by borate electrophoresis at pH 6, electrophoresis in 1 *M* acetic acid, and by paper chromatography in 1-butanol–acetic acid–water (4:1:1).

Reduction of 3′-Keto-N^4-acetylcytidine with $NaBH_4$-^3H.—A reaction between 3′-keto-N^4-acetylcytidine (17.3 mg, 41 μmol) and sodium borohydride-^3H (50 mCi, 2.3 mCi/μmol) was carried out as with the 2′ ketone above. After deacetylation, the mixture was evaporated to dryness and directly applied to a 2 × 45 cm column of Dowex-1 (OH^-) resin equilibrated with methanol–water (1:4). Continued elution with the same solvent gave two well resolved peaks centered about fractions 230 and 290 (15 ml each). The first of these contained cytidine-3′-^3H (3.5 μmol, 8.5%) with a specific activity of 0.62 mCi/μmol, while the second contained 7 μmol (17.1%) of 1-(β-D-xylofuranosyl)cytosine-3′-^3H with a specific activity of 0.54 mCi/μmol. Both products were homogeneous and identical with authentic samples by the electrophoretic and chromatographic systems above.

Registry No.—**5a**, 6698-19-7; **5b**, 6614-56-8; **6a**, 25787-17-1; **6b**, 25767-18-2; **7a**, 25787-19-3; **7b**, 25787-20-6; **8a**, 25787-21-7; **8b**, 25787-22-8; **8c**, 25787-23-9; **9a**, 25787-24-0; **9b**, 25787-25-1; **9c**, 25787-26-2; **10a**, 25787-27-3; **10b**, 25787-28-4; **11a**, 25834-65-5.

Notes

Evidence for a Carbenoid Intermediate in the Corey–Winter Alkene Synthesis[1,2]

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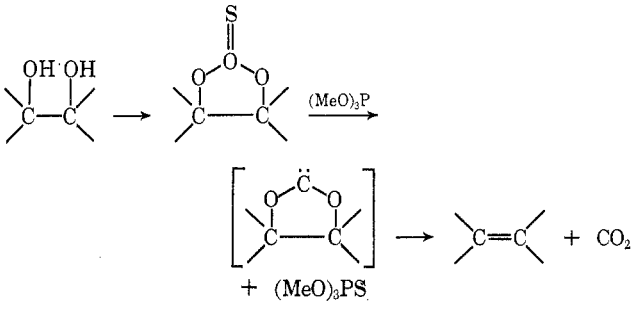
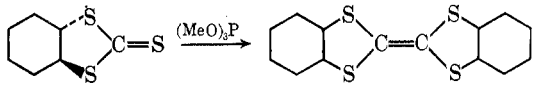
The synthesis of alkenes by treatment of cyclic 1,2-thionocarbonates with a phosphite ester (Corey–Winter alkene synthesis[3]) has proved to be a useful route to unsaturated sugar derivatives.[4–7] It was postulated[3] that the reaction proceeds through a carbene intermediate that is unstable with respect to the alkene and carbon dioxide.



Corey and coworkers[8] extended this synthesis to the preparation of alkenes from trithiocarbonates. The synthetic route permits preparation of highly strained alkenes in good yield. When formation of an alkene is impossible, as with *trans*-cyclohexane-1,2-dithiol 1,2-thionocarbonate, coupling products are obtained. These observations led the authors[8] to propose a



concerted, cycloelimination mechanism for the product-forming step. More recently Corey and Märkl[9] have isolated phosphorus ylides from the reaction of cyclic 1,3-trithiocarbonates with alkyl phosphites, and have been able to inhibit alkene formation from the cyclic 1,2-trithiocarbonates by adding an excess of benzaldehyde to the reaction mixture. Under the latter conditions the product is a ketene dithioacetal formed by a Wittig reaction of the intermediate ylide with the aldehyde. Some systems led only to alkenes, even when an excess of aldehyde was present. It was postulated[9] that ylide intermediates were formed in each case, at least with the trithiocarbonate precursors, and that competitive decomposition of the ylide to alkene, or reaction of the ylide with aldehyde, determined the product obtained.

