saccharides, and panose. In this case the resonance attributable to the unlinked C-6's is a multiplet (62.0 and 61.8 ppm) due to conformational effects (*vide infra*). Comparison of the areas of the resonances due to linked and unlinked C-6's is not nearly as accurate an estimate of the relative amounts of the two linkages because the relaxation mechanisms and nuclear Overhauser enhancements of the two types of C-6 need not be identical. However, the areas do indicate that the 1 → 4 linkage is roughly twice as frequent as the 1 → 6 linkage.

The C-6 resonances of glucose, the terminal reducing glucose unit of maltose, and ring III of panose are doublets (Table I). The relative intensities of the two lines are similar to those of the anomeric carbon atoms of the reducing glucose moieties, indicating that C-6 is sensitive to the presence of α and β anomers at C-1. Thus, it is not unreasonable to suggest that in the glucan, where anomeric purity has been established by chemical methods, the C-6 resonances are sensitive to the nature of the linkage between C-1 of the same glucose unit and the neighboring unit. Thus, approximately equal frequencies of 1 → 4 and 1 → 6 linkages are seen by the C-6's of glucose residues linked at C-4 in the glucan. The only sequence consistent with these data is that shown in Figure 1a.

Similarly, the anomeric resonances of the glucan C-1's involved in 1 → 4 linkages have a multiplet structure. This suggests that, in like fashion to the C-6's, they are sensitive to the nature of the linkage at the C-4 or C-6 position of the same glucose unit. Since the C-1's involved in 1 → 4 links experience approximately equal frequencies of 1 → 4 and 1 → 6 linkages, the polysaccharide sequence must be that represented in Figure 1a.

A further confirmation of the sensitivity of the C-6 resonances to the nature of the linkage at C-1 of the same glucose unit comes from the spectrum of panose (Figure 1d), where there are four C-6 resonances. The resonance at 67.2 ppm is clearly that due to C-6 of ring II. The remaining three resonances are due to the C-6's of rings I and III, which are both primary, but have different frequencies due to the involvement of ring I in a 1 → 6 linkage and the influence on the C-6 of ring III by the α and β anomers at C-1.

Thus, the chemical shifts experienced by carbons 1 and 6, depending on how or whether they are linked, and their long-range conformational sensitivity, have enabled us to determine the composition and sequence of a homopolymer with mixed linkages. This technique provides a very powerful means of structural analysis for carbohydrates.

(8) Issued as N.R.C.C. Publication No. 13030.

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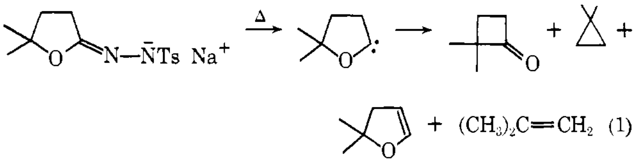
Received October 27, 1972

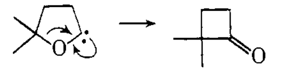
Stereochemical Consequences in the Pyrolysis of Lactone Tosylhydrazone Salts

Sir:

Recently we described the pyrolytic decomposition of several lactone tosylhydrazone salts and suggested that the various observed products arose through rearrangement or fragmentation of intermediate oxycarbenes.[1,2] The species related to isocaprolactone, for example, gave the results shown in eq 1. A point specifically left open was the pathway from oxycarbene to ring-contracted ketone, for which the two simplest possibilities are a concerted alkyl shift from oxygen to carbon (eq 2) and an open alkyl acyl biradical intermediate (eq 3). This question has significance beyond the immediate mechanistic problem, since closely related reactions are involved in the photolysis[3-5] of both cyclobutanones and certain other cyclic ketones, as well as in the thermolysis[6] of cyclobutanones. Furthermore, the ring contraction proceeds in synthetically attractive yields in some cases,[1,2] and the mechanistic question then takes on importance for preparative chemistry.



