solution was cooled to −78 °C and treated with 10.5 mL of 1.6 M *n*-butyllithium/hexane. The resulting mixture was allowed to warm to room temperature and then was cooled to −78 °C and treated with 0.53 g (2.85 mmol) of hexafluorobenzene. This mixture was refluxed overnight and then was cooled and poured into 100 mL of water. After stirring 10 min, the initial pale green slurry turned yellow and was filtered, giving 0.90 g of crude solids. Extraction of these solids for 3 h in a Soxhlet extractor with dichloromethane gave 82 mg of semisolid residue which was slurried in minimal chloroform and filtered, giving 20–25 mg of glistening crystals of II which were recrystallized from 0.5 mL of boiling chlorobenzene. Crystals of II do not melt but turn black above 300 °C.

Anal. Calcd for $C_{24}H_{24}N_6F_6$: C, 56.47; H, 4.74; N, 16.46; F, 22.33; M_r 510.50. Found: C, 56.53; H, 4.80; N, 16.32; F, 22.16. IR (KBr): 2930, 2880, 2800, 1615, 1490 (st), 1440, 1373, 1357, 1329, 1287 (w), 1255, 1240, 1231, 1217, 1182, 1137 (st), 1073, 1051, 1025, 991 915, 893, 825 and 774 cm^{-1}. MS: M^+ at *m/e* 510 with metastable peaks corresponding to the transitions for M − CH_3 and M − F. UV (CH_3CN): λ_{max} 241 nm (ϵ 4.97 × 10^4), shoulder at 320 nm. ^{19}F NMR (C_6H_5Cl solvent at 100 °C, external CF_3CO_2Na/D_2O assigned −77.0 ppm): −162.9 (d, J = 23 Hz) and −175.2 ppm (t, J = 23 Hz).

Crystal Data: *Pccn*, a = 14.514 (3) Å, b = 15.205 (2) Å, c = 9.403 (3) Å, V = 2075Å^3, Z = 8, M_r 510, $C_{24}H_{24}N_6F_6$, ρ_c = 1.63 g/cc. Data were collected on an Enraf-Nonius CAD-4 diffractometer and the structure was solved by using conventional direct methods, Fourier syntheses, and full-matrix least-squares refinements, available in the Enraf-Nonius structure determination package.[6] R = 0.034, R_w = 0.045 for 1751 independent diffracted intensities ($I > 3.0\sigma(I)$), with $2 < \theta < 75°$ (Cu Kα radiation), at room temperature. Anisotropic thermal parameters were employed for all 18 independent non-hydrogen positions. All the hydrogens were located on difference electron density maps. Their positions were refined in the final least-squares cycles, and their thermal parameters were refined isotropically.

Acknowledgment. J.E.R. is indebted to Margaret R. Asirvatham for work which preceeded this.[2] This research was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. II, 92643-59-9; 1,4,7,10,13,16-hexaazacyclooctadecane, 296-35-5; hexafluorobenzene, 392-56-3.

Supplementary Material Available: Structure factor tables, temperature factors, and atomic positional parameters (3 pages). Ordering information is given on any current masthead page.

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Synthesis of (±)-Lineatin by 2 + 2 Cycloaddition of Dichloroketene with a Cyclic Allyl Ether

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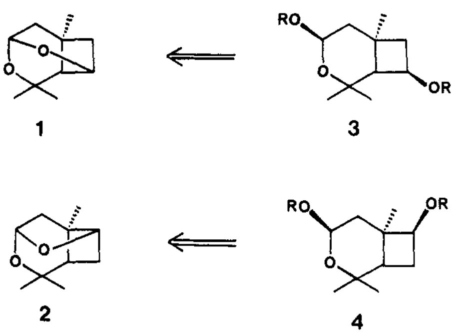
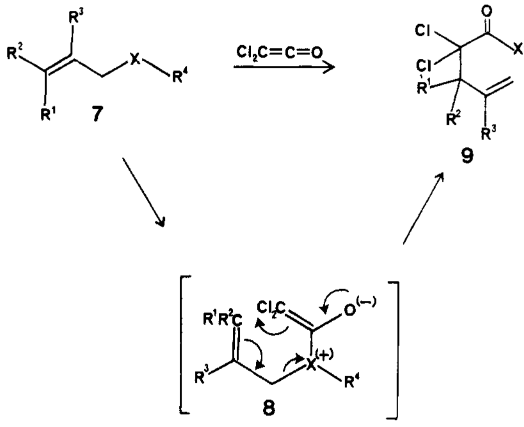
Lineatin (3,3,7-trimethyl-2,9-dioxatricyclo[3.3.1.$0^{4,7}$]nonane, 1) has been shown to be an aggregation pheromone for the bark beetle *Trypodendron lineatum* (Oliver), an economically important forest pest which is responsible for significant damage to fallen and cut timber.[1] The unusual tricyclic acetal structure of 1 has attracted synthetic interest and there have been a number of syntheses reported.[2–8]



