

(421 mg, 58.7%), as crystals: mp 163–164 °C; IR (KBr) 3350, 1790, 1760, 1500, 1300 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.05 (3 H, s), 0.07 (3 H, s), 0.86 (9 H, s), 1.14 (3 H, d, $J = 6.6$ Hz), 3.64 (1 H, dd, $J = 2.0, 2.9$ Hz), 3.80 (3 H, s), 3.93 (3 H, s), 4.00–4.35 (1 H, m), 5.18 (1 H, d, $J = 2.0$ Hz), 6.74 (1 H, br s), 6.92–7.48 (3 H, m).

Anal. Calcd for $\text{C}_{19}\text{H}_{31}\text{O}_6\text{NSSi}$: C, 53.12; H, 7.27; N, 3.26; S, 7.46. Found: C, 53.10; H, 7.33; N, 3.54; S, 7.49.

3(S)-[1(R)-[(*tert*-Butyldimethylsilyl)oxy]ethyl]-4(S)-[(phenylthio)ethynyl]azetidin-2-one (14). To a stirred solution of (phenylthio)acetylene [268 mg, 2 mmol, 0.59 mL of $\text{PhSC}\equiv\text{CH}$ solution in *n*-hexane (3.4 mol/L)] in dry THF (2 mL) was dropwise added 0.67 mL (2 mmol) of ethylmagnesium bromide solution (3 mol/L solution in ether) in dry THF (2 mL) at -40 °C under nitrogen. The mixture was stirred at room temperature for 30 min. The mixture was again cooled at -40 °C, and azetidinone 13 (215 mg, 0.5 mmol) in dry THF (2 mL) was dropwise added. After stirring at room temperature for 1 h, water (10 mL) and 5% HCl solution (1 mL) were added at 0 – 5 °C and extracted with EtOAc (50 mL, twice). The extracts were washed (water, saturated NaHCO_3 solution, water, saturated NaCl solution), dried (MgSO_4), and evaporated to give an oily residue. Purification of this oil by preparative layer chromatography gave 14 (145 mg, 80.3%) as crystals: mp 78–79 °C; IR (KBr) 3100, 2180, 1770 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.08 (6 H, s), 0.88 (9 H, s), 1.25 (3 H, d, $J = 6.0$ Hz), 3.36 (1 H, dd, $J = 2.6, 3.1$ Hz), 4.10–4.40 (1 H, m), 4.58 (1 H, d, $J = 2.6$ Hz), 6.18 (1 H, br s), 7.12–7.50 (5 H, m).

Anal. Calcd for $\text{C}_{19}\text{H}_{27}\text{NO}_2\text{SSi}$: C, 63.07; H, 7.42; N, 3.87; S, 8.85. Found: C, 63.15; H, 7.58; N, 3.94; S, 9.12.

3(S)-[1(R)-[(*tert*-Butyldimethylsilyl)oxy]ethyl]-4(R)-[[[2-[(*p*-nitrobenzyloxy)carbonyl]amino]ethyl]thio]carbonyl]methyl]azetidin-2-one (15). To a stirred solution of 4-acetylenic azetidinone 14 (100 mg, 0.28 mmol) in methylene chloride (2 mL) was added trifluoroacetic acid (158 mg, 1.38 mmol) at room temperature. After 30 min of stirring, the mixture was evaporated under reduced pressure to give an oily residue. This oil was dissolved in AcOEt (20 mL) to which was added water (5 mL), and the solution was stirred at room temperature for 5 min. The organic layer was separated, washed

(saturated NaHCO_3 solution, saturated NaCl solution), dried (MgSO_4), and evaporated to afford a solid substance. Purification of this crude compound by preparative layer chromatography gave 15 (67.2 mg, 64.0%) as crystals: mp 95–98 °C; IR (Nujol) 3175, 3110, 1765, 1725, 1698 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.08 (6 H, s), 0.87 (9 H, s), 1.19 (3 H, d, $J = 6.0$ Hz), 2.25 (3 H, m), 3.70–4.33 (2 H, m), 6.20 (1 H, br s), 7.35 (5 H, s); $[\alpha]_D^{24} +41.8^\circ$ (c 1.6, CHCl_3).

