Cyclization of 1 to 1,2,3,12c-Tetrahydrobenzo[*j*]fluoranthene (5). In a 2-neck flask equipped with magnetic stirrer, condenser, and drying tube were combined 5.0 g (0.019 mol) of diene 1, 5.0 g A-15, and 200 mL of toluene. The mixture was heated at reflux for a total of 100 h with 2.0-mL aliquots removed at 24-h intervals. The samples were filtered through glass wool and the solvent removed under N_2. The oily residues were diluted with 2.0 mL of acetonitrile and analyzed by GC[5] with retention times at 15.0, 15.4, 17.2, 23.2, and 27.2 min for **4a**, **4b**, **4c**, 1, and **5**, respectively. The ratios of these components are given in Table I. No starting material could be detected after 24 h. After 110 h of heating, the warm solution was filtered through Dicalite and concentrated by rotary evaporation to 1.7 g yellow crystals, mp 135–140 °C. Recrystallization from 95% ethanol gave yellow crystals, mp 139–140 °C. These crystals were sublimed at 120 °C (0.05 mm) to give **5**: mp 140.5–141 °C; UV (95% ethanol) λ_{max} 274 nm (log ϵ 4.84); mass spectrum (9 eV), *m/z* (relative intensity) 257 (22.3), 256 ($M^{+}\cdot$, 100), 255 (25.3), 252 (22.3), 228 (65.9); ^1H NMR δ 7.0–8.1 (m, 8 H, Ar H), 3.69 (dd, 1 H, $CH(Ar)_3$), 2.6–3.2 (m, 3 H, overlapping), 2.04–2.4 (m, 2 H, overlapping), 1.04–1.52 (m, 1 H, overlapping); ^{13}C NMR ($CDCl_3$) δ 145.9, 143.4, 139.6, 138.8, 134.8, 132.8, 131.2, 128.8, 127.7, 127.2, 125.9, 125.2, 124.7, 124.0, 119.0, 116.5, 45.2, 26.4, 25.8, 23.4.

Anal. Calcd for $C_{20}H_{16}$: C, 93.71; H, 6.29. Found: C, 93.62; H, 6.31.

Dehydrogenation of 2a to Benzo[*j*]fluoranthene (6). In a 100-mL, round-bottomed flask equipped with a magnetic stirrer, condenser, and argon purge were combined 500 mg (2.0 mmol) of alkene **2a**, 100 mg of 10% Pd/C, and 50 mL of 1-methylnaphthalene. The mixture was heated at reflux for 5 h, cooled, and filtered through Dicalite, and the Dicalite cake was rinsed with warm toluene. Removal of the solvents by distillation followed by trituration of the residue with isohexane afforded 452 mg (1.8 mmol, 92%) of benzo[*j*]fluoranthene: mp 163–164 °C; picrate, mp 193–195 °C (lit.[4a] mp 165 °C; picrate mp 195 °C); mass spectrum of **6** (8 eV), *m/e* (relative intensity) 252 (100), 251 (7), 250 (20), 2126 (7), 57 (8), 43 (8); ^1H NMR (C_6D_6) δ 8.54 (d, 2 H, Ar H), 8.08 (d, 2 H, Ar H), 7.12–7.88 (m, 8 H, Ar H).

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Registry No. 1, 5405-96-9; **2a**, 18522-48-0; **3**, 88730-13-6; **5**, 20162-56-5; **6**, 205-82-3.

Supplementary Material Available: Tables III–VI, listing positional parameters, final anisotropic thermal parameters, bond angles and lengths for hydrocarbon 3, and a list of calculated and observed structure factors (22 pages). Ordering information is given on any current masthead page.

