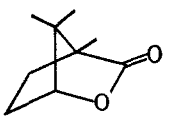
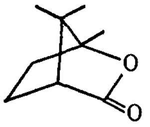
(XII), and this was confirmed by comparison with an independently prepared sample of XII.[10,11]



XII

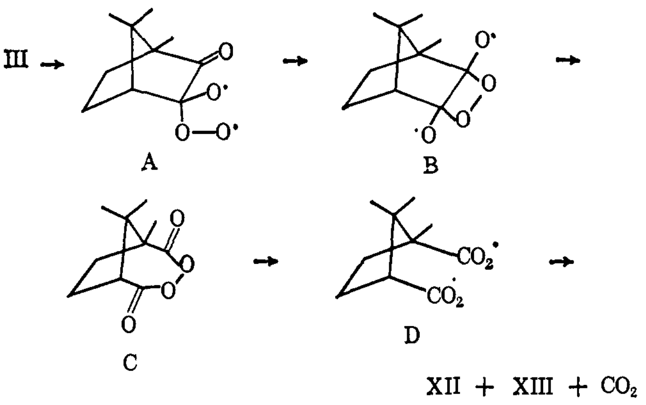


XIII

The third product could not be obtained entirely free of XII and showed a depressed melting range (92.5–105°). Elemental analysis and Rast molecular weight determination again indicated the molecular formula $C_9H_{14}O_2$. A strong infrared absorption at 5.62 μ and nmr peaks corresponding to three C-methyl groups (singlets at τ 9.05, 8.95, and 8.72), with no downfield absorption in the τ 6 region, suggested that this was the isomeric campholytolactone (XIII). Once more, this was confirmed by direct glpc, infrared, and nmr comparison with pure XIII, mp 121.5–122°.[12]

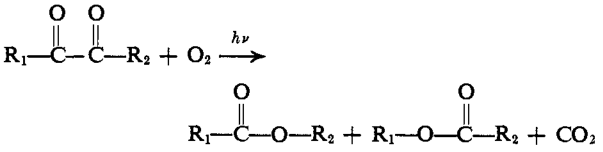
Partial loss of these lactones during work-up makes it difficult to estimate their yields with any accuracy. It does appear that they are formed in about equal amounts, probably in the range of 5–10% each. They obviously arise as a result of a complex sequence of steps. One possible mechanism, shown in Chart II, involves addition of oxygen to III to give an intermediate such as A,[13] which can then proceed *via* B to the cyclic diacyl peroxide C, decomposition of which could be expected to yield XII and XIII, perhaps by decarboxylation of the diradical D.[14,15]

Chart II



Other products formed in the reaction include a benzene-insoluble polymer (*ca.* 15%), the acyloins X and XI (*ca.* 15%), camphoric anhydride (IV; *ca.* 3%), camphoric acid (*ca.* 7%), and a mixture of other acids (*ca.* 40–50%) containing the hydroxy acids corresponding to the lactones XII and XIII and possibly unstable precursors which decompose to these acids during work-up.

In summary, irradiation of camphorquinone in solution leads to reaction only in the presence of oxygen; a variety of oxidation and reduction products are then formed. In benzene, a novel transformation in which one atom of carbon is extruded as carbon dioxide (eq 1) acquires some importance.



$$R_1-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-R_2 + O_2 \xrightarrow{h\nu} R_1-\overset{O}{\overset{\|}{C}}-O-R_2 + R_1-O-\overset{O}{\overset{\|}{C}}-R_2 + CO_2 \tag{1}$$

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[10] W. A. Noyes, *Am. Chem. J.*, **16**, 508 (1894); W. A. Noyes and R. de M. Taveau, *ibid.*, **35**, 385 (1906); J. Bredt, *J. Prakt. Chem.*, **84** (2) 786 (1911).

[11] Although the synthesis of XII according to Noyes could not be repeated, an independently devised synthesis gave a sample of camphonolactone with very close to the reported melting point (161–162.5°, lit.[10] 160–161°) and with appropriate infrared and nmr spectra.

[12] L. L. McCoy and A. Zagalo, *J. Org. Chem.*, **25**, 824 (1960). In our hands, the lead tetraacetate oxidation of camphoric acid gave campholytolactone (XIII) accompanied by about 13% of camphonolactone (XII).

[13] This type of intermediate has been postulated by Professor G. Quinkert to explain some monoketone photooxidation reactions in solution. See G. Quinkert and H. G. Heine, *Tetrahedron Letters*, 1659 (1963); J. Meinwald and R. A. Schneider, *J. Am. Chem. Soc.*, 87, 5218 (1965).

[14] For recent discussions see J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 439–450; F. D. Greene, H. P. Stein, C. C. Chu, and F. M. Vane, *J. Am. Chem. Soc.*, **86**, 2080 (1964).

