(br s, 1 H, OH, exchangeable), 4.9 (d, 1 H, CHOH) ppm. This without further purification was directly oxidized to **18a** by using the following method.

To a magnetically stirred and ice-cold solution of **17a** (682 mg, 2.60 mmol) in acetone (15 mL) was added, dropwise, Jones reagent (2 mL, 5.34 mmol). The mixture was stirred for 15 min in the cold and for 45 min at room temperature. It was cooled in ice. A second aliquot of Jones reagent (2 mL, 5.34 mmol) was added dropwise to the stirred solution. The reaction mixture was stirred cold for 15 min and at room temperature for 2 h. At the end of this period the mixture became completely dark green and was diluted with cold water. The organic material was extracted with ethyl acetate. The extract was washed with water (once) and repeatedly with saturated aqueous $NaHCO_3$ and water and dried (Na_2SO_4). Removal of the solvent gave a brown liquid (92 mg) which was not characterized further. The basic aqueous washing on acidification with cold 6 N HCl gave a white precipitate which was extracted with ethyl acetate to afford the crude acidic product, 160 mg (21%). Crystallization from THF–petroleum ether afforded the pure acid **18a**: 120 mg (16%); mp 209 °C; UV 245 nm (log ϵ 4.1), 294 (3.3). Anal. Calcd for $C_{16}H_{16}O_5$: C, 66.66; H, 5.59. Found: C, 66.41; H, 5.78.

The keto acid **18a** (110 mg, 0.39 mmol) was esterified with CH_2N_2–Et_2O to afford a pale yellow liquid. This, on filtration through a short column of neutral alumina, afforded **19a** as a colorless liquid: 112 mg (91%); IR (film) 1725, 1605, 1595 cm^{-1}; UV 248 nm (log ϵ 4.20), 286 (3.3); NMR (CCl_4) 1.58 (s, 3 H, CCH_3), 3.65 (s, 6 H, 2 CO_2CH_3), 3.70 (1 H, s, COCH), 7.13–7.70 (4 H, m, ArH) ppm; GC 7.2 min (A).

Equilibriation of 19a with NaOMe–MeOH. The keto diester **19a** (80 mg, 0.25 mmol) was treated with 2% NaOMe in MeOH (2 mL,87 mmol) under reflux for 2 h under N_2. The reaction mixture was cooled and diluted with water. Ether extraction revealed the absence of any unhydrolyzed material. The basic aqueous part on acidification allowed the separation of a solid which was extracted with ether to afford **18a**: 70 mg (97%); mp and mmp (with the sample described above) 209 °C. A part of this acid was esterified with Et_2O–CH_2N_2 to afford the starting ester **19a** as revealed by NMR and GC comparisons.

Hydrogenolysis of the Keto Diester 19a to 9a. The keto diester **19a** (24 mg, 0.076 mmol) in dry ethanol (4 mL) was stirred under an atmosphere of hydrogen in presence of Pd/C (10%, 20 mg) and 1 drop of $HClO_4$ (70%) for 24 h. The catalyst was filtered off and washed with ethanol. Powdered $NaHCO_3$ was added portionwise to the combined filtrate and washings until the evolution of CO_2 ceased. The undissolved substance was filtered off, and the filtrate was evaporated to dryness. The residue was digested with ether and filtered through a short column of neutral alumina to afford a solid, mp 81–84 °C. Crystallization from petroleum ether afforded the pure ester **9a**, mp and mmp 89 °C. GC analysis also confirmed the identity.

Hydroboration of the Acid 5b Followed by Oxidation. (±)-1α-Methyl-7-methoxy-9-oxo-1,2,3,4,4a,9a-hexahydrofluorene-1β,4aα-dicarboxylic Acid (18b). The acid **5b** (1 g, 3.49 mmol) in THF (15 mL) was reacted with diborane [generated from $NaBH_4$ (2 g, 52.9 mmol) in diglyme (52 mL) and $BF_3 \cdot Et_2O$ (14 mL) in diglyme (15 mL)] for 23 h under conditions identical with those described for **5a**. After decomposition of the excess diborane with water (5 mL), the organoborane was oxidized with 3 N NaOH (8 mL) and 30% H_2O_2 (8 mL) for 1 h with stirring and heating to 35–40 °C. The organic material was extracted with Et_2O–ethyl acetate by the procedure described earlier to afford the crude triol **17b**: 298 mg (32%); mp 147–153 °C. Crystallization of a part of this material from Et_2O afforded the pure triol **17b**: mp 161 °C; IR (Nujol) 3250, 1615, 1590, 1460 cm^{-1}; UV 278 nm (log ϵ 3.5). A solution of crude **17b** (120 mg, 0.43 mmol) in acetone (10 mL) was oxidized by dropwise addition of Jones reagent (1 mL, 2.67 mmol) in two lots as described for **17a**. The total stirring time was 3 h. The reaction mixture was diluted with water and extracted with ethyl acetate. The ethyl acetate extract was washed with water, NaOH (2%), and water and dried (Na_2SO_4). Removal of the solvent gave a negligible amount of a brown liquid which was rejected. The basic aqueous washing on acidification (6 N HCl) and extraction with ethyl acetate afforded a white solid, 85 mg (65%). Crystallization from THF–petroleum ether afforded the pure acid **18b**, mp 220 °C. Anal. Calcd for $C_{17}H_{18}O_6$: C, 64.14; H, 5.70. Found: C, 64.19; H, 5.87.

