dramatic an increase in the efficiency of mass transfer as is observed for the higher concentration of 1.0 mol %.

Addition of 1.00 equiv of NaBr relative to NaOH to the initial reaction mixture greatly inhibits the rate although the reaction profile suggests autocatalysis (e.g., at 30 min is obtained 3% conversion; 80 min, 17%; 170 min, 62%; 280 min, 98%). It may be concluded therefore that the bromide ion is not the base but competes with the base for extraction. We have shown that the hydroxide ion may be extracted into the organic phase by TOA in the presence of bromide[3] and can catalyse the isomerization of allylbenzene. In that system an induction period is observed which is necessary to attain a steady-state concentration of $[Q^+OH^-]$ in the organic phase. In dehydrobromination, bromide ions are continuously released and $Q^+OH^-_{org}$ must be regenerated by a diffusion-extraction process (most likely at the interface for TOA[13]) that, as we see in both systems, may delay the chemical reaction. The apparent autocatalysis observed is probably due to catalysis of the dehydrobromination by trioctylamine obtained by Hoffmann decomposition of the catalyst with time in the warm basic system.[14] However, the presence of trioctylamine has not been evidenced.

PTC reactions proceeding through the extraction mechanism are characterized by the greater efficiency of organophilic quats.[3,13,15,16] A comparison of TOABr and TEBABr reveals that the organophilic quat induces a higher reactivity. In the presence of TEBABr the reaction follows second-order kinetics for $1^1/_2$ half-lives, and the second-order rate constant is reported in Table I. The mechanism in the presence of TEBA appears to be complicated and is being investigated further.

In conclusion, we have presented and characterized a PTC reaction proceeding via the extraction mechanism and that is diffusion controlled.

Experimental Section

The standard reaction procedure consisted of reacting a solution of 12.30 g of (2-bromoethyl)benzene and 840 mg of toluene (as internal GC standard—total volume 10.00 mL) with 35.0 mL of 50% NaOH in the presence of 364 mg (0.665 mmol) of TOABr and sampling for GC at regular intervals. The reaction was performed in a 100-mL three-necked round-bottomed flask equipped with a mechanical stirrer (Teflon blade), thermometer, and sampling port. The flask was immersed in a stirred thermoregulated (contact thermometer) oil bath ±0.5 °C. Each reaction mixture was stirred 15 min in the absence of catalyst and checked for zero conversion, and then catalyst was added and time taken. Every run was analyzed by at least 12 points determined after conducting a suitable GC calibration graph and correcting concentrations for changes in the volume of the organic phase. The GC was run on a 2-m column 15% SE-30 on Chromosorb operating at 150 °C and a He flow of 2 mL/s. The retention times of toluene, styrene, and (2-bromoethyl)benzene were 1.1, 1.5, and 4.9 min, respectively.

Acknowledgment. A grant from the National Council for Research and Development, Ministry of Science, is gratefully acknowledged.

Registry No. Br^-, 24959-67-9; OH^-, 14280-30-9; TOABr, 14866-33-2; NaOH, 1310-73-2; $PhCH_2CH_2Br$, 103-63-9; $PhCH{=}CH_2$, 100-42-5.

(13) Landini, D.; Maia, A.; Montanari, F. *J. Chem. Soc., Chem. Commun.* **1977**, 112.
(14) March, J. "Advanced Organic Chemistry"; McGraw Hill: New York, 1977; p 935.
(15) Landini, D.; Maia, A.; Montanari, F. *J. Am. Chem. Soc.* **1978**, *100*, 2796.
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Synthesis of Bicyclo[*n*.2.1] Bridgehead Alkenes Acetoxy Substituted at the Opposite Bridgehead Position

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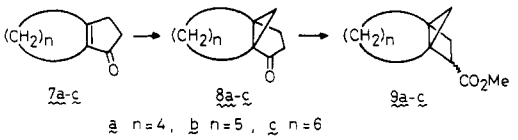
Bridgehead alkenes containing a functional group at the opposite bridgehead position are of considerable interest from theoretical and synthetic points of view as models for examination of the effect of the substituents on the properties of the strained double bond[1] and as synthetic precursors of more strained bridgehead dienes.[2] Concerning bicyclo[*n*.2.1] bridgehead alkenes, only the parent hydrocarbons of the bicyclo[4.2.1] system have been synthesized,[3] while little is known for those functionalized at the opposite bridgehead position.[4] In this paper, we report on the synthesis of a series of bicyclo[*n*.2.1] bridgehead alkenes **2a–c** (*n* = 4–6) substituted at the opposite bridgehead position with an acetoxyl group based on the methodology that was successfully employed in the synthesis of bicyclo[*n*.2.2] bridgehead alkenes,[1] i.e., oxidative decarboxylation of [*n*.2.1]propellanecarboxylic acids **1a–c**[5] with lead tetraacetate. But, in applying this methodology to the [*n*.2.1] case unlike the [*n*.2.2] case, it is anticipated that oxidative cleavage of the central bond of **1a–c** would take place to afford bridgehead diacetates **3a–c** after decarboxylation (path B) in competition with the desirable oxidative decarboxylation (path A) as shown in Scheme I, because it has been well-known that strained cyclopropane derivatives suffer from oxidative cleavage of the σ bond by lead tetraacetate.[2b,7] This problem, however, could be readily solved by converting **3a–c** to **2a–c** by hydrogenation followed by elimination of 1 mol of acetic acid (path C). Furthermore, as a preliminary study on the synthesis of bicyclo[*n*.2.1] bridgehead dienes from **2a–c** by elimination of acetic acid, we also report here on the synthesis of bicyclo[6.2.1] bridgehead diene **6a** means of vapor-phase pyrolysis of **2c**.

