Thermal Cycloaddition to Oxonin

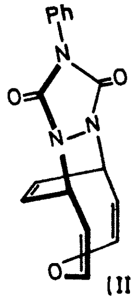
By A. G. ANASTASSIOU* and R. P. CELLURA

(*Department of Chemistry, Syracuse University, Syracuse, New York* 13210)

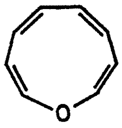
Summary Reaction of oxonin with 4-phenyl-1,2,4-triazoline-3,5-dione at −78° proceeds rapidly, quantitatively, and specifically to yield a "1,8" cycloadduct.

ALL available experimental information attests to the strict symmetry control of concerted cycloadditions.[1] Nevertheless, lack of appropriate chemical models has, in some instances, precluded unambiguous realization of certain key cycloaddition modes. A thermally induced "1,8" addition on to a polyene constitutes a case in point. We describe our experience with oxonin[2] (I) in this connection.

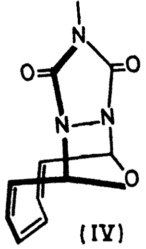
Admixture of equimolar amounts of (I) and 4-phenyl-1,2,4-triazoline-3,5-dione[3] (II) in methylene chloride at −78° leads to rapid and quantitative formation of one product (m.p. 164—165°) characterized as a 1 : 1 adduct on the basis of elemental analysis† and mass-spectral information, *m/e* 295 (M^+; 20%) and 120 [(I); 50%]. In addition, this compound displays prominent i.r. (KBr) bands at 1740, 1420, 1150, 860, and 795 cm^{-1}; u.v. (MeCN) maxima at 262 nm (ϵ 2500), 272 (2250), and 283 (1250); and an n.m.r. spectrum ($CDCl_3$) consisting of a singlet at τ 2·55 (5 H), an AB quartet with doublet components centred at τ 4·13 (2 H; *J ca.* 10·0 Hz) and 4·43 (2 H; *J ca.* 10·0 Hz), a needle-sharp singlet at τ 4·09 (2 H) and a broad singlet at τ 6·66 (2 H; width at half-height *ca.* 4 Hz). The presence in the n.m.r. spectrum of this substance of a single two-proton resonance at high field is indicative of two magnetically equivalent allylic positions, while the appearance of an AB quartet at low fields implicates the presence of two pairs of identical vinylic sites. It follows that the molecule possesses an element of symmetry and that of all possible structures only the three shown in (III), (IV), and (V) ought to be considered seriously. Moreover, the presence in (III) of an enol ether function, coupled with the fact that the adduct lacks n.m.r. and i.r. absorption characteristic of this function,[2,4] enables us tentatively to dismiss structure (III). Pertinent chemical information justifies this rejection and, in addition, distinguishes between (IV) and (V).



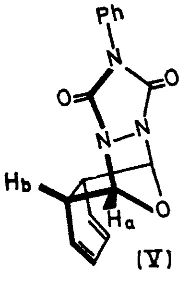
(III)



(I)



(IV)



(V)

On mild treatment (*ca.* −30°) with an excess of dienophile (II), the 1 : 1 adduct is quantitatively converted into a new compound (m.p. 238—239°) shown to be a 2 : 1 adduct of (II) and (I) on the basis of elemental composition and mass-spectral analysis: *m/e* 470 ± 2 (M^+; 100%) and 120 [(I); 66%]. In addition, this product displays strong i.r. (KBr) bands at 1750, 1420, 1240, 1040, 745, and 700 cm^{-1}, and an n.m.r. spectrum [$(CD_3)_2SO$] consisting of broad singlets at τ 2·54 (10 H) and 6·91 (2 H), a well structured multiplet extending from τ 3·55 to 3·74 (4 H), and a broad, poorly resolved, signal extending from τ 4·60 to 4·85 (2 H). The relatively uncomplicated n.m.r. spectrum of this compound is uniquely consistent with a symmetrical structure. To the extent that cycloaddition of (II) on to the initial adduct occurs in a symmetry-allowed "2 + 4" fashion, a symmetrical 2 : 1 cycloadduct‡ can only materialize by way of (V). Also, the ease with which the 1 : 1 adduct reacts with (II) is more in keeping with the coplanar diene segment in (V) than with the puckered triene system present in (IV).

