The Formation of Dihydropyrans from *cis*-Hex-3-ene-2,5-dione and Fulvenes

By M. T. HUGHES and R. O. WILLIAMS*
(*The Department of Chemistry, The College of Technology, Portsmouth*)

FULVENES behave as 1,3-dienes and undergo the Diels–Alder reaction with *cis-* and *trans*-disubstituted dienophiles to give the adducts (I) and (II) respectively.[1] We now report a novel, ready cycloaddition of *cis*-hex-3-ene-2,5-dione[2] to fulvenes.

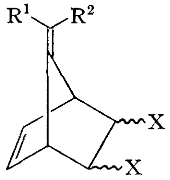
In a typical experiment, this dienophile and dimethylfulvene[3] were heated under reflux in ether for several hours to give in 40% yield a 1 : 1 adduct, $C_{14}H_{18}O_2$, m.p. 73—74°. Chemical and spectroscopic evidence clearly ruled out the expected adduct (I; $R^1 = R^2 = \text{Me}$; $X = \text{Ac}$) but is entirely consistent with the structure (III) or (IV) which can be formulated by exchanging the normal diene and dienophile functions of the reagents.[4] The ultraviolet spectrum λ_{max} (cyclohexane) 250 mμ (ϵ 10,800) is in close agreement with that expected for the diene system,[5] and the n.m.r. spectrum† shows six single-proton resonances which are unambiguously assigned on the basis of chemical shifts for the alternative structures (III) and (IV). The CO·CH_3 protons occur as a singlet at τ 7·99 and the absorptions at τ 8·33 (3H) and 8·41 (6H) correspond to the $=$C–CH_3 and $=$C(CH_3)$_2$ groups. Double-resonance experiments show that the proton H-3, at τ 4·89 is coupled to H-5 ($J_{3,5} = 7{\cdot}7$ c./sec.) and to H-2 at τ 4·39 ($J_{2,3} = 2{\cdot}2$ c./sec.) and is also long-range-coupled to H-1, τ 3·62 ($J_{1,3} = 1{\cdot}5$ c./sec.). Irradiation at τ 6·46 (H-5) has no effect on H-1 or H-2 but reduces the complex signal at τ 7·18 (H-6) to a doublet ($J_{4,6} = 6{\cdot}3$ c./sec.) and sharpens the *gem*-dimethyl response. These and other double-irradiation experiments are fully consistent with (III) and rule out (IV).

Lithium aluminium hydride reduction of (III) gave in excellent yield two epimeric alcohols (Va), m.p. 91—93° and (Vb), m.p. 53–55° which spontaneously rearrange in purified spectroscopic carbon tetrachloride to the ketals (VIa) and (VIb), respectively. The ultraviolet, infrared, and n.m.r. spectra of these compounds are as expected. These intramolecular rearrangements, which are complete within 1—2 hr. at 33°, constitute a

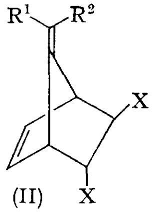
---

† The n.m.r. spectra were measured as solutions in CCl_4 except the alcohols (V) which rearranged and were run in $CDCl_3$.

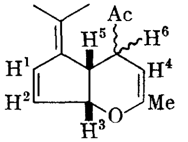
remarkable example of the acid-catalysed addition of alcohols to enol ethers[6] and the ketals formed serve to establish the configuration of the acetyl group in (III) as *trans* to the cyclopentene ring.



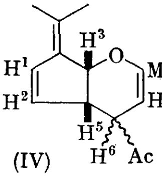
(I)



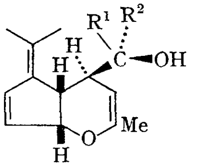
(II)

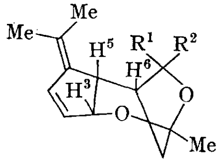


(III)



(IV)





(V) a; R^1=Me, R^2=H
b; R^1=H, R^2=Me

(VI) a; R^1=Me, R^2=H^7
b; R^1=H^7, R^2=Me

Dreiding models of (VI) show that H-5 and H-6 make a dihedral angle of about 90° and should have little or no coupling[7] but if the acetyl group in (III) is *cis*, H-5 and H-6 in models of the corresponding ketals form an angle of approximately 30° and a coupling of about 6 c./sec. would be expected. Irradiation of H-3 (τ 5·24) in (VIa) reduces the doublet centred at τ 6·9 (H-5) to a singlet and since, therefore, there is no measurable coupling between H-5 and H-6, the acetyl group is *trans*. Similarly, the configurations of the CH(OH)Me group in the alcohols (V) are assigned using the MeCH proton signal (H-7) which consists of eight lines centred at τ 5·99 in the ketal (VIa) and is strongly coupled to H-6 ($J_{6,7}$ = 4 c./sec.) but is a pure quartet centred at τ 5·85 in (VIb) ($J_{6,7}$ $\sim$0 c./sec.).

The *trans*-stereochemistry of the acetyl group in (III) is important as it implies that the dihydropyran is formed *via* a transition state of similar stereochemistry to Diels–Alder reactions in which there is maximum overlap of unsaturated centres.[8] A satisfactory explanation for the formation of (III) in preference to (I) is difficult but the geometrical configuration of the $\alpha\beta$-unsaturated ketone is of vital importance. This is shown by the reaction of *trans*-hex-3-ene-2,5-dione[2] with dimethyl-, diethyl-, diphenyl-, and other fulvenes; which, we have found, results in the formation of the normal adducts (II; X = Ac), whereas the *cis*-diketone forms dihydropyrans of type (III) with diethyl-, methylphenyl-, and phenyl-fulvene.

(*Received, April 24th,* 1967; *Com.* 393.)

---

[1] J. H. Day, *Chem. Rev.*, 1953, **53**, 167; K. Alder and R. Ruhrmann, *Annalen*, 1950, **566**, 1.
[2] J. Levisalles, *Bull. Soc. chim. France*, 1957, 997.
[3] E. P. Kohler and J. Kable, *J. Amer. Chem. Soc.*, 1935, **57**, 917; P. Wilder and A. Winston, *ibid.*, 1955, **77**, 5598.
[4] $\alpha\beta$-Unsaturated aldehydes and ketones are known to form dihydropyrans by dimerisation or by addition to olefins but these reactions normally require very severe conditions. M. Mühlstädt and G. Müller, *Tetrahedron Letters*, 1966, 5321; C. W. Smith, D. G. Norton, and S. A. Ballard, *J. Amer. Chem. Soc.*, 1951, **73**, 5267.
[5] A. I. Scott, "Interpretation of the Ultraviolet Spectra of Natural Products," Pergamon, Oxford, 1964, p. 50.
[6] G. F. Woods and D. N. Kramer, *J. Amer. Chem. Soc.*, 1947, **69**, 2246.
[7] M. Karplus, *J. Amer. Chem. Soc.*, 1963, **85**, 2870.
[8] K. Alder and G. Stein, *Angew. Chem.*, 1937, **50**, 510; for a recent Review of the mechanism of the Diels–Alder reaction, see J. Sauer, *Angew. Chem. Internat. Edn.*, 1967, **6**, 16.