The acid **18b** (60 mg, 0.2 mmol) was esterified with CH_2N_2–Et_2O to afford the diester **19b**: 62 mg (94%); colorless liquid; IR (film) 1730, 1710, 1615, 1590, 1490, 1460 cm^{-1}; UV 250 nm (log ϵ 4.2); mass spectrum, *m/e* 346 (M^+), 314, 287, 228, 227, 149; NMR (CCl_4) 1.01–1.45 (m, 4 H, methylenes), 1.60 (s, 3 H, CCH_3), 1.90–2.10 (m, 2 H, methylenes), 3.66 (s, 6 H, 2 $COOCH_3$), 3.70 (s, 1 H, COCH), 3.83 (s, 3 H, OCH_3), 7.03–7.26 (m, 3 H, Ar H) ppm.

Registry No. 4a, 74741-03-0; **4b**, 76403-71-9; **5a**, 76403-72-0; **5b**, 76403-73-1; **6a**, 76403-74-2; **6b**, 76403-75-3; **7a**, 76403-76-4; **8a**, 76403-77-5; **9a**, 76403-78-6; **9b**, 76403-79-7; **10a**, 76403-80-0; **10b**, 76403-81-1; **11a**, 76403-82-2; **12a**, 76403-83-3; **17a**, 76403-84-4; **17b**, 76403-85-5; **18a**, 76403-86-6; **18b**, 76403-87-7; **19a**, 76403-88-8; **19b**, 76403-89-9.

Electrochemical Reduction of Bis(α-bromocyclopropyl) Ketone

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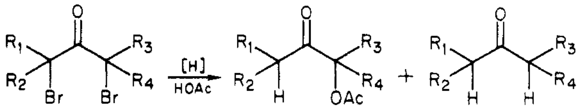
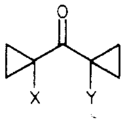
Received November 28, 1980

Reduction of α,α′-dibromo ketones (**1**) in acetic acid affords as major products α-acetoxy ketones (**2**) when the α-carbons bear at least three alkyl substituents; if the latter condition is not fulfilled, the so-called "parent" ketone (**3**) predominates. Reduction may be effected both electrochemically[1] or by finely dispersed mercury.[2] Although product distributions are somewhat different in the two reduction methods, they are on the whole fairly similar.[3,4] In the course of exploring the scope of this reductive acetoxylation process, we had occasion to examine the reduction of bis(α-bromocyclopropyl) ketone (**4**).[5] We describe the anomalous behavior of **4** under our reduction conditions.



1 **2** **3**



4, X = Y = Br
5, X = Br; Y = H
6, X = Y = H

Although α,α′-dibromo ketones are generally reduced in 0.25 to 2 days by ultrasonically dispersed mercury,[2] **4** was recovered (95%) after 8 days. The electrochemical reduction of **4** was also exceptional. Controlled-potential reduction of **4** in acetic acid/1.0 M sodium acetate (HOAc/NaOAc) at −0.80 V (SCE) afforded a mixture of α-bromocyclopropyl cyclopropyl ketone (**5**; 76%) dicyclopropyl ketone (**6**; 14%), and unreacted **4** (10%). Electrolytic reduction of **4** in 9:1 dimethylformamide

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[1] A. J. Fry and J. J. O'Dea, *J. Org. Chem.*, **40**, 3625 (1975).
[2] A. J. Fry and D. Herr, *Tetrahedron Lett.*, 1721 (1978).
[3] A. J. Fry and J. Bujanauskas, *J. Org. Chem.*, **43**, 3157 (1978).
[4] A. J. Fry and A. T. Lefor, *J. Org. Chem.*, **44**, 1270 (1979).
[5] L. Fitjer, *Angew. Chem., Int. Ed. Engl.*, **15**, 763 (1977).

