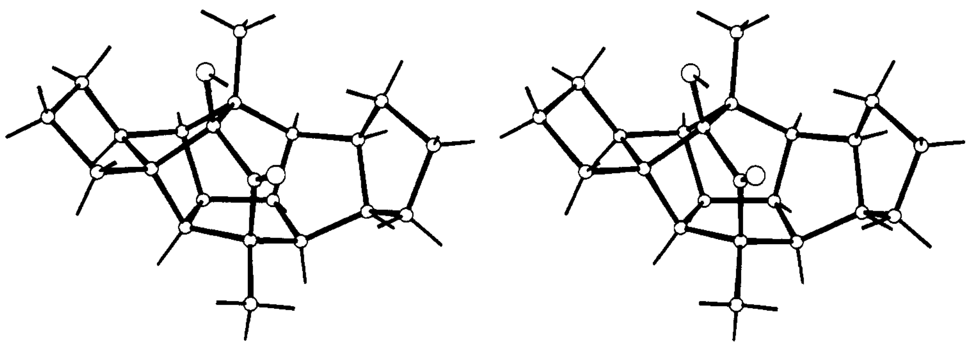
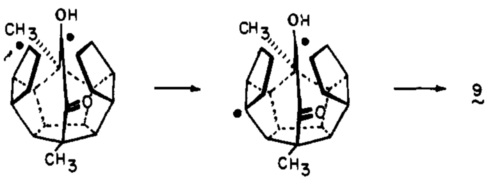


Figure 3. Three-dimensional view of **9** as determined by X-ray analysis.

of this decaquinane is shown in Figure 2.

A novel aspect of the formation of **6** is that precedence would suggest that all of the reactions necessary to go from starting material to product are unlikely, with the exception of the initial hydrogen atom abstraction. The possibility that **6** may have resulted from acid-catalyzed rearrangement of a primary photoproduct was considered, since trace amounts of acids are known to be produced during photochemical reactions in alcoholic solvents. However, irradiations conducted in the presence of either triethylamine or potassium carbonate gave entirely comparable results. Nor was the silica gel employed during purification responsible for promoting secondary chemical changes.

Although the photocyclization of **4** to **6** could involve δ-hydrogen abstraction to give **10**, hydrogen-atom transfer from the ε position (central CH_2 group) cannot be discounted. In either event, subsequent rearrangement to biradical **11** appears to be kinetically favored. This conversion could be the result of two sequential 1,2-hydrogen shifts (little precedented[19]) or more direct 1,3 migration (limited analogy[20]). Such unusual hydrogen shifts may be facilitated by partial relief of the extreme steric congestion in **10** (and **4**). While it is most unusual that biradical cyclization does not occur until hypothetical intermediate **11** is reached, closure at this stage is seen to lead to **9**. In fact, a colorless crystalline solid, mp 132.5–134 °C,[14] identified as **9** could be isolated at shorter reaction times. The structure of this product which exhibits intense infrared peaks (KBr) at 3450, 2940, 1710, and 1062 cm^{-1} and compatible NMR data (^1H, ^{13}C)[21] was established by X-ray analysis (Figure 3).[22] Further irradiation of **9** in mixed solvent systems (e.g., benzene–*tert*-butyl alcohol–acetone, 8:2:1) gave **6**. The presence of acetone was mandatory for the success of this conversion. Since the **9** → **6** process may differ substantively from the **4** → **9** reaction, the assumption of similar mechanisms for these photocyclizations is not warranted.



10 11

The present findings provide groundwork for the belief that α-diketone photochemistry may, under appropriate circumstances, be accompanied by radical rearrangements involving saturated carbon centers.[23]

Supplementary Material Available: Tables of atomic coordinates for compounds **4** and **6** with standard deviations and interatomic distances and angles together with their associated standard deviations for **9** (52 pages). Ordering information is given on any current masthead page.

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(19) Semenov, N. N. "On Some Problems in Chemical Kinetics and Reactivity"; translated by Boudart, M.; Princeton University Press: Princeton, NJ, 1958; Vol. 1, pp 68–73.

(20) Wilt, J. W. *Free Radicals* **1973**, *1*, 278–380.

