3-Hydroxy-4-allylacetanilide (5).—The solutions L_1 and L_2 (see above) were combined and the resulting solution was evaporated under reduced pressure to dryness. The residue (22.5 g, mp 124–139°) was suspended in 500 ml of H_2O. The suspension was heated to the boiling point; EtOH was gradually added until a clear solution was obtained.

The solution was heated for a further 15 min and allowed to stand at room temperature overnight. The crystalline solid was filtered and dried, 15.2 g, mp 161–163°. An analytical sample was recrystallized from an EtOH–H_2O mixture: mp 162–164°; uv max 247 mμ (ε 13,600), 285 (4570); ir, a strong peak at 12.1 μ (characteristic of two adjacent aromatic C–H bonds) and at 11.4 μ (characteristic of an isolated aromatic C–H bond); nmr (Me_2SO) δ 6.9 (s, $H_{5,6}$), 7.3 ppm (s, H_2); tlc, one spot (R_f 0.25). *Anal.* Calcd for $C_{11}H_{13}NO_3$: C, 69.09; H, 6.85; N, 7.33. Found: C, 69.38; H, 6.93; N, 7.23.

2-Allyl-3-acetoxyacetanilide.—A solution of 1.3 ml of AcCl in 15 ml of anhydrous PhH was added dropwise and with stirring to a cooled (10°) mixture of 2 g of 4 and 1.5 ml of pyridine in 85 ml of anhydrous PhH. After the addition was completed, the reaction mixture was stirred for an additional 2 hr and then filtered. The filtrate was shaken with H_2O, $NaHCO_3$ solution and again with H_2O until neutral. The PhH solution was dried (Na_2SO_4) and evaporated. The residue was crystallized from AcOEt to constant melting point (151–152°), tlc one spot (R_f 0.45). *Anal.* Calcd for $C_{13}H_{15}NO_3$: C, 66.93; H, 6.48; N, 6.01. Found: C, 66.94; H, 6.42; N, 5.90.

3-Acetoxy-4-allylacetanilide.—This compound was prepared by a procedure similar to the one used for the 2-allyl isomer. After crystallization from PhH–petroleum ether (bp 30–60°), it melted at 103–104°, uv max 246 mμ (ε 18,500), tlc one spot (R_f 0.35). *Anal.* Calcd for $C_{13}H_{15}NO_3$: C, 66.93; H, 6.48; N, 6.01. Found: C, 66.98; H, 6.42; N, 6.17.

2-Propyl-3-hydroxyacetanilide.—An ethanolic solution of 1.74 g of 4 in 25 ml of EtOH was hydrogenated under 3 atm in the presence of 0.15 g of PtO_2. After 3 hr the reaction mixture was filtered and the filtrate was evaporated to dryness. The residue (1.5 g, mp 163–165°) was crystallized twice from an EtOH–H_2O mixture: mp 167–169°; uv max 278 mμ (ε 2280); tlc one spot (R_f 0.20). *Anal.* Calcd for $C_{11}H_{15}NO_2$: C, 68.39; H, 7.82; N, 7.25. Found: C, 68.51; H, 7.84; N, 7.32.

3-Hydroxy-4-propylacetanilide.—This compound was prepared following the above procedure from 5. After recrystallization from an EtOH–H_2O mixture it melted at 173–175° (lit.[2] mp 173–174.5°): uv max 248 mμ (ε 12,800), 285 (4550); tlc one spot (R_f 0.25). *Anal.* Calcd for $C_{11}H_{15}NO_2$: C, 68.39; H, 7.82; N, 7.25. Found: C, 68.26; H, 7.78; N, 7.32.

2-Methyl-4-acetamidocoumaran (6).—Two grams of 2-allyl-3-hydroxyacetanilide was cyclized by means of fuming hydrobromic acid according to Arnold and McCool.[1] The obtained solid (1.7 g) was crystallized from PhH–petroleum ether to constant melting point (121–123°[8]): uv max 237 mμ (ε 8600), 283 (2550); tlc one spot (R_f 0.55). *Anal.* Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.33. Found: C, 69.25; H, 6.83; N, 7.25.

