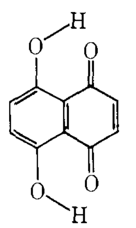
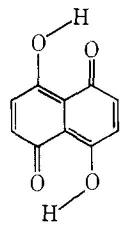
ment against the formulation of naphthazarin in the tautomeric form **5**.[2] With regard to the strong hydrogen bond in naphthazarin,[21] **5** should have a strong shift to lower wave numbers for the C=O vibration compared with **1a**,[22] whereas the observed value for naphthazarin is 1623 cm^{-1} (CCl_4).



4



5

A similar conclusion can be drawn from the shift of the $\pi \rightarrow \pi^*$ transition[23] from 1,4-naphthoquinone (λ_{max} ($CHCl_3$) 335 nm (ϵ 3040)) to 5-hydroxy-1,4-naphthoquinone (λ_{max} ($CHCl_3$) 429 nm (ϵ 3800)) and to naphthazarin (λ_{max} ($CHCl_3$) 524 nm (ϵ 6050)). Assuming a shift of a comparable order (90–100 nm/OH) on introducing one hydroxy group in the peri position of **1** the absorption of **5** should occur at much longer wavelengths than observed for naphthazarin.[24]

Further evidence for the structure of naphthazarin as 5,8-dihydroxy-1,4-naphthoquinone follows from the calculated standard heats of formation[15] for **4** ($\Delta H_f° = -99$, 1 kcal/mol) and **5** ($\Delta H_f° = -85$, 1 kcal/mol). Neglecting entropy and solvation effects the value for the equilibrium constant K (25°) = [**5**]/[**4**] should be $K = 4.9 \times 10^{-11}$.[26]

Our results show that former X-ray studies which describe *one* modification of naphthazarin as 1.5-quinoid[3] permit no conclusions to be made as to the structure of naphthazarin in solution.

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(25) "DMS UV-Atlas of Organic Compounds," Butterworths, London 1966.
(26) The ring protons in the nmr spectrum of naphthazarin are all equivalent.[4,27] As one referee pointed out, this fact may be an indication for the existence of **5** as intermediate. This is not excluded by our findings, but also in this case the equilibrium concentration of **5** is governed by the value of *K*.
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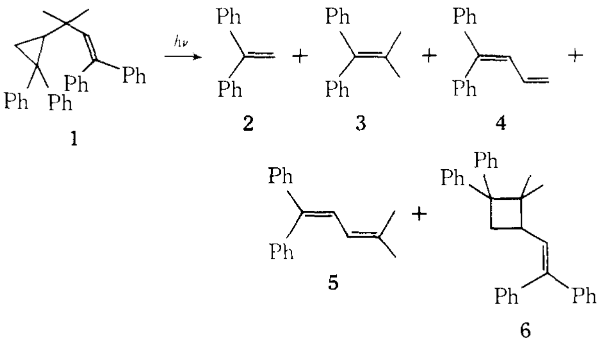
σ–π Interaction. A Cyclopropyl-π-methane Rearrangement. Mechanistic and Exploratory Organic Photochemistry[1,2]

Sir:

One of the most general and synthetically useful of photochemical reactions is the di-π-methane rearrangement.[3] It was therefore of interest to ascertain if the counterpart process in which one π bond is replaced by a three ring will occur.

Presently, (A) we report the photochemistry of 3-(2,2-diphenylcyclopropyl)-3-methyl-1,1-diphenyl-1-butene (**1**) to afford 1,1-diphenylethylene (**2**), 1,1-diphenylisobutylene (**3**), 1,1-diphenyl-1,3-butadiene (**4**), 1,1-diphenyl-4,4-dimethyl-1,3-butadiene (**5**), and 3-(2,2-diphenylvinyl)-2,2-dimethyl-1,1-diphenylcyclobutane (**6**). (B) We also note evidence that diphenylethylene (**2**) and diphenyldimethylbutadiene (**5**) are primary photoproducts, while diphenylisobutylene (**3**) and diphenylbutadiene (**4**) are secondary. (C) We describe the photochemistry of vinylcyclobutane **6** and give evidence that it is the reaction intermediate leading to diphenylisobutylene (**3**) and diphenylbutadiene (**4**). Interesting regiospecificity is noted. (D) We provide evidence that both steps of the reaction are singlet processes. (E) We give results which exclude 3,3-dimethyl-1,1-diphenyl-1-butenylidene (**7**) as an intermediate. (F) We present a mechanism for formation of the primary products which is precisely parallel to that of the ordinary di-π-methane rearrangement.

Direct irradiation[4] of 3-(2,2-diphenylcyclopropyl)-3-methyl-1,1-diphenyl-1-butene (**1**) gave five products (**2**, **3**, **4**, **5**, and **6**) as depicted in eq 1.