Scheme I



Scheme II

Our recent efforts have been directed at development of a relatively simple synthetic scheme for the production of multigram amounts of the pheromone without the coproduction of isolineatin (3,3,7-trimethyl-2,9-dioxatricyclo[4.2.1.$0^{4,7}$]nonane, 2) which has been a coproduct in several previous syntheses. Disconnection of the intramolecular ketal (Scheme I) makes it apparent that a selective synthesis of 1 would require a protocol for the production of a functionalized cyclobutane precursor with the correct regiochemistry (3 rather than 4).

One approach would be to utilize the well-known regioselectivity of dichloroketene cycloadditions with unsymmetric trisubstituted alkenes.[9] Initially, this approach was frustrated by the extreme reluctance of dichloroketene to participate in 2 + 2 cycloaddition reactions with the required alkene substrates. Less than 5% yield of the desired cycloadduct 6 could be isolated from the reaction of 5 with dichloroketene.[3] Compound 5 was eventually abandoned as a precursor to lineatin in part due to the extreme acid sensitivity of cycloadduct 6.

Recent reports[10,11] emphasize that the reaction of dichloroketene with allyl ethers and allyl sulfides typically

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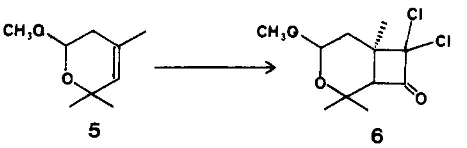


results in rearrangement rather than 2 + 2 cycloaddition (Scheme II).

The proposed mechanism[10] for the formation of **9** was a 3,3-sigmatropic rearrangement of the initially formed dipolar intermediate **8**. In this study, dichloroketene was generated by the zinc dehalogention of trichloroacetyl chloride with concomitant production of $ZnCl_2$. Nucleophilic attack at the carbonyl of dichloroketene leading to intermediate **8** could be facilitated by complexation of $ZnCl_2$ at the carbonyl oxygen.

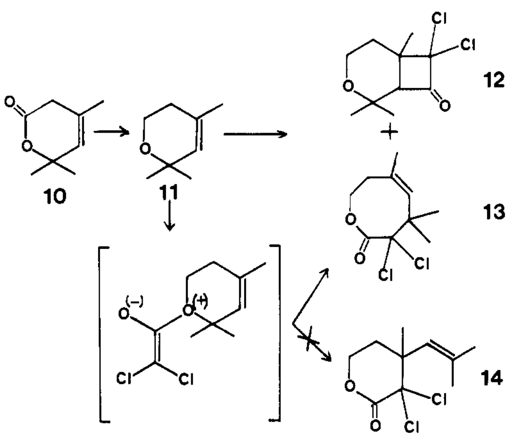
Since it seemed that the most direct route to lineatin utilizing dichloroketene would involve a 2 + 2 cycloaddition reaction with an appropriately substituted allyl ether (e.g., **11**), ways to circumvent the rearrangement product **9** were considered. Krepski and Hassner[12] have reported that the use of phosphorus oxychloride as a sequestering agent for $ZnCl_2$ gives increased yields of 2 + 2 cycloadduct in the reaction of dichloroketene with hindered olefins. Application of this method to the cyclic allylic ether **11** gave, in addition to unreacted starting material, two products separable by chromatography on silica gel. The desired cycloadduct **12** was obtained in only 7% isolated yield while the eight-membered ring compound **13** was the major product (26%) of the reaction. None of the expected 3,3-sigmatropic product **14** could be isolated from the reaction mixture (Scheme III).

Substitution of 1,2-dimethoxyethane for phosphorus oxychloride efficiently suppressed the formation of **13** and a 50% to 60% yield of **12** could be realized. Optimum conditions appeared to be 4 to 6 equiv of 1,2-dimethoxyethane for each equivalent of trichloroacetyl chloride with the reaction carried out in refluxing ether for extended periods of time (4–5 days). Although simple distillation of **12** resulted in only 85–90% purity by GC, this material proved suitable for use in the subsequent steps to form lineatin (Scheme IV).