2-Methyl-6-acetamidocoumaran (7).—This compound was obtained from 5 using the above procedure. After crystallization from PhH–petroleum ether, it had mp 99–101° and was identical (mixture melting point determination, ir and uv analyses) to the acetamidomethylcoumaran derived from the nitro compound prepared as described by Arnold and McCool:[1] uv max 249 mμ (ε 10,200), 291 (5780); tlc one spot (R_f 0.35). *Anal.* Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.33. Found: C, 68.99; H, 7.02; N, 7.45.

Registry No.—**3**, 37439-78-4; **4**, 37439-79-5; **4** acetate, 37439-80-8; **5**, 28583-69-9; **5** acetate, 37439-82-0; **6**, 37439-83-1; **7**, 37439-84-2; 2-propyl-3-hydroxyacetanilide, 37439-85-3; 3-hydroxy-4-propylacetanilide, 28583-72-4.

Acknowledgment.—We are indebted to Miss A. De Leonibus for the microanalyses and to Mrs. M. L. Reviglio Lembo for the tlc data and uv and ir spectra.

(8) This compound was identified previously[1] as 2-methyl-6-acetamidocoumaran, mp 126–126.5° (from water).

An Alternate Synthesis of 5-Thio-D-glucose Pentaacetate[1]

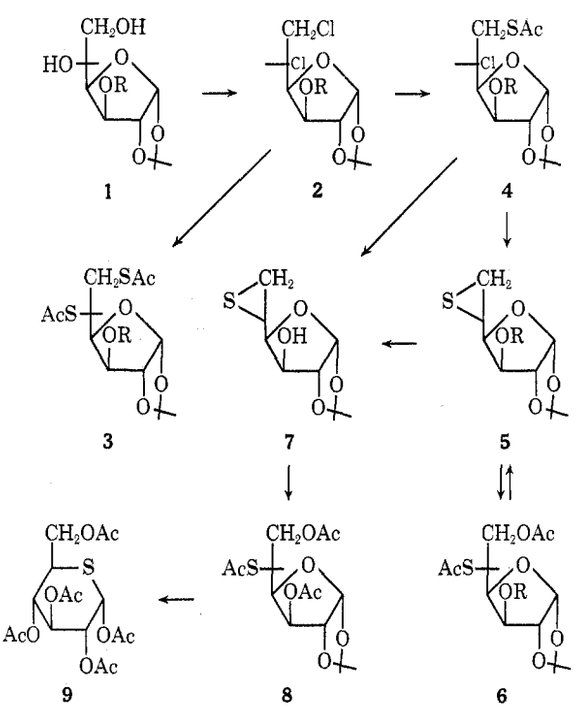
CHUNG-WAI CHIU AND ROY L. WHISTLER*

Department of Biochemistry, Purdue University, Lafayette, Indiana 47907

Received September 1, 1972

Because of growing interest in the biochemistry of 5-thio-D-glucose,[2] a shorter route to its synthesis would be highly desirable. It occurred to us that, since chloro sugars have proved valuable intermediates in the preparation of deoxy[3,4] and amino sugars,[5–7] they might be used to provide a shorter synthesis of 5-thio-D-glucose.

We find that 3-*O*-benzoyl-1,2-*O*-isopropylidene-α-D-glucofuranose (1) can be easily chlorinated to produce 3-*O*-benzoyl-5,6-dichloro-5,6-dideoxy-β-L-idofuranose (2) in 72% yield, by using triphenylphosphine in carbon tetrachloride.[8] The L-ido configuration of compound 2 is established through its conversion to 5,6-dideoxy-5,6-epithio-1,2-*O*-isopropylidene-α-D-glucofuranose (7).[9]



Selective displacement of the primary chloro group on 2 produces 6-*S*-acetyl-5-chloro-5,6-dideoxy-1,2-*O*-isopropylidene-β-L-idofuranose (4) in 60% yield if 1 mol of potassium thioacetate is used at low tempera-

(1) This work was supported by Public Health Service Research Grant No. AM 15641. Journal Paper No. 4861 of the Purdue Agricultural Experiment Station, Lafayette, Indiana 47907.

