The reaction of Diol Thiocarbonates with Methyl Iodide: a Synthesis of 6-Deoxy-sugars

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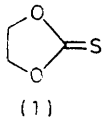
Diol thiocarbonates react with methyl iodide to form *S*-methyl iodo-alcohol thiocarbonates of stereochemistry at the iodine-bearing carbon atom opposite to that of the starting material. Reduction of *S*-methyl *vic*-iodo-alcohol thiocarbonates with zinc or chromium(II) acetate affords mixtures of alkene and *S*-methyl alcohol thiocarbonate, whereas reduction with chromium(II) acetate in the presence of a thiol affords only the latter. Hydrolysis then gives the alcohol. The reactions of a *vic*-diol thiocarbonate with methyl chloro- and fluoro-formate have been studied. The application of thiocarbonate cleavage reactions in carbohydrate chemistry has been adumbrated.

JONES and ANDREADES [1] treated *OO*-ethylene thiocarbonate (1) with methyl iodide to form, through the expected intermediate salt (2), *O*-2-iodoethyl *S*-methyl thiocarbonate (3a). We have examined briefly the application of this reaction in carbohydrate chemistry. During our work Vedejs and Wu [2] reported the reactions of several alicyclic 1,2-diol thiocarbonates with methyl or isopropyl iodide to form the corresponding iodo-thiocarbonates. The more highly reactive iodo-thiocarbonate (3b) underwent a non-stereospecific elimination at the elevated reaction temperature to form *trans*-stilbene in good yields; in all other cases (4a—c) a reduction step was necessary to convert the iodo-thiocarbonate into the corresponding alkene (5a—c) in moderate yield.

Our own investigation was concerned with the synthesis of 6-substituted sugars. We envisaged the conversion of the diol (6a), *via* the thiocarbonate (7) and



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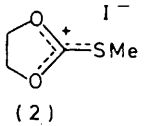

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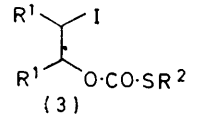
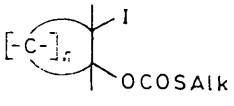


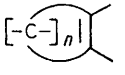
(3)

a; R^1 = H, R^2 = Me
b; R^1 = Ph, R^2 = Pr^i



(4)

a; *n* = 2
b; *n* = 4
c; *n* = 6

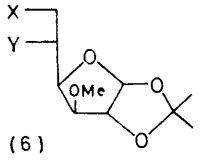


(5)

a; *n* = 2
b; *n* = 4
c; *n* = 6

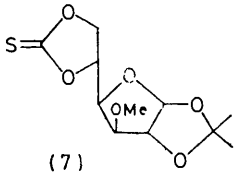
iodo-thiocarbonate (6b), into the alkene (8) and into the 6-deoxy-sugar (6c).

1,2-*O*-Isopropylidene-3-*O*-methyl-α-D-glucofuranose (6a), prepared by methylation (sodium hydride–methyl iodide in tetrahydrofuran) followed by selective acidic hydrolysis, was refluxed with di-imidazol-1-yl thioketone [3,4] in dry tetrahydrofuran to form 1,2-*O*-isopropylidene-3-*O*-methyl-5,6-*O*-thiocarbonyl-α-D-glucofuranose (7). The thiocarbonate (7) was then transformed



(6)

a; X = Y = OH
b; X = I, Y = O·CO·SMe
c; X = H, Y = OH
d; X = H, Y = O·CO·SMe
e; X = Cl, Y = O·CO·SMe
f; X = F, Y = O·CO·SMe



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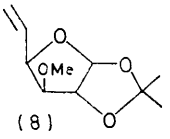


(8)

quantitatively into 6-deoxy-6-iodo-1,2-*O*-isopropylidene-3-*O*-methyl-5-*O*-(methylthio)carbonyl-α-D-glucofuranose (6b) by overnight refluxing in methyl iodide. None of the isomeric 5-iodo-6-*O*-(methylthio)carbonyl compound was detected.

