Table I. Equilibrium Ratios of 2a:2b and 3a:3b (after Butylation)[a]

LDA, mequiv	HMPA, equiv/Li$^+$	additive (mmol)	relative yield, %[b] 2a	2b	3a	3b
1.6	0	none	66	34	63	37
1.6	2.0	none	64	36	64	36
2.2	0	benzophenone (0.4)			66	34
2.2	2.0	benzophenone (0.4)			65	35
2.2	0	diphenylamine (0.4)			69	31
2.2	2.0	diphenylamine (0.4)			70	30

[a] Deprotonation of 2.0 mmol of 1 in THF as described in the text. [b] Determined by ^{1}H NMR spectroscopy, ± 5%.

spectively, of the azaallyllithium reagents or was deduced from the **3a:3b** ratio after butylation (formyl proton signals at δ 6.7 and 6.4, respectively); the results were the same in cases where both methods were used at a specific HMPA:Li$^+$ ratio. In cases where less than 2.0 equiv of HMPA per lithium ion was used for the deprotonation reactions, additional HMPA was added *after* the deprotonation to provide solutions which were suitable for ^{1}H NMR spectroscopy. Typical yields of **3** after butylation were ca. 84%.

Experiments which apparently led to equilibration of **2a** and **2b** showed that the stereoisomeric azaallyllithium reagents formed above had not been equilibrated. These experiments included either use of insufficient base (0.8 equiv) or addition of diphenylamine (0.2 equiv) or benzophenone (0.2 equiv) to the reaction mixtures. In the first two cases, equilibration of **2** by a protonation–deprotonation sequence could occur. Benzophenone could act as an electrophile, permitting equilibration by a reversible aldol condensation as suggested by Rathke[6] for equilibration of 3-pentanone enolates, or could permit electron-transfer reactions. Each of these deprotonations was run in the absence of HMPA and in the presence of 2.0 equiv of HMPA per lithium ion. The results given in Table I show that the equilibrium ratio of **2a:2b** is approximately 65:35.

Thus, deprotonation of **1** in the absence of and in the presence of >2.0 equiv of HMPA gave ratios of **2a:2b** which are far removed from the equilibrium ratio and, further, which are, respectively, greater and less than the equilibrium ratio. In both cases, kinetic products were formed, and the interpretation that distinct transition states for deprotonation exist is supported.[5] Although HMPA may affect the ratio of ketone enolate isomers by activating the system for a reversible aldol condensation leading to equilibration,[6] similar equilibration schemes are less likely for less electrophilic ketone equivalents.

Experimental Section

General Methods. Tetrahydrofuran (THF) was distilled from sodium–benzophenone, diisopropylamine was distilled from calcium hydride, and HMPA was distilled from sodium in vacuo. Reactions were run under nitrogen and syringe transfers were employed.[7] ^{1}H NMR spectra of mixtures of **2** or **3** used for the data in Figure 1 were recorded on a Varian T-60 spectrometer; the formyl protons resonated at the following positions: **2a**, δ 6.2; **2b**, δ 6.6; **3a**, δ 6.7; **3b**, δ 6.4. Spectra of **2** were recorded at ca. 0 °C. In the experiments reported in Table I, the ^{1}H NMR signals of **1** overlapped with those of **2** and **3** at 60 MHz but were resolved at 200 MHz (Varian XL-200, FT with a benzene-d_6 lock).

Deprotonations of 1 in the Absence of HMPA. Deprotonations of **1** followed the general method we have reported.[2] DMH **1** (250 μL, 2.0 mmol) was added dropwise to a THF solution of LDA (2.7 mL, 0.82 N, 2.2 mequiv) at −78 °C. The stirred mixture was warmed to 25 °C for 1 h and then cooled to −78 °C. For ^{1}H NMR analyses, the mixture was cooled to −78 °C, 0.9 mL of HMPA (2.5 equiv per lithium ion) was added, and the mixture was warmed to ca. −23 °C to give a yellow solution. For alkylation reactions, the suspension of **2** at −78 °C was treated with 0.25 mL (2.2 mmol) of 1-iodobutane at −78 °C, and then the mixture was warmed to 25 °C for 0.5 h. The mixture was then cooled to −78 °C and treated with ca. 0.1 mL of water. After warming to 25 °C, the mixtures were analyzed by ^{1}H NMR spectroscopy. GC analysis (SE-30, hexadecane internal standard) indicated that 82–88% yields of **3** were obtained.

