New Synthesis of Cyclopropanes from 1,3-Dicarbonyl Compounds Utilizing Electroreduction of 1,3-Dimethanesulfonates[1]

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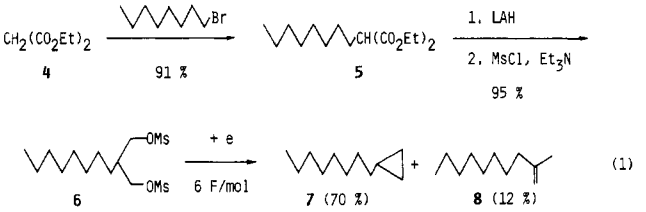
Electroorganic synthesis of cyclopropanes from dimethanesulfonates of 1,3-diols is described. The process involves reduction of 1,3-dicarbonyl compounds with LiAlH followed by esterification with methanesulfonyl chloride and electroreduction.

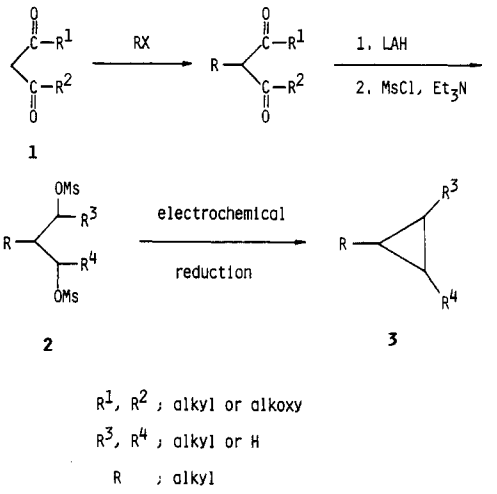
Although electroreductive formation of cyclopropanes from 1,3-dihalides has been known,[2] exploiting new convenient methods of synthesis of a variety of cyclopropanes is desirable, since 1,3-dihalides are rather limited as the starting materials. We describe herein a new electroorganic synthesis of cyclopropanes from dimethanesulfonates (2) of 1,3-diols.[3,4] The process is shown in Scheme I, which indicates that cyclopropanes **3** bearing a variety of substituents can be easily prepared, since the starting 1,3-dicarbonyl compounds **1** are available in great variety and can be alkylated easily with various electrophiles such as alkyl halides and α,β-unsaturated carbonyl compounds.

Preparation of Mono- and 1,1-Disubstituted Cyclopropanes from Diethyl Malonate. Mono- and 1,1-disubstituted cyclopropanes were synthesized by utilizing diethyl malonate (**4**) as a starting compound. The procedure is very simple as exemplified in the synthesis of *n*-octylcyclopropane (**7**, eq 1). The alkylation of **4** with

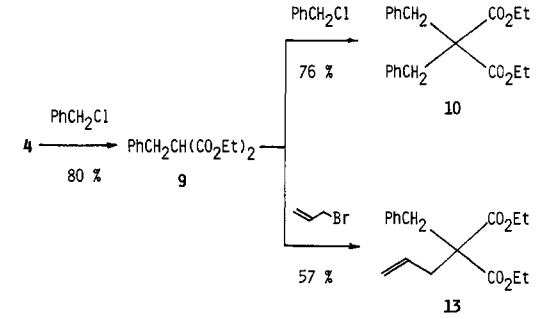


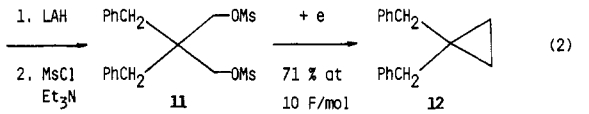
n-octyl bromide followed by LiAlH reduction and esterification with methanesulfonyl chloride yielded dimethanesulfonate **6**, reduction of which was carried out with a constant current by using a divided cell equipped with a ceramic diaphragm, platinum anode, and lead cathode. Thus a solution of **6** in DMF was added dropwise into the catholyte at such a rate that the addition was completed at the time when 3F/mol of electricity was passed. The dropwise addition of **6** increased the yield of cyclopropanes, since 1,3-dimethanesulfonates were not always stable under the reaction conditions. After 6 F/mol of electricity was passed, the expected cyclopropane **7** was obtained in 70% yield together with a minor amount of **8** (12%). As shown in this example, monoalkylation of **4** leads to monoalkylcyclopropanes, while dialkylation of **4** resulted in the formation of 1,1-dialkylcyclopropanes such as 1,1-dibenzylcyclopropane **12** (eq 2). Dialkylation of **4**

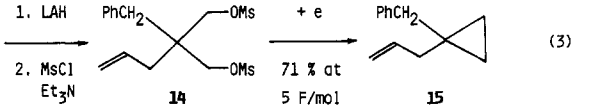
Scheme I



with two different alkyl halides also gave the corresponding 1,1-disubstituted cyclopropanes as shown in eq 3.





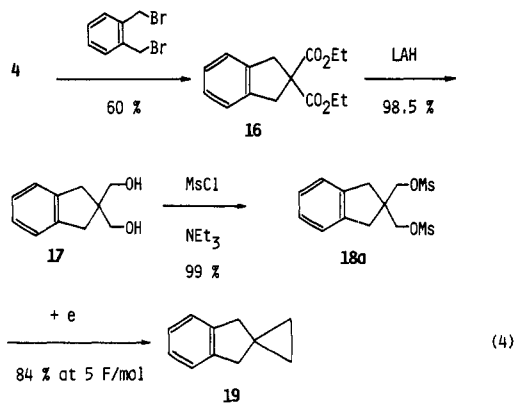


Spiro compound **19** was also obtained from **4** through alkylation with α,α'-dibromo-*o*-xylene (eq 4).

