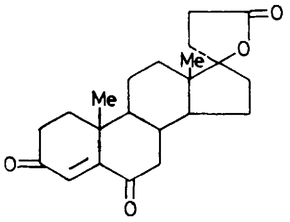
Formation of Dihydropyrans in the Photocycloaddition of a Steroidal Enedione to Olefins and Dienes

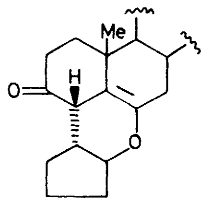
By GEORGE R. LENZ
(*Searle Laboratories, P.O. Box 5110, Chicago, Illinois 60680*)

Summary The photocycloaddition of a steroidal 4-ene-3,6-dione to olefins and dienes yields a regio- and stereospecific [4 + 2]-dihydropyran adduct as well as smaller amounts of a [2+2]-cyclobutane adduct.

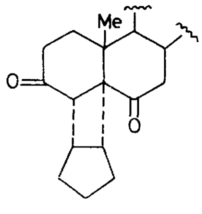
ALTHOUGH the cycloaddition reactions of *transoid*-enones have been extensively studied,[1] the equivalent reactions in the *cisoid*-enone and enedione compounds have been relatively neglected.[2] We report on the novel formation of dihydropyran adducts from the addition of a steroidal enedione (**1**), m.p. 221—223 °C, to olefins and a diene. Irradiation of (**1**) in the presence of cyclopentene leads to rapid formation of two adducts (**2**) (43%) and (**3**) (30%).† The initial adduct (**2**), m.p. 217—219 °C, was identified as a [4+2]-adduct, a dihydropyran, assuming *cis*-addition to the cyclopentene,[3] by its characteristic spectral properties and its 4α-stereochemistry was assigned by the positive o.r.d.–c.d. spectra.‡ The second product (**3**), m.p. 272—274 °C, was identified as the [2+2]-cyclobutane adduct, and its 5α-stereochemistry determined by its characteristic c.d. spectrum and the 4α,5α-*cis*-fusion determined by the recovery of (**3**) after treatment with refluxing sodium methoxide.[4] A similar cycloaddition of (**1**) to dihydropyran furnished the [4+2]-adduct (**4**), m.p. 248—252 °C, in 36% yield as a single isomer. That the enedione had added *cis*- to the dihydropyran double bond was shown by the 2·5 Hz coupling constant typical of acetals in the n.m.r. spectrum. The 4β-proton and the vicinal dihydropyran proton were virtually coupled. However, differential Eu(fod)$_3$ shifts allowed the observation of the 4β-proton as a doublet (*J* 7·5 Hz) which, using the Karplus equation,[5] is only consistent with the all *cis*-stereochemistry indicated in (**4**).



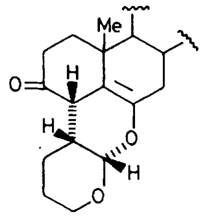
(1)



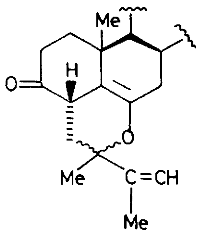
(2)



(3)



(4)



(5)

---

† Irradiations were conducted under argon with toluene–olefin solutions of (**1**) using a 450 W medium pressure mercury arc (Pyrex filter). All new compounds possess microanalytical and spectral data consistent with the assigned structures.

‡ The dihydropyran [4+2]-adducts possess varying degrees of sensitivity towards oxygen. The reaction with oxygen and the further chemical conversions will be described in the full paper.

The photoaddition of (**1**) to 2,3-dimethylbutadiene similarly yielded (**5**), m.p. 244—246 °C, as a single isomer. The structure of the newly formed dihydropyran was indicated by the n.m.r. spectrum, where the 4β-proton appeared as the X-portion of an AMX spin system, the absence of any signals for a proton α to an ether oxygen, and the appearance of an additional tertiary methyl group.

The addition of (**1**) to cyclopentene was quenched by 3,3,4,4-tetramethyl-1,2-diazetidine 1,2-dioxide, implicating the triplet state as the reactive species.[6] Both the [4+2]- and [2+2]-adduct formation can be accommodated by initial bond formation on the α-side of the steroid between C-4 and the olefin to form the more stable diradical. Then 1,4-bonding forms the cyclobutane and 1,6-bonding generates the dihydropyran.

(*Received*, 28*th March* 1977; *Com.* 289.)

[1] P. E. Eaton, *Accounts Chem. Res.*, 1968, **1**, 50; P. DeMayo, *ibid.*, 1971, **4**, 41.

[2] Y. M. Ngan, S. J. Rettig, J. R. Scheffer, and J. Trotter, *Canad. J. Chem.*, 1975, **53**, 2068.

[3] R. M. Bowman, C. Calvo, J. J. McCullough, P. W. Rasmussen, and F. F. Snyder, *J. Org. Chem.*, 1972, **37**, 2084; G. R. Lenz, *Tetrahedron*, 1972, **28**, 2195.

[4] G. Cleve and G.-A. Hoyer, *Tetrahedron*, 1972, **28**, 2637.

[5] N. S. Bhacca and D. H. Williams, 'Applications of N.M.R. Spectroscopy in Organic Chemistry,' Holden-Day, San Francisco, 1964, p. 49.

[6] E. Ullman and P. Singh, *J. Amer. Chem. Soc.*, 1972, **94**, 5077.