Anal. Calcd for $\text{C}_{19}\text{H}_{29}\text{NO}_5\text{SSi}$: C, 60.09; H, 7.64; N, 3.69; S, 8.43. Found: C, 60.04; H, 7.73; N, 3.71; S, 8.56.

3(S)-[1(R)-[(*tert*-Butyldimethylsilyl)oxy]ethyl]-4(R)-[[[2-[(*p*-nitrobenzyloxy)carbonyl]amino]ethyl]thio]carbonyl]methyl]azetidin-2-one (16). To a stirred solution of thiol ester 15 (379 mg, 1.0 mmol) in methylene chloride (5 mL) were added 2-[[[*p*-nitrobenzyloxy]carbonyl]amino]ethanethiol (512 mg, 2.0 mmol) and triethylamine (101 mg, 1.0 mmol) at room temperature, and the solution was kept at room temperature overnight. The mixture was evaporated under reduced pressure to give an oily residue, which was purified by preparative layer chromatography to afford 16 (515 mg, 98%) as an oil: IR (Nujol) 3250, 1760, 1740, 1660 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.06 (6 H, s), 0.86 (9 H, s), 1.16 (2 H, d, $J = 6.0$ Hz), 2.70–3.70 (7 H, m), 3.90–4.25 (2 H, m), 5.20 (2 H, s), 5.55 (1 H, m), 6.65 (1 H, br s), 7.51 (2 H, d), 8.22 (2 H, d).

Anal. Calcd for $\text{C}_{23}\text{H}_{35}\text{N}_3\text{O}_7\text{SSi}$: C, 52.54; H, 6.71; N, 7.99. Found: C, 52.16; H, 6.92; N, 8.20.

Acknowledgment. We thank Mr. N. Ishida for skillful technical assistance. We are also grateful to Dr. T. Kobayashi for helpful discussions.

Registry No. 1, 59995-64-1; 4, 34800-34-5; 5, 98114-06-8; 7, 99765-22-7; 8, 99765-23-8; 9, 99827-42-6; 10, 99765-24-9; 11, 99827-43-7; 12, 99765-25-0; 13, 99765-26-1; 14, 90629-36-0; 15, 90628-93-6; 16, 90628-97-0; 19, 99765-27-2; CH_3CHO , 75-07-0; $\text{PhOCH}_2\text{CO}_2\text{H}$, 122-59-8; $\text{PhSC}\equiv\text{CH}$, 6228-98-4; *p*- $\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{OC(O)NH(CH}_2)_2\text{SH}$, 65750-59-6; *p*-benzoquinone, 106-51-4.

Notes

Iodosobenzene Diacetate, an Efficient Reagent for the Oxidative Decarboxylation of Carboxylic Acids

J. I. Concepción, C. G. Francisco, R. Freire, R. Hernández, J. A. Salazar, and E. Suárez*

Instituto de Productos Naturales Orgánicos del C.S.I.C.,
Carretera La Esperanza 2, La Laguna,
Tenerife, Canary Islands, Spain

Received August 8, 1985

The oxidative decarboxylation of organic acids with concomitant replacement by a halogen (halodecarboxylation), through a radical intermediate, in the Hunsdiecker¹ or modified Hunsdiecker² reaction comprises an extremely useful and selective procedure for the syntheses

of halogenated organic substances. The oxidative elimination of the intermediate radicals to give olefins is an interesting variation of the decarboxylation reaction of acids, which is usually accomplished with lead tetraacetate (LTA)/ $\text{Cu}(\text{OAc})_2$.^{2a}

