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

23-Iodo-24-nor-5β-cholan-3α-yl Acetate (2) Using IBDA/Iodine. A solution of 3α-acetoxy-5β-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 ($CHCl_3$/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-H_2), 4.69 (1 H, m, 3β-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 $C_{25}H_{41}O_2I$ 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 $C_{21}H_{31}I$ 410,1471, found 410.1488.

Compound 6: mp 155–163 °C (CH_2Cl_2/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, 17β-H), 4.58 (1 H, m, 3α-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 $C_{19}H_{27}I$ 382.1158, found 382.1096.

Compound 7: mp 180–182 °C (CH_2Cl_2/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, 17α-H), 4.56 (1 H, m, 3α-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 $C_{19}H_{17}I$ 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, 3α-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 $C_{28}H_{45}O_3I$ 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, 3α-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 $C_{28}H_{44}O_3$ 428.3328, found 428.3308.

Compound 14: nonseparated mixture of C-12 epimers; amorphous; NMR δ 0.79 × 2, 0.84 (9 H, s, 4-Me_2, 10-Me), 0.91, 1.01 (3 H, d, 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-H_2); MS (70 eV), m/e (relative intensity) 404 (M^+, 2), 389 (28), 235 (51), 217 (18), 191 (100); MS, m/e calcd for $C_{19}H_{33}OI$ 404.1577, found 404.1595.

Compound 15: mp 145–149 °C (*n*-hexane); $[\alpha]_D$ +20° (*c* 0.15); IR 1770 cm^{-1}; NMR δ 0.81, 0.85 × 2 (9 H, s, 4-Me_2, 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 $C_{20}H_{32}O_3$ 320.2351, found 320.2367.

Compound 16: mp 196–198 °C (*n*-hexane); $[\alpha]_D$ –34° (*c* 0.106); IR 1770 cm^{-1}; NMR δ 0.80, 0.83, 0.85 (9 H, s, 4-Me_2, 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 $C_{20}H_{32}O_3$ 320.2351, found 320.2362.

23-Chloro-24-nor-5β-cholan-3α-yl Acetate (17) Using IBDA/LiCl. To a solution of 3α-acetoxy-5β-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); $[\alpha]_D$ +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-H_2), 4.69 (1 H, m, 3β-H); MS (70 eV), m/e (relative intensity) 408 (M^+, 0.5), 348 (100), 230 (23), 215 (6); MS, m/e calcd for $C_{25}H_{41}O_2{}^{35}Cl$ 408.2792, found 408.2741.

3α-Acetoxy-24-nor-5β-chol-22-ene (19) Using IBDA/Cu(OAc)$_2$. A solution of 3α-acetoxy-5β-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); $[\alpha]_D$ +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, 3β-H), 4.82 (2 H, m, 23-H_2), 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 $C_{25}H_{40}O_2$ 372.3027, found 372.3032.

Compound 18: mp 135–136 °C (MeOH); $[\alpha]_D$ +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 $C_{25}H_{40}O_2$ 372.3027, found 372.3025.

Compound 20: mp 94–95 °C (MeOH); $[\alpha]_D$ –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, 3α-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 $C_{19}H_{26}$ 254.2033, found 254.2014.

Acknowledgment. This work was supported by the Investigation Programme of the Comisiôn Asesora de Investigaciôn 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.

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

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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

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specific hydroxy groups of polyhydroxy compounds involve the use of protective groups. In order to utilize this methodology efficiently, the ability to selectively protect or deprotect certain hydroxy groups within the polyhydroxy compound is required.

In this paper, we report ferric chloride adsorbed on silica gel as an efficient and selective deprotecting agent for acetals and ketals. The selective cleavage of acetals and ketals by acids in the presence of other acid-labile protective groups such as *tert*-butyldimethylsilyl (TBDMS) ether, triphenylmethyl (trityl) ether, and tetrahydropyranyl (THP) ether is difficult.[3] Other methods reported for the cleavage of acetals and ketals are also not selective.[3]

Ferric chloride–silica gel reagent, a yellow powder, was prepared by mixing silica gel and an acetone solution of hydrated ferric chloride followed by evaporation of the solvent. The reagent was most effective after it was kept under vacuum (0.1 torr) at 60 °C for 30 min.[4]

