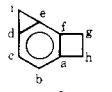
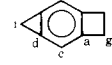


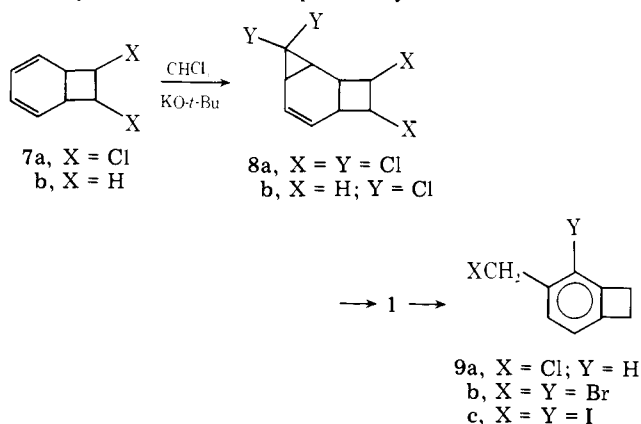
Table I.  $^{13}\text{C}$  NMR Shifts and  $^1\text{H}$  Coupling Constants in **1** and **2**

	Carbon chemical shifts, ppm, <sup>a</sup> and coupling constants (Hz)									Ref
	a	b	c	d	e	f	g	h	i	
	148.0	121.0 (162)	112.4 (166)	126.0	119.6	135.9	31.1 (138)	30.9	19.9 (170)	b
	145.5		110.0 (169)	122.8			29.0 (137)		19.2 (169.5)	c

<sup>a</sup>Peaks measured from  $\text{CDCl}_3$  which was taken as 77.2 ppm downfield from  $\text{Me}_4\text{Si}$ . <sup>b</sup>These assignments are based on relative peak heights, proton-carbon coupling, and comparison of the shifts with those in benzocyclopropene and benzocyclobutene. <sup>c</sup>These values are from ref 2.

smoothly converted into benzocyclopropene (**6**). The rate of conversion of **5** into **6** did, however, appear slower than the rate of conversion of the 3,4 isomer into **6**, and the fact that the double bond in **4** is tetrasubstituted might be critical, particularly if prior rearrangement to the 3,4 position has to occur.<sup>10</sup> Consequently the preparation of an isomer of **4** with the double bond in a different position was investigated.

The diene **7a**, prepared by the chlorination of cyclooctatetraene,<sup>11</sup> was treated with  $\text{KO}-t\text{-Bu}$  and  $\text{CHCl}_3$  to give the dichlorocarbene adduct **8a**, mp 78–79 °C, in 28% yield.<sup>4,5</sup> All attempts to replace the cyclobutyl chlorine atoms with hydrogen were unsuccessful. Bicyclo[4.2.0]octa-2,4-diene (**7b**) was therefore prepared,<sup>12</sup> which on treatment with  $\text{KO}-t\text{-Bu}$  and  $\text{CHCl}_3$  gave the adduct **8b** in 35% yield.<sup>4,5</sup> Treatment of **8b** (1.0 g, 5.3 mmol) with  $\text{KO}-t\text{-Bu}$  (2.24 g, 20 mmol) in  $\text{Me}_2\text{SO}$  (20 mL) at 15 °C for 5 min gave **1** (25 mg, 0.2 mmol, 4%).<sup>13</sup> The mass spectrum (20 eV) had  $m/e$  (rel intensity) 116 ( $\text{M}^+$ , 45%), 115 ( $\text{M}^+ - 1$ , 100%); high resolution (70 eV) 116.0632 ( $\text{C}_9\text{H}_8$  requires 116.0625). The  $^1\text{H}$  NMR spectrum ( $\text{CCl}_4$ ) showed an AB quartet at  $\delta$  7.04 and 6.82 (2 H,  $J = 6.5$  Hz), a singlet at 3.24 (4 H), and a singlet at 3.18 (2 H),<sup>14</sup> and the  $^{13}\text{C}$  NMR spectrum had nine absorptions (Table I). The electronic spectrum (hexane) showed a broad band with maxima at 264 nm (sh,  $\log \epsilon \sim 3.1$ ) 270 ( $\sim 3.2$ ), and 276.5 ( $\sim 3.2$ ).<sup>15</sup> These data are clearly in accord with the assigned structure. Comparison of the  $^{13}\text{C}$  NMR spectra of **1** and **2** is made in Table I, and the chemical shifts found for **1** could be directly derived from those previously found for **2**.



