acetylated to produce **7**. Standard Ireland ester enolate Claisen rearrangement[10] of **7** gave crude silyl ester **8**, which was directly subjected to phenyl selenolactonization[11] to yield **9**. Routine oxidation and elimination produced vinyl lactone **2**[17] in 62% overall yield from **7**.

Vinyl lactone **2** was readily converted to iodide **3** as illustrated in eq 2. After much experimentation, it was found that the
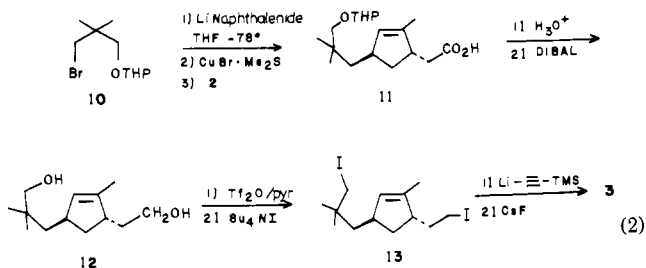
organolithium reagent derived from **10** could be generated by reductive lithiation with 2.0 equiv of lithium naphthalenide (THF, -78 °C).[12] Sequential addition of CuBr–Me$_2$S, followed by **2**, produced **11** as the sole acidic product after acid–base extraction. Although yields were variable, 50–75% of **11** could be isolated under the best conditions. The assignment of anti stereochemistry to **11** was based on model studies[13] and confirmed by ultimate conversion to hirsutene. Crude **11** was directly subjected to acid hydrolysis and reduction to produce diol **12**[17] in 52–64% yield after purification by chromatography or distillation. Diol **12** was then converted to the diiodide **13** via the intermediate ditriflate (64%).[14] Treatment of **13** with 1 equiv of lithium trimethylsilylacetylide (THF, 0 °C),[15] followed by desilylation, produced the cyclization precursor **3**[17] in 78% yield. As expected, the neopentyl iodide was unaffected.

The stage was now set for the key cyclization reaction. In the event, treatment of **3** with tri-*n*-butyltin hydride (C$_6$H$_6$, 0.02 M, catalytic AIBN, reflux 1 h) provided a single major non-tin-containing product in ~80% yield as evidenced by GC and ^{1}H NMR. Purification by medium-pressure liquid chromatography on silica gel with 100% hexanes provided hirsutene in 53% yield. Our synthetic sample was identical in all respects with a sample kindly provided by Professor P. Magnus. Ozonolysis of **1** also gave the well-known norketone.[16]

This short synthesis of hirsutene from the readily available vinyl lactone **2** demonstrates the potential of the tandem hexenyl radical cyclization approach to linear condensed cyclopentanoids. A series of model studies that confirm the generality of the tandem radical cyclization will be reported in a forthcoming paper[13] and extension to the synthesis of more complex hirsutanoids and related capnellenes is under active investigation.

Supplementary Material Available: Spectra and analytical data for **2**, **3**, **9**, **12**, and **13** (2 pages). Ordering information is given on any current masthead page.

(10) Ireland, R. E.; Mueller, R. H.; Willard, A. K. *J. Am. Chem. Soc.* **1976**, *98*, 2868.
(11) Nicolaou, K. C.; Seitz, S. P.; Sipio, W. J.; Blount, J. F. *J. Am. Chem. Soc.* **1979**, *101*, 3884.
(12) Freeman, P. K.; Hutchinson, L. L. *J. Org. Chem.* **1980**, *45*, 1924. Screttas, C. G.; Micha-Screttas, M. *Ibid.* **1979**, *44*, 713. Cohen, T.; Matz, J. R. *J. Am. Chem. Soc.* **1980**, *102*, 6900. We thank Prof. T. Cohen for helpful advice on the reductive lithiation.
(13) Rakiewicz, D. M., unpublished results. These will be described in a forthcoming full paper in *Tetrahedron*, "Symposium in Print", B. Giese, Ed.
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(15) Hansen, R. T.; Carr, D. B.; Schwartz, J. *J. Am. Chem. Soc.* **1978**, *100*, 2244. Verboom, W.; Meijer, J.; Brandsma, L. *Synthesis* **1978**, 577.
(16) We are also grateful to Profs. T. Hudlicky, P. Wender, and R. D. Little for samples and/or spectra of hirsutene and the derived norketone.
(17) Spectra and analytical data for new compounds are included in the supplementary material.