(2) R. L. Whistler and W. C. Lake, *Biochem. J.*, in press.

(3) M. F. Evans, L. Long, Jr., and F. W. Parrish, *J. Org. Chem.*, **33**, 1074 (1968).

(4) B. T. Lawton, D. J. Ward, W. A. Szarek, and J. K. N. Jones, *Can. J. Chem.*, **47**, 2899 (1969).

(5) S. Hanessian and N. R. Plessas, *Chem. Commun.*, 1152 (1967).

(6) B. T. Lawton, W. A. Szarek, and J. K. N. Jones, *ibid.*, 787 (1969).

(7) E. Hardeggar, G. Sanetti, and K. Steiner, *Helv. Chim. Acta*, **46**, 282 (1963).

(8) J. B. Lee and T. J. Nolan, *Can. J. Chem.*, **44**, 1331 (1966).

(9) L. D. Hall, L. Hough, and R. A. Pritchard, *J. Chem. Soc.*, 1537 (1961).

ture (*ca.* 45°). However, if an excess of potassium thioacetate is used or a higher reaction temperature is employed, 5,6-di-*S*-acetyl-3-*O*-benzoyl-5,6-dideoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (**3**) is also formed as the principal product.

5,6-Dideoxy-5,6-epithio-1,2-*O*-isopropylidene-α-D-glucopyranose (**7**) can be obtained in 91% yield from **4** by hydrolysis and cyclization or **4** can be converted to 3-*O*-benzoyl-5,6-dideoxy-5,6-epithio-1,2-*O*-isopropylidene-α-D-glucofuranose (**5**) which gives 6-*O*-acetyl-5-*S*-acetyl-3-*O*-benzoyl-5-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (**6**). Either **5** or **6** can give **7** in 94–97% yield and a cyclization similar to the conversion of **6** to **7** was reported by Owen and coworkers.[10,11]

Nucleophilic ring opening of the episulfide **7** to give 3,6-di-*O*-acetyl-5-*S*-acetyl-5-deoxy-α-D-glucofuranose (**8**) is accomplished essentially according to the published procedure.[12] Acetolysis of **8** produces crystalline 1,2,3,4,6-penta-*O*-acetyl-α-D-glucothiopyranose (**9**) in 69% yield.

Thus, the outlined procedure offers fewer steps to the synthesis of 5-thio-D-glucose starting from normal D-glucose but the overall yield is in the neighborhood of 23% compared to 30% by the longer route.[13] The present route also has two column-chromatographic purification steps not present in the longer synthesis.

Experimental Section

Reactions were monitored by thin layer chromatography (tlc) on silica gel G[14] coated glass plates (5 × 13 cm). Components were located by spraying with 5% sulfuric acid in ethanol and heating until permanent char spots were visible. Column chromatography used alumina and silica gel.[15] Optical rotations were measured yn a Perkin-Elmer Model 141 polarimeter.

3-*O*-Benzoyl-5,6-dichloro-5,6-dideoxy-1,2-*O*-isopropylidene-β-L-idofuranose (2).—A mixture of 3-*O*-benzoyl-1,2-*O*-isopropylidene-α-D-glucofuranose (**1**)[16] (3.5 g), triphenylphosphine (14 g), and anhydrous $CaSO_4$ (2 g) in carbon tetrachloride (150 ml) was refluxed for 5 hr. The reaction mixture was filtered and concentrated to give a solid mass, which was extracted three times with hexane. The combined extracts were evaporated to give a thick syrup which was chromatographed on a silica gel column with a mixture of ether–hexane (1:4, v/v) to yield 3-*O*-benzoyl-5,6-dichloro-5,6-dideoxy-1,2-*O*-isopropylidene-β-L-idofuranose (**2**) as a colorless syrup (2.80 g, 71.7%): $[\alpha]^{25}D$ −5.82° (*c* 1.1, chloroform); ν_{max} (film) 1730 cm^{-1} (OCOPh).