(1) Sakai, Y.; Toyotani, S.; Ohtani, M.; Matsumoto, M.; Tobe, Y.; Odaira, Y. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1474.
(2) (a) Warner, P.; Boulanger, W. *Tetrahedron Lett.* **1980**, *21*, 123. (b) Scott, L. T.; Brunvold, W. R.; Kirms, M. A.; Erden, I. *J. Am. Chem. Soc.* **1981**, *103*, 5216. (c) Tobe, Y.; Ueda, Y.; Matsumoto, M.; Sakai, Y.; Odaira, Y. *Tetrahedron Lett.* **1982**, *23*, 537. (d) Tobe, Y.; Kishimura, T.; Kakiuchi, K.; Odaira, Y. *J. Org. Chem.* **1983**, *48*, 551.
(3) (a) Wiseman, J. R.; Chan, H. F.; Ahola, C. J. *J. Am. Chem. Soc.* **1969**, *91*, 2812. (b) Becker, K. B.; Pfluger, R. W. *Tetrahedron Lett.* **1979**, *3713*.
(4) (a) Carruthers, W.; Qureshi, M. I. *J. Chem. Soc. C* **1970**, 2230. See also: (b) Warner, P. M.; LaRose, R. C.; Palmer, R. F.; Lee, C.; Ross, D. O.; Clardy, J. C. *J. Am. Chem. Soc.* **1975**, *97*, 5507.
(5) Acids **1a–c** were prepared by alkaline hydrolysis of the corresponding methyl esters **9a–c**, which were derived by cyclopropanation of bicyclic enones **7a–c** with dimethylsulfoxonium methylide[6] followed by ring contraction[1] of [*n*.3.1]propellanones **8a–c** (see Experimental Section).



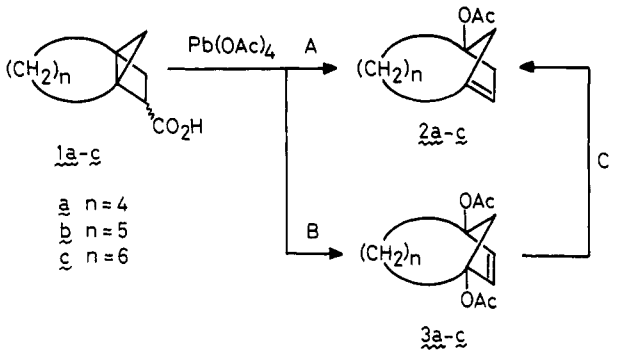
7a-c 8a-c 9a-c

a n=4, b n=5, c n=6

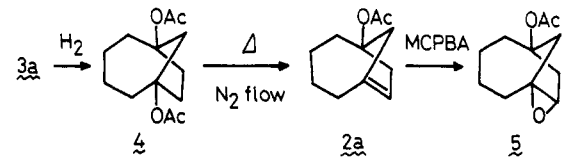
(6) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1353.
(7) For example: (a) Criegee, R.; Rimmelin, A. *Chem. Ber.* **1957**, *90*, 414. (b) Ouellette, R. J.; South, A., Jr.; Shaw, D. L. *J. Am. Chem. Soc.* **1965**, *87*, 2602. (c) Katsushima, T.; Yamaguchi, R.; Iemura, S.; Kawanishi, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3318. (d) Sakai, Y.; Terashima, K.; Tobe, Y.; Odaira, Y. *Ibid.* **1981**, *54*, 2229.

