Thiourea: A Novel Cleaving Agent for 1,3-Dioxolanes

Swapan Majumdar and Anup Bhattacharjya*

Indian Institute of Chemical Biology, 4 Raja S. C. Mullick Road, Calcutta 700 032, India

Received June 10, 1998

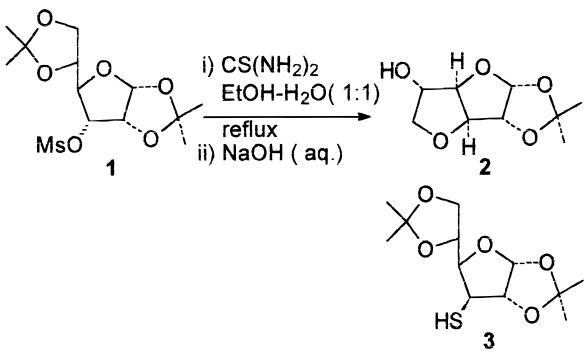
Introduction

One of the most common methods of protecting aldehydes, ketones, and vicinal diols involves the formation of acetals. Aldehydes and ketones are usually protected as their 1,3-dioxolane derivatives, and vicinal diols such as those present in carbohydrate derivatives are protected as 2,2-dimethyl-1,3-dioxolanes. Several methods are available for deprotecting these types of acetals, which mostly utilize acidic cleaving methods.[1] Other cleaving methods involving the use of silica gel[2] or lithium tetrafluoroborate in wet acetonitrile[3] and some nonaqueous cleaving methods have also been reported for this purpose.[4−6] Herein we report that thiourea can effect the cleavage of 1,3-dioxolanes derived from aldehydes and ketones, as well as the selective cleavage of the 5,6-*O*-isopropylidene moiety in 1,2:5,6-di-*O*-isopropylidene hexose derivatives, leading to good to excellent yields of the parent compounds.

Results and Discussion

One of the known methods of preparation of an alkyl thiol from an alkyl halide or sulfonate involves the formation of the corresponding thiouronium salt by treatment with thiourea followed by alkaline hydrolysis.[7] An attempted synthesis of the thiocarbohydrate derivative **3** from the corresponding α-mesylate **1**[8] by heating with a 0.8 M solution of thiourea in ethanol−water (1:1) followed by treatment with aqueous NaOH solution resulted in a mixture of products. The ^{1}H NMR spectrum of one of the products, which was isolated in a very poor yield, revealed the loss of the 5,6-*O*-isopropylidene group of **1** during the reaction (Scheme 1).[9] To our knowledge, there has been no report of such cleavage by thiourea. It was, therefore, of much interest to study whether the method was general for the removal of the 5,6-*O*-isopropylidene groups in other diisopropylidene carbohydrate derivatives, because partial deprotection of such compounds is frequently applied in carbohydrate chemistry. With this end in view, each of the 1,2:5,6-di-*O*-isopropylidene carbohydrate derivatives **4**−**9** (Table 1) was subjected to treatment with a 0.8 M solution of thiourea in ethanol−water (1:1) under reflux. In each case, the corresponding 5,6-deprotected compound was formed in good to very good yields. In all cases, the 1,2-*O*-isopropylidene group remained unaffected under the reaction condition as revealed by the ^{1}H NMR spectra of the products. The utility of this method was immediately apparent when it was discovered that the diisopropylidene aminosugar derivative **8**, which could not be deprotected by treatment with 75% aqueous acetic acid,[10] underwent cleavage by this method.

Scheme 1



The successful removal of the 5,6-*O*-isopropylidene groups of the 1,2:5,6-di-*O*-isopropylidene carbohydrate derivatives with thiourea suggested application of this method for the cleavage of 1,3-dioxolanes derived from aldehydes and ketones. The dioxolane derivative **10** (Table 2) obtained from cyclohexanone was treated with thiourea acccording to the above procedure, and cyclohexanone was indeed obtained in 87% yield as evident from IR, NMR, and GC analyses. Similarly, the dioxolanes **11**−**16** (Table 2) were deprotected to give the corresponding carbonyl compounds in excellent yields. The time required for the cleavage of the dioxolanes listed in Table 2 was found to be shorter than that required for the diisopropylidene carbohydrate derivatives in Table 1.

