LiBr in ether was prepared by reaction of ethylene dibromide with lithium in ether. Addition of 0.44 g of 4 to a mixture of 0.76 g of triflic anhydride and 5.0 mL of LiBr solution at −78 °C gave 0.43 g (95%) of α-bromoacetophenone as determined by GC vs. *n*-dodecane as an internal standard. In a second run, the yield was 92%.

**Reaction of *cis*-2-Butene with Lithium Bromide–Triflic Anhydride.** A solution of 0.78 g of triflic anhydride in 3 mL of ether was cooled to −78 °C and 4 mL of 1.167 M LiBr in ether was added. *cis*-2-Butene (0.5 g) was bubbled into the mixture, which was then slowly warmed to room temperature. A standard aqueous workup and distillation gave 0.36 g of *dl*-2,3-dibromobutane which was identified by NMR spectral comparison with an anthentic sample.

**Acknowledgment** is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

**Registry No.** Bromophenylmagnesium, 100-58-3; iodophenylmagnesium, 16002-63-4; bromo-*p*-tolylmagnesium, 4294-57-9; bromo(*p*-methoxyphenyl)magnesium, 13139-86-1; bromo(*p*-chlorophenyl)magnesium, 873-77-8; bromo(α,α,α-trifluoro-*m*-tolyl)magnesium, 402-26-6; bromo-1-naphthylmagnesium, 703-55-9; bromo(phenylethynyl)magnesium, 6738-06-3; bromooctylmagnesium, 17049-49-9; bromocyclohexylmagnesium, 931-50-0; chlorooctylmagnesium, 38841-98-4; butylchloromagnesium, 693-04-9; benzylchloromagnesium, 6921-34-2; allylchloromagnesium, 2622-05-1; chlorocyclohexylmagnesium, 931-51-1; bromobenzene, 108-86-1; iodobenzene, 591-50-4; *p*-bromotoluene, 106-38-7; *p*-bromoanisole, 104-92-7; 1-bromo-4-chlorobenzene, 106-39-8; *m*-bromo-α,α,α-trifluorotoluene, 401-78-5; 1-bromonaphthalene, 90-11-9; (bromoethynyl)benzene, 932-87-6; 1-bromooctane, 111-83-1; bromocyclohexane, 108-85-0; 1-chlorooctane, 111-85-3; α-chlorotoluene, 100-44-7; chlorocyclohexane, 542-18-7; phenyl trifluoromethyl sulfone, 426-58-4; *p*-tolyl trifluoromethyl sulfone, 383-10-8; *p*-[(trifluoromethyl)sulfonyl]anisole, 15183-74-1; phenylethynyl trifluoromethyl sulfone, 52843-77-3; 1-octyl trifluoromethyl sulfone, 73587-47-0; 1-butyl trifluoromethyl sulfone, 52208-94-3; benzyl trifluoromethyl sulfone, 4855-02-1; allyl trifluoromethyl sulfone, 73587-48-1; cyclohexyl trifluoromethyl sulfone, 73587-49-2; triflic anhydride, 358-23-6.

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# Highly Stereoselective Hydrogenation of 3-Oxo-4-ene and -1,4-diene Steroids to 5β Compounds with Palladium Catalyst[1]

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The catalytic hydrogenation of 3-oxo-4-ene and -1,4-diene steroids is a convenient and widely employed route to 5β steroids.[2] Usually palladium catalysts are preferred for this purpose. The stereoselectivity to 5β, however, greatly depends on the reaction medium[2] and also on the functional groups in steroids.[2,3] The following media have been known to be effective for the favorable formation of 5β compounds: methanol or ethanol with potassium hydroxide,[2] pyridine,[4] and acetic acid with hydrobromic acid.[5] Among these media, pyridine appears to be the most useful in view of high stereoselectivity and lack of side reactions as well as its excellent property as a solvent for steroids.[6] With some steroids, however, stereoselectivity to 5β is not satisfactory even in pyridine. For example, in the hydrogenation of 11-oxoprogesterone in pyridine, Suvorov and Yaroslavtseva obtained the corresponding 5β ketone only in 17.4% yield, compared to 77.9% yield with progesterone.[4] Combe, Henbest, and Jackson also studied the effect of some nitrogen bases, but a solvent which is more stereoselective than pyridine has not been reported.[7]

In this study, various nitrogen bases have been surveyed in the hydrogenation of 3-oxo-4-ene and -1,4-diene steroids in order to find a more stereoselective solvent than pyridine and also to know the effects of the 1,2-unsaturation and the functional groups at C-11 and C-17 upon the stereochemistry of hydrogenation in basic media. Some 19-norsteroids have also been hydrogenated to see the effect of the angular methyl group at C-10. All hydrogenations were performed at room temperature and atmospheric pressure, using palladium black as the catalyst.