Anal. Calcd for $C_{16}H_{18}Cl_2O_5$: C, 53.21; H, 5.02; Cl, 19.63. Found: C, 53.62; H, 5.16; Cl, 19.29.

5,6-Di-*S*-acetyl-3-*O*-benzoyl-5,6-dideoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (3).—To a solution of **2** (800 mg) in dry acetone (20 ml) was added potassium thioacetate (1.01 g), and the mixture was refluxed under stirring in a current of nitrogen for 4 hr. The reaction mixture was filtered and concentrated to a syrup, which was washed with cold water, dried, and purified by silica gel column chromatography using ethyl acetate–carbon tetrachloride (1:19, v/v) as eluent. Compound **3** was obtained in 82.7% yield (848 mg). Recrystallization from hexane gave fine needles: mp 114–115°; $[\alpha]^{25}D$ −65.5° (*c* 1.2, chloroform); ν_{max}^{Nujol} 1730 (–OCOPh) and 1680 cm^{-1} (–SCOCH$_3$); nmr ($CDCl_3$) δ 1.33, 1.57 (2 s, 6 H, CMe_2), 2.15, 2.33 (2 s, 6 H, *S*-acetyl), 2.9–5.0 (m, 5 H, H-2,4,5,6), 5.48 (d, 1 H, $J_{3,4}$ = 3 Hz, H-3), 6.0 (d, 1 H, $J_{1,2}$ = 4 Hz, H-1), 7.2–8.3 (m, 5 H, aromatic protons).

Anal. Calcd for $C_{20}H_{24}O_7S_2$: C, 54.53; H, 5.49; S, 14.55. Found: C, 54.51; H, 5.64; S, 14.70.

6-*S*-Acetyl-3-*O*-benzoyl-5-chloro-5,6-dideoxy-1,2-*O*-isopropylidene-β-L-idofuranose (4). A.—A mixture of **2** (200 mg) and potassium thioacetate (95 mg) in dry acetone (20 ml) was stirred under nitrogen at a temperature of 40–45°. After 16 hr, the reaction mixture was filtered and the filtrate was concentrated to a pale yellow syrup, which was chromatographed on a silica gel column using ether–hexane (2:3, v/v) as eluent. Starting material was recovered as an oil (90 mg) and the product **4** was collected as a colorless syrup (232 mg, 70%): $[\alpha]^{25}D$ −37.3° (*c* 1.56, chloroform); nmr ($CDCl_3$) δ 1.35, 1.57 (2 s, 6 H, CMe_2), 2.21 (s, 3 H, *S*-acetyl), 3.33 (m, 2 H, H-6), 4.0–4.8 (m, 1 H, H-5), 4.48 (d, 1 H, $J_{3,4}$ = 3 Hz, H-4), 4.71 (d, 1 H, $J_{1,2}$ = 4 Hz, H-2), 5.54 (d, 1 H, $J_{3,4}$ = 3 Hz, H-3), 6.03 (d, 1 H, $J_{1,2}$ = 4 Hz, H-1), 7.2–8.3 (m, 5 H, aromatic protons).

Anal. Calcd for $C_{18}H_{21}ClO_6S$: C, 53.93; H, 5.28; S, 7.99; Cl, 8.84. Found: C, 54.03; H, 5.52; S, 7.90; Cl, 8.60.

B.—A mixture of **2** (200 mg) and potassium thioacetate (63 mg, 1 mol) in dry acetone was treated under nitrogen at a temperature of 50° for 24 hr. After treatment as above, 12 mg of the starting material, 59 mg of **3** (25.8%), and 131 mg (63%) of **4** were obtained.