Deprotonations of 1 in the Presence of HMPA. The method described above was used with the exceptions that HMPA was added to the LDA solutions before **1** was added and the deprotonation reactions were maintained at ca. −23 °C for 1.5 h. For ^{1}H NMR analyses of the mixtures containing <2.0 equiv of HMPA per lithium ion, the reaction mixtures were cooled to −78 °C, and the total amount of HMPA was brought to 2.5 equiv per lithium ion.

Equilibration Studies. Deprotonation reactions were conducted with 0.0 or 2.0 equiv of HMPA per lithium ion as described above. For the reactions initially containing no HMPA, the mixtures were subsequently cooled to −78 °C and 2.5 equiv of HMPA per lithium ion was added. The mixtures were warmed to ca. −23 °C and, when appropriate, an additive was added. The mixtures were maintained at ca. −23 °C for 2 h, then cooled to −78 °C, and treated with 1-iodobutane as described above.

Acknowledgment. This work was supported by a grant from the National Institutes of Health (GM 26268). The Varian XL-200 NMR spectrometer used in this research was purchased with the aid of a National Science Foundation grant (CHE78-27411) to Texas A&M University.

Registry No. 1, 7422-93-7; 2, 66970-40-9; 3a, 72215-77-1; 3b, 72215-76-0.

(7) Brown, H. C. "Organic Syntheses via Boranes"; Wiley-Interscience: New York, 1975.

Facile Oxetane Formation in a Rigid Bicyclo[2.2.2]octane System[1a]

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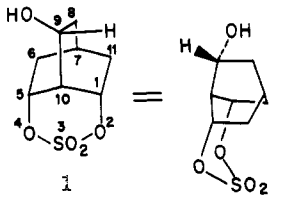
Introduction

In connection with studies on the stereoelectronic preference of heterolytic fragmentations[2] we have prepared the racemic hydroxy sulfate **1** and have investigated its reactions in the presence of nonnucleophilic bases. The fundamental stereoelectronic requirement of this reaction

(1) (a) Taken from the Ph.D. thesis of S.E.D., ETH-Zurich, No. 6665, July 1980. (b) Address correspondence to School of Chemical Sciences, University of Illinois, Urbana, IL 61801.

(2) (a) Eschenmoser, A.; Frey, A. *Helv. Chim. Acta* **1952**, *35*, 166. Reviews: Becker, K. B.; Grob, C. A. In "The Chemistry of Double Bonded Functional Groups"; Patai, S., Ed.; Wiley-Interscience: New York, **1977**; Vol. 2, p 653; (b) Grob, C. A.; Schiess, P. W. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 1.

0022-3263/81/1946-3144$01.25/0



1

is the anti-periplanarity of the breaking bonds (b–c, d–x, (d′–x′), I in Figure 1) as established by Wharton[3a,b] and Grob.[3c] The existence of an additional stereoelectronic component derived from the relative orientation of the incipient double bonds remains unaddressed. The selection of 1 as an ideal model was based on several considerations. First, it satisfies the well-known fundamental requirement requirement mentioned above. Second, the rigidity of the molecule enforces a defined geometry of the incipient double bonds during the reaction. Formulas II and III in Figure 1 illustrate how the model embodies two stereoelectronically distinct fragmentation geometries, i.e., an anti-periplanar relationship of the incipient double bonds (a–b, c–d, II, Figure 1) and a syn-clinal relationship (a–b, c–d′, III, Figure 1). Finally, the products of fragmentation via these two pathways are enantiomers. Thus, the stereoselectivity of the fragmentation (with optically active 1) would provide a direct measure of the preference for reaction via one of the available pathways. We report herein the preparation of racemic 1 and its facile and surprising conversion to the tricyclic oxetane 2.

Results and Discussion

The synthesis of 1, which began with the known bicyclo[2.2.2]octane-2,6,7-trione[4] 3, is outlined in Scheme I. The mixture of isomeric triols[5] was treated with an excess of phenylboronic acid in methanol solution to provide a 24% yield[6] (based on 3) of the cyclic boronic ester 4, mp 127–128 °C. Protection of the remaining hydroxyl group was achieved by conversion to the *tert*-butyldimethylsilyl ether[7] 5, mp 74–75.5 °C, in 93% yield. Selective removal of the cyclic boronate function was achieved, using a two-phase hydrolysis with 3 M NaOH and ether at 20 °C for 4 days. In this manner the diol 6, mp 46–47.5 °C, was obtained in 89% yield along with a 7% recovery of 5.