Ab Initio Study of the Infrared Spectrum of Methylenecyclopropene

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Methylenecyclopropene (**1**) has recently been synthesized by Billups[1] and Staley[2] independently and found to be a highly reactive molecule that can only be observed at low temperature. Its synthesis was confirmed primarily by NMR and IR spectroscopy. Because of the unusual nature of **1** we have undertaken

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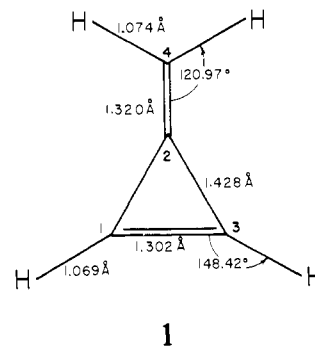
an ab initio study of its IR spectrum for comparison with the experimental spectrum reported by Billups.[1] It has been shown that such studies can be useful both in confirming the structures[3–7] of unstable species and in making assignments of their IR bands.[8]

Pople's 6-31G* basis set, which has been found to give reliable predictions of the IR spectra of cyclobutadiene[6] and ethylene oxide,[8] was used to give the fully optimized structure **1** of methylenecyclopropene with an energy of -153.669 777 au and a dipole moment of 2.3384 D. The structure was optimized with the assumption of C_s geometry with atoms 2 and 4 in the single reflection plane. The fact that the force constant matrix of this structure has only positive eigenvalues shows the structure is still optimum if the symmetry assumption is removed.[12] The best previous calculation of **1** was by Johnson and Schmidt[11] who used an MC-SCF wave function. Their single-point calculation was done at the optimized MNDO geometry, and they obtained an energy of -153.605 53 au and a dipole moment of 1.33 D. While this latter value is considerably lower than ours, as they noted the actual MC-SCF dipole moment might be somewhat different since their calculation was not done at the optimized MC-SCF geometry.

Computation of the IR frequencies and intensities of **1** was

(1) Billups, W. E.; Lin, L.-J.; Casserly, E. W. *J. Am. Chem. Soc.* **1984**, *106*, 3698–3699.
(2) Staley, S. W.; Norden, T. D. *J. Am. Chem. Soc.* **1984**, *106*, 3699–3700.
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(7) Hess, B. A., Jr.; Schaad, L. J.; Čársky, P. *Pure Appl. Chem.* **1983**, *55*, 255–260.
(8) Hess, B. A., Jr.; Schaad, L. J.; Polavarapu, P. *J. Am. Chem. Soc.* **1984**, *106*, 4348–4352.
(9) All computations were done with GAUSSIAN 80: Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, J. B.; Topiol, S.; Kahn, L. R.; Pople, J. A., GAUSSIAN 80, Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN. We thank Professor John Yates, University of Pittsburgh, for a DEC version of this program.
(10) Pople, J. A. In "Modern Theoretical Chemistry"; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; pp 1–27.
(11) Johnson, R. P.; Schmidt, M. W. *J. Am. Chem. Soc.* **1981**, *103*, 3244–3249.
(12) Čársky, P.; Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1983**, *105*, 396–402.

Table I. Computed IR Spectrum of Methylenecyclopropene **1** and Deuterated Derivatives[a,c]

C_4H_4 (1)		1-*1,3,4,4*-d_4		1-*1,3*-d_2		1-*4,4*-d_2		sym-metry	description
freq	rel int	freq	rel int	freq	rel int	freq	rel int		
3502	0.01	2679	0.04	2678	0.04	3502	0.00	A_1	sym C–H str, ring H's
3460	0.00	2550	0.02	2550	0.00	3460	0.00	B_2	antisym C–H str, ring H's
3419	0.08	2547	0.04	3419	0.08	2548	0.06	B_2	antisym C–H str, CH_2
3337	0.02	2439	0.01	3337	0.02	2440	0.02	A_1	sym C–H str, CH_2
1960	1.00	1894	1.07	1923	1.10	1936	0.93	A_1	sym ring deformation strongly coupled with $C_2=C_4$ stretch
1741	0.20	1654	0.08	1657	0.06	1733	0.27	A_1	$C_1=C_3$ stretch coupled with $C_2=C_4$ stretch
1599	0.03	1234	0.01	1598	0.03	1248	0.02	A_1	CH_2 scissoring
1258	0.07	1170	0.04	1232	0.03	1240	0.08	B_2	b
1183	0.02	986	0.00	1090	0.01	1091	0.00	B_2	b
1124	0.02	948	0.02	1022	0.03	1076	0.00	A_1	sym ring H in-plane deformation coupled with sym ring deformation
967	0.02	778	0.02	833	0.02	861	0.02	B_2	b
918	0.01	715	0.00	722	0.00	873	0.00	A_1	see 1124
878	0.40	717	0.29	878	0.38	698	0.09	B_1	methylene H out of plane
791	0.22	645	0.00	669	0.08	794	0.34	B_1	ring H out of plane
493	0.07	422	0.10	434	0.09	474	0.09	B_1	$C_2=C_4$ out-of-plane bend
393	0.01	332	0.01	368	0.01	352	0.00	B_2	b