The electronic spectrum shows the expected hypsochromic shift compared with that of **2**, but the deviation from the trend observed by Thummel and Nutakul<sup>16</sup> for benzenes annelated in the 1,2:3,4 positions by larger rings is less than that for **2** with its related systems.<sup>17</sup>

Treatment of **1** with  $\text{HCl}$  in  $\text{CCl}_4$  gave **9a**,<sup>4,5</sup> identical with the compound obtained by a similar treatment of **2**, and therefore having the constitution shown. Treatment of **1** with  $\text{Br}_2$  gave **9b**, mp 77–78 °C,<sup>4,5</sup> and with  $\text{I}_2$  gave **9c**, mp 79–81 °C,<sup>4,5</sup> the substitution pattern being assumed on the basis of the structure of **9a**.<sup>18,19</sup>

We are currently engaged in a comparative study of the chemistry of **1** and **2**.

**Acknowledgment.** We thank the SRC (U.K) for a graduate award (to M.M.M.) and the Pahlavi Foundation for a grant (to D.D.). We thank Dr. A. G. Loudon for the high resolution mass spectral determinations, and BASF (Ludwigshafen) for a gift of cyclooctatetraene.

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- Satisfactory microanalytical and/or high resolution mass spectral data have been obtained for this compound.
- $^1\text{H}$  NMR ( $\delta$ ): **3a** ( $\text{CDCl}_3$ ), 5.53 (s, 1 H), 5.12 (s, 2 H), 4.70 (s, 1 H), 2.10 (m, 6 H); **3b** ( $\text{CDCl}_3$ ), 5.66 (s, 1 H), 5.23 (s, 2 H), 4.76 (s, 1 H), 2.13 (m, 6 H); **4** ( $\text{CDCl}_3$ ), 2.62 (m, 2 H), 2.45 (m, 2 H), 1.94 (m, 6 H); **8a** ( $\text{CDCl}_3$ ), 6.12 (ddd, 1 H,  $J = 9, 6, 1$  Hz), 5.84 (dd, 1 H,  $J = 10, 2$  Hz), 4.30 (m, 2 H), 3.38 (t, 1 H,  $J = 10$  Hz), 2.86 (m, 1 H), 2.18 (m, 2 H); **8b** ( $\text{CDCl}_3$ ), 6.0 (m, 2 H), 3.2–1.2 (m, 8 H); **9a** ( $\text{CCl}_4$ ), 6.96 (m, 3 H), 4.40 (s, 2 H), 3.06 (s, 4 H); **9b** ( $\text{CCl}_4$ ), 7.24, 6.90 (dd, 2 H,  $J = 7.5$  Hz), 4.52 (s, 2 H), 3.12 (s, 4 H); **9c** ( $\text{CCl}_4$ ), 7.24, 6.88 (dd, 2 H,  $J = 7.5$  Hz), 4.50 (s, 2 H), 3.02 (s, 4 H).
- Decomposition occurred under the reaction conditions.
- The properties of cyclopropa[*a*]naphthalene, which has now been prepared,<sup>9</sup> suggest that even if formed this compound would not have survived our isolation procedure.
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- Also, unlike the case of the 3,4 isomer, elimination of  $\text{HCl}$  from **5** can proceed in two ways, and one of the dienes so produced requires more extensive bond rearrangement to give **6**.
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- The method of isolation was similar to that described by Billups et al.<sup>9</sup> Compound **1** has a pungent smell, similar to benzocyclopropene, and the yield without distillation is  $\sim 10\%$  (NMR).
- At 60 MHz with  $\text{CDCl}_3$  as solvent, a single resonance is observed for the cyclopropyl and cyclobutyl hydrogens.
- These are minimal values for the extinction coefficients.
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- It is not at present possible to compare the degree or direction of bond fixation in these two systems. The  $^{13}\text{C}$  NMR spectra indicate that both systems are similarly hybridized at comparable carbon atoms, but the significance of the large bathochromic shift in the electronic spectrum of **2** is not known.
- The  $^1\text{H}$  NMR spectrum of **9c** shows two low intensity singlets at 4.32 and 3.12 (1:2), probably due to the other isomer.
- Chemical proof for the substitution pattern in **9b** and **9c** is currently being sought.