3-*O*-Benzoyl-5,6-dideoxy-5,6-epithio-1,2-*O*-isopropylidene-α-D-glucofuranose (5).—A mixture of **4** (150 mg) and triethylamine (5 ml) in methanol (15 ml) was stirred overnight at 40°. The solution was evaporated to dryness, and the syrup was washed with ice water (2 × 5 ml). After drying in a vacuum desiccator, the episulfide **5** was collected as a colorless syrup in quantitative yield (121 mg): $[\alpha]^{25}D$ −91.0° (*c* 1.44, chloroform); nmr ($CDCl_3$) δ 1.33, 1.52 (2 s, 6 H, CMe_2), 2.5 (m, 2 H, H-6), 3.10 (m, 1 H, H-5), 3.86 (q, 1 H, $J_{3,4}$ = 3 Hz, $J_{4,5}$ = 8 Hz, H-4), 4.68 (d, 1 H, $J_{1,2}$ = 4 Hz, H-2), 5.53 (d, 1 H, $J_{3,4}$ = 3 Hz, H-3), 6.03 (d, 1 H, $J_{1,2}$ = 4 Hz, H-1), 7.2–8.3 (m, 5 H, aromatic protons).

Anal. Calcd for $C_{16}H_{18}O_5S$: C, 59.61; H, 5.63; S, 9.94. Found: C, 59.42; H, 5.90; S, 9.66.

When 1 mol of methanolic potassium hydroxide was used instead of triethylamine, only 80.6% of **5** was isolated and compound **7** was obtained as a minor product in 9.2% yield.

5,6-Dideoxy-5,6-epithio-1,2-*O*-isopropylidene-α-D-glucofuranose (7). A. From 5.—To a cold methanolic solution of episulfide **5** (50 mg), a methanolic potassium hydroxide solution (1 equiv) was added dropwise. After 20 min, the solution was treated with Amberlite IR-120 (H^+). The reaction mixture was filtered and evaporated to give crystalline **7**, which was purified by passing through an alumina column using ether–hexane (1:10, v/v) as the eluent to yield 31.8 mg (94%). It melted at 140–141°: $[\alpha]^{25}D$ −75.8° (*c* 1.2, chloroform) [lit.[16] mp 138–140°; $[\alpha]^{25}D$ −76.2° (*c* 1.9, chloroform)].

B. From 4.—**4** (80 mg) was dissolved in anhydrous methanol and cooled to 0°. Methanolic potassium hydroxide solution (2 equiv) was added dropwise. After treatment as above, **7** was isolated in 91.5% yield (40 mg).

3,6-Di-*O*-acetyl-5-*S*-acetyl-5-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (8).—Compound **8** was prepared according to the published procedure[9] with slight modification.

Thus, a crude product of **7**, prepared from 50 mg of **5** as described in the above section (omitting the purification step by chromatography), was dissolved in a mixture of acetic acid and acetic anhydride (1:10, v/v, 3 ml). Potassium acetate (30 mg) was added and the mixture was heated at 140° for 12 hr. The resulting yellow solution was coevaporated with toluene to give a solid mixture which was extracted three times with ether and evaporated to dryness. The slightly yellow crystals thus obtained were pure enough for the next reaction. Pure **8** could be obtained, after column chromatography, as a white, crystalline compound (52 mg, 92% based on **5**), mp 149–150°, $[\alpha]^{25}D$ +7.5° (*c* 1.5, chloroform) [lit.[9] mp 149°, $[\alpha]^{25}D$ +7.2° (*c* 1.8, chloroform)].

1,2,3,4,6-Penta-*O*-acetyl-α-D-glucothiopyranose (9).—Crude **8** (25 mg) was acetolyzed with 3 ml of a mixture of acetic anhydride–acetic acid–sulfuric acid (70:30:1, v/v). After 3 days, anhydrous ether (20 ml) was added, followed by sodium acetate (300 mg). The mixture was filtered and the residue was washed with ether (2 × 20 ml). The combined solutions were coevaporated with toluene to give a thick syrup, which was chromatographed on a silica gel column using ether–hexane (1:4, v/v) as eluent. Pure pentaacetate **9** was collected as white crystals (20 mg, 68.6%). Recrystallization from ether–hexane gave long needles, mp 103°, $[\alpha]^{25}D$ +213° (*c* 1.4, chloroform) [lit.[9] mp 103°, $[\alpha]^{25}D$ +213° (*c* 1.35, chloroform)].