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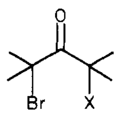
Table I. Polarographic Half-Wave Potentials of Selected Bromides and Dibromides[a]

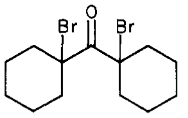
compd	$E_{1/2}$, V (vs. SCE)
4	−0.85, −1.15
4[b]	−0.88, −1.33
5	−1.18
7	−0.23
8	−0.34
9	−0.27
1-bromopropane[c]	−2.17
1,6-dibromohexane[d]	−2.13
1,3-dibromopropane[d]	−1.91

[a] Measured in this laboratory in HOAc/1.0 M NaOAc, except where noted. [b] Acetonitrile/0.1 M TEAB. [c] DMF/0.1 M TEAB. See ref 9. [d] DMF/0.1 M tetrabutylammonium perchlorate: M. R. Rifi, *Tetrahedron Lett.*, 1043 (1969).

(DMF):HOAc/NaOAc or DMF/tetraethylammonium bromide (TEAB) at −0.80 V afforded **5** as the exclusive product. In contrast, reduction in acetic acid containing media of the dibromo ketones **7** and **9**, either electrochemically or by ultrasonically dispersed mercury, affords the corresponding α-acetoxy ketones in high yield,[1,2] and in fact we have not observed behavior such as that exhibited by **4** with any other of the ca. 50 dibromo ketones of widely varying structure which we have examined to date in this laboratory.



7, X = Br
8, X = H



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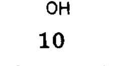
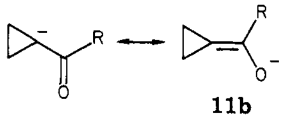
A clue to the unusual behavior exhibited by **4** may be obtained by comparing its polarographic behavior with some other mono- and dibromides (Table I). The data in Table I exhibit two notable features: first, it is clear that **4** is substantially harder to reduce than other dibromo ketones; secondly, the second bromine of **4** is reduced with markedly greater difficulty than is the first, behavior also unlike that exhibited by other mono- and dibromo ketone pairs, e.g., **7** and **8**. The failure of **4** to undergo reduction by mercury may be understood from these data. Reduction of dibromo ketones such as **7** or bis(α-bromocyclohexyl) ketone (**9**) in acetic acid is nearly thermoneutral,[2] and the negative shift in the reduction potential of **4** relative to **7** or **9** is apparently large enough to render reduction by mercury impossible. This experiment sets a lower limit of −0.85 V for the reducing ability of mercury under our conditions. The separation of 0.33 V between the two reduction steps of **4** accounts for the isolation of **6** in the electrolytic reduction. Failure to isolate an α-acetoxy ketone in this reaction, even though **4** is fully substituted at the α-positions, is presumably because the requisite precursor,[1] hydroxyallyl cation **10**, derives no stabilization from the cyclopropyl rings, as a consequence of the fact that the electron density and banana bonds of these rings are orthogonal to the allylic π system.[6]



10

The very negative reduction potentials of **4** and **5** are not associated with the cyclopropyl rings per se, since the polarographic reduction potentials of bromocyclopropane, 2-bromopropane, and bromocyclohexane are practically identical (−2.36, −2.26, and −2.29 V, respectively, in DMF/TEAB).[7] Rather, the relative difficulty of reduction probably arises because the resulting anions (**11**) derive much less stabilization from enolate structure **11b** than do the corresponding open-chain species from, e.g., **7**, **8**, or **9**. For presumably similar reasons, cyclopropyl ketones undergo proton exchange at the α-position at much slower rates than do the corresponding isopropyl ketones.[8]



11a **11b**

The reason for the large difference between the reduction potentials of **4** and **5** is not clear. A calculation based upon the expected inductive effect of one bromine atom upon the polarographic reduction potential of the other using the relationship[9] shown in eq 1 and a value[10] of

$$E_{1/2} = 0.325\sigma^* + 0.12E_s - 2.165 \qquad (1)$$

+1.00/2.8 for the σ^* of $BrCH_2CH_2$, together with reasonable estimates[10] of E_s for this group, suggests that a 1,3-dibromide should be 0.05–0.08 V easier to reduce than the corresponding monobromide. However all of the available experimental evidence indicates that larger separations are the norm. Thus, note the 0.11-V difference between $E_{1/2}$'s of **8** and **7**, or the differences (0.22 and 0.26 V, respectively) between the reduction potential of 1,3-dibromopropane and those of either 1,6-dibromohexane or 1-bromopropane. It is known[11] that 1,3-dibromides are strongly adsorbed on mercury[12] and that their reduction potentials can be quite substantially affected thereby;[11] therefore, the substantial difference between the $E_{1/2}$'s of **4** and **5** and from the calculated value of 0.05–0.8 V may arise simply from differing degrees of adsorption for the two substances.