0022-3263/84/1949-2012$01.50/0

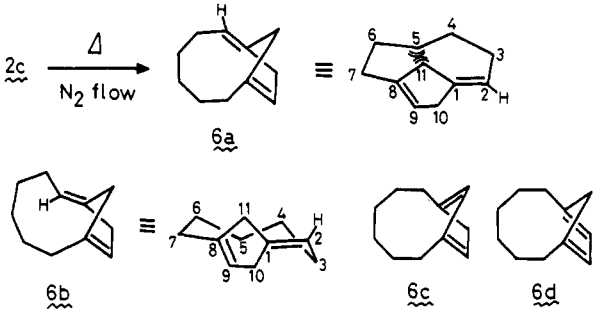
Scheme I



Oxidative decarboxylation of [6.2.1]propellanecarboxylic acid (**1c**) was carried out by heating a solution of **1c**, lead tetraacetate (1.2 equiv), and pyridine (0.6 equiv) in benzene under reflux for 1 h.[8] As expected, acetoxy-substituted alkene **2c** formed via path A was obtained successfully in 58% yield, while any product from oxidative cleavage (path B) was not detected.[9] In the oxidation of [5.2.1]propellane **1b** under similar conditions except for using a large excess (20 equiv) of pyridine, both A and B pathways took place simultaneously to afford acetoxy alkene **2b** and diacetate **3b** in 30% and 8% yields, respectively.[9] On the other hand, oxidation of highly strained [4.2.1]propellane **1a** gave diacetate **3a** derived via path B in 33% yield as the only isolable product but the desired alkene **2a** was not obtained. So, we next tried to synthesize **2a** by elimination of 1 mol of acetic acid by means of vapor-phase pyrolysis from diacetate **4**, which was derived from **3a** by catalytic hydrogenation (83%). As expected (path C),[12] pyrolysis of a hexane solution of **4** with a nitrogen flow at 400 °C afforded the $\Delta^{1,8}$ isomer **2a** selectively (>90%)[13] in 42% yield after purification by preparative GLC. The position of the double bond was determined on the basis of the similarity of the vinyl proton signal in the ^{1}H NMR spectrum (δ 5.35, br s) to that of the parent hydrocarbon[3] and was further established by oxidative derivation (MCPBA) to the known epoxide **5**.[14] Thus an entry to bicyclo[*n*.2.1] bridgehead alkenes acetoxy substituted at the opposite bridgehead position was exploited on the basis of lead tetraacetate oxidation of [*n*.2.1]propellanecarboxylic acids **1a–c**.



Furthermore, in order to explore a facile route to bicyclo[*n*.2.1] bridgehead dienes from the obtainable olefins **2a–c**, pyrolysis of **2c** was examined. When a hexane solution of **2c** was passed through a Pyrex column heated at 400 °C, a diene was isolated as an almost sole product in 50% yield after purification by preparative GLC. Although it may be possible in principle that two types of 1,3-dienes **6c** and **6d** and two stereoisomers of 1,4-dienes (*Z*,*Z*)-**6a** and (*E*,*Z*)-**6b** are formed depending on the position and direction of the hydrogen eliminated, the ^{1}H NMR spectrum of the product clearly exclude the possibility of 1,3-dienes **6c** and **6d**. Namely, the vinyl proton signal of the newly introduced double bond (H(2)) appeared as a doublet of doublet at δ 4.76 with coupling constants of 5 and 10 Hz. Moreover, of the two stereoisomeric 1,4-dienes **6a** and **6b**, **6b** may be excluded on the basis of the following reasons: (i) Examination of molecular models[15] clearly shows that (*E*,*Z*)-**6b** is apparently more strained than (*Z*,*Z*)-**6a**, though the relative strain of them is uncertain at present. (ii) Molecular model study indicates that **6a** has a planar conformation while **6b** has a conformation in which the methylene protons of C(5) are located over one of the bridgehead double bond (C(8)–C(9)). In the off-resonance decoupled ^{13}C NMR spectrum of the pyrolysis product, a triplet signal was observed at considerably high field (δ 19.7). This is assigned to C(5) carbon of **6a**, which is sterically congested by C(11) because of the planar conformation. (iii) In the ^{1}H NMR spectrum of the product, no high-field resonance (δ < 1.0) due to shielding by the bridgehead double bond was observed. It is, therefore, deduced that bicyclo[6.2.1] bridgehead diene **6a** was readily prepared in a selective manner by pyrolysis of **2c**.

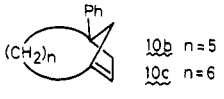


Experimental Section[17]

[*n*.3.1]Propellanones 8a–c were prepared by cyclopropanation of **7a–c** according to the procedure of Corey et al.[6] except that, in the case of **7a**, a large excess (5 equiv) of trimethyloxosulfonium iodide was used in order to accelerate the cyclopropanation.[2b] In the cases of the reaction with **7a** and **7b**, 7-formyl[4.3.1]propellane and 8-formyl[5.3.1]propellane were obtained, respectively, as minor products. **8a** (43%): IR (neat) 1710, 1075 cm^{-1}; MS, *m*/*e* (relative intensity) 150 (M$^+$, 43), 108 (100), 93 (56), 79 (43); ^{1}H NMR ($CDCl_3$) δ 0.9–2.5 (m); ^{13}C NMR ($CDCl_3$) δ 215.56 (s), 36.43 (s), 33.17 (s), 32.94 (t), 29.91 (t), 29.57 (t), 24.99 (t), 21.90 (t), 21.73

(8) Since oxidation of both exo and endo epimers of **1a–c** gave essentially the same results, a mixture of isomers was used in the preparative oxidation.

(9) In addition to the acetates **2b** and **2c**, a small amount of phenyl-substituted alkenes **10b** and **10c** derived via path A were obtained. Though the detailed mechanistic pathway for the formation of them is not clear, they might be formed by radical reaction[10] rather than via carbocationic rearrangement.[1] Moreover, a small mount of some unidentified products were obtained in the oxidation of **1b,c** which may arise from oxidation of alkenes **2b,c** and **10b,c** by lead tetraacetate[11] in competition with oxidative decarboxylation of **1b,c**.



