Tetrahedron Letters No. 49, pp 4313 - 4316, 1975. Pergamon Press. Printed in Great Britain.

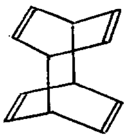
# PHOTOCYCLOADDITION OF CIS-1,2-DIHYDROPHTHALIC ANHYDRIDE TO BENZENE AND ARENES

N. C. Yang,*[1] Charles V. Neywick, and Kasturi Srinivasachar

Department of Chemistry, University of Chicago, Chicago, Illinois 60637

(Received in USA 27 August 1975; received in UK for publication 24 October 1975)

Tricyclo[4.2.2.2$^{2,5}$]dodeca-3,7,9,11-tetraene (1) and tricyclo[4.2.2.2$^{2,5}$]dodeca-3,7,9-triene (2) contain a number of isolated π-systems in spatial proximity and thus are expected to exhibit interesting chemical and physical properties. Although the photocycloadditions of cyclic 1,3-dienes to aromatic hydrocarbons yield several novel products,[2-5] benzene itself does not react photochemically with 1,3-cyclohexadiene to give the expected adduct (2). The major volatile products of this reaction are isomeric 1,3,5-hexatrienes under a variety of experimental conditions,[6] in direct contrast to the photocycloaddition of furan to benzene which gives the $4\pi_s+4\pi_s$ adduct (3), recently reported by Cantrell and by Berridge, Bryce-Smith and Gilbert.[4,5] Apparently, benzene may transfer its excitation energy to 1,3-cyclohexadiene which then undergoes a conrotatory ring-opening to give cis-1,3,5-hexatriene,[7] while such an energy transfer cannot occur with furan. If the ring opening is retarded by appropriate substituents in the cyclohexadiene moiety, the $4\pi_s+4\pi_s$ photocycloaddition between benzene and the substituted 1,3-cyclohexadiene may proceed to give a substituted 2 among its products. We wish to report the photocycloaddition of cis-1,2-dihydrophthalic anhydride (4) to benzene, naphthalene, and anthracene to give 5-7 respectively. These compounds may be the key intermediates in the syntheses of homo- and heterodimers of benzene including 1 and other novel cyclic systems, such as 8 and 9.



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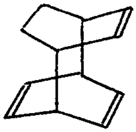

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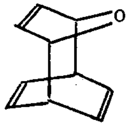

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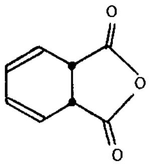

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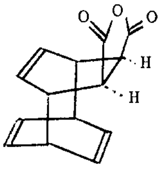

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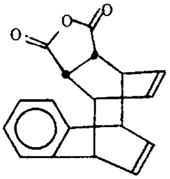

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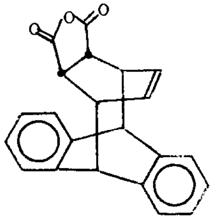

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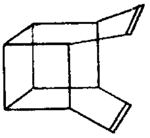

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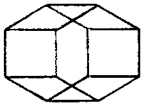

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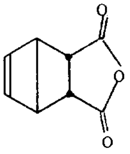
Irradiation of a 1.67X10$^{-2}$ M solution of 4 in benzene (1 g/400 ml) under nitrogen with a Hanovia 450-w Hg-arc through a Vycor filter yielded a mixture including a copious amount of an insoluble yellow deposit which was not identified. Evaporation of the benzene solution yielded 880 mg of a residue, from which two major products could be isolated by chromatography on silica gel, bicylo[2.2.0]hex-5-ene 2,3-dicarboxylic acid anhydride 10 isolated as the diacid (145 mg, 29%)[8] and 5 (76 mg, 5%), plus traces of several minor products. The crude yields of 5 and 10 may be estimated from the nmr spectrum of the reaction mixture to be 13% and 51% respectively. Recrystallization of 5 from benzene-hexane yielded an analytical sample, mp 149-150° (dec); uv end absorption; ir (KBr) 1785 and 1850 cm$^{-1}$; mass spec (70 ev) parent ion (m/e) 228; anal. found C, 73.53 and H, 5.35; nmr δ(CDCl$_3$) 3.39 (m, 2), 3.50 (m, 2), 3.86 (s, 2), 6.00 (sextet, 2), 6.29 (sextet, 2) and 6.52 ppm (sextet, 2). Spin decoupling experiments substantiated the structure assignment. Photocycloaddition of 4 to naphthalene and anthracene in dichloromethane proceeded smoothly to give 6 (85%) and 7 (69%), respectively. The structure of 6 and 7 were established by spectroscopic and elemental analyses. The hydrogens α- to the anhydride function occupy the endo positions as indicated by the lack of coupling with the neighboring bridgehead hydrogens in their nmr spectra [δ 3 ppm (s)]. The structure of 6 was further substantiated by the xanthone sensitized photocyclization to 11 [66% yield; mp 240-241°; ir (KBr) 1840 and 1745 $cm^{-1}$; uv max (ethanol) 273.5 ($\epsilon$ 128) and 264 nm ($\epsilon$ 177); nmr $\delta$ ($CDCl_3$) 2.62 (s, 2), 2.90-3.15 (m, 4), 3.73 (m, 2), 4.10 (m, 2) and 7.10-7.25 ppm (m, 4); anal. found C, 77.21 and H, 5.01].

Since 10 is the major product in the irradiation of a very dilute solution of 4 in benzene, in which virtually all the incident light was absorbed by benzene, energy transfer from excited benzene to 4 is still the major reaction pathway. The excited singlet energy levels of 1,3-cyclohexadiene ($\lambda_{max}$ 264 nm, $\epsilon$ 8,000) and 4 ($\lambda_{max}$ 264 nm, $\epsilon$ 5,000) are not known. Judging from their uv spectra and our experimental results, they must be quite close to each other as well as to that of benzene such that a minor modification in the structure of 1,3-cyclohexadiene to 4 enables the $4\pi_s+4\pi_s$ addition to occur.

Preliminary investigations indicated that 5 also undergoes xanthone sensitized photocyclization to 12. The conversion of 5 to other ring systems and the substituent effect in aromatic hydrocarbons on their photocycloaddition to 4 are currently under investigation in our laboratory.



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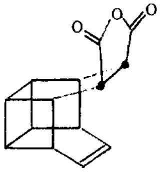

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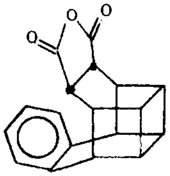

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Acknowledgement. The authors wish to thank the National Institute of General Medical Sciences, grant GM-20329, and the National Science Foundation, grant MPS-22579, for the support of this work. The high resolution nmr spectrometers used were purchased with funds from equipment grants made by the National Science Foundation (GP-33116) and the National Cancer Institute through the University of Chicago Cancer Research Center (CA-14599).

## Footnotes

(1) Guggenheim Fellow, 1974-5.

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