[a] Frequencies are in cm^{-1}, and intensities are given relative to the 1960-cm^{-1} band of C_4H_4. [b] These bands are a result of strong coupling of antisymmetric ring deformation, $C_2=C_4$ in-plane bend, ring H antisymmetric in-plane deformation, and CH_2 rock. [c] In addition to the IR-active bands two A_2 Raman frequencies are computed at 588 and 1025 cm^{-1} for **1** at 427 and 833 cm^{-1} for the d_4, at 581 and 833 cm^{-1} for the *1,3*-d_2 and at 437 and 1024 cm^{-1} for the *4,4*-d_2 derivatives. They result from CH_2 torsion and antisymmetric ring H out of plane.
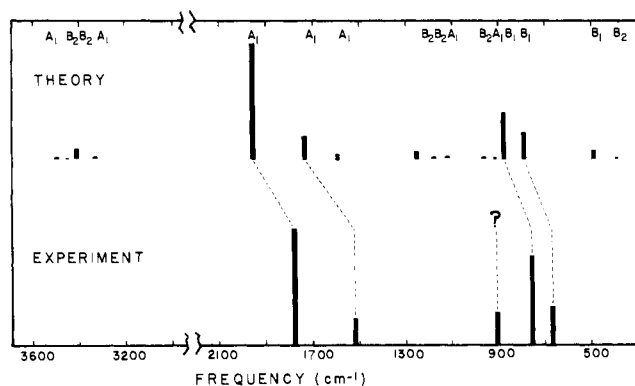

Figure 1. Comparison of the theoretical 6-31G* spectrum with the experimental spectrum of methylenecyclopropene reported by Billups.[1] Relative intensities are shown by bar heights.

carried out as previously described.[4–8] Force constants were gotten from finite differences of analytically computed gradients. The dipole moment derivatives used in the intensity calculations were evaluated from internal coordinate displacements. In Table I these are given along with those for three yet unknown deuterated derivatives of **1**. Also given are the individual symmetries of the bands and a description of the corresponding predominant motions as given by the eigenvectors of the GF matrix.

In Figure 1 the computed spectrum of **1** is compared with the experimental spectrum reported by Billups.[1] His spectrum contains many weak bands which he was unable to assign to methylene-cyclopropene (in part due to impurities), and we have therefore plotted only the five bands which were attributed to **1**. It is seen that the computed spectrum contains four intense bands while five relatively intense bands are found experimentally. There is good agreement for the two higher wave number bands. They are of A_1 symmetry and arise from strong coupling between the exo double bond stretch and ring deformation, in agreement with Billups' tentative assignment. However, at longer wavelengths we predict only two intense bands (B_1). These are due to the out-of-plane bending of the two types of hydrogens. We suggest these two correspond to the experimental 754- and 664-cm^{-1} bands and that the experimental band at 904 cm^{-1} is likely due to an impurity, perhaps isobutylene.[13]

Although the theoretical spectrum in Figure 1 is for isolated molecules at 0 K while the experimental spectrum was taken in

(13) We have recently been informed by Professor Billups that the absorption at 904 cm^{-1} is not due to methylenecyclopropene. This now brings the experimental spectrum into good agreement with the theoretical spectrum.

an argon matrix at 15 K, and although computed frequencies are all higher (as is usual) than the corresponding observed lines, the strong similarity in pattern of the two spectra does support Billups' and Staley's report of the first successful synthesis of methylenecyclopropene.

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An Inverted Reactivity Series in the Reaction of *tert*-Butyl Radical with Nucleophiles[1]
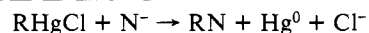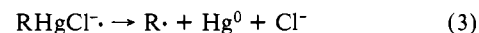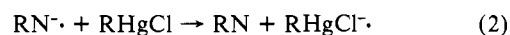
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Alkylmercury halides will participate in $S_{RN}1$ reactions with certain nucleophiles (Scheme I)[2] and undergo analogous chain

Scheme I

$$R\cdot + N^- \rightarrow RN^-\cdot \qquad (1)$$

$$RN^-\cdot + RHgCl \rightarrow RN + RHgCl^-\cdot \qquad (2)$$

$$RHgCl^-\cdot \rightarrow R\cdot + Hg^0 + Cl^- \qquad (3)$$

$$RHgCl + N^- \rightarrow RN + Hg^0 + Cl^-$$

reactions with neutral radicalphiles such as pyridines,[3] tetramethylphenylenediamine,[3] 1,1-di-*p*-anisylethylene,[4] or benzyl isocyanide.[4]

Table I lists anions that we found capable of undergoing a photostimulated reaction with *t*-BuHgCl. The yields in Table I were those observed for the reaction of equimolar amounts of the nucleophiles and *t*-BuHgCl in Me_2SO or HMPA at 35 °C when

(1) Electron Transfer Processes. 33. This work was supported by a grant from the donors of the Petroleum Research Fund, administered by the American Chemical Society.

(2) Russell, G. A.; Hershberger, J.; Owen, K. *J. Am. Chem. Soc.* **1979**, *101*, 1312; *J. Organomet. Chem.* **1982**, *225*, 43. The relative reactivities of alkylmercuric chlorides toward $Me_2C=NO_2^-$ are $PhCH_2$ (4.70) > Me_3C (1.00) > Me_2CH (0.07) > n-C_6H_{13} (<0.005). This suggests that reactions 2 and 3 of Scheme I may occur in a concerted fashion.

(3) Unpublished results with Deliang Guo.

(4) To yield with *t*-BuHgCl, $Me_3CCH=C(p$-$OCH_3C_6H_4)_2$, and $PhCH_2NHCOCMe_3$ after hydrolysis.