

NOVEL PHOTOCHEMICAL 1,3-ADDITION OF TRIMESIC ACID ESTERS
TO DIPHENYLACETYLENE

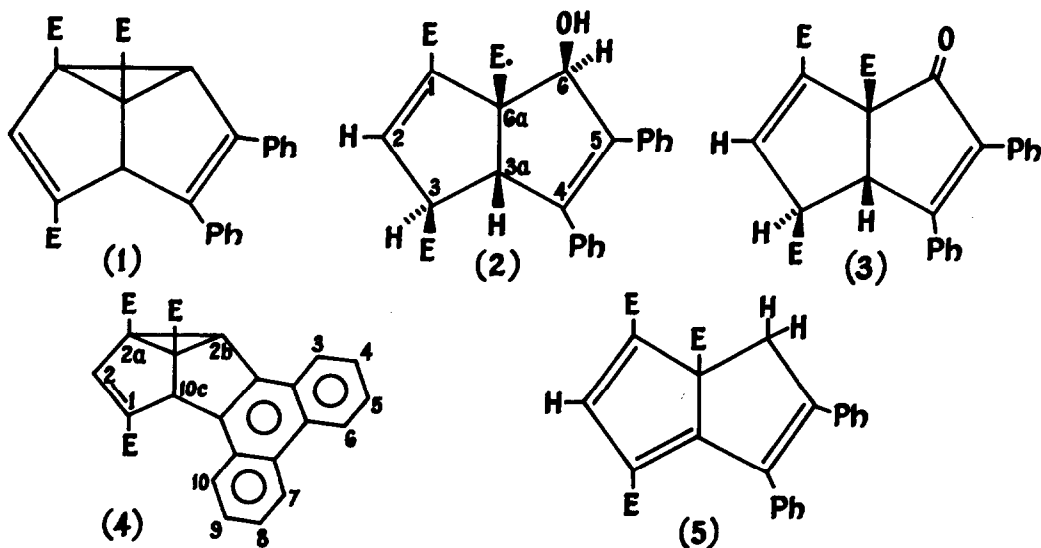
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Benzene when photochemically excited undergoes cycloadditions to alkenes in a 1,2-, 1,3-, and 1,4-manners although the 1,3-addition is favoured on orbital symmetry grounds,^{1,2,3} whereas the photochemical additions between benzene and various acetylenes take place solely in the 1,2-fashion.^{4,5} However, it has been shown that the excited species in this case is the acetylene rather than the benzene.⁶ In this context, the photo-additions of the excited benzene to an acetylene are of interest. We report here the novel photochemical 1,3-addition of a benzene derivative to diphenylacetylene.

Ultraviolet irradiation through Pyrex-filter for 6 days of a solution of trimesic trimethylester and diphenylacetylene (1:1 mixture) in methylene chloride gave predominantly one 1:1 adduct (5%) which could not be isolated in a pure state. Based on the pmr spectrum together with the following chemical and spectral evidence the structure (I, E=CO₂Me) has been assigned; δ (CDCl₃): s, 3.16 (3H; OMe), s, 3.73 (3H; OMe), s, 3.85 (3H; OMe),



s, 4.48 (1H), s^{*}, 4.61 (1H), s, 6.64 (1H), and m, 6.8-7.4 (Ar-H). Chromatography of (1) on alumina converted it to the hydrated crystalline compound (2, E=CO₂Me), m.p. 168-172°⁷; $\nu_{\text{max}}^{\text{KBr}}$ 3640 cm⁻¹ (OH); $\lambda_{\text{max}}^{\text{EtOH}}$ (ϵ), 263 (9,350) and 225 nm (23,400) which retains the stilbene chromophore; m/e (%), 448 (91) (molecular ion), 430 (43), 390 (35), 389 (100), 357 (44), 297 (48), 241 (41), 239 (36), 178 (33), 57 (35), 43 (38), others less than 33%, and δ (CDCl₃)⁸ at d, 3.30 (1H; J_{6,OH} 7.6 Hz; OH), dd, 3.36 (1H; J_{2,3} 3.1 Hz, J_{3,3a} 2.3 Hz; H-3), dd, 4.89 (1H; J_{3,3a} 2.3 Hz, J_{3a,6} 2.7 Hz; H-3a), dd, 5.69 (1H; J_{3a,6} 2.7 Hz, J_{6,OH} 7.6 Hz; H-6), dd, 6.74 (1H; J_{2,3} 3.1 Hz, J 0.4 Hz; H-2), s^{*} 7.2 (10H; Ar-H) and three nonequivalent methyls at 3.68, 3.76 and 3.86. The stereochemistry of (2, E=CO₂Me) with a cis junction between the two rings joined by 1,3-photoaddition of the benzene derivative is supported by the pmr spectrum. The coupling constant (J_{3,3a} 2.3 Hz) indicates a trans configuration of H-3 and H-3a as examination of models shows that a large coupling (ca. 10Hz) would be expected for a cis arrangement. In addition, the observed value (J_{3a,6} 2.7 Hz) is in agreement with other reported homoallylic couplings,⁹ is identical with that reported for the transoid configuration of tetraethyl 3,7-dioxobicyclo-[3,3,0]octene-2,4,6,8-tetracarboxylate,¹⁰ the closest structure to (2) found in the literature.