Reversible Retro-Diels–Alder Reactions of Bicyclo[4.1.0]hept-2-ene Systems

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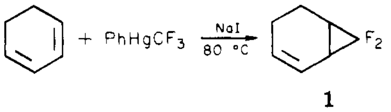
The synthesis and thermal isomerizations of 7,7-difluorobicyclo[4.1.0]hept-2-ene (1) and spiro[bicyclo-[4.1.0]hept-2-ene-7,1′-cyclopropane] (12) are described. 1 and 12 undergo reversible formal retro-Diels–Alder reactions with activation parameters which uniquely describe the highly ordered transition state for the Diels–Alder reaction. The relationship of the inherent strain of these bicyclic systems to the ability to observe such isomerizations is discussed.

The first to comment on the unusual effects of fluorine substitution on cyclopropane were O'Neal and Benson[1] who estimated that an increase in ring strain of 4.5–5 kcal/mol per fluorine substituent was produced. Hoffman predicted that fluorine should weaken the bond opposite the carbon bearing the fluorine substituent whereas the adjacent bonds should be slightly strengthened.[2] In a series of studies to obtain quantitative data on the kinetic and thermodynamic consequences of geminal fluorine substitution, we have found that the bond opposite to the CF_2 group is weakened by 8–10 kcal/mol[3] while there is a much less significant weakening of the adjacent bond of 0–2 kcal/mol,[4] results largely in keeping with these early predictions.

A study of the thermal rearrangements of 2,2-difluoro-1-vinylcyclopropanes[5] demonstrated a facile [1,3]-sigmatropic process involving the preferential initial homolytic cleavage of the C_1–C_3 bond of these molecules. We wish to report in this paper a detailed analysis of the thermal isomerization of a cis-fused difluorovinylcyclopropane, 7,7-difluorobicyclo[4.1.0]hept-2-ene (1). We compare its interesting thermal behavior with that of its hydrocarbon analogue and describe the preparation and thermal rearrangement of a hydrocarbon of similar ring strain.

Table I. Rate and Equilibrium Data for 1 ⇄ 2

temp, °C	$k_1 + k_{-1}$ ($\times 10^5$ s)	k_1	k_{-1}	K_{eq}
160.1	1.55	0.84	0.71	1.132
167.5	2.86	1.64	1.22	1.346
171.8	4.06	2.39	1.67	1.437
179.25	7.38	4.70	2.68	1.752
185.0	13.22	8.73	4.49	1.948
196.8	31.53	22.17	9.36	2.368



1

Results and Discussion

7,7-Difluorobicyclo[4.1.0]hept-2-ene (1) was prepared via Seyferth's[6] method of difluorocarbene addition to cyclohexa-1,3-diene in 56% yield. 1 was unambiguously char-

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[1] O'Neal, H. E.; Benson, S. W. *J. Phys. Chem.* **1968**, *72*, 1866.

[2] (a) Hoffmann, R.; Stohrer, W. P. *J. Am. Chem. Soc.* **1971**, *93*, 6941. (b) Hoffmann, R. *Tetrahedron Lett.* **1970**, 2907.

[3] (a) Dolbier, W. R., Jr.; Enoch, H. O. *J. Am. Chem. Soc.* **1977**, *99*, 4352. (b) Dolbier, W. R., Jr. *Acc. Chem. Res.* **1981**, *14*, 195.

[4] (a) Dolbier, W. R., Jr.; Fielder, T. H., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 5577. (b) Dolbier, W. R.; Al-Sader, B. H.; Sellers, S. F.; Elsheimer, S. *Ibid.* **1981**, *103*, 715.

[5] Dolbier, W. R., Jr.; Sellers, S. F. *J. Am. Chem. Soc.* **1982**, *104*, 2494.

[6] Seyferth, D.; Hopper, S. P *J. Org. Chem.* **1972**, *37*, 4070.