(10) (a) Kochi, J. K.; Bacha, J. D. *J. Org. Chem.* **1968**, *33*, 2746. (b) Scheldon, R. A.; Kochi, J. K. *Org. React. (N.Y.)* **1972**, *19*, 279.

(11) Moriarity, R. M. "Selective Organic Transformations"; Thyagarajan, B. S., Ed.; Wiley-Interscience, New York, 1972; Vol. 2, p 183.

(12) It is reasonable to expect that the double bond might be selectively introduced to C(1)–C(8) position in preference to C(1)–C(2) or C(1)–C(9) position by pyrolysis of **4**, because it has been shown that the parent hydrocarbon of **2a** was prepared by pyrolysis of a bridgehead quaternary ammonium hydroxide in 80% selectivity[3a] or by that of a bridgehead acetate in 90% selectivity[3b] over the $\Delta^{1,2}$ isomer.

(13) Minor products were not investigated.

(14) Tobe, Y.; Ohtani, M.; Kakiuchi, K.; Odaira, Y. *Tetrahedron Lett.* **1983**, *24*, 3639.

(15) A flexible molecular model that can at least reproduce torsion (deviation from coplanarity) and out of plane bending (deviation form sp^2 hybridization) of the bridgehead double bonds[16] was used for the model examination.

(16) Shea, K. J. *Tetrahedron* **1980**, *36*, 1683.

(17) The instruments were the same as used in the previous works.[2d]

(t), 20.25 (t). Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 79.70; H, 9.54.

7-Formyl[4.3.1]propellane (8%): IR (neat) 3050, 2700, 1720, 1010 cm^{-1}; MS, *m/e* (relative intensity) 164 (M^+, 49), 135 (100), 93 (64), 91 (64), 79 (64); ^1H NMR (CCl_4) δ 0.30 (d, J = 4 Hz, 1 H), 0.52 (d, J = 4 Hz, 1 H), 1.0–2.2 (m, 12 H), 2.68 (dd, J = 4, 7 Hz, 1 H), 9.52 (d, J = 4 Hz, 1 H). Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.09; H, 9.62.

8b (63%): IR (neat) 3060, 1720, 1075, 1055 cm^{-1}; MS, *m/e* (relative intensity) 164 (M^+, 89),122 (100), 107 (55), 93 (65), 79 (62); ^1H NMR (CCl_4) δ 1.0–2.6 (m); ^{13}C NMR ($CDCl_3$) δ 215.64 (s), 42.49 (s), 38.01 (s), 35.15 (t), 33.27 (t), 32.42 (t), 28.33 (t), 27.22 (t), 26.77 (t), 26.18 (t). Semicarbazone, mp 198–200 °C. Anal. Calcd for $C_{12}H_{19}N_3O$: C, 65.12; H, 8.65; N, 18.99. Found: C, 65.17; H, 8.55; N, 19.04.

8-Formyl[5.3.1]propellane (7%): IR (neat) 2730, 1710, 1170 cm^{-1}; MS, *m/e* (relative intensity) 178 (M^+, 42), 149 (100), 107 (34), 93 (37), 81 (53), 67 (76); ^1H NMR (CCl_4) δ 0.24 (d, J = 5 Hz, 0.2 H), 0.42 (d, J = 5 Hz, 0.8 H), 0.62 (d, J = 5 Hz, 0.2 H), 0.79 (d, J = 5 Hz, 0.8 H), 1.0–2.4 (m, 14 H), 2.42–2.85 (m, 1 H), 9.53 (d, J = 4 Hz, 0.8 H), 9.68 (d, J = 4 Hz, 0.2 H). Semicarbazone, mp 202–205 °C. Anal. Calcd for $C_{13}H_{21}N_3O$: C, 66.35; H, 9.00; N, 17.86. Found: C, 66.42: H, 8.98; N, 17.84.

8c (91%): mp 79–80 °C; IR (KBr) 3080, 1705, 1070, 1030, 1010 cm^{-1}; MS, *m/e* (relative intensity) 178 (M^+, 100), 149 (26), 121 (50), 107 (47), 93 (53), 79 (57); ^1H NMR (CCl_4) δ 0.59 (d, J = 4 Hz, 1 H), 0.95 (d, J = 4 Hz, 1 H), 1.1–2.6 (m, 16 H). Semicarbazone, mp 210–211 °C. Anal. Calcd for $C_{13}H_{21}N_3O$: C, 66.35; H, 9.00; N, 17.86. Found: C, 66.15; H, 8.97; N, 17.74.

Methyl [*n*.2.1]Propellanecarboxylates 9a–c. Ring contraction of **8a–c** was carried out by the procedure involving photochemical Wolff rearrangement of α-diazo derivatives of **8a–c** as previously described.[1] Exo and endo esters were separated by column chromatography on silica gel with 3% either–petroleum ether eluent. In the case of **8a**, [4.3.1]propell-8-en-7-one and 9-methoxy[4.3.1]propellan-7-one were also obtained from irradiation of the α-diazopropellanone.