We now present direct evidence to support the hypothesis of a carbene intermediate in the conversion of the thionocarbonate of a 1,2-diol into an alkene. The 5,6-thionocarbonate (**1**) of 1,2-*O*-isopropylidene-α-D-glucofuranose when treated with refluxing trimethyl phosphite for 70 hr gave, in addition to the 5,6-alkene **2** (isolated crystalline in 75% yield) as earlier reported,[5] a second product (**3**), isolated crystalline in 1% yield after column chromatography of the mother liquors from crystallization of **2**. Compound **3** proved to be identical in all respects with 1,2-*O*-isopropylidene-α-D-glucofuranose 3,5,6-orthoformate,[10] an authentic sample of which was prepared in 94% yield by condensation of 1,2-*O*-isopropylidene-α-D-glucofuranose with triethyl orthoformate.

(1) Part XI in the series Synthesis and Reactions of Unsaturated Sugars. For part X, see D. M. Clode, D. Horton, M. H. Meshreki, and H. Shoji, *Chem. Commun.*, 693 (1969).

(2) Supported, in part, by the Agricultural Research Service, U. S. Department of Agriculture, Grant No. 12-14-100-9201(71) (OSURF Project 2573) administered by the Northern Utilization Research and Development Division, Peoria, Ill.

(3) E. J. Corey and R. A. E. Winter, *J. Amer. Chem. Soc.*, **85**, 2677 (1963).

(4) D. Horton and W. N. Turner, *Tetrahedron Lett.*, 2531 (1964).

(5) D. Horton and W. N. Turner, *Carbohyd. Res.*, **1**, 444 (1966); D. Horton, J. K. Thomson, and C. G. Tindall, Jr., *Methods Carbohyd. Chem.*, **6**, in press.

(6) E. L. Albano, D. Horton, and T. Tsuchiya, *Carbohyd. Res.*, **2**, 349 (1966).

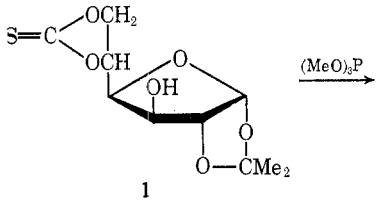
(7) D. Horton and C. G. Tindall, Jr., *Abstr. Pap. Amer. Chem. Soc. Meeting*, **158**, CARB6 (1969).

(8) E. J. Corey, F. A. Carey, and R. A. E. Winter, *J. Amer. Chem. Soc.*, **87**, 934 (1965).

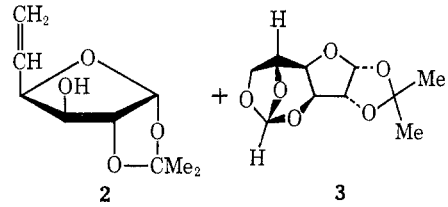
(9) E. J. Corey and G. Märkl, *Tetrahedron Lett.*, 3201 (1967).

(10) K. Freudenberg and W. Jacob, *Ber.*, **80**, 325 (1947); E. J. Hedgley and O. Mérész, *Proc. Chem. Soc.*, 399 (1964).

The structure of **3** is fully supported by 100-MHz nmr spectral assignments verified by spin decoupling, and by mass spectrometry; a major ion having *m/e* 215 corresponding to loss of a methyl radical from the molecular ion is observed. Full spectral details are recorded in the Experimental Section, where 100-MHz nmr data verified by spin decoupling are also recorded for the thionocarbonate **1**, together with mass spectral data.