As described in the above examples, a malonic ester can be regarded as an equivalent for cyclopropane in this electroreductive reaction. Thus, the Michael addition of

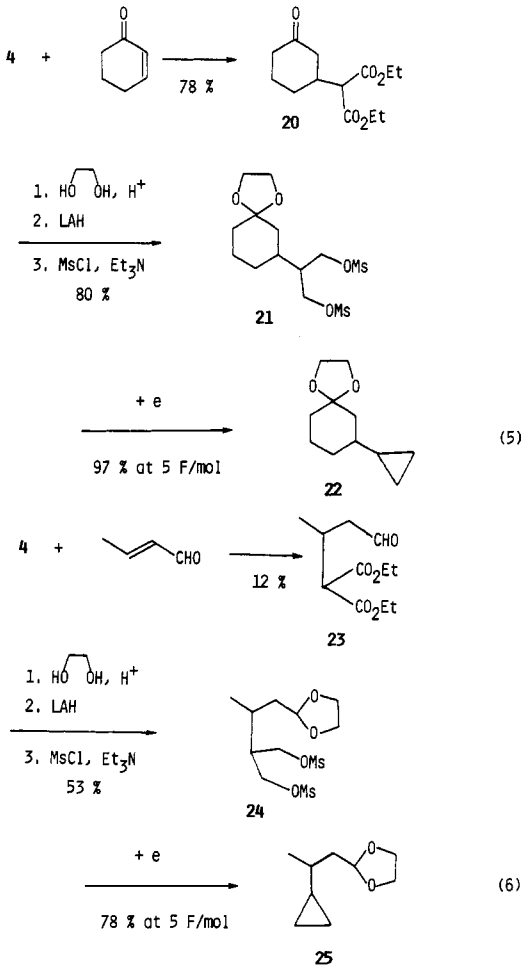
(1) Electroorganic Chemistry. 58.
(2) For example: (a) Rifi, M. R. *J. Am. Chem. Soc.* **1967**, *89*, 4442. (b) Adachi, T.; Iwasaki, T.; Miyoshi, M.; Inoue, I. *J. Chem. Soc., Chem. Commun.* **1977**, 248.
(3) To our knowledge, the reduction of a 1,3-dimethanesulfonate by chemical reducing agents such as disolving metals has not been reported.
(4) Electrochemical reduction of a monomethanesulfonate: Shono, T.; Matsumura, Y.; Tsubata, K.; Sugihara, Y. *Tetrahedron Lett.* **1979**, 2157.

0022-3263/82/1947-3090$01.25/0



(4)

a malonic ester to α,β-unsaturated carbonyl compounds followed by protection of the carbonyl group, reduction with LiAlH, esterification with methanesulfonyl chloride, and electroreduction is an effective method of synthesizing β-cyclopropyl-substituted carbonyl compounds as exemplified in eq 5 and 6.



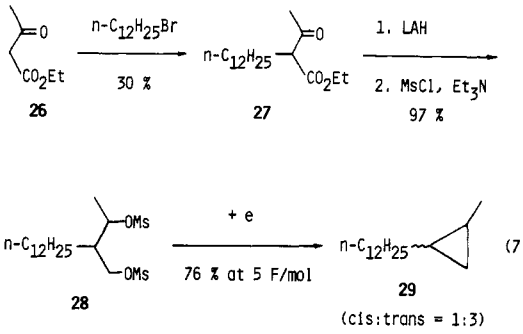
(5)

(6)

The processes shown in eq 5 and 6 are considered to be equivalent to the Michael addition of cyclopropyl anion to α,β-unsaturated carbonyl compounds,[5] though such Michael addition is not always a simple process.

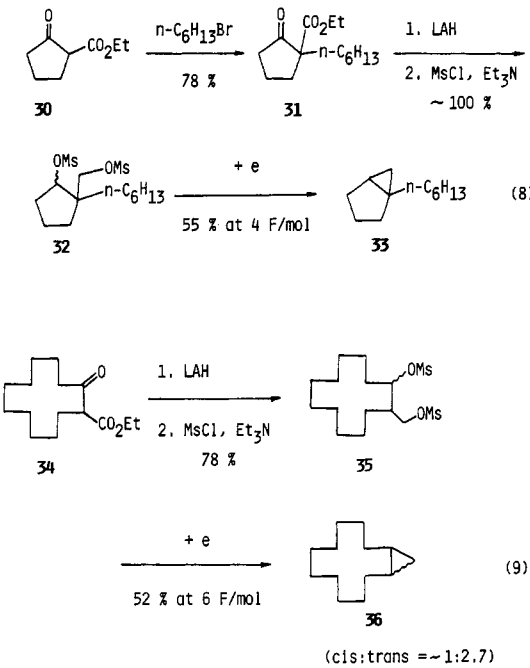
Preparation of 1,2-Disubstituted and 1,1,2-Trisubstituted Cyclopropanes from β-Keto Esters. When β-keto esters were used as starting dicarbonyl compounds, 1,2-disubstituted and 1,1,2-trisubstituted cyclopropanes could also be synthesized (eq 7–9).

