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PHOTOREARRANGEMENT OF PHOTOCYCLOADDUCTS FROM ARENES AND 1,3-CYCLOHEXADIENE

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Summary: The $4\pi_s+4\pi_s$ photoadduct from an arene and 1,3-cyclohexadiene may undergo a photochemical rearrangement to the $4\pi_s+2\pi_s$ adduct.

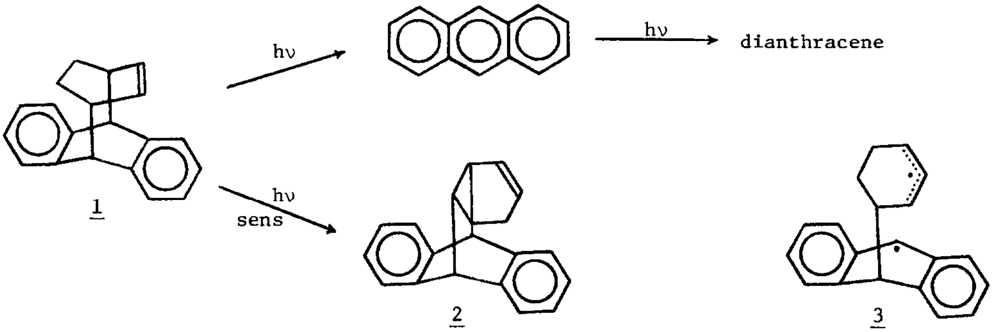
Photocycloadditions of 1,3-dienes to arenes have been applied to the synthesis of a variety of novel cyclic compounds.[3] The mechanism of these reactions has been a subject of current interest and dispute.[4-7] One of the bases of dispute is the difference in the composition of products formed in a given reaction from different laboratories using different experimental conditions. Although the major product formed in these reactions is the formal $4\pi_s+4\pi_s$ adduct, e. g., 1 from anthracene (An) and 1,3-cyclohexadiene (CHD), and its formation may be rationalized via a concerted process in accordance with the rule of conservation of orbital symmetry,[8] substantial amounts of other products also may be formed including formal $4\pi_s+2\pi_s$ adducts such as 2. Kaupp has proposed an alternate mechanism in which both products are formed via a common biradical intermediate 3.[5] However, the relative yields of these adducts often depend upon the ratio of reactants, their concentrations, the solvent, and the wavelength of exciting light.[4-6] The present investigation demonstrates that $4\pi_s+4\pi_s$ adducts from CHD and arenes undergo secondary photochemical reactions to give the corresponding $4\pi_s+2\pi_s$ adducts in variable yields, whereas $4\pi_s+2\pi_s$ adducts are stable under comparable conditions. The results not only do not support the contention of a common biradical intermediate in the formation of both types of adducts but also enable us to control the pathway of these reactions leading to the formation of either adduct as the major adduct for synthetic purposes.[3]

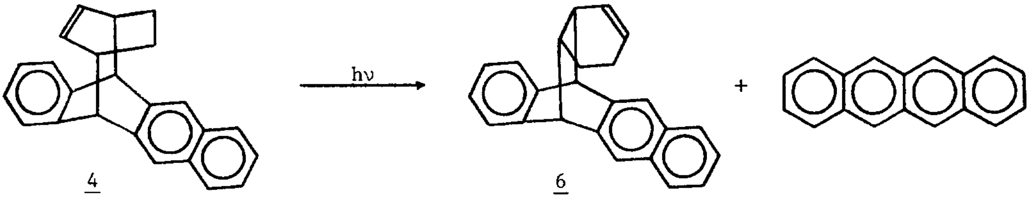
Although 1 sublimes without decomposition under reduced pressure at 200°C, it undergoes photodecomposition under both direct and sensitized conditions. Direct irradiation of 1 in acetonitrile with Vycor filtered light causes mainly its dissociation to An which subsequently photodimerizes. However, irradiation of a benzene solution of 1, with light absorbable

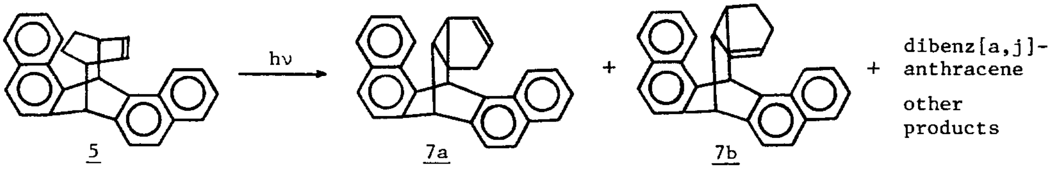
Table[a]

Adduct	Solvent	Filter	Sensitizer	Products		
				Adduct	Arene Dimer	Other
1	CD_3CN	Vycor	--	2,<5%	>95%	-[b]
2	CD_3CN	Vycor	--	-	-	-
1	C_6H_6 or C_6D_6	Pyrex	benzene	2,92%	8%	-
2	C_6H_6 or C_6D_6	Pyrex	benzene	-	-	-
1	$CDCl_3$ or CD_3CN	Uranyl	xanthone	2,80%	20%	-
2	$CDCl_3$ or CD_3CN	Uranyl	xanthone	-	-	-
4	C_6D_6	Pyrex	--[c]	6,50%	50%	-
5	C_6H_6	Pyrex	--[c]	7a&b,15%	-	39%, a,j-DBA 46%, unknown

[a] All irradiations were carried out with a Hanovia 450-watt Hg-arc with an appropriate filter. Reactions carried out in deuterated solvents were analyzed by nmr spectrosocpy while those in non-deuterated solvents were analyzed by chromatography followed by nmr spectroscopy. [b] None detected. [c] No distinction was made between direct and sensitized irradiation.







by benzene, results in its rearrangement to 2. Since benzene is a common solvent used in the photocycloadditions of arenes to 1,3-dienes,[4,5] improper filtering of the incident light may cause the decomposition of the primary photoproduct thus altering the product distribution. Photoexcited benzene can intersystem cross to a triplet state and function as a high energy sensitizer for the activation of either isolated olefinic systems or substituted benzenoid groups in compounds like 1.[9] The results (Table) suggest that excited 1 mainly undergoes "allowed" retrocycloaddition in the singlet manifold but mainly rearranges to the more stable isomer 2 in the triplet manifold. This is substantiated by the formation of 2 and a lesser amount of dianthracene in the xanthone-sensitized irradiation of 1 in CD_3CN or $CDCl_3$ (Table), with light absorbable only by the sensitizer (uranyl glass filtered). The rearrangement is likely to proceed via a biradical intermediate 3 which cyclizes to give the less strained 2. Adduct 2 is photostable under both direct and sensitized conditions (Table). Formation of less dianthracene when the sensitizer is benzene rather than xanthone may be attributed to the difference in the triplet energy levels of the sensitizers; the E_T of benzene is 84.3 kcal/mole but that of xanthone is only 74.1 kcal/mole.[9] Triplet benzene therefore may transfer energy to both 1 and dianthracene, while xanthone can transfer its energy only to the cyclohexenoid double bond of 1.

The photolability of $4\pi_s+4\pi_s$ adducts appears to be general (Table). Irradiation of 4 or 5, the major photoproduct formed between CHD and tetracene or dibenz[a,j]anthracene,[4c] respectively, led to their facile rearrangement to the corresponding $4\pi_s+2\pi_s$ adduct 6 or 7a&b[4c] as well as dissociation to the parent arene in benzene.

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References and Notes.

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