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SENSITIZING ACTIONS OF AROMATIC KETONES ON ISOMERIZATION OF NORBORNADIENE TO QUADRICYCLENE

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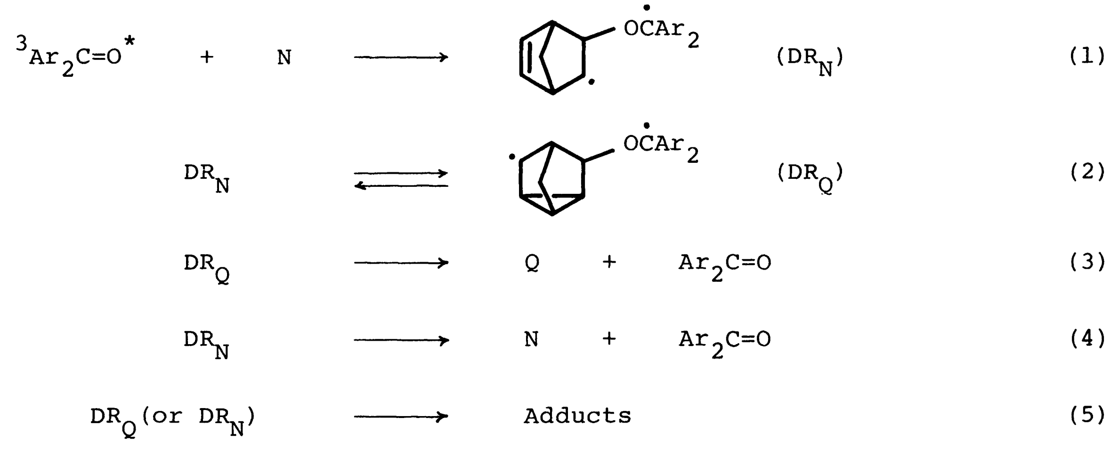
The quantum yields for norbornadiene to quadricyclene isomerization were measuerd in acetonitrile using several triplet sensitizers. Among benzophenones employed as sensitizers which have nearly the same triplet excitation energies, those with electron-donating substituents exhibited higher efficiency than those with electron-accepting substituents.

Currently much attention has been paid to photochemical isomerization of norbornadiene (N) to quadricyclene (Q) for chemical conversion and storage of solar energy.$^{1-4)}$ However, N exhibits absorption bands only at shorter wavelengths than 300 nm. For utillization of longer wavelength light, one possible way is use of suitable sensitizers and another is introduction of appropriate substituents in N to extend the absorption bands to longer wavelength and to improve the quantum yield for isomerization.$^{5,6)}$ Triplet sensitizers like benzophenone and Michler's ketone are known to sensitize the isomerization;$^{1-4)}$ however, there are not enough reports to understand the mechanism for the triplet sensitized isomerization and what kinds of triplet sensitizers are effective has not yet been clear. We now wish to report the effect of triplet sensitizers on the isomerization and to show that among the substituted benzophenones with nearly the same triplet energies, those with electron-donating groups are more effective in sensitization than those with electron-accepting groups.

The quantum yields for sensitized isomerization of N (0.1 mol l^{-1}) to Q were determined at low conversion using several triplet sensitizers (0.1 mol l^{-1}) in deaerated acetonitrile solutions. The results are summarized in Table 1 together with the triplet excitation energies (E_T) of the sensitizers employed. Figure 1 plots the quantum yields against the triplet energies of sensitizers. As Fig. 1 indicates, the sensitization efficiency is not governed by the triplet energies of sensitizers. Thus, triphenylene (E_T: 66.5 kcal mol^{-1}, 1 kcal = 4.184 kJ)$^{7)}$ is far less effective than benzophenone (E_T: 69.2 kcal mol^{-1})$^{7)}$ and even than 4-phenylbenzophenone (E_T: 60.7 kcal mol^{-1}).$^{7)}$ However, it is noticeable that along the quantum yield axis are scattered the plots for benzophenones with nearly the same triplet excitation energies, i.e., unsubstituted benzophenone, mono- and di-substituted benzophenones with methoxy, methyl, and chloro substituents. Figure 2 plots the quantum yields for these benzophenones against the Hammett sigma constants of the substituents of the benzophenones. This figure shows that the benzophenones carrying the electron-donating substituents act as more effective sensitizers. Accordingly, it is clear that the efficiency of the sensitizer is not fully controlled by its triplet excitation energy, but among the benzophenones employed some electronic effects of the substituents play an important role in the sensitization.

To get insight into the quenching process of the triplet benzophenones the efficiency of quenching by N and Q was investigated by transient spectroscopy. The sensitizers (4×10^{-4} mol l^{-1}) were excited by nitrogen laser in argon-purged acetonitrile solutions in the presence of varying concentrations of N and Q, and the decay of the resulting triplet states was followed at the T-T absorption maxima to get the quenching rate constants. The typical results are listed for unsubstituted benzophenone (BP), 4,4'-dichlorobenzophenone (CBP), and 4,4'-dimethoxybenzophenone (MBP) in Table 2. The fact that the rate constants for Q decrease in the order of CBP, BP, and MBP indicates a significant contribution of electron transfer interaction to this quenching process.[8)] N quenches more effectively the triplet state of CBP than that of BP or MBP. This cannot be explained only in terms of the typical triplet energy transfer because the triplet energy of CBP is lower than those of BP and MBP. Electron transfer interaction will not be so important in the case of N, because of the endothermicity of the electron transfer process (ΔG=13, 15, and 18 kcal mol^{-1}, for CBP, BP, and MBP, respectively).