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Muzammil M. Mansuri

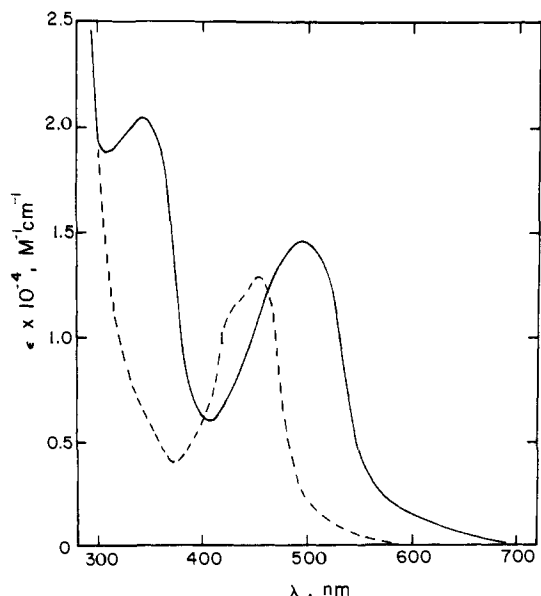
Department of Chemistry, University College London  
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Received August 24, 1977

## On the Nature of $\text{Ru}(\text{bpy})_3^+$ in Aqueous Solution<sup>1</sup>

Sir:

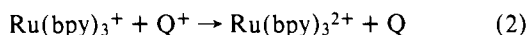
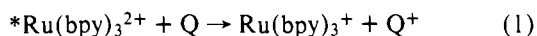
$\text{Ru}(\text{bpy})_3^+$  (bpy = 2,2'-bipyridine) is generated<sup>2–5</sup> upon the reductive quenching of  $^*\text{Ru}(\text{bpy})_3^{2+}$  and is thermodynamically capable of reducing  $\text{H}_2\text{O}$  to  $\text{H}_2$ .<sup>6,7</sup> Thus,  $\text{Ru}(\text{bpy})_3^+$  could be



**Figure 1.** Absorption spectrum of  $\text{Ru}(\text{bpy})_3^{2+}$  (—) and  $\text{Ru}(\text{bpy})_3^{2+}$  (---) in aqueous solution. The spectrum of  $\text{Ru}(\text{bpy})_3^{2+}$  is obtained by pulse radiolysis and is independent of pH (5–13) and the mode of generation (reduction by  $e_{\text{aq}}^-$ ,  $\cdot\text{CH}_2\text{O}^-$ ,  $\text{CH}_3\text{CHO}^-$ , and  $(\text{CH}_3)_2\text{CO}^-$ ). Correction is made for depletion of the substrate.

visualized as the reactive intermediate in some catalyzed photodissociation cycle;<sup>8</sup> the use of  $\text{Ru}(\text{bpy})_3^{2+}$  and its derivatives for solar energy conversion is being enthusiastically investigated.<sup>9–12</sup>

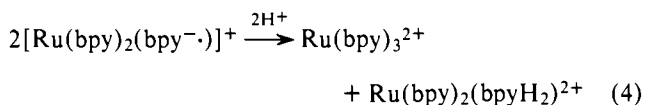
One serious problem in the investigation of photochemically generated  $\text{Ru}(\text{bpy})_3^+$  in aqueous solution is associated with its very fast back-electron-transfer reaction with the oxidized form of the reductive quencher (eq 1 and 2);  $\text{Ru}(\text{bpy})_3^+$  is a very powerful reducing agent and reported values of  $k_2$  are in the range  $10^7$ – $10^{10} \text{ M}^{-1} \text{ s}^{-1}$  depending upon the nature of  $\text{Q}^+$ .<sup>3–5</sup> Although  $\text{Ru}(\text{bpy})_3^+$  can be generated electrochemically<sup>5–7</sup> in  $\text{CH}_3\text{CN}$ , its nature in aqueous solution has not been investigated in that way. The techniques of radiation chemistry (continuous and pulse) permit the generation of  $\text{Ru}(\text{bpy})_3^+$  in aqueous solution to be accomplished in the absence of Q and nonaqueous solvents.



