

PHOTOCHEMICAL TRANSFORMATIONS XXV: QUENCHING EXPERIMENTS IN THE TRIPLET-SENSITIZED CONVERSION OF NORBORNADIENE TO QUADRICYCLENE

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Summary

The photochemical isomerization of norbornadiene to quadricyclene, sensitized by acetone, acetophenone and benzophenone, is investigated. Quenching of these reactions with piperylene and with 2,5-dimethyl-2,4-hexadiene indicates that triplet excitation transfer from these ketones to norbornadiene occurs with rate constants of about $10^9 \text{ l mol}^{-1} \text{ s}^{-1}$. The initial products of excitation transfer to norbornadiene either have lifetimes of less than 1 ns or are converted almost completely to quadricyclene, regardless of whether they undergo "natural" decay or whether they decay by interaction with quencher.

1. Introduction

Reference should be made to Part XXIV [1]. The photochemical transformation of norbornadienes to quadricyclenes was first reported [2] almost 25 years ago. The conversion of norbornadiene (I) itself to quadricyclene (II) has been reported [3] to be sensitized by ketones. This photo-reaction has continued to be of interest, as it became a model [4] for intramolecular [2 + 2] photocycloadditions. (The first report [5] of intramolecular cyclobutane formation preceded the norbornadiene-quadricyclene experiment by almost half a century.) It is also part of a cycle in a candidate method for the practical conversion of light energy into chemical energy [6]. In this work we report information on the nature of the intermediate produced in the I to II photovalence isomerization.

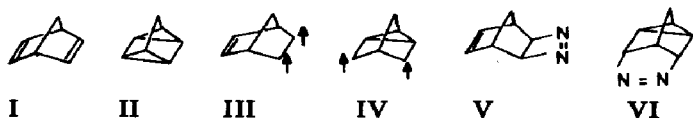
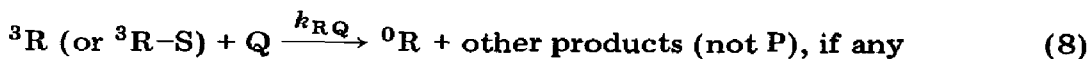
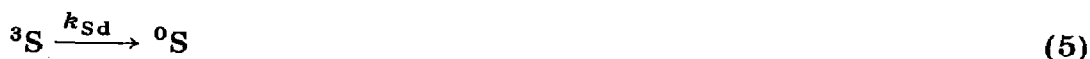


Fig. 1.

A method has been described recently [7] for the quantitative treatment of quenching results in photosensitized reactions. With this method rate constants for the excitation transfer from triplet sensitizer S to reactive substrate R, as well as lifetimes of the triplet substrate 3R (or triplet sensitizer-substrate exciplex ^3R-S) leading to product P, can be obtained. The relationship has the form

$$\frac{\phi_0}{\phi_q} = 1 + \frac{k_{SQ}[Q]}{k_{SR}[R]} + \left(1 + \frac{k_{SQ}[Q]}{k_{SR}[R]}\right) k_{RQ} \tau_{^3R} [Q] \quad (1)$$

where ϕ_0 and ϕ_q are quantum yields of product P in the absence and presence of quencher Q respectively, where the rate constants are given by reactions (2) - (8), and where the concentrations of R and Q are large enough so that $k_{SR}[R] \gg k_{Sd}$, *i.e.* substantially all of the sensitizer transfers excitation to R or to Q.



It can be seen from eqn. (1) that a plot of ϕ_0/ϕ_q , measured at various values of [Q] but with constant [Q]/[R] ratios, gives a line from whose intercept the ratio k_{SQ}/k_{SR} can be determined and whose slope divided by the intercept gives $k_{RQ} \tau_{^3R}$. Inherent in the derivation is the assumption (reaction (8)) that interaction of triplet substrate with quencher does not lead to product P, *i.e.* excitation transfer from 3R (or ^3R-S) to Q directs 3R away from P. Under such circumstances positive slopes are obtained and lifetimes of 3R as low as 1 - 2 ns can be measured, assuming k_{RQ} values of $5 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$. The method fails to give lifetimes, and indeed negative slopes will be seen, when excitation transfer from 3R to Q results in the perturbation of the fate of 3R such that more of the excited intermediate is directed towards P by interaction with Q than by "natural" decay (absence of Q). An example of this has been reported [8].

The ϕ_0/ϕ_q plot will have a zero slope under certain circumstances.

(1) It will have a zero slope when the lifetime of the intermediate is so short that it cannot be trapped by quenching processes, *i.e.* $k_P + k_{Rd} \gg k_{RQ} [Q]$. With the methods used for the quantum yield measurements, approximately

1 - 2 ns is the lower limit for lifetimes in which we have confidence. (2) The plot will have a slope of zero when 3R gives the same ratio of product P formation to other fates in its quenched decay as in its "natural" decay. This would seem to be most likely when the excited reactant has a structure close to that of the product (and separated by a considerable difference in energy from a structure resembling R), so that the easiest path for any decay of 3R is to give product. Such cases are expected to occur in systems where ϕ_o is high (assuming that reactions (2) and (3) are efficient).