Similarly, methyl 2,3-di-*O*-methyl-α-D-glucopyranoside was converted into 6-deoxy-6-iodo-2,3-di-*O*-methyl-4-*O*-(methylthio)carbonyl-α-D-glucopyranoside without characterisation of the intermediate thiocarbonate. This shows that the reaction sequence can be applied also to 1,3-diols.

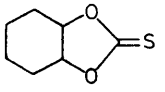
The iodo-thiocarbonate (6b) was unaffected by tetra-n-butylammonium iodide in refluxing acetonitrile or anhydrous tin(II) chloride in pyridine. Reduction with activated zinc dust or zinc couple (copper, mercury, or

[1] F. N. Jones and S. Andreades, *J. Org. Chem.*, 1969, **34**, 3011.
[2] E. Vedejs and E. S. C. Wu, *J. Org. Chem.*, 1974, **39**, 3641.
[3] H. A. Staab and G. Walther, *Annalen*, 1962, **657**, 98.
[4] T. J. Pullukat and G. Urry, *Tetrahedron Letters*, 1967, 1953.

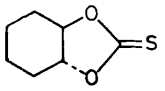
silver [5]), in either refluxing ethanol or acetic acid, produced mixtures of 5,6-dideoxy-1,2-*O*-isopropylidene-3-*O*-methyl-α-D-*xylo*-hex-5-enofuranose (8) and 6-deoxy-1,2-*O*-isopropylidene-3-*O*-methyl-5-*O*-(methylthio)-carbonyl-α-D-glucofuranose (6d). The highest yield of isolated alkene (8) was 50%. The thiocarbonate (7) in refluxing trimethyl phosphite [6,7] was converted into the alkene (8) [8] in 85% yield.

Reduction of the iodo-thiocarbonate (6b) with chromium(II) acetate in refluxing ethanol or dimethylformamide (100 °C) again afforded mixtures of the alkene (8) and the thiocarbonate (6d). The highest yield of the alkene was 40%. However, addition of butane-1-thiol to the chromium(II) acetate–dimethylformamide system [9] allowed a nearly quantitative conversion of the iodo-thiocarbonate (6b) into the thiocarbonate (6d). Hydrolysis with sodium methoxide in methanol then converted the thiocarbonate (6d) into 6-deoxy-1,2-*O*-isopropylidene-3-*O*-methyl-α-D-glucofuranose (6c) [10] in quantitative yield.

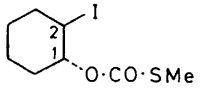
The stereochemistry of the reaction of 1,2-diol thiocarbonates with methyl iodide was investigated as follows. *cis*- and *trans-OO*-Cyclohexane-1,2-diyl thiocarbonate, (9) and (10), were prepared according to the method for compound (7). In refluxing methyl iodide the *cis*-thiocarbonate (9) was converted exclusively into *O*-(*trans*-2-iodocyclohexyl) *S*-methyl thiocarbonate (11),



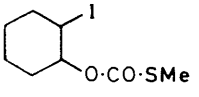
(9)



(10)



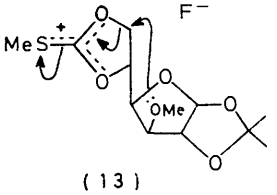
(11)



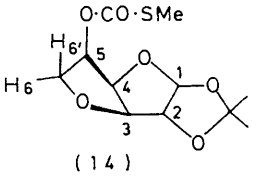
(12)

whereas the *trans*-thiocarbonate (10) was converted into the corresponding *cis*-iodo-thiocarbonate (12). Assignment of the relative stereochemistry of compounds (11) and (12) was based on n.m.r. measurements, compound (11) having $J_{1,2}$ 10 Hz and compound (12) $J_{1,2}$ 2.5 Hz. Thus the ring-opening reaction of compounds (9) and (10) with methyl iodide proceeds stereospecifically and with inversion of configuration at one carbon centre, an observation also made by Vedejs and Wu [2] in the case of an *OO*-cyclobutane-1,2-diyl thiocarbonate.