Thus, a 1,2-disubstituted cyclopropane (**29**) was obtained from ethyl acetoacetate (**26**, eq 7). The stereochemistry of stereoisomers of **29**, being separable by GLC, was determined by comparison of their NMR spectra with those of 1,2-disubstituted cyclopropanes.[6]



(7)

Fused bicyclic cyclopropanes could also be synthesized by utilizing 2-carbethoxycycloalkanones as β-keto esters. For example, alkylation of 2-carbethoxycyclopentanone (**30**) with *n*-hexyl bromide followed by the conversion to the methanesulfonate and electroreduction afforded 1-*n*-hexylbicyclo[3.1.0]hexane (**33** eq 8). A bicyclic cyclopropane in which the cyclopropane ring is fused with a large ring was also obtained when 2-carbethoxycyclododecanone (**34**) was used as the starting compound (eq 9). The stereoisomers of **36** were separated by GLC, and their stereochemistry was determined in the same way as for **29**.



(8)

(9)

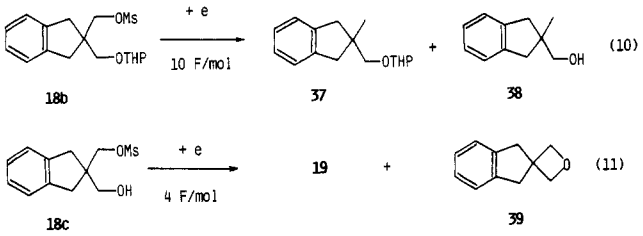
Discussion

Two methanesulfonate groups seem essential to carry out this 1,3-elimination satisfactorily, since other leaving groups such as OH and OTHP brought about the formation of a mixture of products. Thus, the products from **18b** were **37** and **38** in 70% and 23% yields, respectively, and **18c** gave cyclopropane **19** (45%) and **39** (47%) (eq 10 and 11).

Although the mechanism is not clear as yet, the electroreductive formation of cyclopropanes may involve the initial generation of a carbanion through the electroreductive cleavage of the C–O bond of a methanesulfonate

(5) Marino, J. P.; Browne, L. J. *J. Org. Chem.* **1976**, *41*, 3629.

(6) (a) Longone, D. T.; Miller, A. H. *J. Chem. Soc., Chem. Commun.* **1967**, 447. (b) Casanova, J.; Waegell, B. *Bull. Soc. Chim. Fr.* **1971**, 1289.



and subsequent intramolecular nucleophilic displacement of another methanesulfonate group by the carbanion.[7] However, the route involving the coupling of a biradical formed by one-electron reduction of the C–O bonds of both methanesulfonate groups is not necessarily ruled out. That the mechanism still remains vague does not diminish the potentiality of this new synthetic method of cyclopropane.

Experimental Section

Melting points were taken with a Yanako micro melting point apparatus and are uncorrected as are boiling points. ^1H NMR spectra were recorded on a Varian Associates EM-390 or EM-360 spectrometer. IR spectra were taken with a Hitachi 215 spectrophotometer. Gas chromatographic analyses were performed on a Yanaco GCG 550T gas chromatograph.

DMF was dried over calcium hydride or molecular sieves.

Preparation of Alkylated 1,3-Dicarbonyl Compounds 5, 9, 10, 13, 16, 20, 23, 27, 31, and 34. Diethyl *n*-octylmalonate (5) was prepared by a method similar to that of Polgar and Robinson:[9] bp 110–123 °C (0.9–1.0 mm); IR (neat) 2930, 2860, 1735, 1465, 1372, 1338, 1300, 1155, 1120, 1098, 1035, 860 cm^{-1}; NMR (CCl_4) δ 0.88 (t, 3 H), 1.27 (t, 6 H), 1.30 (br s, 12 H), 1.82 (m, 2 H), 3.15 (t, 1 H), 4.15 (q, 4 H); mass spectrum, *m/e* 272 (M^+), 227 ($M^+ - C_2H_5O$).

Diethyl benzylmalonate (9) was prepared according to the method described in the literature;[10] bp 115–123 °C (0.9 mm) [lit.[10] 163–190 °C (12 mm)].

Diethyl dibenzylmalonate (10) was prepared by the method described in the literature.[10]

Diethyl allylbenzylmalonate (13) was prepared by a method similar to that of Wallingford and co-workers:[11] bp 126–132 °C (1 mm); IR (neat) 3060, 3025, 2975, 2935, 1718, 1635, 1602, 1440, 1363, 1280, 1243, 1208, 1182, 1140, 1092, 1080, 1040, 920, 860, 738, 698 cm^{-1}; NMR (CCl_4) δ 1.20 (t, 6 H), 2.52 (d, 2 H), 3.15 (s, 2 H) 4.10 (q, 4 H), 4.84–6.25 (m, 3 H), 7.11 (br s, 5 H); mass spectrum, *m/e* 290 (M^+).

Diethyl hydrindene-2,2-dicarboxylate (16) was prepared by the method of Baeyer and Perkin:[12] bp 120–128 °C (0.7 mm) [lit.[13] bp 186 °C (19 mm)]; IR (neat) 2980, 1730, 1460, 1370, 1283, 1255, 1193, 1070, 862, 755, 740 cm^{-1}; NMR (CCl_4) δ 1.21 (t, 6 H), 3.41 (s, 4 H), 4.04 (q, 4 H), 6.94 (s, 4 H); mass spectrum, *m/e* 262 (M^+).

Diethyl (3-oxocyclohexyl)malonate (20) was prepared by a method similar to that described in the literature:[14] bp 154–158 °C (2 mm); IR (neat) 2930 (br), 1740 and 1705 (br), 1442, 1365, 1218, 1140, 1025, 960, 860 cm^{-1}; NMR (CCl_4) δ 0.93–2.79 (m 9 H), 1.26 (t, 6 H), 3.21 (d, 1 H), 4.18 (q, 4 H); mass spectrum, *m/e* 256 (M^+).