[15] Several other types of mechanism might be invoked to account for lactone formation. Preliminary attempts to prepare the diacyl peroxide *C* independently, and to examine its thermal and photochemical reactions, have given only ambiguous results so far. We hope to pursue this possibility, along with the possible role of singlet oxygen in this transformation, in future work.

New Rearrangements of Hexose 4- and 5-*O*-Sulfonates

Sir:

In this communication we wish to report the discovery of a ring contraction which occurs during attempted displacements of the 4-*O*-sulfonate esters Ia–c of pyranoside Id.[1] Further, an additional 1,5 methoxyl migration has been observed with mesylate Ia under conditions less conducive to S_N2 displacements.

Mesylate Ia, mp 128–129°, was synthesized from the known[2] methyl 2,3-*O*-isopropylidine-α-D-mannopyranoside following a method previously successful in the glucose series.[3] Treatment of Ia with lithium aluminum hydride afforded the alcohol Id, $[\alpha]^{27}\mathrm{D}$ 15.2° (*c* 1.4),[4] *via* O–S cleavage, which in turn could be converted to tosylate Ib, mp 59°, $[\alpha]^{27}\mathrm{D}$ $-23.9°$ (*c* 1.1). The physical constants of Ib and d agreed with those of their L enantiomers prepared from L-rhamnose,[5] thus also establishing the structure of Ia.

All attempted displacement reactions on sulfonates Ia and b and on brosylate Ic, mp 44–46°, resulted in ring contraction to give furanoside products. Thus, treatment of Ia with acetate ion in refluxing dimethylformamide (DMF) afforded (after saponification) a 65% yield of a mixture of D-*talo*-IIa and L-*allo*-IIIa, ratio 7 : 1.[6]

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[1] A previous report (C. L. Stevens, P. Blumbergs, and R. P. Glinski, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, Abstracts, p 5C) indicated that displacement of Ia with acetate ion, while difficult, proceeded normally. Later data have shown that the previous structural data, while perhaps consistent with proposed structures, was, in fact, equivocal. Thus, the structures presented in the above reference are corrected herein.

[2] R. G. Ault, W. N. Haworth, and E. L. Hirst, *J. Chem. Soc.*, 517 (1935).

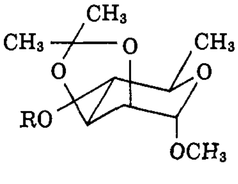
[3] C. L. Stevens, P. Blumbergs, D. H. Otterbach, J. L. Strominger, M. Matsuhashi, and D. N. Dietzler, *J. Am. Chem. Soc.*, **86**, 2937 (1964).

[4] The solvent for rotations was methanol.

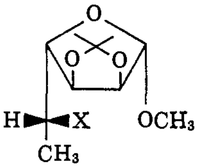
[5] (a) P. A. Levine and J. Compton, *J. Am. Chem. Soc.*, **57**, 2306 (1935); (b) I. E. Muskat, *ibid.*, **56**, 2653 (1934).

[6] Determined by vapor phase chromatography (vpc). Compounds IIa and IIIa usually comprised over 80% of the crude reaction mixture.

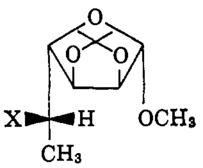
Formation of IIa results from inversion at C-4 and retention (or double inversion) at C-5 of Ia, while formation of IIIa is a result of inversions at both C-4 and C-5. Separation of the IIa–IIIa mixture was effected *via* their crystalline brosylates.



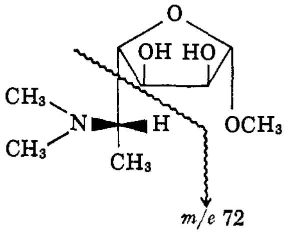
α-D-*manno*
Ia, R = Mes
b, R = Tos
c, R = Bros
d, R = H



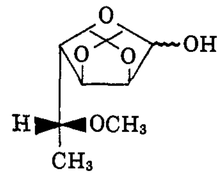
α-D-*talo*
IIa, X = OH
b, X = OBros
c, X = $C_6H_5CO_2$
d, X = OCH_3
e, X = NH_2
f, X = phthalimido



β-L-*allo*
IIIa, X = OH
b, X = OBros
c, X = OTos
d, X = N_3
e, X = NH_2
f, X = $N(CH_3)_2$