The inability to introduce the sulfate moiety by direct methods[8] dictated an indirect approach which began by treating 6 with a freshly prepared solution of *N,N′*-thionyldiimdazole[9] to afford a 94% yield of the unstable sulfurous esters 7 followed by oxidation of the mixture of sulfites with RuO_4 to a single sulfate 8, mp 79.5–80.5 °C, in 72% yield.

The final deprotection step proved more difficult than anticipated. Attempted desilylation under a wide range of conditions[10] afforded either recovery of 8 or highly polar, hygroscopic materials. It appeared that conditions under which desilylation was occurring (n-$Bu_4N^+F^-$/THF/−20 °C) were producing the alkoxide derived from 1 which was undergoing facile side reactions (fragmentation?) prior to workup. However, desilylation with liquid hydrogen fluoride[11] at −78 °C in a Teflon tube provided the target hydroxy sulfate 1, mp 109–110 °C dec, in 88% yield.

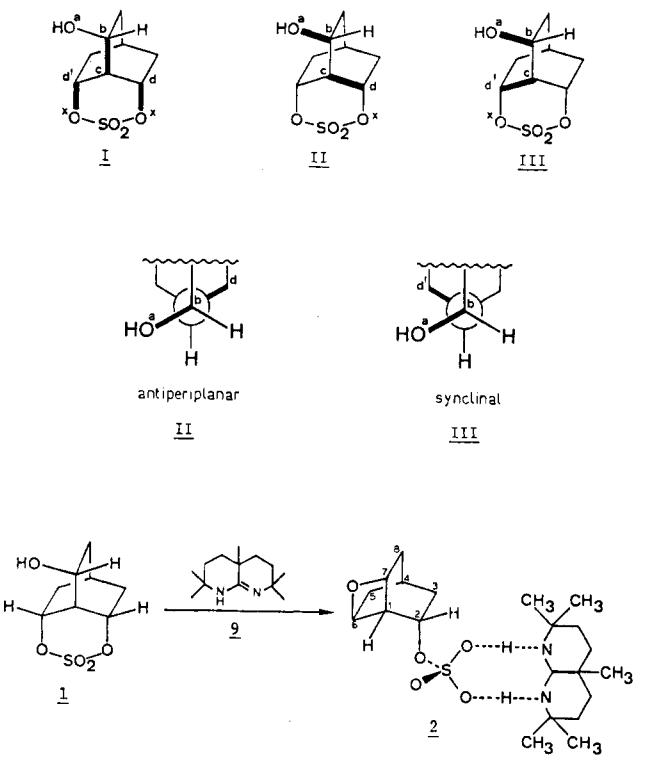


Figure 1.

Subjection of 1 to standard fragmentation conditions (NaH or KO-*t*-Bu) completely consumed the educt, but nothing could be isolated. However, when DMF solutions 0.43 M in 1 and 0.91 M (2 equiv) in amidine base[12] 9 were allowed to stand at 20 °C, a white, crystalline material slowly precipitated. The crystalline precipitate, mp 208–209 °C, gave a correct elemental analysis for $C_{21}H_{36}N_2O_5S$, establishing a 1:1 stoichiometry of the reactants from which a 46% yield for the reaction could be calculated. The structure of the adduct 2 was deduced spectroscopically. In particular, the lack of a carbonyl absorption in the IR and the absence of resonances in both the ^1H and ^{13}C NMR spectra due to olefinic carbon atoms (other than the amidinium portion) indicated that 2 was not derived from a fragmentation. Evidence that the bicyclo[2.2.2]octane skeleton was still intact was obtained from the ^1H NMR spectrum at 360 MHz in which the resonances due to the amidine base and the rest of the molecule are well separated. Irradiation of the three-proton multiplet at δ 4.46 (H-2, H-6, H-7) caused the quartetoid signal at δ 3.83 (H-1) to collapse to a singlet. Complementary irradiation at δ 3.83 changed only the signal at δ 4.64, indicating it was coupled to no other protons. The four-proton multiplet (H-3, H-5, H-8, H-4) at δ 2.20 was significantly affected by irradiation at δ 4.64, while the three-proton multiplet (H′-3, H′-5, H′-8) was not. Further, the ^{13}C NMR spectrum was qualitatively similar to that obtained from boronate 4, the only major perturbation being the downfield shift (ca. 15 ppm) of the C-6 and C-7 resonances, consistent with their confinement in an oxetane ring.[13,14]

(3) (a) Wharton, P. S. *J. Org. Chem.* **1961**, *26*, 4781. (b) Wharton, P. S.; Heigel, G. A. *Ibid.* **1965**, *30*, 3254. (c) Grob, C. A.; Kiefer, H. R.; Lutz, H.; Wilkens, H. *Tetrahedron Lett.*, **1964**, 2901. (d) Clayton, R. B.; Henbest, H. B. *Chem. Ind.* **1953**, 1315.