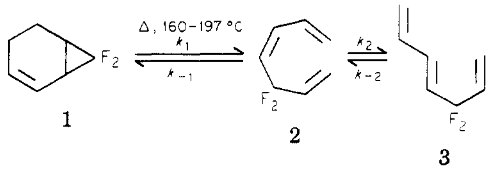
0022-3263/84/1949-1033$01.50/0

Table II. Activation Parameters for 1 ⇄ 2

	log *A*	$E_a{}^a$	$\Delta H^{\ddagger a,b}$	$\Delta S^{\ddagger b,c}$	$\Delta G^{\ddagger a,b}$
k_1	13.3 (0.3)	36.5 (0.6)	35.6	−0.38	35.8
k_{-1}	9.1 (0.3)	28.3 (0.65)	27.4	−19.6	36.2

[a] kcal/mol. [b] Mean temp 176.6 °C. [c] cal/deg.

acterized by its spectral properties notably its ^{1}H and ^{19}F NMR spectra (see Experimental Section). The thermal isomerization of 1 was carried out in the gas phase in a well-conditioned Pyrex vessel. It was found that 1 underwent a relatively low activation energy thermal equilibration at 160 °C with the acyclic species, *cis*-5,5-difluorohepta-1,3,6-triene (2). This rearrangment is probably best thought of as a retro-Diels–Alder reaction. The rates of reaction and equilibrium positions were determined for six temperatures, 160–197 °C (Table I). In one instance the equilibrium position was obtained from both directions and found to be identical. Yields of 2 (determined by the use of an internal standard) were very high, >95%, during the first half-life at each temperature. However, the formation of a second product, identified as the trans isomer of the triene (3) could also be observed. After five half lives, approximately 10% of 3 had accumulated at 250 °C. In a study carried out at 240.5 °C, where the interconversion of 2 and 3 was more rapid, the following four rate constants were estimated: $k_1 = 6.1 \times 10^{-3}$, $k_{-1} = 1.2 \times 10^{-3}$, $k_2 = 1.6 \times 10^{-5}$ and $k_{-2} = 1.2 \times 10^{-6}$. It can be seen that the rates of the more rapid 1 ⇄ 2 equilibrium are >300 times those of the 2 ⇄ 3 equilibrium. Thus the formation of 3 was ignored for the purposes of the kinetic and thermodynamic analyses presented in Table I.



From the results in Table I, the following Arrhenius data (Table II) were obtained by the method of least squares; quoted error limits are standard deviations.

A van't Hoff plot of the equilibrium data in Table I gave the result below.

$$1 \rightleftarrows 2:$$

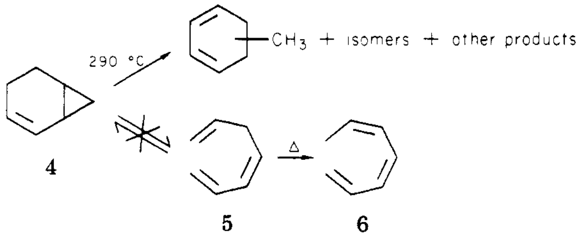
$$\Delta H^0 = +8.26\ (0.28)\ \text{kcal/mol}$$

$$\Delta S^0 = +19.33\ (0.13)\ \text{eu}$$

$$\Delta G^0 = 0.43\ \text{kcal/mol}$$

It is apparent that entropy factors strongly favor the acyclic triene 2 while enthalpy favors 1. The Arrhenius parameters clearly show that the transition state for the interconversion has a structure very close to the ring-closed form. Almost *no* change in entropy is required for 1 to reach the transition state ($\Delta S^{*}{}_1 = -0.4$ kcal/mol), whereas a great *loss* of entropy is required to attain this same transition state from 2 ($\Delta S^{*}{}_2 = -19.6$ kcal/mol). For a point of reference the entropies of activation for the Diels–Alder dimerizations of cyclopentadiene[7] and butadiene[8] are −32.8 and −26.7 eu, respectively.