Finally, we point out that, inasmuch as the method of Fitjer[5] is not readily adaptable to the synthesis of **5**, the electrochemical reduction of **4** constitutes a convenient synthetic route to this substance.

Experimental Section

Electrochemical experiments were carried out with a Princeton Applied Research Model 170 electrochemistry system. NMR spectra were recorded on Varian A60-A and HA-100 spectrometers, and mass spectra were recorded on a Perkin Elmer-Hitachi Model RMU-6L spectrometer.

Electrolysis of bis(α-bromocyclopropyl) ketone was carried in a manner previously described;[1] electrolysis in DMF containing 0.1 M TEAB afforded α-bromocyclopropyl cyclopropyl ketone (90%), shown to be free of **4** and **6** by VPC; after isolation by preparative VPC, **5** exhibited mass spectral peaks at *m/e* 188 and 190 (parent) and 109 (M − Br) and NMR multiplets at δ 2.6, 1.55,

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(6) M. Hanack, T. Bassler, W. Eymann, W. E. Heyd, and R. Kopp, *J. Am. Chem. Soc.*, **96**, 6686 (1974).

(7) F. L. Lambert and K. Kobayashi, *J. Am. Chem. Soc.*, **82**, 5324 (1960).

(8) (a) W. Th. van Wijnen, H. Steinberg, and Th. J. deBoer, *Tetrahedron*, **28**, 5423 (1972); (b) Harold W. Pinnick, Y.-H. Chang, S. C. Foster, and M. Govindan, *J. Org. Chem.*, **45**, 4505 (1980), and references therein.

(9) F. L. Lambert, *J. Org. Chem.*, 31, 4184 (1966).

(10) R. W. Taft, Jr. in "Steric Effects in Organic Chemistry", M. S. Newman, Ed., Wiley, New York, 1956, p 556 ff.

(11) O. R. Brown and E. R. Gonzalez, *J. Electroanal. Chem.*, **43**, 215 (1973).

(12) We have observed strong polarographic maxima for most of the dibromo ketones we have studied. Monobromo ketones generally exhibit no (or very small) maxima. Dibromide 4 does not exhibit a maximum.

and 0.95 (ratios 1:4:4, respectively). Anal. Calcd for C_7H_9BrO: C, 44.47; H, 4.80. Found: C, 44.88; H, 5.09.

Bis(α-bromocyclohexyl) ketone (**9**) was prepared[1] in 58% yield, mp 100–101 °C (toluene–hexane). Electrochemical reduction at −0.18 V in HOAc/KOAc afforded α-acetoxydicyclohexyl ketone and dicyclohexyl ketone in a 3.5:1 ratio (VPC); reduction by mercury afforded the same two substances in a 10.4:1 ratio.

Acknowledgment. Financial support, including a postdoctoral fellowship for J.A., was provided by the National Science Foundation. Dr. L. Fitjer kindly supplied details on the synthesis of 4.

Registry No. 4, 60538-60-5; **5**, 74605-55-3; **6**, 1121-37-5; **7**, 17346-16-6; **8**, 3212-63-3; **9**, 76447-11-5.

Oxidation of Benzyl Ethers[1]

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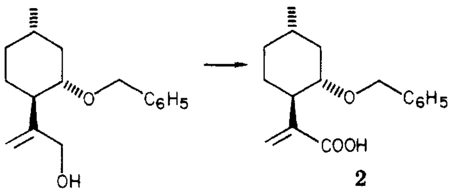
Received August 28, 1980

Benzyl ethers are commonly used to protect alcohols because of the ease of formation, stability to a variety of reagents, and specific removal methods.[2] In connection with a recent synthetic effort, the transformation of benzyl ether **1** into the corresponding acid **2** was required (eq 1).