In an attempt to extend the utility of the thiocarbonate–methyl iodide reaction the thiocarbonate (7) was heated with the ' masked ' alkyl halide, methyl chloroformate. Apart from unchanged starting material, the product consisted of 6-chloro-6-deoxy-1,2-*O*-isopropylidene-3-*O*-methyl-5-*O*-(methylthio)carbonyl-α-D-glucofuranose (6e) (62%). Presumably the reaction proceeds through the chloride salt corresponding to the salt (2), the chloride ion being formed by concomitant loss of carbon dioxide from the chloroformate anion. The corresponding reaction of the thiocarbonate (7) with methyl fluoroformate,[11,12] designed to produce the 6-deoxy-6-fluoro-compound (6f), was not successful. Initial *S*-methylation to form the fluoride salt (13) was presumably followed by an intramolecular attack of the methoxy-group on the electrophilic C-6. *O*-Demethylation by the weakly nucleophilic fluoride ion then formed 3,6-anhydro-1,2-*O*-isopropylidene-5-*O*-(methylthio)-carbonyl-α-D-glucofuranose (14). The identification of



(13)



(14)

compound (14) was unambiguous in that H-6 and H-6', held rigid in a furanose ring system, gave rise in the n.m.r. spectrum to an AB quartet split further into eight lines by H-5. Also H-6' was significantly deshielded relative to H-6 by the adjacent methylthiocarbonyl function. The anhydro-sugar (14) was shown not to be an intermediate in the conversion of the thiocarbonate (7) into the iodo-thiocarbonate (6b) by its failure to react with refluxing methyl iodide.

The ring opening reactions of diol thiocarbonates may find useful application in carbohydrate chemistry.

EXPERIMENTAL

M.p.s were taken with a Kofler hot-stage apparatus. N.m.r. spectra were taken with a Varian T-60 or HA-100 instrument (tetramethylsilane as internal standard). T.l.c. (Merck GF_{254}) and column chromatography were performed on silica gel with the appropriate ether–light petroleum mixtures as eluants. All evaporations were carried out with a rotary evaporator under vacuum.

1,2-O-*Isopropylidene*-3-O-*methyl*-5,6-O-*thiocarbonyl*-α-D-*glucofuranose* (7).—The diol (6a) (10.1 g) was dissolved in tetrahydrofuran (90 ml.) and di-imidazol-1-yl thioketone (8.40 g) was added. The mixture was refluxed (0.5 h) under nitrogen and then evaporated. The solid residue was dissolved in dichloromethane (400 ml), washed with cold hydrochloric acid (50 ml; 2N) and cold water (10 ml), and dried ($MgSO_4$). Evaporation and crystallisation yielded the *thiocarbonate* (7) (9.45 g, 80%), m.p. 111.5—112° (from ethyl acetate–light petroleum), $[\alpha]_D^{23}$ −46.5° (*C* 1.0 in $CHCl_3$), $\lambda_{max.}$ (EtOH) 234 nm (ε 3 300), τ($CDCl_3$) 4.06 (1 H, d, H-1, $J_{1,2}$ 3.5 Hz), 4.63—4.98br (1 H, m), 5.12—5.49

[5] J. M. Conia and C. Girard, *Tetrahedron Letters*, 1973, 2767.
[6] E. J. Corey and R. A. E. Winter, *J. Amer. Chem. Soc.*, 1963, **85**, 2677.
[7] D. Horton and W. N. Turner, *Tetrahedron Letters*, 1964, 2531.
[8] J. S. Josan and F. W. Eastwood, *Carbohydrate Res.*, 1968, **7**, 161.
[9] D. H. R. Barton and N. K. Basu, *Tetrahedron Letters*, 1964, 3151; D. H. R. Barton, N. K. Basu, R. H. Hesse, F. S. Morehouse, and M. M. Pechet, *J. Amer. Chem. Soc.*, 1966, **88**, 3016.
[10] E. Vischer and T. Reichstein, *Helv. Chim. Acta*, 1944, **27**, 1332.
[11] C. W. Tullock and D. D. Coffman, *J. Org. Chem.*, 1960, **25**, 2016.
[12] G. A. Olah and J. Welch, *Synthesis*, 1974, 654.

