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Photochemical Transformations of 1-Pyrazolyl-*cis*-1,2-dibenzoylalkenes. A Laser Flash Photolysis Investigation[1]

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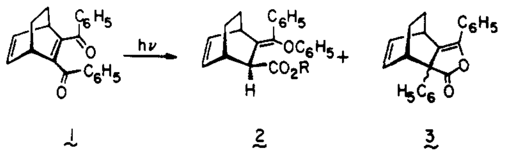
Photorearrangements of several pyrazolyl-*cis*-1,2-dibenzoylalkenes **8**–**12** (Scheme III) are reported. Photolysis of **8** in benzene gave a mixture of the butenoic acid **21** and the tetrahydroisoquinoline **33**, whereas in methanol, a mixture of the butenoic ester **26** and **33** is formed. Similar results were obtained in the irradiation of **9** both in benzene and methanol. The photolysis of **10**–**12** in benzene gave exclusively the corresponding butenoic acids **23**–**25**, whereas in methanol, the corresponding butenoic esters **28**–**30** were formed. In the case of **10** and **11**, however, the methanol irradiation gave the corresponding bis(pyrazolyl) derivatives **43** and **44** also. Photolysis of the pyrazolyl fumarate **14** gave the bis(pyrazolyl) succinate **45**, whereas the irradiation of **16** gave a mixture of the pyrazole **4a** and *cis*-dibenzoylethylene. Laser flash photolysis (337.1 nm) of **8**–**12** in benzene and methanol leads to (a) formation of short-lived transients ($\tau \leq 20$ ns), absorbing in the spectral region 400–550 nm and assigned as the triplets of **8**–**12**, (b) pronounced end-of-pulse bleaching in the region of ground-state absorption (300–380 nm), (c) formation of oxygen-insensitive transients ($\tau = 0.3$–33 μs), characterized by dual maxima at ~400 and ~600 nm, and (d) growth (oxygen insensitive) of a methanol adduct, with absorption maxima at 370–390 nm in methanol and benzene plus methanol (0.5–5 M) mixtures ($\tau = 0.8$–6 μs). Triplet sensitization studies using pulse-generated and γ-radiolytically generated biphenyl triplet photolysis suggest that the formation of the 400/600-nm species is triplet mediated while the methanol related reaction as well as the phototransformation leading to the butenoic ester derivatives occurs via intermediates from the singlet state (S_1). We attribute the 400/600-nm species to a zwitterion (**40**, Scheme V) and the methanol related growth to the reaction of the ketene **18** with the alcohol (Scheme III).

Introduction

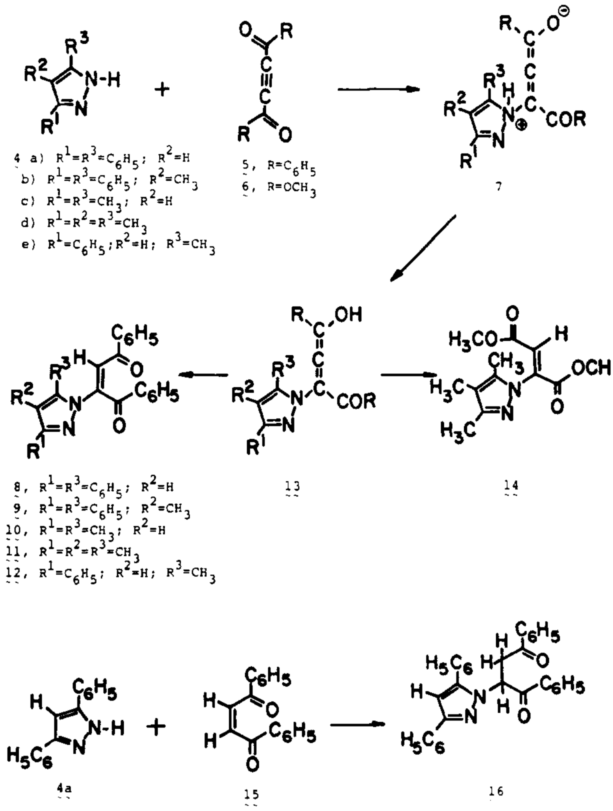
Dibenzoylethylenes undergo interesting photorearrangements to give the corresponding ketene-derived products and lactones, in addition to cis–trans isomerization.[3-8] For example, the photolysis of *cis*-1,2-dibenzoylstilbene in ethanol gives ethyl 2,4-diphenyl-4-phenoxy-3-butenoate as the major product. The observed regioselectivity of this rearrangement has been attributed to the stability of the diradical intermediates involved. Zimmerman et al.[9] had suggested, on the basis of quenching studies, that these photoreactions proceed primarily from their excited singlet states. Recent studies[6,10,11] have shown that substrates, wherein the cis–trans isomerization is prevented through geometric constraints, undergo predominantly the expected photorearrangements. Thus, the photolysis of 2,3-dibenzoylbicyclo[2.2.2]octa-2,5-diene (**1**) in methanol gives a mixture of methyl 6-(phenoxyphenylmethylene)bicyclo[2.2.2]oct-2-ene-5-*exo*-carboxylate (**2**) and the lactone **3**, as major products (Scheme I).

Our objective was to examine the photoreactions of a few unsymmetrical 1-pyrazolyl-1,2-dibenzoylalkenes through steady-state and laser flash photolysis studies. The substrates that we have examined include 2-[1-(3,5-diphenylpyrazolyl)]-1,4-diphenylbut-2-ene-1,4-dione (**8**), 2-[1-(3,5-diphenyl-4-methylpyrazolyl)]-1,4-diphenylbut-2-ene-1,4-dione (**9**), 2-[1-(3,5-dimethylpyrazolyl)]-1,4-di-

Scheme I



Scheme II



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phenylbut-2-ene-1,4-dione (**10**), 2-[1-(3,4,5-trimethylpyrazolyl)]-1,4-diphenylbut-2-ene-1,4-dione (**11**), 2-[1-(5-methyl-3-phenylpyrazolyl)]-1,4-diphenylbut-2-ene-1,4-dione (**12**) and 2-[1-(3,5-diphenylpyrazolyl)]-1,4-diphenylbutane-1,4-dione (**16**).

Results and Discussion

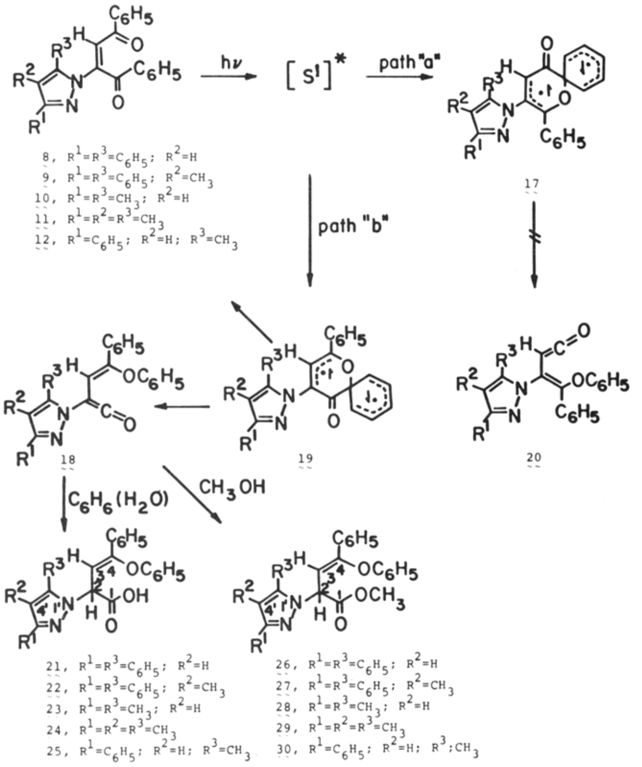
(1) Preparation of Starting Materials. Nucleophiles add to acetylenic ketones to give the corresponding 1:1 adducts.[12] We have prepared the 1-pyrazolyl-1,2-dibenzoylalkenes **8**–**12** in yields ranging between 70–90%, through the addition of the corresponding pyrazoles (**4a**–**e**) to dibenzoylacetylene (DBA, **5**) (Scheme II). Similarly, the dimethyl fumarate **14**[13] was prepared through the reaction of 3,4,5-trimethylpyrazole (**4d**) with dimethyl acetylenedicarboxylate (DMAD, **6**), whereas the dibenzoylalkane **16** was prepared through the reaction of 3,5-diphenylpyrazole (**4a**) with *cis*-1,2-dibenzoylethylene (DBE, **15**). The structures of all these adducts have been established on the basis of analytical results and spectral data. The geometry of the carbon–carbon double bond in the adducts **8**–**12** has been assigned the *E* configuration on the basis of the electronic spectra.[12,14]