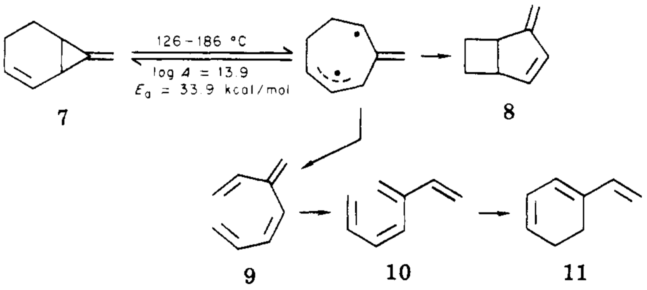
This rearrangement was unexpected in view of the fact that the analogous thermal rearrangement is not observed in the parent hydrocarbon system. We verified a report[9] that bicyclo[4.1.0]hept-2-ene (4) is stable at temperatures



less than 250 °C, rearranging to a complex mixture of products with a half-life of 65 min at 291 °C. We also established that *cis*-1,3,6-heptatriene (5)[10] exclusively undergoes an apparently lower energy [1,5]-hydrogen shift to form *cis*-1,3,5-heptatriene (6) at temperatures between 200–300 °C. While 4 should certainly be favored thermodynamically over 5 even more than 1 over 2, the Diels–Alder cyclization of 5 should be inhibited relative to that of 2 because of the expected activating effect of the fluorine substituents of 2. Moreover there is no low-energy F-shift process comparable to the H-shift process of 5 to 6 to divert 2 from its equilibrium with 1. A recent report[12] detailing the photochemistry of 4 at 185–230 nm identifies 5 as a primary product with evidence supporting a concerted mechanism from the singlet state.

The failure of 4 or 5 to exhibit thermal chemistry analogous to 1 and 2 led us to examine hydrocarbons where substituents increased the cyclopropyl ring strain.

Billups[13] describes the thermolysis of 7-methylenebicyclo[4.1.0]hept-2-ene (7) to two products, 8 and 11, in approximately equal amounts. A diradical mechanism involving a common intermediate was proposed. 8 represents the product of a vinylcyclopropane rearrangement. Proposed tetraene intermediate 9 may have derived from the diradical or it may alternatively have arisen directly from 7 by a retro-Diels–Alder process, product 11 then deriving reasonably from electrocyclic ring closure as shown. Apparently, the introduction of that additional strain due to the methylene group (estimated to be 13–14 kcal/mol[14]) causes the rearrangement of 7 to divert from the behavior of 4 to a pathway similar to that observed for 1.



In order to further investigate the relationship of the strain in the bicyclic structure relative to its ability to undergo the retro-Diels–Alder process, we prepared spiro[bicyclo[4.1.0]hept-2-ene-7,1′-cyclopropane] (12). It was

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(7) Benford, G. A.; Wassermann, A. *J. Chem. Soc.* **1939**, 362.

(8) Rowley, D.; Steiner, H.; *Disc. Faraday Soc.* **1951**, *10*, 198.

(9) Miconov, V. A.; Fedorovich, A. P.; Mil'vitskaya, I. M.; Korner, C. Ya; Akhrem, A. A. *Dokl. Akad. Nauk SSSR* **1972**, *203*, 347.

(10) Prepared by the treatment of 4-bromohepta-1,6-diene[11] with solid potassium hydroxide.

(11) Beckwith, A. L. J.; Moad, G. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1726.

(12) Leigh, W. J.; Srinivasan, R. *J. Am. Chem. Soc.* **1983**, *105*, 514.

(13) Billups, W. E.; Baker, B. A.; Chow, W. Y.; Leavell, K. H.; Lewis, E. S. *J. Org. Chem.* **1975**, *40*, 1702.

(14) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976; p 274.