(1)



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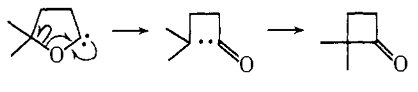
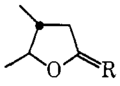


(3)

We have now prepared and pyrolyzed tosylhydrazone salts related to the three lactones **1a–3a** in order to assess the stereochemical consequences of this decomposition. The lactones were prepared by known methods[7] and then converted to tosylhydrazones **1b–3b**[8] *via* the ortholactones **1c–3c** following a procedure previously described.[1] Hydrolysis of **1b–3b** in aqueous acid furnished **1a–3a**, respectively, and confirmed that no loss of stereochemistry had occurred in these transformations. The derived dry sodium salts **1d–3d** were then thermally decomposed at 310° (0.1 Torr), and the products were analyzed, all according to methods employed earlier.[2] Structures were assigned to the enol ethers on the basis of spectroscopic properties and



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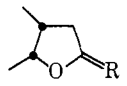

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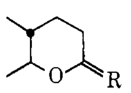

3

a, R = O
b, R = NNHTs
c, R = $(OC_2H_5)_2$
d, R = NN̄Ts Na$^+$

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(1) A. B. Smith, III, A. M. Foster, and W. C. Agosta, *J. Amer. Chem. Soc.*, **94**, 5100 (1972).

(2) A. M. Foster and W. C. Agosta, *ibid.*, **94**, 5777 (1972).

(3) P. Yates, *Pure Appl. Chem.*, **16**, 93 (1968); W. C. Agosta and D. K. Herron, *J. Amer. Chem. Soc.*, **90**, 7025 (1968).

(4) N. J. Turro and D. M. McDaniel, *ibid.*, **92**, 5727 (1970).

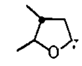
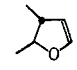
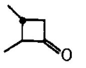
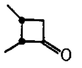
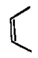
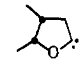
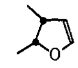
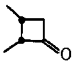
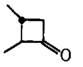
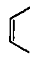
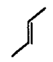
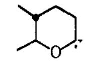
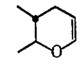
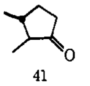
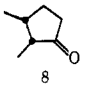
(5) H. A. J. Carless, J. Metcalfe, and E. K. C. Lee, *ibid.*, **94**, 7221 (1972), and references cited therein.

(6) J. Metcalfe, H. A. J. Carless, and E. K. C. Lee, *ibid.*, **94**, 7235 (1972), and references cited therein.

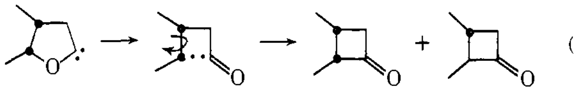
(7) Lactones 1a and 2a: J.-F. Laporte and R. Rambaud, *C. R. Acad. Sci., Paris, Ser. C*, **262**, 1095 (1966); M. Tokuda, Y. Yokoyama, and T. Taguchi, *J. Org. Chem.*, **37**, 1859 (1972). Lactone 3a: S. Dew and C. Rai, *J. Indian Chem. Soc.*, **34**, 266 (1957); E. Honkanen, T. Moisio, P. Karvonen, A. I. Virtanen, and J. Paasivirta, *Acta Chem. Scand.*, **22**, 2041 (1968).

(8) These new compounds gave acceptable elemental analyses (±0.1%) for carbon, hydrogen, and nitrogen.