Particularly, iododecarboxylation of carboxylic acids to alkyl iodides has been effected by reaction of the free acid with *tert*-butyl hypoiodite^{2a,b} or with combinations of $\text{LTA}^{2a,b}$ or mercuric oxide^{2c} with iodine and also treating the silver carboxylate with iodine.^{2d} It is known that several other oxidizing metal ions such as Ce^{IV} , Mn^{III} , Co^{III} , and Ti^{III} can also effect the decarboxylation of acids.^{2e,3}

We have recently reported⁴ the functionalization of nonactivated carbon atoms, through intramolecular hydrogen abstraction by alkoxy radicals generated by photolysis of the corresponding alcohols in the presence of iodosobenzene diacetate (IBDA)⁵ and iodine. Inasmuch

(1) Johnson, R. G.; Ingham, R. K. *Chem. Rev.* **1956**, *56*, 219. Wilson, C. V. *Org. React. (N.Y.)* **1957**, *9*, 332.

(2) (a) Sheldon, R. A.; Kochi, J. K. *Org. React. (N.Y.)* **1972**, *19*, 279. (b) Barton, D. H. R.; Faro, H. P.; Serebryakov, E. P.; Woolsey, N. F. *J. Chem. Soc.* **1965**, 2438. (c) Cristol, J. S.; Firth, W. C. *J. Org. Chem.* **1961**, *26*, 280. (d) Oldham, J. W. H.; Ubbelohde, A. R. *J. Chem. Soc.* **1941**, 368. (e) McKillop, A.; Bromley, D.; Taylor, E. C. *J. Org. Chem.* **1969**, *34*, 1172. (f) Kochi, J. K. *J. Am. Chem. Soc.* **1965**, *87*, 2500. (g) Patrick, T. B.; Johri, K. K.; White, D. H. *J. Org. Chem.* **1983**, *48*, 4158.

(3) Laude, S. S.; Kochi, J. K. *J. Am. Chem. Soc.* **1968**, *90*, 5196. Sheldon, R. A.; Kochi, J. K. *Ibid.* **1968**, *90*, 6688. Anderson, J. M.; Kochi, J. K. *Ibid.* **1970**, *92*, 1651, 2450; *J. Org. Chem.* **1970**, *35*, 986. Kochi, J. K.; Bethea, T. W. *Ibid.* **1968**, *33*, 75.

(4) Concepción, J. I.; Francisco, C. G.; Hernández, R.; Salazar, J. A.; Suárez, E. *Tetrahedron Lett.* **1984**, *25*, 1953.

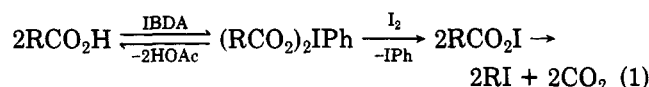
(5) For recent reviews on polivalent iodine compounds, see: Varvoglis, A. *Chem. Soc. Rev.* **1981**, *10*, 377. Banks, D. F. *Chem. Rev.* **1966**, *66*, 243.

Table I. Decarboxylation of Acids with Iodosobenzene Diacetate

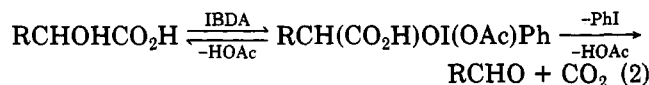
entry	acid	reagent ^a	solvent	time, h	products (yield, %)
1	1	A(1.1/1)	C ₆ H ₁₂	1	2 (80)
2	1	A(1.1/1)	CCl ₄	1.5	2 (94)
3	3	A(1.1/1)	C ₆ H ₁₂	1	4 (89)
4	5	A(1.1/1)	C ₆ H ₁₂	1.5	6 (23), 7 (55)
5	5	A(1.1/1)	CCl ₄	1	6 (24), 7 (56)
6	8	A(1.1/1)	C ₆ H ₁₂	1	9 (78), 10 (14)
7	8	A(1.1/1)	CCl ₄	0.25	9 (76), 10 (5)
8	11	A(1.1/1)	C ₆ H ₁₂	1.5	12 (94)
9	13	A(2/1)	C ₆ H ₁₂	1	14 (60), 15 (6), 16 (4)
10	1	B(1.1/1.1)	C ₆ H ₆	2	17 (15), 1 (65)
11	1	B(5/5)	C ₆ H ₆	8	17 (40), 1 (30)
12	1	C(2/0.2)	C ₆ H ₆	8	19 (40), 18 (9)
13	1	C(5/0.2)	C ₆ H ₆	8	19 (80), 18 (19)
14	5	C(5/0.2)	C ₆ H ₆	8	20 (79)