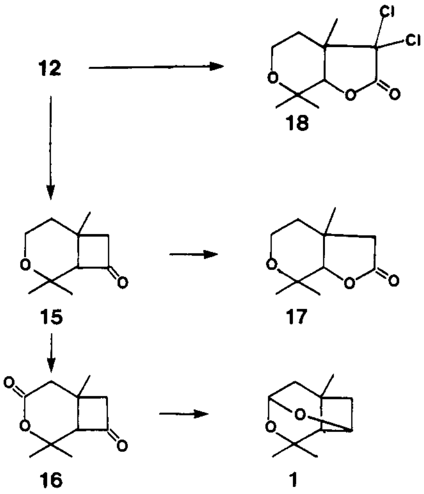
Dechlorination of **12** (58%) was effected by treatment with Zn in methanol saturated with ammonium chloride.[13] Oxidation of cyclobutanone–ether **15** with catalytic amounts of RuO_4[14] in a two-phase (CCl_4/H_2O) system containing $NaIO_4$ as the cooxidant resulted in formation of crystalline cyclobutanone–lactone **16** (61%) which could be recrystallized to a high state of purity. Use of NaOCl (commercial bleach) as a cooxidant[15] for RuO_4 resulted in only Baeyer–Villiger type products (i.e., **17**, **18**) from either dichlorocyclobutanone **12** or cyclobutanone **15**. Finally, reduction of **16** with diisobutylaluminum hydride (Dibal) in hexane/ether,[2,6,8] followed by an acidic workup, yielded lineatin. The overall yield of lineatin from **11** was 10–12%.

In summary, lineatin (**1**) has been prepared by using a short synthetic sequence which is suitable for multigram quantities. The synthesis involves a modified procedure for dichloroketene cycloadditions with allyl ethers to produce moderate yields of cyclobutanones which should be of value in the synthesis of similar four-membered ring systems.

Scheme III



Scheme IV



Experimental Section

^1H NMR spectra were recorded on a Bruker WM400 spectrometer. Mass spectra were obtained by use of a Hewlett-Packard 5985B GC/MS system operating at 70 eV. Elemental analyses were performed by Mr. M. Yang of Simon Fraser University, Department of Biological Sciences, using a Perkin-Elmer Model 240 elemental analyzer. Gas chromatographic analysis utilized a Hewlett-Packard 5880A with a J+W fused silica DB-1 capillary column (15 m × 0.25 mm), a flame ionization detector, and a suitable linear oven temperature gradient.

Solvents and reagents were used as supplied from commercial sources with the following exceptions. Ether and dimethoxyethane were distilled from $LiAlH_4$ immediately prior to use. Zinc was activated by the method of Krepski and Hassner.[12]

2,2,4-Trimethyl-5,6-dihydro-2*H*-pyran (11). Lithium tetrahydridoaluminate (52 g, 1.4 mol) was stirred with dry ether (2 L) and cooled with an ice bath while lactone **10**[5] (265 g, 1.9 mol) was added dropwise over 1 h. The cooling bath was removed and the reaction stirred at ambient temperature for 16 h. The reaction mixture was then carefully poured (caution! foaming) into ice-cold 2 M sulfuric acid (3 L). After stirring at room temperature for 1 h, the ether layer was separated and the aqueous acid extracted with additional ether (2 × 500 mL). The combined extracts were washed with saturated $NaHCO_3$ solution (300 mL) and dried over anhydrous $MgSO_4$. Removal of the solvent through a 20-cm Vigreaux column at atmospheric pressure, followed by distillation of the residue, yielded **11** (197 g, 83%): bp 130–133 °C (750 mmHg); IR (neat film) 2975 (s), 2920 (s), 2863 (m), 1677 (w), 1463 (m), 1440 (m), 1385 (m), 1360 (s), 1272 (m), 1243 (m), 1223 (m), 1200 (m), 1180 (m), 1125 (s), 1098 (s), 1087 (m), 939 (m), 872 (m),

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838 (m), 770 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.29 (1 H, vinyl H, sextet, J = 1.5 Hz), 3.78 (2 H, OCH_2, t, J = 5.6 Hz), 1.93 (2 H, allylic CH_2, brt, J = 5.4 Hz), 1.67 (3 H, allylic CH_3, br s), 1.20 (6 H, 2 methyls, s); mass spectrum, *m/e* (relative intensity) 126 (3), 112 (6), 111 (100), 43 (7). Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.31; H, 11.03.