The above findings of the nature of the isomerization efficiency relatively insensitive to the triplet energy of the sensitizers employed and of the less efficient sensitizing action of triphenylene than the aromatic carbonyl compounds[9)] suggest that the sensitization by benzophenone proceeds, at least in part, through addition of the $n\pi^*$ triplet state to N followed by subsequent steps as depicted in Scheme 1. The substituent effects of benzophenones on the sensitization efficiency could be explained by 1) the change in contribution of the addition and energy transfer mechanisms, and/or 2) the change in equilibrium between DR_N and DR_Q and that in rate constants of the elimination steps to produce Q and N from DR_Q and DR_N, respectively.[10)]



Scheme 1.

Table 1. Quantum yields for N→Q Isomerization ($\Phi_{N\rightarrow Q}$) in Acetonitrile[a)]

Sensitizer	E_T/kcal mol^{-1} b)	$\Phi_{N\rightarrow Q}$	$\Sigma\sigma$ c)
Benzil (1)	54.3	0.009	
4-Phenylbenzophenone (2)	60.7	0.23	
Michler's ketone (3)	62	0.04	
Triphenylene (4)	66.5	0.02	
4-Cyanobenzophenone (5)	67.0[d)]	0.33	0.66
4-Benzoylpyridine (6)	67.2	0.40	
2-Benzoylpyridine (7)	67.4	0.35	
4-Hydroxybenzophenone (8)	68.3[d)]	0.42	-0.37
4,4'-Dichlorobenzophenone (9)	68.4[d)]	0.29	0.46
4-Chlorobenzophenone (10)	68.8	0.29	0.23
4-Methoxybenzophenone (11)	69.0	0.53	-0.27
3-Benzoylpyridine (12)	69.0	0.36	
Benzophenone (13)	69.2	0.45	0
4-Methylbenzophenone (14)	69.2	0.50	-0.17
4,4'-Dimethylbenzophenone (15)	69.3	0.59	-0.34
4,4'-Dimethoxybenzophenone (16)	70.3	0.56	-0.54

a) Concentration of N, 0.1 mol l^{-1}. b) Triplet excitation energies of sensitizers taken from ref. 7, unless otherwise indicated. c) Hammett's sigma constants for substituted benzophenones (O. Exner, "Advances in Linear Free Energy Relationships," ed by N. B. Chapman and J. Shorter, Plenum, (1972)). d) Estimated from phosphorescence spectra measured in EPA at 77 K.

Table 2. Typical Rate Constants (k_q) for Quenching of Triplet Benzophenones with N and Q in Acetonitrile

Sensitizer	Quencher	τ/µs a)	k_q/l mol^{-1} s^{-1}
4,4'-Dichlorobenzophenone	N	21	7.8×10^{8}
	Q	22	1.8×10^{9}
Benzophenone	N	26	3.4×10^{8}
	Q	31	6.9×10^{8}
4,4'-Dimethoxybenzophenone	N	13	4.6×10^{8}
	Q	14	3.0×10^{7}

a) Lifetimes of sensitizer triplets in the absence of quencher in acetonitrile.

Finally, it should be noted that, though the sensitization mechanism is still not clear, the present results of the effects of electron-donating substituents on the benzophenones to enhance the N→Q isomerization will contribute to desirable designs of molecules to store solar energy as chemical one.

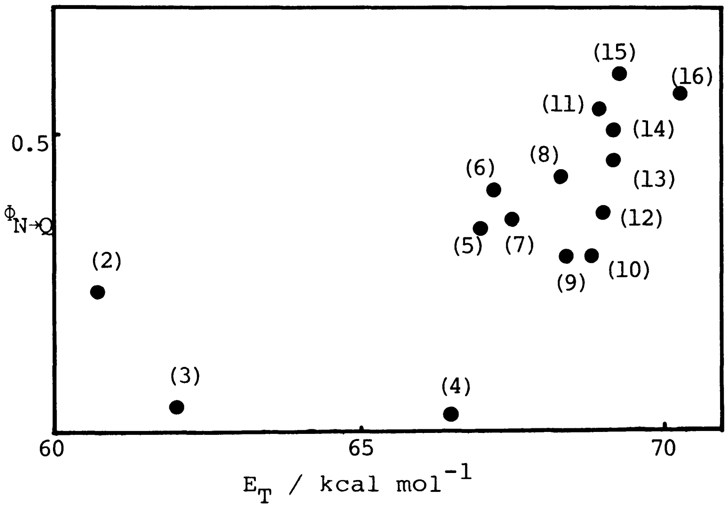


Fig. 1. Plot of the isomerization quantum yields ($\Phi_{N\to Q}$) against the triplet energies (E_T) of sensitizers. The numerals refer to the sensitizers in Table 1.

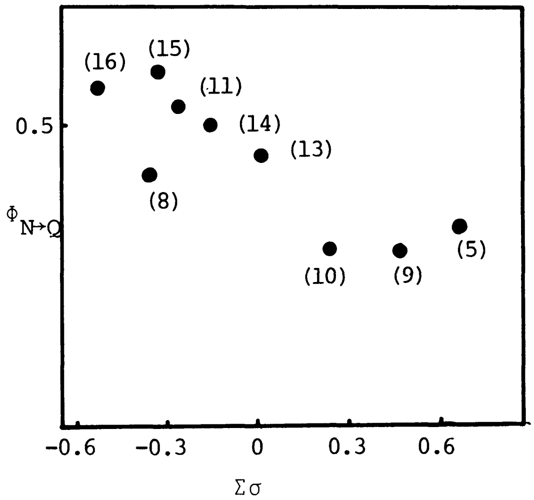


Fig. 2. Plot of the isomerization quantum yields ($\Phi_{N\to Q}$) against the Hammett's sigma constants. The numerals refer to the sensitizers in Table 1.

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