^a A, moles of IBDA/moles of iodine per mole of acid; B, moles of IBDA/moles of LiCl per mole of acid. C, moles of IBDA/moles of Cu(OAc)₂ per mole of acid.

as an alkyl hypoiodite is expected to be involved in this reaction, we decided to investigate if this reagent is able to react with carboxylic acids to generate acyl hypoiodites which eventually iododecarboxylate (eq 1).



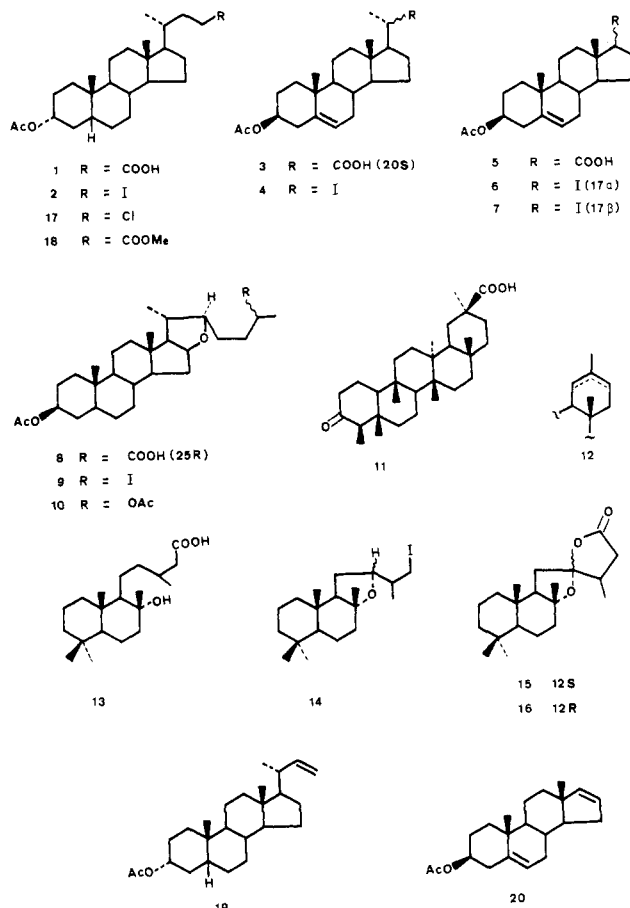
In fact, it has also been reported that α -hydroxy carboxylic acids undergo oxidative decarboxylation with IBDA to give aldehydes, an iodine(III) ester being proposed as intermediate⁶ (eq 2).



We present here the results of this study which show that the system IBDA/iodine is a good alternative to the methods outlined above for the decarboxylation of carboxylic acids. This reagent avoids some of the difficulties associated with the use of heavy metal derivatives, especially in large-scale reactions, such as toxicity, troublesome workup procedures, and the need to use an excess of oxidizing agent.

Examination of the results summarized in Table I indicates that primary and secondary aliphatic acids undergo successful iododecarboxylation in good yields (entries 1–7, 9). The tertiary acid 11 gave under these conditions a mixture of the tertiary olefins 12 (entry 8). In all cases 1.1 mmol of IBDA and 1 mmol of iodine per mmol of acid were used except for 13 (entry 9), and the reactions were performed in cyclohexane or carbon tetrachloride at reflux temperature under irradiation with two 100-W tungsten-filament lamps. Carbon tetrachloride can be used advantageously as it is a better solvent for carboxylic acids, but mixtures with cyclohexane or cyclohexane alone can be used without significant decrease of yield. Hence, although in the case of acid 1 a better yield of alkyl iodide is obtained with carbon tetrachloride as solvent instead of cyclohexane (entries 1 and 2), similar yields were found for compounds 5 (entries 4 and 5) and 8 (entries 6 and 7).