9a (39%, exo:endo = 2:1). *exo*-**9a**: IR (neat) 3050, 1730, 1190, 1170, 1030 cm^{-1}; MS, *m/e* (relative intensity) 180 (M^+, 39), 121 (100), 93 (52), 91 (35), 79 (65); ^1H NMR ($CDCl_3$) δ 0.38 (dd, J = 1, 5 Hz, 1 H), 0.98 (d, J = 5 Hz, 1 H), 1.0–2.2 (m, 10 H), 2.90 (dd, J = 5, 10 Hz, 1 H), 3.56 (s, 3 H). Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.16; H, 9.13.

endo-**9a**: IR (neat) 3050, 1730, 1185, 1155 1020 cm^{-1}; MS, *m/e* (relative intensity) 180 (M^+, 78), 121 (91), 93 (87), 91 (74), 79 (100); ^1H NMR ($CDCl_3$) δ 0.57 (dd, J = 1, 5 Hz, 1 H), 0.78 (d, J = 5 Hz, 1 H), 0.9–1.9 (m, 9 H), 2.24 (ddd, J = 2, 5, 10 Hz, 1 H), 2.75 (t, J = 5 Hz, 1 H), 3.64 (s, 3 H). Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.17; H, 9.10.

[4.3.1]Propell-8-en-7-one (4%): IR (neat) 3050, 1700, 1560, 1120, 830, 740 cm^{-1}; MS, *m/e* (relative intensity) 148 (M^+, 58), 120 (54), 108 (72), 91 (100), 79 (60); ^1H NMR (CCl_4) δ 0.9–2.5 (m, 10 H), 5.50 (d, J = 5 Hz, 1 H), 7.47 (d, J = 5 Hz, 1 H). Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.65; H, 8.26.

8-Methoxy[4.3.1]propellan-7-one (4%): IR (neat) 1720, 1090 cm^{-1}; MS, *m/e* (relative intensity) 180 (M^+, 100), 150 (76), 120 (66), 91 (66), 79 (93); ^1H NMR (CCl_4) δ 0.9–2.5 (m, 12 H), 3.08 (dd, J = 2, 6 Hz, 1 H), 3.27 (s, 3 H). Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.13; H, 9.10.

9b (61%, exo:endo = 3:2). *exo*-**9b**: IR (neat) 3070, 1730, 1195, 1170, 1030 cm^{-1}; MS, *m/e* (relative intensity) 194 (M^+, 22), 135 (100), 93 (49), 91 (24), 81 (24), 79 (36), 67 (40); ^1H NMR (CCl_4) δ 0.66 (br s, 2 H), 0.9–2.1 (m, 12 H), 2.79 (dd, J = 4, 10 Hz, 1 H), 3.55 (s, 3 H). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.09; H, 9.37.

endo-**9b**: IR (neat) 3070, 1730, 1195, 1165 cm^{-1}; MS, *m/e* (relative intensity) 194 (M^+, 41), 135 (100), 134 (52), 105 (42), 93 (73), 91 (55), 79 (73), 67 (50); ^1H NMR (CCl_4) δ 0.38 (d, J = 4 Hz, 1 H), 0.8–1.2 (m, 4 H), 1.4–2.0 (m, 8 H), 2.17 (ddd, J = 2, 5, 10 Hz, 1 H), 2.43 (t, J = 5 Hz, 1 H), 3.62 (s, 3 H). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73.96; H, 9.50.

9c (53%, exo:endo = 2:3). *exo*-**9c**: IR (neat) 3070, 1730, 1180, 1160, 1080 cm^{-1}; MS, *m/e* (relative intensity) 208 (M^+, 11), 149 (72), 138 (53), 119 (34), 107 (40), 105 (34), 93 (68), 91 (64), 81 (53), 79 (100), 77 (43), 67 (81); ^1H NMR (CCl_4) δ 0.20 (dd, J = 2, 4 Hz, 1 H), 0.92 (d, J = 4 Hz, 1 H), 1.2–2.3 (m, 14 H), 2.97 (dd, J = 4, 10 Hz, 1 H), 3.58 (s, 3 H). Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.66; H, 9.61.

endo-**9c**: IR (neat) 3070, 1730, 1185, 1160, 1080 cm^{-1}; MS, *m/e* (relative intensity) 208 (M^+, 13), 149 (60), 148 (43), 138 (38), 119 (32), 107 (53), 105 (45), 93 (79), 91 (68), 79 (100), 67 (62); ^1H NMR (CCl_4) δ 0.58 (dd, J = 2, 4 Hz, 1 H), 0.66 (d, J = 4 Hz, 1 H), 0.9–2.1 (m, 13 H), 2.38 (ddd, J = 2, 5, 10 Hz, 1 H), 2.40 (t, J = 5 Hz, 1 H), 3.67 (s, 3 H). Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.68; H, 9.62.