Diethyl (2-formyl-1-methylethyl)malonate (23) was prepared by the method of Warner and Moe.[15]

Ethyl 2-*n*-dodecylacetoacetate (27) was prepared by a method similar to that of Marvel and Hager:[16] bp 149–152 °C (1.1 mm); IR (neat) 2910, 2845, 1705 (br), 1418, 1353, 1240, 1140, 1020 cm^{-1}; NMR (CCl_4) δ 0.6–2.45 (m, 28 H), 2.12 (s, 3 H), 3.11 (t, 1 H), 4.11 (q, 2 H); mass spectrum, *m/e* 256 ($M^+ - CH_2{=}C{=}O$).

2-*n*-Hexyl-2-carbethoxycyclopentanone (31) was prepared according to the method of Barco and co-workers:[17] bp 103–112 °C (0.6 mm); IR (neat) 2950, 2925, 2860, 1740, 1708, 1680, 1622, 1460, 1410, 1378, 1353, 1303, 1225, 1140, 1053, 917, 858, 772 cm^{-1}; NMR (CCl_4) δ 0.69–2.73 (m, 22 H), 4.11 (q, 2 H); mass spectrum, *m/e* 240 (M^+).

2-Carbethoxycyclododecanone (34) was prepared by the method described in the literature.[18]

Synthesis of Dimethanesulfonates 6, 11, 14, 18a, 21, 24, 28, 32, and 35. The general procedure for the synthesis of dimethanesulfonates except **21** and **24** is as follows. To a stirred suspension of lithium aluminum hydride (1.7 g, 45 mmol) in ether (80 mL) was added dropwise a solution of the 1,3-dicarbonyl compound (30 mmol) in ether (20 mL). After the addition was completed, the reaction mixture was refluxed for 2–3 h. An excess of water (2–3 equiv) was added dropwise to the cooled mixture, and the reaction mixture was stirred at room temperature for 1 h. The product was collected by filtration, and the solid was washed with methylene chloride (In the case of the diol derived from **34**, ethyl acetate was used as the solvent for washing.) The combined organic solution was evaporated to give diol which could be purified by column chromatography on silica gel (*n*-hexane–AcOEt), though it was in general pure enough to use directly in the following step. To a stirred solution of the diol (15 mmol) and triethylamine (3.54 g, 35 mmol) in CH_2Cl_2 (30 mL) was added dropwise methanesulfonyl chloride (4 g, 35 mmol). The reaction temperature was maintained at 0–5 °C during the reaction. After the reaction mixture was stirred for 1–2 h, it was diluted with CH_2Cl_2 (20 mL) and was washed with cold water (15 mL), cold 5% HCl (15 mL), aqueous $NaHCO_3$ (15 mL), and brine (15 mL) successively. The organic solution was dried over anhydrous magnesium sulfate, and the drying agent was filtered off. The solvent was evaporated, and the residue was purified by column chromatography on silica gel (*n*-hexane–AcOEt) to afford the dimethanesulfonate.

Dimethanesulfonates **21** and **24** were prepared in a similar way after the ketone and aldehyde had been protected,[19] respectively.

6: mp 52 °C (CCl_4); IR (KBr) 3030, 2925, 2855, 1485, 1350, 1168, 1105, 985, 958, 940, 840, 830, 755 cm^{-1}; NMR ($CDCl_3$) δ 0.89 (t, 3 H), 1.10–1.60 (m, 14 H), 2.15 (m, 1 H), 3.02 (s, 6 H), 4.04–4.40 (m, 4 H). Anal. Calcd for $C_{13}H_{28}O_6S_2$: C, 45.33; H, 8.19; S, 18.61. Found: C, 45.21; H, 8.30; S, 18.49.

11: mp 108–109 °C (*n*-hexane–AcOEt, 2:1); IR (KBr) 3030, 2935, 1592, 1490, 1458, 1450, 1355, 1332, 1320, 1262, 1163, 975, 940, 845, 818, 740, 722, 697 cm^{-1}; NMR ($CDCl_3$) δ 2.73 (s, 4 H), 2.90 (s, 6 H), 3.88 (s, 4 H), 7.16 (s, 10 H). Anal. Calcd for $C_{19}H_{24}O_6S_2$: C, 55.32; H, 5.87; S, 15.54. Found: C, 55.02; H, 5.84; S, 15.39.

14: IR (neat) 3055, 3015, 2935, 1635, 1598, 1455, 1350, 1172, 957, 830, 735, 702 cm^{-1}; NMR ($CDCl_3$) δ 2.12 (d, 2 H), 2.73 (s, 2 H), 3.02 (s, 6 H), 4.00 (s, 4 H), 4.99–6.27 (m, 3 H), 7.28 (br s, 5 H). Anal. Calcd for $C_{15}H_{22}O_6S_2$: C, 49.71; H, 6.12; S, 17.69. Found: C, 49.42; H, 5.89; S, 17.68.

18a: mp 84–85 °C (AcOEt); IR (KBr) 3040, 3020, 2980, 2945, 2900, 2850, 1465, 1438, 1340 (br), 1238, 1185, 1167, 1095, 995, 955, 875, 860, 835, 805, 780, 745 cm^{-1}; NMR ($CDCl_3$) δ 2.90 (s, 4 H), 2.96 (s, 6 H), 4.14 (s, 4 H), 7.07 (s, 4 H). Anal. Calcd for $C_{13}H_{18}O_6S_2$: C, 46.69; H, 5.43; S, 19.17. Found: C, 46.64; H, 5.45; S, 19.03.