Table I shows the yields of saturated 5β ketones obtained with various nitrogen bases as solvents. It is seen that the most stereoselective is 4-methoxypyridine with which yields as high as 95–99.9% were obtained for most of the steroids hydrogenated. The effectiveness of 4-methoxypyridine is especially remarkable with the compounds **1e**, **1f**, and **2b**, where the yields of 5β ketones were rather low in the other solvents. The use of 4-methoxypyridine is also advantageous in that it is an excellent solvent for steroids and hydrogenation can be conducted in high concentration without loss in high stereoselectivity, as shown in preparative runs described in the Experimental Section.

4-Methoxypyridine ($pK_a$ = 6.6) is a weaker base than 2,4,6-trimethylpyridine ($pK_a$ = 7.4), 1-methylimidazole ($pK_a$ = 7.06), and piperidine ($pK_a$ = 11.1), although it is a stronger base than pyridine ($pK_a$ = 5.2) and 4-methylpyridine ($pK_a$ = 6.0). It is also noted that stereoselectivity is lower with triethylamine than with piperidine. These facts suggest that the nucleophilicity of nitrogen bases, rather than their $pK_a$'s, is an important factor for the favorable formation of 5β compounds. The above results prompted us further to examine a substituted pyridine which is more basic than 4-methoxypyridine. Thus some steroids have been hydrogenated in the presence of 4-(dimethylamino)pyridine ($pK_a$ = 9.7) which has been found to be a powerful catalyst for the acylation of hydroxyl groups.[8] The effect of 4-(dimethylamino)pyridine, however, is not so straightforward, as shown in Table II. Although stereoselectivity increased with **1e** and **1f** in pyridine and with **2b** in 4-methoxypyridine, it decreased in the cases of **1e** and **1f** in 4-methoxypyridine. Thus the effect of 4-(dimethylamino)pyridine is rather complex and further detailed studies are needed.

The effects of various substituents in steroids on the stereochemistry of hydrogenation in basic media appear

(1) (a) Partly presented at the ACS/CSJ Chemical Congress: "Abstracts of Papers Part II", Honolulu, HI, Apr, 1979, ORGN 432. (b) Stereochemistry of the Palladium Catalyzed Hydrogenation of 3-Oxo-4-ene Steroids. 4. For paper 3, see ref 3.

(2) For reviews, see (a) H. J. E. Loewenthal, *Tetrahedron*, **6**, 269 (1959). (b) R. L. Augustine, "Organic Reactions in Steroid Chemistry," Vol. 1, J. Fried and J. A. Edwards, Eds., Van Nostrand Reinhold Company, New York, 1972, p 111. (c) R. L. Augustine, *Adv. Catal.*, **25**, 56 (1976).

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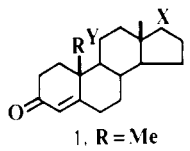
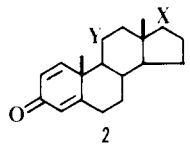
Table I. Yields of 5β Compounds (%) in Hydrogenation of 3-Oxo-4-ene and -1,4-diene Steroids in Nitrogen Bases[a]