[*n*.2.1]Propellanecarboxylic Acids 1a–c. Hydrolysis of **9a–c** was carried out with 2% aqueous potassium hydroxide at 65–70 °C for 17–20 h to afford each epimer of **1a–c** in 87–95% yield, which was recrystallized from petroleum ether.

exo-**1a**: mp 67–68 °C; IR (KBr) 3500–2500, 1690, 1240, 1215, 1020, 920 cm^{-1}; MS, *m/e* (relative intensity) 166 (M^+, 57), 121 (76), 93 (81), 91 (48), 79 (100); ^1H NMR ($CDCl_3$) δ 0.46 (dd, J = 1, 5 Hz, 1 H), 1.02 (d, J = 5 Hz, 1 H), 1.1–2.3 (m, 10 H), 3.02 (dd, J = 5, 10 Hz, 1 H), 9.75 (br s, 1 H). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.09; H, 8.59.

endo-**1a**: mp 76–77 °C; IR (KBr) 3500–2500, 1690, 1235, 1220, 1020, 950 cm^{-1}; MS, *m/e* (relative intensity) 166 (M^+, 64), 121 (68), 93 (94), 91 (59), 79 (100); ^1H NMR ($CDCl_3$) δ 0.61 (dd, J = 1, 5 Hz, 1 H), 0.80 (d, J = 5 Hz, 1 H), 0.9–2.1 (m, 9 H), 2.45 (ddd, J = 2, 5, 10 H, 1 H), 2.64 (t, J = 5 Hz, 1 H), 10.62 (br s, 1 H). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.12; H, 8.54.

exo-**1b**: mp 78–9 °C; IR (KBr) 3500–2400, 1690, 1230, 935 cm^{-1}; MS, *m/e* (relative intensity) 180 (M^+, 45), 135 (100), 93 (100), 91 (59), 79 (96); ^1H NMR (CCl_4) δ 0.74 (br s, 2 H), 1.0–2.2 (m, 12 H), 2.89 (dd, J = 5, 10 Hz, 1 H), 11.82 (br s, 1 H). Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.16; H, 8.97.

endo-**1b**: mp 65–67 °C; IR (KBr) 3500–2400, 1690, 1225, 1175, 1045, 930 cm^{-1}; MS, *m/e* (relative intensity) 180 (M^+, 44), 135 (95), 93 (100), 91 (67), 79 (95); ^1H NMR (CCl_4) δ 0.41 (d, J = 4 Hz, 1 H), 0.8–1.4 (m, 4 H), 1.5–2.4 (m, 8 H), 2.20 (ddd, J = 2, 5, 10 Hz, 1 H), 2.53 (t, J = 5 Hz, 1 H), 12.20 (br s, 1 H). Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30, H, 8.95. Found: C, 73.53; H, 9.02.

exo-**1c**: mp 80–81 °C; IR (KBr) 3500–2500, 1695, 1240, 930 cm^{-1}; MS, *m/e* (relative intensity) 194 (M^+, 24), 124 (91), 93 (70), 79 (100); ^1H NMR (CCl_4) δ 0.20 (br d, J = 4 Hz, 1 H), 1.00 (d, J = 4 Hz, 1 H), 1.1–2.3 (m, 14 H), 3.03 (dd, J = 4, 9 Hz, 1 H), 11.55 (br s, 1 H). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73.79; H, 9.30.

endo-**1c**: mp 58–59 °C; IR (KBr) 3500–2500, 1695, 1250, 920 cm^{-1}; MS, *m/e* (relative intensity) 194 (M^+, 20), 124 (73), 93 (85), 79 (100); ^1H NMR (CCl_4) δ 0.67 (br s, 2 H), 1.0–2.2 (m, 13 H), 2.38 (ddd, J = 2, 5, 10 Hz, 1 H), 2.51 (t, J = 5 Hz, 1 H), 12.04 (br s, 1 H). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73.82; H, 9.30.

Oxidation of 1c with Lead Tetraacetate. A solution of **1c** (2.50 g, 12.9 mmol), pyridine (0.60 g, 7.6 mmol), and lead tetraacetate (6.80 g, 15.4 mmol) in 125 mL of benzene was heated under nitrogen at reflux temperature for 1 h. After being filtered, the filtrate was washed with 1 N hydrochloric acid, sodium carbonate solution, and water and then dried ($MgSO_4$). The solvent was evaporated and the residue chromatographed on silica gel. Elution with 3% ether–petroleum ether gave 0.435 g (15%) of phenyl alkene **10c** and then 1.54 g (58%) of acetoxy alkene **2c**. Analytical samples of **2c** and **10c** were obtained by preparative GLC.

2c: IR (neat) 3040, 1735, 1650, 1255, 1235, 1030, 785 cm^{-1}; MS, *m/e* (relative intenisity) 208 (M^+, trace), 148 (75), 106 (58), 105 (100), 92 (63); ^1H NMR (CCl_4) δ 0.7–1.1 (m, 2 H), 1.4–2.9 (m, 17 H, s at 1.91), 5.24 (dd, J = 1, 3 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 170.75 (s), 142.23 (s), 123.06 (d), 91.22 (s), 42.69 (t), 41.84 (t), 39.37 (t), 31.84 (t), 30.93 (t), 30.28 (t), 29.30 (t), 26.83 (t), 22.35 (q). Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 75.05; H, 9.77.

