

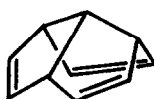
DOMINO DIELS-ALDER REACTIONS. II. A FOUR-STEP CONVERSION OF  
CYCLOPENTADIENIDE TO TRIQUINACENE<sup>1</sup>

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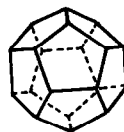
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Triquinacene (1) has been a focal point of chemical interest in recent years primarily since Woodward's suggestion that its appropriate dimerization could provide access to dodecahedrane (2).<sup>3</sup> In continuation of previous triquinacene research in this laboratory,<sup>4</sup> a four-



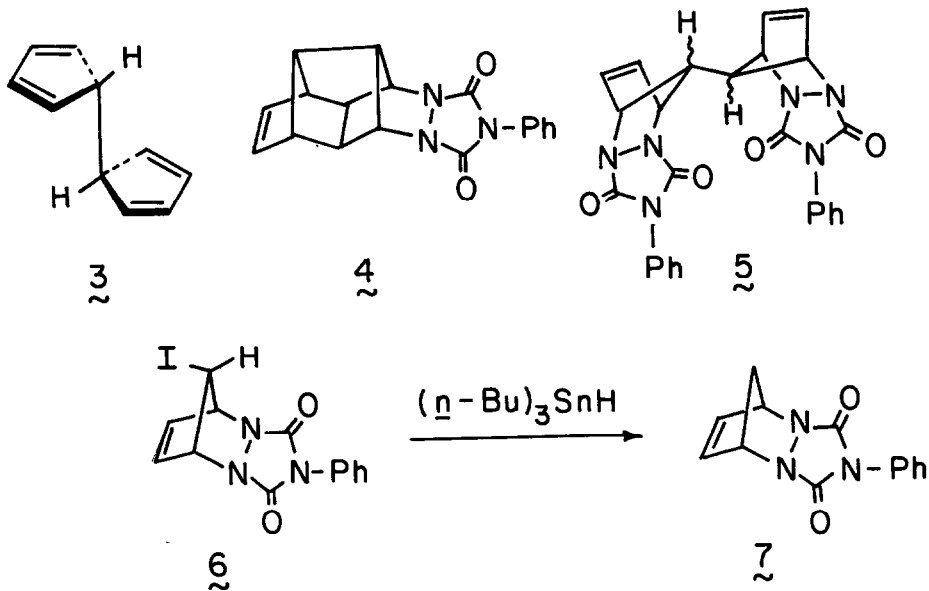
1



2

step synthesis of 1 from cyclopentadienide anion was projected which involves as its key step a Domino Diels-Alder reaction.<sup>1</sup> Conceptually, the route involves the construction of a precursor of the tricyclic skeleton containing one double bond and an azo group positioned such that ejection of nitrogen will result in unmasking of the other two olefinic centers. The successful reduction to practice of this novel route to 1 is herein described.

