Conversion of Vicinal Diols into Olefins *via* the Derived Bisdithiocarbonates

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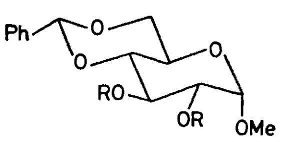
Summary Reaction of vicinal diol bisdithiocarbonates with tri-n-butyltin hydride in toluene or benzene gives the corresponding olefin in high yield.

ALCOHOLS are mildly and conveniently deoxygenated by reaction of the derived dithiocarbonate and tri-n-butyltin hydride.[1] The intermediacy of the alkyl radical suggested a possible route to olefins from reaction of vicinal bisdithiocarbonates and tri-n-butyltin hydride (Scheme).

Reaction of the glucoside diol (**1a**) and sodium hydride in tetrahydrofuran with imidazole catalysis, carbon disulphide, and methyl iodide in sequence gave the derived bisdithiocarbonate (**1b**) in high yield.



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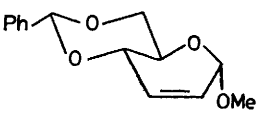

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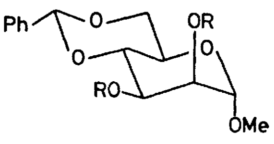

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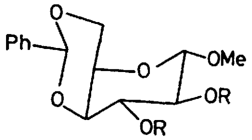

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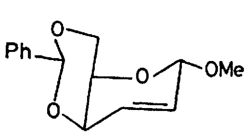

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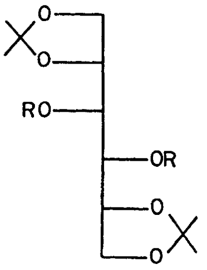

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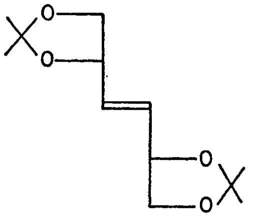

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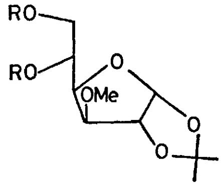

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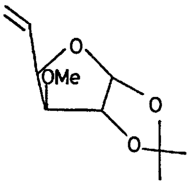
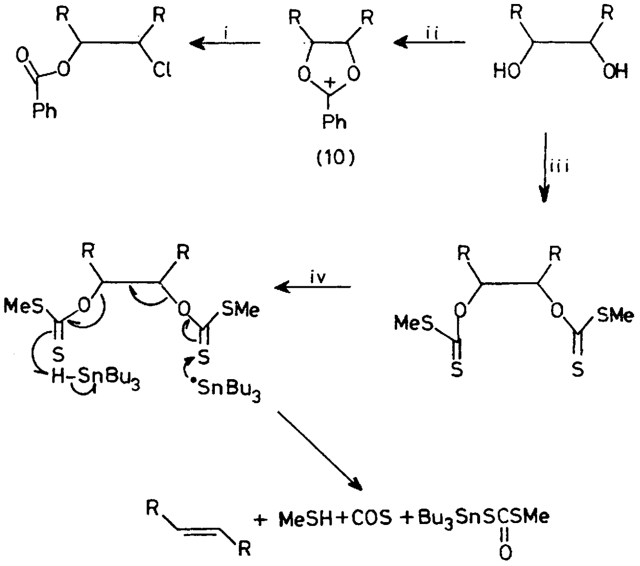


(9)

a; R = H
b; R = CS$_2$Me

Attempted preparation of vicinal dibenzoates from diols and the Vilsmeier reagent (Me$_2$N$^+$=CClPhCl$^-$) gave the corresponding vicinal chloro-benzoate derivatives[2] *via* the cyclic cation (**10**) (see Scheme). Since analogues of such species cannot be formed in bisdithiocarbonate preparation, the compounds (**3b**), (**4b**), (**6b**), and (**8b**) were prepared in high yield from the diols (**3a**), (**4a**), (**6a**), and (**8a**).