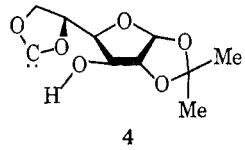


1



2 major + **3** minor

The formation of the orthoformate **3** as a side product in the conversion of thionocarbonate **1** into alkene **2** can be attributed to the intramolecular insertion of a carbene intermediate (**4**) into the O–H bond of the hydroxyl group at C-3, and provides strong evidence that the same carbene **4** is an intermediate in formation of the alkene **2**. It would be difficult to reconcile the observed formation of **3** as a side product if a reaction intermediate of the ylide type were involved in the conversion of **1** into **2**.



4

Experimental Section

General Methods.—Nmr spectra were measured at 100 MHz, and chemical shifts refer to an internal standard of tetramethylsilane (τ 10.00); the latter also provided a lock signal. Signal assignments were verified by spin decoupling. Deuteration was performed by adding 1 drop of deuterium oxide to the prepared sample. Mass spectra were recorded by C. R. Weisenberger with an AEI MS-902 high-resolution, double-focusing spectrometer with an accelerating potential of 8 kV, an ionizing potential of 70 eV, and a direct-insertion probe with an inlet temperature of 250°. Thin layer chromatography (tlc) was performed with 0.25-mm layers of silica gel G (E. Merck, Darmstadt, Germany) activated at 120° as the adsorbent and sulfuric acid as the indicator.

1,2-*O*-Isopropylidene-α-D-glucofuranose 5,6-Thionocarbonate (1).—This compound was prepared as described previously,[5] mp 205–206°, $[\alpha]^{20}D$ −18° (*c* 1, acetone); 100-MHz nmr data in acetone-d_6 τ 3.98 (1-proton doublet, $J_{1,2}$ = 3.4 Hz, H-1), 4.62 (1-proton, symmetrical eight-line multiplet, $J_{4,5}$ = 2.6 Hz, H-5), 5.26 (2-proton, apparent doublet, $J_{5,6} \sim 8$ Hz, H-6,6′), 5.37 (1-proton triplet, $J_{3,4}$ = 3.5 Hz, H-4), 5.46 (1-proton doublet, $J_{2,3} \sim 0$ Hz, H-2), 5.68 (1-proton, broad peak, becoming a doublet after deuteration, H-3), 7.12 (1-proton, broad peak, disappears on deuteration, OH), 8.58, 8.75 (3-proton singlets, CMe_2); mass spectral data (relative peak intensity and assignment in parentheses) *m/e* 262 (1, M^+), 247 (1, M − CH_3), 187 (65, M − CH_3 − CH_3CO_2H), 159 (6), 129 (9), 127 (18), 101 (9), 100 (4), 86 (42), 85 (90), 73 (20), 71 (15), 69 (34), 68 (5), 60 (100, $CH_3CO_2H \cdot^+$), 59 (100, $CH_3COCH_3H^+$), 58 (20), 57 (27), 56 (5), 55 (25), 45 (14), 44 (10), 43 (60, CH_3CO^+).

Reaction of 1 with Trimethyl Phosphite.—The following is an adaptation of an earlier procedure.[5] A solution of **1** (5.0 g, 19 mmol) in freshly distilled trimethyl phosphite (20 ml) was heated to reflux under an atmosphere of nitrogen. The bath temperature was maintained for 60 hr at 150°, during which time the mixture ceased to reflux. The solution was cooled and poured into 250 ml of 1 *M* aqueous sodium hydroxide and the mixture was stirred vigorously until a permanently basic, homogeneous solution resulted. The solution was extracted with four 250-ml portions of chloroform, and the dried (magnesium sulfate) extract was evaporated to a colorless syrup (2.78 g) that crystallized spontaneously. Tlc of the product (3:1 dichloromethane–ether) showed a major component (**2**), R_f 0.5, and a minor component (**3**), R_f 0.9. The solid was dissolved in the minimum volume of ether, and Skellysolve[11] C (50 ml) was added. The solution was then concentrated at 15–20° until it became slightly turbid, whereupon it was seeded with **2** and refrigerated for 12 hr, to give **5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hex-5-enofuranose (2)**, yield 1.92 g (in two crops). The residual mother liquors were chromatographed on a column (3 × 30 cm) of silica gel (type 7734, 70–325 mesh ASTM, E. Merck) with 3:2 petroleum ether (bp 60–110°)–ether as eluent. The first product to be eluted was **1,2-*O*-isopropylidene-α-D-glucofuranose 3,5,6-orthoformate (3)**, yield 50 mg (0.22 mmol, 1%), identical with an authentic sample of **3** by mixture melting point and ir and nmr spectra. Further elution of the column gave an additional 0.62 g of **2**, total yield of **2** 2.54 g (13 mmol, 72%), mp 61–65°, $[\alpha]^{20}D$ −60° (*c* 2, chloroform).