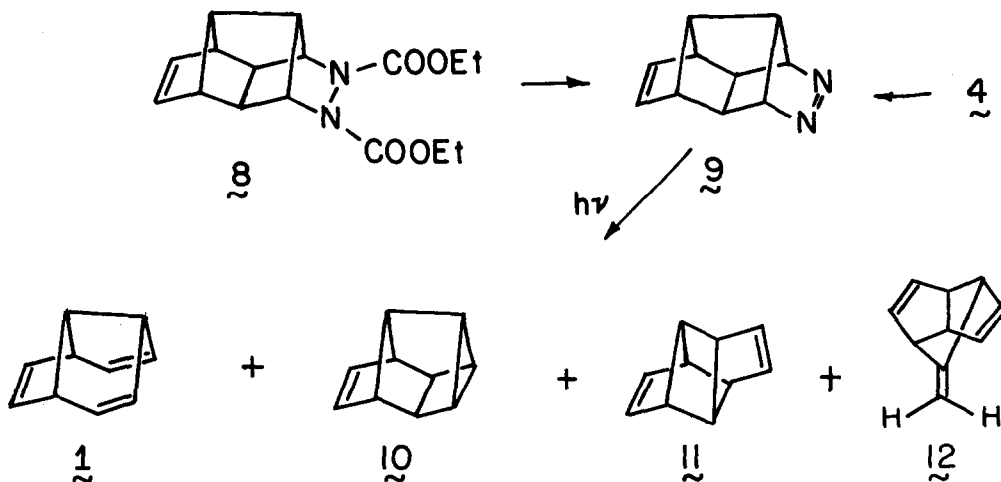
Treatment of a cold (-78<sup>o</sup>) tetrahydrofuran solution of 9,10-dihydrofulvalene (3), generated in situ at this temperature by oxidative coupling of sodium cyclopentadienide with iodine,<sup>1,5</sup> with the highly reactive N-phenyltriazolinedione (PTAD), followed by warming to room temperature and chromatography on silica gel, led to separation of the resulting adducts 4-7. The pmr spectra of 6<sup>6</sup> and 7<sup>7</sup> proved identical to those given in the literature and their structural interrelationship was further substantiated by tri-n-butyltin hydride reduction of 6. The third adduct, mp 228-229<sup>o</sup> dec,<sup>8</sup> proved expectedly to be polycondensed. Its pmr spectrum (CDCl<sub>3</sub>) which consists of an aromatic singlet at  $\delta$  7.40 (5H), an olefinic triplet ( $J = 2$  Hz) at 5.87 (2H), and multiplets of area 2 at 4.6, 2.9, 2.5, and 2.2 is uniquely accommodated by structure 4. In particular, the appearance of paired transitions attests to the C<sub>s</sub> symmetry inherent in the structure.<sup>9</sup> As concerns the final product, elemental and pmr analysis showed it to be a bis-adduct of PTAD and unrearranged 3. Because several stereoisomeric formulations



for such an adduct are possible and pursuit of this matter was not of direct relevance to our goal, the precise stereochemistry of 5 and indeed the possibility that a mixture was in hand have not been elucidated.<sup>10</sup>

When recourse was made to the less reactive diethyl azodicarboxylate reagent, no iodine-containing or multiple addition products were isolated and obtention of 8<sup>11</sup> was consequently somewhat more practical.<sup>12</sup> Hydrolysis (KOH, *i*-PrOH, reflux) and oxidation (MnO<sub>2</sub> or CuCl<sub>2</sub>) of either 4 or 8 gave the desired azo compound 2 (64-79% after sublimation).<sup>13</sup>

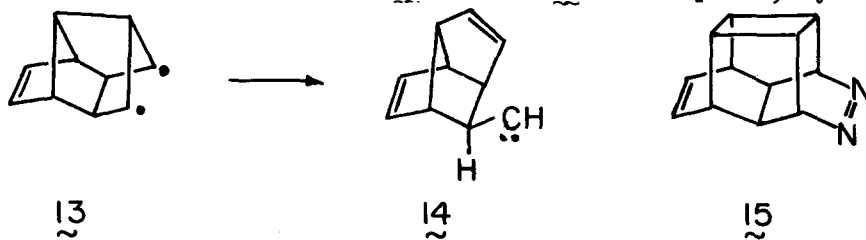
Through-Pyrex irradiation of 2 in purified pentane (0.0025-0.01 M) at ambient temperature with a medium-pressure Hanovia light source (450 W) resulted in the production of a mixture consisting (vpc analysis) of 58-61% triquinacene (1), 25-30% of the new (CH)<sub>10</sub> isomer 10, 9-10% of 11, and 3% of triene 12. The individual hydrocarbons may be separated gas chromatographically (5% SE-30 on Chromosorb G, 70°) or more conveniently by column chromatography on silica gel (pentane elution). The characteristic<sup>3</sup> two sharp pmr (CDCl<sub>3</sub>) singlets ( $\delta$  5.62 and 3.73) of 1 in the ratio of 6:4 define unequivocally the triquinacene molecule, the formation of which corresponds to cleavage of that C-C bond  $\beta, \beta'$ -oriented to the departing azo group. Photoproduct 11 has previously been characterized as the (CH)<sub>10</sub> system into which hypostrophene is converted irreversibly upon warming to 80°.<sup>14</sup> The genesis of 11 can be economically rationalized in terms of intermediate biradical 13 in which 1,2-shift of the remote apical



carbon atom leads directly to this diene.