(2) Preparative Photochemistry and Product Identification. Irradiation of **8** in benzene gave a mixture of 2-[1-(3,5-diphenylpyrazolyl)]-4-phenoxy-4-phenyl-3-butenoic acid (**21**) and *erythro*-5,6-dibenzoyl-2-phenylpyrazolo[5,1-*a*]-5,6-dihydroisoquinoline (**33**) in 37% and 26% yields, respectively. Similar results were obtained when the irradiation was carried out in acetone. On the other hand, when the irradiation of **8** was carried out in methanol, a mixture of methyl 2-[1-(3,5-diphenylpyrazolyl)]-4-phenoxy-4-phenyl-3-butenoate (**26**, 13%) and **33** (56%) was obtained. The structures of **21**, **26**, and **33** have been assigned on the basis of analytical results and spectral information. The structures of **21** and **26** were further confirmed by converting **21**–**26** through the reaction with diazomethane. Further confirmation of the structure of **33** was based on chemical evidence. Thermolysis of **33** gave 2,5,7-triphenylfuro[3,4-*c*]pyrazolo[5,1-*a*]isoquinoline (**35**), whereas treatment of **33** with hydrazine gave the dihydrazone **36** (Scheme IV).

Similarly, the photolysis of **9** in benzene (or acetone) gave a mixture of 2-[1-(3,5-diphenyl-4-methylpyrazolyl)]-4-phenoxy-4-phenyl-3-butenoic acid (**22**) and *erythro*-5,6-dibenzoyl-1-methyl-2-phenylpyrazolo[5,1-*a*]-5,6-dihydroisoquinoline (**34**) in 44% and 24% yield, respectively. The irradiation of **9** in methanol, on the other hand gave a mixture of methyl 2-[1-(3,5-diphenyl-4-methylpyrazolyl)]-4-phenoxy-4-phenyl-3-butenoate (**27**, 12%) and **34** (48%).

Photolysis of **10** in benzene (or acetone) gave a 76% yield of 2-[1-(3,5-dimethylpyrazolyl)]-4-phenoxy-4-phenyl-3-butenoic acid (**23**), whereas in methanol, a mixture of methyl 2-[1-(3,5-dimethylpyrazolyl)]-4-phenoxy-4-phenyl-3-butenoate (**28**, 19%) and *meso*-2,3-bis[1-(3,5-dimethylpyrazolyl)]-1,4-diphenylbutane-1,4-dione (**43**, 36%) was formed. Similarly, the irradiation of **11** in benzene (or acetone) gave a 67% yield of 2-[1-(3,4,5-trimethylpyrazolyl)]-4-phenoxy-4-phenyl-3-butenoic acid (**24**), whereas in methanol, a mixture of methyl 2-[1-(3,4,5-trimethylpyrazolyl)]-4-phenoxy-4-phenyl-3-butenoate (**29**, 38%) and *meso*-2,3-bis[1-(3,4,5-trimethylpyrazolyl)]-1,4-diphenylbutane-1,4-dione (**44**, 42%) was obtained. The photolysis of **12** in benzene (or acetone) gave a 62% yield of 2-[1-(5-methyl-3-phenylpyrazolyl)]-4-phenoxy-4-phenyl-3-butenoic acid (**25**), while the methanol photolysis gave only methyl 2-[1-(5-methyl-3-phenylpyrazolyl)]-4-phenoxy-4-phenyl-3-butenoate (**30**). The structure of all the photoproducts has been established on the basis of analytical results and spectral data. Further confirmation of the structures **43** and **44** was derived through their formation by the addition of the pyrazoles **4c** and **4d** to **10** and **11**, respectively.

Scheme III

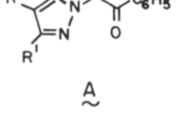


8, $R^1=R^3=C_6H_5$; $R^2=H$
9, $R^1=R^3=C_6H_5$; $R^2=CH_3$
10, $R^1=R^3=CH_3$; $R^2=H$
11, $R^1=R^2=R^3=CH_3$
12, $R^1=C_6H_5$; $R^2=H$; $R^3=CH_3$

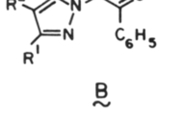
21, $R^1=R^3=C_6H_5$; $R^2=H$
22, $R^1=R^3=C_6H_5$; $R^2=CH_3$
23, $R^1=R^3=CH_3$; $R^2=H$
24, $R^1=R^2=R^3=CH_3$
25, $R^1=C_6H_5$; $R^2=H$; $R^3=CH_3$

26, $R^1=R^3=C_6H_5$; $R^2=H$
27, $R^1=R^3=C_6H_5$; $R^2=CH_3$
28, $R^1=R^3=CH_3$; $R^2=H$
29, $R^1=R^2=R^3=CH_3$
30, $R^1=C_6H_5$; $R^2=H$; R^3;CH_3

The formation of the different products in the photolysis of the pyrazolyl-1,2-dibenzoylalkenes, **8**–**12**, can be understood in terms of the pathways shown in Schemes III–V. One of the possible pathways, proceeding from the singlet excited state, would involve the singlet diradical intermediate **19** (path "b", Scheme III), which can give the ketene **18** or revert back to the starting material (**8**–**12**). The ketne **18** will subsequently react with the moisture present in solvent to give the carboxylic acids **21**–**25** or with methanol to give the methyl esters **26**–**30**. The exclusive formation of the acids **21**–**25** and the esters **26**–**30** from the pyrazolyl-1,2-dibenzoylalkenes **8**–**12**, respectively, would suggest that the alternate ketene **20**, arising through the singlet diradical **17** (path "a", Scheme III), is not involved in these reactions. The exact reason for this regioselectivity is not clear; however, it is likely that the ground-state conformations of **8**–**12** may have a strong influence. The starting dibenzoylalkenes **8**–**12** would prefer to exist chiefly in the less hindered conformer A than the alternate conformer B. The A conformer preferentially leads to **19** and **18** and ultimately, the observed products.