10c: IR (neat) 3040, 1655, 1600, 815, 790, 760, 700 cm^{-1}; ^1H NMR (CCl_4) δ 0.6–1.1 (m, 2 H), 1.3–3.0 (m, 14 H), 5.47 (dd, J = 2, 4 Hz, 1 H), 7.11 (s, 5 H); ^{13}C NMR ($CDCl_3$) δ 152.57 (s), 142.82 (s), 128.00 (d, 2C), 126.21 (d, 2C), 125.15 (d), 124.83 (d), 52.02 (s), 49.42 (t), 42.60 (t), 41.42 (t), 31.92 (t), 31.72 (t), 30.86 (t), 29.73 (t), 28.02 (t). Anal. Calcd for $C_{17}H_{22}$: C, 90.20; H, 9.80. Found: C, 89.91; H, 9.68.

Oxidation of 1b with Lead Tetraacetate. Oxidation of **1b** (900 mg, 5.0 mmol) as described above except for using a large excess (7.9 g, 100 mmol) of pyridine afforded 272 mg (30%) of

acetoxy alkene **2b**, 89 mg (8%) of diacetate **3b**, 80 mg (8%) of phenyl alkene **10b**, and 58 mg of unreacted **1b** after chromatography on silica gel.

2b: IR (neat) 3040, 1735, 1640, 1250, 1230, 1040, 790 cm^{-1}; MS, *m/e* (relative intensity) 194 (M^+, 2), 134 (84), 119 (59), 105 (69), 92 (100), 91 (94); ^1H NMR ($CDCl_3$) δ 1.3–2.9 (m, 17 H, s at 1.96), 5.39 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 170.77 (s), 143.99 (s), 122.06 (d), 90.86 (s), 45.06 (t), 43.06 (t), 40.37 (t), 34.48 (t), 29.56 (t), 28.83 (t), 26.32 (t), 22.17 (q). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73.92; H, 9.59.

3b: mp 52–53 °C; IR (KBr) 3010, 1730, 1250, 1230, 1090, 1065, 1015, 940, 860, 800, 780, 735 cm^{-1}; MS, *m/e* (relative intensity) 252 (M^+, not detected), 192 (38), 150 (68), 122 (68), 108 (66), 107 (100); ^1H NMR (CCl_4) δ 1.0–1.4 (m, 3 H), 1.5–2.3 (m, 13 H, s at 1.90), 2.49 (d, J = 15 Hz, 1 H), 2.83 (d, J = 15 Hz, 1 H), 6.11 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 170.11 (s, 2 C), 136.89 (d, 2 C), 92.37 (s, 2 C), 51.62 (t), 38.11 (t, 2 C), 28.13 (t, 2 C), 26.47 (t), 22.16 (q, 2 C). Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99. Found: C, 66.74; H, 7.99.

10b: IR (neat) 3040, 1640, 1600, 790, 760, 700 cm^{-1}; MS, *m/e* (relative intensity) 212 (M^+, 100), 169 (65), 156 (94), 155 (88), 129 (89), 91 (88); ^1H NMR ($CDCl_3$) δ 1.3–3.0 (m, 14 H), 5.52 (br s, 1 H), 7.04–7.42 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 151.06 (s), 144.97 (s), 128.04 (d, 2 C), 126.05 (d, 2 C), 125.35 (d), 123.04 (d), 54.13 (s), 48.93 (t), 46.29 (t), 42.96 (t), 35.69 (t), 29.52 (t), 28.95 (t), 26.60 (t). Anal. Calcd for $C_{16}H_{20}$: C, 90.50; H, 9.50. Found: C, 90.24; H, 9.73.

Oxidation of 1a with Lead Tetraacetate. Oxidation of **1a** (1.00 g, 6.02 mmol) was carried out with an excess of lead tetraacetate (6.65 g, 15.0 mmol) to afford 473 mg (33%) of **3a** after chromatography on silica gel.

3a: IR (neat) 1735, 1260, 1235, 1075, 1030, 780 cm^{-1}; MS, *m/e* (relative intensity) 238 (M^+, 3), 136 (100); ^1H NMR ($CDCl_3$) δ 1.4–1.7 (m, 4 H), 1.8–2.2 (m, 10 H, s at 1.98), 2.30 (d, J = 12 Hz, 1 H), 3.15 (d, J = 12 Hz, 1 H), 6.12 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 170.16 (s, 2 C), 135.82 (d, 2 C), 89.09 (s, 2 C), 47.70 (t), 35.42 (t, 2 C), 22.99 (t, 2 C), 21.92 (q, 2 C). Anal. Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.28; H, 7.69.

Hydrogenation of 3a. Hydrogenation of **3a** (597 mg, 2.5 mmol) with a catalytic amount of palladium on charcoal in 10 mL of methanol at atmospheric pressure of hydrogen gave 500 mg (83%) of **4**: IR (neat) 1730, 1235, 1075, 1045, 1030, 1010, 940 cm^{-1}; MS, *m/e* (relative intensity) 240 (M^+, trace), 137 (100), 120 (79), 109 (58), 96 (68); ^1H NMR ($CDCl_3$) δ 1.4–2.3 (m, 19 H, s at 1.94), 2.85 (d, J = 12 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 170.21 (s, 2 C), 87.43 (s, 2 C), 46.58 (t), 38.46 (t, 2 C), 36.74 (t, 2 C), 23.04 (t, 2 C), 22.07 (q, 2 C). Anal. Calcd for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 64.66; H, 8.21.