(4 H, m), 6.07 (1 H, d, H-3, $J_{2,3}$ 0.0, $J_{3,4}$ 4.0 Hz), 6.58 (3 H, s, OCH_3), and 8.48 and 8.65 (6 H, d, CMe_2) (Found: C, 47.7; H, 5.85; S, 11.75. $C_{11}H_{16}O_6S$ requires C, 47.8; H, 5.85; S, 11.6%).

6-*Deoxy*-6-*iodo*-1,2-O-*isopropylidene*-3-O-*methyl*-5-O-(*methylthio*)*carbonyl*-α-D-*glucofuranose* (6b).—The thiocarbonate (7) (2.76 g) was refluxed (20 h) under nitrogen with methyl iodide (15 ml). Evaporation yielded a solid which was dissolved in dichloromethane (100 ml); the solution was washed with sodium thiosulphate and water, dried, and evaporated. Recrystallisation yielded the *iodo-thiocarbonate* (6b) (4.00 g, 95%), m.p. 85—86° (from methanol–water), $[\alpha]_D^{23}$ −60.9° (*c* 1.0 in $CHCl_3$), $\lambda_{max.}$ (EtOH) 211 (ε 2 400) and 253 nm (ε 400), $\nu_{max.}$ (Nujol) 1 715 cm^{-1} (C=O), τ ($CDCl_3$) 4.20 (1 H, d, H-1, $J_{1,2}$ 3.5 Hz), 5.08—5.33 (1 H, m, H-5), 5.51 (1 H, d, H-2, $J_{2,3}$ 0.0 Hz), 5.73 and 5.82 (1 H, ABq, H-4, $J_{3,4}$ 3.0, $J_{4,5}$ 9.0 Hz), 6.24—6.56 (3 H, m, H-3, -6, and -6'), 6.69 (3 H, s, OCH_3), 7.69 (3 H, s, SCH_3), and 8.53 and 8.72 (6 H, d, CMe_2) (Found: C, 34.65; H, 4.65; I, 30.2; S, 7.5. $C_{12}H_{19}IO_6S$ requires C, 34.45; H, 4.68; I, 30.35 S, 7.65%).

Reduction of the Iodo-thiocarbonate (6b) *with Zinc*.—The iodo-thiocarbonate (6b) (420 mg) was dissolved in solvent (refluxing ethanol or acetic acid; 4 ml) and treated (12 h) with zinc (activated dust, or as couple with copper, mercury, or silver; 650 mg). The zinc was filtered off and washed with ether (3 × 10 ml) and the combined filtrates were evaporated. A solution of the residual oil in ether (50 ml) was washed with dilute hydrochloric acid and sodium hydrogen carbonate, dried, and evaporated to yield an oil; n.m.r. ($CDCl_3$) showed the presence of the alkene (8) and the thiocarbonate (6d) in various proportions. High-vacuum distillation then allowed isolation of the pure alkene (8) (100 mg, 50%).

5,6-*Dideoxy*-1,2-0-*isopropylidene*-3-O-*methyl*-α-D-xylo-*hex*-5-*enofuranose* (8).—The thiocarbonate (7) (275 mg) was refluxed (24 h) under nitrogen in trimethyl phosphite (2 ml) and the mixture was evaporated. A solution of the residue in ether (50 ml) was washed with water, dried, and evaporated to yield an oil. Chromatography then afforded the alkene (8) (170 mg, 85%), identical with material prepared by the method of Josan and Eastwood.[8]

Reduction of the Iodo-thiocarbonate (6b) *with Chromium*(II) *Acetate*.—To the iodo-thiocarbonate (6b) (840 mg) in solvent (refluxing ethanol or dimethylformamide at 100 °C; 6 ml) was added chromium(II) acetate (1.2 g), and the mixture was stirred (12 h) under nitrogen. Evaporation and trituration with ether (100 ml) gave, after evaporation, a pale green oil. Chromatography then yielded a colourless oil; n.m.r. ($CDCl_3$) showed the presence of the alkene (8) and the thiocarbonate (6d) in equal proportions. High-vacuum distillation allowed isolation of the pure alkene (8) (160 mg, 40%).