Table III. Equilibrium Data for **12** $\rightleftarrows$ **13**

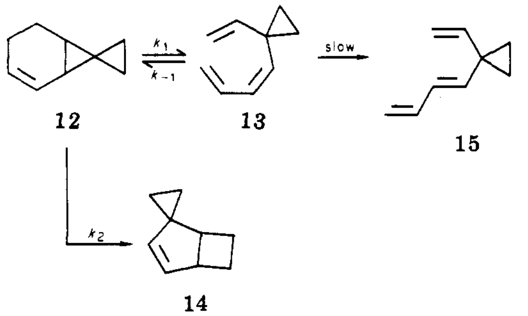
temp, °C	199.75	207.0	213.0	219.25	225.0	232.75
K_{eq}	10.58	11.81	12.80	13.81	14.95	16.58

Table IV. Rate Data for (**12** $\rightleftarrows$ **13**) → **14**

temp, °C	$(k_1 + k_{-1}) \times 10^5$, s	k_{-1}	k_1	K_{calcd}	k_2
188.0	5.58	0.562	5.02	8.933	0.216
193.75	8.20	0.766	7.44	9.705	0.359
199.25	12.58	1.091	11.49	10.526	
206.75	24.61	1.942	22.67	11.673	1.23
209.25	30.21	2.302	27.91	12.125	1.93
214.0	41.20	2.962	38.24	12.910	1.94

synthesized in 44% yield by the reaction of diazomethane with **7** (prepared in the manner of Billups[13]) utilizing palladium diacetate to direct the addition to the exocyclic double bond.[15]

Thermolysis of **12** in a well-conditioned Pyrex vessel in the gas phase at 188–214 °C gave two products, the major one, 1-(*cis*-1,3-butadienyl)-1-ethenylcyclopropane (**13**), being formed at a rate ~20 times that of the minor product, spiro[bicyclo[3.2.0]hept-2-ene-4,1′-cyclopropane] (**14**). Thus, while the major observed pathway of rearrangement of **12** is the retro-Diels–Alder process, as in the case of **1**, one can detect the competing vinylcyclopropane rearrangement. A third product, apparently the trans-triene **15** is formed irreversibly after long reaction times. (After four half-lives at 206.75 °C, **15** is present to the extent of 6% of **13**.) Equilibrium constants for **13**/**12** were obtained at six temperatures (199.75–232.75 °C) (Table III), and a van't Hoff analysis of these data led to the following thermodynamic values (mean temperature 217.13 °C).



$$\mathbf{12} \rightleftarrows \mathbf{13}:$$

$$\Delta H^0 = +6.4 \pm 0.1 \text{ kcal/mol}$$

$$\Delta S^0 = +18.2 \pm 0.1 \text{ eu}$$

$$\Delta G^0 = -2.54 \text{ kcal/mol}$$

The equilibration of **12** and **13** was examined kinetically at six temperatures (188–214 °C) (Table IV) and treated as a reversible, first-order process, ignoring the slower formations of **14** and **15**. The equilibrium constants for each of these runs were calculated from the van't Hoff data. Acceptable Arrhenius plots were obtained by a least-squares treatment of the data in Table IV, leading to the activation parameters in Table V. While the kinetic data for **12** $\rightleftarrows$ **13** is not as reliable as that of **1** $\rightleftarrows$ **2** (the $\Delta S^\ddagger$ for k_{-1}, for example, is probably closer to the −18.2 eu reflected in the more precise thermodynamic values derived from Table III), there is obviously a great similarity in the data for the two systems.

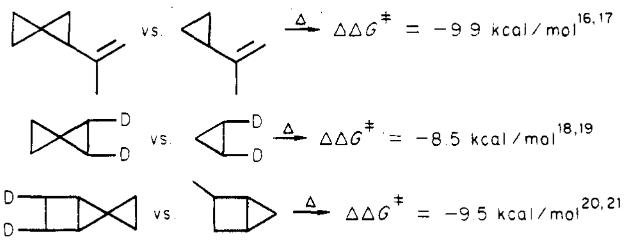
Table V. Activation Parameters for **12** $\rightleftarrows$ **13**

	E_a[a]	log A	$\Delta H^{\ddagger a,b}$	$\Delta S^{\ddagger a,b}$	$\Delta G^{\ddagger a,b}$
k_1	36.0 (1.0)	12.7 (0.5)	35.0	−3.3	36.6
k_{-1}	29.6 (1.0)	8.8 (0.5)	28.7	−21.4	38.8

[a] kcal/mol. [b] Mean temp 202.8 °C.