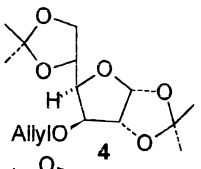
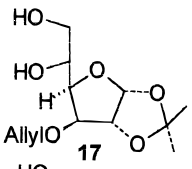
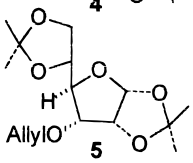
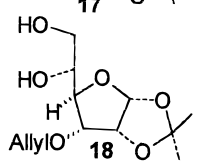
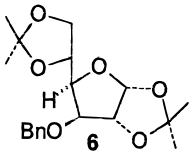
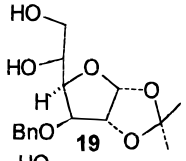
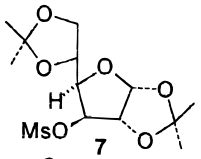
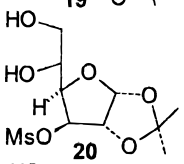
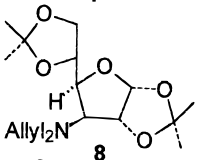
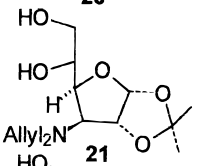
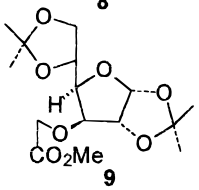
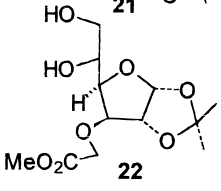
The time required for the completion of the cleavage reaction was found to depend on the concentration of thiourea. The extent of deprotection of the diisopropylidene derivative **4** was insignificant even after 20 h when a 0.25 M solution of thiourea in ethanol−water (1:1) was used. However, during the same period the use of a 0.5 M solution led to 50% conversion, whereas a 0.8 M solution of thiourea afforded the cleaved product in 77% yield. Interestingly, when the deprotection of **4** was carried out in a 5 M solution of thiourea in water the reaction was over in only 6 h and the 1,2-*O*-isopropylidene glucose derivative **17** was obtained in 75% yield.

Thiourea-mediated cleavage was also found to be effective for the removal of dimethyl acetal and THP ether, as evident from the efficient deprotection of ben-

(1) For general methods, see: Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis;* John Wiley and Sons: New York, 1991.
(2) Huet. F.; Lechevalier, A.; Pellet, M.; Conia, J. M. *Synthesis* **1978**, 63.
(3) Lipshutz, B. H.; Harvey, D. F. *Synth. Commun.* **1982**, *12*, 267.
(4) Marcantoni, E.; Nobili, F. *J. Org. Chem.* **1997**, *62*, 4183 and references therein.
(5) Sen, S. E.; Roach, S. L.; Boggs, J. K.; Ewing, G. J.; Magrath, J. *J. Org. Chem.* **1997**, *62*, 6684 and references therein.
(6) Kaur, G.; Trehan, A.; Trehan, S. *J. Org. Chem.* **1998**, *63*, 2365.
(7) Speziale, A. J. *Organic Synthesis*; Wiley: New York, 1963; Collect. Vol. IV, p 401.
(8) Meyer zu Reckendrof, W. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 967.
(9) The product was assigned the structure **2**[22] (Scheme 1) on the basis of ^{1}H and ^{13}C NMR analyses. The structure of **2** was independently verified by its preparation from **1** by removal of the 5,6-isopropylidene group by known hydrolytic procedure[10] followed by treatment of the resulting diol with NaOEt.
(10) (a) Shing, T. K. M.; Elsley, D. A.; Gillhouley, J. G. *J. Chem. Soc., Chem. Commun.* **1989**, 1280. (b) Yadav, J. S.; Chander, M. C.; Reddy, K. K. *Tetrahedron Lett.* **1992**, *33*, 135.

