References and Notes

(1) C. B. Ziegler, Jr., and R. F. Heck, *J. Org. Chem.*, **43**, 2941 (1978).
(2) R. F. Heck, *J. Am. Chem. Soc.*, **90**, 5542 (1968).
(3) H. A. Dieck and R. F. Heck, *J. Org. Chem.*, **40**, 1083 (1975).
(4) B. A. Patel and R. F. Heck, *J. Org. Chem.*, **43**, 3898 (1978).
(5) T. G. H. Jones and R. Robinson, *J. Chem. Soc.*, **111**, 918 (1917).
(6) I. E. Muskat, B. C. Becker, and J. S. Lowenstein, *J. Am. Chem. Soc.*, **52**, 329 (1930).
(7) T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer, and G. Wilkinson, *J. Chem. Soc.*, 3632 (1965).

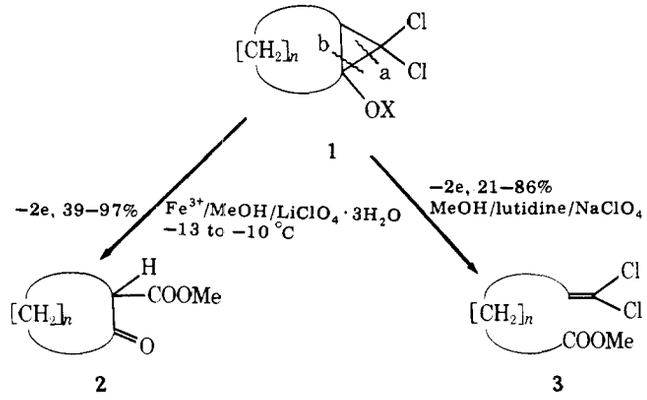
Selective Cleavage of 1-Methoxy-2-(phenylthio)cyclopropane Homologues by Electrolytic Procedure

Sigeru Torii,* Tsutomu Inokuchi, and Nobuharu Takahasi

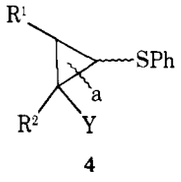
Department of Industrial Chemistry, School of Engineering, Okayama University, Okayama Japan 700

Received July 6, 1978

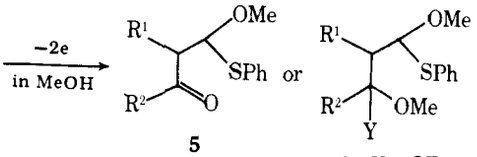
In our last report, 1-trimethylsiloxybicyclo[*n*.1.0]alkanes (**1**, X = $SiMe_3$) were shown to undergo regiospecific cleavage of the type a by the electrolysis with iron(III) nitrate in alcohols at −10 to −13 °C to give 2-alkoxycarbonylcycloalkanones (**2**),[1] contrasting to Schäfer's results of the type b fission of 1-ethoxybicyclo[*n*.1.0]alkanes (**1**, X = Et), giving **3**.[2]



We report in this paper that the type a ring opening of 1-methoxy-2-(phenylthio)cyclopropanes (**4**)[3] can be carried out anodically under a constant applied voltage in a two-compartment cell in the presence of potassium carbonate. The reaction provides a convenient procedure for the preparation of 2-[methoxy(phenylthio)methyl]alkanone analogues **5** or **6**.[4]



4



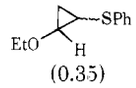
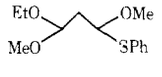
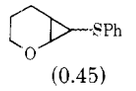
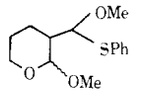
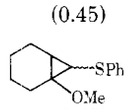
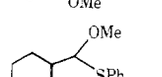
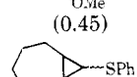
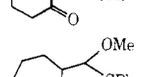
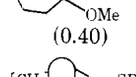
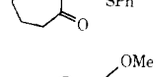
5

6a, Y = OEt
b, Y = OMe

Electrolysis of a solution of **4** ($R^1 = R^2 = -(CH_2)_4-$, 0.43 mmol) and tetraethylammonium tosylate in methanol in the presence of potassium carbonate (50–120 mg) in an anode compartment (cell voltage 3 V, anode potential 0.9 V vs. SCE,[5] 0.8–1.2 mA/cm^2) consumed 5.8 F/mol, affording **5** in 98% yield (75% of conversion). The electrolysis conditions of **4**, conversion percentages, and yields of **5** and **6** are listed in Table I.

