The Photochemistry of Cyclohexa-2,5-dien-1-ones. Intramolecular Cycloaddition of a Furan to an Intermediate Oxyallyl Zwitterion

Arthur G. Schultz,*[a] Salvador Puig,[a] and Yu Wang[†][b]

[a] *Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181, U.S.A.*
[b] *Department of Chemistry, National Taiwan University, Roosevelt Rd., Section 4, Taipei, Taiwan, Republic of China*

Photorearrangement of 4-furfuryloxy-2,4,6-trimethylcyclohexa-2,5-dien-1-one (**1**) gives the bridged furan adduct (**4**) in 80% yield.

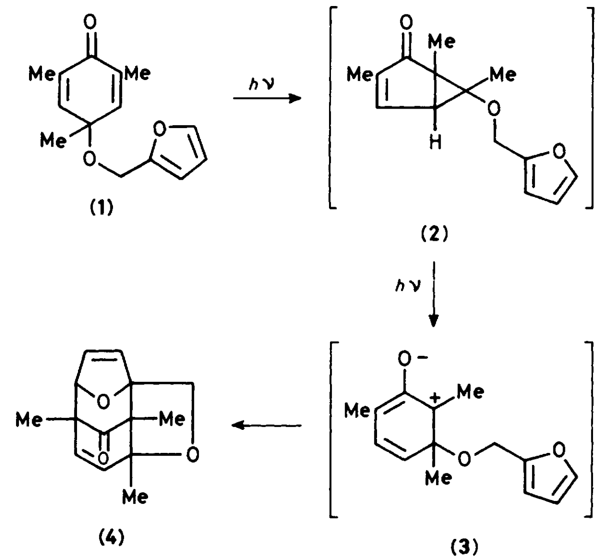
Additions of furan to intermediates generated from photolysis of 2,5-cyclohexadienones at low temperature have been reported by Chapman and co-workers.[1] These reactions presumably involve photorearrangement of cyclohexa-2,5-dienones to bicyclo[3.1.0]hex-3-en-2-ones, from which secondary photorearrangement provides dienophilic oxyallyl zwitterions. There do not appear to be any recorded examples of intramolecular cycloadditions of dienes to photochemically generated oxyallyl zwitterions;[2] however, the novel photorearrangement of 4-azidoalkylcyclohexa-2,5-dienones to bridged triazenes has been reported.[3] Herein, we report the first example of an intramolecular cycloaddition of a furan ring to an intermediate oxyallyl zwitterion generated by ambient temperature photorearrangement of a cyclohexa-2,5-dienone; *i.e.*, (**1**) → (**4**).

Irradiation of 4-furfuryloxy-2,4,6-trimethylcyclohexa-2,5-dien-1-one (**1**)[‡] in dry, degassed benzene solution (6×10^{-3} M) with a 366 nm light source[3] for 1 h followed by flash chromatography on silica gel (ethyl acetate–hexane, 2 : 8) provided the bridged furan adduct (**4**) (m.p. 129—130 °C from pentane) in 80% isolated yield. The formulation of (**4**) is

---

[†] Address correspondence concerning crystal data to this author.

[‡] Cyclohexadienone (**1**) (oil) was prepared in low yield by solvolysis of a mixture of 4-chloroacetyloxy-2,4,6-trimethylcyclohexa-2,5-dien-1-one and 6-chloroacetyloxy-2,4,6-trimethylcyclohexa-2,4-dien-1-one in furfuryl alcohol at 65 °C.



supported by spectroscopic data§ and an *X*-ray structure determination. The molecular structure of (**4**) is shown in Figure 1.¶

We propose that the conversion of (**1**) into (**4**) occurs by photorearrangement of (**1**) to bicyclohexenone (**2**); photoinduced cleavage of the internal cyclopropane bond in (**2**) produces zwitterion (**3**), from which intramolecular cycloaddition gives (**4**). It is noteworthy that zwitterion addition to the furan ring occurs from an *endo* orientation. *endo* Addition has been reported for the intermolecular process.[1] Also of interest is the observation that the vinyl substituted zwitterionic unit in (**3**) reacts exclusively as a two-electron component in cycloaddition to the furan ring.

