The compounds to be hydrogenated were added after the catalyst had been shaken with hydrogen in the reaction medium for 30–60 min. The products were analyzed, usually after complete hydrogenation, by GC using OV-17 or OV-101 as a stationary phase. Optical rotatory dispersion and circular dichroism were measured on a JASCO J-20 spectropolarimeter. Melting points were determined in capillaries and are corrected.

Nitrogen Bases. 4-Methoxypyridine was prepared by catalytic reduction of 4-methoxypyridine *N*-oxide (Aldrich) with Raney nickel in methanol.[13] Care was taken not to let the reaction become too violent by adding the *N*-oxide in portions; bp 89 °C (24 mm). 4-(Dimethylamino)pyridine (Aldrich) was purified by passing through alumina and/or recrystallization from pyridine. Other nitrogen bases of commercial origin were used without further purification but with drying over potassium hydroxide.

Solvent. Tetrahydrofuran was purified by treatment with lithium aluminum hydride or with a ruthenium catalyst and hydrogen, followed by distillation under nitrogen.[14]

Catalyst. The palladium black used as the catalyst was prepared by reduction of palladium hydroxide with hydrogen in water.[14]

Hydrogenation of Testosterone (1c) in 4-Methoxypyridine. The compound **1c** (500 mg) was hydrogenated with 51 mg of palladium black in 1.5 mL of 4-methoxypyridine for 42 h. After the catalyst was removed, the reaction mixture was treated with ether and 10% hydrochloric acid. The ether solution was washed with water and then with 5% sodium hydrogen carbonate solution and dried over anhydrous sodium sulfate. Evaporation of the ether gave the product containing 98.5% of 5β-androstan-17β-ol-3-one (GC analysis). Recrystallization of the product from 1:1 acetone–hexane yielded 352 mg (70% yield) of the compound of a high purity (99.6% by GC analysis): mp 142–142.5 °C; $[\theta]^{26}_{290}$ −1421 and a = −20.3 (c 0.25, MeOH) (lit. mp 142–144 °C;[15] $[\theta]_{289}$ −1485 and a = −22 (MeOH)[16]).

Hydrogenation of Androsta-1,4-diene-3,17-dione (2b) in 4-Methoxypyridine. The compound **2b** (1 g) was hydrogenated with 50 mg of palladium black in 1.7 mL of 4-methoxypyridine. The hydrogenation was complete within 14 h to give the product containing 98.3% of 5β-androstane-3,17-dione (GC analysis). Recrystallization of the product from acetone–hexane gave 772 mg (77% yield) of the compound of a high purity (99.7% by GC analysis): mp 133–133.5 °C; $[\alpha]^{22}_{D}$ +114° (c 0.96, EtOH) (lit.[17] mp 130–131 °C; $[\alpha]^{26}_{D}$ +112° (c 0.139, EtOH)).

Hydrogenation of 19-Norandrost-4-ene-3,17-dione (3b) in Tetrahydrofuran and Hydrobromic Acid. 3b (500 mg) was hydrogenated with 20 mg of palladium black in 2 mL of tetrahydrofuran containing 0.02 mL of concentrated hydrobromic acid. The hydrogenation was complete in 3 h to give the product containing 97.9% 19-nor-5β-androstane-3,17-dione (GC analysis). Recrystallization of the product from acetone gave 367 mg (73% yield) of the pure compound (no 5α isomer by GC analysis): mp 181–181.5 °C; $[\alpha]^{25}_{D}$ +114° (c 1, $CHCl_3$) (lit.[18] mp 179–181 °C; $[\alpha]^{25}_{D}$ +111.6° (c 1, $CHCl_3$).

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Registry No. 1a, 601-57-0; **1b**, 63-05-8; **1c**, 58-22-0; **1d**, 1045-69-8; **1e**, 57-83-0; **1f**, 382-45-6; **1g**, 2872-90-4; **1h**, 481-30-1; **2b**, 897-06-3; **2c**, 846-48-0; **2d**, 2363-59-9; **3b**, 734-32-7; **3c**, 434-22-0; **3d**, 1425-10-1; 5β-cholestan-3-one, 601-53-6; 5β-androstane-3,17-dione, 1229-12-5; 5β,17β-17-hydroxyandrostan-3-one, 571-22-2; 5β,17β-17-acetoxyandrostan-3-one, 1164-92-7; 5β-pregnane-3,20-dione, 128-23-4; 5β-androstane-3,11,17-trione, 1429-06-7; 5β-androstan-3-one, 18069-68-6; 5β-androstane-3,17-dione, 1229-12-5; 5β,11β-11-hydroxyandrostan-3-one, 571-22-2; 5β,11β-11-acetoxyandrostan-3-one, 1164-92-7; 5β-estrane-3,17-dione, 5696-51-5; 5β,11β-11-hydroxyestran-3-one, 19468-31-6; 5β,11β-11-acetoxyestran-3-one, 2302-77-4; Pd, 7440-05-3.