(4) Theilacker, W.; Schmidt, W. *Justus Liebigs Ann. Chem.* **1950**, *570*, 15.

(5) Heyns, H.; Rüdiger, G.; Paulsen, H. *Chem. Ber.* **1972**, *105*, 1028.

(6) Unless otherwise indicated yields refer to isolated, chromatographically homogeneous material.

(7) Corey, E. J.; Venkateswarlu, A. *J. Am. Chem. Soc.* **1972**, *94*, 6190.

(8) Unseccessful attempts included: SO_2Cl_2, sulfuryl *N,N*-bis(3-methylimidazolium)bis(methyl sulfate), SO_3–pyridine complex.

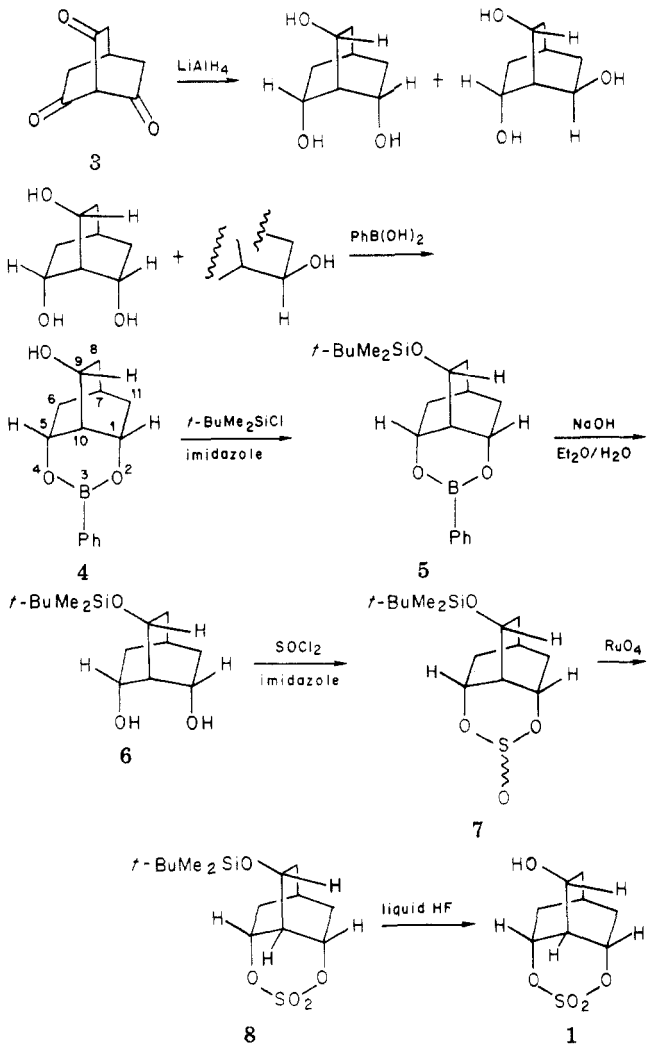
(9) Staab, H. A.; Wendel, K. *Angew. Chem.* **1961**, *73*, 26.

(10) (n-Bu)$_4N^+F^-$/THF/−60 °C $Et_3N^+HF^-/Et_2O$/20 °C, KF/MeOH/0 °C. AcOH/20 °C, CF_3CO_2H/Et_2O/20 °C 2 N HCl/Et_2O/20 °C.

(11) The successful use of this reagent for the cleavage of C–Si bonds has been documented recently in these laboratories: Jenkins, P. R.; Gut, R.; Wetter, H.; Eschenmoser, A. *Helv. Chim. Acta* **1979**, *62*, 1922.

(12) 3,3,6,6,9-Pentamethyl-2,10-diazabicyclo[4.4.0]dec-1-ene: Heinzer, F.; Soukup, M.; Eschenmoser, A. *Helv. Chim. Acta* **1978**, *61*, 2851.