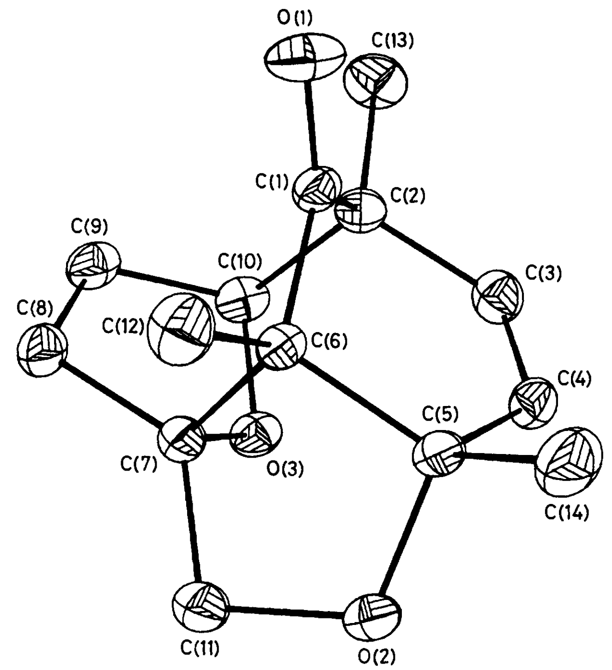


Figure 1. Molecular structure of (**4**). Bond lengths are O(1)–C(1) 1.212(2), O(2)–C(5) 1.472(2), O(2)–C(11) 1.450(2), O(3)–C(7) 1.426(2), O(3)–C(10) 1.417(2), C(1)–C(2) 1.503(2), C(1)–C(6) 1.511(2), C(2)–C(3) 1.518(2), C(2)–C(10) 1.582(2), C(2)–C(13) 1.516(2), C(3)–C(4) 1.318(2), C(4)–C(5) 1.513(2), C(5)–C(6) 1.534(2), C(5)–C(14) 1.527(2), C(6)–C(7) 1.578(2), C(6)–C(12) 1.524(2), C(7)–C(8) 1.518(2), C(7)–C(11) 1.508(2), C(8)–C(9) 1.317(2), C(9)–C(10) 1.518(2) Å.

We thank the National Institutes of Health for support of this work.

Received, 21st February 1985; Com. 230

References

1 L. L. Barber, O. L. Chapman, and J. D. Lassila, *J. Am. Chem. Soc.*, 1969, **91**, 3664; O. L. Chapman, J. C. Clardy, T. L. McDowell, and H. E. Wright, *ibid.*, 1973, **95**, 5086.

2 B. Föhlisch and R. Herter, *Chem. Ber.*, 1984, **117**, 2580; in this paper, the intramolecular cycloaddition of the related allylium-2-oleates (oxyallyl cations) to the furan nucleus is described.

3 A. G. Schultz, S. O. Myong, and S. Puig, *Tetrahedron Lett.*, 1984, **25**, 1011.

---

§ *Spectroscopic data for* (**4**): N.m.r. ^{1}H (CDCl$_3$), δ 6.43 (d, 1H, *J* 6 Hz), 6.36 (dd, 1H, *J* 6, 2 Hz), 5.96 (d, 1H, *J* 10 Hz), 5.62 (d, 1H, *J* 10 Hz), 4.18 (d, 1H, *J* 2 Hz), 4.15 (d, 1H, *J* 9 Hz), 4.08 (d, 1H, *J* 9 Hz), 1.25 (s, 3H), 1.13 (s, 3H), and 1.08 (s, 3H); $\nu_{(CO)}$ 1710 cm^{-1} (KBr). A satisfactory elemental analysis was obtained.

¶ *Crystal data for* (**4**): $C_{14}H_{16}O_3$, triclinic, space group $P\bar{1}$, a = 6.920(1), b = 8.780(1), c = 10.278(2) Å, α = 97.69(1), β = 90.34(1), γ = 111.45(1)°, Z = 2, D_m = 1.34, D_c = 1.30 g cm^{-3}, λ = 0.7107 Å, $R_w(F)$ = 0.030 with 2232 reflections. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.