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Highly Convenient Electrolysis Procedure for the Preparation of α-Halogenated Ketones and Acetals from Enol Acetates, Enol Ethers, and Silyl Enol Ethers

Sigeru Torii,* Tsutomu Inokuchi, Seiji Misima, and Takesi Kobayashi

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

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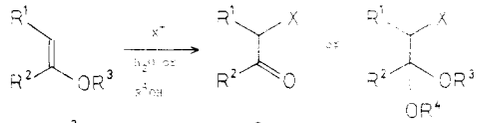
Although numerous methods are available for halogenation of the α-position of alkanones using unstable and troublesome halogenating reagents,[1] none are satisfactory for the preparation of α-halogenated carbonyl compounds **2** and their acetals **3** from enol ethers **1** under mild and



1a, R^3 = Ac
b, R^3 = $SiMe_3$
c, R^3 = Me
d, R^1 = R^3 = alkyl, R^2 = H

2

3

X = Cl, Br, I

neutral conditions such as for an electrolytic procedure with halide salts. To our knowledge, only one literature[2] method deals with the electrochemical haloalkoxylation of 6-alkoxydihydropyran,[3] and the electrochemical halofunctionalization on enol acetates[4] **1a** and silyl enol ethers[5] **1b** has not been attempted yet. We, therefore, endeavored to develop an electrochemical procedure for the conversion of **1** into α-halogenated ketones **2** and their congeners **3**. We describe here a simple and general synthetic procedure for obtaining **2** and **3** from **1** by electrolysis with halide salts in an undivided cell. The most fascinating features of the present anodic halogenation of **1** are concerned not only with an easily utilizable technique but also with a regioselective monohalogenating procedure, resulting in high yields of α-halogenated products whose halogen atom can be chosen by using an appropriate halide salt, either NH_4Cl, NH_4Br, or NH_4I.

Preparation of α-Halogenated Ketones and Their Acetals. Electrolysis of a mixture of enol acetate **1a** [R^1, R^2 = $-(CH_2)_{10}-$] in a MeCN–H_2O–NH_4Br–(Pt–Pt) system under a constant current of 6.7 mA/cm^2 at 0.7–0.8 V vs.

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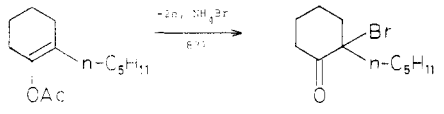
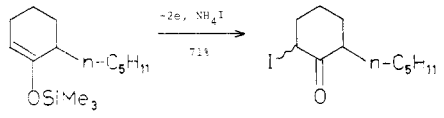
Ag wire with 2.3 F/mol of electricity afforded 2-bromocyclododecanone (**2**, X = Br; R^1, R^2 = $-(CH_2)_{10}-$) in 95% yield (Table I, entry 1). Similarly, 2-chlorocyclododecanone (**2**, X = Cl; R^1, R^2 = $-(CH_2)_{10}-$) was obtained in 95% yield by electrolysis of **1a** [R^1, R^2 = $-(CH_2)_{10}-$] with NH_4Cl as a halogenating reagent (entry 2). Results for the electrolytic halogenation of a series of alicyclic and aliphatic enol acetates **1a** are presented in Table I.

2-Iodoalkanones **2**[6] (X = I) were obtained by electrolysis of silyl enol ethers **1b** in MeCN–H_2O–NH_4I (entries 12, 13). On the other hand, electrolysis of methyl enol ethers **1c** with MeOH–NH_4X (X = halides) provided α-halogenated acetals **3** (R^3 = R^4 = Me) in good yields (entries 8–11).

It was also possible to obtain regioselective α-halogenation of unsymmetrical ketones by electrolysis of enol derivatives such as **4** and **6**. For example, thermodynamically favorable enol acetate **4** can be converted into the corresponding 2-bromo derivative **5** in 83% yield, whereas kinetically favored silyl enol ether **6** afforded the corresponding 6-iodo derivative **7** in 71% yield.



4 **5**

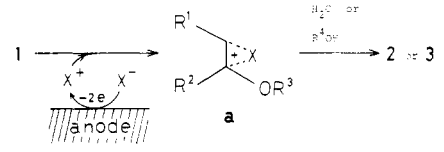


6 **7**

Electrosynthesis of α-Halogenated Acetals. The electrochemical conversion of 6-methoxydihydropyran has been carried out by Kruglikova et al.[2] in MeOH–NH_4Br, giving a 45% yield of 3-bromo-2,6-dimethoxytetrahydropyran. More recently, White and Coleman[7] reported a preparative procedure of acetals of α-chloro aldehydes from alkanols by an electrolytic reaction. In a practical sense, however, synthetic utility of the electrochemical procedures has not been recognized yet. In an effort to ascertain how the double bond of **1d** [R^1, R^3 = $-(CH_2)_3-$] could be halogenated predictably, a series of electrolytic haloacetalizations with a variety of halides were investigated (entries 14–30).

In entries 14–16, each haloacetalization with NH_4X (X = Cl, Br, I) was conducted in 70–96% yields, and the best result (97%) was provided with Et_4NBr as a halogen source (entry 17). In contrast to ammonium halides, alkali bromides decreased the yield of **3** (R^4 = Me, X = Br) slightly (entries 18–21). Electrolysis of **1d** [R^1, R^3 = $-(CH_2)_3-$] in either ethanol, propanol, or allyl alcohol gave the corresponding alkoxylated **3** (R^4 = Et, Pr, CH_2CH=CH_2; X = Br) in good yields (entries 22–24). The haloacetalization can be successfully extended to congeners of enol ethers **1d** (R^1, R^3 = $-CH_2CH_2(OEt)CH-$; R^1, R^3 = $-CH(Me)CH_2CH_2-$; R^1, R^3 = $-CH_2CH_2-$; R^1 = H, R^3 = Et), giving the corresponding acetals of the α-halo aldehydes smoothly (entries 25–30).