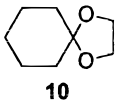
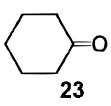
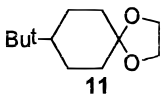
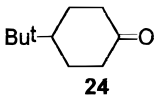
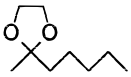
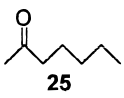
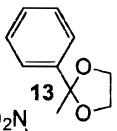
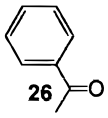
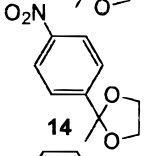
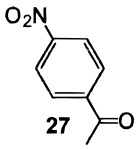
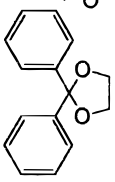
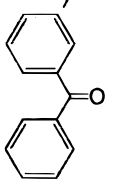
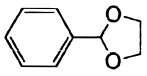
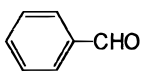
10.1021/jo981115c CCC: $18.00
Published on Web 07/02/1999

Table 1. Cleavage of 5,6-Isopropylidene Groups from 1,2:5,6-di-*O*-Isopropylidene Furanoses

Substrate[a]	Product[b]	Time[c] (h)	Yield[d] (%)
 **4**	 **17**	20	77
 **5**	 **18**	20	75
 **6**	 **19**	22	86
 **7**	 **20**	24	64
 **8**	 **21**	18	82
 **9**	 **22**	6	93

[a] 1,2:5,6 di-*O*-isopropylidene derivatives **4**-**5**[15], **6**[16] and **7**[17] were prepared by known methods [b] products were characterised by IR, ^{1}H, ^{13}C NMR and EI mass spectra; products **17**[18] and **19**[16] were reported previously [c] reaction condition was refluxing substrates with 0.8 M thiourea in alcohol-water (1:1) [d] yields of products isolated by column chromatography.

Table 2. Deprotection of Ethylene Acetals by Thiourea

Substrate[a]	Product[b]	% GLC Yield (min)	Time (h)	Isolated Yield (%)
 **10**	 **23**	100 (15)	5	87
 **11**	 **24**	97 (15)	5	89
 **12**	 **25**	99 (15)	6	89
 **13**	 **26**	100 (15)	6	87
 **14**	 **27**	100 (20)	18	83
 **15**	 **28**	98 (20)	6	82
 **16**	 **29**	97 (15)	6	84

[a] ethylene acetals were prepared by known methods [19] and characterised by their IR and NMR spectra [b] products were characterised by IR and NMR spectra which were identical with those of authentic compounds.

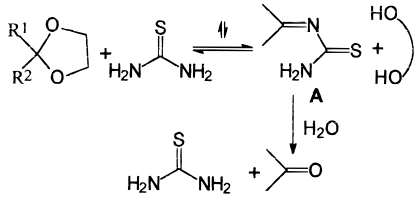
zaldehyde dimethyl acetal **31** (87%) and the THP ether of cyclohexanol **32** (86%) (Table 3). It was also established that under the condition of the cleavage reaction dioxolanes could be selectively deprotected in the presence of two important hydroxyl protecting groups, TBDMS and MOM, because the doubly protected derivatives **30** and **33** could be converted to the singly protected **34** and **36** without any noticeable deprotection of the other protecting groups (Table 3).

The mechanism of the above cleavage of dioxolanes by thiourea is not clear at present. The usual removal of the 5,6-*O*-isopropylidene group in the aforementioned carbohydrate derivatives generally requires a mildly acidic medium. The pH values of 0.25, 0.5, and 1.0 M thiourea in ethanol−water were found to be 6.6, 6.0, and 5.6, respectively, and that of 5.0 M thiourea in water was 5.4. The pH of the solvent medium without thiourea or of the individual solvents was found to be nearly 7.0. It was also observed that the deprotection did not proceed without thiourea in the reaction medium.[11] It is possible that under the condition of the reaction, the iminothiol tautomer of thiourea with an acidic thiol group is involved in the hydrolytic removal of the dioxolane moiety.[12]

In conclusion, thiourea-induced cleavage of 1,3-dioxolanes in ethanol−water provides an efficient and operationally simple procedure for deprotection of ethylene acetals, as well as the selective deprotection of 1,2:5,6-diisopropylidene carbohydrate derivatives or similar compounds. The method is expected to be one of choice for this purpose as a result of the essentially neutral reaction medium employed for the cleavage reaction.