A



B

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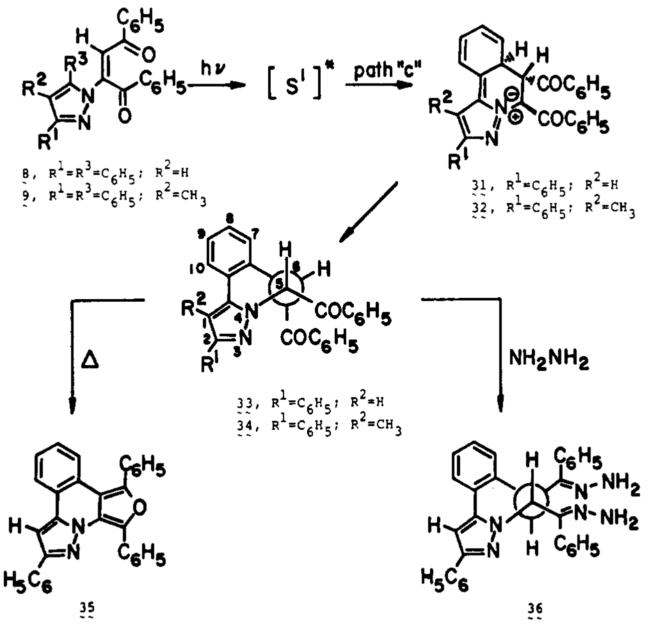
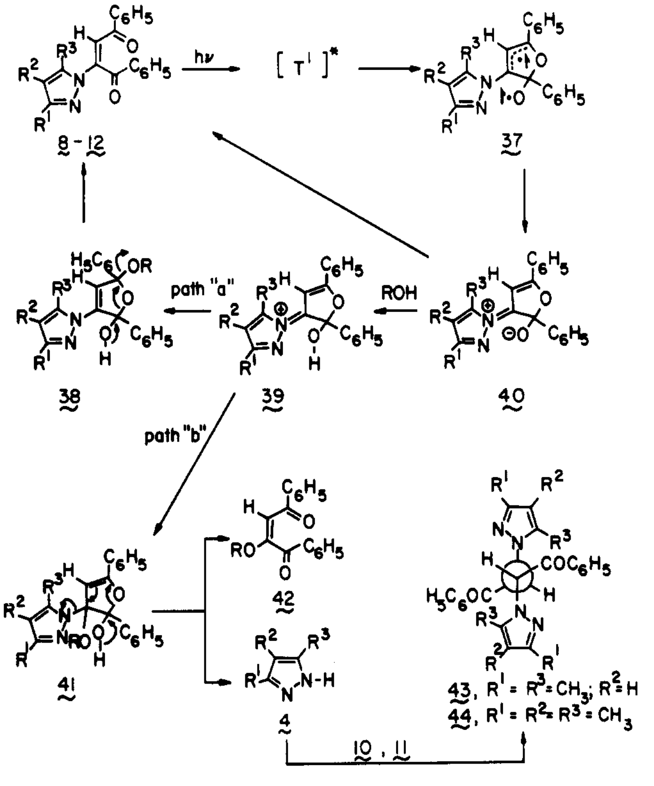
Scheme IV



Scheme V



An alternative pathway, for substrates **8** and **9**, containing C-5′ phenyl groups, would be an electrocyclic ring closure (10 or 14 electrons) to give the zwitterionic intermediates **31** and **32**, which will then give **33** and **34**, respectively, through prototropic shifts (path "c", Scheme IV).

The formation of the bis(pyrazole) adducts **43** and **44** can be understood in terms of Scheme V. The triplet excited states of the starting materials (**8–12**) could give the triplet diradical intermediate **37**, which can lead to the zwitterionic intermediate **40**, through electron demotions. Reaction of **40** with alcohol will result in the 1,4-adduct **38** (path "a", Scheme V) or the 1,2-adduct **41** (path "b", Scheme V). Subsequent fragmentation of **38** will give back the starting materials (**8–12**), whereas **41** will lead to the alkoxy substituted dibenzoylalkene **42** and the pyrazole **4**. Further reaction of **4** with **10** and **12** under thermal conditions, for example, will lead to the bis adducts **43** and **44**, respectively.

Scheme VI

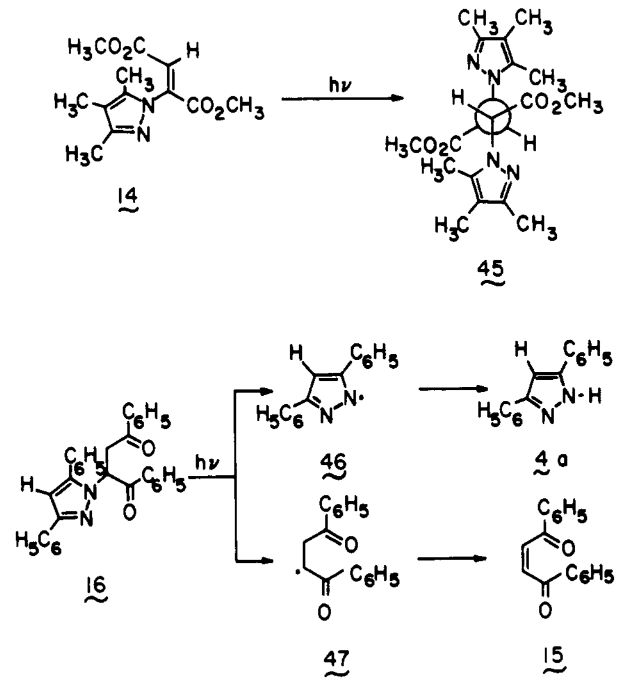


Table I. Quantum Yields of Disappearance of Substrates 8–12 under Steady-State Irradiation (334 nm) and from Pulsed Laser Photolysis (337.1 nm)

no.	ϕ_{dis}[a,c] benzene	ϕ_{dis}[a,c] methanol	ϕ_{dep}[b,c]
8	0.31 (0.27)	0.26 (0.24)	0.16 (0.14)
9	0.30 (0.29)	0.29 (0.26)	0.12 (0.12)
10	0.36 (0.24)	0.29 (0.31)	0.26 (0.21)
11	0.31 (0.26)	0.25 (0.20)	0.25 (0.19)
12	0.24 (0.19)	0.25 (0.26)	0.15 (0.14)

[a] ±15%; λ_{ex} = 334 nm (steady state) and λ_{mon} = 350–375 nm. [b] Solvent: benzene; ±20%; λ_{ex} = 337.1 nm (laser pulse) and λ_{mon} = 330 nm. [c] The data in parentheses were obtained in air-saturated solutions and the others under deoxygenated conditions.

In continuation, we have examined the photochemistry of the dimethyl fumarate **14**, which cannot undergo the 1,2-dibenzoylalkene rearrangement, and also the electrocyclic ring closure to see whether it will lead to the bis(pyrazole) adducts, similar to **43** and **44**. Irradiation of a benzene solution of **14** for 2.5 h gave a 14% yield of *meso*-dimethyl 2,3-bis[1-(3,4,5-trimethylpyrazolyl)]succinate (**45**)[13] (Scheme VI). The formation of **45** may take place through the pathway shown in Scheme V, involving a zwitterionic intermediate, analogous to **40**.

In contrast, the photolysis of the pyrazolyl-1,2-dibenzoylalkane **16** gave rise to fragmentation products. Thus, the irradiation of **16** gave a mixture of 3,5-diphenylpyrazole (**4a**, 54%) and *cis*-1,2-dibenzoylethylene (**15**, 55%). The formation of **4a** and **15** could occur through the radical intermediates **46** and **47**, respectively, shown in Scheme VI.

(3) Steady-State Quantum Yield Studies. The quantum yields (ϕ_{dis}) of disappearance of the dibenzoylalkenes **8–12**, under steady-state lamp excitation at 334 nm, were determined from the decrease in absorbance at 350–375 nm. There was practically no absorption of the major photoproducts **21–25** and **33**, **34**, **43**, and **44** at these wavelengths. The data for ϕ_{dis} under deoxygenated and air-saturated conditions (Table I) show that the presence

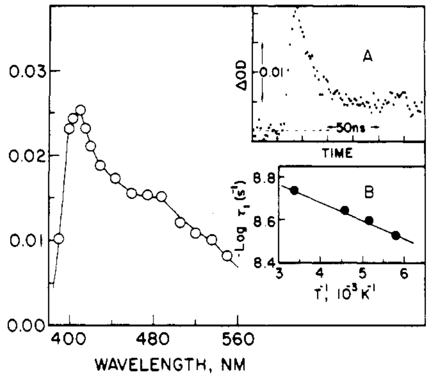


Figure 1. Transient absorption spectrum (end-of-pulse) of the short-lived species (τ_1 = 18 ns) observed upon 337.1-nm laser flash photolysis of substrate **9** in degassed methanol. Inset A: an experimental trace for the decay at 420 nm. Inset B: Arrhenius plot for the rate constant (τ_1^{-1}) for decay in methanol in the temperature range 173–295 K.

