

THE CATION RADICAL ROUTE TO DIENE TRIPLETS

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Abstract: Diene triplets in predominantly the s-cis conformation are formed efficiently by back electron transfer to diene cation radicals in DMF and dichloromethane.

The formation of conjugated diene cation radicals by photosensitized electron transfer to 1,4-dicyanobenzene (DCB) in acetonitrile solution and their subsequent efficient and selective participation in the cation radical Diels-Alder reaction are now well established.¹⁻³ It has now been observed that the cyclodimerizations of 1,3-cyclohexadiene (1) and 2,4-dimethyl-1,3-pentadiene (2) in N,N-dimethylformamide (DMF) and dichloromethane (DCM) solution follow a dramatically different course, resulting in formation of cyclobutane/Diels-Alder dimer mixtures indicative of the triplet states of 1 and 2. The cation radical (or back electron transfer) route to diene triplets is only a minor side-reaction in the DCB-sensitized dimerization of 1 and 2 in acetonitrile. In contrast, triplet formation appears to be the exclusive reaction mode of 1 and 2 in DMF and also of 2 in DCM.

Results of photosensitized cyclodimerization of 1 and 2 in DMF and of 2 in DCM with DCB as photosensitizer are illustrated in the Scheme and Table. Conversions after ca. 20h of photolysis were as high as 85% in the case of 2 (in DCM) and 40% in the case of 1 (DMF). As required, the distribution of cyclodimers of 1 is virtually the same as in the conventional triplet-sensitized dimerization.⁴ Triplet-sensitized dimerization of 2 has not been reported, and could not be effected using benzophenone or several other common triplet sensitizers. Fluorenone sensitization, however, is effective, giving a cyclodimer distribution very different from that obtained via the cation radical route. In particular, the latter reaction

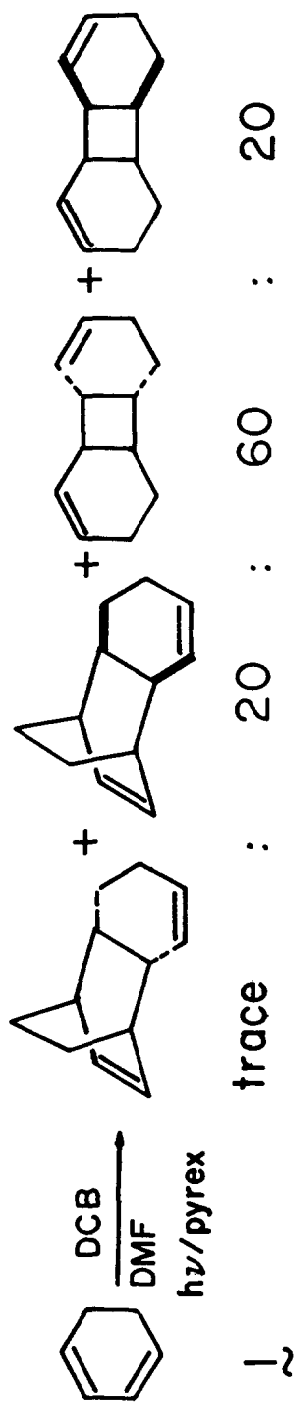
TABLE

Sensitizer/Solvent	Dimeric Products from <u>2</u> ^a			Conversion
	<u>%3</u>	<u>%4</u>	<u>%5</u>	
DCB/CH ₃ CN/hv	95.3	4.0	0.7	71
DCB/DMF/h	70.0	22.6	7.4	1
DCB/DCM/h	72.1	21.1	6.7	85
Fluorenone/neat <u>2</u> /h	43.0	39.0	18.0	--
DCB/DMF/TMB/h	67.0	26.0	7.0	0.01