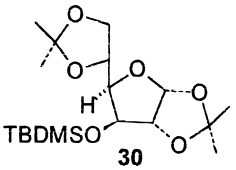
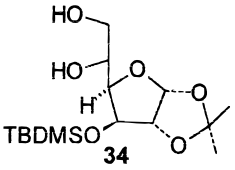
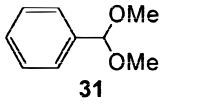
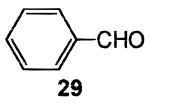
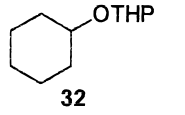
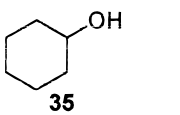
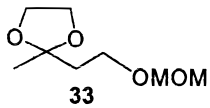
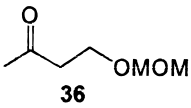
(11) In control experiments, the pH of a medium consisting of alcohol and water was adjusted to pH 6 by addition of acetic acid, and **6** (Table 1) and **15** (Table 2) were separately heated under reflux in this medium for 10 h and 6 h, respectively. Both were observed to be completely deprotected.

(12) Another possibility suggested by one of the referees is the involvement of the following equilibrium:



However, attempted reaction of the dioxolane **16** with thiourea in ethanol in the absence of water to isolate the corresponding *N*-carbamoyl imino intermediate **A** failed because the starting material remained unchanged, and the involvement of such a mechanism is inconclusive.

Table 3. Removal of Other Protecting Groups by Thiourea

Substrate[a]	Product[b]	Time (h)	Yield [c](%)
 **30**	 **34**	40	77
 **31**	 **29**	6	87
 **32**	 **35**	12	86
 **33**	 **36**	20	*d*

[a] substrates **30**[5], **31**[20], and **32**[21] were prepared according to literature procedure [b] products were characterised by ^{1}H NMR spectral analysis [c] isolated yield [d] The ^{1}H NMR spectrum of the product revealed the presence of **33** and **36** in a ratio of 1:3 (vide experimental)

Experimental Section

Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions at 300 and 75 MHz, respectively. Reactions were monitored by thin-layer chromatography using Merck 60 F_{254} precoated silica gel plate (no. 5554). Gas−liquid chromatography was performed using a HP-5890 series II instrument with HP-1 (megabore) capillary column (30 m × 0.53 mm × 0.88 μm) fitted with FID, and quantitation was done using HP integrator (HP 3396A). Silica gel of mesh size 60−120 (SRL, India) was used for column chromatography. Organic extracts were dried over anhydrous sodium sulfate. Alcohol was distilled from calcium oxide prior to use. Solvents were removed in a rotary evaporator under reduced pressure. Thiourea was crystallized from dehydrated alcohol.

3-Deoxy-3-*N*,*N*-diallylamino-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (8). Anhydrous K_2CO_3 (3.4 g, 24.6 mmol) and allyl bromide (3 mL) were added at 25 °C to a stirred solution of 3-deoxy-3-amino-1,2:5,6-di-*O*-isopropylideneglucofuranose[13] (2.54 g, 9.8 mmol) in dry acetone (50 mL), and stirring was continued at 50 °C for 20 h. Filtration of the mixture and removal of solvent from the filtrate afforded a syrupy residue, which was chromatographed on silica gel (hexanes−ethyl acetate, 19:1) to give **8** as a syrupy liquid (3.1 g, 93%): $[\alpha]^{24}_D$ −24.6 (*c* 1.0, $CHCl_3$); IR (neat) 2984, 1642, 1455, 1376, 1251, 1213, 1165, 1071 cm^{-1}; ^{1}H NMR δ 5.81 (m, 3H), 5.32−5.11 (m, 4H), 4.72 (d, J = 3.6 Hz, 1H), 4.30 (m, 1H), 4.10 (m, 2H), 3.97 (m, 1H), 3.46 (d, J = 4.8 Hz, 1H), 3.40 (bd, J = 13.2 Hz, 2H), 3.03 (dd, J = 14.7, 7.2 Hz, 2H), 1.50 (s, 3H), 1.41 (s, 3H), 1.36 (s, 3H), 1.31 (s, 3H); ^{13}C NMR δ 134.2 (d), 116.2 (t), 109.8 (s), 109.1 (s), 103.5 (d), 80.1 (d), 78.8 (d), 71.1 (d), 66.0 (t), 64.2 (d), 52.6 (t), 25.3 (q), 25.0 (q), 24.0 (q), 23.7 (q); MS (EI) *m*/*z* 339 (M^+), 324 (M^+ − 15), 298, 240, 169. Anal. Calcd for $C_{18}H_{29}O_5N\cdot H_2O$: C, 60.46; H, 8.74; N, 3.92; Found: C, 60.60; H, 8.47; N, 3.57.