21: IR (neat) 3025, 2947, 2895, 1355, 1178, 1080, 1040, 980, 950 (br), 840, 750 cm^{-1}; NMR ($CDCl_3$) δ 0.7–2.38 (m, 10 H), 3.05 (s, 6 H), 3.93 (s, 4 H), 4.32 (m, 4 H). Anal. Calcd for $C_{13}H_{24}O_8S_2$:

(7) The similar mechanism has been suggested in the electrochemical reduction of 1,3-dihalides.[8]

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(9) Polgar, N.; Robinson, R. *J. Chem. Soc.* **1943**, 615.

(10) Cope, A. C.; Holmes, H. L.; House, H. O. *Org. React.* **1957**, *9*, 107.

(11) Wallingford, V. H.; Thrope, M. A.; Homeyer, A. H. *J. Am. Chem. Soc.* **1942**, *64*, 580.

(12) Baeyer, A.; Perkin, W. H. *Chem. Ber.* **1884**, *17*, 122.

(13) Thole, F. B.; Thorpe, J. F. *J. Chem. Soc.* **1911**, *99*, 2183.

(14) Spencer, T. A.; Newton, M. D.; Baldwin, S. W. *J. Org. Chem.* **1964**, *29*, 787.

(15) (a) Warner, D. T.; Moe, O. A. *J. Am. Chem. Soc.* **1948**, 70, 3470. (b) *Ibid.* **1949**, *71*, 2586.

(16) Marvel, C. S.; Hager, F. D. "Organic Syntheses"; Wiley: New York, 1967; Collect. Vol. 1, p 248.

(17) Barco, A.; Benetti, S.; Pollini, G. P. *Synthesis* **1973**, 316.

(18) Rhoads, S. J.; Gilbert, J. C.; Decora, A. W.; Garland, T. R.; Spangler, R. J.; Urbigkit, M. J. *Tetrahedron* **1963**, *19*, 1625.

(19) Acetals were prepared by refluxing the mixture of carbonyl compounds and excess ethylene glycol in ethyl orthoformate containing a catalytic amount of *p*-toluenesulfonic acid.

C, 41.92; H, 6.49; S, 17.22. Found: C, 42.16; H, 6.68; S. 16.96.

24: IR (neat) 3020, 2960, 2940, 2890, 1352, 1175, 980, 955, 835, 745 cm^{-1}; NMR ($CDCl_3$) δ 1.06 (d, 3 H), 1.49–2.7 (m, 4 H), 3.07 (s, 6 H), 3.91 (m, 4 H), 4.29 (d, 4 H), 4.91 (t, 1 H). Anal. Calcd for $C_{11}H_{22}O_8S_2$: C, 38.14; H, 6.40; S, 18.51. Found: C, 37.98; H, 6.37; S, 18.78.

28: mp 78–80 °C (*n*-hexane); IR (KBr) 2915, 2850, 1470, 1350, 1332, 1178, 993, 978, 962, 920, 853, 838 cm^{-1}; NMR ($CDCl_3$) δ 0.64–2.26 (m, 29 H), 2.94 (s, 6 H), 4.10 (m, 2 H), 4.85 (m, 1 H). Anal. Calcd for $C_{18}H_{38}O_6S_2$: C, 52.14; H, 9.24; S, 15.47. Found: C, 52.22; H, 9.05; S, 15.53.

32: IR (neat) 3022, 2930, 2855, 1462, 1350, 1175, 960, 840, 755 cm^{-1}; NMR (CCl_4) δ 0.65–2.78 (m, 19 H), 2.99 (s, 6 H), 3.72–4.32 (m, 2 H), 4.82 (t, 1 H). Anal. Calcd for $C_{14}H_{28}O_6S_2$: C, 47.17; H, 7.92; S, 17.98. Found: C, 47.33; H, 8.03; S, 17.73.

35: mp 114.5–115.5 °C (*n*-hexane–AcOEt, 1:2); IR (KBr) 3025, 2935, 2855, 1468, 1355, 1340, 1330, 1167, 970, 908, 868, 855, 838, 825, 808, 755, 720 cm^{-1}; NMR ($CDCl_3$) δ 0.8–2.6 (m, 21 H), 3.0 (s, 6 H), 4.12 (d, 2 H), 4.86 (m, 1 H). Anal. Calcd for $C_{15}H_{30}O_6S_2$: C, 48.62; H, 8.16; S, 17.31. Found: C, 48.72; H, 8.31; S, 17.35.

Synthesis of Diol 17. Diol **17** was obtained by LiAlH reduction of **16** in a 98.5% yield: mp 109–112.5 °C (*n*-hexane–AcOEt, 3:2); IR (KBr) 3250 (br), 2890, 2845, 1455, 1355, 1285, 1235, 1115, 1078, 1020, 955, 930, 735 cm^{-1}; NMR ($CDCl_3$) δ 2.68 (m 2 H, OH), 2.78 (s, 4 H), 3.68 and 3.72 (br s, 4 H), 7.06 (s, 4 H). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.86; H, 7.96.