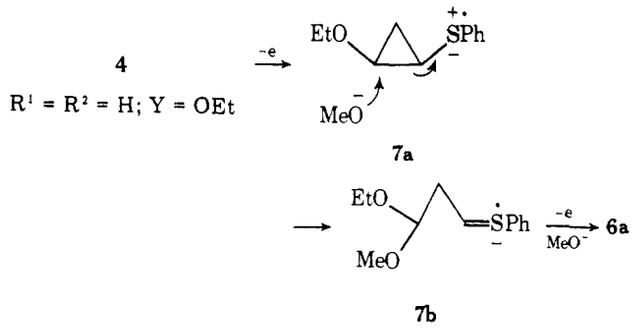
When **4** ($R^1 = R^2 = H$; Y = OEt) was electrolyzed without potassium carbonate it was converted into **6b** ($R^1 = R^2 = H$; Y = OMe) in 72% yield as well as ~20% of diphenyl disulfide after passage of 2.3 F/mol. Since on continuing the electrolysis the solution becomes weakly acidic, the acetal **6a** initially formed would undergo trans acetalization to form **6b**. However, analogous electrolysis with appreciable amounts of potassium carbonate provided **6a** ($R^1 = R^2 = H$; Y = OEt) in 93% yield as a sole product. The latter results suggest that the intermediate **7a**, generated by one-electron discharge on the anode, could be trapped immediately with methanol without scrambling of alkoxides. In the conditions of the formation of **6b**, partially generated thiophenol would also be oxidized

Table I. Conditions and Results of Electrolysis of 1-Methoxy-2-(phenylthio)cyclopropane Homologues in Methanol[a]

entry	substrate 4 (mmol)	registry no.	current, mA/cm^2	applied voltage, V	F/mol	conversion, %	product 5 or 6	registry no.	yield,[b] %
1	 (0.35)	52565-43-2	0.8–1.2	3	4.0	100		68002-01-7	93
2	 (0.45)	68036-09-9	0.8–1.2	3	3.5	89		68002-02-8	82
3	 (0.45)	68001-98-9	0.8–1.2	3	5.8	75		68002-03-9	98
4	 (0.40)	68001-99-0	0.8–1.2	4	2.3	100		68002-04-0	79
5	 (0.32)	68002-00-6	0.8–1.2	5	2.3	100		68002-05-1	78

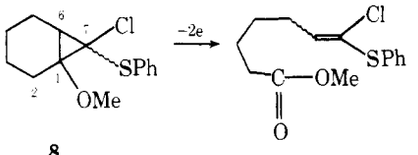
[a] Electrolyzed using a divided cell fitted with platinum electrodes in the presence of Et_4NOTs at 20–30 °C for 6–12 h. [b] Based on isolated product.

0022-3263/78/1943-5020$01.00/0



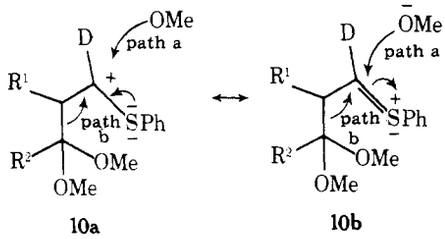
anodically, giving diphenyl disulfide.[6] On the other hand, addition of dimethylformamide (42 mL) in methanol (1.5 mL) gave a mixture of **6a** (63%) and diphenyl disulfide (30%). Hydrolysis of the dimethoxy ketal function of the alicyclic compounds **6** ($R^1 = R^2 = -(CH_2)_n-$) occurred, when the crude ketals were eluted on a silica gel column.

In the same electrolysis conditions, anodic cleavage of 7-chloro-1-methoxy-7-(phenylthio)bicyclo[4.1.0]heptane (**8**) gave methyl 7-chloro-7-(phenylthio)-6-heptenoate (**9**) in 40%



8 **9**

yield (87% conversion after passing 4.5 F/mol), indicating that the important factor determining productselectivity is the type of substituents on the cyclopropane ring. We suggest tentatively that the chlorine atom at the C-7 position of **8** may stabilize the carbonium ion **10** (D = Cl) rather than **10** (D = H)[7] derived from **4**, and this would tend to promote migration of the bond electron as shown in path b.