3-*O*-Carbomethoxymethyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (9). 1,2:5,6-di-*O*-isopropylidene glucose[14] (5 g, 19.2 mmol) was added in portions to a suspension of NaH (1.6 g, 40% suspension in mineral oil), prewashed with hexane (2 × 5 mL) and dried under vacuum, in THF (50 mL) and cooled to 0 °C. After the mixture was stirred for 30 min, methylbromoacetate (3 mL, 28.8 mmol) was added, and the reaction mixture was heated under reflux for 15 h. After the completion of the reaction as revealed by TLC, the reaction mixture was poured onto ice and extracted with $CHCl_3$ (3 × 25 mL). The combined organic layer was washed with water (3 × 25 mL), dried, and concentrated. The syrupy residue solidified on trituration with cyclohexane, and crystallization from cyclohexane gave **9** as a colorless solid (4.5 g, 60%): mp 102−103 °C; $[\alpha]^{24}_D$ − 3.9 (*c* 2.3, $CHCl_3$); IR (KBr) 2988, 1737, 1443, 1382, 1225, 1139, 1070, 1016, 883, 852, 697 cm^{-1}; ^{1}H NMR δ 5.90 (d, J = 3.6 Hz, 1H), 4.71 (d, J = 3.6 Hz, 1H), 4.36−4.29 (m,1H), 4.26 (s, 2H), 4.14−4.09 (m, 2H), 4.03−3.96 (m, 2H), 3.77 (s, 3H), 1.49 (s, 3H), 1.42 (s, 3H), 1.35 (s, 3H), 1.32 (s, 3H); ^{13}C NMR δ 171.0 (s), 112.2 (s), 109.4 (s), 105.6 (d), 84.1 (d), 83.7 (d), 81.5 (d), 73.0 (d), 68.7 (t), 67.7 (t), 52.3 (q), 27.2 (2q), 26.6 (q), 25.7 (q); MS (EI) *m*/*z* 317 (M^+ − 15), 303, 259, 245, 236, 199. Anal. Calcd for $C_{15}H_{24}O_8$: C, 54.20; H, 7.27. Found: C, 53.45; H, 7.21.

2-(2-Methoxymethyloxy)ethyl-2-methyl-1,3-dioxolane (33). NaH (0.5 g) was added at 0 °C to a stirred solution of 2-(2-hydroxy)ethyl-2-methyl-1,3-dioxolane[19b] (1.0 g, 7.5 mmol) in THF (20 mL). Methoxymethyl chloride (1 mL) was added to this, and the mixture was stirred for 1 h. Excess NaH was destroyed by the addition of crushed ice, and the residue obtained after removal of THF was extracted with ether (3 × 20 mL). The combined organic layer was washed with water (3 × 20 mL) and dried, and removal of solvent gave **33** as a colorless syrup (1.1 g, 82%): IR (neat) 2954, 1442, 1216 cm^{-1}; ^{1}H NMR δ 4.74 (s, 1H), 4.72 (s, 1H), 3.95 (m, 4H), 3.74 (t, 2H), 3.39 (s, 3H), 1.99 (t, 2H), 1.34 (s, 3H); ^{13}C NMR δ 108.7 (s), 96.3 (t), 64.4 (t, 2C), 63.5 (t), 54.9 (q), 38.7 (t), 24.1 (q); MS (EI) *m*/*z* 175 (M^+ − 1), 161 (M^+ − 15), 114, 101, 87, 71.

General Method for Cleavage of 1,3-Dioxolanes by Thiourea. The general method is illustrated by the cleavage of the 1,2:5,6-di-*O*-isopropylidene carbohydrate derivative **8**.