7,7-Dichloro-2,2,6-trimethyl-3-oxabicyclo[4.2.0]octan-8-one (12). Zinc–copper couple (100 g, 1.5 mol) was added to a stirred mixture of anhydrous ether (2 L) and anhydrous 1,2-dimethoxyethane (500 mL). The reaction was maintained under N_2 while ether 11 (126 g, 1 mol) was added, followed by dropwise addition of trichloroacetyl chloride (250 g, 1.4 mol) over 1 h. After 48 h at reflux, further portions of dimethoxyethane (500 mL), zinc (100 g), and trichloroacetyl chloride (250 g) were added. After an additional 48 h at reflux, the reaction was terminated by filtration and concentration in vacuo to a volume of ~350 mL. The dark-colored concentrate was poured in a thin stream into petroleum ether (30–60 °C) (3 L) with rapid stirring. Insoluble material was removed by suction filtration and the petroleum ether solution was then stirred with ice-cold saturated $NaHCO_3$ solution (1.5 L) for a period of 1 h. The organic phase was washed with an additional portion of saturated $NaHCO_3$ (1 L), water (2 × 500 mL), and saturated NaCl solution (500 mL). After drying over anhydrous $MgSO_4$, concentration in vacuo gave a dark brown syrup which was subjected to vacuum distillation to yield partially purified adduct **12** (141 g, 85% pure by GC), bp 70–85 °C (0.1 mmHg). An analytical sample was further purified by flash chromatography (hexane:ethyl acetate, 10:1): IR (neat film) 2970 (s), 2925 (m), 2870 (m), 1803 (s), 1478 (m), 1452 (m), 1436 (m), 1384 (m), 1368 (m), 1346 (m), 1321 (m), 1289 (m), 1272 (m), 1237 (m), 1210 (m), 1170 (m), 1130 (m), 1079 (m), 1020 (m), 992 (m), 928 (m), 900 (m), 872 (m), 812 (m), 790 (m), 748 (m), 714 (m), cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 150 (8), (1 H, C_4H, ddd, J_{gem} = 12, J_{cis} = 5, J_{trans} = 2.2 H), 3.68 (1 H, C_4H', dt, $J_{gem} = J_{trans}$ = 12, J_{cis} = 1.8 Hz), 3.24 (1 H, C_1H, d, $J_{1,5}$ = 1.9 Hz), 1.84 (1 H, C_5H, m, J_{gem} = 15, J_{trans} = 12, J_{cis} = 5 Hz), 1.66 (1 H, C_5H', dq, J_{gem} = 15, $J_{trans} \approx J_{cis} \approx J_{1,5} \approx 2$ Hz), 1.59 (3 H, CH_3, d, J = 0.8 Hz), 1.49 (3 H, CH_3, s), 1.21 (3 H, CH_3, s); mass spectrum, *m/e* (relative intensity) 238 (0.1), 236 (0.1), 152 (5), 150 (8), 138 (7), 136 (10), 83 (100), 55 (30). Anal. Calcd for $C_{10}H_{14}O_2Cl_2$: C, 50.65; H, 5.95. Found: C, 50.64; H, 5.79.