10a **10b**

Experimental Section

Melting points and boiling points are uncorrected. IR spectra were determined with a JASCO Model IRA-1 spectrometer. ^{1}H-NMR spectra were determined at 60 MHz with a Hitachi Model R-24 spectrometer and ^{13}C-NMR spectra were determined at 25.05 MHz with a JEOL pulsed Fourier transform spectrometer, Model FX-100. The chemical shift values are expressed in δ values (ppm) relative to a Me_4Si as an internal standard. Elemental analyses were performed in our laboratory.

1-Methoxy-7-(phenylthio)bicyclo[4.1.0]heptane (4, $R^1 = R^2 = -(CH_2)_4-$; Y = OMe). To a vigorously stirred solution of 1-methoxy-1-cyclohexene[8] (100 mg, 0.89 mmol), (phenylthio)methyl chloride[9] (190 mg, 1.2 mmol), and benzyltrimethylammonium chloride[3] (5 mg) in CH_2Cl_2 (5 mL) was added dropwise 50% aqueous KOH (2 mL) at 0–3 °C. The mixture was stirred with a vibrator for 4 h at 20 °C and extracted with ether. The extracts were worked up in the usual manner to give 149 mg (71%) of 4 ($R^1 = R^2 = -(CH_2)_4-$; Y = OMe): bp 60–63 °C (0.004 mm); IR (neat) 3054, 2832, 1582, 1479, 1436, 732, 688 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.05–2.45 (m, 10, CH_2, CH), 3.23 (s, 3, CH_3O), 6.75–7.70 (br d, 5, S–Ph); ^{13}C NMR ($CDCl_3$) δ 21.05 (t), 21.59 (t), 23.98 (t), 27.58 (t), 27.73 (d, C-6), 30.41 (d, C-7), 54.43 (q, C-12), 65.05 (s, C-1), 124.60 (d, C-11), 126.41 (d, C-9), 128.59 (d, C-10), 139.03 (s, C-8).

Anal. Calcd for $C_{14}H_{18}OS$: C, 71.77; H, 7.74. Found: C, 71.86; H, 7.63.

1-Ethoxy-2-(phenylthio)cyclopropane (4, $R^1 = R^2 = H$; Y = OEt) was prepared from 1-ethoxyethylene by the same procedure described above for 4 ($R^1 = R^2 = -(CH_2)_4-$; Y = OMe) in 57% yield: bp 74–76 °C (5 mm); IR (neat) 3080, 3059, 1586, 1480, 1437, 742, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.73–0.98 (m, 1, CH), 1.07–1.46 (t, m, 4, CH_3, CH), 2.06–2.41 (m, 1, CH–S), 3.37–3.80 (q, m, 3, CH_2–O–CH), 7.04–7.62 (m, 5, S–Ph).

Anal. Calcd for $C_{11}H_{14}OS$: C, 68.02; H, 7.27. Found: C, 68.04; H, 7.27.

1-Methoxy-8-(phenylthio)bicyclo[5.1.0]octane (4, $R^1 = R^2 = -(CH_2)_4-$; Y = OMe) was obtained in 62% yield by the same procedure as described above: bp 65–67 °C (0.005 mm); IR (neat) 3074, 3052, 2825, 1588, 1480, 1439, 739, 688 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.75–2.80 (m, 12, CH_2, CH), 3.15, 3.18 (s, s, 3, CH_3O), 6.66–7.40 (m, 5, S–Ph).

Anal. Calcd for $C_{15}H_{20}OS$: C, 72.55; H, 8.12. Found: C, 72.41; H, 8.00.

