

Intramolecular Cycloadditions with Oxidopyrylium Ylides

Peter G. Sammes* and Leslie J. Street

Department of Organic Chemistry, The University, Leeds LS2 9JT, U.K.

3-Oxopyrans, bearing unsaturated side chains, can undergo intramolecular cycloaddition reactions, either by thermal or base-catalysed processes, to yield bicyclic adducts and affording, for example, a simple entry into the perhydroazulene system.

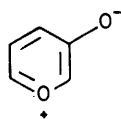
Recently, Hendrickson and Farina reported the trapping of the oxidopyrylium species (**1**) by reaction with certain 1,3-dipolarophiles.¹ Since the oxidopyrylium intermediates are formed from the readily generated 3-oxopyrans, *e.g.* (**2**), their facility for intramolecular cycloadditions across unsaturated bonds has been explored.

Reaction of furfuraldehyde with 1-(bromomagnesio)pent-4-ene gave the alcohol (**3**), which was treated with bromine in methanol at -45°C to give the acetal (**4**) as a mixture of epimers.² After acid hydrolysis and acetylation with acetic anhydride in pyridine, the acetal (**4**) gave the pyranulose ester (**5**), also as a mixture of epimers, in greater than 80%

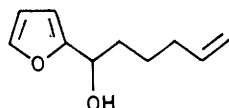
yield from furfuraldehyde. In a similar manner the homologue (**6**) and the acetylene (**7**) could also be prepared.[†]

On heating the pentenyl derivative (**5**) at 150°C for 16 h in acetonitrile solution (sealed tube) a major product formed (61%), identified as the enone (**8**). Reaction of this material with lithium dimethylcuprate afforded the ketone (**11**). The relative stereochemistry of the latter was confirmed by an X-ray crystallographic analysis on the derived 2,4-dinitrophenyl-

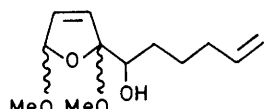
[†] All new compounds gave satisfactory microanalytical and spectroscopic data.



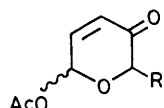
(1)



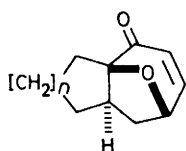
(3)



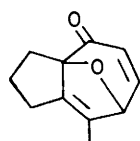
(4)



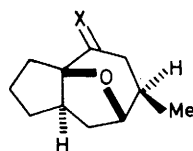
- (2) R = H
 (5) R = [CH₂]₃C=CH₂
 (6) R = [CH₂]₄CH=CH₂
 (7) R = [CH₂]₃C≡C·CH₃



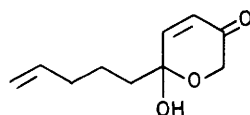
- (8) n = 1
 (9) n = 2



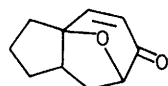
(10)



(11) X = O

(12) X = 2,4-(NO₂)₂C₆H₃NH·N

(13)



(14)

hydrazone (12), m.p. 185 °C;‡ this analysis confirms that intramolecular reaction favours *exo*-addition of the isolated double bond to the presumed oxidopyrylium intermediate [*cf.* (1)]. Heating either the hexenyl derivative (6) or the acetylene (7) under similar conditions also gave good yields of the corresponding cycloadducts, (9) and (10), respectively.

Hendrickson and Farina noted that treatment of the acetate (2) with triethylamine afforded dimers, again presumably formed from the intermediate zwitterion (1). For derivatives such as (5) the side chain should again act as an intramolecular trap for such an intermediate when generated with base, thus avoiding dimerisation. Treatment of (5) with triethylamine in dichloromethane at room temperature caused a slow reaction (several days) producing the cycloadduct (8) (40%). This reaction could be stimulated by use of a stronger base, such as 1,5-diazabicyclo[4.3.0]non-5-ene, when the product (8) was formed in 75% yield; this method thus provides a more convenient process for the formation of the cycloadduct.

The intramolecular cycloadditions described above appear to be general, giving access, for example, to a variety of substituted perhydroazulenes. Thus, reaction of furfuryl alcohol in tetrahydrofuran with two equivalents of *n*-butyl-lithium followed by 1-bromopent-4-ene, using hexamethylphosphoric triamide as co-solvent, gave 1-hydroxymethyl-5-(pent-4-en-1-yl)furan (70%). Oxidation of the latter alcohol with *m*-chloroperbenzoic acid⁸ afforded the pyranone (13) (82%), pyrolysis of which, at 150 °C for 16 h in acetonitrile containing a catalytic amount of acetic acid, gave the cycloadduct (14) (52%).

We thank the S.E.R.C. and Shell Research Ltd., Sittingbourne, for a CASE Studentship (to L. J. S.).

Received, 7th June 1982; Com 645

References

- 1 J. B. Hendrickson and J. S. Farina, *J. Org. Chem.*, 1980, **45**, 3359, 3361.
- 2 O. Achmatowicz, Jr., P. Bukowski, B. Szechner, Z. Zwierzchowska, and A. Zamojski, *Tetrahedron*, 1971, **27**, 1973.
- 3 Y. Lefebvre, *Tetrahedron Lett.*, 1972, 133.

‡ We thank Dr. W. S. McDonald, Department of Inorganic & Structural Chemistry, University of Leeds, for this analysis.