(21) ^1H NMR (δ, $CDCl_3$) 3.50 (s, 1 H), 3.5–0.8 (series of m, 21 H), 1.22 (s, 3 H), and 1.13 (s, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 221.56, 89.63, 64.75, 62.63, 61.29, 60.75, 59.72, 59.59, 58.87, 58.68, 58.50, 51.22, 49.82, 46.85, 32.04, 31.31, 27.37, 23.91, 23.24 (2 C), 23.06, 22.94, and 22.39 (one C signal not evident). *m/e* calcd: 324.2089; found: 324.2096.

(22) The crystals of **9** were orthorhombic, space group $P2_12_12_1$, with a = 8.581 (2), b = 10.963 (3), c = 17.619 (5) Å; d_{calcd} = 1.300 g cm^{-3} for Z = 4 ($C_{22}H_{28}O_2$, M_r 324.46). A total of 1312 reflections were measured for $\theta < 57°$, of which 1247 were considered to be observed. The final discrepancy indexes are R = 0.035 and wR = 0.042 for the remaining 1245 observed reflections. The final difference map has no peaks greater than ±0.2 e $Å^{-3}$.

(23) The financial support of this work by a grant by the National Institutes of Health (AI-11490) is gratefully acknowledged.

Model Approach to the Pentagonal Dodecahedrane. Synthesis and Properties of a Monoseco Derivative

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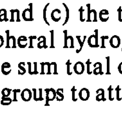
Any stepwise synthetic elaboration of the magnificently symmetric dodecahedrane molecule **1** must overcome the strong penchant shown by its partially constructed precursors for transannular bonding, framework isomerization, and noncyclopentanoid cyclization.[1] Generally, these undesirable processes gain their kinetic prominence from (a) the need to enclose a solvent-free cavity, (b) the onset of large allosteric effects[2] which force the partially constructed systems to become markedly nonspherical, and (c) the topological requirement that nearest-neighbor peripheral hydrogens ultimately become perfectly eclipsed. It is the sum total of these and other factors which have caused several groups to attempt convergent approaches to **1**,[3] but



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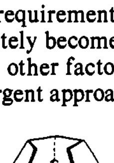

2

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(1) (a) Balogh, D. W.; Paquette, L. A. *J. Org. Chem.* **1980**, *45*, 3038. (b) Hales, N. J.; Paquette, L. A. *Ibid.* **1979**, *44*, 4603. (c) Paquette, L. A.; Begley, W. J.; Balogh, D.; Wyvratt, M. J.; Schallner, O.; Muthard, J. L.; Begley, W. J.; Blankenship, R. M.; Balogh, D. *Ibid.* **1979**, *44*, 3616 and relevant references cited in these papers.

(2) Koshland, D. E., Jr. *Enzymes* **1970**, *1*, 341–296.

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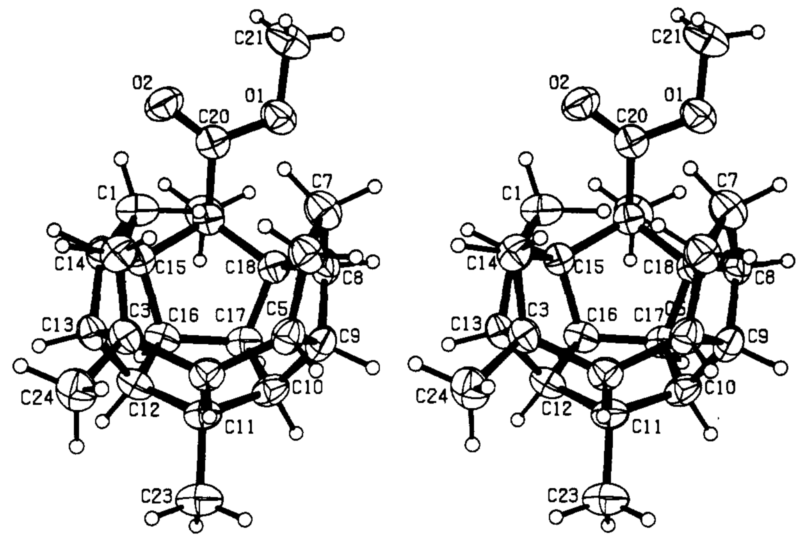
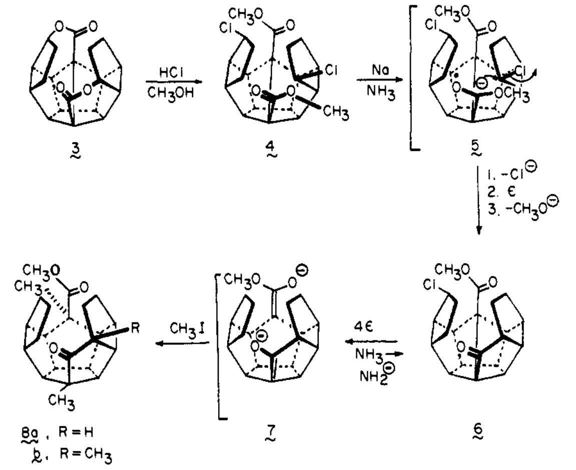