Synthesis of Monomethanesulfonates 18b,c. To a stirred solution of diol **17** (0.801 g, 4.5 mmol) and dihydropyran (0.378 g, 4.5 mmol) in CH_2Cl_2 (10 mL) was added a catalytic amount of *p*-toluenesulfonic acid (0.03 g, 1.16 mmol), and the reaction mixture was stirred at room temperature for 30 min. Water (10 mL) was added to the solution, and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL), and the combined organic solution was dried over anhydrous magnesium sulfate. After the drying agent was removed by filtration, the solvent was evaporated, and the residue was purified by column chromatography on silica gel (ether) to afford a monohydroxyl compound (0.632 g, 54% yield). This compound was transformed into methanesulfonate **18b** by treating the alcohol with 1.1 equiv of metanesulfonyl chloride in the usual manner, as described above: quantitative yield; mp 88 °C (*n*-hexane–AcOEt, 7:1); IR (KBr) 3008, 2960, 2935, 2850, 1380, 1175, 1120, 1032, 973, 948, 855, 840, 750 cm^{-1}; NMR (CCl_4) δ 1.20–2.00 (m, 6 H), 2.87 (s, 7 H), 3.10–4.00 (m, 4 H), 4.15 (s, 2 H), 4.50 (m, 1 H), 7.06 (s, 4 H). Anal. Calcd for $C_{17}H_{24}O_5S$: C, 59.98; H, 7.10; S, 9.42. Found: C, 59.68; H, 7.10; S, 9.57.

The conversion of diol **17** to methanesulfonate **18c** was carried out by treating **17** with 1.05 equiv of methanesulfonyl chloride in a similar manner except that the reaction temperature was −20 °C: 77% yield; IR (neat) 3550, 3400, 3020, 2930, 2845, 1453, 1428, 1340,1220, 1165, 1068, 1028, 942, 825, 785, 732 cm^{-1}; NMR ($CDCl_3$) δ 2.35 (br s, 1 H), 2.86 (s, 4 H), 3.01 (s, 3 H), 3.63 (s, 2 H), 4.27 (s, 2 H), 7.18 (s, 4 H). Anal. Calcd for $C_{12}H_{16}O_4S$: C, 56.24; H, 6.29; S, 12.51. Found: C, 55.95; H, 6.52; S, 12.41.

Electroreductive Synthesis of Cyclopropanes 7, 12, 15, 19, 22, 25, 29, 33, and 36. Electrochemical reduction of dimethanesulfonates was carried out in a divided cell equipped with a lead cathode and a platinum anode. To a stirred solution of dry DMF (50 mL) containing tetraethylammonium *p*-toluenesulfonate (5 g, 17 mmol) as a supporting electrolyte was added dropwise a solution of dimethanesulfoante (5 mmol) in dry DMF (5 mL) over the period in which 3 F/mol of electricity had been passed. The current was constant (0.2 A), and the current density was 5.7 mA/cm^2. The cathode potential was about −2.5 V vs. SCE.[20] During the reaction, the solution was stirred and cooled in an ice–water bath. After 4–10 F/mol of electricity was passed, the cathodic solution was poured into cold 5% hydrochloric acid (100 mL), and the product was extracted with pentane (3 × 50 mL). The combined organic layer was dried over anhydrous mangesium sulfate. After the drying agent was removed by filtration, the solvent was evaporated, and the residual oil was purified by column chromatography on silica gel (pentane) to afford cyclopropane derivatives which were further purified by GLC to obtain samples for identification. The products **7** and **8** were separated from their mixture by GLC. In the case of disubstituted cyclopropanes **29** and **36**, cis and trans isomers were also separated by GLC. The stereochemistry of each isolated isomer was determined on the basis of its NMR spectra since the cis methine proton on a cyclopropane ring generally appears at higher field than the trans methine proton.[6] The results were summarized in Table I.

(20) The formation of cyclopropanes proceeded effectively at the cathode potential of −2.5 V vs. SCE, whereas the yields of cyclopropanes were negligible at −2.3 V vs. SCE.

Table I. Electroreductive Synthesis of Cyclopropanes

methanesulfonate	electricity passed, F/mol	product (% yield)[a]
6	6	**7** (70), **8** (12)
11	10	**12** (71)
14	5	**15** (71)
18a	5	**19** (84)
21	5	**22** (97)
24	5	**25** (78)
28	5	**29** (76)[b]
32	4	**33** (55)
35	6	**36** (52)[c]

[a] The isolated yield determined after purification by column chromatography. [b] The ratio of cis to trans isomers is 1:3. [c] The ratio of cis to trans isomers is ~1:2.7.

7: IR (neat) 3075, 3000, 2953, 2925, 2850, 1460, 1070, 820 cm^{-1}; NMR (CCl_4) δ −0.17 to +0.15 (m, 2 H), 0.15–0.72 (m, 3 H), 0.87 (t, 3 H), 1.28 (br s, 14 H); mass spectrum, *m/e* 154 (M^+).

8: IR (neat) 3080, 2955, 2930, 2860, 1647, 1455, 1375, 1263, 1100, 1028, 885, 785 cm^{-1}; NMR (CCl_4) δ 0.87 (t, 3 H), 1.28 (br s, 12 H), 1.69 (s, 3 H), 1.97 (t, 2 H), 4.60 (s, 2 H); mass spectrum, *m/e* 154 (M^+).

12: IR (neat) 3060, 3020, 2910, 2840, 1597, 1492, 1450, 1073, 1030, 1015, 903, 763, 735, 697 cm^{-1}; NMR (CCl_4) δ 0.48 (s, 4 H), 2.50 (s, 4 H), 7.06 (s, 10 H); mass spectrum, *m/e* 222 (M^+), 131 ($M^+ - PhCH_2$), 91 ($PhCH_2^+$).