(10) A. M. Creighton and L. N. Owen, *J. Chem. Soc.*, 1024 (1960).
(11) L. W. C. Miles and L. N. Owen, *ibid.*, 817 (1952); J. S. Harding and L. N. Owen, *ibid.*, 1528 (1954); P. S. Fitt and L. N. Owen, *ibid.*, 2240 (1957).
(12) R. M. Rowell and R. L. Whistler, *J. Org. Chem.*, **31**, 1514 (1966).
(13) U. G. Nayak and R. L. Whistler, *ibid.*, **34**, 97 (1969).
(14) L. Merk Ag, Darmstadt, Germany. Distributors: Brinkman Instruments Inc., Westbury, N. Y. 11590.
(15) J. T. Baker Chemical Co., Phillipsburg, N. J.
(16) E. Fischer, *Ber.*, **48**, 268 (1915).

6-*O*-Acetyl-5-*S*-acetyl-3-*O*-benzoyl-5-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (6).—A mixture of **5** (34 mg) and potassium acetate (300 mg) in 5 ml of acetic acid–acetic anhydride (1:5, v/v) was heated at 140°. After 16 hr, the reaction mixture was coevaporated with toluene to dryness, extracted with ether, and concentrated. The crystalline product was purified by column chromatography on silica gel, using ether–hexane (2:3, v/v) as eluent to give **6** (440 mg, 96.7%), mp 129–30°, $[\alpha]^{25}D$ −80.8° (*c* 0.5, chloroform).

Anal. Calcd for $C_{20}H_{24}O_8S$: C, 56.57; H, 5.69; S, 7.55. Found: C, 56.75; H, 5.83; S, 7.50.

Reaction of 6 with Sodium Methoxide.—Compound **6** (100 mg) was dissolved in anhydrous methanol (10 ml) and cooled to 0°. A solution of sodium methoxide in methanol was added and the pH was adjusted to 10. Progress of the reaction was monitored by tlc using ether–hexane (2:3, v/v) as the irrigant. After 1 hr, the reaction mixture was neutralized with Amberlit IR-120 (H^+) resin, evaporated, and chromatographed on alumina with ether–hexane (1:10, v/v) to give **7** (40 mg, 77.81 %).

Registry No.—**1**, 37614-73-6; **2**, 37614-74-7; **3**, 37614-75-8; **4**, 37614-76-9; **5**, 37614-77-0; **6**, 37614-78-1; **7**, 37614-79-2; **8**, 10227-17-5; **9**, 10227-18-6.

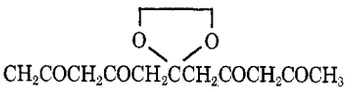
Protection of Carbonyl Groups as Bromomethylethylene Ketals

E. J. COREY* AND RONALD A. RUDEN

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

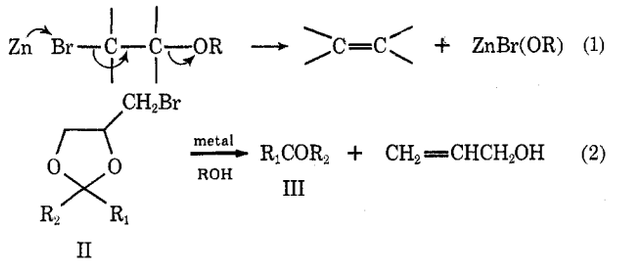
Received October 2, 1972

Ketalization has proven to be an invaluable method for the protection of a carbonyl group during various transformations. However, a ketal protecting group necessitates the use of acid catalysis for its removal. During the course of studies directed toward a total synthesis of the spiro alkaloid histrionicotoxin,[1] a carbonyl protecting group which could be removed under neutral conditions was required. Other instances of the inadequacy of conventional methods for carbonyl protection have been noted previously; *e.g.*, removal of the ketal blocking group from the polyketide I could not be achieved.[2]



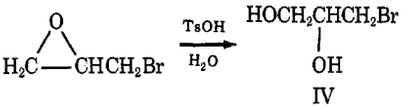
I

A promising approach seemed to be the use of a bromomethylethylene ketal which could be cleaved by the familiar β-bromo ether reductive elimination (eq 1; *cf.* ref 3). More specifically, the simplest cyclic ethylene ketal (II) was selected for use, the unmasking step then being expressed by eq 2.