6-*Deoxy*-1,2-O-*isopropylidene*-3-O-*methyl*-5-O-(*methylthio*)-*carbonyl*-α-D-*glucofuranose* (6d).—The iodo-thiocarbonate (6b) (1.25 g) was dissolved in dimethylformamide (6 ml) and butane-1-thiol (1.6 ml) and chromium(II) acetate (1.7 g) were added. The mixture was stirred (17 h; 60 °C) under nitrogen, evaporated, and triturated with ether; evaporation then left an oil which was chromatographed and distilled under high vacuum to yield the *thiocarbonate* (6d) (790 mg, 90%), $[\alpha]_D^{23}$ −26.3° (*c* 1.0 in $CHCl_3$), $\lambda_{max.}$ (EtOH) 212 nm (ε 1 600), $\nu_{max.}$ 1 725 cm^{-1} (C=O), τ ($CDCl_3$) 4.16 (1 H, d, H-1, $J_{1,2}$ 3.5 Hz), 4.64—4.97 (1 H, octet, H-5, J_{5,CH_3} 6.5 Hz), 5.49 (1 H, d, H-2, $J_{2,3}$ 0.0 Hz), 5.89 and 5.98 (1 H, ABq, H-4, $J_{3,4}$ 2.5, $J_{4,5}$ 9.0 Hz), 6.32 (1 H, d, H-3), 6.68 (3 H, s, OCH_3), 7.70 (3 H, s, SCH_3), 8.53 and 8.72 (6 H, d, CMe_2), and 8.62 (3 H, d, CH_3) (Found: C, 49.05; H, 7.05; S, 10.75. $C_{12}H_{20}O_6S$ requires C, 49.3; H, 6.9; S, 10.95%).

6-*Deoxy*-1,2-O-*isopropylidene*-3-O-*methyl*-α-D-*glucofuranose* (6c).—The thiocarbonate (6d) (450 mg) in methanol (2 ml) was added to sodium (70 mg) in methanol (2 ml) under nitrogen, and the mixture was kept at room temperature (12 h). Acetic acid was then added (pH 7), the solution evaporated, and the residue dissolved in ether (50 ml). The solution was washed with aqueous sodium hydrogen carbonate, dried, and evaporated to yield an oil. Chromatography and high-vacuum distillation yielded the alcohol (6c) (335 mg, 100%), $[\alpha]_D^{23}$ −64.4° (*c* 1.0 in $CHCl_3$) {lit.,[10] $[\alpha]_D^{16}$ −51.3° (*c* 3.627 in Me_2CO)}, $\nu_{max.}$ 3 450br cm^{-1} (OH), τ ($CDCl_3$) 4.13 (1 H, d, H-1, $J_{1,2}$ 4.0 Hz), 5.47 (1 H, d, H-2, $J_{2,3}$ 0.0 Hz), 5.82—6.22 (3 H, m, H-3, -4, and -5), 6.60 (3 H, s, OCH_3), 7.52br (1 H, s, OH), 8.53 and 8.69 (6 H, d, CMe_2), and 8.71 (3 H, d, CH_3, $J_{5,Me}$ 6.0 Hz).

cis-OO-*Cyclohexane*-1,2-*diyl Thiocarbonate* (9).—By the procedure described for preparing the thiocarbonate (7), *cis*-cyclohexane-1,2-diol [13] (2.32 g) and di-imidazol-1-yl thioketone (3.92 g) in refluxing tetrahydrofuran (40 ml; 4 h) yielded, after work-up, column chromatography, and high vacuum distillation, the thiocarbonate (9) (2.60 g, 82%), identical with material prepared by Kardouche and Owen.[14]

trans-OO-*Cyclohexane*-1,2-*diyl Thiocarbonate* (10).—*trans*-Cyclohexane-1,2-diol [15] (2.32 g) and di-imidazol-1-yl thioketone (3.92 g) in refluxing tetrahydrofuran (50 ml; 4 h) yielded, after work-up and column chromatography, the crystalline thiocarbonate (10) (1.75 g, 56%), m.p. 108.5—110° (from ether–light petroleum) (lit.,[16] 109°).