Mechanism. The direct anodic oxidation of enol acetates (1.8–2.0 V vs. SCE)[8] and enol ethers (1.3–1.7 V vs. SCE)[9] has been shown to proceed at relatively high potentials. However, the lack of product selectivity which occurred upon straightforward oxidation of the enol ethers caused us to investigate a different method for the electrochemical functionalization of **1** with halides which can be oxidized at ca. 0.4–0.8 V vs. Ag wire.[10] Obviously, under our indirect electrolysis conditions, halonium ions generated by a discharge at the anode would be trapped by the enolic double bond to give α-halogenated ketones **2** and acetals **3** via a bridged halonium intermediate through through a concerted or stepwise nucleophilic attack of water or alcohols.



a

Experimental Section

Melting points are uncorrected, and boiling points are indicated by an air-bath temperature without correction. IR spectra were determined with a JASCO IRA-1 grating spectrometer. ^1H NMR spectra were obtained with Hitachi R-24 (60 MHz) and/or JEOL FX-100 (100 MHz) spectrometers. Chemical shifts (δ) are expressed in parts per million downfield from internal Me_4Si. Current–potential measurements were carried out by using a Kowa Electronics Model PGS-1550 potentiogalvanostat and a FG-102A function generator. Elemental analyses were performed in our laboratory.

Materials. Enol acetates **1a**,[4a,b] trimethylsilyl enol ethers **1b**,[11] and methyl enol ethers **1c**[12] were prepared according to the procedures in the literature. Commercially available dihydropyrans and dihydrofuran **1d** were distilled over sodium before use.

1- and 2-Octen-2-yl Acetates 1a (R^1 = n-C_6H_{13}, R^2 = H and R^1 = n-C_5H_{11}, R^2 = CH_3). A mixture of 2-octanone (1.02 g, 7.92 mmol), isopropenyl acetate (1.9 g, 19 mmol), and p-TsOH (50 mg) was refluxed for 48 h. The mixture was worked up in the usual manner to give 1.32 g (90%) of 1- and 2-octen-2-yl acetates: bp 54–57 °C (11 mm) [lit.[13] bp 108 °C (42.5 mm)].

2-Pentyl-1-cyclohexen-1-yl Acetate (4). A mixture of 2-pentylcyclohexanone[14] (504 mg, 3.0 mmol), Ac_2O (3 mL), and p-TsOH (30 mg) was heated at 110–125 °C for 12 h. The mixture was poured into cold aqueous $NaHCO_3$ and worked up in the usual manner to give 593 mg (94%) of **4**: bp 141–142 °C (28 mm); IR (neat) 1755 (AcO), 1698 (C=C), 1211, 1108 cm^{-1}; ^1H NMR (60 MHz) δ 0.88 (t, 3, J = 6 Hz, CH_3), 1.05–2.22 (m, 16, CH_2), 2.02 (s, 3, $COCH_3$). Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.29; H, 10.74.

1-(Trimethylsiloxy)-6-pentyl-1-cyclohexene (6). To a solution of i-Pr_2NLi (856 mg, 8.0 mmol) in THF (4 mL) and hexane (5 mL) was added a solution of 2-pentylcyclohexanone (672 mg, 4.0 mmol) in THF (2 mL) at −70 °C, and the mixture was stirred

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Table I. Conditions[a] and Results of Electrochemical Halogenation of Enolic Olefins 1

entry	1 R³	1 R¹	1 R²	amt of 1, mmol	halide salt (amt, mmol)	solvent[b]	applied voltage (current density) V (mA/cm²)	F/mol	time, h	product (R⁴, X, % yield[c])
1	Ac	$-(CH_2)_{10}-$		0.15	NH_4Br (0.21)	a	3.0–5.0 (6.7)	2.3	0.4	2 (Br, 95)
2	Ac	$-(CH_2)_{10}-$		0.15	NH_4Cl (0.15)	a	3.5–5.0 (6.7)	2.4	0.5	2 (Cl, 95)[d]
3	Ac	$-(CH_2)_5-$		1.0	NH_4Br (1.48)	a	2.0 (6.7–10.0)	2.4	2.5	2 (Br, 84)[e]
4	Ac	$-(CH_2)_5-$		1.0	NH_4Cl (1.5)	a	3.0 (3.3–10.0)	2.3	5.0	2 (Cl, 83)[f]
5	Ac	$-(CH_2)_4-$		2.0	NH_4Br (2.14)	a	1.5–2.0 (6.7)	2.1	5.5	2 (Br, 55)[g]
6	Ac	$-(CH_2)_4-$		2.1	NH_4Cl (2.1)	a	3.5–4.0 (6.7)	2.1	5.5	2 (Cl, 62)[h]
7	Ac	n-C_5H_{11}	CH_3[i]	1.0	NaBr (1.53)	a	3.5–4.0 (13.3)	2.2	1.5	2 (Br, 95)[j]
8	Me	$-(CH_2)_{10}-$		1.0	NH_4Br (1.2)	b	2.5 (1.1–5.6)	2.3	2.7	3 (Me, Br, 94)
9	Me	$-(CH_2)_{10}-$		1.0	NH_4Cl (1.2)	b	2.0 (2.7–6.7)	2.4	6.3	3 (Me, Cl, 88)
10	Me	$-(CH_2)_5-$		1.0	NH_4Br (1.2)	b	2.0 (3.0–7.3)	2.3	6.5	3 (Me, Br, 85)
11	Me	$-(CH_2)_4-$		1.0	NH_4Br (1.2)	b	2.0 (3.0–6.0)	2.3	6.2	3 (Me, Br, 94)
12	$SiMe_3$	$-(CH_2)_{10}-$		0.12	NH_4I (0.14)	a	2.0 (2.0–2.7)	2.4	1.5	2 (I, 97)
13	$SiMe_3$	n-C_5H_{11}	CH_3[k]	0.16	NH_4I (0.23)	a	1.5 (2.0–2.7)	2.5	1.5	2 (I, 82)[l]
14	$-(CH_2)_3-$		H	1.0	NH_4Br (1.2)	b	2.0 (1.3–6.0)	2.1	8.3	3 (Me, Br, 96)[m]
15	$-(CH_2)_3-$		H	1.0	NH_4Cl (1.2)	b	2.2 (1.0–5.0)	2.1	15.5	3 (Me, Cl, 70)[n]
16	$-(CH_2)_3-$		H	1.0	NH_4I (1.2)	b	1.5 (1.6–5.0)	3.5	7.5	3 (Me, I, 93)
17	$-(CH_2)_3-$		H	1.0	Et_4NBr (1.2)	b	2.0 (0.3–1.8)	2.1	28.0	3 (Me, Br, 97)
18	$-(CH_2)_3-$		H	1.0	LiBr (1.2)	b	2.0 (1.0–4.7)	2.1	14.0	3 (Me, Br, 76)
19	$-(CH_2)_3-$		H	1.0	NaBr (1.2)	b	2.0 (1.3–2.6)	2.1	11.0	3 (Me, Br, 74)
20	$-(CH_2)_3-$		H	1.0	KBr (1.2)	b	2.0 (1.0–2.7)	2.1	14.0	3 (Me, Br, 69)
21	$-(CH_2)_3-$		H	1.0	$MgBr_2$ (1.2)	b	2.0 (0.1–1.7)	2.1	71.0	3 (Me, Br, 69)
22	$-(CH_2)_3-$		H	1.0	NH_4Br (1.2)	c	2.0 (1.3–5.3)	2.1	10.0	3 (Et, Br, 84)[o]
23	$-(CH_2)_3-$		H	1.0	NH_4Br (1.2)	d	2.0 (0.7–1.4)	2.1	17.0	3 (Pr, Br, 95)
24	$-(CH_2)_3-$		H	1.0	NH_4Br (1.2)	e	2.0 (0.3–1.3)	2.1	62.0	3 ($CH_2CH{=}CH_2$, Br, 91)
25	$-CH(OEt)CH_2CH_2-$		H	1.0	NH_4Br (1.2)	c	2.0 (0.4–3.1)	2.1	24.0	3 (Et, Br, 86)[p]
26	$-CH_2CH_2CH(Me)-$		H	1.0	NH_4Br (1.2)	b	2.0 (6.3–21.7)	2.1	2.5	3 (Me, Br, 92)
27	$-CH_2CH_2-$		H	1.0	NH_4Br (1.2)	b	2.0 (5.0–23.3)	2.1	3.0	3 (Me, Br, 72)[q]
28	Et	H	H	1.0	NH_4Br (1.2)	f	2.5 (0.8–1.7)	2.1	22.0	3 (CH_2CH_2OMe, Br, 87)
29	Et	H	H	1.0	NH_4Cl (1.2)	f	2.5 (1.1–1.8)	2.1	23.0	3 (CH_2CH_2OMe, Cl, 92)
30	Et	H	H	1.0	NH_4I (1.2)	f	1.5 (1.6–2.8)	2.1	8.3	3 (CH_2CH_2OMe, I, 60)