The ferric chloride–silica gel reagent smoothly cleaved the ketal groups of compounds **1–3** and the acetal group of compound **4**. On the other hand, the cleavage of TBDMS ethers **5** and **6** and trityl ethers **7** and **8** with the same reagent was sluggish. When the reagent was applied to the more complex molecules **9**, **11**, and **13**, it selectively cleaved the 5,6-*O*-isopropylidene group to afford compounds **10**, **12**, and **14**, respectively, in high yield. The ferric chloride–silica gel reagent also selectively cleaved the benzylidene acetal of compound **15** without affecting the glycosidic linkage.

Based on these results, we anticipated that the ferric chloride–silica gel reagent would be used as the selective deprotecting agent for acetal and ketal protective groups in complex molecules which also contain other acid-labile protective groups such as TBDMS ether and trityl ether. Indeed, when compound **16** containing both isopropylidene group and TBDMS ether linkage was stirred with the ferric chloride–silica gel reagent in chloroform at room temperature for 8 h, the 5,6-*O*-isopropylidene group was selectively hydrolyzed and compound **17** was obtained in 79% yield. Selectivity of the reagent toward acetal and ketal groups was also shown in the hydrolysis of compound **18**. Thus, compound **18** was transformed into compound **19** in 74% yield by ferric chloride–silica gel reagent in chloroform. On the other hand, sulfuric acid or acetic acid hydrolyzed both the isopropylidene group and the TBDMS ether linkage of compounds **16** and **18** to afford a mixture of products. The ferric chloride adsorbed on silica gel, however, could not preferentially cleave the isopropylidene group in the presence of the trityl ether linkage of compound **20**. Prolonged reaction time and high temperature resulted in the cleavage of both protective groups of **20**. We have also established that ferric chloride–silica gel was unable to distinguish between the isopropylidene group and the THP ether linkage, though the rate of hydrolysis of THP ethers by the reagent was a little slower than that of acetals and ketals.

In acetone ferric chloride–silica gel selectively cleaved the TBDMS ether linkage of compound **18** without affecting the isopropylidene group to give compound **1** in 66% yield. The reagent also hydrolyzed the trityl ether linkage but did not affect the isopropylidene group of compound **20** in acetone to afford compound **1** in 85% yield. This solvent effect can be readily explained by the fact that the hydrolysis is in equilibrium and the excess acetone simply maintains the equilibrium in favor of the isopropylidene group. Hydrolysis of compounds **6** and **8** was not influenced very much by the change of solvents. Other solvents such as acetonitrile and ether gave almost the same results as chloroform.

Aluminum chloride or zinc chloride adsorbed on silica gel could also hydrolyze acetals and ketals but was not as effectve as ferric chloride–silica gel.

Experimental Section

All melting points and boiling points are uncorrected. Infrared spectra were run on a Shimadzu Model IR-435 or on a Perkin-Elmer IR 710B spectrophotometer. ^{1}H NMR spectra were obtained on a Varian EM-360L spectrometer in chloroform-*d* with tetramethylsilane as the internal standard. Microanalyses were performed in Korea Research Institute of Chemical Technology, Daejon, Korea. GC analyses were accomplised on a Hewlett-Packard Model 5750B flame ionization instrument by using a column of 10% UCW-982 on Chromosorb W. Solvents for the deprotecting procedure wrere distilled without drying, but solvents for other purposes were dried and distilled prior to use.

Preparation of Ferric Chloride Adsorbed on Silica Gel. To a solution of ferric chloride hexahydrate (1.2 g) in acetone (16 mL) was added silica gel (10 g, 70–230 mesh, E. Merck Kiesegel 60) at room temperature. The solvent was evaporated using a rotary evaporator at 30 °C under reduced pressure (15 torr). The mixture was further kept under vacuum (0.1 torr) at 60 °C for 30 min. The resulting yellow powder can be stored for extended periods under nitrogen at room temperature without change.