O-(trans-2-*Iodocyclohexyl*) S-*Methyl Thiocarbonate* (11).—By the procedure for the preparation of the iodo-thiocarbonate(6b), the thiocarbonate (9) (850 mg) in refluxing (24 h) methyl iodide (5 ml) yielded, after work-up, colour chromatography, and high-vacuum distillation, the *iodo-thiocarbonate* (11) (1.55 g, 95%), $\lambda_{max.}$ (EtOH) 215 (ε 1 700) and 258 nm (ε 550), $\nu_{max.}$ (film) 1 715 cm^{-1} (C=O), τ($CDCl_3$) 4.88—5.14br (1 H, sextet, H-1, $J_{1,2}$ 10 Hz), 5.76—6.03 (1 H, octet, H-2), and 7.70 (3 H, s, SCH_3) (all other signals constituted the methylene envelope) (Found: C, 31.85; H, 4.5. $C_8H_{13}IO_2S$ requires C, 32.0; H, 4.35%).

O-(cis-2-*Iodocyclohexyl*) S-*Methyl Thiocarbonate* (12).—The thiocarbonate (10) (800 mg) in refluxing (18 h) methyl iodide (5 ml) yielded, after work-up, column chromatography, and high-vacuum distillation, the *iodo-thiocarbonate* (12) (1.10 g, 74%), $\lambda_{max.}$ (EtOH), 216 (ε 1600) and 256 nm (ε 600), $\nu_{max.}$ (film) 1 715 cm^{-1} (C=O), τ($CDCl_3$) 5.30—5.64br (2 H, m, H-1 and -2, $J_{1,2}$ 2.5 Hz), and 7.68 (3 H, s, SCH_3) (all other signals constituted the methylene envelope) (Found: C, 32.3; H, 4.3%).

6-*Chloro*-6-*deoxy*-1,2-O-*isopropylidene*-3-O-*methyl*-5-O-(*methylthio*)*carbonyl*-α-D-*glucofuranose* (6e).—The thiocarbonate (7) (280 mg) in methyl chloroformate (2 ml) was heated (100 °C) in a sealed tube (43 h). Evaporation and chromatography yielded crystalline *chloro-thiocarbonate* (6e) (200 mg, 62%), m.p. 81.5—82° (from methanol–water

[13] A. I. Vogel, 'Practical Organic Chemistry,' Longmans, London, 3rd edn., 1970, p. 895.
[14] N. G. Kardouche and L. N. Owen, *J.C.S. Perkin I*, 1975, 2186.
[15] Ref. 13, p. 894.
[16] T. J. Adley, A. K. M. Anisuzzaman, and L. N. Owen, *J. Chem. Soc.* (*C*), 1967, 807.

$[\alpha]_D^{23}$ −42.7° (*c* 1.1 in $CHCl_3$), $\lambda_{max.}$ (EtOH) 215 nm (ε 1600), $\nu_{max.}$ (Nujol) 1710 cm^{-1} (C=O), τ ($CDCl_3$) 4.12 (1 H, d, H-1, $J_{1,2}$ 3.5 Hz), 4.45—4.80 (1 H, m, H-5), 5.42 (1 H, d, H-2, $J_{2,3}$ 0.0 Hz), 5.52 and 5.67 (1 H, ABq, H-4, $J_{3,4}$ 3.5, $J_{4,5}$ 9.0 Hz), 5.83—6.40 (3 H, m, H-3, -6, and -6′), 6.59 (3 H, s, OCH_3), 7.61 (3 H, s, SCH_3), and 8.50 and 8.67 (6 H, d, CMe_2) (Found: C, 44.35; H, 5.9; Cl, 10.55; S, 9.6. $C_{12}H_{19}ClO_6S$ requires C, 44.1; H, 5.85; Cl, 10.85; S, 9.8%).