7-(Phenylthio)-2-oxabicyclo[4.1.0]heptane (4, $R^1 = R^2 = -(CH_2)_3O-$; Y = OMe) was obtained in 50% yield by the same manner as described above: bp 60–63 °C (0.004 mm); IR (neat) 3085, 3065, 2875, 1586, 1479, 1438, 737, 687 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.00–2.15 (m, 6, CH_2, CH), 3.00–3.85 (m, 3, CH_2, CH), 6.80–7.35 (m, 5, S–Ph).[10]

1-Methoxy-13-(phenylthio)bicyclo[10.1.0]tridecane (4, $R^1 = R^2 = -(CH_2)_{10}-$; Y = OMe). To a stirred solution of *t*-BuOK (1.1 g, 9.82 mmol) in hexane (3 mL), 1-methoxy-1-cyclododecene (200 mg, 1.02 mmol) and $C_6H_5SCH_2Cl$ (320 mg, 2.14 mmol) in hexane (3 mL) was added dropwise at −40 °C for 15 min. The mixture was stirred at −35 to −30 °C for 8 h, allowed to warm up to room temperature, and quenched with cold water. The organic phase was worked up in the usual manner to give 173 mg (53%) of 4 ($R^1 = R^2 = -(CH_2)_{10}-$; Y = OMe) after chromatography (SiO_2, hexane–benzene 2/1): mp 77–78 °C; IR (Nujol) 3050, 1584, 1478, 725, 680 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.00–1.95 (br, 22, 10 CH_2, 2 CH), 3.28 (s, 3, CH_3O), 7.03–7.40 (br, 5, S–Ph); ^{13}C NMR ($CDCl_3$) δ 21.88 (t), 22.90 (t), 24.07 (t), 27.19 (t), 27.44 (t), 27.78 (t), 27.92 (t), 30.36 (d, C-13), 34.40 (d, C-12), 54.63 (q, C-18), 70.22 (s, C-1), 124.60 (d, C-17), 126.21 (d, C-15), 128.59 (d, C-16), 139.31 (s, C-14).

Anal. Calcd for $C_{20}H_{30}OS$: C, 75.43; H, 9.50. Found: C, 75.67; H, 9.62.

7-Chloro-1-methoxy-7-(phenylthio)bicyclo[4.1.0]heptane (8) was obtained in the similar manner to that described above:[11] bp 66–68 °C (0.01 mm); IR (neat) 3058, 3036, 2822, 1577, 1478, 1435, 1203, 1072, 907, 735, 685, 675 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.18–2.35 (m, 9, CH_2, CH), 3.35 (s, 3, CH_3O), 7.10–7.55 (m, 5, S–Ph); ^{13}C NMR ($CDCl_3$) δ 20.13 (t), 20.56 (t), 21.64 (t), 24.27 (t), 33.19 (d, C-6), 54.38 (q, C-12), 61.21 (s, C-7), 67.68 (s, C-1), 126.16 (d, C-11), 128.45 (d, C-9), 128.74 (d, C-10), 135.28 (d, C-8).

Anal. Calcd for $C_{14}H_{17}ClOS$: C, 62.55; H, 6.38. Found: C, 62.52; H, 6.28.

Electrolysis Apparatus. A modified H-type two-compartment cell (100-mL volume) was employed. The anode compartment, fitted with a drying tube ($CaCl_2$), a thermometer, and a magnetic stirrer bar, was divided from the cathode compartment by a 3-cm diameter glass-frits plate. Two platinum electrodes (1.5 × 2.0 cm^2) were placed parallel to each other 4 cm apart. Regulated DC power was supplied by a Metronix Model 543B instrument.

A General Procedure for Electrolysis of 1-Methoxy-2-(phenylthio)cyclopropane Analogues. A solution of 4 ($R^1 = R^2 = -(CH_2)_4-$; Y = OMe, 100 mg, 0.43 mmol), K_2CO_3 (120 mg), and *p*-$CH_3C_6H_4SO_3NEt_4$ (2 g) in dry MeOH (40 mL) was charged in the anode compartment. To the cathode compartment, a solution of *p*-$CH_3C_6H_4SO_3NEt_4$ (1 g) in dry MeOH (20 mL) was poured. The mixture was electrolyzed under a constant applied voltage of 3 V at a current of 0.80–1.20 mA/cm^2 (anode voltage ~0.9 V vs. SCE) at 20–30 °C. After 5.8 F/mol of electricity were passed, the anode solution was concentrated and the residue was taken up in ether. The extracts were washed with 5% aqueous $NaHCO_3$ and brine, dried (Na_2SO_4), and concentrated. The crude product was chromatographed (SiO_2, hexane-ether 50:1) to give 80 mg (98% yield) of 5 ($R^1 = R^2 = -(CH_2)_4-$) along with 25 mg (25%) of the recovered 4 ($R^1 = R^2 = -(CH_2)_4-$) (75% of conversion). The conditions and results of electrolysis of 4 in MeOH are shown in Table I.