Preparation of Protected Hydroxy Compounds. Compounds **1**, **9**, **13**, and **15** were prepared by well-established procedures (see references in Table I). Ketalization and acetalization of simple diols were performed by refluxing a benzene solution of a diol with an appropriate ketone or aldehyde on Dean–Stark trap. Trityl ethers and TBDMS ethers were readily prepared by the reaction of alcohols with trityl chloride and TBDMS chloride, respectively, in the presence of 4-(dimethylamino)pyridine as a catalyst in methylene chloride.[5]

1,2-*O*-(*p*-Nitrobenzylidene)-1,2-*trans*-cyclohexanediol (4). The title compound was produced in 65% yield: mp 110–111 °C; IR (Nujol) 1518, 1345 cm^{-1}; ^{1}H NMR δ 1.15–2.20 (m, 8 H), 3.15–3.45 (m, 2 H), 6.03 (s, 1 H), 7.90 (q, 4 H). Anal. Calcd for $C_{13}H_{15}NO_3$: C, 66.94; H, 6.48; N, 6.00. Found: C, 66.85; H, 6.35; N, 6.10.

***tert*-Butyldimethylsilyl 2-Heptyl Ether (6).** The title compound was formed in 92% yield: bp 93–95 °C (12 mm); IR (neat) 1250 cm^{-1}; ^{1}H NMR δ 0.16 (s, 6 H), 0.80 (s, 9 H), 1.04–1.68 (m, 15 H). Anal. Calcd for $C_{13}H_{30}OSi$: C, 67.75; H, 13.12. Found: C, 67.80; H, 12.90.

Cyclohexylmethyl Trityl Ether (8). The title compound was obtained as a colorless syrup in 79% yield: ^{1}H NMR δ 0.90–1.80 (m, 11 H), 3.13 (d, J = 5.5 Hz, 2 H), 7.10–7.60 (m, 15 H). Anal. Calcd for $C_{26}H_{28}O$: C, 87.60; H, 7.91. Found: C, 87.65; H, 7.85.

3-*O*-(*tert*-Butyldimethylsilyl)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (16). The title compound was obtained as a colorless syrup from **9** in 72% yield: IR (neat) 1255 cm^{-1}; ^{1}H NMR δ 0.14 (s, 6 H), 0.92 (s, 9 H), 1.33 (s, 6 H), 1.41 (s, 3 H), 1.50 (s, 3 H), 3.93–4.40 (m, 6 H), 5.88 (d, J = 3.5 Hz, 1 H). Anal. Calcd for $C_{18}H_{34}O_6Si$: C, 57.52; H, 9.15. Found: C, 57.85; H, 9.05.

1-*O*-(*tert*-Butyldimethylsilyl)-2,3-*O*-isopropylideneglycerol (18). The title compound was obtained as a colorless syrup from **1** in 68% yield: IR (neat) 1250 cm^{-1}; ^{1}H NMR δ 0.20 (s, 6 H), 1.10 (s, 9 H), 1.47 (s, 3 H), 1.52 (s, 3 H), 3.70–4.32 (m, 5 H). Anal. Calcd for $C_{12}H_{26}O_3Si$: C, 58.49; H, 10.63. Found: C, 58.45; H, 10.69.

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(4) When the reagent was kept under vacuum (0.1 torr) at 60 °C for 12 h, it became brown powder which was not effective. By addition of ~5% (w/w) of water, the brown powder turned into yellow powder which was then effective for the hydrolysis of acetals and ketals.

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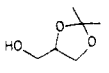
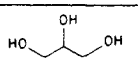
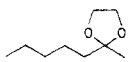
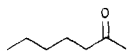
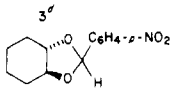
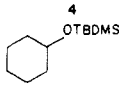
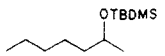
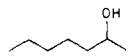
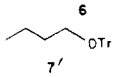
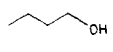
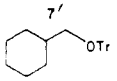
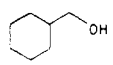
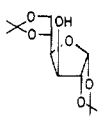
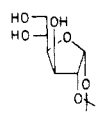
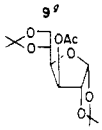
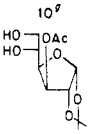
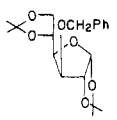
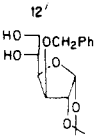
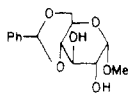
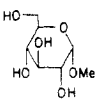
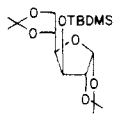
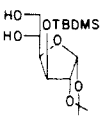
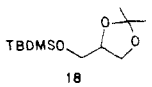
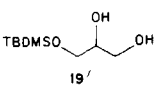
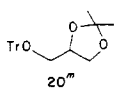
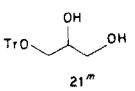
Table I. Cleavage of Protective Groups Using Ferric Chloride Adsorbed on Silica Gel