Conclusion

It has been demonstrated in a number of systems that the kinetic, rate-enhancing effect of a substituting a spiropentyl group for a cyclopropyl group is about −(9–10) kcal/mol in $\Delta G^\ddagger$, while the *incremental* strain due to a spiropentane (vs. two cyclopropanes) is considered to be ~8.3 kcal/mol. Therefore it is not surprising that **12** and **1** behave similarly inasmuch as the *gem*-difluoro substituents of **1** have been demonstrated to give rise to a kinetic enhancement of a ring cleavage of 9–10 kcal/mol, and the incremental strain due to *gem*-difluoro substitution has been estimated to be 12–14 kcal/mol.[22]



It is also not surprising that the methylenecyclopropane-containing system **7** gives rise to more vinylcyclopropane-type rearrangement than **1** or **12**, since the vinylcyclopropane rearrangement is considered to take place via a diradial intermediate and the intermediate deriving from **7**, a trimethylenemethane species, would be a stabilized diradical in comparison to those that would be derived from **1** or **12**.

The activation parameters for the retro-Diels–Alder processes of **1** and **12** show remarkable similarity, the $\Delta\Delta G^\ddagger$ for the two sytems being only 0.7 kcal/mol, with $k_1(\mathbf{1})/k_1(\mathbf{12}) = 2.3$ at 180 °C. While the thermodynamic parameters for the two equilibria do not *quantitatively* reflect the expected differences based upon published strain estimates for *gem*-difluorocyclopropanes and spiropentanes,[14] such variation can probably be attributed to the greater complexity and unknown actual strain values of **1** and **12**.

While the present lack of precise kinetic data for the formation of vinylcyclopropane rearrangement product **14** will not allow unambiguous confirmation of such a conclusion, it seems probable from the equilibrium kinetic data and on the basis of mechanistic precedent that interconversion of **1** and **2** and of **12** and **13** are via [2 + 4] pericyclic processes while the competitive conversion of **12** to **14** proceeds via a diradical intermediate.

The observed kinetic parameters for reversible intramolecular Diels–Alder reactions present perhaps the most clear-cut and dramatic examples of the precise relationship of the transition state of a Diels–Alder reaction to both the starting materials and the adduct. The fact that virtually *all* of the entropy loss in the forming product is lost

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(15) Suda, M. *Synthesis* **1981**, 714.

(16) Gajewski, J. J. *J. Am. Chem. Soc.* **1970**, *92*, 3688.

(17) Frey, H. M.; Marshall D. C. *J. Chem. Soc.* **1962**, 3981.

(18) Gilbert, J. C. *Tetrahedron* **1969**, *25*, 1459.

(19) Rabinovitch, B. S.; Schlag, E. W.; Wiberg, K. B. *J. Chem. Phys.* **1958**, *28*, 504.

(20) Roth, W. R.; Enderer, K. *Liebigs Ann. Chem.* **1970**, *733*, 44.

(21) Chesick, J. P. *J. Am. Chem. Soc.* **1962**, *84*, 3250.

(22) Roth, W. R.; Kirmse, W.; Hoffman, W.; Lennartz, H.-W. *Chem. Ber.* **1982**, *115*, 2508.

in reaching the transition state is dramatically demonstrated by the two equilibria presented in this paper.