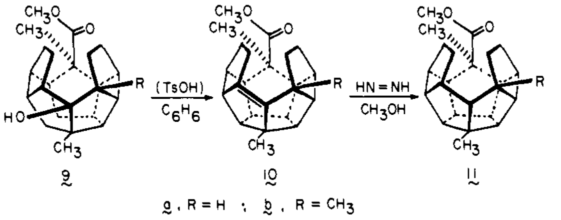
Figure 1. Three-dimensional view of **11b** as determined by X-ray analysis.

these have, to date, been uniformly unsuccessful.[4] We have for some time[5] envisioned a serial synthesis of **1** which deploys all 20 ring carbons in their proper spatial relationship and which bypasses by suitable experimental strategy the many pitfalls earlier encountered. Herein we describe the realization of these goals as applied to the C_{2v} symmetric monoseco hydrocarbon **2**.

Ester carbonyl groups are rarely photoactive, and dilactone **3**[1d] proved not to be an exception to this rule. Our first concern, then, was to effect its conversion into a more highly condensed ketonic intermediate which would prove chemically responsive to irradiation. Since the conversion of **3** to dichloro diester **4** had been earlier accomplished,[1d] the scheme **3** → **4** → **8** suggested itself. In hypothetical terms, the dissolving metal reduction of **4** in liquid ammonia was perceived as a viable means of generating radical anion **5** whose proximity considerations were expected to favor S_N2 displacement of chloride ion[6] and generation of **6**. Continued reduction of the latter intermediate would lead via central bond cleavage to **7**.[1c,d,8] In the final result, treatment of such reaction mixtures with an excess of methyl iodide gave **8a** and **8b**[7] in a combined yield in excess of 65%. The mechanistic considerations just presented are seen to deny ring closure from materializing a second time on the opposite face of the sphere. Nonetheless, the transformation has the undeniable value of catapulting the synthetic scheme to the tetraseco stage of construction. There is no question that **8b** is formed during workup as a consequence of the alkalinity of the medium and the presence of residual alkylating agent. In practice, conditions can be controlled so that **8a** predominates widely.



The keto esters **8a**[9] and **8b**,[10] when independently irradiated through Pyrex in a solvent system comprised of 20% *tert*-butyl alcohol in benzene containing a few drops of triethylamine,[11] were converted to **9a** and **9b**[7] in 85–95% yield. To establish that the cyclizations had occurred in the desired fashion,[12] **9a** and **9b** were subjected to acid-catalyzed dehydration (71–92%) and diimide reduction (H_2NNH_2, H_2O_2, quantitative).[13] At this point, the structural assignment to **11b** was substantiated by X-ray methods (Figure 1).[14] Certain C–C bonds, e.g., C(3)–C(4) and C(4)–C(5),