When the bisdithiocarbonate (**1b**) is heated to reflux with tri-n-butyltin hydride in toluene, the olefin (**2**) is obtained in 59% yield. The corresponding mannoside *cis*-bisdithiocarbonate (**3b**) gave the same olefin (**2**) in 79% yield. In a typical procedure the bisdithiocarbonate in toluene (or benzene) was added slowly to a solution of tri-n-butyltin hydride (5—10 mol. equiv.) in toluene (or benzene) under reflux. After 5—12 h the solution was cooled, washed with aqueous KOH, dried (Na$_2$SO$_4$), evaporated, and chromatographed. This transformation has been applied to several bisdithiocarbonates (Table) giving good yields of olefins from *cis* and *trans* cyclic and acyclic substrates. The bisdithiocarbonate (**6b**) gave only the *trans* isomer (**7**).



Scheme. i, Cl$^-$; ii, PhC(Cl)=$^+$NMe$_2$Cl$^-$; iii, (1) NaH (2) CS (3) MeI; iv, Bu$_3$SnH.

Table

Bisdithiocarbonate M.p./°C ([α]$_D$/°)[a]	Yield %	Olefin M.p./°C ([α]$_D$/°)[a]	Yield %
(**1b**) 98—101 (−38)	95	(**2**)[d] 115—117 (+135)	59
(**3b**)[b] 167—169 (−27)	94	(**2**) 115—117 (+130)	79
(**4b**)[c] 145—146·5 (+154)	83	(**5**) 148—150 (−85)	49
(**6b**) 82—84·5 (+101)	90	(**7**)[e] 78—80 (+51)	65
(**8b**)[g]	94	(**9**)[f] Oil, b.p. 101 °C at 5 mmHg (−44, EtOH)	62

[a] Optical rotations were measured in CHCl$_3$ unless otherwise stated. [b] J. Honeyman and J. W. W. Morgan, *J. Chem. Soc.*, 1954, 744; G. J. Robertson, *ibid.*, 1934, 330. [c] E. Sorkin and T. Reichstein, *Helv. Chim. Acta*, 1945, **28**, 11; B. Capon, W. G. Overend, and M. Sobell, *Tetrahedron*, 1961, **16**, 106. [d] Lit. m.p. 119—120 °C, [α]$_D$ + 129° (F. H. Newth, *J. Chem. Soc.*, 1956, 471). [e] Lit. m.p. 80—82 °C, [α]$_D$ + 55° (ref. 3). [f] Lit. b.p. 80 °C at 2 mmHg, [α]$_D$ −43° (J. S. Josan and F. W. Eastwood, *Carbohydrate Res.*, 1968, **7**, 161). [g] D. H. R. Barton, R. V. Stick, and R. Subramanian, *J.C.S. Perkin I*, 1976, 2112.

The olefin synthesis described herein is carried out at low temperature under mild neutral conditions and should find wide application. Alternative olefin syntheses *via* the ortho-ester or -amide,[3,4] or dimethanesulphonate[5] have the respective disadvantages of acidic reaction conditions and failure with some diol stereochemistries (S_N2 reactions). The Corey–Winter process[6] is also based on a cyclic intermediate.

(*Received, 9th September* 1977; *Com.* **939**.)

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[1] D. H. R. Barton and S. W. McCombie, *J.C.S. Perkin I*, 1975, 1574.

[2] T. G. Back, D. H. R. Barton, and B. L. Rao, *J.C.S. Perkin I*, 1977, 1715.

[3] F. W. Eastwood, K. J. Harrington, J. S. Josan, and J. L. Pura, *Tetrahedron Letters*, 1970, 5223; T. vanEs, *Carbohydrate Res.*, 1967, **5**, 282.

[4] J. S. Josan and F. W. Eastwood, *Austral. J. Chem.*, 1968, **21**, 2013.

[5] H. L. Slates and N. C. Wendler, *J. Amer. Chem. Soc.*, 1956, **78**, 3749.

[6] E. J. Corey and R. A. E. Winter, *J. Amer. Chem. Soc.*, 1963, **85**, 2677.