Scheme I



Finally, there exists substantial literature precedent for the formation of oxetanes from γ-halo or γ-pseudohalo alcohols as side reactions to fragmentation[15,16] or as sole observable products.[17]

Experimental Section[18]

Melting points were taken in sealed capillaries on a Büchi melting point apparatus and are corrected. NMR spectra were recorded on the following instruments: ^{1}H NMR, Varian HA-100 (100 MHz) and Bruker HXS-360 (360 MHz); ^{13}C NMR, Varian XL-100 (25 MHz). In all cases $CDCl_3$ was used as solvent with Me_4Si, or $CHCl_3$ (for Si-containing compounds, δ 7.24) as internal standards. IR spectra were recorded on a Perkin-Elmer PE 125 spectrophotometer. Mass spectra were recorded on Hitachi RMU 6d or 6M instruments at 70 EV. THF, Et_2O, and dioxane were distilled prior to use over sodium benzophenone ketyl. DMF was distilled from CaH_2 and stored over activated 4-Å sieves, hexane was distilled from $LiAlH_4$, and CCl_4 and CH_2Cl_2 were distilled from P_2O_5.

Other reagents were purified as follows. *t*-$BuMe_2SiCl$ was distilled under N_2, imidiazole was recrystallized from benzene, thionyl chloride was distilled, RuO_4 solutions were prepared by the method of Nakata[19] and titrated gravimetrically, and HF (Ugine-Kuhlman) was distilled three times (last time from AgF) and stored in chromnickel steel 18-8 cyclinders.

(1*S,5*R*,9*R*)-9-Hydroxy-3-phenyl-2,4-dioxa-3-boratricyclo[5.3.1.0^{5,10}]undecane (4).** A solution of 6.27 g (41.2 mmol) of triketone[4] **3** in 250 mL of dioxane was reduced with a suspension of 5.86 g (150.5 mmol) of $LiAlH_4$ in 400 mL of THF according to the procedure of Paulsen.[5] The crude triol solution obtained after desalting with ion-exchange resins was concentrated to 50 mL and treated with a solution of 5.0 g (41.0 mmol) of $PhB(OH)_2$ in 30 mL of MeOH followed by 100 mL of H_2O. The milky emulsion was cooled to 2 °C overnight and the crystalline precipitate collected, washed with H_2O, and dried (3.90 g). Recrystallization from 250 mL of hexane afforded 2.36 g (24% based on **3**) of **4**: mp 127–128 °C; ^{1}H NMR (100 MHz, $CDCl_3$) δ 7.92–7.62 (m, 2 H), 7.52–7.20 (m, 3 H), 4.74–4.50 (m, 1 H), 4.40–4.18 (m, 1 H), 4.18–3.92 (m, 1 H), 2.50–1.10 (methylene envelope, 9 H); ^{13}C NMR (25 MHz, $CDCl_3$) δ 133.49 (2 d), 130.45 (d), 127.40 (2 d), 65.24 (d), 65.09 (d), 63.16 (d), 40.25 (d), 37.70 (t), 36.63 (t), 35.41 (t), 22.82 (d), carbon bearing boron not visible; IR ($CHCl_3$) 3610, 1440, 1410, 1321, 1230 cm^{-1}; mass spectrum, *m/e* 256 (M^+, 100), 243 (25), 226 (45), 185 (60), 159 (62), 105 (35), 104 (29), 79 (33), 78 (40). Anal. Calcd for $C_{14}H_{17}BO_3$: C, 68,89; H, 7.02. Found: C, 68.91; H, 7.11.

(1*S,5*R*,9*R*)-3-Phenyl-9-[(*tert*-butyldimethylsilyl)oxy]-2,4-dioxa-3-boratricyclo[5.3.1.0^{5,10}]undecane (5).** A solution of 2.30 g (9.42 mmol) of alcohol **4**, 3.55 g (23.6 mmol) of *t*-$BuMe_2SiCl$, and 3.21 g (47.1 mmol) of imidazole in 250 mL of DMF was heated at 100 °C for 2 h. After the solution cooled to 20 °C the DMF was removed in vacuo and the residue triturated with 50 mL of Et_2O. The heavier, oily phase was drawn off and the ether layer washed with water, dried ($MgSO_4$), and evaporated to give 3.22 g of a pale yellow solid. Chromatographic purification of this solid on 60 g of silica gel (Merck Kieselgel 60) with Et_2O–hexane (1/1) afforded 3.14 g (93%) of off-white crystals, **5**, mp 74–75.5 °C. An analytical probe was obtained by recrystallization from methanol: ^{1}H NMR (100 MHz, $CDCl_3$) δ 7.86–7.72 (m, 2 H), 7.42–7.24 (m, 3 H), 4.70–4.46 (m, 1 H), 4.36–4.12 (m, 1 H), 4.12–3.88 (dt, J_d = 9, J_t = 3 Hz, 1 H), 2.44–1.08 (methylene envelope, 8 H), 0.85 (s, 9 H), 0.04 (s, 6 H); IR (CCl_4) 2935, 1311, 1058 cm^{-1}; mass spectrum, *m/e* 358 (M^+, 3), 301 (100), 179 (M^+/2, 33), 79 (38). Anal. Calcd for $C_{20}H_{31}BO_3Si$: C, 67.02; H, 8.74. Found: C, 66.80; H, 8.79.