In early work, Hammond and coworkers [3, 9, 10] have shown that norbornadiene (I) has a rather low triplet energy and that its conversion to II is sensitized by benzophenone ($E_T = 69 \text{ kcal mol}^{-1}$) with a quantum yield of 0.51 in ether. It has also been observed that the I \rightarrow II conversion has a quantum yield of 0.91 with acetophenone, it is sensitized by acetone and goes essentially to completion. Gorman and coworkers [11] have observed that, in benzene, the maximum quantum yields for I \rightarrow II conversion are 0.54 for benzophenone sensitization and 0.96 for acetophenone sensitization. They have also reported that k_{SR} is $9.7 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ for excitation transfer from benzophenone to I (using pulse radiolysis techniques and assuming that $k_{sd} = 1.5 \times 10^5 \text{ s}^{-1}$), whereas that for acetophenone is 4 times greater.

2. Results and discussion

In this work we report results using the quenching treatment method [7] developed in our laboratory for the I \rightarrow II conversion, sensitized with acetone, acetophenone and benzophenone, quenched by piperylene or 2,5-dimethyl-2,4-hexadiene, and using acetonitrile as solvent.

The acetone-sensitized experiments were conducted with 300 nm lamps, whereas those with acetophenone and benzophenone were conducted with 350 nm lamps. The reactions were carried out to less than 5% conversion. The peak areas for II obtained from gas chromatograms of irradiated mixtures containing varying amounts of diene, and with constant ratios of diene to I present, were compared with similar areas for irradiations of 0.2 - 0.5 M I without piperylene (these ketone triplets are essentially completely quenched by I at concentrations as low as 0.05 M). The results of a typical experiment are shown in Fig. 2 and the results of several experiments are tabulated in Table 1.

From an inspection of the data in Table 1 it is concluded that, if a theoretically quenchable intermediate exists in this system (quenchable away from product II), it has a lifetime which is indistinguishable, within the limits of our measurements ($\pm 1 - 2 \text{ ns}$), from zero. This will be discussed later. The k_{SQ}/k_{SR} values are also of interest. Clearly norbornadiene is an excellent quencher of ketones; it is much better than simple mono-olefins [12], with rate constants k_{SR} of the order of $8 \times 10^8 - 2 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ if k_{SQ} values of $5 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ are assumed [8]. When the solvent difference,

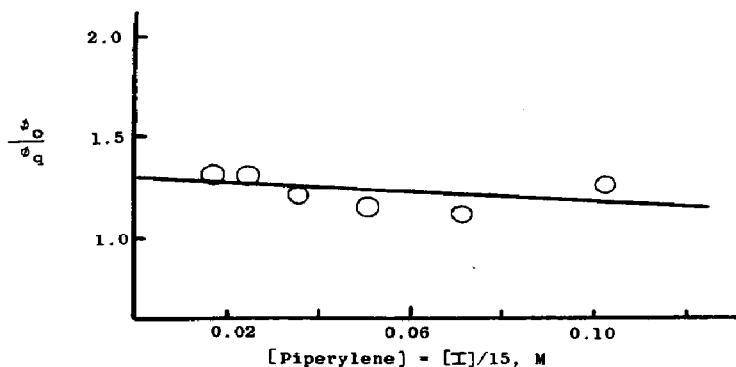


Fig. 2. Quenching of the acetone-sensitized rearrangement of norbornadiene (I) to quadricyclene (II) by piperylene in 30% acetone-acetonitrile.

the relative difficulties of our method and the considerable assumptions made are taken into consideration, our value for k_{SR} from benzophenone to norbornadiene of $8 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ is in remarkable agreement with that ($9.7 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$) obtained by direct measurement of phosphorescence quenching [11]. Also transfer from acetophenone occurs at about 2.5 times the rate from benzophenone, again in fair agreement with the results of Gorman and coworkers [11]. Our method, which has only minimal equipment requirements, would thus appear to give useful and reliable, if not precise, results; therefore, within these limits, it is a useful alternative to the much more sophisticated procedures otherwise necessary.

The high rate of excitation acceptance by norbornadiene from ketone triplets, even from one with a triplet energy as low as that of benzophenone, suggests that interaction between the two double bonds in I is involved at the time of excitation transfer and that the triplet biradical produced directly from I is better represented by IV than by III. Thus, as discussed earlier, "natural" decay (with intersystem crossing (ISC)) and decay by quenching both lead to quadricyclene rather than to norbornadiene. Alternatively, the transfer from the triplet biradical state surface connecting *I and *II to that of the S_0 ground state surface, whether by "natural" decay or by energy transfer to quencher, would appear to require less reorganization and therefore less activation energy in the transformation to II than to I.