2,2,6-Trimethyl-3-oxabicyclo[4.2.0]octan-8-one (15). A mixture of Zn powder (125 g, 1.9 mol) and methanol saturated with NH_4Cl (1 L) was stirred while partially purified **12** (140 g, 0.59 mol) was added dropwise at a rate sufficient to maintain a gentle reflux. After the addition was complete (~2 h), the reaction was maintained at reflux for an additional 4.5 h by external heating. After cooling to room temperature and filtration, the methanol was removed in vacuo and the semicrystalline residue was shaken with a mixture of ether (1.5 L) and 2 M H_2SO_4 (800 mL). When the zinc salts had dissolved, the organic phase was separated and the aqueous phase extracted with additional ether (2 × 300 mL). The combined ether extracts were washed with saturated $NaHCO_3$ solution (500 mL) and water (500 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo. The residue was distilled to give **15**; bp 55–60 °C (0.3 mmHg), 58 g, 58% yield; 90% pure by GC. An analytical sample was further purified by flash chromatography (hexane:ethyl acetate, 4:1): IR (neat film) 2975 (s), 2930 (s), 2875 (s), 1780 (s), 1464 (m), 1383 (m), 1365 (m), 1348 (m), 1323 (m), 1291 (m), 1273 (m), 1237 (m), 1208 (m), 1163 (m), 1083 (m), 1062 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.70 (2 H, C_4H, m), 2.76 (1 H, C_7H, dd, J_{gem} = 16, $J_{1,7}$ = 1.8 Hz), 2.67 (1 H, C_1H, br s), 2.60 (1 H, C_7H, dd, J_{gem} = 16, $J_{1,7}$ = 1.5 Hz), 1.80 (1 H, C_5H, dm, J_{gem} = 14.5 Hz), 1.63 (1 H, C_5H', m), 1.49 (3 H, CH_3, s), 1.44 (3 H, CH_3, s), 1.22 (3 H, CH_3, s); mass spectrum, *m/e* (relative intensity) 168 (2), 154 (12), 125 (10), 111 (100), 100 (25), 83 (20), 72 (13), 55 (14). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.60; H, 9.64.

2,2,6-Trimethyl-3-oxabicyclo[4.2.0]octane-4,8-dione (16). A mixture of **15** (32 g, 190 mmol) in CCl_4 (400 mL) and aqueous $NaIO_4$ (120 g, 560 mmol in 1 L of water) was stirred while $RuCl_3 \cdot 3H_2O$ (1.5 g, 5.7 mmol) was added in one portion. After 18 h of stirring at ambient temperature, the organic phase remained yellow when the stirring was stopped and the reaction was judged to be complete. Insoluble material was removed by suction filtration and the aqueous phase was extracted with CH_2Cl_2 (3 × 250 mL). The combined extracts were treated with 2-propanol (5 mL) to destroy the remaining RuO_4 and concentrated to yield a black syrup. This material was dissolved in ether (1.2 L) and washed with saturated $NaHCO_3$ solution (300 mL). The black insoluble RuO_2 remained in the aqueous layer after shaking for ~10 min. The organic layer was separated, washed with water (100 mL), and dried over anhydrous $MgSO_4$. Removal of the solvent gave a grey semicrystalline residue which was recrystallized from hexane:ethyl acetate (4:1) to yield 21.0 g (61%) of compound **16**: mp 97–98 °C (lit.[8] mp 99–100 °C); IR (Nujol mull) 1773 (s), 1725 (s), 1340 (m), 1290 (m), 1203 (m), 1145 (m), 1075 (m), 995 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.97 (1 H, C_1H, s), 2.90 (2 H, C_5H, m), 2.84 (1 H, C_7H, d, J_{gem} = 16.8 Hz), 2.73 (1 H, C_7H', d, J_{gem} = 16.8 Hz), 154 (3 H, CH_3, s), 1.53 (3 H, CH_3, s), 1.41 (3 H, CH_3, s); mass spectrum, *m/e* (relative intensity) 182 (1), 141 (10), 126 (10), 125 (100), 123 (22), 97 (32), 96 (39), 83 (15), 82 (16), 81 (17), 55 (12). Anal. Calcd for $C_8H_{14}O_3$: C, 65.86; H, 7.74. Found: C, 66.19; H, 7.75.

2,2,6-Trimethyl-3,9-dioxabicyclo[4.3.0]nonan-8-one (17). To a solution of **15** (100 mg, 0.60 mmol) in CCl_4 (20 mL) was added 5% aqueous NaOCl solution (Javex bleach, 10 mL, ~13 mmol) and $RuCl_3 \cdot 3H_2O$ (20 mg, 0.08 mmol). After stirring at room temperature for 5 h, the CCl_4 layer was withdrawn and the aqueous layer further extracted with CCl_4 (2 × 10 mL). The combined extracts were treated with 2-propanol (0.5 mL) and filtered through a short silica gel column. The column was washed with ether, and the combined solution was concentrated in vacuo to yield **17** as a crystalline solid (106 mg, 91%): mp 54–56 °C; IR (KBr pellet) 3005 (m), 2995 (m), 2925 (m), 2890 (m), 1780 (s), 1712 (m), 1480 (w), 1435 (m), 1390 (w), 1368 (m), 1307 (m), 1285 (m), 1260 (m), 1223 (m), 1204 (s), 1185 (m), 1130 (m), 1086 (s), 1043 (m), 1015 (m), 1005 (m), 996 (m), 965 (m), 873 (w), 804 (m), 753 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.75 (1 H, C_1H, s), 3.67 (2 H, C_4H, m), 2.42 (1 H, C_7H, d, J_{gem} = 17 Hz), 2.32 (1 H, C_7H, d, J_{gem} = 17 Hz), 1.71 (1 H, C_5H, m), 1.35 (1 H, C_5H, m), 1.23 (3 H, CH_3, s), 1.22 (3 H, CH_3, s), 1.20 (3 H, CH_3, s); mass spectrum, *m/e* (relative intensity) 184 (7), 169 (10), 98 (100), 83 (24), 70 (20), 69 (32), 59 (18). Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.20; H, 8.76. Found: C, 64.90; H, 9.10.

