used, carbon–carbon bond forming reactions in cubane chemistry are conspicuously absent, except for the recently reported phenylation of cubane, using the cubyl anion formed via reverse transmetalation and subsequent addition to benzyne formed from either dehydrohalogenation of bromobenzene or metal–metal exchange upon 1,2-dibromobenzene.[6] As interesting as this demonstration of arylation is, the structural precondition of a (diisopropylamino)carbonyl group for ortho activation is a limitation.

A desirable goal is the direct arylation of cubane without the necessarily of ortho activation, and we now report this via lead tetraacetate radical oxidative decarboxylation in a reaction akin to Kochi's free-radical halodecarboxylation.[7] Thus, 1,4-cubanedicarboxylic acid methyl ester (**1**),[8] upon reflux and irradiation in benzene solution, yields methyl 1-phenylcubane-4-carboxylate (**2**) in 66% yield.[9] Similarly, chlorobenzene yielded a mixture



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[5] The various decarboxylation methods applied to cubane are the following: RCOOH → RH using *N*-hydroxypyridine-2(1*H*)-thione (Della, E. W.; Tsanaktsides, J. *Aust. J. Chem.* **1986**, *39*, 2061), i.e., the Barton reaction (Barton, D. H. R.; Crich, D.; Motherwell, W. B. *Tetrahedron* **1985**, *41*, 3901), and RCOOH → RI (Abeywickrema, R. S.; Della, R. S. *J. Org. Chem.* **1980**, *45*, 4226) using *tert*-butyl hypo iodite (Moriarty, R. M.; Khosrowshahi, J. S.; Dalecki, T. M. *J. Chem. Soc., Chem. Commun.* **1987**, 675) and using $PhI(OAc)_2–CCl_4–I_2$ are all radical processes, but only RX and RH have been obtained to date.

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