3-Deoxy-3-*N*,*N*-diallylamino-1,2-*O*-isopropylidene-α-D-glucofuranose (21). A solution of **8** (1.15 g, 3.39 mmol) in 0.85 M thiourea solution in (1:1) EtOH−H_2O (20 mL) was heated under reflux for 18 h. The reaction mixture was concentrated under reduced pressure, and the residue was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layer was washed with water (3 × 20 mL), dried, and then concentrated to give a brown syrup, which on chromatography over silica gel (ethyl acetate) gave the diol **21** as a colorless syrup (0.84 g, 82%): $[\alpha]^{25}_D$ −16.0 (*c* 0.6, $CHCl_3$); IR (neat) 3446 (broad), 2982, 1643, 1378, 1216, 1166, 1066 cm^{-1}; ^{1}H NMR δ 5.86 (d, J = 3.9 Hz, 1H), 5.78 (m, 2H), 5.24 (m, 4H), 4.77 (d, J = 3.9 Hz, 1H), 4.24(m,1H), 3.86 (m, 2H), 3.67 (m, 1H), 3.56 (d, J = 5.9 Hz, 1H), 3.40 (dd, J = 13.8, 5.4 Hz, 2H), 2.97 (dd, J = 13.8, 8.1 Hz, 2H), 1.49 (s, 3H), 1.25 (s, 3H); ^{13}C NMR δ 134.7 (d), 119.3 (t), 111.5 (s), 106.1 (d), 79.3 (d), 71.5 (d), 67.1 (d), 65.0 (t), 55.0 (t), 27.1 (s), 26.4 (s); MS (EI) *m*/*z* 299 (M^+), 297 (M^+ − 2), 284 (M^+ − 15), 268, 258, 199. Anal. Calcd for $C_{15}H_{25}O_5N$: C, 60.16; H, 8.42; N, 4.68. Found: C, 59.46; H, 8.08; N, 5.09.

All other dioxolanes were cleaved according to the above procedure. For the dioxolanes derived from aldehydes and ketones, essentially the same procedure was adopted, except extraction was done with hexane or ether and the purification by chromatography was not necessary.

3-*O*-Allyl-1,2-isopropylidene-α-D-allofuranose (18). Oil; $[\alpha]^{25}_D$ +116.3 (*c* 0.6, $CHCl_3$); IR (Neat) 3446, 2930, 1647, 1455, 1379 cm^{-1}; ^{1}H NMR δ 6.03−5.92 (m, 1H), 5.78 (d, J = 3.6 Hz, 1H), 5.29 (m, 2H), 4.65 (t, J = 3.9 Hz, 1H), 4.27 (dd, J = 6.3, 5.4 Hz, 1H), 4.07 (m, 2H), 3.91 (dd, J = 8.7, 4.2 Hz, 1H), 3.73 (m,

(13) Brimacombe, J. S.; Bryan, J. G. H.; Husain, A.; Stacey, M.; Tolley, M. S. *Carbohydr. Res.* **1967**, *3*, 318.
(14) Schimdt, O. T. *Methods in Carbohydrate Chemistry*; Academic Press Inc.: New York and London, 1963; Vol. II, p 318.
(15) Bhattacharjee, A.; Chattopadhyay, P.; Kundu, A. P.; Mukhopadhyay, R.; Bhattacharjya, A. *Indian J. Chem.* **1996**, *35B*, 69.
(16) Brimacombe, J. S.; Ching, O. A. *Carbohydr. Res.* **1968**, *8*, 82.
(17) de Belder, A. N. *Adv. Carbohydr. Chem.* **1977**, *34*, 179.
(18) Smith, A. B., III; Rivero, R. A.; Hale, K. J.; Vaccaro, H. A. *J. Am. Chem. Soc.* **1991**, *113*, 2092.
(19) (a) Daignault, R. A.; Eliel, E. L. *Organic Synthesis*; Wiley: New York, 1973; Collect. Vol. V, pp 303−306. (b) Meskens, F. A. J. *Synthesis* **1981**, 501.
(20) McMurry, J. E.; Erion, M. D. J. *Am. Chem. Soc.* **1985**, *107*, 2712.
(21) Miyashita, N.; Yoshikoshi, A.; Grieco, P. A. *J. Org. Chem.* **1977**, *42*, 3772.
(22) Buchanan, J. G.; Oakes, E. M. *Carbohydr. Res.* **1965**, *1*, 242.

1H), 2.53 (d, J = 3.6 Hz, 1H), 2.48 (dd, J = 7.5, 6.0 Hz, 1H), 1.59 (s, 3H), 1.36 (s, 3H); ^{13}C NMR δ 134.2 (d), 119.1 (t), 113.6 (s), 104.5 (d), 79.3 (d), 77.8 (d), 77.7 (d), 71.7 (t), 71.3 (d), 63.4 (t), 27.1 (q), 26.9 (q); MS (EI) m/z 245 ($M^+ - 15$), 199, 141, 127. Anal. Calcd for $C_{12}H_{20}O_6$: C, 55.35; H, 7.74. Found: C, 54.11; H, 7.47.