2-(Methoxy(phenylthio)methyl)cyclohexanone (5, $R^1 = R^2 = -(CH_2)_4-$): bp 55–56 °C (0.004 mm); IR (neat) 3043, 2805, 1712, 1582, 1437, 1300, 1074, 743, 684 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.15–3.00 (m, 9, CH_2, CH), 3.37 (s, 3, CH_3O), 4.87–5.10 (d, d, J = 4.2, 7.2 Hz, 1, O–CH–S), 7.12–7.60 (m, 5, S–Ph).

Anal. Calcd for $C_{14}H_{18}O_2S$: C, 67.18; H, 7.25. Found: C, 67.03; H, 7.21.

1-Ethoxy-1,3-dimethoxy-3-(phenylthio)propane (6a, $R^1 = R^2 = H$; Y = OEt): IR (neat) 3045, 2817, 1586, 1477, 1439, 1375, 1125–

1050, 749, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.21 (t, 3, J = 7.0 Hz, CH_3), 2.07 (d, d, 2, J = 6.6 Hz, CH_2), 3.35 (s, 3, CH_3O), 3.55 (s, 3, CH_3O), 3.67 (q, 2, J = 7.0 Hz, CH_2O), 4.73 (t, 1, J = 6.6 Hz, S-CH-O), 4.80 (t, 1, J = 7.3 Hz, O-CH-O), 7.28-7.80 (m, 5, S-Ph).

Anal. Calcd for $C_{13}H_{20}O_3S$: C, 60.92; H, 7.87. Found: C, 61.12; H, 8.11.

2-[Methoxy(phenylthio)methyl]cycloheptanone (5, $R^1 = R^2 = -(CH_2)_5-$): bp 67-69 °C (0.005 mm); IR (neat) 3057, 2825, 1706, 1584, 1476, 1096, 747, 690 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.87-2.77 (m, 11, CH_2, CH), 3.35-3.42 (m, 3, CH_3O), 4.83-5.11 (m, 1, O-CH-S), 7.19-7.65 (m, 5, S-Ph).

Anal. Calcd for $C_{15}H_{20}O_2S$: C, 68.16; H, 7.63. Found: C, 68.21; H, 7.70.

2-[Methoxy (phenylthio)methyl]cyclododecanone (5, $R^1 = R^2 = -(CH_2)_{10}-$): bp 97-99 °C (0.005 mm); IR (neat) 3049, 2815, 1710, 1582, 1471, 1443, 1090, 741, 717, 691 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.05-2.00 (br, 18, CH_2), 2.25-2.80 (m, 3, CH_2, CH), 3.40 (s, 3, CH_3O), 4.54 (d, 1, J = 9.5 Hz, S-CH-O), 7.13-7.55 (m, 5, S-Ph); ^{13}C NMR ($CDCl_3$) δ 21.61 (t), 22.08 (t), 22.37 (t), 23.84 (t), 24.13 (t), 26.01 (t), 26.30 (t), 27.42 (t), 38.81 (t), 55.77 (d, C-12), 56.30 (q, C-18), 91.76 (d, C-13), 128.00 (d, C-17), 128.75 (d, C-15), 131.75 (d, C-16), 134.15 (s, C-14), 211.71 (s, C-1).

Anal. Calcd for $C_{20}H_{30}O_2S$: C, 71.82; H, 9.04. Found: C, 71.72; H, 9.08.

2-Methoxy-3-[methoxy(phenylthio)methyl]tetrahydropyran (5, $R^1 = R^2 = -(CH_2)_3O-$): bp 54-56 °C (0.005 mm); IR (neat) 3025, 1586, 1438, 1180, 1109, 1076, 961, 752, 688 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.10-2.10 (m, 5, CH_2, CH), 3.21-3.50 (m, 8, CH_3O, CH_2O), 4.18-4.90 (m, 2, CH), 7.05-7.60 (m, 5, S-Ph).