The reaction of labdanolic acid (13) (entry 9) deserves further comments; intramolecular abstraction of hydrogen by the alkoxy radical⁴ with subsequent decarboxylation of the carboxy radical leads to the C-12 epimeric iodo derivatives 14. The unexpected formation of isomeric lac-



tones 15 and 16 can be explained by a double hydrogen abstraction originated by the carboxy and alkoxy radicals. However, as carboxy radicals decarboxylate so rapidly that the hydrogen abstraction is practically unobserved,⁷ an alternative mechanism based on the formation of a C-12 radical through hydrogen abstraction promoted by the alkoxy radical and subsequent attack of the acid should be considered.

Attempts to produce chlorodecarboxylations^{2f} using a mixture of IBDA with LiCl as reagent were partially successful (entries 10 and 11), as only 15% of chloro compound 17 was obtained in the decarboxylation of acid 1 with 1 mol of the reagent, while with a large excess of reagent (fivefold) a modest 40% of 17 was achieved.

The decarboxylation of acids with oxidative elimination of the alkyl radical intermediates to form alkenes^{2a} can be conveniently accomplished using IBDA with catalytic amounts of cupric acetate. Thus acid 1 produces the olefin 19 in good yield with a fivefold excess of reagent (entry 13). The formation of alkene 20 (entry 14) from acid 5 is another example of this reaction.

Experimental Section

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. Optical rotations were measured for solutions in CHCl₃. ¹H NMR spectra were recorded with a Bruker WP-200 SY (200 MHz) instrument for solutions in CDCl₃ with tetramethylsilane as internal reference. Infrared spectra were measured on a Perkin-Elmer 257 instrument in CHCl₃. Low- and high-resolution mass spectra were determined with a VG Micromass ZAB-2F spectrometer. Thin-layer chromatography (TLC) was performed on Merck silica gel 60 and column chromatography on Merck silica gel (0.063–0.2 mm). The spray reagent for TLC was vanillin (1 g) in H₂SO₄–EtOH (4:1; 200 mL). Iodosobenzene

(6) Griegee, R.; Bencker, H. *Ann. Chem.* **1939**, *541*, 218. Vaidyanathan, K.; Venkatasubramanian, N. *Indian J. Chem.* **1973**, *11*, 1146.

(7) Barton, D. H. R.; Beckwith, A. L. J.; Goosen, A. *J. Chem. Soc.* **1965**, 181.

dietate (98%) was purchased from Aldrich and was used without purification. 3 α -Acetoxy-5 β -cholan-24-oic acid (1) (Sigma) and 3 β -acetoxy-23,24-bisnor-5-cholen-22-oic acid (3) (Steraloids) were recrystallized before use. 3 β -Acetoxy-5-androstene-17 β -carboxylic acid (5) was prepared from 3 β -acetoxy-pregn-5-en-20-one.⁸

23-Iodo-24-nor-5 β -cholan-3 α -yl Acetate (2) Using IBDA/Iodine. A solution of 3 α -acetoxy-5 β -cholan-24-oic acid (1) (1 mmol) in carbon tetrachloride (75 mL) containing IBDA (0.55 mmol) and iodine (0.5 mmol) was irradiated with two 100-W tungsten-filament lamps for 45 min at reflux temperature, another portion of IBDA (0.55 mmol) and iodine (0.5 mmol) was then added, and the irradiation at this temperature was continued for 45 min. The reaction mixture was washed with diluted sodium thiosulfate and water. Silica gel column chromatography of the crystalline residue (eluant, 90:10 *n*-hexane-ethyl acetate) gave the iodo compound 2 with 94% yield: mp 207–210 °C (CHCl₃/MeOH); IR 1720, 1250 cm⁻¹; NMR δ 0.64 (3 H, s, 13-Me), 0.89 (3 H, d, *J* = 5.9 Hz, 20-Me), 0.90 (3 H, s, 10-Me), 2.01 (3 H, s, OAc), 3.03, 3.11 (2 H, m, 23-H₂), 4.69 (1 H, m, 3 β -H); MS (70 eV), *m/e* (relative intensity) 500 (M⁺, 1.3), 440 (90), 425 (20), 230 (55), 215 (100); MS, *m/e* calcd for C₂₅H₄₁O₂I 500.2151, found 500.2176.