(2*R,6*S*,7*R*)-7-[(*tert*-Butyldimethylsilyl)oxy]bicyclo[2.2.2]octane-2,6-diol (6).** A solution of 3.00 g (8.37 mmol) of boronic ester **5** in 125 mL of Et_2O and 125 mL of 3 N NaOH solution was stirred vigorously at 20 °C for 4 days. The ether layer was separated and the aqueous layer saturated with NaCl and extracted three times with 150-mL portions of Et_2O. The combined extracts were dried (Na_2SO_4) and concentrated to a pale yellow oil (2.44 g). Chromatography of this oil on 120 g of silica gel with Et_2O–hexane (2/1) afforded 240 mg (8%) of recovered **5** and 2.06 g (90%) of **6** as a colorless oil which crystallized in vacuo. Recrystallization of **6** from concentrated hexane solutions at −78 °C afforded 2.00 g (95% based on consumed **5**) of white, crystalline diol **6**: mp 46–47.5 °C; ^{1}H NMR (100 MHz, $CDCl_3$) δ 4.52–4.22 (m, 1 H), 4.08–3.70 (m, 2 H), 3.78 (s, 1 H), 3.31 (d, *J* = 6 Hz, 1 H) 2.36–1.02 (methylene envelope, 8 H), 0.84 (s, 9 H), 0.00 (s, 6 H); IR ($CHCl_3$) 3620, 3400–3100, 2860, 1256, 1083 cm^{-1}; IR (CCl_4, 0.02% in 50-mm cells) 3621 (free OH), 3540 (intra OH) cm^{-1}; mass spectrum, *m/e* no M^+, 255 (M^+–OH, 1), 215 (27), 139 (39), 95 (56), 93 (32), 79 (100), 73 (42), 61 (31), 41 (23). Anal.

(13) Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972, pp 269–277.

(14) More convincing evidence for this structure would be its conversion to a symmetric tricyclic oxetane. All attempts to effect elimination of the SO_4^{2-} unit, reduction of the C–OSO_3 bond, or even hydrolytic cleavage of the sulfate unit were uniformly unsuccessful.

(15) (a) Clayton, R. B.; Henbest, H. B.; Smith, M. *J. Chem. Soc.* **1957**, 1982. (b) Searles, S. in "Heterocyclic Compounds with Three- and Four-Membered Rings"; Weisberger, A., Ed.; Interscience: New York, **1964**; Part II, p 983. (c) Zurfluh, R.; Wall, E. N.; Siddall, J. B.; Edwards, J. A. *J. Am. Chem. Soc.* **1968**, *90*, 6224.

(16) An analogous state of affairs exists in the reactions of γ-halo amines: (a) Grob, C. A. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 535; (b) Grob, C. A.; Rich, R. *Helv. Chim. Acta* **1979**, *62*, 2793 and references cited therein.

(17) (a) Henbest, H. B.; Millward, B. B. *J. Chem. Soc.* **1960**, 3575. (b) Köll, P.; Schulz, J. *Tetrahedron Lett.* **1978**, 49.

(18) The assistance of the following people is acknowledged for the determination of spectroscopic and physical data: Ms. B. Brandenberg (^{1}H NMR), Mr. K. Hiltbrunner (^{13}C NMr), Mr. H. Hediger (IR), Ms. L. Golgowski and Professor J. Seibl (mass spectra), and Mr. W. Manser (microanalyses).

(19) Nakata, H. *Tetrahedron* **1963**, *19*, 1959.

Calcd for $C_{14}H_{28}O_3Si$: C, 61.72; H, 10.36. Found: C, 61.79; H, 10.45.