On catalytic hydrogenation (10% Pd/C; 1 atm.) the 1 : 1 adduct absorbs 2 mole-equiv. of hydrogen to produce a crystalline (m.p. 148—149°) $C_{16}H_{17}N_3O_3$ compound (M^+ at *m/e* 299) which displays prominent i.r. (KBr) bands at 1750, 1420, 1160, 850, 800, and 700 cm^{-1}; u.v. (MeCN) absorption in the form of a shoulder at 255 nm (ϵ 300); and an n.m.r. spectrum ($CDCl_3$) consisting of a singlet at τ 2·55 (5 H), a needle-sharp singlet at τ 4·27 (2 H) and broad multiplets extending from τ 7·45 to 7·75 (2 H) and τ 8·15 to 8·90 (8 H). Hydrogen uptake obviously requires that the 1 : 1 adduct contain only two double bonds and, consequently, that it possess the structure shown in (V). Of course, our conclusion in this connection draws heavily upon the assumption that all olefinic functions of the 1 : 1 adduct are amenable to saturation under the hydrogenation conditions employed, and consequently that the sharp low-field resonance present in the n.m.r. spectrum of both the adduct and its hydrogenated counterpart is not due to "vinylic protons." This is no doubt the case, since the function responsible for the key singlet fully survives hydrogenation conditions (10% Rh/C; 1 atm.) that are sufficiently forcing to saturate completely the aromatic ring present in the adduct. The fully saturated $C_{16}H_{23}N_3O_3$ compound (m.p. 138—139°) thus produced displays prominent i.r. (KBr) absorption at 2890, 1720, 1400, 1275, and 890 cm^{-1} and an n.m.r. spectrum ($CDCl_3$) consisting of an exceedingly sharp singlet at τ 4·40 (2 H) and a broad multiplet extending from τ 7·50 to 8·90 (21 H).

In terms of both shape and chemical shift, the sharp low-field resonance is best ascribed to the two rigidly-held, electron-deficient, H_a protons in (V). Indeed, careful examination of a Dreiding molecular model of (V) strongly supports this assignment on account of an orthogonal disposition between H_a and its sole neighbour, H_b. The pronounced sharpness of the H_a resonance strongly favours

---

† Acceptable elemental analyses were obtained for all new compounds described.

‡ We believe this to be a normal Diels–Alder adduct but are uncertain as to stereochemical detail.

the stereochemical disposition shown in (V) over the alternative arrangement in which the oxygen bridge and the diene segment are disposed *anti* to one another, and for which the H_a–H_b dihedral angle is estimated at *ca.* 30°.

With regard to mechanism, (V) may materialize along one of two symmetry-allowed paths.[1] Thus, formation of this product may entail either direct "2 + 2 + 2" cycloaddition of (II) on to (I) or initial interaction of these two compounds in a "2 + 8" fashion to produce (IV) which could then undergo disrotatory bonding across the end carbons of its triene segment.§¶

We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for support of this work. We also thank Badische Anilin and Soda-Fabrik AG for a gift of cyclo-octatetraene.

(*Received, January 30th*, 1970; *Com.* 143.)

¶ All our preliminary observations on the reaction of (II) with *N*-ethoxycarbonylazonin[5] indicate that the azonin is substantially less reactive than oxonin in this connection.

§ Experiments designed to provide a choice between these two mechanistic alternatives are currently under way in our laboratories. The following preliminary observations seem pertinent: (a) treatment of (I) with an *equimolar quantity* of (II) at −30° produces the 2 : 1 adduct to the virtual exclusion of (V); and (b) (V) reacts with (II), at −78°, *more* rapidly than does (I) (k_V/k_I *ca.* 1·7) and leads to the exclusive production of the 2 : 1 adduct. This information, considered in conjunction with the fact that admixture of equimolar amounts of (I) and (II), at −78°, leads to the exclusive formation of the 1 : 1 adduct (V), appears to implicate the initial formation, at −78°, of a highly labile intermediate which is less reactive toward (II) than either (I) or (V).

[1] R. B. Woodward and R. Hoffmann, *Angew. Chem.*, 1969, **81**, 797.
[2] A. G. Anastassiou and R. P. Cellura, *Chem. Comm.*, 1969, 903.
[3] R. C. Cookson, S. Giliani, and I. D. Stevens, *J. Chem. Soc.* (*C*), 1967, 1905.
[4] J. K. Crandall and R. J. Watkins, *Tetrahedron Letters*, 1967, 1717.
[5] A. G. Anastassiou and J. H. Gebrian, *J. Amer. Chem. Soc.*, 1969, **91**, 4011.