Baxendale and Fiti<sup>13</sup> generated  $\text{Ru}(\text{bpy})_3^+$  in aqueous solution via

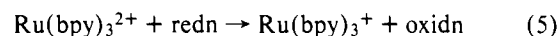


for which  $k_3 = 8.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ; they reported an intense absorption band at 510 nm ( $\epsilon 1.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) and a weaker band at  $\sim 600 \text{ nm}$ . In the presence of 0.5 M *tert*-butyl alcohol as an OH radical scavenger ( $(\text{CH}_3)_3\text{COH} + \text{OH} \rightarrow \cdot\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH} + \text{H}_2\text{O}$ ;  $k = 5.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ), they reported that  $\text{Ru}(\text{bpy})_3^+$  decayed via second-order kinetics ( $k = 3.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ) in neutral solution which was attributed to a bimolecular disproportionation reaction.  $\text{Ru}(\text{bpy})_3^+$  was described as a bpy electron-adduct radical coordinated to a  $\text{Ru}^{\text{II}}$  center and reaction 4 was written to represent its decay. No  $\text{H}_2$  was observed to be generated in neutral solution.

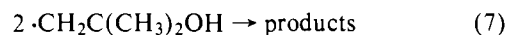
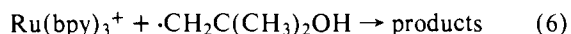


In the course of our examination of the radiolytic one-electron reduction of bpy and its coordination complexes in

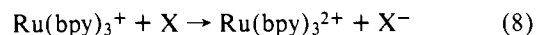
aqueous solution, we have found that  $\text{Ru}(\text{bpy})_3^+$  (Figure 1), generated from the reaction of  $\text{Ru}(\text{bpy})_3^{2+}$  with  $\cdot\text{CH}_2\text{O}^-$ , or  $\text{CH}_3\text{CHO}^-$ , or  $(\text{CH}_3)_2\text{CO}^-$  radicals in alkaline (pH 11–13) solution ( $k_5 = 2.9 \times 10^9$ ,  $7.0 \times 10^9$ , and  $4.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , respectively), is rather long-lived, decaying via first-order kinetics independent of  $[\text{OH}^-]$ ,  $[\text{Ru}(\text{bpy})_3^{2+}]$ , or the nature and concentration of the alcohol used to generate the reducing radicals. The value of the first-order rate constant at low radiation doses ( $<250 \text{ rads}$ ) is  $0.2 \text{ s}^{-1}$ . No  $\text{H}_2$  or free bpy are generated in the reaction. The spectral changes observed upon continuous radiolysis in alkaline solution are essentially the same as those seen by Baxendale and Fiti in neutral solution. When *tert*-butyl alcohol is present, but not in sufficient concentration to scavenge OH radicals, the decay of  $\text{Ru}(\text{bpy})_3^+$  is unaffected. However, when  $\cdot\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$  radicals are generated, the decay of  $\text{Ru}(\text{bpy})_3^+$  becomes rapid and complex.



It is clear that  $\text{Ru}(\text{bpy})_3^+$  reacts readily with  $\cdot\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$  radicals so that the rapid second-order decay of  $\text{Ru}(\text{bpy})_3^+$  observed by Baxendale and Fiti<sup>13</sup> represents reaction 6 in competition with reaction 7 ( $k_7 = 7.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ )<sup>14</sup> rather than reaction 4.  $\text{Ru}(\text{bpy})_3^+$  also reacts efficiently with  $\cdot\text{CH}_2\text{OH}$ ,  $\text{CH}_3\text{CHOH}$ ,  $(\text{CH}_3)_2\text{CHOH}$ , and  $\cdot\text{CO}_2^-$  radicals,<sup>15</sup> as well as  $\cdot\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$ , in neutral solution. It should be noted that these radicals do not reduce  $\text{Ru}(\text{bpy})_3^{2+}$  ( $k_5 < 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ).