Table II. Lifetimes Associated with Transient Processes Observed upon 337.1-nm Laser Flash Photolysis of 8–12 in Degassed Benzene and Methanol

no.	solvent	τ_1,[a] ns	τ_2,[b] μs	τ_3,[c] μs
8	C_6H_6	*d*	0.42	5.5[e]
	MeOH	20	0.30	1.7 (0.96)[f]
9	C_6H_6	*d*	33	3.6[e]
	MeOH	18	25	2.3 (0.94)[f]
10	C_6H_6	*d*	1.1	3.4[e]
	MeOH	~10	0.37	1.3 (1.1)[f]
11	C_6H_6	*d*	28	2.6[e]
	MeOH	~10	15	0.84 (0.70)[f]
12	C_6H_6	*d*	0.70	3.2[e]
	MeOH	~10	0.40	1.0 (0.59)[f]

[a] Lifetimes of short-lived transients absorbing at 400–450 nm; ±20%. [b] Lifetimes of transient species with absorption maxima at ~400 and ~600 nm; ±15%. [c] Lifetimes associated with the growth of transient absorption at 380–390 nm in solutions containing methanol; ±15%. [d] ≤5 ns. [e] In benzene containing 2.5 M MeOH. [f] The data in parentheses are lifetimes for the growth processes in MeOH containing 5% water and 5.6 mM tetramethylammonium hydroxide.

of oxygen in the solutions in most cases makes no substantial difference in ϕ_{dis}.

(4) Laser Flash Photolysis and Pulse Radiolysis. The dibenzoylalkenes were subjected to laser flash photolysis studies with 337.1-nm nitrogen laser excitation (2–3 mJ, ~8 ns). Also, with a few of them, attempts were made to observe triplet-related transient phenomena under energy-transfer sensitization by biphenyl triplet ($^3BP^*$) generated by pulse radiolysis[15] in benzene.

The important features in transient processes observed at 290–700 nm upon 337.1-nm laser excitation of the five dibenzoylethylenes (**8–12**) in benzene and methanol are (a) very short-lived transients ($\tau \leq 20$ ns) with spectral absorptions at 400–450 nm, (b) pronounced ground-state depletion (negative absorbance changes) at short wavelengths (300–380 nm), (c) transients characterized by dual absorption maxima at 400 and 600 nm and decaying with first-order kinetics on the microsecond time-scale, and (d) growth of transient absorptions at 360–390 nm in methanol and benzene plus methanol mixtures. The lifetimes (τ_i) associated with the processes described under a, c, and d and designated by subscripts 1, 2, and 3, respectively, are summarized in Table II.

(a) Short-Lived Transients Absorbing at 390–450 nm. Figure 1 and its inset A show the absorption spectrum

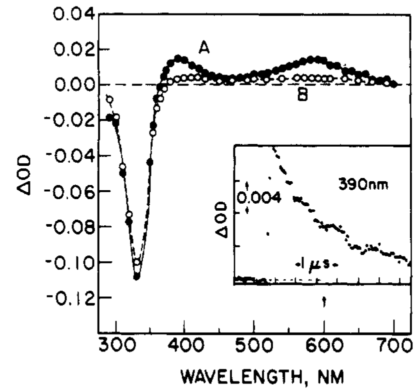


Figure 2. Transient absorption spectra (A, 0.2 μs; B, 3 μs following laser flash) observed upon 337.1-nm laser flash photolysis of substrate **10** in degassed benzene. Inset: experimental trace for decay at 390 nm.

and a representative kinetic trace, respectively, for the short-lived transient, derived from **9**. Detailed experiments with **9** as the substrate in methanol show that the 400-nm transient is quenchable by oxygen (k_q = ~1 × 10^9 M^{-1} s^{-1}) and that on lowering the temperature from 296 K to 173 K, its lifetime becomes longer only to a small extent (40%). A similar lack of pronounced temperature dependence on τ_1 has also been noticed for the 400-nm species from substrates **8** and **10–12**. The Arrhenius plot (inset B in Figure 1) for the decay rate constants (τ_1^{-1}) in the case of **9** in methanol gives 0.5 kcal/mol as the activation energy.

Among the most plausible candidates for the assignment of the short-lived transients, namely, singlets, triplets, and biradical intermediates (**19**, Scheme III), the triplet biradical intermediates appear highly unlikely since similar biradicals have been recognized[6,16] to have much longer lifetimes (13–16 μs) in previous studies on related systems. The fluorescence lifetime[17] of **9** in degassed methanol is considerably shorter than the observed τ_1 (20 ns); this rules out a singlet assignment. Thus, it appears that the triplets of the dibenzoylethylenes are responsible for the fast-decaying transient absorption under examination. Note that on quenching biphenyl triplet (produced pulse radiolytically in degassed benzene containing 0.05 M biphenyl) by dibenzoylethylenes **8**, **9**, and **10** (at 0.5–1 mM) no transient absorptions attributable to relatively long-lived triplets of the latter were observed as a result of the quenching. Only the weakly absorbing transients characterized by maxima at 400 and 600 nm and identified as species other than the triplets (see later) were produced in these experiments. The reason for the unusually short lifetimes of the dibenzoylethylene triplets can be ascribed to twisting[18] about the olefinic double bond and/or their fast transformation (intersystem crossing) from biradicaloid structures to zwitterionic forms (ground state) owing to the presence of the pyrazolyl group (see later).

(b) Ground-State Bleaching at 300–360 nm. With dibenzoylethylene **10** as a representative case, the transient absorption spectra observed at 0.1 and 3 μs following 337.1-nm laser flash excitation in benzene and methanol are presented in Figures 2 and 3, respectively. The most prominent feature of these spectra is the large negative absorbance change in the spectral region 300–380 nm

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(15) For a description of pulse radiolytic generation of triplets, see: Bensasson, R.; Land, E. J. *Trans. Faraday Soc.* **1971**, *67*, 1904–1915.

(16) Small, R. D., Jr.; Scaiano, J. C. *J. Phys. Chem.* **1978**, *82*, 2064–2066.

(17) By time-correlated single-photon counting of the emission at 420–430 nm; for a description of the apparatus, see ref 29c.

(18) The triplets of chalcones are reportedly very short-lived (τ = 5–29 ns in methanol), presumably because of twisting about the double bond. Caldwell, R. A.; Singh, M. *J. Am. Chem. Soc.* **1983**, *105*, 5139–5140.

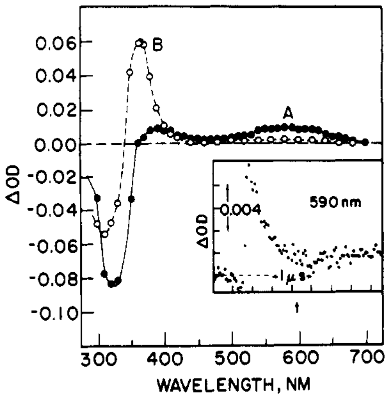

Figure 3. Transient absorption spectra (A, 0.2 μs; B, 3 μs following laser pulse) observed upon 337.1-nm laser flash photolysis of substrate **10** in degassed methanol. Inset: experimental trace for decay at 590 nm.