Experimental Section

Addition of Difluorocarbene to Cyclohexa-1,3-diene. Sodium iodide (2.9 g, 0.193 mol), 2.2 g of (trifluoromethyl)phenylmercury (0.0063 mol), 10 mg of tetra-*n*-butylammonium iodide, and 10 mg of 18-crown-6 ether were placed in a 25-mL Carius tube in a dry box. The Carius tube was attached to a vacuum line and evacuated, and 0.7 g of cyclohexa-1,3-diene (0.00875 mol) was condensed into the tube from calcium hydride. The tube was sealed in vacuo and heated at 85 °C for 15 h. The tube was cooled in dry ice and opened, and all volatile materials were vacuum transferred to a liquid nitrogen cooled trap. The mixture was separated by GLPC, 20 ft × $^1/_4$ in. 10% TCP on Chrom P, 100 °C, 40 mL min^{-1}, to give only cyclohexa-1,3-diene and **1**, 0.49 g (56% yield): IR ν_{max} 1470 cm^{-1}, $\nu_{C=C}$ weak 1647 cm^{-1}; ^{1}H NMR δ 5.04 (vinyl, complex m, 2 H), 1.0–2.6 (br m, 6 H); ^{19}F ϕ 132.5 (midpoint) (AB, J_{AB} = 148.8 Hz, $\delta\ \nu_{AB}$ = 2390.67 Hz; upfield F br s, downfield F complex m); MS, *m/e* 130.0593 ± 0.000693 (M$^+$, 5.33 ppm); calcd 130.0594 [dev = 0.0008 (0.6 ppm)]; bp 109–110 °C.

Pyrolysis of 1. Pyrolysis was carried out in the gas phase, in Pyrex vessels heated in a thermostatted salt bath. The apparatus, as well as the gas-handling techniques have been described earlier.[5]

1 was pyrolyzed at 225 °C for 30 min, and the products were condensed into a liquid nitrogen cooled trap and separated by GLPC, 20 ft × $^1/_4$ in., 20% SE 30 on Chrom P 30/80, 105 °C, 40 mL min^{-1} to give recovered **1** and **2**.

2: IR ν_{max} 1125, $\nu_{C=C}$ 1600, 1660 cm^{-1}; NMR (0 °C) ^{1}H NMR δ 5.0–7.0 ppm (overlapping complex m); ^{19}F, ϕ 88.52 (complex dd, J = 9.4, 12.8 Hz); ^{13}C δ 135.56 (t, $^3J_{C-F}$ = 6.71 Hz), 132.86 (t, $^2J_{C-F}$ = 29.9 Hz), 131.81 (S), 123.53 (t, $^1J_{C-F}$ = 29.8 Hz), 123.18 (s), 119.89 (t, $^3J_{C-F}$ = 9.2 Hz), 118.92 (t, $^1J_{C-F}$ = 235 Hz); MS, *m/e* 130.0594 ± 0.00058 (M$^+$, 4.4 ppm); calcd 130.0594 [dev = 0.00003 (0.2 ppm)]; λ_{max} (EtOH) 224 nm (28 100).

At long pyrolysis time, a third component becomes the dominant product. MS/GC, 20 ft × $^1/_4$ in. 15% ODPN, 60 °C, 30 mL min^{-1} gives an MS almost identical with **2**. An NMR spectrum of the crude pyrolysis mixture gives an additional ^{19}F reasonance ϕ 94.26 (complex t, J = 10 Hz).

Reaction of 7-Methylenebicyclo[4.1.0]hept-2-ene with Diazomethane. To 1.5 g (0.014 mol) of olefin and 0.01 g of palladium diacetate in 5 mL of ethyl ether was added dropwise 30 mL of ethyl ether containing diazomethane prepared from 3.5 g Diazald (0.0163 mol). The reaction, virtually instantaneous as evidenced by the evolution of N_2, was filtered and the bulk of the ether was removed by fractional distillation, leaving a yellow oil. This was separated by GLPC, 10 ft × $^1/_4$ in., 10% SE 30 on Chrom P, 130 °C; 50 mL/min, to give starting material plus a single product.

12: 0.75 g (44% yield); IR (neat, film) 3062, 3030, 2995, 2915, 2850, 1640, 1440, 1047, 1017, 1003, 933, 893, 813, 772, 711 cm^{-1}; ^{1}H NMR δ 5.95 (vinyl, complex m, 1 H), 5.55 (vinyl, complex m, 1 H), 2.00–1.45 (cyclohexyl CH_2 and CH, m, 6 H), 0.78–0.58 (cyclopropyl CH_2, m, 4 H); ^{13}C δ 47.2, 5.57 (cyclopropyl CH_2), 16.54, 19.21 (cyclohexyl CH), 18.10, 22.00 (cyclohexyl CH_2), 19.21 (quarternary C), 123.19, 127.19 (vinyl CH); MS, *m/e* 120.0934 ± 0.0004 (M$^+$, 3.6 ppm); calcd for C_9H_{12}, 120.0939 [dev = 0.0004 (3.9 ppm)].