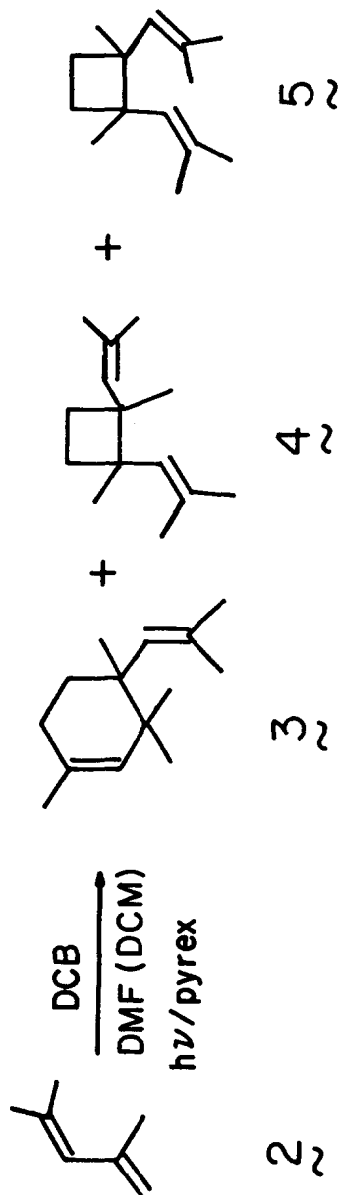
^aPhotochemical experiments were conducted at 0.25 M diene concentration, 1:1 sensitizer:diene ratio, at ambient temperature for ca. 20h using a Hanovia 450W medium pressure mercury lamp with a pyrex filter.

is characterized by a much higher Diels-Alder:cyclobutane adduct ratio (3:4+5) than the former. This disparity is, of course, permissible in view of the conformational mobility of 2 (in contrast to 1) and the known tendency of s-trans diene triplets to produce cyclobutane adducts almost exclusively but of s-cis diene triplets to afford, in addition, substantial amounts of Diels-Alder type adducts.⁵ The cycloadduct mixtures obtained from 2 via the cation radical route appear to emanate purely from triplet 2 rather than from a mixture of triplet chemistry and cation radical Diels-Alder cycloaddition. This is alluded to by the virtually identical product distributions obtained in the two different solvents (DCM and DMF) and more strongly supported by the fact that the product distribution is independent of diene (2) concentration. Specifically, the rate of cation radical Diels-Alder addition via an exciplex is dependent on the diene concentration, whereas back electron transfer to a diene cation radical is not. Cation radical Diels-Alder cycloaddition via a chain process, involving separated ion radicals formed in a rate limiting diffusive separation, is also excluded by the observation that the product distribution is also unchanged by added 1,3,5-trimethoxybenzene (TMB), even though the cycloaddition is strongly (but not completely) quenched. The cycloadduct distribution emanating from 2 in the solvents DMF and DCM, therefore appears to reflect only cycloadditions of triplet 2 to ground state 2. The rather strong preference for the Diels-Alder mode suggests that the diene cation radicals which are precursors to triplet 2 exist predominantly in the s-cis conformation, giving rise to primarily s-cis triplets. The involvement of s-cis diene cation radicals as dienophiles in the cation radical Diels-Alder has previously been inferred from the "cis-propenyl effect."⁶ It should also be noted that diene triplets relatively rich in the s-cis conformer have been generated using triplet sensitizers of slightly lower triplet energy than that of the s-trans diene.⁵ The

SCHEME



40% CONVERSION



cyclodimerization of 1 in DCM, in contrast to the results in DMF and to the behavior of triplet 1, yields substantial quantities of the endo Diels-Alder adduct (28% of the total dimer), indicative of a competing cation radical Diels-Alder reaction. Indeed, added trimethoxybenzene strongly and selectively suppresses this product and returns the distribution to one close to that observed for triplet 1 (5:22:51:21, respectively, referring to the products in the sequence illustrated in the scheme).

The generality of the cation radical route to diene triplets is circumscribed by diene ionizability, failing, of course, where the diene is too difficultly ionizable (butadiene, mono- and di-alkylated butadienes, electron deficient dienes) and also where the diene is too easily ionized (dicyclopentenyl, 2,4-dimethyl-hexadiene, 1-methoxycyclohexadiene). The problem in the latter case is insufficient energy to generate diene triplets via the back electron transfer. The strong preference for back electron transfer over Diels-Alder cycloaddition in DMF (in contrast to acetonitrile) is attributed, at least in part, to the more efficient solvation of the diene cation radicals in DMF, which strongly retards cycloaddition. In DCM, in contrast, slow ion separation from the exciplex appears a more likely explanation. Thus, acetonitrile emerges as the ideal solvent for the photosensitized cation radical Diels-Alder reaction.

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NOTES AND REFERENCES

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