1, R = Me
3, R = H



2

| | | | solvent | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | pyridine | | | | | | | |
| compd | X | Y | H | 4-Me | 4-MeO | 2,6-$Me_2$ | 2,4,6-$Me_3$ | 1-methyl-imidazole | piper-idine | triethyl-amine |
| 1a | β-$C_8H_{17}$ | H | 98.7 | 99.2 | 99.5 | 96.8 | 98.2 | 98.3 | 99.4 | 93.9 |
| 1b | =O | H | 91.2 | 92.1 | 98.4 | 82.1 | 78.5 | 92.3 | 84.9 | 63.4 |
| 1c | β-OH | H | 90.6 | 95.8 | 97.1 | 86.4 | 88.6 | 93.6 | 93.8 | 76.8 |
| 1d | β-OAc | H | 98.2 | 96.8 | 98.9 | 93.6 | 93.6 | 96.2 | 96.0 | 87.5 |
| 1e | β-Ac | H | 82.8 | 83.4 | 98.1 | 85.7 | 70.0 | 85.2 | 82.4 | 62.1 |
| 1f | =O | =O | 26.8 | 43.6 | 79.1 | 57.7 | 40.0 | 45.5 | 21.0 | |
| 1g | H | H | 97.2 | 97.5 | 98.9 | 94.9 | 88.7 | 96.1 | | 90.3 |
| 1h | α-OH | H | 96.3 | | 99.9 | | | | | |
| 2b | =O | H | 88.0 | 88.8 | 97.3 | 77.9 | 80.5 | 90.3 | 89.2 | 63.2 |
| 2c | β-OH | H | 87.1 | 91.3 | 95.3 | 90.4 | 86.3 | | 97.0 | 90.0 |
| 2d | β-OAc | H | 95.4 | 94.9 | 98.4 | 95.1 | 91.6 | 97.7 | 98.6 | 88.1 |
| 3b | =O | H | 88.5 | 86.5 | 93.8 | 58.0 | 58.1 | 60.4 | | 55.9 |
| 3c | β-OH | H | 83.2 | 82.8 | 91.6 | 61.3 | 62.8 | 71.1 | 93.6 | 72.0 |
| 3d | β-OAc | H | 92.6 | 89.6 | 96.2 | 52.8 | 72.7 | 91.3 | 92.3 | 56.7 |

[a] The compound (5–50 mg) was hydrogenated in 0.2–1.0 mL of the solvent with 0.5–5 mg of palladium catalyst. The products were analyzed by GC, usually after complete hydrogenation.

Table II. Effect of the Addition of 4-(Dimethylamino)pyridine[a]

| compd[b] | medium | yield of 3-oxo-5β-steroid, %[c] |
|---|---|---|
| 1e | Py | 82.8 |
| | Py/4-$Me_2$N-Py | 85.3 |
| | 4-MeO-Py | 98.1 |
| | 4-MeO-Py/4-$Me_2$N-Py | 95.6 |
| 1f | Py | 26.8 |
| | Py/4-$Me_2$N-Py | 45.9 |
| | 4-MeO-Py | 79.1 |
| | 4-MeO-Py/4-$Me_2$N-Py | 77.4 |
| 2b | 4-MeO-Py | 97.3 |
| | 4-MeO-Py/4-$Me_2$N-Py | 98.3 |

[a] The compound (50–500 mg) was hydrogenated over 10–50 mg of palladium catalyst in 1.2–3.7 mL of pyridine or 4-methoxypyridine with addition of 0.30–0.76 g of 4-(dimethylamino)pyridine. [b] For the compound structure, see Table I. [c] GC analysis.

Table III. Hydrogenation of 19-Nor-3-oxo-4-ene Steroids in Tetrahydrofuran and Hydrobromic Acid[a]

| compd[b] | yield of 3-oxo-5β-steroid, %[c] |
|---|---|
| 3b | 97.9[d] |
| 3c | 98.6 |
| 3d | 99.8[e] |

[a] The compound (30–500 mg) was hydrogenated with 5–50 mg of palladium catalyst in 1–2 mL of tetrahydrofuran containing 0.002–0.02 mL of concentrated hydrobromic acid. [b] For the compound structure, see Table I. [c] GC analysis. [d] 97.7% yield in acetic acid-hydrobromic acid. [e] 99.2% yield in acetic acid-hydrobromic acid.

very similar to those observed in neutral or acidic conditions.[3] Functional groups $\Delta^1$, 17β-hydroxy, 17-oxo, 17β-acetyl, and 11,17-dioxo decreased the stereoselectivity to 5β. The degree of the decreasing effect is roughly in the order indicated above.