[a] Electrolyses were carried out by using Pt (3 cm²) electrodes at 5–25 °C in an undivided cell. [b] Solvent system: a, MeCN (6 mL)-H_2O (2 mL); b, MeOH (6 mL); c, EtOH (6 mL); d, PrOH (6 mL); e, $CH_2{=}CHCH_2OH$; f, $MeOCH_2CH_2OH$ (6 mL). [c] Isolated yields based on added 1. [d] Mp 55–56.5 °C (lit.[15] mp 59–60 °C). [e] Bp 46–49 °C (15 mm) [lit.[4b] bp 83 °C (3.5 mm)]. [f] Bp 41–44 °C (15 mm) [lit.[16] bp 109–111 °C (27 mm)]. [g] Bp 82–85 °C (9 mm) [lit.[4b] bp 74 °C (3.8 mm)]. [h] Bp 81–83 °C (9 mm) [lit.[16] bp 77–80 °C (3 mm)]. [i] Containing ca. 22% of 1-octen-2-yl acetate. [j] Containing ca. 22% of 1-bromo-2-octanone: bp 51–53 °C (11 mm) [lit.[17] bp 77.4–79 °C (3 mm)]. [k] Containing ca. 20% of 2-(trimethylsiloxy)-1-octene. [l] Containing ca. 20% of 1-iodo-2-octanone: bp 61–63 °C (3 mm) [lit.[6] bp 63 °C (1 mm)]. [m] Bp 88–89 °C (13 mm) [lit.[18] bp 88–89 °C (18 mm)]. [n] Bp 64–65 °C (13 mm) [lit.[3d] bp 73–75 °C (14 mm)]. [o] Bp 86–88 °C (13 mm) [lit.[18] bp 94–96 °C (18 mm)]. [p] Bp 80–81 °C (1 mm) [lit.[19] bp 102–104 °C (34 mm)]. [q] Bp 82–83 °C (29 mm).[20]

at −70 °C for 4 h. To this solution was added a mixture of Me_3SiCl (869 mg, 8.0 mmol) and Et_3N (178 mg, 1.76 mmol), and the solution was stirred at −70 °C for 1 h and at −30 °C for 1 h. The mixture was poured into cold aqueous $NaHCO_3$ and worked up in the usual manner. The crude product was distilled to give 865 mg (90%) of **6**: bp 136–139 °C (24 mm); IR (neat) 3020, 1658 (C=C), 1242, 1165, 910, 835 cm^{-1}; ^1H NMR (60 MHz) δ 0.05 (s, 9, CH_3), 0.80 (t, 3, J = 6 Hz, CH_3), 0.98–2.04 (m, 15, CH_2, CH), 4.57 (t, 1, J = 3 Hz, HC=). Anal. Calcd for $C_{14}H_{28}OSi$: C, 69.93; H, 11.74. Found: C, 70.21; H, 11.53.