(1)

Table I. Quantum Yield Determinations

				Quantum yield			
Run	Reactant	λ_{irrad}, nm	% Conv	Diphenyl ethylene **2**	Diene **5**	Diphenyl isobutylene **3**	Diphenyl butadiene **4**
1	**1**	250	4.3	0.018	0.018	0.0010	0.0009
2	**1**	250	8.4	0.017	0.016	0.0019	0.0016
3	**6**	250	1.8	$<10^{-4}$[a]	$<10^{-4}$[a]	0.056	0.054
4	**6**	250	4.9	$<10^{-4}$[a]	$<10^{-4}$[a]	0.060	0.058
5	**6**[b]	325	0.4	$<10^{-5}$[a]	$<10^{-5}$[a]	0.0011	0.0010

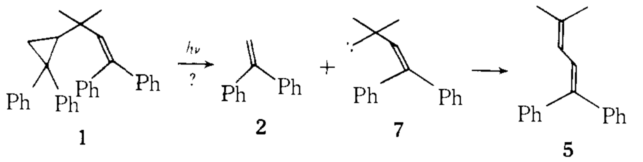
[a] Maximum value, below the limits of detection. [b] *m*-Methoxyacetophenone, 4.4×10^{-3} *M*, was added.

The quantum yields for formation of diphenylethylene (**2**) and diphenyldimethylbutadiene (**5**) remained constant at low conversions (<9%) where product light absorption was not a problem. In contrast, diphenylisobutylene (**3**) and diphenylbutadiene (**4**) exhibited quantum yields which increased with extent of conversion. This suggests that these arise from some primary product. Note Table I.

This primary product proved to be vinylcyclobutane **6** which could be detected using 270-MHz nmr. This compound was independently synthesized, and it was found that direct irradiation of vinylcyclobutane **6** indeed does give diphenylisobutylene (**3**) and diphenylbutadiene (**4**) but no diphenylethylene (**2**) or diphenyldimethylbutadiene (**5**). This regiospecificity, while interesting in itself, provided support for the postulated secondary nature of products **3** and **4**.

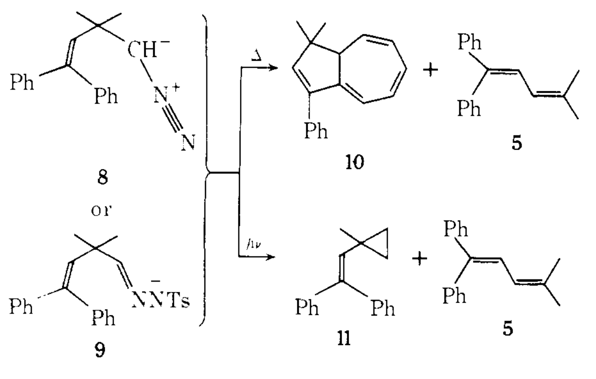
Both steps of the reaction, namely reaction of cyclopropylvinylmethane **1** and reaction of vinylcyclobutane **6**, proved to be singlet processes. *m*-Methoxyacetophenone sensitization gave no reaction from **1** and little from **6**. Note Table I.

Of the four alkene and diene products (**2**, **3**, **4**, and **5**), the diphenylethylene (**2**) and the diphenyldimethylbutadiene (**5**) could conceivably have arisen by a Griffin fragmentation[5] of cyclopropylvinylmethane **1** to give carbene **7** and diphenylethylene (**2**). Rearrangement of this carbene with vinyl migration might then afford diphenyldimethylbutadiene (**5**). This mechanism is shown in eq 2.



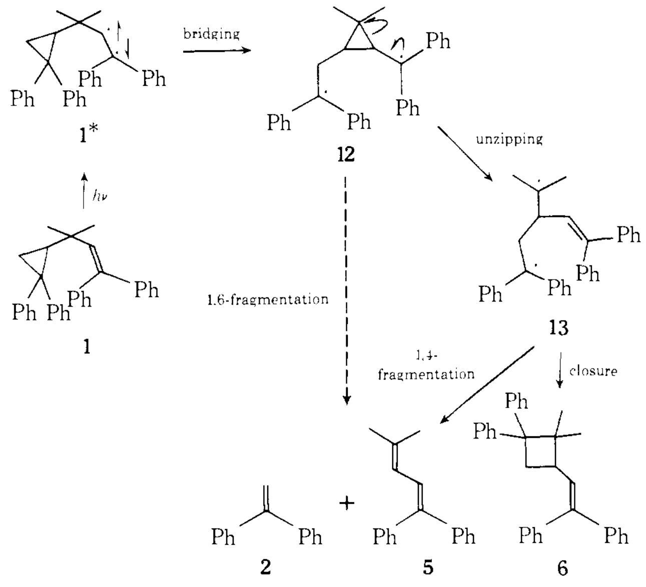
(2)

To test this possibility the carbene (*i.e.*, **7**) was generated independently, both from diazo compound **8** and from tosylhydrazone anion **9**. Interestingly, the product distributions from thermal and photochemical generation of the carbene depended on the mode of generation and differed from that observed in the photochemistry of cyclopropylvinylmethane **1**. Note eq 3. Thus, evidence is available that carbene **7** is not involved in the photochemistry of cyclopropylvinylmethane **1**.



(3)

Chart I. Mechanism for the Cyclopropylvinylmethane Rearrangement



Finally, we note that a single mechanism is capable of accounting for both the fragmentation products and for the vinylcyclobutane (*i.e.*, **6**). This mechanism is precisely parallel to that of the normal di-π-methane process with cyclopropyl-vinyl bridging of the excited state replacing the usual vinyl-vinyl bonding. However, presently, there is partial diversion of the biradical species involved (**12** or **13**) resulting in fragmentation (Chart I).

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(1) This is Paper 92 of the series.

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