Anal. Calcd for $C_{14}H_{20}O_3S$: C, 62.67; H, 7.51. Found: C, 62.53; H, 7.55.

Methyl 7-Chloro-7-(phenylthio)-6-heptenoate (9). Electrolysis of 8 was carried out in the same manner as described above to give **9** in 40% yield: bp 73-75 °C (0.002 mm); IR (neat) 3039, 2852, 1735, 1585, 1480, 1442, 1205, 1170, 1020, 740, 686 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.16-2.00 (m, 4, CH_2), 2.00-2.59 (m, 4, CH_2), 3.67 (s, 3, CH_3O), 6.21 (t, 1, J = 7.8 Hz, HC=C), 7.11-7.47 (br s, 5, S-Ph).

Anal. Calcd for $C_{14}H_{17}ClO_2S$: C, 59.03; H, 6.02. Found: C, 59.11; H, 6.21.

3-(Phenylthio)-1,1,3-trimethoxypropane (6b, $R^1 = R^2 = H$; Y = OMe). A solution of 4 ($R^1 = R^2 = H$, Y = OEt, 70 mg, 0.36 mmol) and p-$CH_3C_6H_4SO_3NEt_4$ (2 g) in dry MeOH (40 mL) was charged in the anode compartment. A solution of p-$CH_3C_6H_4SO_3NEt_4$ (1 g) in dry MeOH (20 mL) was poured into the cathode compartment. The mixture was electrolyzed under a constant applied voltage of 3 V at a current of 1.20-1.33 mA/cm^2 at 20-30 °C. After passage of 2.3 F/mol of electricity, the anode solution was concentrated and the residue was taken up in ether. The extracts were washed with brine, dried (Na_2SO_4), and concentrated. The crude product was chromatographed (SiO_2, hexane-ether 40:1) to give 63 mg (72%) of **6b** ($R^1 = R^2 = H$, Y = OMe) along with 5.5 mg (18%) of diphenyl disulfide, **6b:** IR (neat) 3040, 1588, 1477, 1440, 1130, 1080, 1028, 972, 750, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.02 (t, 2, J = 6.5 Hz, CH_2), 3.31 (s, 6, CH_3O), 3.50 (s, 3, CH_3O), 4.56 (t, 1, J = 6.5 Hz, O-CH-O), 4.70 (t, 1, J = 6.5 Hz, O-CH-S), 7.13-7.59 (m, 5, S-Ph).

Anal. Calcd for $C_{12}H_{18}O_3S$: C, 59.49; H, 7.49. Found: C, 59.40; H, 7.55.

Registry No.—**6b** ($R^1 = R^2 = H$; Y = OMe), 68002-06-2; **8**, 68002-07-3; **9**, 68002-08-4; 1-methoxy-1-cyclohexene, 931-57-7; phenylthiomethyl chloride, 7205-91-6; 1-ethoxyethylene, 109-92-2; 1-methoxy-1-cyclododecane, 32400-32-1.

References and Notes

(1) S. Torii, T. Okamoto, and N. Ueno, *Chem. Commun.*, 293 (1978).
(2) M. Klehr and H. J. Schäfer, *Angew. Chem., Int. Ed. Engl.*, **14**, 247 (1975).
(3) U. Schöllkopf, G. J. Lehmann, J. Paust, and H.-D. Härtl, *Chem. Ber.*, **97**, 1527 (1964); G. Boche and D. R. Schneider, *Tetrahedron Lett.*, 4247 (1975).
(4) Synthetic utilities of the alkoxy(alkylthio)methyl group have been reported: B. M. Trost and C. H. Miller, *J. Am. Chem. Soc.*, **97**, 7182 (1975).
(5) The considerably lower oxidation potential of **4** ($R^1 = R^2 = -(CH_2)_4-$), compared to those of phenyl sulfide derivatives (1.45 V vs. SCE: S. Torii, K. Uneyama, K. Iida, and K. Sasaki, *Tetrahedron Lett.*, 4513 (1972)) and alkoxycyclopropane (1.64 V vs. SCE),[2] reveals that the contribution of the electron-donating groups such as both phenylthio and alkoxy functions attached to the cyclopropane ring would cause the suppression of the oxidation potential of **4**.
(6) K. Uneyama and S. Torii, *Tetrahedron Lett.*, 329 (1971).
(7) Sulfur-stabilized cation has been discussed: (a) B. M. Trost and Y. Tamaru, *J. Am. Chem. Soc.*, **97**, 3528 (1975); (b) B. M. Trost and K. Hiroi, *ibid.*, **98**, 4313 (1976).
(8) R. A. Wohl, *Synthesis*, 38 (1974).
(9) B. M. Trost and R. A. Kunz, *J. Org. Chem.*, **39**, 2648 (1974).
(10) M. Saquet, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **275**, 283 (1972).
(11) U. Schöllkopf, F. P. Woerner, and E. Wiskott, *Chem. Ber.*, **99**, 806 (1966).