Electrolysis Apparatus. An undivided cell was equipped with two platinum electrodes (3 cm^2), a gas lead pipe, and a thermometer. Regulated dc power was supplied by a Metronix 543B instrument.

General Procedure for Electrolysis of Enol Acetates 1a. A solution of **1a** [R^1, R^2 = $-(CH_2)_{10}-$; 30 mg, 0.134 mmol] and NH_4Br (19.7 mmol, 0.201 mmol) in MeCN (6 mL) and H_2O (2 mL) was electrolyzed under a constant current of 6.7 mA/cm^2 at 3.0–5.0 V (anode voltage ~0.75 V vs. Ag wire) at 20–25 °C. After 2.3 F/mol of electricity was passed, the mixture was concentrated, and the residue was taken up in benzene–AcOEt (1:1). The usual workup gave 33.3 mg (95%) of **2** [R^1, R^2 = $-(CH_2)_{10}-$, X = Br], mp 50.5–51.5 °C (pentane) (lit.[4b] mp 52.0–53.5 °C).

Details of the reaction conditions and results are given in Table I, and physical and spectra data of the products **2** are well consistent with reported ones.

2-Bromo-2-pentylcyclohexanone (5) was prepared in the same manner as described above in 83% yield by electrolysis of 4 (101 mg, 0.48 mmol) with NH_4Br (70 mg, 0.71 mmol) at 2.1–2.8 V (current density 6.7 mA/cm^2) for 1.9 h (2.9 F/mol): bp 133–139 °C (22 mm); IR (neat) 1710 (C=O), 782, 760 cm^{-1}; ^1H NMR (60 MHz) δ 0.89 (t, 3, J = 6 Hz, CH_3), 1.05–2.50 (m, 15, CH_2), 2.90–3.45 (m, 1, CH_2). Anal. Calcd for $C_{11}H_{19}BrO$: C, 53.45; H, 7.75. Found: C, 53.68; H, 7.51.

General Procedure for Electrolysis of Silyl Enol Ethers 1b. A solution of **1b** [R^1, R^2 = $-(CH_2)_{10}-$; 26.9 mg, 0.12 mmol) and NH_4I (33.3 mg, 0.23 mmol) in MeCN (6 mL) and H_2O (2 mL) was electrolyzed at 2.0 V (anode voltage 0.45 V vs. Ag wire; current density 2.0–2.7 mA/cm^2) for 1.5 h (2.4 F/mol) at 5–10 °C. The usual workup gave 35.8 mg (97%) of **2** [R^1, R^2 = $-(CH_2)_{10}-$, X = I] as a white solid: mp 47.0–48.5 °C (pentane); IR (Nujol) 1709 (C=O), 1240, 1206, 1132, 1118, 1016, 946, 736, 720 cm^{-1}; ^1H NMR (100 MHz) δ 1.31 (br s, 14, CH_2), 1.50–2.06 (m, 3, CH_2), 2.34–2.68 (m, 2, $COCH_2$, CH_2), 3.01 (dd, 1, J = 6.8, 4 Hz, $COCH_2$), 4.70 (dd, 1, J = 15, 4 Hz, CHI). Anal. Calcd for $C_{12}H_{21}IO$: C, 46.77; H, 6.87. Found: C, 46.58; H, 6.86.

6-Iodo-2-pentylcyclohexanone (7) was prepared in the same manner as described above in 71% yield by electrolysis of **6** (120 mg, 0.5 mmol) with NH_4I (109 mg, 0.75 mmol) at 1.5 V (current density 2.1–2.3 mA/cm^2) for 12 h (5.9 F/mol): IR (neat) 1710 (C=O), 1150, 1130, 868, 785 cm^{-1}; ^1H NMR (60 MHz) δ 0.88 (t, 3, J = 6 Hz, CH_3), 1.05–2.50 (m, 15, CH_2, CH), 4.46–4.92 (m, 1, CHI). Anal. Calcd for $C_{11}H_{19}IO$: C, 44.91; H, 6.51. Found: C, 45.19; H, 6.79.

General Procedure for Electrolysis of Methyl Enol Ethers 1c. A solution of **1c** [R^1, R^2 = $-(CH_2)_4-$, 112.3 mg, 1.0 mmol] and NH_4Br (117.6 mg, 1.2 mmol) in MeOH (6 mL) was electrolyzed at 2.0 V (anode voltage 0.6 V vs. Ag wire; current density 3.0–6.0 mA/cm^2) for 6.2 h (2.2 F/mol) at 20–25 °C. The mixture was concentrated and extracted with hexane. The usual workup gave 209 mg (94%) of **3** [R^1, R^2 = $-(CH_2)_4-$, R^4 = Me, X = Br] after chromatography (SiO_2, hexane–ether, 10:1): bp 48–49 °C (12 mm); IR (neat) 1448, 1370, 1308, 1275, 1250, 1166, 1111, 1055, 945, 890, 800 cm^{-1}; ^1H NMR (100 MHz) δ 1.30–2.40 (m, 8, CH_2), 3.20, 3.23 (s, 6, OCH_3), 4.33 (m, 1, CHBr). Anal. Calcd for $C_8H_{15}BrO_2$: C, 43.07; H, 6.78. Found: C, 43.25; H, 6.91.

2-Bromocyclododecanone dimethyl acetal [3; R^1, R^2 = $-(CH_2)_{10}-$, R^4 = Me, X = Br]: mp 76–77 °C; IR (Nujol) 1224, 1130, 1062, 1048, 966, 932, 870, 767, 721 cm^{-1}; ^1H NMR (100 MHz) δ 1.30 (br s, 18, CH_2), 2.66–2.81 (m, 2, CH_2), 3.49 (s, 6, OCH_3), 4.38 (dd, 1, J = 13, 5 Hz, CHBr). Anal. Calcd for $C_{14}H_{27}BrO_2$: C, 54.72; H, 8.86. Found: C, 54.78; H, 8.91.