By monitoring the decay of  $\text{Ru}(\text{bpy})_3^+$  in the presence of oxidants, the rate constants for reaction 8 can be obtained. The values of  $k_8$  for  $\text{O}_2$ ,  $\text{Co}(\text{bpy})_3^{3+}$ , and  $\text{Ni}(\text{CN})_4^{2-}$  are  $7.4 \times 10^9$ ,  $1.6 \times 10^9$ , and  $4.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ , respectively, at pH 11 in 0.1 M  $\text{CH}_3\text{OH}$ . The possible photocatalytic applications of  $\text{O}_2^-$  generated in reaction 8 have already been pointed out.<sup>5</sup> Reaction 8 with  $\text{Ni}(\text{CN})_4^{2-}$  generates  $\text{Ni}(\text{CN})_4^{3-}$  which is known<sup>16</sup> to react further to give  $\text{Ni}_2(\text{CN})_6^{4-}$ , a species capable of reducing  $\text{H}_2\text{O}$  to  $\text{H}_2$ .<sup>17</sup> The characteristic absorption of  $\text{Ni}_2(\text{CN})_6^{4-}$  at 313 nm<sup>17</sup> is observed; the yield of this species is consistent with the disappearance of  $\text{Ru}(\text{bpy})_3^+$  via reaction 8.



In summary, the absorption spectrum of  $\text{Ru}(\text{bpy})_3^+$  in aqueous solution obtained by pulse radiolysis is very similar to that obtained by flash photolysis in  $\text{CH}_3\text{OH}$ ,<sup>5</sup>  $\text{CH}_3\text{CN}$ ,<sup>5</sup> and  $\text{H}_2\text{O}$ .<sup>3,18</sup> The band at 360 nm is in the same spectral region as that of the one-electron reduction product of free bpy in aqueous solution<sup>19</sup> and can be assigned as a coordinated ligand radical localized transition; the band at 495–510 nm has been suggested to arise from a metal-to-ligand charge-transfer transition.<sup>3</sup> Although  $\text{Ru}(\text{bpy})_3^+$  does not appear to reduce  $\text{H}_2\text{O}$  in neutral<sup>13</sup> or alkaline solution at a measurable rate, it can serve as an intermediate to drive the reduction of  $\text{H}_2\text{O}$  via other energy-rich species.  $\text{Ru}(\text{bpy})_3^+$  is a very strong reducing agent and reacts rapidly with free radicals in solution. Any bimolecular disproportionation reaction (such as 4) must have a rate constant at least  $10^3$  times smaller than that attributed in the past.  $\text{Ru}(\text{bpy})_3^+$  has a rather long intrinsic lifetime in aqueous solutions. Its mode of decay appears to be with  $\text{H}_2\text{O}$ , possibly through the intermediacy of a covalent hydrate species; free bpy is known<sup>20</sup> to interact with  $\text{H}_2\text{O}$  in that way.

**Acknowledgments.** We thank the Linac staff of C.N.R. and Dr. M. G. Simic of U.S. Army Natick Research and Development Command for assistance.

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 Received May 31, 1977

### Divergent Cycloaddition Pathways for Reaction of Singlet Stilbene and Stilbene Excimer with Dimethyl Fumarate

Sir:

The intermediacy of excimers and exciplexes in photochemical cycloaddition reactions is firmly established.<sup>1</sup> Furthermore, excimers and exciplexes often have sufficiently long lifetimes to be intercepted by a third molecule.<sup>2-6</sup> Such interception can result in the formation of a triplex,<sup>2</sup> exciplex substitution to form a new exciplex,<sup>3</sup> deactivation to ground-state molecules,<sup>4,5</sup> or new or enhanced chemical reactions.<sup>6</sup> We wish to report that different cycloadducts are formed upon quenching of singlet *trans*-stilbene and stilbene excimer by dimethyl fumarate. Divergent modes of cycloaddition for a singlet monomer and excimer are without precedent and offer a promising avenue for extending the synthetic scope of the photochemical cycloaddition process.

