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PHOTOCHEMICAL CYCLOADDITION REACTIONS. III[1].

A FACILE SYNTHESIS OF DIMETHYL 2,3-PLEIADIENEDICARBOXYLATE

Joan E. Shields*, Dragan Gavrilovic* and Jan Kopecký**

*Department of Chemistry, C. W. Post College of Long Island University,
Brookville, New York

**Institute of Industrial Hygiene and Occupational Diseases,
Prague, Czechoslovakia

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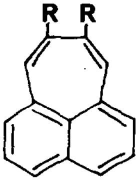
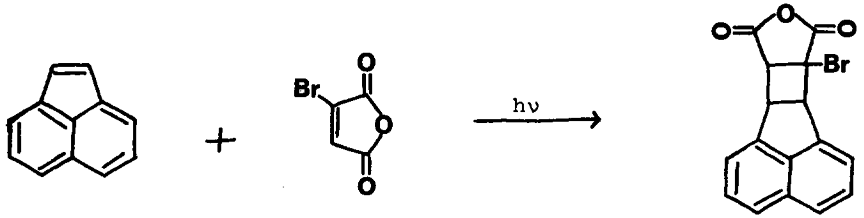
Pleiadiene and related nonalternant hydrocarbons have long been a subject of theoretical interest[2]. The synthesis of the parent compound, pleiadiene (I), has been reported[3,4]. However, extremely low yields from lengthy synthetic schemes have precluded an investigation of the physical and chemical properties of this substance. We now report the facile preparation of dimethyl cyclohepta[de]naphthalene-8,9-dicarboxylate (II), thereby providing an entry into this interesting 14 Π electron pleiadiene ring system.

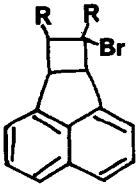


I, R = H
II, R = CO_2CH_3

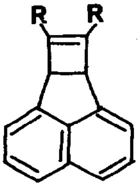
Aside from the well-known photodimerization[5], photochemical cycloadditions to acenaphthylene have been reported only with duroquinone[6], chloranil[7], and acrylonitrile[8]. Taking advantage of the heavy-atom effect observed in the photodimerization of acenaphthylene[9] and in its cycloaddition to acrylonitrile[8], we have found that brief irradiation[10] of an ethyl bromide solution, containing equimolar amounts of bromomaleic anhydride and acenaphthylene, led to deposition of III[11], $C_{16}H_9BrO_3$, as colorless crystals (45%), mp 240-242°, (from acetone-hexane). It should be noted that no cycloadduct was observed from irradiation of these addends in the absence of a heavy-atom solvent. Photolysis in acetone, benzene, cyclohexane, ether or hexane afforded only acenaphthylene dimer. Hydrolysis of anhydride III in a refluxing solution of acetone-water (2:1) gave the anticipated diacid IV, $C_{16}H_{11}BrO_4$, mp 248-249° (from acetone) in quantitative yield. Treatment of IV with diazomethane afforded 100% yield of



III



IV, R = CO_2H
V, R = CO_2CH_3



VI, R = CO_2CH_3

diester V, $C_{18}H_{15}BrO_4$, as colorless needles, mp 108-109° (from diethyl ether). Dehydrobromination of V with triethylamine in refluxing tetrahydrofuran gave 75% yield of colorless crystalline cyclobutene diester VI, $C_{18}H_{14}O_4$, mp 131.5-133° (from diethyl ether). The nmr spectrum ($CDCl_3$) of VI shows the presence of two carbomethoxy groups (δ3.81, singlet), two bridgehead protons (δ4.84, singlet) and six aromatic protons (δ7.38-7.80, multiplet).

Conversion of VI to the desired dimethyl 2,3-pleiadienedicarboxylate (II) was accomplished by heating a solution of VI in diphenylmethane under reflux (265°) for ten minutes. This valence isomerization was accompanied by the appearance of a brick-red solution. Chromatography of this solution on a silica gel column resulted in the separation of diphenylmethane (elution with hexane) and pleiadiene diester II (elution with 5% diethyl ether-hexane). The latter fraction, after recrystallization from diethyl ether-hexane, gave 80% yield of II, $C_{18}H_{14}O_4$, as orange-red needles[12], mp 107-108°. Proof of structure of II was based on elemental analysis, molecular weight and the following spectral evidence. The nmr spectrum ($CDCl_3$) exhibits a singlet of six methyl protons at δ3.78 and a multiplet of eight protons centered at δ7.21. The ultraviolet-visible spectrum is strikingly similar to that reported[3] for pleiadiene (I).

Further investigations, especially those directed toward the photochemical synthesis of pleiadiene and other derivatives, are now in progress.

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10. Irradiations were carried out in a Solidex reactor equipped with a Hanovia 100 w mercury-quartz high-pressure lamp cooled by a water jacket.
11. The structure assigned each new compound (II - VI) has been confirmed by spectral data (ir, uv and nmr), elemental analysis and molecular weight determination.
12. Pleiadiene (I) was reported as a red crystalline solid, (ref. 3).