Table I. Pyrolysis Products from **1d**–**3d**

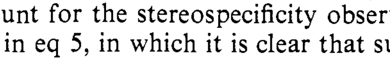
	Presumed carbene	Products, % yield Enol ether	Ketone (ret)	Ketone (inv)	Alkene (ret)	Alkene (inv)	Cyclopropane (ret)	Cyclopropane (inv)
1		 24	 15	 1.3	 32	 <1	 3.6	 2.3
2		 17	 11	 11	 42	 3	 2.5	 0.5
3		 6	 41	 8				

previous experience,[2] while the remaining compounds were identified by comparison with authentic samples.[9] Table I presents a summary of the results, and we wish to draw particular attention to several of these findings. First, there is appreciable loss of stereochemical integrity in the ring contraction leading to ketone. The amount of inversion varies considerably in the three examples, but in series **2** it amounts to 50%, and in series **3** it has gone well past the reported equilibrium trans:cis ratio of 19:1.[10] The results are inconsistent with contraction solely by a concerted pathway (eq 2) or by any mechanism leading to the equilibrium distribution of isomers, and they suggest that part or all of the reaction proceeds through a biradical intermediate which may lose stereochemical integrity (eq 4). Both


(4)

concerted and biradical pathways have been discussed[4] for the reverse photochemical conversion of cyclobutanones to oxycarbenes, and in that case a biradical intermediate was favored.

The second result of interest is that, in contrast to ring contraction, the fragmentation leading from **1d** and **2d** to 2-butenes (and presumably ketene) is highly stereospecific. This fragmentation thus appears to involve intermediates other than the biradicals implicated in ring contraction (eq 4), and we suggest that a concerted, symmetry-allowed [4 + 2] cycloreversion[11] can account for the stereospecificity observed. This is depicted in eq 5, in which it is clear that such a process


(5)

is tantamount to a reverse 1,3-dipolar cycloaddition with ketene functioning uniquely as a 1,3 dipole.[12]

The process of eq 5 is of course unknown in the opposite direction; it not only would be highly endothermic but also would necessarily compete with the facile [2 + 2] cycloaddition of olefin to ketene. In this connection it is noteworthy that recent extensive study[5] of the gas-phase photolysis of the 2,3-dimethylcyclobutanones has also demonstrated fragmentation to the 2-butenes with retention of stereochemistry. To account for their results the investigators were led to postulate[5] two distinguishable biradical intermediates, one which maintained stereochemistry and went on to 2-butene, and another which gave other products with loss of stereochemistry. Concerning the postulated biradical which maintains its steric configuration these authors noted further that "it is conceivable that it is correlated with" an oxycarbene intermediate. Our present findings provide evidence that an oxycarbene intermediate can indeed fragment stereospecifically to olefin, as this suggestion requires.

Finally a brief comment concerning the cyclopropanes should be made. The yields are too low to permit rigorous conclusions, but there is clearly greater loss of stereochemistry in the trans (**1**) series than in the isomeric cis (**2**) series. This is reminiscent of the unexplained observation that gas-phase pyrolysis of both *cis*- and *trans*-2,3-dimethylcyclobutanone yields 1,2-dimethylcyclopropane chiefly as the cis isomer.[6]

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Received November 13, 1972

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[9] The authentic 2,3-dimethylcyclobutanones were generously provided by Professor N. J. Turro and Dr. P. Lechtken, Columbia University (see ref 10).

[10] D. Varech, C. Ouannes, and J. Jacques, *Bull. Soc. Chim. Fr.*, 1662 (1965). The ratio for the 2,3-dimethylcyclobutanones is 3.26:1 [N. J. Turro and R. B. Gagosian, *J. Amer. Chem. Soc.*, **92**, 2036 (1970)].

[11] R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

[12] For the application of orbital symmetry considerations to 1,3-dipolar cycloadditions, see A. Eckell, R. Huisgen, R. Sustmann, G. Wallbillich, D. Grashey, and E. Spindler, *Chem. Ber.*, **100**, 2192 (1967).

Migration of Alkoxy Groups from Carbon to Nitrogen. A Novel Rearrangement

Sir:

The migration of alkoxy groups in molecular rearrangements is not common, and alkoxy migration from carbon to nitrogen is rare.[1] We now report such a rearrangement.

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[1] Alkoxy groups migrate to a minor extent in the decomposition of certain alkoxycarbonylnitrene precursors, giving alkoxyisocyanates.[2–4]