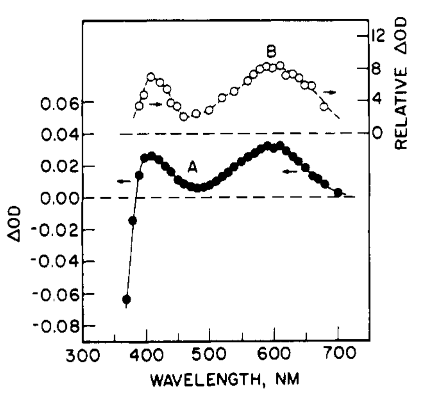

Figure 4. (A) Transient absorption spectra observed at 0.2 μs following 337.1-nm laser flash photolysis of substrate **9** in degassed benzene. (B) Same, observed upon pulse radiolysis of degassed benzene containing 0.05 M biphenyl and 1 mM substrate **9** (following the decay of biphenyl triplet).

following closely the ground-state absorption spectra. In benzene solutions of **8**–**12**, the depletions near the maxima (~330 nm) remain nearly unrecovered over ~100 μs, although the species responsible for the transient absorption with λ_{max}'s at ~400 and ~600 nm (see later) decay completely (for **8**, **10**, and **12**) or nearly completely (for **9** and **11**) over this time scale. On the other hand, in methanol solutions of **8**–**12**, partial recoveries of the ground-state depletion occur via first-order kinetics, but on time scales different from those of the decay of the 400/600-nm species. These observations suggest that the primary cause of the depletion could be primary photochemical process(es) other than the one related with the formation of the transients absorbing in the visible (λ_{max} 400 and 600 nm).

On the basis of the assumption that the primary products of laser photolysis absorb negligibly at 330 nm (relative to the substrate ground states), we have made use of the end-of-pulse absorbance changes (negative) due to depletion at this wavelength in benzene solutions to estimate the quantum yields of photochemical loss (ϕ_{dep}). This was done by comparison with absorbance changes due to benzophenone triplet ($\phi_T = 1$, $\epsilon_{max}^{TT} = 7.6 \times 10^3$ M^{-1} cm^{-1} at 532 nm)[19] in a solution of benzophenone in benzene optically matched at 337.1 nm with the solutions of **8**–**12**. ϕ_{dep} data are given in Table I. The fact that ϕ_{dep}'s are generally smaller than ϕ_{dis}'s appears to be due to the inadequacy of our assumption that the extinction coefficients of the primary photoproducts at 330 nm are negligible compared with those of the ground states of **8**–**12**.

(c) Transient Species with Absorption Maxima at 400 and 600 nm. The transient spectra and decay kinetics associated with the 400/600-nm species in the case of **10** are illustrated in Figures 2 and 3 and their insets. That, for a particular substrate, the same species is responsible for the transient absorptions at the two wavelength maxima is shown by the fact that the decay lifetimes (τ_2) are identical when the transient absorption is monitored at either of the two wavelengths. Interestingly, the transient species generated from **9** and **11** (τ_2 = 15–30 μs) are much longer-lived than those from **8**, **10**, and **12** (τ_2 = 0.3–1.2 μs). On going from benzene to methanol, τ_2's become shorter for all of the substrates. That this shortening is due to a bimolecular interaction with methanol is established by the observation of the enhancement of decay kinetics in benzene solutions upon gradual addition of methanol in molar concentrations. The bimolecular quenching rate constants, estimated in a few cases, are however very small, namely, ~1 × 10^5 and ~5 × 10^3 M^{-1} s^{-1} for the species derived from **10** and **11**, respectively. Protonation is a characteristic reaction of the 400/600-nm species as shown by the fact that perchloric acid quenches them efficiently with rate constants in the range 1.9–4.0 × 10^9 M^{-1} s^{-1} (in methanol containing 5% water). Bases such as tetramethylammonium hydroxide and *n*-butylamine have no effect on τ_2's.

No shortening of τ_2's is observed in the presence of ~0.01 M oxygen (O_2-saturated solutions) and ≤0.05 M di-*tert*-butylnitroxide (stable free radical). Also, azulene and ferrocene, typical low-energy triplet quenchers[20] (E_T = 38–40 kcal/mol) do not have any quenching effect on the lifetimes in all these cases. All these results firmly rule out the assignment of the 400/600-nm species as the triplets of **8**–**12**. A study of the laser intensity dependence shows that the formation of these transients is monophotonic in origin. Since no transient absorption attributable to solvated electron is observed at long wavelengths (650–750 nm) upon laser flash photolysis of methanol solutions, it is highly unlikely that the 400/600-nm species are radical cations (nonquenchable by oxygen) produced as a result of photoionization.

We carried out a few pulse radiolysis experiments[15] in which biphenyl triplet (^{3}BP*), generated by energy transfer from solvent triplets in benzene solutions containing 0.05 M biphenyl (BP), was quenched by substrates **9**, **10**, and **11** present in the solutions at relatively small concentrations (0.5–1 mM). The rate constants for the quenching of ^{3}BP* by the dibenzoylethylenes are 2–3 × 10^9 M^{-1} s^{-1}. Interestingly, following the completion of the decay of ^{3}BP* in the presence of **9**, **10**, and **11** at 1 mM, transient absorption spectra (λ_{max}'s 400 and 600 nm) reminiscent of those obtained in the course of the laser flash photolysis of these substrates in benzene are observed. This is shown in Figures 4 and 5 with **9** and **11** as the substrates, respectively. The similarity of the spectra as well as the decay lifetimes (τ_2) measured under the two conditions strongly suggests that the 400/600-nm species is a triplet-mediated photoproduct. To put this on a quantitative basis, the following experiments were done with **9** as the substrate in benzene. We measured the absorbance at 600 nm due to the 400/600-nm species under nearly complete quenching of pulse radiolytically generated ^{3}BP*, relative to that due to ^{3}BP* monitored at its maximum (360 nm) in the absence of a quencher. This was compared with the

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[19] Bensasson, R.; Land, E. J. *Photochem. Photobiol. Rev.* **1978**, *3*, 163–191.

[20] Herkstroeter, W. J. *J. Am. Chem. Soc.* **1975**, *97*, 4161–4167.

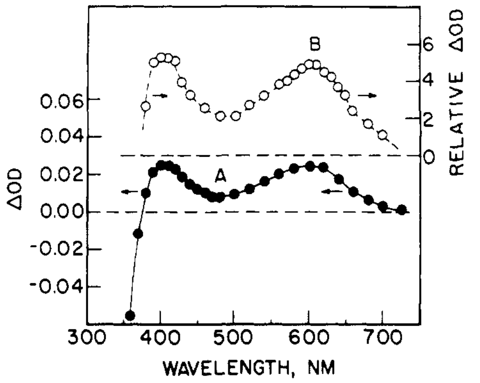

Figure 5. Transient absorption spectra observed at 0.2 μs following 337.1-nm laser flash photolysis of substrate **11** in degassed benzene. (B) Same, observed upon pulse radiolysis of degassed benzene containing 0.05 M biphenyl and 1 mM substrate **11** (following the completion of decay of biphenyl triplet).

absorbance at 600 nm due to the same species produced under 337.1-nm laser excitation of a solution of **9** in benzene, the latter being normalized with respect to the absorbance due to $^3BP^*$ at 360 nm observed in a separate solution containing benzophenone and ~0.01 M BP (optically matched with the solution of **9**). We found that the yield of the 400/600-nm transient via the triplet route with $^3BP^*$ as the sensitizer was approximately twice as high as that obtained under 337.1-nm excitation. Similar experiments with **11** showed that the relative yield under triplet sensitization was even higher (about 4 times that under direct 337.1-nm excitation). Admittedly, these observations cannot be used as evidence against the singlets (S_1) being precursors of the 400/600-nm species; however, these are compatible with a scheme with the triplets (T_1) as the predominant precursors of them, the significantly lower yields under direct excitation being a reflection of intersystem crossing yields much lower than unity (~0.5 and ~0.2 for **9** and **11**, respectively, based on the assumption that the 400/600-nm species are produced solely through the intermediacy of the triplets).