7,7-Dichloro-2,2,6-trimethyl-3,9-dioxabicyclo[4.3.0]nonan-8-one (18). Treatment of **12** with RuO_4/NaOCl as described for the preparation of **17** from **15** yielded **18** as a crystalline solid in 85% yield: mp 82–87 °C; IR (KBr pellet) 3005 (m), 2995 (m), 2950 (m), 2890 (m), 1805 (s), 1465 (m), 1393 (m), 1370 (m), 1275 (m), 1215 (s), 1170 (m), 1113 (m), 1086 (m), 1040 (m), 990 (s), 975 (s), 902 (m), 842 (m), 820 (m), 767 (m), 738 (m), 690 (m), 664 (m), 580 (m), 530 (m), 503 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.10 (1 H, C_1H, s), 3.83–3.67 (2 H, C_4H, 14 peak multiplet), 1.90–1.50 (2 H, C_5H_2, m), 1.46 (3 H, CH_3, s), 1.38 (3 H, CH_3, s), 1.33 (3 H, CH_3, s); mass spectrum, *m/e* (relative intensity) 254 (7), 252 (10), 239 (20), 237 (28), 169 (12), 168 (18), 167 (19), 166 (27), 161 (19), 159 (52), 150 (13), 139 (14), 137 (18), 133 (36), 131 (100), 123 (10), 115 (13), 110 (11), 103 (12), 101 (10), 95 (12), 87 (10), 79 (14), 77 (12), 75 (10), 67 (15), 65 (23), 59 (10), 58 (10), 53 (11), 51 (10), 43 (33), 41 (15). Anal. Calcd for $C_{10}H_{14}O_3Cl_2$: C, 47.45; H, 5.58. Found: C, 47.61; H, 5.57.

3,3,7-Trimethyl-2,9-dioxatricyclo[3.3.1.0^{4,7}]nonane (1). Bicyclic keto lactone **16** (38 g, 0.21 mol) was added to dry ether (500 mL) and cooled in an ice bath. To the stirred heterogeneous mixture was added dropwise a 1 M hexane solution of Dibal (500 mL, 0.50 mol) over 1.5 h with the temperature maintained at 5–7 °C. After a further 0.5 h at 5 °C, the reaction mixture was poured into ice-cold 10% aqueous tartaric acid (800 mL) and stirred until a clean separation into two layers occurred (~45 min). The organic phase was separated and the aqueous phase extracted with ether (2 × 100 mL). The combined organic extracts were washed with saturated $NaHCO_3$ (100 mL), water (100 mL), and saturated NaCl (100 mL), dried over anhydrous $MgSO_4$, and concentrated by distillation through a 30-cm Vigreaux column. The residue was vacuum distilled to yield **1** (24.6 g, 70%), bp 61 °C (2.5 mmHg) (lit.[5] bp 70 °C (12 mmHg)). This material was >98% pure by GC and had spectral data in complete accord with earlier reports.[1-7]

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Registry No. (±)-1, 71899-16-6; 10, 22954-83-2; 11, 55130-14-8; 12, 92958-26-4; 15, 92958-27-5; 16, 76946-39-9; 17, 92958-28-6; 18, 92958-29-7; trichloroacetyl chloride, 76-02-8.