2-Chlorocyclododecanone dimethyl acetal [3; R^1, R^2 = $-(CH_2)_{10}-$, R^4 = Me, X = Cl]: mp 80.5–82.0 °C; IR (Nujol) 1131, 1062, 1044, 968, 870, 779, 728 cm^{-1}; ^1H NMR (60 MHz) δ 1.35 (br s, 18, CH_2), 1.68–2.17 (m, 2, CH_2), 3.22, 3.32 (s, 6, OCH_3), 4.01 (d, 1, J = 10 Hz, CHCl). Anal. Calcd for $C_{14}H_{27}ClO_2$: C, 63.98; H, 10.36. Found: C, 64.17; H, 10.51.

2-Bromocycloheptanone dimethyl acetal [3; R^1, R^2 = $-(CH_2)_5-$, R^4 = Me, X = Br]: bp 45–46 °C (2 mm); IR (neat) 1454, 1432, 1170, 1102, 1087, 1049, 1014, 997, 904 cm^{-1}; ^1H NMR (100 MHz) δ 1.30–2.56 (m, 10, CH_2), 3.22, 3.49 (s, 6, OCH_3), 4.29–4.44 (m, 1, CHBr). Anal. Calcd for $C_9H_{17}BrO_2$: C, 45.58; H, 7.23. Found: C, 45.75; H, 7.42.

3-Iodo-2-methoxytetrahydropyran [3; R^1, R^3 = $-(CH_2)_3-$, R^4 = Me, X = I]: bp 44–45 °C (2.5 mm); IR (neat) 1200, 1135, 1095, 1075, 1045, 955, 877, 707 cm^{-1}; ^1H NMR (100 MHz) δ 1.36–2.32 (m, 4, CH_2), 3.45 (s, 3, OCH_3), 3.48–3.69 (m, 1, CHI). Anal. Calcd for $C_6H_{11}IO_2$: C, 29.77; H, 4.58. Found: C, 29.67; H, 4.75.

3-Bromo-2-propoxytetrahydropyran [3; R^1, R^3 = $-(CH_2)_3-$, R^4 = Pr, X = Br]: bp 94–96 °C (26 mm); IR (neat) 1207, 1134, 1096, 1076, 1026, 1005, 870, 728 cm^{-1}; ^1H NMR (100 MHz) δ 0.95, 0.97 (t, 3, J = 7 Hz, CH_3), 1.40–2.56 (m, 6, CH_2), 3.31–4.04 (m, 5, CH_2O, CHBr), 4.57 (d, J = 5 Hz, O–CHO), 4.68 (d, J = 3 Hz, O–CHO). Anal. Calcd for $C_8H_{15}BrO_2$: C, 43.07; H, 6.78. Found: C, 43.15; H, 6.77.

3-Bromo-2-(2-propenoxy)tetrahydropyran [3; R^1, R^3 = $-(CH_2)_3-$, R^4 = $CH_2CH{=}CH_2$, X = Br]: bp 109–111 °C (13 mm); IR (neat) 3080, 1650 (C=C), 1203, 1135, 1075, 1030, 955, 875, 735 cm^{-1}; ^1H NMR (100 MHz) δ 1.25–2.13 (m, 3, CH_2), 2.19–2.56 (m, 1, CH_2), 3.44–3.68 (m, 1, CHBr), 3.72–4.15 (m, 2, CH_2O), 4.20, 4.33 (d, t, 2, J = 5, 1 Hz, $C{=}CCH_2O$), 4.64 (d, J = 4 Hz, O–CHO), 4.75 (d, J = 3 Hz, O–CHO), 5.18 (complex d, 1, J = 9 Hz, HC=), 5.32 (complex d, 1, J = 16 Hz, HC=), 5.74–6.15 (m, 1, HC=). Anal. Calcd for $C_8H_{13}BrO_2$: C, 43.46; H, 5.92. Found: C, 43.30; H, 6.09.

3,4-*cis*-3-Bromo-4-methyl-2-methoxytetrahydropyran [3; R^1, R^3 = $-CH_2CH_2CH(Me)-$, R^4 = Me, X = Br]: bp 102–104 °C (34 mm); IR (neat) 2830, 1218, 1130, 1108, 1058, 946, 885, 837, 780, 688 cm^{-1}; ^1H NMR (60 MHz) δ 0.97, 1.04 (d, 3, J = 6 Hz, CH_3), 1.23–2.30 (m, 3, CH_2, CH), 3.32 (s, 3, OCH_3), 3.35–3.76 (m, 2, CH_2O), 3.97 (m, 1, CHBr), 4.55, 4.72 (m, 1, O–CHO). Anal. Calcd for $C_7H_{13}BrO_2$: C, 40.21; H, 6.27. Found: C, 40.29; H, 6.42.

3,4-*trans*-3-Bromo-4-methyl-2-methoxytetrahydropyran [3; R^1, R^3 = $-CH_2CH_2CH(Me)-$, R^4 = Me, X = Br]: bp 104–106 °C (34 mm); IR (neat) 2850, 1380, 1209, 1198, 1158, 1130, 1077, 948, 888, 720 cm^{-1}; ^1H NMR (60 MHz) δ 0.98, 1.13 (d, 3, J = 6 Hz, CH_3), 1.25–2.25 (m, 3, CH_2, CH), 3.16–4.05 (m, 3, CH_2O, CHBr), 3.41 (s, 3, OCH_3), 4.18 (d, 1, J = 7 Hz, O–CHO). Anal. Calcd for $C_7H_{13}BrO_2$: C, 40.21; H, 6.27. Found: C, 40.42; H, 6.38.

