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HETEROCYCLOPENTADIENE PHOTOCHEMISTRY

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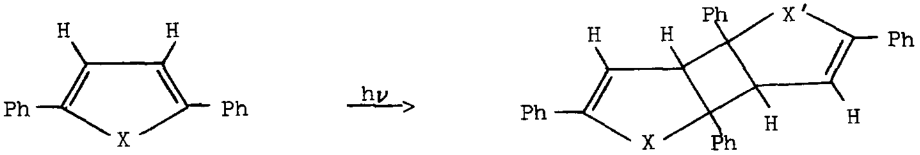
Current interest in the photochemistry of five-membered ring heterocycles(1-7) prompts us to report some results of an investigation of the photochemical behavior of a series of 2,5-diphenylheterocyclopentadienes. The choice of substituents might appear unwise, as Wynberg(8) found no photoproducts resulting from extensive irradiation of 2,5-diphenylthiophene, but was dictated by synthetic availability.

Irradiation(9) of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene(10)(Ia) in ether solution resulted in rapid formation of a colorless crystalline dimer (IIa)(mp 197-8°) and an unidentified polymer. Dimer IIa was identified from its elemental analysis, mass spectrum and nmr spectrum which showed a multiplet (22H) for the aromatic and olefinic protons centered at δ 7.09, a doublet (J=3.6 Hz) for the two allylic protons at δ 4.26 and two singlets (6H each) at δ 0.31 and -0.31 for the methyl protons. The spectral data does not necessitate a "head-to-tail" dimer nor does it specify the stereochemistry of the cyclobutane ring.(11)

This rather dramatic change in photochemical lability in replacing a sulfur atom by another heteroatom was found not to be specific for silicon. Irradiation(9) of 1,1-dimethyl-2,5-diphenyl-1-germacyclopentadiene(12)(Ib) under identical conditions again provided a "2+2" dimer (IIb)(mp 215-17°) whose nmr spectrum was virtually identical with that of IIa [complex multiplet (22H) δ 7.30, doublet (2H) δ 4.37, two singlets (6H each) δ 0.45 and -0.18]. Perhaps not surprisingly 1,1-dimethyl-2,5-diphenyl-1-stannacyclopentadiene(10)(Ic) upon irradiation(9) suffered Sn-C cleavage leading to polymeric products. Such photochemical cleavage of a vinyl tin is well precedented.(13)

Since the analogous thiophene was photochemically inactive, our results were presumed to be due to the fact that there was no aromatic stability to be lost in the dimerizations. Indeed the irradiation(9) of 1,2,5-triphenylpyrrole(14)(Id) provided no conversions even after nine hours. However, when 1,2,5-triphenylphosphole(15)(Ie), a ring system for which various claims of aromatic character have been made(16), was irradiated(9) in 50% THF/Et_2O solution for seven hours considerable loss of phosphole resulted and dimer IIe was isolated in good yield. Dimer IIe (white solid, mp 229-30°) was identified from elemental analysis, mass spectrum and nmr spectrum which showed only aromatic and olefinic protons (32H) centered at ca. δ 7.03 and a multiplet (2H) at δ 4.88 which collapsed to a doublet upon irradiation at phosphorus (24.2897 MHz). The ease of formation of IIe would seem to cast some doubt upon assignment of aromatic stabilization of the phosphole ring.



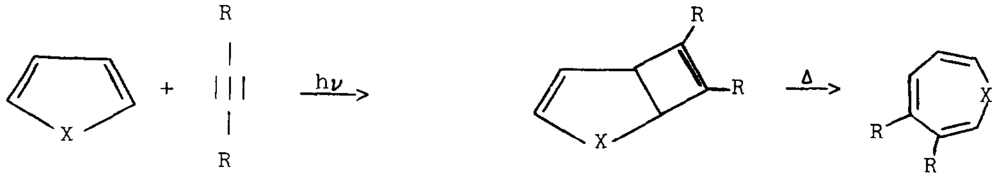
Ia, X=$(CH_3)_2Si$
Ib, X=$(CH_3)_2Ge$
Ic, X=$(CH_3)_2Sn$
Id, X=Ph-N
Ie, X=Ph-P
If, X=Te

IIa, X = $(CH_3)_2Si$
IIb, X = $(CH_3)_2Ge$
IIe, X = Ph-P
IIg, X = $(CH_3)_2Si$
X'= Ph-P

The inability of thiophenes to undergo photodimerization is presumably derived from their aromatic nature. Tellurophene (If) has been claimed(17) to possess aromatic character although qualitative consideration of the π-bond energy to be gained from 5p-2p overlap places this claim in a position of some incredulity. However, when 2,5-diphenyltellurophene(12)(If) was subjected to irradiation under similar conditions no photoproducts were formed and recovery of starting material was quantitative. Preliminary experiments in our laboratory have also confirmed the aromatic character of the tellurophene ring system. This character is perhaps best exemplified by inability to act as a diene in a Diels-Alder reaction even under forcing conditions.

It should be noted that at least in the cases of IIa and IIe the dimerization is reversible if light of a higher energy (no filter) is employed. Attempts to trap the excited intermediate with added olefins or acetylenes have been unsuccessful to date even though ten-fold molar excesses of trapping agent were used. Thus a large preference for photodimerization is exhibited by these systems. The only successful diversion of this reaction was formation of the mixed dimer (IIg)(mp 248-9°) upon irradiation of an equimolar solution of Ia and Ie.

Work is continuing on the "2+2" addition of acetylenes to the heterocyclopentadiene systems in an attempt to provide a synthetic pathway to heterocycloheptatrienes. Such cycloadditions have recently been reported for benzo[b]thiophene(18), a ring system which is known to undergo photodimerization in the oxidized (sulfone) form(19).



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(9) A 450-watt Hanovia medium-pressure mercury arc lamp was employed with a Pyrex filter unless otherwise stated. Nitrogen was continuously passed through the solution during the photolysis. All concentrations were one gram per 350 ml of solvent.

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(11) Structures of Ia, Id, Ie, and IIa are presently under investigation by Dr. J. C. Clardy using x-ray crystallography.

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