Pyrolysis of 4. A solution of **4** (455 mg, 1.90 mmol) in 50 mL of hexane was passed with a nitrogen flow through a Pyrex column packed with Pyrex chips which was heated at 400 °C (contact time about 20 s). Products were collected in a cold trap containing powdered potassium carbonate. The solvent was evaporated and the products were analyzed by GLC. Preparative GLC gave 144 mg (42%) of **2a**: IR (neat) 1730, 1260, 1240, 1035, 1020, 825, 790, 730 cm^{-1}; MS, *m/e* (relative intensity) 180 (M^+, 26), 120 (100), 96 (63), 92 (95), 91 (74); ^1H NMR ($CDCl_3$) δ 1.0–3.0 (m, 15 H, s at 1.95), 5.35 (br m, 1 H); ^{13}C NMR ($CDCl_3$) δ 170.97 (s), 143.28 (s), 125.47 (d), 90.25 (s), 41.90 (t), 41.79 (t), 36.19 (t), 31.79 (t), 25.39 (t), 22.64 (t), 22.10 (q). Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 72.96; H, 8.86.

Pyrolysis of 2c. Pyrolysis of **2c** (236 mg, 1.13 mmol) was carried out as described above to afford 99 mg (59%) of **6a** after purification by preparative GLC. **6a**: IR (CCl_4) 3020, 1660, 915 cm^{-1}; MS, *m/e* (relative intensity) 148 (M^+, 80), 106 (63), 105 (77), 91 (100), 79 (59); ^1H NMR ($CDCl_3$) δ 1.0–3.2 (m, 14 H), 4.76 (dd, J = 5, 10 Hz, 1 H), 5.82 (dd, J = 2, 4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 151.63 (s), 149.19 (s), 132.01 (d), 114.84 (d), 38.78 (t), 33.62 (t), 33.26 (t), 27.53 (t), 23.51 (t), 23.27 (t), 19.65 (t). Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 89.18; H, 10.93.

Registry No. *exo*-**1a**, 89398-38-9; *endo*-**1a**, 89460-83-3; *exo*-**1b**, 89398-39-0; *endo*-**1b**, 89460-84-4; *exo*-**1c**, 89398-40-3; *endo*-**1c**, 89460-85-5; **2a**, 88226-68-0; **2b**, 89398-41-4; **2c**, 89398-42-5; **3a**, 89398-43-6; **3b**, 89398-44-7; **4**, 89398-45-8; **6a**, 89398-46-9; **7a**, 22118-00-9; **7b**, 769-32-4; **7c**, 38262-50-9; **8a**, 20990-27-6; **8b**, 89398-47-0; **8b** semicarbazone, 89398-48-1; **8c**, 89398-49-2; **8c** semicarbazone, 89398-50-5; *exo*-**9a**, 89398-51-6; *endo*-**9a**, 89460-86-6; *exo*-**9b**, 89398-52-7; *endo*-**9b**, 89460-87-7; *exo*-**9c**, 89398-53-8; *endo*-**9c**, 89460-88-8; **10b**, 89398-54-9; **10c**, 89398-55-0; [4.3.1]-propell-8-en-7-one, 89398-56-1; 8-methoxy[4.3.1]propellan-7-one, 89398-57-2; 8-formyl[5.3.1]propellane, 89398-58-3; 8-formyl-[5.3.1]propellane semicarbazone, 89398-59-4; 7-formyl[4.3.1]-propellane, 89398-60-7; trimethyloxosulfonium iodide, 1774-47-6; lead tetraacetate, 546-67-8.

Generation of the Dianion of *N*-(Trimethylsilyl)acetamide and Reaction of the Dianion with Electrophilic Reagents

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Aliphatic esters are readily converted to enolate anions by strong bases, and numerous examples of condensations of the anions with electrophilic reagents have been reported.[1] These reactions are sometimes complicated by self-condensation leading to β-keto esters. One method for circumventing this problem involves enolate anions prepared from salts of the corresponding carboxylic acids;[2] the resulting dianions are more basic and nucleophilic than the corresponding ester anions.

Anions of carboxamides have received relatively little study; many of the investigations have been with monoanions of *N,N*-disubstituted amides. Dianions of monosubstituted amides have been investigated by Hauser and co-workers.[3] Although the dianion of acetanilide could not be formed with KNH_2 in liquid ammonia, it was prepared satisfactorily with 2 equiv of *n*-butyllithium in ethereal solvent. Other monosubstituted amides formed dianions similarly; the anions reacted selectively with electrophiles at the α-methylene position. Problems arise with unsubstituted amides, other than special cases such as phenylacetamide.[4] The anions frequently have poor solubility in ethereal solvents, making it difficult to effect secondary ionization at the α position.[5] A second ionization at nitrogen may precede enolate anion formation. Furthermore, it has been reported that treatment of acetamide with strong bases under forcing conditions causes dehydration to form the anion of acetonitrile.[5,6] In cases where preparation of the N,C-dianion may be possible, it is not clear that electrophiles will react exclusively on carbon.

In synthetic studies of compounds related to pretetramide presently being carried out in this laboratory, the need arose for synthons that are equivalent to the enolate anion of acetamide for use in acylation reactions. The

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