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(3) (a) Woodward, R. B.; Fukunaga, T.; Kelly, R. C. *J. Am. Chem. Soc.* **1964**, *86*, 3162. (b) Repic, O. Ph.D. Dissertation, Harvard University, 1976. (c) Eaton, P. E.; Mueller, R. H. *J. Am. Chem. Soc.* **1972**, *94*, 1014. (d) Eaton, P. E.; Mueller, R. H.; Carlson, G. R.; Cullison, D. A.; Cooper, G. F.; Chou, T.-C.; Krebs, E.-P. *Ibid.* **1977**, *99*, 2751. (e) Eaton, P. E.; Andrews, G. D.; Krebs, E.-P.; Kunai, A. *J. Org. Chem.* **1979**, *44*, 2824. (f) Paquette, L. A.; Farnham, W. B.; Ley, S. V. *J. Am. Chem. Soc.* **1975**, *97*, 7273. (g) Paquette, L. A.; Itoh, I.; Farnham, W. B. *Ibid.* **1975**, *97*, 7280. (h) Paquette, L. A.; Itoh, I.; Lipkowitz, K. *J. Org. Chem.* **1976**, *41*, 3524.

(4) Review: Eaton, P. E. *Tetrahedron* **1979**, *35*, 2189.

(5) (a) Paquette, L. A. *Pure Appl. Chem.* **1978**, *50*, 1291. (b) Paquette, L. A. *Ibid.*, in press.

(6) Some of Professor Bertrand's recent work makes use of a similar concept: Bertrand, M.; Teissière, P.; Pelerin, G. *Tetrahedron Lett.* **1980**, 2051, 2055.

(7) All new compounds exhibited spectra consistent with the assigned structures and gave satisfactory elemental analysis and/or high-resolution mass spectra.

(8) Paquette, L. A.; Snow, R. A.; Muthard, J. L.; Cynkowski, T. *J. Am. Chem. Soc.* **1978**, *100*, 1600; **1979**, *101*, 6991.

(9) ^1H NMR (δ, $CDCl_3$) 4.0–0.8 (series of m, 21 H), 3.62 (s, 3 H), 1.39 (s, 3 H), and 1.21 (s, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 228.73, 176.90, 64.51, 63.96, 63.72, 62.45, 59.47 (2 C), 56.62, 56.50, 55.95, 53.04, 52.86, 50.86 (2 C), 50.55, 38.90, 34.96, 34.04, 30.95, and 30.71; *m/e* calcd: 354.2195; found: 354.2203.

(10) Mp 160–162 °C; ^1H NMR (δ, $CDCl_3$) 4.4–0.8 (series of m, 20 H), 3.56 (s, 3 H), 1.36 (s, 3 H), 1.21 (s, 3 H), and 1.10 (s, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 231.30, 176.87, 65.15, 64.18, 62.02, 61.75, 61.38, 60.96, 59.41, 59.20, 56.68, 55.98, 53.16, 50.88 (2 C), 50.58, 43.24, 38.72, 34.98, 31.62, 31.31, 30.16, 27.85, and 24.85; *m/e* calcd: 368.2351; found: 368.2340.

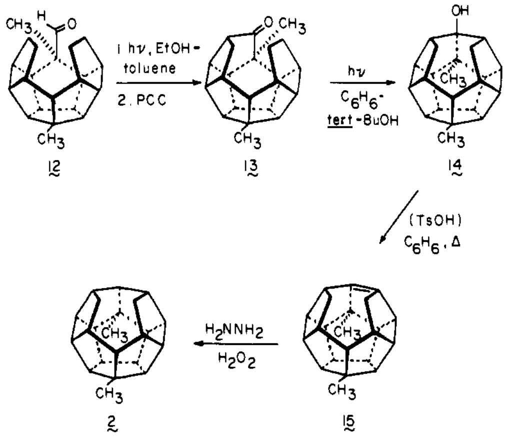
(11) The presence of small amounts of triethylamine in the photolysis mixture prevented spontaneous dehydration of the newly formed tertiary alcohol.

(12) Compare with the unusual photochemical behavior of a structurally allied α-diketone: Balogh, D. W.; Paquette, L. A.; Engel, P. *J. Am. Chem. Soc.* **1980**, accompanying paper.