compd	product	time, h	solvent	yield,[a,b] %
 1[c]		6	$CHCl_3$	85
 2[d]		8	$CHCl_3$	(97)
 3[d]		2.5	$CHCl_3$	(100)
 4		8	$CHCl_3$	75
 5[e]		18	$CHCl_3$	(21)
 6		18 18	$CHCl_3$ Me_2CO	(32) (52)
 7[f]		20	$CHCl_3$	(30)
 8		24 24	$CHCl_3$ Me_2CO	(22) (22)
 9[g]	 10[g]	1	$CHCl_3$	82
 11[h]	 12[f]	4	$CHCl_3$	83
 13[f]	 14[f]	4	$CHCl_3$	75
 15[k]		10	$CHCl_3$	64
 16	 17	8	$CHCl_3$	79
16	**9**	18	Me_2CO	30
 18	 19[f]	4	$CHCl_3$	74
18	**1**	12	Me_2CO	66
 20[m]	 21[m]	12	$CHCl_3$	10
20	**1**	14	Me_2CO	85

[a] Isolated yield. [b] The yields in parentheses were determined by GC. [c] Renoll, M.; Newman, M. S. In "Organic Synthesis"; Horning, E. C., Ed.; Wiley: New York, 1955; Collect Vol. III, p 502. [d] Feugeas, Cl. *Bull. Soc. Chim. Fr.* **1963**, 2568. [e] Kita, Y.; Haruta, J.; Fuji, T.; Segawa, J.; Tamura, Y. *Synthesis* **1981**, 451. [f] Norris, J. F.; Young, R. C. *J. Am. Chem. Soc.* **1930**, *52*, 753. [g] Schmidt, O. T. In "Methods in Carbohydrate Chemistry"; Whistler, R. L., Wolfrom, M. L., Eds.; Academic Press: New York, 1963; Vol. II, p 318. [h] Muskat, I. E. *J. Am. Chem. Soc.* **1934**, *56*, 2449. [i] Akhrem, A. A.; Zaitseva, G. V.; Mikhailopulo, I. A. *Carbohydr. Res.* **1973**, *30*, 223. [j] Whistler, R. L.; Lake, W. C. In "Methods in Carbohydrate Chemistry"; Whistler, R. L.; BeMiller, J. N., Eds.; Academic Press: New York, 1972; Vol. VI, p 286. [k] Richtmyer, N. K. In "Methods in Carbohydrate Chemistry"; Whistler, R. L.; Wolfrom, M. L., Eds.; Academic Press: New York, 1962; Vol. I, p 107. [l] Ogilvie, K. K.; Hakimelahi, G. H. *Carbohydr. Res.* **1983**, *115*, 234. [m] Molotkovskii, Y. G.; Bergelson, L. D. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1967**, *11*, 2498.

General Procedure for Cleavage of Protective Groups Using Ferric Chloride Adsorbed on Silica Gel. A mixture of 5 mmol of a protected hydroxy compound and 0.10 g of $FeCl_3$–SiO_2 reagent in 20 mL of $CHCl_3$ or CH_3COCH_3 was stirred at room temperature. The reaction was monitored by GC or TLC. After completion of the reaction, the mixture was filtered, and the filtrate was concentrated under reduced pressure. The product was purified by distillation, crystallization, or column chromatography.

3-*O*-(*tert*-Butyldimethylsilyl)-1,2-*O*-isopropylidene-α-D-glucofuranose (17). The title compound was obtained as a syrup: IR (neat) 1250 cm^{-1}; ^1H NMR δ 0.16 (s, 6 H), 0.83 (s, 9 H), 1.32 (s, 3 H), 1.50 (s, 3 H), 2.00 (br s, 1 H), 2.51 (br s, 1 H), 3.75–4.40 (m, 6 H), 5.93 (d, J = 3.7 Hz, 1 H). Anal. Calcd for $C_{15}H_{30}O_6Si$: C, 53.86; H, 9.04. Found: C, 53.80; H, 8.97.