3,6-*Anhydro*-1,2-O-*isopropylidene*-5-O-(*methylthio*)*carbonyl*-α-D-*glucofuranose* (14).—(*a*) The thiocarbonate (7) (550 mg) in methyl fluoroformate (1 ml) was heated (65 °C) in a sealed tube (55 h). Ether (50 ml) was then added and the solution washed with aqueous sodium hydrogen carbonate and water, dried, and evaporated to yield an oil. Chromatography and high-vacuum distillation then yielded the *anhydro-sugar* (14) (250 mg, 46%), $[\alpha]_D^{20}$ 52.2° (*c* 0.32 in $CHCl_3$), $\nu_{max.}$ (film) 1725 cm^{-1} (C=O), τ ($CDCl_3$) 4.11 (1 H, d, H-1, $J_{1,2}$ 3.5 Hz), 4.73—4.94 (1 H, sextet, H-5), 5.08 (1 H, t, H-4, $J_{4,5}$ 4.5 Hz), 5.47 (1 H, d, H-2, $J_{2,3}$ 0.0 Hz), 5.54 (1 H, d, H-3, $J_{3,4}$ 4.0 Hz), 6.03 (1 H, d of ABd, H-6′, $J_{6,6'}$ 9.0, $J_{5,6'}$ 7.0 Hz), 6.28 (1 H, d of ABd, H-6, $J_{5,6}$ 6.5 Hz), 7.70 (3H, s, SCH_3), and 8.56 and 8.71 (6 H, d, CMe_2) (Found: C, 47.55; H, 5.85; S, 11.3. $C_{11}H_{16}O_6S$ requires C, 47.8; H, 5.85; S, 11.6%), *m/e* 261 ($M^+ - 15$).

(*b*) The anhydro-sugar (14) (28 mg) was heated in refluxing methyl iodide (0.5 ml; 24 h). T.l.c. showed no reaction and only starting material (20 mg) was isolated.

Methyl 6-*Deoxy*-6-*iodo*-2,3-*di*-O-*methyl*-4-O-(*methylthio*)*carbonyl*-α-D-*glucopyranoside*.— Methyl 2,3-di-*O*-methyl-α-D-glucopyranoside [17] (3.33 g) in tetrahydrofuran (30 ml) was added dropwise with stirring to di-imidazol-1-yl thioketone (2.94 g) in refluxing tetrahydrofuran (30 ml). After further refluxing (0.5 h) the mixture was evaporated, chloroform (200 ml) was added, and the solution was washed with 2N-hydrochloric acid (20 ml; saturated with sodium chloride), saturated aqueous sodium hydrogen carbonate, and brine, dried, and evaporated to yield an oil (3.85 g). T.l.c. showed the presence of the 4,6-thiocarbonate.[18] Methyl iodide (10 ml) was added and the mixture refluxed (15 h); methylene chloride (100 ml) was added and the solution washed with dilute aqueous sodium thiosulphate and water, dried, and evaporated to yield an oil. Chromatography then yielded the title *compound* (2.40 g, 40%), m.p. 144—144.5° (from ethyl acetate–light petroleum), $[\alpha]_D^{20}$ +66.0° (*c* 0.565 in $CHCl_3$), $\lambda_{max.}$ (EtOH) 211 (ε 3100) and 253 nm (ε 600), $\nu_{max.}$ (Nujol) 1 720 cm^{-1} (C=O), τ ($CDCl_3$) 5.21 (1 H, d, H-1, $J_{1,2}$ 3.0 Hz), 5.30 (1 H, t, H-4, $J_{3,4} = J_{4,5} =$ 9.0 Hz), 6.06—7.06 (5 H, m, H-2, -3, -5, -6, and -6′), 6.57br (9 H, s, 3 × OCH_3), and 7.69 (3 H, s, SCH_3) (Found: C, 32.8; H, 5.0; I, 31.25; S, 8.0. $C_{11}H_{19}IO_6S$ requires C, 32.5; H, 4.7; I, 31.25; S, 7.9%).

We thank Professor L. N. Owen and Dr. S. M. McCombie for discussion.

[5/454 *Received*, 10*th March*, 1975]

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