(1*S,5*R*,9*R*)-9-[(*tert*-Butyldimethylsilyl)oxy]-3-oxo-2,4-dioxa-3-thiatricyclo[5.3.1.0^{5,10}]undecane (7).** A solution of *N,N'*-thionyldiimidazole was prepared by dissolving 899 mg (13.2 mmol) of imidazole in 20 mL of THF, cooling to 2 °C, and adding 238 mL (3.31 mmol) of thionyl chhloride. The resulting suspension was added dropwise via cannula through a glass filter frit to a cold (-15 °C), stirred solution of 300 mg (1.10 mmol) of diol **6**. The cooling bath was removed and the reaction mixture stirred for 1 h. After evaporation of ca. 75% of the solvent, the clear, residual oil was chromatographed on 35 g of silica gel with Et_2O-hexane (1/2), affording 331 mg (94%) of the mixture of sulfurous esters **7** as a clear colorless oil: ^1H NMR (360 MHz) δ 4.90-4.83 (m, 1 H), 4.54-4.48 (m, 1 H), 3.98-3.89 (m, 1 H), 3.57 (q, J = 4 Hz, 0.6 H), 2.76-2.67 (d, J = 16 Hz, 1.2 H), 2.51 (q, J = 4 Hz, 0.4 H), 2.19-2.08 (m, 1 H), 2.00-1.70 (methylene envelope, 4 H), 1.31-1.22 (m, 1 H); ^1H NMR (100 MHz) δ 5.04-4.81 (m, 1 H), 4.68-4.46 (m, 1 H), 4.10-3.86 (m, 1 H), 3.60 (q, J = 4 Hz, 0.6 H), 2.82 (q, 0.4 H), 2.67 (q, 0.4 H), 2.52 (q, J = 4 Hz, 0.4 H), 2.34-1.10 (methylene envelope, 6.2 H), 0.86 (s, 9 H), 0.03 (s, 6 H); IR ($CHCl_3$) 2955, 1185, 1101 cm^{-1}; mass spectrum, m/e 318 (M$^+$, 1), 261 (10), 197 (84), 153 (26), 79 (70), 77 (100), 59 (27), 41 (25).

(1*S,5*R*,9*R*)-9-[(*tert*-Butyldimethylsilyl)oxy]-3,3-dioxo-2,4-dioxa-3-thiatricyclo[5.3.1.0^{5,10}]undecane (8).** To a solution of 445 mg (1.40 mmol) of **7** in 10 mL of CCl_4 was added 35.8 mL (1.68 mmol) of a 0.048 M solution of RuO_4 in CCl_4. The black RuO_2 precipitate was filtered off and washed twice with 5-mL portions of CCl_4 and the filtrate concentrated to a yellow oil which crystallized in vacuo (400 mg). Recrystallization from 5 mL of hexane afforded 334 mg (72%) of sulfate **8** as white plates: mp 79.5-80.5 °C; ^1H NMR (100 MHz) δ 5.38-5.12 (m, 1 H), 5.02-4.78 (m, 1 H), 4.18-3.97 (dt, J_t = 9, J_d = 4 Hz, 1 H), 3.08 (q, J = 4 Hz, 1 H), 2.56-1.63 (methylene envelope, 6 H), 1.42-1.16 (dq, J_d = 15 Hz, 1 H), 0.83 (s, 9 H), 0.04 (s, 6 H); IR ($CHCl_3$) 2955, 1383, 1195, 990, 977 cm^{-1}; mass spectrum, m/e 334 (M$^+$, 1), 277 (100), 197 (37), 79 (45), 75 (97). Anal. Calcd for $C_{14}H_{26}O_5SSi$: C, 50.27; H, 7.83; S, 9.59. Found: C, 50.29; H, 7.69; S, 9.68.

(1*S,5*R*,9*R*)-3,3-Dioxo-2,4-dioxa-3-thiatricyclo-[5.3.1.0^{5,10}]undecan-1-ol (1).** Hydrogen fluoride is an extremely dangerous reagent. All reactions using this substance must be done in a well-ventilated hood, taking the utmost precautions against inhalation of or contact with the vapor.[20]