Registry No. 1, 100-79-8; 2, 4352-95-8; 3, 4352-98-1; 4, 99605-24-0; 5, 67124-67-8; 6, 99605-25-1; 7, 6226-44-4; 8, 99605-26-2; 9, 582-52-5; 10, 18549-40-1; 11, 16713-80-7; 12, 24807-96-3; 13, 18685-18-2; 14, 22529-61-9; 15, 3162-96-7; 16, 99605-27-3; 17, 99605-28-4; 18, 99605-29-5; 19, 85951-08-2; 20, 5330-64-3; 21, 18325-46-7; 1,2,3-propanetriol, 56-81-5; 2-heptanone, 110-43-0; 2-pentanone, 107-87-9; *trans*-1,2-cyclohexanediol, 1460-57-7; cyclohexanol, 108-93-0; 2-heptanol, 543-49-7; 1-butanol, 71-36-3; cyclohexylmethanol, 100-49-2; methyl α-D-glucopyranoside, 97-30-3; ferric chloride, 7705-08-0.

Reinvestigation on the Adducts Derived from *N*-Alkyloxaziridine and Phenyl Isothiocyanate

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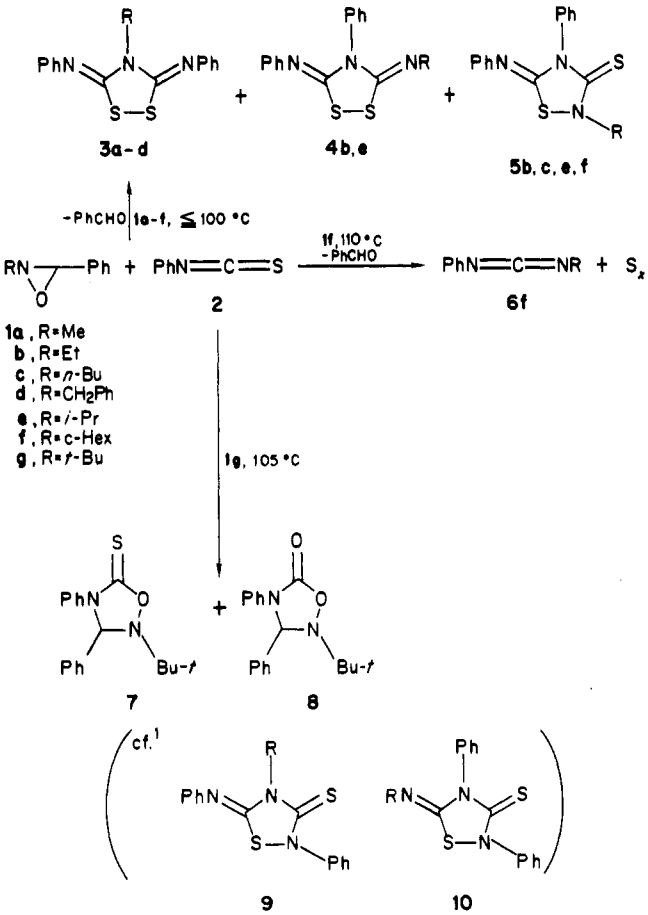
Received July 9, 1985

Previously we reported reactions of *N*-alkyloxaziridines **1** with sulfur-containing heterocumulenes such as carbon disulfide and phenyl isothiocyanate (**2**) leading to heterocyclic compounds or to another heterocumulene with incorporation of an alkylnitrene moiety.[1] The reaction of **1f** (R = c-Hex) with **2**, for example, afforded thiadiazolidine derivative **5f** at 90 °C but *N*-cyclohexyl-*N'*-phenylcarbodiimide (**6**) at 110 °C as illustrated in Scheme I. When the N-substituent of **1** was a *tert*-butyl group (**1g**), 1:1 cycloadducts **7** and **8** were isolated. However, the structures of the products **3** and **5** were assigned as thiadiazolidines **9** and **10**, respectively, in the preceding paper.[1] Similar reactions, viz., alkyl azides with isothiocyanates, were extensively studied by L'abbé et al., who assigned structures of the products mainly by ^{13}C NMR[2] and revealed rearrangement reactions among the products.[3]