15: IR (neat) 3060, 3020, 2990, 2905, 2845, 1635, 1605, 1493, 1440, 1422, 1073, 1013, 998, 912, 760, 720, 697 cm^{-1}; NMR (CCl_4) δ 0.37 (br s, 4 H), 1.93 (d, 2 H), 2.52 (s, 2 H), 4.86–5.16 (m, 2 H), 5.40–6.20 (m, 1 H), 7.11 (br s, 5 H); mass spectrum, *m/e* 172 (M^+), 144 ($M^+ - C_2H_4$), 131 ($M^+ - C_3H_5$), 91 ($PhCH_2^+$).

19: IR (neat) 3070, 3045, 3020, 2990, 2922, 2890, 2838, 1585, 1483, 1460, 1433, 1308, 1213, 1045, 1023, 1012, 1005, 955, 750, 728 cm^{-1}; NMR (CCl_4) δ 0.57 (s, 4 H), 2.84 (s, 4 H), 6.97 (s, 4 H); mass spectrum, *m/e* 144 (M^+), 116 ($M^+ - C_2H_4$).

22: IR (neat) 3072, 2980, 2935, 2870, 1447, 1358, 1145, 1073, 1040, 1015, 962, 947, 935, 915, 855, 840, 820, 803 cm^{-1}; NMR (CCl_4) δ 0–2.05 (m, 14 H), 3.79 (s, 4 H); mass spectrum, *m/e* 182 (M^+).

25: IR (neat) 3070, 2987, 2950, 2863, 2765, 1455, 1430, 1408, 1372, 1215, 1130 (br), 1030 (br), 940, 893, 818, 703 cm^{-1}; NMR (CCl_4) δ −0.16 to +2.03 (m, 11 H), 3.74 (m, 4 H), 4.81 (t, 1 H); mass spectrum, *m/e* 156 (M^+).

***trans*-29**: IR (neat) 3050, 2980, 2918, 2850, 1455, 1375, 1073, 1015, 865 783, 718 cm^{-1}; NMR (CCl_4) δ 0–0.6 (m, 4 H), 0.63–1.66 (m, 28 H); mass spectrum, *m/e* 224 (M^+), 125 ($M^+ - C_7H_{15}$), 111 ($M^+ - C_8H_{17}$), 97 ($M^+ - C_9H_{18}$), 83 ($M^+ - C_{10}H_{21}$), 69, ($M^+ - C_{11}H_{23}$), 55 ($M^+ - C_{12}H_{25}$).

***cis*-29**: IR (neat) 3050, 2980, 2918, 2850, 1450, 1375, 1073, 1020, 840, 718 cm^{-1} NMR (CCl_4) δ −0.37 (m, 1 H), 0.43–1.83 (m, 31 H); mass spectrum, *m/e* 224 (M^+), 125, 111, 97, 83, 69, 55.

33: IR (neat) 3050, 2920, 2852, 1450, 1377, 1015, 757 cm^{-1}; NMR (CCl_4) δ 0–0.40 (m, 2 H), 0.56–2.26 (m, 20 H); mass spectrum, *m/e* 166 (M^+), 95 ($M^+ - C_5H_{11}$), 81 ($M^+ - C_6H_{13}$).

***trans*-36**: IR (neat) 3055, 2990, 2925, 2852, 1465, 1442, 1347, 1305, 1250, 1080, 1020, 970, 885, 808, 780, 715 cm^{-1}; NMR (CCl_4) δ 0–0.94 and 0.94–2.55 (m, 24 H); mass spectrum, *m/e* 180 (M^+), 96 ($M^+ - C_6H_{12}$), 95 ($M^+ - C_6H_{13}$), 82 ($M^+ - C_7H_{14}$), 81 ($M^+ - C_7H_{15}$).

***cis*-36**: IR (neat) 3055, 2980, 2925, 2855, 1468, 1445, 1340, 1305, 1280, 1020, 978, 847, 823, 795, 758 cm^{-1}; NMR (CCl_4) δ −0.32 (m, 1 H), 0.35–2.10 (m, 23 H); mass spectrum, *m/e* 180 (M^+), 96, 95, 82, 81.

Electrochemical Reduction of 18b and 18c. Electrochemical reduction was carried out in a similar procedure as described

above. Electroreduction of **18b** gave **37** and **38** in 70% and 23% yields, respectively. From **18c** were obtained **19** and **39** in 45% and 47% yields, respectively.

37: IR (neat) 3060, 3020, 2930, 2860, 2850, 1452, 1435, 1372, 1350, 1200, 1120, 1075, 1058, 1030, 993, 970, 902, 865, 810, 733 cm^{-1}; NMR (CCl_4) δ 1.17 (s, 3 H), 1.60 (m, 6 H), 2.76 (dd, 4 H), 3.04-4.03 (m, 4 H), 4.49 (m, 1 H), 6.96 (s, 4 H); mass spectrum, *m/e* 246 (M^+), 145 ($M^+ - C_5H_9O_2$), 144 ($M^+ - C_5H_{10}O_2$), 85 ($C_5H_9O^+$).

38: IR (neat) 3350 (br), 3065, 3020, 2950, 2920, 2870, 1460, 1433, 1378, 1300, 1227, 1035, 978, 795, 735 cm^{-1}; NMR (CCl_4) δ 1.10 (s, 3 H), 2.15 (s, 1 H), 2.67 (dd, 4 H), 3.55 (s, 2 H), 6.93 (s, 4 H); mass spectrum, *m/e* 162 (M^+), 145 ($M^+ - OH$), 130 ($M^+ - CH_3OH$).

39: IR (neat) 3060, 3020, 2922, 2855, 1475, 1458, 1430, 1323, 1300, 1282, 1245, 1218, 1123, 1082, 1022, 973, 950, 828, 785, 740, 717 cm^{-1}; NMR (CCl_4) δ 3.19 (s, 4 H), 4.49 (s, 4 H), 7.03 (s, 4 H); mass spectrum, *m/e* 160 (M^+), 130 ($M^+ - CH_2O$).