Preparative photolysis of *trans*-stilbene ( $7 \times 10^{-3}$  M) and dimethyl fumarate ( $7 \times 10^{-2}$  M) in benzene has previously been reported to yield dimethyl  $\mu$ - and *neo*-truxinate (**1** and **2**) as the major and minor isolated products.<sup>7</sup> Photolysis of a more concentrated solution of stilbene (0.20 M) and dimethyl fumarate (0.22 M) followed by silica gel chromatography led

Table I. Quantum Yields for Stilbene Isomerization and Cycloaddition<sup>a</sup>

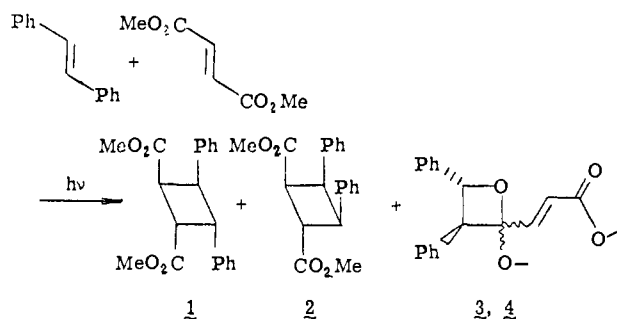
[ <i>trans</i> -Stilbene], M	[Dimethyl fumarate], M	$\Phi_t$	$\Phi_1$	$\Phi_3$
0.010	0.13	0.31	0.0080	0.0010
0.010	0.17	0.28	0.0094	0.0012
0.010	0.25	0.25	0.014	0.0014
0.010	0.39	0.20	0.017	0.0013
0.10	0.13	0.33	0.0081	0.036
0.10	0.17	0.29	0.0096	0.037
0.10	0.25	0.24	0.012	0.036
0.10	0.33	0.21	0.015	0.036
0.010	0.10	0.35	0.0069	0.0017
0.050	0.10	0.39	0.0070	0.013
0.10	0.10	0.38	0.0069	0.036
0.25	0.10	0.25	0.0061	0.16
0.55	0.10	0.20	0.0051	0.24

<sup>a</sup> Degassed 1% pyridine/benzene solutions irradiated using monochromatic 334-nm light at 25 °C. Analysis by gas chromatography at <5% conversion on a 5 ft  $\times$  1/8 in. 5% SF96 on Chromosorb G column at 220 °C. Light intensities determined by benzophenone-benzylhydrol actinometry. Limits of error:  $\pm 10\%$  for stilbene isomerization,  $\pm 20\%$  for cycloadduct formation.

Table II. Wavelength Dependence of Quantum Yields<sup>a,b</sup>

$\lambda$ , nm <sup>c</sup>	$\Phi_t$	$\Phi_1$	$\Phi_3$
334	0.16	0.018	0.035
365	0.04	0.035	0.012

<sup>a</sup> Degassed benzene solutions containing 0.11 M *trans*-stilbene and 0.42 M dimethyl fumarate. <sup>b</sup> See note for Table I. <sup>c</sup> Wavelength of irradiation.



to isolation of **1** and **2** along with two previously unreported isomeric oxetanes (**3** and **4**).<sup>8,9</sup> At low *trans*-stilbene conversions, *cis*-stilbene, **1**, and **3** were the only products detected by GC. As the stilbene photostationary state was approached, **2** and **4** were detected. Michler's ketone and benzil sensitized the isomerization of *trans*-stilbene (0.01 M) in the presence of dimethyl fumarate (0.10 M); however, no cycloadducts were observed at moderate to high conversions of *trans*- to *cis*-stilbene.

Quantum yields for *trans*-stilbene isomerization ( $\Phi_t$ ) and formation of **1** and **3** were determined as a function of both dimethyl fumarate and *trans*-stilbene concentration (Table I). Stilbene and dimethyl fumarate form a weak ground-state complex ( $K \sim 1.0 \pm 0.5$  by the method of Rose and Drago<sup>10</sup>); however, for all of the data in Table I, essentially all ( $\geq 98\%$ ) of the 334-nm light is absorbed by uncomplexed *trans*-stilbene. Selective excitation of the ground-state complex can be accomplished by irradiation of concentrated solutions at 365 nm and results in different product quantum yields than those obtained with 334-nm irradiation (Table II). The fluorescence of dilute ( $10^{-4}$  M) *trans*-stilbene is efficiently quenched by dimethyl fumarate with the concomitant appearance of weak exciplex fluorescence ( $\lambda_{\max}$  470 nm, benzene solution).

The failure of triplet sensitization to effect either cyclobu-