The observed properties of the 400/600-nm species strongly suggest that it is a zwitterion. The triplet biradical analogue of **19** (Scheme III) is ruled out as a candidate on the basis of the insensitivity toward oxygen and di-*tert*-butylnitroxide, as well as the fact that the formation of butenic acid/ester derivatives with this as the precursor is not observed under triplet sensitization (see later). On the other hand, the zwitterionic intermediate **40** (Scheme V) may be tentatively assigned[21] to the 400/600-nm species. The former may be visualized as the outcome of intramolecular electron transfer (or electron "demotion") in the triplet state (diradical), **37** (Scheme V). The possible mode of reaction with methanol leading to the formation of pyrazoles, which in turn, react with the substrates to produce bis(pyrazolyl) diones **43** and **44** is explained by path "b" in Scheme V.

(d) Growth of Transient Absorption at 360–390 nm in Solutions Containing Methanol. The transient spectrum B in Figure 3 exemplifies the absorption spectrum of the methanol-related photoproduct in the case of **10** in methanol. For substrates **8**, **9**, and **12**, the corresponding transient phenomena (methanol related) show up only in terms of partial recovery of the ground-state absorption at 360–390 nm (see the kinetic traces in Figure 6). Interestingly, when the methanolic solution is made basic by adding tetramethylammonium hydroxide in millimolar concentrations, the growth processes become very prominent in all the cases at 380–410 nm. Understandably, this is due to the red shift in the absorption maximum of the methanol adducts at high pH. τ_3's are found to be shorter under alkaline conditions (see the data in parentheses in Table II); they are, however, independent of tetramethylammonium hydroxide concentrations (1–10 mM).

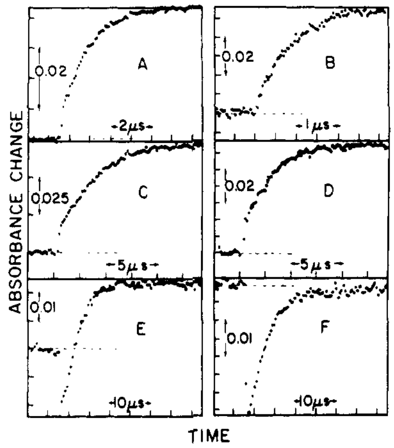

Figure 6. Growths of transient absorption (at 380 nm) due to methanol adducts. A and B correspond to substrates **10** and **11** in methanol and C–F correspond to **10**, **11**, **12**, and **8**, respectively, in benzene plus 2.5 M methanol.

The kinetics of the growth processes at 380–390 nm are totally insensitive to O_2 concentrations in solutions and bear no correlation with the decay of the corresponding 400/600-nm species. For instance, the lifetime τ_3 (1.3 μs) for the growth of the 380-nm species is much longer than that of the decay of the 400/600-nm species (τ_2 = 0.37 μs) for **10** in methanol, whereas the reverse is the case with **11** in methanol, that is, τ_2 = 15 μs and τ_3 = 0.84 μs.

Again, pulse radiolysis experiments were carried out in benzene solutions containing 0.5–1.5 M methanol to ascertain if the methanol related growth is due to a photoproduct coming from the triplets of **8–12** (generated via sensitization by $^3BP^*$, as described earlier). Interestingly, neither growth of a transient absorption nor recovery of an initial negative absorbance change is observed under the conditions of sensitization. Note that at the concentrations (0.5–1.5 M) of methanol used in these experiments, distinct growth processes occur on the microsecond time scale in the course of laser flash photolysis (see Figure 6, part C and D). This result proves that the species reacting with methanol originates from the singlets under direct excitation.

Zimmerman and co-workers[9,22] have shown that the photorearrangements of *cis*-dibenzoylethylenes leading to butenoic acid/ester derivatives are predominantly singlet mediated. In order to sort out if a similar mechanism is operative in the case of the pyrazolyldibenzoylethylenes, a benzene solution containing 0.05 M of BP, 2 mM of **10**, and 0.1 M of methanol was subjected to γ-radiolysis in a Co^{60} γ-cell. Obviously, under these conditions, we expected $^3BP^*$-sensitized formation of the triplet of **10** and the photochemical loss of **10**, if any, due to triplet-mediated photoreactions (particularly, the photorearrangement of Scheme III giving the methyl ester, **28**). Upon γ-radiolysis for 30 min, during which a solution of 0.05 M BP, 0.6 mM O_2, and 0.05 mM diphenylisobenzofuran contained in a

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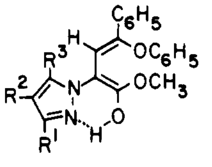
[21] Other zwitterionic structures may also be written for the 400/600-nm species; however, there are no additional supporting evidences in favor of these structures.

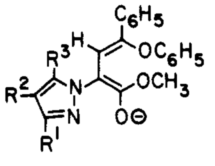
[22] Zimmerman, H. E.; Hull, V. J. *J. Am. Chem. Soc.* **1970**, *92*, 6515–6520.

separate cell showed 69% consumption of diphenylisobenzofuran (via reaction with singlet oxygen formed as a result of oxygen quenching of ^{3}BP*), the experimental solution containing BP, **10**, and methanol showed practically no loss of absorbance due to **10** at 350–380 nm. Following extensive γ-radiolysis (for 5.5 h) the solution was concentrated and then subjected to thin-layer chromatography (silica gel/*n*-ehxane + 5% di-*tert*-butyl ether); the presence of the ester **28** was not detectable. This experiment strongly suggests that as with dibenzoylethylenes,[9,22] the phototransformation of **10**, as well as other pyrazolyldibenzoylethylenes (by analogy) leading to butenoic acid/ester derivatives, takes place primarily from their singlet states (S_1).

It seems plausible that the single-mediated, methanol-related growth seen in laser flash photolysis is a manifestation of the reaction of methanol with the ketene **18**, formed in high yields as a result of singlet-mediated intramolecular phenyl group migration (path "b" in Scheme III). Specifically, the species absorbing at 380–410 nm could be the enol (**48a**) or the enolate anion (**48b**), depending upon the pH of the medium; this subsequently undergoes ketonization, following protonation if necessary, to form the ester on a longer time scale.[23] This interpretation is supported by the observation that *cis*-dibenzoylethylene also exhibits a similar growth in methanol containing 5% water and 5.6 mM tetramethylammonium hydroxide although the signal is poor with this substrate.



48a



48b

The yields of the methanol adduct (**48**) measured in terms of the plateau absorbance following its growth in the course of laser flash photolysis of **10** and **11** in benzene plus 2.5 M methanol are essentially the same in deoxygenated vs. air-saturated solutions; this suggests that the precursors of the ketene, particularly the singlet biradical (**19** in Scheme III), are insensitive toward oxygen, possibly because of short lifetimes.

Experimental Section

All melting points are uncorrected and were determined on a Mel-Temp melting point apparatus. The IR spectra were recorded on a Perkin-Elmer Model 580 infrared spectrometer. The electronic spectra were recorded on Cary 17D or 219 spectrophotometers. ^{1}H NMR traces were recorded on Bruker WP-80, WP-90, WH-250, or Varian XL-100 NMR spectrometers and ^{13}C NMR traces on Bruker WP-20 or Varian XL-15 NMR spectrometers with tetramethylsilane as internal standard. The mass spectra were recorded on a Varian Mat CH7 or Hitachi RMU-6E single-focusing mass spectrometer at 70 eV. All irradiation experiments were carried out in a Srinivasan-Griffin Rayonet photochemical reactor.