Bromoacetaldehyde Ethyl 2-Methoxyethyl Acetal (3; R^1 = H, R^3 = Et, R^4 = $CH_2CH_2OCH_3$, X = Br): bp 52–53 °C (13 mm); IR (neat) 1450, 1373, 1348, 1200, 1125, 1063, 848 cm^{-1}; ^1H NMR (100 MHz) δ 1.21, 1.25 (t, 3, J = 7 Hz, CH_3), 3.79 (s, 3, OCH_3), 3.40 (d, 2, J = 6 Hz, CH_2Br), 3.51–3.83 (m, 6, CH_2O), 4.75 (t, 1, J = 6 Hz, O–CHO). Anal. Calcd for $C_7H_{15}BrO_3$: C, 37.02; H, 6.66. Found: C, 37.19; H, 6.88.

Chloroacetaldehyde Ethyl 2-Methoxyethyl Acetal (3; R^1 = H, R^3 = Et, R^4 = $CH_2CH_2OCH_3$, X = Cl): bp 52–53 °C (11 mm); IR (neat) 1450, 1377, 1344, 1201, 1130, 1070, 1030, 850, 761 cm^{-1}; ^1H NMR (100 MHz) δ 1.24 (t, 3, J = 7 Hz, CH_3), 3.39 (s, 3, OCH_3), 3.54 (d, 2, J = 6 Hz, CH_2Cl), 3.56–3.88 (m, 6, CH_2O), 4.71 (t, 1, J = 6 Hz, O–CHO). Anal. Calcd for $C_7H_{15}ClO_3$: C, 46.03; H, 8.28. Found: C, 46.08; H, 8.53.

Iodoacetaldehyde Ethyl 2-Methoxyethyl Acetal (3; R^1 = H, R^3 = Et, R^4 = $CH_2CH_2OCH_3$, X = I): bp 56–58 °C (12 mm); IR (neat) 1450, 1418, 1375, 1347, 1203, 1127, 1062, 1007, 977, 914 cm^{-1}; ^1H NMR (100 MHz) δ 1.21, 1.23 (t, 3, J = 7 Hz, CH_3), 3.25 (d, 2, J = 6 Hz, CHI), 3.40, 3.41 (s, 3, OCH_3), 3.42–3.79 (m, 6, CH_2O), 4.69 (t, 1, J = 6 Hz, O–CHO). Anal. Calcd for $C_7H_{15}IO_3$: C, 30.67; H, 5.52. Found: C, 30.63; H, 5.70.

Registry No. **1** (R^1,R^2 = $(CH_2)_{10}$; R^3 = Ac), 32399-66-9; **1** (R^1,R^2 = $(CH_2)_5$; R^3 = Ac), 14477-74-8; **1** (R^1,R^2 = $(CH_2)_4$; R^3 = Ac), 1424-22-2; **1** (R^1 = n-C_5H_{11}; R^2 = CH_3; R^3 = Ac), 26735-85-3; **1** (R^1,R^2 = $(CH_2)_{10}$; R^3 = Me), 32400-32-1; **1** (R^1,R^2 = $(CH_2)_5$; R^3 = Me), 50438-50-1; **1** (R^1,R^2 = $(CH_2)_4$; R^3 = Me), 931-57-7; **1** (R^1,R^2 = $(CH_2)_{10}$; R^3 = $SiMe_3$), 51584-36-2; **1** (R^1 = n-C_5H_{11}; R^2 = CH_3; R^3 = $SiMe_3$), 69843-64-7; **1** (R^3,R^1 = $(CH_2)_3$; R^2 = H), 110-87-2; **1** (R^3,R^1 = $CH(OEt)CH_2CH_2$; R^2 = H), 103-75-3; **1** (R^3,R^1 = $CH_2CH_2CH_2$-(Me); R^2 = H), 2270-61-3; **1** (R^3,R^1 = CH_2CH_2; R^2 = H), 1191-99-7; **1** (R^3 = Et; R^2,R^1 = H), 109-92-2; **2** (R^1,R^2 = $(CH_2)_{10}$; X = Br), 31236-94-9; **2** (R^1,R^2 = $(CH_2)_{10}$; X = Cl), 35951-28-1; **2** (R^1,R^2 =