Recently, we reexamined cyclic adducts **3b** etc. by means of X-ray diffraction and also by ^{13}C NMR and determined the molecular structures of the products **3** and **5**: the formerly proposed structures **9** and **10** were not correct. Structures of cycloadducts **7** and **8** (R = *t*-Bu) were correct, judging from their spectral and analytical data or identification with an authentic sample.[1]

Scheme I



A careful workup of the reaction of **1b** (R = Et) with **2** carried out at 80 °C in benzene afforded not only the adducts **3b** and **5b** but also a third isomeric cycloadduct (**4b**), previously a contaminant of **3b**.[4] Conclusive evidence for the structures of **3b** and **5b** has been obtained by X-ray crystallography.[5] Clearly, the molecule assigned as **9b** (R = Et) was found to be 4-ethyl-3,5-bis(phenylimino)-1,2,4-dithiazolidine (**3b**, Figure 1) and **10b** (R = Et) to be 2-ethyl-4-phenyl-5-(phenylimino)-1,2,4-thiadiazolidine-3-thione (**5b**, Figure 1). ^{13}C NMR spectra of compounds **3b** and **5b** were in good agreement with X-ray data.

Efforts to obtain suitable crystals of **4b** for X-ray analysis failed. In the ^1H NMR spectrum of **4b**, the methylene protons appear in higher field than those of **3b** by ca. 1 ppm. The ^{13}C NMR spectrum clearly shows that the structure of **4b** is not symmetrical and no thione carbon[3] but two types of imino carbons were observed. The IR spectrum of **4b** exhibited rather weak absorption due to the C=N bond at 1615 cm^{-1}, while relatively wide absorption of the C=N bond of **3b** was observed at around 1580 cm^{-1}. These data as well as that of mass spectrum supported the 3,5-bis(imino)-1,2,4-dithiazolidine structure of **4b**.

Similarly we reexamined the cycloadducts having other *N*-alkyl substituents by NMR and IR spectral data (Table

(1) Komatsu, M.; Ohshiro, Y.; Yasuda, K.; Ichijima, S.; Agawa, T. *J. Org. Chem.* **1974**, *39*, 957.
(2) L'abbé, G. *Tetrahedron* **1982**, *38*, 3537; *J. Heterocycl. Chem.* **1984**, *21*, 627 and references cited therein.
(3) L'abbé, G.; Van Loock, E.; Velherst, G.; Toppet, S. *J. Org. Chem.* **1975**, *40*, 607. L'abbé, G.; Velherst, G.; Toppet, S. *Ibid.* **1977**, *42*, 1159.

(4) A trace amount of a cycloadduct consisting of PhN=C=S, PhN=C=NEt, and NEt was isolated and the structure was determined to be 2,4-diethyl-3,5-bis(phenylimino)-1,2,4-thiadiazolidine by spectral analysis: mp 82–83 °C; IR (Nujol) 1620 cm^{-1} (C=N); ^1H NMR ($CDCl_3$) δ 0.92 (t, 3 H, Me), 1.37 (t, 3 H, Me), 2.95 (q, 2 H, CH_2), 4.06 (q, 2 H, CH_2), 6.7–7.4 (m, 10 H, 2 Ph); ^{13}C NMR ($CDCl_3$) 148.0 (s, PhN=), 148.2 (s, PhN=), 150.0 (s, C=N), 153.3 ppm (s, C=N); MS, m/e 324 (M^+). Anal. Calcd for $C_{18}H_{20}N_4S$: C, 66.35; H, 6.21; N, 17.27; S, 9.88. Found: C, 66.74; H, 6.17; N, 17.29; S, 9.85.
(5) For details: Kuriyama, M.; Yasuoka, N.; Kasai, N.; Komatsu, M.; Ohshiro, Y.; Agawa, T. *Bull. Chem. Soc. Jpn.*, in contribution.

0022-3263/86/1951-0407$01.50/0