Compound 4: a nonseparated 3:2 mixture of the epimeric 20-iodo as determined by NMR; IR 1720, 1250 cm⁻¹; MS (70 eV), *m/e* (relative intensity) 410 (M⁺ - AcOH, 20), 283 (100), 267 (42), 253 (31); MS, *m/e* calcd for C₂₁H₃₁I 410.1471, found 410.1488.

Compound 6: mp 155–163 °C (CH₂Cl₂/MeOH) [lit.⁹ mp 154–159 °C]; IR 1720, 1250 cm⁻¹; NMR δ 0.82 (3 H, s, 13-Me), 1.01 (3 H, s, 10-Me), 2.02 (3 H, s, OAc), 4.35 (1 H, d, *J* = 6.2 Hz, 17 β -H), 4.58 (1 H, m, 3 α -H), 5.36 (1 H, m, 6-H); MS (70 eV), *m/e* (relative intensity) 382 (M⁺ - AcOH, 34), 367 (2), 255 (78), 254 (100), 239 (41); MS, *m/e* calcd for C₁₉H₂₇I 382.1158, found 382.1096.

Compound 7: mp 180–182 °C (CH₂Cl₂/MeOH) [lit.⁹ mp 182–183 °C]; IR 1720, 1250 cm⁻¹; NMR δ 0.81 (3 H, s, 13-Me), 1.01 (3 H, s, 10-Me), 2.01 (3 H, s, OAc), 3.74 (1 H, t, *J* = 9.5 Hz, 17 α -H), 4.56 (1 H, m, 3 α -H), 5.35 (1 H, m, 6-H); MS (70 eV), *m/e* (relative intensity) 382 (M⁺ - AcOH, 100), 367 (2), 255 (78), 254 (12), 239 (11); MS, *m/e* calcd for C₁₉H₁₇I 382.1158, found 382.1163.

Compound 9: amorphous; IR 1720, 1250 cm⁻¹; NMR δ 0.76 (3 H, s, 13-Me), 0.81 (3 H, s, 10-Me), 0.98 (3 H, d, *J* = 6.5 Hz, 20-Me), 1.91 (3 H, d, *J* = 6.8 Hz, 25-Me), 2.00 (3 H, OAc), 3.3 (1 H, m, 22-H), 4.2 (2 H, m, 16-H, 25-H), 4.6 (1 H, m, 3 α -H); MS (70 eV), *m/e* (relative intensity) 556 (M⁺, 1.5), 481 (1), 429 (11), 428 (4), 386 (22), 373 (25), 315 (100); MS, *m/e* calcd for C₂₈H₄₅O₃I 556.2413, found 556.2392.

Compound 10: amorphous; IR 1720, 1250 cm⁻¹; NMR δ 0.75 (3 H, s, 13-Me), 0.81 (3 H, s, 10-Me), 0.96 (3 H, d, *J* = 6.5 Hz, 20-Me), 1.17 (3 H, d, *J* = 6.8 Hz, 25-Me), 2.00 (6 H, s, OAc), 3.3 (1 H, m, 22-H), 4.2 (1 H, m, 16-H), 4.7 (2 H, m, 3 α -H, 25-H); MS (70 eV), *m/e* (relative intensity) 488 (M⁺, 1), 428 (10), 386 (49), 373 (11), 344 (32), 315 (100); MS, *m/e* calcd for C₂₈H₄₄O₃ 428.3328, found 428.3308.