(13) The unsaturated esters proved remarkably inert to catalytic hydrogenation even at 1400 psi of hydrogen.

are seen to be somewhat long and the eight cyclopentane rings come in a variety of conformations. Of major interest are the distances between atoms where bonds are needed to complete the dodecahedrane framework. These are C(2)–C(6), 3.27; C(1)–C(20), 3.15; C(7)–C(20), 3.31 Å; all are well within achievable range.[15]

Because it was already obvious that the carbomethoxy group in **11a** could not be enticed into chemical reaction by photochemical means, the decision was made to proceed with aldehyde **12**. This substance was arrived at in excellent yield by sequential diisobutylaluminum hydride reduction and pyridinium chlorochromate oxidation.[16] The fact that the CHO group was bonded to a fully substituted carbon now had to be contended with. The literature dealing with the photochemical cyclization of aldehydes to cyclobutanols[17] leaves no doubt that these structural features are most conducive to decarbonylation. While **12** was certainly prone to carbon monoxide extrusion, a 29% yield of the epimeric "homo-Norrish" cyclopentanols could be realized in deoxygenated toluene–ethanol (9:1) solution at −78 °C (450-W Hanovia lamp, Pyrex). With subsequent pyridinium chlorochromate oxidation, the diseco ketone **13** was obtained. Furthermore, not only could **13** be photocyclized reproducibly in high yield, but removal of the tertiary hydroxyl group in **14** and saturation of the double bond in **15** were encouragingly simple and efficient steps.



With arrival at the beautifully crystalline secododecahedrane **2** (mp 235–240 °C, sublime), a return to C_{2v} symmetry materializes, a phenomenon reflected in the appearance of only eight lines in its ^{13}C NMR spectrum.[18] The infrared spectrum is characterized by an unusually high absorption at 3150 cm^{-1}, assumed to be caused by the sterically compressed opposed methylene hydrogens. Molecular models of this decaquinane reveal that the opposed methylene groups must experience substantial steric repulsion adequate to force a skewed orientation.[20] Preliminary efforts to uncover a dehydrogenation catalyst effective on **2** or an isomerization catalyst which would cyclize **15** have yet to be successful. While investigations along the preceding lines continue, other workable solutions to this final maneuver and to the removal (or noninstallment) of the vestigial methyl groups are currently being examined.[19]

Supplementary Material Available: Final atomic (Table I) and anisotropic thermal parameters (Table II), bond lengths (Table III), bond angles (Table IV), and torsion angles (Table V) for **11b** (6 pages). Ordering information is given on any current masthead page.

† Presidential Fellow, 1979–1980.

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(14) The crystals were triclinic, space group $P\bar{1}$, with a = 8.517 (3), b = 8.738 (2), c = 13.191 (5) Å; α = 70.86 (3)°, β = 80.94 (3)°, γ = 85.01 (2)°; d_{calcd} = 1.279 g cm^{-3} for Z = 2 ($C_{24}H_{32}O_2$, M_r 352.52). The intensity data were measured with a Hilger–Watts diffractometer (Ni-filtered Cu Kα radiation, θ–2θ scans, pulse-height discrimination). A crystal measuring approximately 0.15 × 0.35 × 0.6 mm was used for data collection. A total of 2472 reflections were measured for $\theta < 57°$, of which 2244 were considered to be observed [$I > 2.5\sigma(I)$]. The structure was solved by a multiple solution procedure [Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368] and was refined by full-matrix least squares. In the final refinement anisotropic thermal parameters were used for the heavier atoms and isotropic temperature factors were used for the hydrogen atoms. The hydrogen atoms were refined isotropically. The final discrepancy indices are R = 0.045 and wR = 0.059 for the 2244 observed reflections. The final difference map has no peaks greater than ±0.2 e Å^{-3}.

(15) This is particularly so for ketone photochemistry in the solid state where it has been shown that the $>{=}O\cdots H_a{-}C<$ distance should be ≤2.5 Å, the $>(HO)\dot{C}\cdots\dot{C}<$ distance ≤3.5 Å, and the $-H_2/O{=}C<$ angle approximately 90° with H_a ≤10° out of the carbonyl plane: Scheffer, J. R.; Dzakpasu, A. A. *J. Am. Chem. Soc.* **1978**, *100*, 2163.

(16) Mp 132–134 °C; ^{1}H NMR (δ, $CDCl_3$) 9.98 (s, 1 H), 3.8–0.7 (series of m, 21 H), 1.20 (s, 3 H), and 1.12 (s, 3 H); m/e calcd: 308.2140; found: 308.2150.