1,2-*O*-Isopropylidene-α-D-glucofuranose 3,5,6-Orthoformate (3).—Into a 25-ml flask was placed 1,2-*O*-isopropylidene-α-D-glucofuranose (5.0 g, 22.6 mmol) and triethyl orthoformate (3.4 ml, 22.6 mmol) and 1 ml of acetic acid. The mixture was heated under an atmosphere of nitrogen for 4 hr at 120°. The cooled mixture was evaporated and three 15-ml portions of toluene were evaporated from the residue to remove acetic acid. Sublimation of the resultant solid at 0.05 Torr and 120° gave a white powder that was recrystallized from ethyl acetate to give pure **3**, yield 4.9 g (21.2 mmol, 94%), mp 201–203°, $[\alpha]^{20}D$ −41.5° (*c* 0.3, chloroform); R_f 0.9 (3:1 dichloromethane–ether); nmr data in chloroform-*d* τ 3.94 (1-proton doublet, $J_{1,2}$ = 3.2 Hz, H-1), 4.03 (1-proton singlet, orthoformate CH), 5.22 (1-proton, broad multiplet, width 12 Hz, H-5), 5.44 (1-proton doublet, $J_{2,3} \sim 0$ Hz, H-2), 5.65 (1-proton doublet, $J_{3,4}$ = 3.0 Hz, H-3), 5.92 (1-proton doublet and 1-proton multiplet, $J_{6,6'}$ = 8.0 Hz, $J_{5,6} \sim 0$, H-6, H-4), 6.11 (1-proton quartet, $J_{5,6}$ = 4.6 Hz, H-6′), 8.52, 8.78 (3-proton singlets, CMe_2); mass spectral data (relative intensities and assignments given in parentheses) *m/e* 215 (60, M − CH_3), 187 (<1, M − CH_3CO), 159 (<1, M − 71), 155 (<1, M − CH_3 − CH_3CO_2H), 129 (70), 127 (20), 114 (5), 113 (15), 101 (20), 100 (50), 85 (85), 71 (10), 69 (21), 61 (11), 59 (41, $CH_3COCH_3H^+$), 43 (100, CH_3CO^+).

For this compound prepared by a different procedure the following constants have been reported:[10] mp 201–203°, $[\alpha]D$ −40.9° (chloroform), τ 3.90 (H-1), 3.99 (orthoformate CH).

Fusion of **3** (1 g) with triphenylacetic acid (0.1 g) at 210° led to quantitative recovery of unchanged **3**, which sublimed from the reaction vessel and no conversion[12] into **2** was observed.

Registry No.—**1**, 25356-81-4; **3**, 3891-47-2.

(11) Petroleum ether fractions, bp 90–97°, Skelly Oil Co., Kansas City, Mo.

(12) G. Crank and F. W. Eastwood, *Aust. J. Chem.*, **17**, 1392 (1964).

The Synthesis of Cherylline

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The isolation, structure, and *S* configuration of cherylline (**8**), a new representative of the rare phenolic *Amaryllidaceae* alkaloids, was recently reported[1] and

(1) A. Brossi, G. Grethe, S. Teitel, W. C. Wildman, and D. T. Bailey, *J. Org. Chem.*, **36**, 1100 (1970).