The stereoselectivity to 5β also decreased with 19-nor-steroids (compare **3b–d** with **1b–d**, respectively, in Table I). This is in contrast to the results in acidic medium where high yields of 5β compounds were obtained with 19-norsteroids.[5] Thus, the results with 19-norsteroids are in line with those reported with $\Delta^{1,9}$-2-octalone where high yields of *cis*-2-decalone were obtained in acidic media rather than in basic media.[2c] Recently, we have found that a combination of tetrahydrofuran and hydrobromic acid is as effective as or even more effective than acetic acid and hydrobromic acid which have been recommended previously.[5] The use of tetrahydrofuran with hydrobromic acid is particularly useful, e.g., for 19-nortestosterone where acetylation of the 17β-hydroxyl group may occur during hydrogenation in acetic acid and hydrobromic acid. The use of tetrahydrofuran is also advantageous in view of its excellent property as a solvent for most steroids as well as in the easiness of working up the reaction mixture. Typical examples are shown in Table III and also in the Experimental Section. Hydrogenation of $\Delta^{1,9}$-2-octalone in tetrahydrofuran and hydrobromic acid gave a 99.5% yield of *cis*-2-decalone.[9]

A remarkable effect of hydrogen halide in tetrahydrofuran has previously been described in the stereoselective hydrogenation of 3-oxo steroids to axial alcohols with rhodium catalyst.[10] Augustine has also noted that use of nonhydroxylic solvents is effective for formation of *cis*-2-decalone in the hydrogenation of $\Delta^{1,9}$-2-octalone in presence of hydrogen chloride.[11] Note further that the amounts of hydrogen halides required for obtaining an optimal selectivity are much smaller in tetrahydrofuran than in a hydroxylic solvent.[10,12]

## Experimental Section

**General.** All hydrogenations were carried out at room temperature and atmospheric pressure in an Erlenmeyer flask with a magnetic stirrer or in a small glass apparatus driven vibrationally.

(9) Unpublished results.
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(11) R. L. Augustine, D. C. Migliorini, R. E. Foscante, C. S. Sodano, and M. J. Sisbarro, *J. Org. Chem.*, **34**, 1075 (1969).
(12) It has also been observed that the amount of hydrobromic acid given in Table III can be reduced to one-tenth to effect the same high stereoselectivity in hydrogenation of 19-nortestosterone.

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 5$\beta$-androstan-17$\beta$-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 5$\beta$-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-5$\beta$-androstane-3,17-dione (GC analysis). Recrystallization of the product from acetone gave 367 mg (73% yield) of the pure compound (no 5$\alpha$ 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, $CHCl_3$).

**Acknowledgment.** This work was partially supported by a Grant-in-Aid for Scientific Research (No. 284022) from the Ministry of Education of Japan.

**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; 5$\beta$-cholestan-3-one, 601-53-6; 5$\beta$-androstane-3,17-dione, 1229-12-5; 5$\beta$,17$\beta$-17-hydroxyandrostan-3-one, 571-22-2; 5$\beta$,17$\beta$-17-acetoxyandrostan-3-one, 1164-92-7; 5$\beta$-pregnane-3,20-dione, 128-23-4; 5$\beta$-androstane-3,11,17-trione, 1429-06-7; 5$\beta$-androstan-3-one, 18069-68-6; 5$\beta$-androstane-3,17-dione, 1229-12-5; 5$\beta$,11$\beta$-11-hydroxyandrostan-3-one, 571-22-2; 5$\beta$,11$\beta$-11-acetoxyandrostan-3-one, 1164-92-7; 5$\beta$-estrane-3,17-dione, 5696-51-5; 5$\beta$,11$\beta$-11-hydroxyestran-3-one, 19468-31-6; 5$\beta$,11$\beta$-11-acetoxyestran-3-one, 2302-77-4; Pd, 7440-05-3.

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# Highly Convenient Electrolysis Procedure for the Preparation of $\alpha$-Halogenated Ketones and Acetals from Enol Acetates, Enol Ethers, and Silyl Enol Ethers

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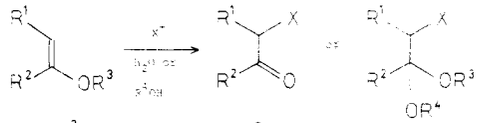
Although numerous methods are available for halogenation of the $\alpha$-position of alkanones using unstable and troublesome halogenating reagents,[1] none are satisfactory for the preparation of $\alpha$-halogenated carbonyl compounds **2** and their acetals **3** from enol ethers **1** under mild 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 $\alpha$-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 $\alpha$-halogenated products whose halogen atom can be chosen by using an appropriate halide salt, either $NH_4Cl$, $NH_4Br$, or $NH_4I$.

**Preparation of $\alpha$-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.

(1) H. O. House, "Modern Synthetic Reactions", 2nd ed., W. A. Benjamin, Menlo Park, CA, 1972, p 459.
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