3-*O*-Methanesulfonyl-1,2-isopropylidene-α-D-glucofuranose (20). Oil; $[\alpha]^{25}_D$ −49.2 (*c* 1.2, $CHCl_3$); IR (neat) 3490, 2984, 2930, 1360, 1217, 1175, 1080, 1021, 949, 886, 784, 727 cm^{-1}; ^{1}H NMR δ 5.95 (d, J = 3.6 Hz, 1H), 5.12 (d, J = 2.7 Hz, 1H), 4.75 (d, J = 3.6 Hz, 1H), 4.25 (dd, J = 9.0, 3.0 Hz, 1H), 3.89 (dd, J = 12.9, 5.5 Hz, 1H), 3.75 (m, 2H), 3.15 (s, 3H), 2.93 (d, J = 5.4 Hz, 1H), 2.13 (bm, 1H), 1.51 (s, 3H), 1.32 (s, 3H); ^{13}C NMR δ 113.4 (s), 105.7 (d), 84.0 (d), 82.7 (d), 79.1 (d), 68.9 (d), 64.5 (t), 38.8 (q), 27.1 (q), 26.6 (q); MS (EI) m/z 283 ($M^+ - 15$), 237, 209, 188. Anal. Calcd for $C_{10}H_{18}O_8S$: C, 40.24; H, 6.08; Found: C, 40.14; H, 6.16

3-*O*-Carbomethoxymethyl-1,2-isopropylidene-α-D-glucofuranose (22). Oil; $[\alpha]^{25}_D$ −76.3 (*c* 0.6, $CHCl_3$); IR (neat) 3446, 2934, 1738, 1381, 1237, 1131, 1086, 1017 cm^{-1}; ^{1}H NMR δ 5.94 (d, J = 3.3 Hz, 1H), 4.73 (bs, 1H), 4.50 (d, J = 3.3 Hz, 1H), 4.36−3.68 (m, 7H), 3.80 (s, 3H), 1.48 (s, 3H), 1.31 (s, 3H); ^{13}C NMR δ 172.8 (s), 112.4 (s), 105.6 (d), 83.6 (d), 82.3 (d), 80.4 (d), 69.1 (d), 66.1 (t), 64.7 (t), 53.0 (q), 27.1 (q), 26.7 (q); MS (EI) m/z 292 (M^+), 277 ($M^+ - 15$), 231, 216, 204. Anal. Calcd for $C_{12}H_{20}O_8$: C, 49.29; H, 6.90. Found: C, 49.22; H, 6.86.

4-Methoxymethyloxybutane-2-one (36). The deprotection of **33** (0.2 g, 1.14 mmol) by the above method gave after 20 h a colorless syrup (130 mg), which was found from the analysis of the ^{1}H NMR spectrum of the mixture to consist of **33** and **36** in a ratio of 1:3: IR (neat, mixture) 2944, 1714, 1458, 1355, 1216, 1114, 992 cm^{-1}; ^{1}H NMR (mixture, data for **36**) δ 4.75 (s, 1H), 4.72 (1H), 3.83 (t, 2H), 3.38 (s, 3H), 2.70 (t, 2H), 2.18 (s, 3H).

Deprotection of 4 with 5 M Thiourea Solution. Compound **4** (0.1 g, 0.33 mmol) was heated under reflux with aqueous 5 M thiourea solution (5 mL) for 6 h. After the completion of the reaction as revealed by TLC, the reaction mixture was extracted with $CHCl_3$ (3 × 15 mL), and the combined organic layer was washed with water (3 × 15 mL), dried, and concentrated to give a syrupy liquid. Chromatography of the material over silica gel (ethyl acetate) furnished the diol **17** as a colorless syrup (0.065 g, 75%).

Acknowledgment. A.B. is grateful to DST, India for financial assistance. The award of a Senior Research Fellowship by UGC, India to S.M. is gratefully acknowledged. Thanks are due to Dr. V. S. Giri and Dr. Ranjan Mukhopadhyay for NMR analysis.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra of **8**, **9**, **18**, **20**, **21**, **22**, **33**, and **36**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO981115C