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THE PHOTOLYSIS OF exo-1,6-DIMETHYL-7,8-DIPHENYL TRICYCLO [4.2.1.0^{2,5}]NONA-3,7-DIEN-9-ONE. PART 1. ISOLATION AND CHARACTERISATION OF A STABLE BICYCLO[4.2.0]OCTA-2,4,7-TRIENE

> I.W. McCay and R.N. Warrener Department of Chemistry, S.G.S., Australian National University, Canberra A.C.T. 2600, Australia

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A great deal of interest has been displayed recently in the challenging rearrangements observed to occur in $(CH)_n$ hydrocarbons. In the C_8H_8 series cyclooctatetraene, semibullvalene and barrelene have been linked photochemically on a common energy surface interrelating these isomers (1), while the thermal system is more complex (2). Studies on the bicyclo[4.2.0]octa-2,4,7-trienes (biCOTs) have been limited in the past due to their facile thermal isomerisation to the cyclooctatetraene (COT) form (3). Those studies which have been done (1,4) suggest that fragmentation to an aromatic hydrocarbon plus an acetylene occurs, rather than entry onto the C_8H_8 energy surface. In this and the accompanying paper (5) we describe a convenient entry into the biCOT system, but reserve a discussion of the photochemistry to a later date (6).

Our approach takes advantage of the well documented photodecarbonylation of α , β -unsaturated ketones (7,8). Thus irradiation of acetone solutions of the tricyclo[4.2.1.0^{2,5}]nona-3,7-dien-9-one (I) (9) (low pressure Hg-lamp, vycor filter) over the temperature range -50° to +40° caused rapid decarbonylation to form the related bicyclo[4.2.0]octa-2,4,7-triene (II) in fair yield; prolonged irradiation

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caused significant production of the aromatic hydrocarbon (III), and acetylene (10) (Scheme 1) and other photoproducts (6).



The bicyclic isomer (II) proved to be quite stable (p.m.r. studies showed appreciable stability at 65°, $t_{\frac{1}{2}}$ ca. 90 min.) and could be isolated, contaminated with minor amounts of other hydrocarbon photoproducts (6), by thick-layer chromatography (silica gel/n-hexane) as an almost colourless oil, λ max 280, 290, 297 inf, and general absorption finally trailing off at 360 nm. The p.m.r. spectrum (fig. 1) is consistent with the assigned structure, and this is borne out by comparison with model bi- and tricyclic systems [IV (11), V (3b) and VI (4)], and clearly distinguishes it from that expected for a cyclooctatetraene [cf. VII (12) and (5)].







FIGURE 1

Chemical evidence bearing on the assigned structure follows from its reaction with dienophiles under conditions which are characteristic of the biCOT system (3,5). Thus reaction occurs rapidly at room temperature with maleic anhydride or with 4-methyl-1,2,4-triazoline-3,5-dione at -78°. The p.m.r. spectra of these adducts retain the resonances characteristic of the cyclobutene moeity, thus supporting cycloaddition to the cyclic diene. [e.g. adduct (VIII), m.p. 212°, p.m.r. $CDCl_3 : \delta$ 7.40 - 6.78 (m, 10H, phenyl); δ 6.40 (s, 2H, cyclobutenyl); δ 3.24 (s,2H,cyclobutenyl); δ 3.10 (s,3H,N-CH₃); δ 1.63 (s,6H,C-CH₃)].



Further characterisation of biCOT (II) was obtained from its reaction with 3,6-di-(2'-pyridyl)-1,2,4,5-tetrazine (IX), a reagent which reacts rapidly with cyclobutene dienophiles (13). In this case reaction of (II) and (IX) in chloroform solution occurred at ca. -40° (see Scheme 2 above). Here, typically, the initially formed adduct (X) loses nitrogen (gas evolution observed) to yield the 4,5-diazatricyclo[6.4.0.0^{2,7}]-dodeca-3,5,9,11-tetraene derivative (XI), stable at -20• [p.m.r. (CDC1₂) : δ 8.85 - 6.60 (m's, 18H, phenyl plus pyridyl); δ 4.76, 3.67 (m, m, 2H, 2H, cyclobuty1) & 1.52 (s, 6H, C-methy1)]. This compound fragments below room temperature, via a symmetry forbidden thermal process, to give the aromatic hydrocarbon (III) and 3,6-di(2'-pyridyl)-pyridazine (XIII). A sîmilar fragmentation has been reported (11) for the related carbocyclic system (IV), which forms two moles of benzene. Compound (XI) forms a mono-adduct on reaction with 4-methyl-1,2,4-triazoline-3,5-dione, the p.m.r. of which supports addition to the carbocyclic diene moeity - [p.m.r. (CDCl₂) : & 8.8 - 6.9 (m's, 18H, phenyl plus pyridyl); & 4.26, 3.09 (m, m, 2H, 2H, cyclobutyl); & 3.04 (s, 3H, N-methyl); δ 1.76 (s, 6H, C-methy1)].

Further studies on the thermal stability of the bicyclic compound (VI) are described in the accompanying communication and are completely in agreement with the assigned structure.

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