IV, β-L-*allo*



V, D-*talo*

The configurations of IIa and IIIa were determined as follows. Hydrogenation with Raney nickel of brosylate IIb, mp 85–86°, afforded IIa as an oil which was purified through its benzoate derivative IIc, mp 93–94°, $[\alpha]^{27}\text{D}$ 35.6° (*c* 0.92). Saponification of IIc and distillation gave pure IIa, $[\alpha]^{27}\text{D}$ 57.5 (*c* 1.27). Acid hydrolysis and phenylhydrazine treatment converted IIa to the osazone of 6-deoxy-D-talose,[7] mp 171–173°. In addition, the physical constants of IIa and c agreed with those reported for their L counterparts.[7] In much the same way, brosylate IIIb, mp 142–143°, was hydrogenated to give pure IIIa, $[\alpha]^{27}\text{D}$ 81.5° (*c* 0.84), and, again, IIIa gave the osazone of 6-deoxy-L-allose, mp 183–184°. The physical constants reported for the counterparts of IIIa,c[8] and the osazone[7,8] agree. Interconversion of IIa and IIIa with acetate ion in DMF and the synthesis of nitrogen derivatives with nucleophiles in DMF indicated that displacement reactions at C-5 of the furanose derivatives proceeded without further rearrangement. This result was, however, strictly dependent on reaction conditions (see below).

From brosylate IIb, amine IIIe (HCl), mp 233–234°, was prepared *via* azide IIId. Reductive methylation of IIIe gave the dimethylamino derivative IIIf (HCl), mp 155–156°. An nmr spectrum ($CDCl_3$) of the free base IIIf clearly revealed that the N-C-H proton, a broad multiplet at δ 2.34, was adjacent to the C-methyl group. Also, a mass spectrum of compound IV (picrate mp 194–195°) revealed an intense peak at *m/e* 72.[9]

The D-*talo* amine IIe (HCl), mp 183–184°, and phthalimido derivative IIf, mp 158–159°, were also prepared from IIIb by displacements in DMF. Lithium azide displacements in DMF attempted on the pyranose 4-*O*-sulfonates Ia and b gave complex mixtures from which, after reduction, the D-*talo* amine IIe (25%) was the only basic product isolated. Likewise, potassium phthalimide (DMF) with sulfonates Ia and c gave the D-*talo*-IIf (20%).

When mesylate Ia was heated at 170° (sealed tube) in dioxane–water (9:1) containing excess sodium bicarbonate or sodium hydroxide, three products, IIa, IIIa, and an unknown V, were formed in about 90% yield (ratios 1:2:6). The unknown V, a liquid, could be isolated (vpc) in 51% yield; $[\alpha]^{27}\text{D}$ −2.5° (*c* 0.48).

The mass spectrum of V indicated a 5-methoxy formulation, and its stereochemistry was shown by synthesis. Mild acid hydrolysis of V followed by phenylhydrazine treatment afforded a new osazone, VI, mp 195–196°. This same osazone was prepared from IId, $[\alpha]^{27}\text{D}$ 64.5° (*c* 2.8), which in turn had been prepared by silver oxide–methyl iodide treatment of IIa. The position of the isopropylidene bridge in V was confirmed when methylation of V produced a two-component mixture (2:1), the major product of which was IId (vpc). Acid hydrolysis of the mixture and phenylhydrazine treatment afforded, again, osazone VI. Had the isopropylidine bridged C-1 and C-2 in V, the above reaction sequence should not have produced osazone VI.

It was considered possible that Ia, under reaction conditions, had rearranged to an intermediate 5-*O*-mesyl-β-L-allofuranoside which then underwent the C-1–C-5 methoxyl migration. As a preliminary test of this consideration the brosylate IIIb was treated at 130° with 9:1 dioxane–water containing sodium hydroxide. Methoxyl migration did indeed occur, producing a reaction mixture (∼90% yield) containing 89% V, 9% IIa, and 2% IIIa.

A 1,4 methoxyl migration has been shown to occur in an attempted displacement reaction on an open-chain lyxose derivative.[10,11] To our knowledge the pyranose–furanose ring contraction and accompanying 1,5 methoxyl migration described in this communication are new. Further work on the mechanism and scope of these rearrangements is in progress.

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[7] E. J. Reist, L. Goodman, and B. R. Baker, *J. Am. Chem. Soc.*, **80**, 5775 (1958).

[8] P. A. Levine and J. Compton, *J. Biol. Chem.*, **116**, 199 (1936).

[9] For mass spectral determination of nitrogen position in amino sugars, see D. C. DeJongh and S. Hanessian, *J. Am. Chem. Soc.*, **87**, 3744 (1965).

[10] N. A. Hughes and P. R. H. Speakman, *Chem. Commun.*, 199 (1965).

[11] Previous attempted displacements of the sulfonate ester group of a 4-*O*-tosylate enantiomeric with I (L-rhamnose series) has led to conflicting results: see ref 5b and P. A. Levene and J. Compton, *J. Am. Chem. Soc.*, **57**, 2306 (1935).

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Rearrangement on Deoxygenation of Nitrosobenzene

Sir:

Current interest in deoxygenation of aromatic nitroso and nitro compounds with tervalent organophosphorus compounds stems from a parallelism of these reactions and the pyrolysis or photolysis of corresponding azides.