Compound 14: nonseparated mixture of C-12 epimers; amorphous; NMR δ 0.79 \times 2, 0.84 (9 H, s, 4-Me₂, 10-Me), 0.91, 1.01 (3 H, d, *J* = 6.5 Hz, 13-Me), 1.07, 1.10 (3 H, s, s, 8-Me), 2.8–4.3 (3 H, m, 12-H, 14-H₂); MS (70 eV), *m/e* (relative intensity) 404 (M⁺, 2), 389 (28), 235 (51), 217 (18), 191 (100); MS, *m/e* calcd for C₁₉H₃₃OI 404.1577, found 404.1595.

Compound 15: mp 145–149 °C (*n*-hexane); [α]_D +20° (*c* 0.15); IR 1770 cm⁻¹; NMR δ 0.81, 0.85 \times 2 (9 H, s, 4-Me₂, 10-Me), 1.07 (3 H, d, *J* = 6.4 Hz, 13-Me), 1.28 (3 H, s, 8-Me); MS (70 eV), *m/e* (relative intensity) 320 (M⁺, 2), 305 (100), 251 (27), 191 (48); MS, *m/e* calcd for C₂₀H₃₂O₃ 320.2351, found 320.2367.

Compound 16: mp 196–198 °C (*n*-hexane); [α]_D -34° (*c* 0.106); IR 1770 cm⁻¹; NMR δ 0.80, 0.83, 0.85 (9 H, s, 4-Me₂, 10-Me), 1.07 (3 H, d, *J* = 7.1 Hz, 13-Me), 1.12 (3 H, s, 8-Me); MS (70 eV), *m/e* (relative intensity) 320 (M⁺, 15), 305 (100), 251 (16), 191 (49); MS, *m/e* calcd for C₂₀H₃₂O₃ 320.2351, found 320.2362.

23-Chloro-24-nor-5 β -cholan-3 α -yl Acetate (17) Using IBDA/LiCl. To a solution of 3 α -acetoxy-5 β -cholan-24-oic acid (1) (1 mmol) in dry benzene (40 mL) were added IBDA (5 mmol)

and LiCl (5 mmol) portionwise, at the rate of 1 mmol each every 90 min at reflux temperature under argon. The reaction mixture was then washed with water and the residue chromatographed over silica gel (eluant 1:1 benzene-*n*-hexane) to give starting material (30%) and the chloro derivative 17 (40%): mp 160–163 °C (*n*-hexane); [α]_D +43° (*c* 0.1); IR 1715, 1250 cm⁻¹; NMR δ 0.64 (3 H, s, 13-Me), 0.90 (3 H, d, *J* = 6 Hz, 20-Me), 0.90 (3 H, s, 10-Me), 2.00 (3 H, s, OAc), 3.49 (2 H, m, 23-H₂), 4.69 (1 H, m, 3 β -H); MS (70 eV), *m/e* (relative intensity) 408 (M⁺, 0.5), 348 (100), 230 (23), 215 (6); MS, *m/e* calcd for C₂₅H₄₁O₂Cl 408.2792, found 408.2741.

3 α -Acetoxy-24-nor-5 β -chol-22-ene (19) Using IBDA/Cu(OAc)₂. A solution of 3 α -acetoxy-5 β -cholan-24-oic acid (1) (1 mmol) in dry benzene (40 mL) containing Cu(OAc)₂ (0.2 mmol) and pyridine (0.7 mmol) was stirred for 15 min under argon. To this solution IBDA (5 mmol) was added in portions, 1 mmol every 90 min, and the mixture refluxed for 8 h. The reaction mixture was then washed with dilute hydrochloric acid and water. Silica gel column chromatography of the residue (eluant 60:40 benzene-*n*-hexane) gave methyl ester 18 (19%) and the olefin 19 (80%): mp 96–97 °C (MeOH); [α]_D +28° (*c* 0.27); IR 1715, 1250 cm⁻¹; NMR δ 0.65 (3 H, s, 13-Me), 0.91 (3 H, s, 10-Me), 0.99 (3 H, d, *J* = 6.6 Hz, 20-Me), 2.00 (3 H, s, OAc), 4.70 (1 H, m, 3 β -H), 4.82 (2 H, m, 23-H₂), 5.64 (1 H, m, 22-H); MS (70 eV), *m/e* (relative intensity) 372 (M⁺, 0.7), 357 (2), 312 (15), 297 (16), 257 (100), 215 (34); MS, *m/e* calcd for C₂₅H₄₀O₂ 372.3027, found 372.3032.