$(CH_2)_5$; X = Br), 766-65-4; **2** (R^1,R^2 = $(CH_2)_5$; X = Cl), 766-66-5; **2** (R^1,R^2 = $(CH_2)_4$; X = Br), 822-85-5; **2** (R^1,R^2 = $(CH_2)_4$; X = Cl), 822-87-7; **2** (R^1 = n-C_5H_{11}; R^2 = CH_3; X = Br), 51134-60-2; **2** (R^1,R^2 = $(CH_2)_{10}$; X = I), 69381-33-5; **2** (R^1 = n-C_5H_{11}; R^2 = CH_3; X = I), 73746-49-3; **3** (R^1,R^2 = $(CH_2)_{10}$; R^3,R^4 = Me; X = Br), 73746-46-0; **3** (R^1,R^2 = $(CH_2)_{10}$; R^3,R^4 = Me; X = Cl), 73746-47-1; **3** (R^1,R^2 = $(CH_2)_5$; R^3,R^4 = Me; X = Br), 73746-48-2; **3** (R^1,R^2 = $(CH_2)_4$; R^3,R^4 = Me; X = Br), 1728-17-2; **3** (R^3,R^1 = $(CH_2)_3$; R^2 = H; R^4 = Me; X = Br), 5324-21-0; **3** (R^3,R^1 = $(CH_2)_3$; R^2 = H; R^4 = Me; X = Cl), 6581-61-9; **3** (R^3,R^1 = $(CH_2)_3$; R^2 = H; R^4 = Me; X = I), 67038-72-6; **3** (R^3,R^1 = $(CH_2)_3$; R^2 = H; R^4 = Et; X = Br), 39150-42-0; **3** (R^3,R^1 = $(CH_2)_3$; R^2 = H; R^4 = Pr; X = Br), 39150-11-3; **3** (R^3,R^1 = $(CH_2)_3$; R^2 = H; R^4 = $CH_2CH{=}CH_2$; X = Br), 73746-50-6; **3** (R^3,R^1 = $CH(OEt)CH_2CH_2$; R^2 = H; R^4 = Et; X = Br), 3149-11-9; **3** (R^3,R^1 = $CH_2CH_2CH(Me)$; R^2 = H; R^4 = Me; X = Br), 73746-51-7; **3** (R^3,R^1 = CH_2CH_2; R^2 = H; R^4 = Me; X = Br), 33691-61-1; **3** (R^3 = Et; R^1,R^2 = H; R^4 = CH_2CH_2OMe; X = Br), 73746-52-8; **3** (R^3 = Et; R^1,R^2 = H; R^4 = CH_2CH_2OMe; X = Cl), 73746-53-9; **3** (R^3 = Et; R^1,R^2 = H; R^4 = CH_2CH_2OMe; X = I), 73746-54-0; **4**, 73746-55-1; **5**, 73746-56-2; **6**, 73746-57-3; **7**, 73746-58-4; 1-octen-2-yl acetate, 26735-84-2; 2-(trimethylsiloxy)-1-octene, 55314-45-9; 1-bromo-2-octanone, 26818-08-6; 1-iodo-2-octanone, 63641-50-9.

Communications

Primary Tritium Isotope Effect on Hydride Transfer from Sodium Borohydride to Cyclopropenium Ion[‡]

Summary: Reduction of a cyclopropenium perchlorate with tritium-labeled sodium borohydride shows a primary kinetic isotope effect, suggesting that hydride transfer is at least partially rate-determining and thus demonstrating that formation of the encounter complex between cation and hydride is reversible.

Sir: The 1,2-disubstituted cyclopropene function occurs in the center of the fatty acid chain of lipids from plants belonging to the order *Malvales*. Cottonseed and kapok oils, which contain two of these unusual fatty acids, are consumed in large amounts by the world's population. Cottonseed flour finds increasing use as a source of protein for human consumption. These cyclopropenoid fatty acids are responsible for certain physiological disorders in farm and laboratory animals. Some of these disorders[1] are delayed sexual development in females, impaired reproduction, altered fat metabolism, pink discoloration in avian egg whites during storage, and liver damage.[2] More importantly, cyclopropenoid fatty acids have been reported to be potent cocarcinogens[3] and carcinogens in rainbow trout.[4]

There has been considerable interest in synthetic cyclopropenoid fatty acids, and in particular sterculic acid, a Δ^9-19-carbon acid. All of the synthetic procedures,[5] except for one,[6] utilize the special stability of the cyclopropenium ion which is reduced by hydride to the corresponding cyclopropene. Reduction appears to occur only at the 3-position; none of the above procedures[5] mention the occurrence or separation of an isomeric 1,3-disubstituted cyclopropene. We have reduced a series of seven 1,2-dialkylcyclopropenium perchlorates with sodium borohydride. The product contains no isomeric cyclopropenes, as indicated by the absence of vinylic cyclopropene proton resonance in the τ 2.99 region.[7]

Breslow and co-workers[7] report three equivalent propyl groups in the NMR spectrum of tripropylcyclopropenyl perchlorate, indicating that the positive charge is evenly distributed around the ring. Also, the propyl groups in the three cations tripropylcyclopropenyl, dipropylcyclopropenyl, and propyldiphenylcyclopropenyl perchlorate are relatively shifted to the same extent. Differences in chemical shift between the α- and β-methylene hydrogens are very similar for the propyl groups in each of these three cations. These data convincingly support the concept that each carbon of the cyclopropenyl cation has a similar charge structure, with essentially one-third of the charge at each ring carbon.

Long-lived carbonium ions have the ability to discriminate between nucleophiles. For example, triphenylmethyl cation, $pK_{R+} = -6.63$, has a competition factor, k_y/k_0, of 2.8×10^5 for azide ion in 50% aqueous acetone.[8] Although the competition factor has not been determined for the more stable dialkylcyclopropenium ions, $pK_{R+} = 2.7$,[9] one would expect it to be considerably more selective. As already mentioned, these cyclopropenium ions show a selectivity for site of reaction, allowing the less hindered positions to react more readily, rather than a combination dependent only upon their diffusion together. Ritchie[10] has documented the regularity of reactivity of anions with organic cations.

We are surprised to observe that cyclopropenium ions not only show a high degree of selectivity in their combination with hydride, but the reaction also exhibits a primary kinetic isotope effect. Sterculic acid was prepared by dropping the corresponding cyclopropenium perchlorate[7] into Me_2SO containing tritium-labeled sodium borohydride (26.7 mCi/mmol) at 5 °C. The product incorporated 6.8 times less label than was present in the sodium borohydride, or $k_H/k_T = 6.8$. Although this effect is smaller than the theoretical maximum for a primary kinetic isotope effect, it demonstrates that the reaction is not solely diffusion controlled. The cation–hydride approach must be somewhat reversible with hydride transfer at least partially rate determining.

Registry No. Sodium borohydride, 16940-66-2; cyclopropenium ion, 20829-57-6.

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Norman E. Pawlowski,* Russell O. Sinnhuber
Department of Food Science and Technology
Oregon State University
Corvallis, Oregon 97331
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