Facile Synthesis of Triimidazo[1,3,5]triazine Derivatives

Roland Verhé, Norbert De Kimpe,*[1] Laurent De Buyck, and Niceas Schamp

Laboratory of Organic Chemistry, Faculty of Agricultural Sciences, State University of Gent, B-9000 Gent, Belgium

J. P. Declercq,[1] G. Germain, and M. Van Meersche

Laboratory of Physical Chemistry and Crystallography, University of Louvain, B-1348 Louvain-La-Neuve, Belgium

Received July 25, 1978

During the preparation of 1-alkyl-4-methoxy-5,5-dimethyl-2-imidazolidinones **2** (X = O)[2] by reaction of α-chloroaldimines **1** with potassium cyanate in methanol, small amounts of high-melting side products were isolated. It was assumed that these compounds were directly derived from the methoxyimidazolidinones **2** (X = O) and not from a further reaction of the imidazolidinones with potassium cyanate. We now describe the synthesis and structural determination of these byproducts.

Heating of 1-alkyl-4-methoxy-5,5-dimethyl-2-imidazolidinones **2** (X = O) at 150 °C in vacuo afforded the same compounds in high yields (Table I). In all cases only one isomer was obtained by crystallization. Even in the mother liquor no isomeric compound was detectable (vide infra). The structure elucidation was obtained by X-ray diffraction studies on the *tert*-butyl compound. The structure was shown to be 3,7,11-tri-*tert*-butyl-4,4,8,8,12,12,-hexamethyl-1*H*,2*H*,5*H*,6*H*,9*H*,10*H*-triimidazo[3,4-*a*;3′,4′-*c*;3″,4″-*e*]-[1,3,5]triazine-2,6,10-trione (**5d**). The compound crystallized in the monoclinic space group $P2_1$ with $Z = 2$, $a = 11.184$ (5), $b = 10.148$ (7), $c = 13.746$ (5) Å, and $\beta = 106.49$ (3)°. The molecular structure and the ORTEP drawing are given in Figure 1. The atom numbering system used, the positional and thermal parameters, the intramolecular bond distances, the valence angles, and the torsional angles are listed in tables included in the microfilm edition of this journal. The formation of the hexahydro[1,3,5]triazines can be explained by loss of methanol from the 4-methoxy-2-imidazolidinones **2** on heating to give the intermediate 2-imidazolidinones **4** (X = O) which rapidly trimerized into **5.** An analogous elimination of methanol has been observed during the in situ preparation of 1-phenyl-3-imidazolin-2,5-diones from 5-methoxy-3-phenylhydantoines.[3,4]

Other trimerizations of imino compounds have been reported in the case of 3,4-diazanorcaradiene,[5] β,β-dimethylindolenine,[6] (2-chloro-2-methylpropylidene)imine[7] and the dehydrohalogenation of *N*-chloropiperidine.[8,9] In our case compounds **4** (X = O) trimerized very rapidly due to activation of an additional carbonyl group on the nitrogen of the imino function. It is known that *N*-acylimines rapidly undergo nucleophilic addition at the activated carbon–nitrogen double bond.[10]

The corresponding thione compounds **6** were obtained in the same way from the 1-alkyl-5,5-dimethyl-4-methoxy-2-imidazolidinethiones **3**,[11] except when R = *t*-Bu. Compound **3** (R = *t*-Bu) did not lose methanol even on prolonged heating at 200 °C.

The structure of compounds **5** and **6** was further confirmed

0022-3263/78/1943-5022$01.00/0