Turro *et al.* [13] have recently discussed the photochemistry of the azoalkanes V and VI. The triplets of both V and VI give I and II in a ratio of 1:9 and apparently in high yield. These authors have proposed, based on their results and on theory, that there is no energy barrier separating the triplets III and IV and that the energy surface connecting III and IV has a minimum at a structure which is well represented by IV. Our results are consistent with their proposal, at least as far as the location of an energy minimum is concerned. However, our results are equally consistent with an energy surface in which III and IV are real species separated by an energy barrier small enough to be traversed in the III- to -IV direction in times of 1 ns or less.

TABLE 1

Diene quenching of ketone-sensitized photoisomerization of norbornadiene (I) to quadricyclene (II) in acetonitrile solution

Sensitizer	Quencher	Principal irradiation (nm)	[I]/[Q]	Slope ^c (l mol ⁻¹ s ⁻¹)	Intercept ^c $k_{RQ}I_0^3 R^c$ (l mol ⁻¹)	k_{SQ}/k_{SR} ^c
Acetone	Piperylene ^a	300	15	-4 ± 2	1.4	6
Acetone	Piperylene ^a	300	20	-4 ± 3	1.3	6
Acetophenone	2,5-diMeHex ^b	350	27	5 ± 9	1.1	3
Benzophenone	2,5-diMeHex ^b	350	11	4 ± 4	1.6	7

^a A mixture of *cis*- and *trans*-piperylene was used.

^b 2,5-Dimethyl-2,4-hexadiene.

^c From eqn. (1).

3. Experimental

Norbornadiene (b.p. 83 - 84 °C), acetophenone, 2,5-dimethyl-2,4-hexadiene and piperylene (*cis-trans* mixture) were obtained from Aldrich Chemical Co. and were purified using fractional distillation prior to use. Acetonitrile and acetone were of spectral quality; acetonitrile was stored over molecular sieves. The analytical work was carried out on a Hewlett-Packard 5750B instrument equipped with dual flame ionization detectors, and the peak areas were measured either by cutting and weighing or by integration using a Hewlett-Packard 3380S digital integrator. Gas chromatography was performed on a $\frac{1}{8}$ in aluminum column 5 ft in length containing OV-101 on 100 - 120 mesh Chromosorb G at 50 °C. The retention times on this column were 5.0 min for I, 10 min for II and 13 min for n-octane. A $\frac{1}{8}$ in aluminum column 4 m long containing Carbowax 1540 on 100 - 120 mesh Chromosorb W at 60 °C was also used. The retention times were 4.2 min for n-octane, 6.0 min for I, 11.0 min for II and 14 min for acetonitrile.

The irradiations were carried out in a carousel apparatus using a Rayonet RPR-208 reactor with either 3000 Å or 3500 Å lamps. Corning O-52 filters were used with the 3500 Å lamps. Solutions were placed in Vycor or Pyrex tubes, were degassed by four freeze-pump-thaw cycles and were sealed at pressures below 10^{-5} Torr. In order to avoid gas phase reactions the tubes were wrapped with aluminum foil except at the carousel window sites.

For the acetone-sensitized reactions a solution of 30% (by volume) acetone in acetonitrile was used for the preparation and dilution of all samples. In a typical run 1.37 g (14.9 mmol) of norbornadiene and 2 ml of a 0.516 M solution (1.03 mmol) of piperylene were diluted to 10 ml. Successive dilutions were made and 3 ml of each concentration was pipetted into Vycor tubes. A second solution of 0.458 g (4.97 mmol) of norbornadiene without quencher was diluted to 10 ml. Two samples (3 ml) of this solution were pipetted into Vycor tubes. All tubes were degassed and irradiated at 3000 Å for 3.5 h. (In some runs the irradiation times were varied so that the per cent reactions were more nearly the same.) After irradiation 50 μ l of a 0.0778 g ml^{-1} solution of n-octane was added (3.89 mg tube^{-1}). Analysis was carried out using gas chromatography and the peak areas were computed by cutting and weighing. The results are tabulated in Table 2 and are plotted in Fig. 2.

For the acetophenone-sensitized reactions samples were prepared with acetonitrile solvent, with 0.221 M acetophenone as the sensitizer and with 2,5-dimethyl-2,4-hexadiene as the quencher. Pyrex tubes, 3500 Å lamps and Corning O-52 filters were used. Similar conditions were used with 0.050 M benzophenone as the sensitizer. The results are summarized in Table 1.

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TABLE 2

Formation of quadricyclene (II) by irradiation of norbornadiene (I)-piperylene mixtures at 3000 Å for 3.5 h in 30% acetone-acetonitrile

Tube	Initial [I] (M)	[Piperylene] (M)	Area of II/Area of n-octane	ϕ_0/ϕ_q
1	0.497	0.00	2.49 ± 0.27	—
2	0.497	0.00	2.39 ± 0.07	—
3	0.250	0.0173	1.85	1.32
4	0.358	0.0247	1.85 ± 0.02	1.32
5	0.511	0.0353	2.03 ± 0.19	1.20
6	0.730	0.0505	2.10 ± 0.09	1.16
7	1.04	0.0721	2.16 ± 0.05	1.13
8	1.49	0.103	1.94 ± 0.06	1.26

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