Starting Materials. Pyrazoles, **4a**, mp 197 °C, **4b**, mp 223–224 °C, **4c**, mp 139 °C, **4d**, mp 137–138 °C,[24] and **4e**, mp 128 °C, were prepared by reported procedures. Similarly, DBA (**5**),[25,26] mp 110–111 °C, DBE (**15**),[27] mp 135 °C, and DMAD (**6**),[28] bp 95–98 °C (19 nm) were prepared by reported procedures. Solvents for photolysis were purified and distilled before use, whereas Aldrich Gold label solvents were used for laser studies. Petroleum ether used was the fraction with bp 60–80 °C.

Preparation of 2-(1-Pyrazolyl)-1,4-diphenylbut-2-ene-1,4-diones (8–12). A general procedure for the preparation of **8–12** was to reflux a mixture of the appropriate pyrazole (**4a–e**, 10 mmol) with DBA (**5**, 10 mmol) in benzene (50 mL) for 6–8 h. The reaction mixture, on cooling, was diluted with petroleum ether (50 mL) to give the corresponding adducts.

Pyrazolyl-1,2-dibenzoylalkene **8** (90%), mp 168 °C, after recrystallization from a mixture (1:1) of benzene and petroleum ether: IR ν_{max} (KBr) 3060 (CH), 1690, 1660 (C=O) and 1600 (C=C) cm^{-1}; UV λ_{max} (CH_3CN) 248 nm (ε 38 290), 345 (13 270); ^{1}H NMR ($CDCl_3$) δ 6.82 (1 H, s, vinylic proton), 7.22 (1 H, s, pyrazolyl proton), 7.5 (20 H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 108.21 (C-4′), 115.27, 125.54, 126.09, 126.89, 127.23, 127.42, 127.82, 128.23, 128.43, 128.63, 129.37, 131.70, 133.06, 136.35, 137.42, 146.41, 147.93 (C-2), 153.53 (C-3), 190.00 (C=O); mass spectrum, *m/e* (relative intensity) 454 (M^+, 3), 349 ($M^+ - COC_6H_5$, 20), 321 ($M^+ - COC_6H_5 - CO$, 19) and other peaks.

Anal. Calcd for $C_{31}H_{22}N_2O_2$: C, 81.93; H, 4.84; N, 6.16. Found: C, 82.16; H, 4.61; N, 6.38.

Compound **9** (82%), mp 190–191 °C, after recrystallization from a mixture (1:1) of benzene and petroleum ether: IR ν_{max} (KBr) 3060 (CH), 1690, 1655 (C=O), 1600 and 1580 (C=C) cm^{-1}; UV λ_{max} (CH_3CN) 244 nm (ε 38 490), 345 (23 420); ^{1}H NMR ($CDCl_3$) δ 2.1 (3 H, s, methyl), 6.95 (1 H, s, vinylic proton), 7.6 (20 H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 9.23 (CH_3), 112.41, 117.91, 124.94, 126.24, 126.68, 127.02, 127.19, 127.92, 128.41, 128.61, 129.14, 129.31, 130.41, 132.56, 132.92, 136.51, 137.42, 148.60, 154.16, 190.10 (CO); mass spectrum, *m/e* (relative intensity) 468 (M^+, 8) and other peaks.

Anal. Calcd for $C_{32}H_{24}N_2O_2$: C, 82.00; H, 5.1; N, 6.0. Found: C, 81.66; H, 4.79; N, 6.4.

Compound **10** (72%), mp 130–131 °C, after recrystallization from a mixture (2:5) of methylene chloride and petroleum ether: IR ν_{max} (KBr) 3060, 2980 (CH), 1690, 1650 (C=O), 1600 and 1585 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 258 nm (ε 25 360), 326 (23 070); ^{1}H NMR ($CDCl_3$) δ 2.22 (3 H, s, CH_3), 2.24 (3 H, m, CH_3), 6.0 (1 H, s, H$^{4'}$-pyrazolyl), 7.71 (11 H, m, aromatic and vinylic); ^{13}C NMR ($CDCl_3$) 13.57 (CH_3), 13.81 (CH_3), 106.06, 111.27, 112.39, 128.38, 128.59, 128.81, 129.15, 129.41, 129.54, 133.12, 133.47, 135.41, 136.07, 137.53, 140.72, 142.00, 149.19, 152.25, 191.13 (C=O), 192.59 (C=O).

Anal. Calcd for $C_{21}H_{18}N_2O_2$: C, 76.36; H, 5.46; N, 8.48. Found: C, 76.08; H, 5.44; N, 8.0.

Compound **11** (70%), mp 164–165 °C, after recrystallization from a mixture (2:5) of methylene chloride and petroleum ether: IR ν_{max} (KBr) 3080, 2920 (CH), 1695, 1650 (C=O), 1600 and 1590 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 257 nm (ε 28 500), 330 (24 140); ^{1}H NMR ($CDCl_3$) δ 1.85 (3 H, s, CH_3), 2.22 (3 H, s, CH_3), 2.24 (3 H, s, CH_3), 7.6 (11 H, m, aromatic and vinylic).

Anal. Calcd for $C_{22}H_{20}N_2O_2$: C, 76.74; H, 5.81; N, 8.14. Found: C, 77.00; H, 5.57; N, 8.43.

Compound **12** (76%), mp 164–165 °C, after recrystallization from a mixture (1:1) of benzene and petroleum ether: IR ν_{max} (KBr) 3060, 2920 (CH), 1680 and 1655 (C=O), 1590 and 1580 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 252 nm (ε 36 570), 340 (27 800); ^{1}H NMR ($CDCl_3$) δ 2.1 (3 H, s, CH_3), 6.2 (1 H, s, H$^{4'}$-pyrazolyl), 6.7 (1 H, s, vinylic), 7.7 (15 H, m, aromatic).

Anal. Calcd for $C_{26}H_{20}N_2O_2$: C, 79.59; H, 5.10; N, 7.14. Found: C, 79.88; H, 4.98; N, 6.88.

Preparation of Dimethyl 2-[1-(3,4,5-Trimethylpyrazolyl)]fumarate (14). A solution of DMAD (**6**, 1.42 g, 10 mmol) in benzene (10 mL) was gradually added to a benzene solution (50 mL) of **4d** (1.1 g, 10 mmol) at room temperature, with constant stirring (0.25 h). After 0.5 h, the solid that separated out was filtered and further purified by chromatographing over

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[23] Conventional lamp flash photolysis of **10** and **11** in methanol show that the methanol adducts decay over milliseconds with half-lives of 0.8–1.2 ms. We are grateful to Dr. G. Ferraudi for assistance in performing these experiments (for details of the apparatus, see: Ferraudi, G. *Inorg. Chem.* **1979**, *18*, 1005–1013).

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silica gel. Elution with a mixture (1:1) of benzene and petroleum ether gave 2.2 g (88%) of **14**, mp 96 °C, after recrystallization from a mixture (1:1) of benzene and petroleum ether: IR ν_{max} (KBr) 3000, 2980, 2920 (CH), 1750 and 1710 (C=O), 1630 (C=C) cm^{-1}; UV λ_{max} (CH_3CN) 295 nm (ε 18 500); ^1H NMR ($CDCl_3$) δ 2.0 (3 H, s, CH_3), 2.20 (3 H, s, CH_3), 2.30 (3 H, s, CH_3), 3.8 (3 H, s, OCH_3), 4.0 (3 H, s, OCH_3), 6.1 (1 H, s, vinylic).