Pyrolysis of 12. **12** was pyrolyzed at 225 °C for 16 h; the products were condensed into a liquid N_2 cooled trap and separated by GLPC, 10 ft × $^1/_4$ in., 10% SE 30 on Chrom P, 150 °C, 50 mL/min to give **13** and **14**.

13: ^{1}H NMR ($CDCl_3$) δ 6.85–4.80 (vinylic H's, complex, 8 H), 0.85 (cyclopropyl CH_2, S, 4 H); ^{13}C NMR ($CDCl_3$) δ 15.87 (cyclopropyl CH_2), 21.00 (q C), 111.57, 117.67, 132.22, 133.47, 133.71, 143.71 (vinylic C's).

14: ^{1}H NMR ($CDCl_3$) δ 5.74 (vinylic, dd, J = 2.5, 5.4 Hz, 1 H), 5.27 (d, J = 5.4 Hz, 1 H), 3.8–3.1 (m, 1 H), 2.50–1.50 (cyclobutyl CH_2 and CH, m, 5 H), 0.70–0.53 (cyclopropyl CH_2, m, 4 H); ^{13}C NMR ($CDCl_3$) δ 7.36, 15.25 (cyclopropyl CH_2), 25.05, 25.79 (cyclobutyl CH_2), 43.41, 45.85 (CH), 132.74, 138.05 (vinyl), the quaternary carbon was not observed.

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Registry No. **1**, 88703-78-0; **2**, 88703-79-1; **3**, 88703-83-7; **5**, 55758-72-0; **6**, 30915-44-7; **7**, 36398-96-6; **12**, 88703-80-4; **13**, 88703-81-5; **14**, 88703-82-6; 4-bromohepta-1,6-diene, 58794-16-4; 1,3-cyclohexadiene, 592-57-4; diazomethane, 334-88-3; difluorocarbene, 2154-59-8; (trifluoromethyl)phenylmercury, 24925-18-6.

Alkylation and Aldol Condensation Reactions of 1,3-Oxathiolanones[1]

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Reactions of 2,2,4-trimethyl-1,3-oxathiolan-5-one (**1b**) with alkyl halides in the presence of LDA and HMPA give alkylation products only with very reactive halides. In contast, 2,2-dimethyl-1,3-oxathiolan-5-one (**1a**) affords no alkylation products. Both **1a** and **1b** react with aldehydes and ketones to give diastereomeric mixtures of aldol products. Conjugated enones afford predominantly 1,2- or 1,4-addition depending on the structure of the reactants.

Recently, we described the reduction of substituted 1,3-oxathiolan-5-ones (**1**) as a preparative route to 2-mercaptoaldehydes[4] which are of value in the preparation of 2,5-dihydrothiophenes and their derived products.[5] Compounds **1** were prepared from the corresponding 2-mercaptoacids. When this preparation is used, access to **1** which bear complex substituents with further function-

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(4) McIntosh, J. M.; Siddiqui, M. A. *Can. J. Chem.* **1983**, *61*, 1872.

(5) McIntosh, J. M.; Goodbrand, H. B.; Masse, G. M. *J. Org. Chem.* **1974**, *39*, 202. McIntosh, J. M.; Steevensz, R. S. *Can. J. Chem.* **1977**, *55*, 2442 and reference cited therein. McIntosh, J. M.; Sieler, R. A. *J. Org. Chem.* **1978**, *43*, 4431. McIntosh, J. M.; Khalil, H. *Can. J. Chem.* **1975**, *53*, 209.

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