Registry No. **4**, 105-53-3; **5**, 1472-85-1; **6**, 64923-67-7; **7**, 1472-09-9; **8**, 13151-27-4; **9**, 607-81-8; **10**, 597-55-7; **11**, 82044-43-7; **12**, 65933-61-1; **13**, 82044-44-8; **14**, 82044-45-9; **15**, 82056-40-4; **16**, 66014-45-7; **17**, 82044-46-0; **18a**, 82044-47-1; **18b**, 82044-48-2; **18c**, 82044-49-3; **19**, 7198-71-2; **20**, 22274-75-5; **21**, 82044-50-6; **22**, 82044-51-7; **23**, 23904-39-4; **24**, 82044-52-8; **25**, 82044-53-9; **26**, 141-97-9; **27**, 5397-53-5; **28**, 82044-54-0; *trans*-**29**, 82056-41-5; *cis*-**29**, 82044-55-1; **30**, 611-10-9; **31**, 36370-13-5; **32**, 82044-56-2; **33**, 82044-57-3; **34**, 4017-60-1; **35**, 82044-58-4; *trans*-**36**, 1731-44-8; *cis*-**36**, 1731-42-6; **37**, 82044-59-5; **38**, 73739-59-0; **39**, 82044-60-8; $PhCH_2Cl$, 100-44-7; *n*-$C_{12}H_{25}Br$, 143-15-7; *n*-$C_6H_{13}Br$, 111-25-1; 1-bromooctane, 111-83-1; allyl bromide, 106-95-6; 1,2-dibromomethylbenzene, 91-13-4; 2-cyclohexenone, 930-68-7; 2-butenal, 4170-30-3.

Allylic vs. Vinylic Deprotonation Reactions of Cyclic Vinyl Ethers. 7-Lithio-2,3,4,5-tetrahydrooxepin: Synthesis and Carbon-13 Nuclear Magnetic Resonance Spectrum

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2,3,4,5-Tetrahydrooxepin treated with either *n*-butyllithium or *tert*-butyllithium affords 7-lithio-2,3,4,5-tetrahydrooxepin. The question of allylic vs. vinylic deprotonation of cyclic vinyl ethers was examined by varying ring size and degree of unsaturation. Carbon-13 spectral data for the anions obtained from 2,5-dihydrofuran, 2,3-dihydrooxepin, and 2,3,4,5-tetrahydrooxepin are reported. In contrast to 2,3,4,5-tetrahydrooxepin, 2,3-dihydrooxepin undergoes allylic deprotonation, possibly as a result of a slightly larger C—C=C bond angle in the dihydrooxepin as compared to that of the tetrahydrooxepin.

Introduction

Recently we reported that vinyl anions obtained from the deprotonation of the cyclic vinyl ethers 2,3-dihydrofuran (**1**) and 2,3-dihydro-4*H*-pyran (**2**) can be readily observed by carbon-13 NMR; formation of the α-lithiated species results in a large downfield shift of the resonance of the vinylic carbon bonded to oxygen.[1] Allylic deprotonation by alkyllithium reagents of these two cyclic ethers has not been observed. The magnitude of the internal angle of the possible vinyl or allyl anions is one of several factors expected to affect the site of deprotonation.[2] For example, a C=C—O angle of about 113° is favored for vinyl anions,[3] whereas a C—C—C angle of approximately 132° is preferred for allyl anions.[4] An important difference between the allyl and vinyl anions, and another factor affecting the site of deprotonation, is the presence of the oxygen atom which is expected to inductively stabilize the vinyl anion and conjugatively destabilize the allyl anion. Allylic deprotonation should be favored by an opening up of the C—C=C angle in vinyl ethers, while vinyl deprotonation is favored by a contraction of the C=C—O angle; calculations suggest that such a contraction occurs upon formation of the vinyl anion.[3] Restricting appreciable contraction, and thus discouraging vinyl deprotonation, might be accomplished by incorporating the C=C—O moiety within a suitable sized ring and by extending the conjugation (compare 2,3,4,5-tetrahydrooxepin (**3**) and 2,3-dihydrooxepin (**4**)). The expected effect of ring size on the internal angle may be approximated by considering the C=C—C angle in relevant cycloalkenes:[5,6] cyclopentene (111.8°), cyclohexene (123.5°), cycloheptene (125.5°), cyclooctene (121.0°), and 1,3-cycloheptadiene (129.1°). These data suggest that in the corresponding cyclic vinyl ether series 2,3,4,5-tetrahydrooxepin (**3**) and 2,3-dihydrooxepin (**4**) are the best candidates for allylic deprotonation provided that the bond angle considerations are not dominated by the effects of the oxygen atom mentioned above.

In the present paper we report on an NMR study of the deprotonation reactions of 2,3,4,5-tetrahydrooxepin (**3**), 2,3-dihydrooxepin (**4**), and 2,5-dehydrofuran (**5**). Deprotonation reactions of **3** have not been previously published to the best of our knowledge. The deprotonation reactions of 2,3-dihydrooxepin and 2,5-dihydrofuran have been noted previously[7,8] although the carbon-13 spectra have not been reported for their respective anions.

Results and Discussion

The carbon-13 chemical shifts for various ethers of interest are shown in Table I along with $^1J_{^{13}C-^1H}$ values and the percent *s* character of the carbon orbitals of the C-H bonds. The effect of the oxygen atom is to increase the

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