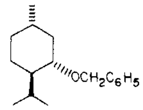
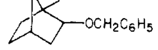
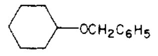
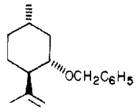


1 2 (1)

Jones reagent[3] seemed the logical choice to accomplish this goal; however, when compound **1** was allowed to react with Jones reagent at 0 °C for 1 h, a host of products resulted. These included the corresponding α,β-unsaturated aldehyde plus carboxylic acid(s) and a benzoate ester. Another reaction which was allowed to stir at 0 °C for 3–4 min gave only the aldehyde.

The oxidation of benzyl ethers with Jones reagent is a general one. Table I shows the results from the Jones oxidation of a variety of benzyl ethers.[4] For example, the benzyl ether of 2-octanol gives a 79% yield of 2-octanone and 21% 2-octyl benzoate in addition to 61% benzoic acid. In most of the systems studied, the ketone is formed in a larger proportion than the benzoate ester.

Table I. Jones Oxidation of Benzyl Ethers[a]

ether	products, % yield[b] ketone[c]		
	ketone[c]	benzoate[c]	benzoic acid[d]
$CH_3(CH_2)_5CH(CH_3)OCH_2C_6H_5$	79	21	61
	57	28	53
$C_6H_5CH(CH_3)OCH_2C_6H_5$	56	21	52
	63	24	47
	16	40	16
	30	32	31

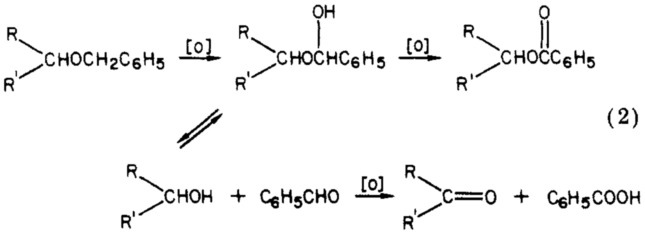
[a] All reactions were run for 12 h at 0 °C, using 4 equiv of Jones reagent. [b] (Millimoles/millimole of starting material) × 100%. [c] Average of percentages independently determined from GC and NMR data and weight of material obtained. [d] Isolated.

Table II. Rate of Oxidation of Benzyl Ethers[a]

addtn time, min	reacn time, min	% benzyl ether reacted[b]
2	5	55
10	10	57
10	30	61
10	60	67
10	100	80
10	110	87
10	155	100

[a] Using 2-octyl benzyl ether and 4 equiv of Jones reagent at 0 °C. [b] 100 × (millimoles of starting ether − millimoles of ether left)/millimoles of starting ether.

The products apparently arise by initial formation of a hemiacetal, as postulated in electrochemical oxidation of benzyl ethers,[5] followed by oxidation to the ester, ketone, and benzoic acid (eq 2). Exposure of 2-octyl benzoate to the reaction conditions and workup gave a 96% recovery of starting material, thus ruling out the benzoate ester as a precursor for the ketone and benzoic acid. In addition, the ratio of products does not change as a function of percent reaction.



(2)

The oxidation reaction is remarkably fast, using 4 equiv of Jones reagent[6] (see Table II). Thus, over half of the benzyl ether of 2-octanol is consumed within 20 min of combined addition and stirring time. In addition, the reaction is complete after 2.5 h. When only 1 equiv of

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(1) Presented at the Southeast-Southwest Regional Meeting of the American Chemical Society, Dec 10–13, 1980, New Orleans, LA, Abstract 475.

(2) Reese, C. B. In "Protective Groups in Organic Chemistry"; McOmie, J. F. W., Ed.; Plenum: New York, 1973; pp 98–100.

(3) (a) Bowden, K.; Heilbron, I. M.; Jones, E. R. H.; Weedon, B. C. L. *J. Chem. Soc.* **1946**, 39. (b) Bowers, A.; Halsall, T. G.; Jones, E. R. H.; Lemin, A. H. *ibid.* **1953**, 2548. (c) Note: the CrO_3 is critical since dark CrO_3 will give a reagent which gives only poor oxidation results.

(4) All benzyl ethers were prepared in over 90% yields from the corresponding alcohols with benzyl bromide and sodium hydride in dimethylformamide.

(5) (a) Weinreb, S. M.; Epling, G. A.; Comi, R.; Reitano, M. *J. Org. Chem.* **1975**, *40*, 1356. (b) Boyd, J. W.; Schmalzl, P. W.; Miller, L. L. *J. Am. Chem. Soc.* **1980** *102*, 3856 and references cited therein.

(6) Although only 2–3 equiv of Jones reagent is required (see eq 2), the use of 4 equiv allows the reaction to go to completion without difficulty.

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