(17) (a) Orban, I.; Schaffner, K.; Jeger, O. *J. Am. Chem. Soc.* **1963**, *85*, 3033. (b) Schaffner, K. *Chimia* **1965**, *19*, 575; (c) Agosta, W. C.; Herron, D. K. *J. Am. Chem. Soc.* **1968**, *90*, 7025. (d) Coyle, J. D. *J. Chem. Soc. B* **1971**, 2254. (d) Lischewski, M.; Adam, G.; Serebryakov, E. P. *Tetrahedron Lett.* **1980**, 45.

(18) ^{13}C NMR (ppm, $CDCl_3$) 78.40 (s), 70.15 (d), 68.16 (d), 66.08 (d), 58.99 (d), 52.29 (d), 33.64 (q), and 32.58 (t).

(19) The National Institutes of Health (Grant No. AI-11490) provided the financial support which made this research possible.

(20) **Note Added in Proof**: Dr. Peter Engel (Bern) has recently confirmed the structural assignment to **2** by X-ray analysis.

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^{13}C NMR Spectra of Carbonium Ions in the Solid State: The *sec*-Butyl Cation

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Received May 27, 1980

The use of magic angle spinning in combination with NMR pulse techniques allows moderately high resolution ^{13}C NMR spectroscopy in the solid state.[1] With the inclusion of variable temperature capability,[2] solid-state ^{13}C NMR is a powerful tool for the study of very reactive intermediates. We report procedures that allow preparation of solid samples of thermally unstable carbonium ions and subsequent manipulation of samples for solid-state NMR studies at temperatures close to 77 K.[3] A study of the *sec*-butyl cation exemplifies these procedures.

2-Butanol-*3*-^{13}*C* (55 atom % enriched) was prepared from acetic acid-*1*-^{13}*C* by a standard sequence, and the alcohol was converted to 2-chlorobutane.[4,5] An intimate mixture of the alkyl chloride (1.5 mmol) and SbF_5 (~13 mmol) was deposited at ~10^{-5} torr on a cooled surface with the use of a vapor deposition apparatus (Figure 1). Our apparatus and deposition procedures are similar to those described by Saunders.[6] The O-ring joint on the reactor permits rapid detachment of the reactor base. Concentric jets

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† Department of Chemistry, Harvey Mudd College, Claremont, CA 91711.

(1) Schaefer, J.; Stejskal, E. O.; Buchdahl, R. *Macromolecules* **1977**, *10*, 384.

(2) Fyfe, C. A.; Mossbrugger, H.; Yannoni, C. S. *J. Magn. Reson.* **1979**, *36*, 61.

(3) Well-resolved ^{13}C NMR spectra have been reported for stable carbonium ion salts. (Lyerla, J. R.; Yannoni, C. S.; Bruck, D.; Fyfe, C. A. *J. Am. Chem. Soc.* **1979**, *101*, 4770.)

(4) The sequence used was

$$CH_3{}^*CO_2H \xrightarrow[C_6H_5OH]{SOCl_2} CH_3{}^*CO_2C_6H_5 \xrightarrow[\text{diglyme}]{LiAlH_4} \xrightarrow[\text{distill}]{HOCH_2CH_2OH}$$

$$CH_3{}^*CH_2OH \xrightarrow{HBr} CH_3{}^*CH_2Br \xrightarrow[n\text{-}Bu_2O]{Mg} \xrightarrow{CH_3CHO} \xrightarrow[\text{distill}]{HOCH_2CH_2OH}$$

$$CH_3CH(OH){}^*CH_2CH_3 \xrightarrow[ZnCl_2]{HCl}$$

$$\underset{(75\%)}{CH_3CHCl{}^*CH_2CH_3} + \underset{(25\%)}{CH_3{}^*CHClCH_2CH_3}$$

where * denotes the ^{13}C label.

(5) The small volume of the rotors (~60 μL) and the use of excess SbF_5 necessitated the use of ^{13}C-enriched samples to minimize data acquisition time.

(6) Saunders, M.; Cox, D.; Lloyd, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 6656.

0002-7863/81/1503-230$01.00/0