Compound 18: mp 135–136 °C (MeOH); [α]_D +37° (*c* 0.16); IR 1720, 1250 cm⁻¹; NMR δ 0.61 (3 H, s, 13-Me), 0.88 (3 H, d, *J* = 6 Hz, 20-Me), 0.89 (3 H, s, 10-Me), 2.00 (3 H, s, OAc), 3.63 (3 H, s, OMe), 4.69 (1 H, m, 3-H); MS (70 eV), *m/e* (relative intensity) 372 (M⁺ - AcOH, 60), 357 (24), 257 (37), 230 (24), 215 (100); MS, *m/e* calcd for C₂₅H₄₀O₂ 372.3027, found 372.3025.

Compound 20: mp 94–95 °C (MeOH); [α]_D -81° (*c* 0.27); IR 1720, 1250 cm⁻¹; NMR δ 0.77 (3 H, s, 13-Me), 1.04 (3 H, s, 10-Me), 2.01 (3 H, s, OAc), 4.58 (1 H, m, 3 α -H), 5.38 (1 H, m, 6-H), 5.69, 5.82 (2 H, m, 16-H, 17-H); MS (70 eV), *m/e* (relative intensity) 254 (M⁺ - AcOH, 100), 239 (64), 211 (7), 183 (18), 159 (25); MS, *m/e* calcd for C₁₉H₂₆ 254.2033, found 254.2014.

Acknowledgment. This work was supported by the Investigation Programme of the Comisión Asesora de Investigación Científica y Técnica. J.I.C. expresses his gratitude to the Excmo. Cabildo Insular de La Palma for a fellowship.

Registry No. 1, 4057-84-5; 2, 99707-18-3; 3, 1474-14-2; 4 (epimer 1), 99707-19-4; 4 (epimer 2), 99707-27-4; 5, 51424-66-9; 6, 6570-64-5; 7, 35581-53-4; 8, 99707-20-7; 9, 99707-21-8; 10, 99707-22-9; 11, 50656-72-9; 12, 99707-24-1; 13, 469-11-4; 14 (epimer 1), 99707-25-2; 14 (epimer 2), 99780-93-5; 15, 99780-91-3; 16, 99780-92-4; 17, 99707-26-3; 18, 3253-69-8; 19, 50630-72-3; 20, 1236-14-2.

Efficient and Selective Cleavage of Acetals and Ketals Using Ferric Chloride Adsorbed on Silica Gel

Kwan Soo Kim,* Yang Heon Song, Bong Ho Lee, and Chi Sun Hahn

Department of Chemistry, Yonsei University, Seoul 120, Korea

Received May 6, 1985

Selective reactions on a hydroxy group of polyhydroxy compounds are extremely useful in organic synthesis, especially in the field of carbohydrate and nucleoside chemistry. Recently, we reported selective oxidation methods for various alcohols and a polyhydroxy compound.^{1,2} Indirect methods for the selective reaction on

(8) Staunton, J.; Eisenbraun, E. J. In "Organic Syntheses"; Baumgarten, H. E., Ed.; Wiley: New York, 1973; Collect. Vol. V, p 8.

(9) Biollaz, M.; Kalvoda, J. *Helv. Chim. Acta* 1972, 55, 366.

(1) Kim, K. S.; Cho, I. H.; Yoo, B. K.; Song, Y. H. *J. Chem. Soc., Chem. Commun.* 1984, 762.