The facile hydration of (1) under basic conditions is consistent with the presence of a cyclopropane ring. Although electrophilic addition to cyclopropane is well known, nucleophilic additions are rare. However, α -carbanion stabilising substituents, such as ester groups, render the cyclopropane skeleton exceedingly reactive towards nucleophilic attack.¹¹

The hydroxy compound (2, E=CO₂Me) is oxidised under mild condition¹² to the ketone (3, E=CO₂Me), m.p. 141-146°⁷; m/e (%) at 447 (33), 446 (100) (molecular ion), 386 (42), 355 (31), 328 (31), 178 (23), other peaks less than 23%; $\nu_{\text{max}}^{\text{KBr}}$ at 1740 (ester), 1720 (cyclopentanone), and 1705 cm⁻¹ (ester); $\lambda_{\text{max}}^{\text{EtOH}}$ (ϵ) at 301 (10,700), 266 (7,500) (inflexion), 250 (11,200) (inflexion), and 228 nm (21,000) which shows a large bathochromic shift due to the Ph-C=C=O chromophore; and δ (CDCl₃)⁸ at dd, 3.45 (1H; J_{2,3} 3.1 Hz, J_{3,3a} 2.9 Hz; H-3), s, 3.73 (3H; OMe), s, 3.79 (3H; OMe), s, 3.83 (3H; OMe), d, 4.85 (1H; J_{3,3a} 2.9 Hz; H-3a), d, 6.87 (1H; J_{2,3} 3.1 Hz; H-2) and m, 7.1-7.4 (10H; Ar-H). Apart from the absence of a proton at C-6 and its coupling to H-3a the spectrum is little different to that of (2, E=CO₂Me) which indicates that no skeletal change occurred during oxidation, and that the coupling from the H-6 proton in (2) is of a long range type rather than a vicinal coupling.

Irradiation of trimesic acid triethylester under similar conditions gave compound (2, E=CO₂Et) in better yield (14.6%), m.p. 89-92°⁷; m/e (%) at 490 (98) (molecular ion) 473 (45), 417 (100), 371 (46), others less than 45%; the pmr spectrum of which is superimposable with that of (2, E=CO₂Me) except for the signals of the ester groups. A second compound, m.p. 190-196.5°⁷, was isolated from the reaction mixture by chromatography on silicic acid. The molecular ion at 470 (100%) in the mass spectrum indicates a loss of two hydrogen atoms from the structure (1, E=CO₂Et). The striking similarity of the ultraviolet spectrum of this compound, $\lambda_{\max}^{\text{EtOH}}$ (ϵ) at 316 (7,800) (shoulder), 303 (7,700), 273 (10,200), 258 (35,900), and 250 nm (34,500) (shoulder) to that¹³ of 9,10-dimethylphenanthrene suggests the structure (4). The absence of two aromatic protons, when compared with (1, E=CO₂Me) and the unusually large downfield spread of the aromatic protons in the pmr spectrum: δ (CDCl₃)⁸ at t's, 1.18, 1.28, 1.39 (3H's; splitting 7 Hz; OCH₂CH₃); q's, 4.05, 4.21, 4.57 (2H's; splitting 7 Hz; OCH₂CH₃), s, 5.14 (1H; H-2b), d, 5.30 (1H; J_{2,10c} 0.65 Hz; H-10c), d, 6.42 (1H; J_{2,10c} 0.65 Hz; H-2), m, 7.45-8.8 (8H; Ar-H), supports the presence of the phenanthrene nucleus. The H-2b at 5.14 is at much lower field than has been observed for other protons of this type. The downfield shift can be explained by its position in the deshielding plane of the phenanthrene ring current. Similar photocyclisation of the stilbene moiety under these conditions has been found in this laboratory.¹⁴

Oxidation of compound (2, E=CO₂Et) gave the ketone (3, E=CO₂Et), m.p. 125-129°⁷; m/e (%) at 489 (33), 488 (100), (molecular ion), 414 (21), 413 (39), 368 (41), 341 (28), 296 (31), 239 (21), 178 (30), 149 (19), 105 (19), others less than 19%; ν_{\max}^{KBr} 1745 (ester), 1730 (ketone), 1710 (ester), and 1645 cm⁻¹ (double bond); $\lambda_{\max}^{\text{EtOH}}$ (ϵ) at 300 (12,200), 250 (11,700) (inflexion), and 225 nm (26,300); the pmr spectrum is identical to that of (3, E=CO₂Me) except for the resonance due to ester groups.

Treatment of compound (2, E=CO₂Et) with a trace of p-toluenesulphonic acid in boiling benzene afforded a yellow compound in high yield, m.p. 106-110°⁷. The spectroscopic data show a loss of water; m/e (%) at 472 (100) (molecular ion), 425 (50), 399 (85), 398 (90), 252 (67), others less than 50%; ν_{\max}^{KBr} no absorption band for the hydroxyl; a large bathochromic shift (134 nm), ν_{\max}^{EtOH} (ϵ) at 397 (14,800), 273 (15,200) and 240 nm (18,500), and δ (CDCl₃)⁸ at, d, 2.86 (1H; J_{gem} -15.7 Hz; H-6), d, 3.61 (1H; J_{gem} -15.7 Hz; H-6), s, 7.99 (1H; H-2), m, 7.0-7.4 (10H; Ar-H), together with signals for three nonequivalent ethyl groups. Based on

this evidence the structure (5, E=CO₂Et) is proposed which can logically be arrived at by initial loss of the hydroxyl group followed by a 1,4-sigmatropic hydrogen shift¹⁵ and then loss of a proton. The Dreiding model shows that the hydrogen atom at C-3a is in a preferable position to migrate to the site of the developing positive charge at C-6. The formation of a stable tertiary carbonium ion at C-3a no doubt provides the driving force for this hydride shift and the reaction is further favoured by the formation of the highly conjugated molecule (5).

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