II

Following the procedure of Winstein and Goodman, the requisite starting material, 1,2-dihydroxy-3-bromopropane[4] (IV), was prepared in one step from epibromohydrin. Three substrates, V–VII, were chosen to



IV

illustrate the generality of the sequence ketalization–deketalization. The first step, ketalization, was accomplished in excellent yield by treatment of an aldehyde or ketone with bromoglycol IV in refluxing benzene using *p*-toluenesulfonic acid as a catalyst (Table I). Deketalization was attempted using a variety of

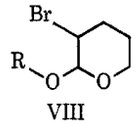
TABLE I

Carbonyl compd	Yield of Ketal,[a,b] %	Yield of deketalized material,[a,c] %
4-*tert*-Butylcyclohexanone (V)	98[d]	89
$CH_3(CH_2)_4COCH_2COOCH_3$ (VI)	95[e]	96
$CH_3(CH_2)_{10}CHO$ (VII)	93[f]	89

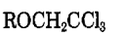
[a] Evaporatively distilled. [b] The ketals showed the expected spectral and analytical properties. [c] Infrared and nmr spectra were identical with those of authentic material. [d] Mass spectrum M^+ calcd 290.0082, found 290.0879. [e] ($M^+ - CH_3OM$) calcd 277, found 277 (no parent ion). [f] M^+ calcd 320.1350, found 320, 1342.

metals and conditions.[3,5] After some experimentation, it was found that treatment of the bromo ketal with activated zinc in refluxing methanol afforded an excellent yield of the deketalized compound (Table I).

The bromomethylethylene ketal unit has been found to be stable to a variety of reagents which are commonly used in synthesis. Thus, treatment of the ketal obtained from 4-*tert*-butylcyclohexanone with *m*-chloroperbenzoic acid, liquid ammonia, $NaBH_4$ in ethanol at room temperature, MeLi in ether at 0° for 1 hr, or Jones (CrO_3) reagent led to a *quantitative recovery* of starting ketal. In addition, it should be noted that there are many hydroxyl, amino, and carbonyl protecting groups which can survive the deketalization conditions and only a few, for example the alcohol protecting groups VIII and IX, which cannot.



VIII



IX

Experimental Section

The following experiments illustrate the procedures utilized.

Ketalization.—Dodecanal (634 mg, 3.40 mmol) in 2 ml of benzene was added portionwise to a refluxing benzene solution (50 ml) of bromoglycol IV (5.3 g, 34.0 mmol) and *p*-toluenesulfonic acid (50 mg) over 10 hr. The solution was heated at reflux for an additional 5 hr, and the product was isolated after washing with water and removal of benzene to afford 1.10 g (100%) of crude bromo ketal. Evaporative distillation (120°,

(1) J. W. Daley, I. Karle, C. W. Meyers, T. Tokuyama, J. A. Waters, and B. Witkop, *Proc. Nat. Acad. Sci. U. S.*, 1870 (1971).

(2) A. J. Birch, P. Fitton, D. C. C. Smith, D. E. Steerie, and A. R. Stelfox, *J. Chem. Soc.*, 2209 (1963).

(3) H. O. House and R. S. Ro, *J. Amer. Chem. Soc.*, **80**, 182 (1958).

(4) S. Winstein and L. Goodman, *ibid.*, **76**, 4368 (1954).

(5) Representative metals tried were Zn, Al–Hg, Mg–Hg, Zn–Cu, Zn–Hg, and Li–Hg.