Collapse of this same hypothetical intermediate with accompanying bridging leads to production of a bicyclo[2.1.0]pentane moiety and may represent the mode of formation of **10**. The pmr spectrum ( $\text{CDCl}_3$ ) of this stable oily hydrocarbon<sup>8</sup> shows the customary downfield triplet ( $\delta$  5.52, 2H, olefinic) in addition to multiplets centered at 2.94 (1H), 2.83 (2H), 2.21 (2H), 2.05 (2H), and 1.27 (1H). In its upfield region, this spectrum is reminiscent of that of cuneane.<sup>15</sup> Double irradiation studies of **10** at 100 MHz established that the signal at 2.94 arises from the apical proton proximal to the  $\pi$  bond, the 2.83, 2.21, and 2.05 multiplets from the allylic, bicyclopentyl, and homoallylic hydrogen pairs, respectively, and the most upfield peak (1.27) to the remaining cyclopropyl proton.

Structural assignment to **12** is based upon (a) the presence of a terminal spin-isolated methylene group (s,  $\delta$  4.74); (b) a pair of additional olefinic absorptions (2H each) at  $\delta$  6.20 and 5.67 which are nearly identical in multiplicity to the comparable signals exhibited by lumibullvalene;<sup>16</sup> and (c) two likewise paired allylic methine transitions at  $\delta$  3.03 and 2.65 which accord with the  $C_2$  symmetry of the molecule. The genesis of **12** is most easily envisioned as the result of rearrangement of **13** to carbene **14** and subsequent 1,2-hydride shift.



When pyrolyzed in a flow system ( $N_2$ ) through a quartz chip packed quartz reactor at  $380^\circ$  and 40 mm, azo compound **2** suffered loss of nitrogen and conversion not to **1** but to a mixture of dihydrofulvalenes in which the 1,5-dihydro isomer predominated.<sup>17</sup> Catalytic hydrogenation of this mixture furnished bicyclopentyl exclusively. This ready fragmentation, which contrasts strikingly with the reported thermal stability of **15**,<sup>18</sup> can be viewed as the result of a symmetry-allowed [ $\pi^2_s + \sigma^2_s + \sigma^2_s + \sigma^2_s + \sigma^2_s$ ] fragmentation, although the data of course do not demand this.

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#### FOOTNOTES AND REFERENCES

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- (8) Satisfactory combustion analyses have been obtained for all new compounds reported here.
- (9) We recognize that the two apical hydrogens in **4** reside in differing chemical environments. However, molecular models show that these protons are projected rather acutely away from the 2- and 3-positions of the norbornyl moiety. Moreover, using the chemical shifts of the bridge protons in **77** as a point of reference, it is clear that the external influences on the AB pair are nearly identical. As will be seen, only small accentuated differences appear in these adducts even when the two nitrogen atoms take on the form of an azo group as in **2**.
- (10) Mp 216-217° dec; pmr ( $CDCl_3$ )  $\delta$  7.40 (s, 1OH, aryl), 6.45 (m, 4H, olefinic), 5.18 (m, 2H,  $>CHN<$ ), 4.85 (m, 2H,  $>CHN<$ ), 3.07 (br d,  $J \approx 8$  Hz, 1H), and 2.05 (br d,  $J \approx 8$  Hz, 1H).
- (11) Obtained in two crystalline forms, mp 70-71.5° and 78-79.5°; pmr ( $CDCl_3$ )  $\delta$  5.82 (t,  $J=2$ Hz, 2H), 4.56 (d,  $J=3$  Hz, 2H), 4.18 (q,  $J=7$  Hz, 4H), 2.90 (m, 2H), 2.30 (br m, 2H), 2.03 (m, 2H), and 1.28 (t,  $J=7$  Hz, 6H).
- (12) We do not yet consider the yields of **4** and **8** optimized. In part, yield calculations suffer from our ignorance of the efficiency of the coupling reaction and the requisite transfer of the cyclopentadienide solution to remove the alumina (from  $Na/Al_2O_3$ ) employed in its generation. To date, we have typically isolated 5.1 g of **8** from runs involving 50 g of cyclopentadiene. The amounts of **4** produced are somewhat lower.
- (13) Mp 65.8-66.5° (sealed tube); pmr ( $CDCl_3$ ) 5.86 (t,  $J=2$ Hz, 2H), 5.21 (d,  $J=3$  Hz, 2H), 3.02 (m, 2H), 2.56 (m, 1H), 2.44 (m, 1H), and 1.96 (m, 2H).
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