Nucleophilic Reactivity of Anions Associated with a Lipophilic Proton Cryptate, $[H^+\subset(1.1.1,C_{14})]$

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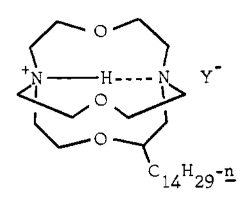
The reactivity of an ion pair A^+X^- in a condensed phase reaches the highest values when at least two fundamental conditions are achieved: (1) a good solubility in non-polar media; (2) a large cation–anion separation.[1] These conditions are especially fulfilled by onium quaternary salts, bearing long and/or bulky alkyl chains,[1] and by multidentate ligands which surround metal cations giving rise to lipophilic macrocations.[2] Within the latter species, lipophilic cryptates are of particular interest, since they probably represent the best model of "solvent-separated ion pair".[3,4]

In a series of papers we have studied the anionic reactivity of lipophilic cryptates[3,5,6] compared with that of quaternary onium salts[7,8] and complexed crown ethers.[4]

We have also reported[9] the synthesis of $[H^+\subset(1.1.1,C_{14})]Y^-$ cryptates 1, following a route which directly affords the proton cryptated species. It was shown by Lehn[10] that the unsubstituted [1.1.1] cryptand 2 is capable of selectively binding one or two protons inside its intramolecular cavity. Whereas one proton can be removed from the dicationic species, it is practically impossible to remove the last proton from the one-proton cryptate.[10] Cryptates 1 are readily soluble in non-polar media. Since the anionic reactivity of cryptates is independent of the nature of metal cation, which only affects[11] the stability constant of the complex, it was interesting to know about the reactivity of the anions associated with the "unique" species of a lipophilic proton cryptate.



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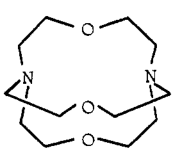

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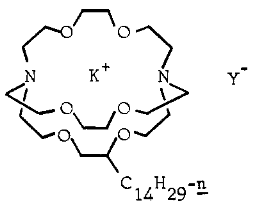

3

Results and Discussion

Rates of displacement of the methanesulfonic group in *n*-octyl methanesulfonate by a series of anions (Cl^-, Br^-, I^-, N_3^-) associated with the cation $[H^+\subset(1.1.1,C_{14})]$ have been measured in anhydrous chlorobenzene at 60 °C (eq 1).

$$n\text{-}C_8H_{17}OSO_2Me + [H^+\subset(1.1.1,C_{14})]Y^- \xrightarrow[60\ ^\circ C]{PhCl} n\text{-}C_8H_{17}Y + [H^+\subset(1.1.1,C_{14})]MeSO_3^- \quad (1)$$

a, Y = Cl; **b**, Y = Br; **c**, Y = I; **d**, Y = N_3; **e**, Y = ClO_4

The same reactions were studied by using tetraoctylammonium salts 4 as a source of anions. In all cases

$$\underset{\mathbf{4}}{(n\text{-}C_8H_{17})_4N^+Y^-} \qquad \underset{\mathbf{5}}{n\text{-}C_{16}H_{33}P^+Bu_3Y^-}$$

comparable amounts of substrate [(2–6) × 10^{-2} M] and nucleophile [(0.8–2.4) × 10^{-2} M] were used. The rates were measured by potentiometric titration of the nucleophile. Under these conditions reactions follow a second-order kinetic equation (eq 2) up to at least 80% conversion.

$$\text{rate} = k[\text{substrate}][\text{cryptate}] \quad (2)$$

Rate constants are reported in Table I together with those, previously measured under the same conditions, for $[K^+\subset(2.2.2,C_{14})]Y^-$ cryptates 3 and hexadecyltributylphosphonium salts 5. Results indicate that the reactivity of anions associated with $[H^+\subset(1.1.1,C_{14})]$ cation is high and comparable with the reactivities measured in the presence of the best anionic activators (quaternary salts and metal cryptates).

All the attempts for obtaining the free ligand from the proton cryptates failed. For example, when 1c was treated with $NaBH_4$ and $LiAlH_4$ in tetrahydrofuran (THF), anion exchange and decomposition of the cryptate were observed, respectively;[9b] nor was it possible to remove the proton when a toluene solution of 1c was stirred for several days in the presence of 50% aqueous NaOH. In other words, the proton included into the ligand $[1.1.1,C_{14}]$ behaves as an ordinary cryptated metal cation.

The smaller size and the higher charge localization of 1 compared with that of 3 is likely responsible for its anionic reactivity (1.5–3.5 times less, depending on the anion) (Table I). Compared with bulky tetraoctylammonium salts 4, cryptates 1 represent a more rigid and a less hindered system. Indeed, these factors, altogether,

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