In a Teflon test tube (2 × 15 cm) fitted with Teflon stopper and Teflon inlet and outlet tubes was placed 259 mg (0.772 mmol) of **8**. The test tube was then cooled in a dry ice-*i*-PrOH bath and ca. 5 mL of HF was condensed in the tube. The vessel was swirled gently and then transferred to a -20 °C bath (dry ice-*i*-PrOH), and a stream of argon was passed over the surface to remove the HF (ca. 1.5 h). The yellow residue was partitioned between H_2O and CH_2Cl_2 (2 mL each). The aqueous layer was separated and extracted with three 5-mL portions of CH_2Cl_2. The combined CH_2Cl_2 extracts were dried ($MgSO_4$) and evaporated to give an off-white oil which crystallized in vacuo (166 mg). Recrystallization from CH_2Cl_2 (2 mL)-hexane (5 mL) afforded 150 mg (88%) of **1** as off-white crystals: mp 109-110 °C dec; ^1H NMR (100 MHz) δ 5.42-5.19 (m, 1 H), 5.07-4.86 (m, 1 H), 4.37-4.08 (m, 1 H), 3.20 (q, J = 4 Hz 1 H), 2.56-1.60 (methylene envelope, 7 H), 1.45-1.18 (dm, J_d = 15 Hz, 1 H); IR ($CHCl_3$) 3610, 2950, 1383, 1193, 984, 955 cm^{-1}; mass spectrum, m/e no M$^+$, 122 (27), 96 (25), 95 (39), 79 (56), 78 (100), 77 (25), 41 (29), 40 (25). Anal. Calcd for $C_8H_{12}O_5S$: C, 43.62; H, 5.49; S, 14.56. Found: C, 43.77; H, 5.44; S, 14.45.

3,3,6,6,9-Pentamethyl-2-azonia-10-azabicyclo[4.4.0]dec-1-ene 6,7-oxybicyclo[2.2.2]oct-2-yl Sulfate (2). To a solution of 50 mg (0.227 mmol) of **1** in 500 μL of DMF in a small test tube (7 × 60 mm) fitted with a rubber septum under Ar was added 103 μL (0.45 mmol, d^{20}_4 0.918) of **9**. A white, crystalline precipitate slowly formed overnight. After 9 days TLC analysis of the supernatant liquid indicated complete consumption of the educt. The mixture was diluted with 200 μL of Et_2O and 500 μL of hexane. The crystals were collected by filtration and dried in vacuo (50 mg). Recrystallization from CH_2Cl_2-Et_2O followed by drying at 40 °C in vacuo gave 44.5 mg (46%) of **2** as white, fluffy needles: mp 208-209 °C; ^1H NMR (100 MHz) δ 9.10-8.80 (s, 2 H), 4.70-4.45 (m, 3 H), 3.91-3.70 (m, 1 H), 2.40-1.20 (methylene envelope, 15 H), 1.36 and 1.30 (2 s, 15 H); ^{13}C NMR (25 MHz) δ 167.52 (s), 80.31 (d), 79.88 (d), 69.20 (d), 54.44 (s), 39.44 (d), 37.81 (t), 34.32 (t), 34.08 (t), 32.08 (s), 31.03 (2 t), 30.92 (2 t), 30.70 (2 q), 29.84 (2 q), 25.23 (d), 24.61 (q); IR ($CHCl_3$) 3220, 3110, 3005, 2975, 2950, 1642, 1255, 1242, 1021, 950 cm^{-1}; mass spectrum, m/e 427 (M$^+$ - 1,1) 193 (100), 180 (37), 165 (27), 84 (26), 81 (52), 69 (84), 57 (36), 55 (34), 45 (44), 44 (59), 43 (39), 41 (47). Anal. Calcd for $C_{21}H_{36}N_2O_5S$: C, 58.85; H, 8.47; N, 6.54; S, 7.48. Found= C, 58.77; H, 8.52; N, 6.41; S, 7.52.

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Activation of Reducing Agents. Sodium Hydride Containing Complex Reducing Agents. 16.[1] FeCRACO, a New Reagent for Carbonylation of Primary, Secondary, and Tertiary Alkyl Halides at Atmospheric Pressure

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In recent years, complex reducing agents "NaH-RONa-MX_n"[2] (termed CRA and MCRA when the nature of the metallic salt must be specified) have been described as versatile, inexpensive reagents in organic synthesis and useful applications have already been devised.[3] In particular, it seemed that CRA, prepared under carbon monoxide, could be used for the generation of transition-metal carbonyl species under very mild conditions in an aprotic medium. Thus, it has been found that "NaH-Am-*t*-ONa-$Co(OAc)_2$-CO" led to the generation (room temperature, 1 atm) of $NaCoCO_4$ in a multicomponent medium,[4] termed CoCRACO. Furthermore it has been evidenced that the simultaneous presence of NaH and Am-*t*-ONa promotes $S_{RN}1$ condensations of $NaCoCO_4$ with aryl halides,[4] thus allowing catalytic carbonylation of aryl halides[5] under unusually mild conditions for cobalt carbonyl species.

On the other hand, we have also briefly reported[6] that "NaH-Am-*t*-ONa-$FeCl_3$-CO" led to iron carbonyl species

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