Anal. Calcd for $C_{12}H_{16}N_2O_4$: C, 57.14; H, 6.30; N, 11.11. Found: C, 56.84; H, 6.39; N, 11.48.

Preparation of 2-[1-(3,5-Diphenylpyrazolyl)]-1,4-diphenylbutane-1,4-dione (16). A mixture of 3,5-diphenylpyrazole (**4a**, 2.2 g, 1 mmol) and DBE (**15**, 2.36 g, 1 mmol) in benzene (50 mL) was refluxed for 20 h. The solvent was removed under vacuum to give a residue, which was chromatographed over silica gel. Elution with a mixture (1:4) of benzene and petroleum ether gave 1.5 g (30%) of **16**, mp 153 °C, after recrystallization from a mixture (1:1) of benzene and petroleum ether: IR ν_{max} (KBr) 3060, 2920 (CH), 1700 and 1690 (C=O), 1600 (C=C) cm^{-1}; UV λ_{max} ($CHCl_3$) 248 nm (ε 25 960); ^1H NMR ($CDCl_3$) δ 4.1 (2 H, m, methylene), 6.5 (1 H, m, methine), 6.53 (1 H, s, $H^{4'}$-pyrazolyl) 7.65 (20 H, m, aromatic).

Anal. Calcd for $C_{31}H_{24}N_2O_2$: C, 81.57; H, 5.26; N, 6.14. Found: C, 81.39; H, 5.50; N, 5.73.

Continued elution with a mixture (1:1) of benzene and petroleum ether gave 1.06 g (45%) of **15**, mp 135 °C (mixture melting point), after recrystallization from ethanol.

Further elution with benzene gave 1.12 g (51%) of **4a**, mp 197 °C (mixture melting point), after recrystallization from benzene.

Irradiation of 2-[1-(3,5-Diphenylpyrazolyl)]-1,4-diphenylbut-2-ene-1,4-dione (8). A solution of **8** (0.15 g, 0.33 mmol) in benzene (150 mL) was irradiated for 2 h. The solvent was removed under vacuum to give a residue which was chromatographed over silica gel. Elution with a mixture (1:1) of benzene and petroleum ether gave 40 mg (26%) of **33**, mp 152–153 °C, after recrystallization from a mixture (1:1) of benzene and petroleum ether: IR λ_{max} (KBr) 3080 and 3060 (CH), 1687 (C=O), 1595 and 1580 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 225 nm (ε 21 940 sh) and 250 (31 350); ^1H NMR ($CDCl_3$) δ 5.31 (1 H, d, $J_{5,6}$ = 3 Hz, H^6-proton), 6.31 (1 H, d, $J_{5,6}$ = 3 Hz, H^5 proton), 6.89 (1 H, s, H^1-pyrazolyl), 7.5 (19 H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 49.25 (C-6), 62.11 (C-5), 98.37 (C-1), 124.62, 125.79, 127.22, 127.74, 128.52, 128.91, 133.12, 133.85, 134.62, 136.66, 140.47, 152.56 (C-2), 193.88 (C=O), 196.34 (C=O); mass spectrum, *m/e* (relative intensity) 454 (M^+, 7), 349 ($M^+ - COC_6H_5$, 22) and other peaks.

Anal. Calcd for $C_{31}H_{22}N_2O_2$: C, 81.93; H, 4.8; N, 6.1. Found: C, 82.22; H, 4.70; N, 5.78.

Continued elution with benzene gave 58 mg (37%) of **21**, mp 191–192 °C, after recrystallization from a mixture (1:1) of benzene and petroleum ether: IR ν_{max} (KBr) 3060 and 3020 (CH), 3000–2500 (OH, intermolecularly hydrogen bonded), 1740 (C=O), 1660 and 1595 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 252 nm (ε 48 460); ^1H NMR ($CDCl_3$) δ 6.13 (1 H, d, $J_{2,3}$ = 9 Hz, D_2O-exchangeable, methine proton), 6.4 (1 H, d, $J_{2,3}$ = 9 Hz, vinylic proton), 6.62 (1 H, s, $H^{4'}$-pyrazolyl), 7.67 (1 H, s (broad), D_2O-exchangeable, OH), 7.25 (20 H, m, aromatic); ^{13}C NMR ($CDCl_3$) 57.04 (C-2), 103.95 (C-4′), 110.71, 116.03, 122.15, 125.92, 126.57, 128.78, 129.03, 129.40, 132.42, 133.58, 146.71, 152.17 (C-4), 153.47 (C-3), 156.32, 170.50 (C=O); mass spectrum, *m/e* (relative intensity) 454 ($M^+ - H_2O$, 2), 428 ($M^+ - CO_2$, 7), 335 ($M^+ - CO_2 - OC_6H_5$, 36) and other peaks.

Anal. Calcd for $C_{31}H_{24}N_2O_3$: C, 79.18; H, 5.08; N, 5.93. Found: C, 79.18; H, 4.91; N, 6.08.

In a repeat run, when the irradiation of **8** was carried out in acetone under analogous conditions, a mixture of **33** (28%) and **21** (38%) was obtained.

In Methanol. A solution of **8** (0.1 g, 0.22 mmol) in methanol (100 mL) was irradiated for 2 h. The photolysis was repeated several times to photolyze, in all, 1.0 g (2.2 mmol) of **8**. Removal of the solvent under vacuum gave a product, which was fractionally recrystallized from a mixture (1:1) of benzene and petroleum ether to give 560 mg (56%) of **33**, mp 152–153 °C (mixture melting point). The mother liquor, after removal of the solid product, was concentrated and chromatographed over neutral alumina. Elution with a mixture (1:4) of benzene and petroleum ether gave 140 mg (13%) of **26**, mp 128 °C, after recrystallization from a mixture (1:4) of benzene and petroleum ether: IR ν_{max} (KBr) 3040 and 2940 (CH), 1745 (C=O), 1650 and 1580 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 248 nm (ε 51 630); ^1H NMR ($CDCl_3$) δ 3.72 (3 H, s, OCH_3), 5.85 (1 H, d, $J_{2,3}$ = 9 Hz, D_2O-exchangeable, methine proton), 6.1 (1 H, d, $J_{2,3}$ = 9 Hz, vinylic proton), 6.5 (1 H, s, $H^{4'}$-pyrazolyl), 7.25 (20 H, m, aromatic); mass spectrum, *m/e* (relative intensity) 486 (M^+, 0.28), 427 ($M^+ - CO_2CH_3$, 9), 393 ($M^+ - OC_6H_5$, 100), 334 ($M^+ - CO_2CH_3 - OC_6H_5$, 68) and other peaks.

Anal. Calcd for $C_{32}H_{26}N_2O_3$: C, 79.01; H, 5.35; N, 5.76. Found: C, 79.33; H, 5.47; N, 5.68.

Reaction of 2-[1-(3,5-Diphenylpyrazolyl)]-4-phenoxy-4-phenyl-3-butenoic Acid (21) with Diazomethane. To a solution of **21** (150 mg, 0.31 mmol) in ether was added an ether solution (5%, 1 mL) of diazomethane at 0 °C and the reaction mixture was stirred for 0.5 h. Removal of the solvent under vacuum gave a residue, which was recrystallized from a mixture (1:4) of benzene and petroleum ether to give 138 mg (89%) of **26**, mp 128 °C (mixture melting point).

Thermolysis of *erythro*-5,6-Dibenzoyl-2-phenylpyrazolo[5,1-*a*]-5,6-dihydroisoquinoline (33). A sample of **33** (0.1 g, 0.22 mmol) was heated in a sealed tube at ca. 350 °C for 2 h. The reaction mixture was chromatographed over silica gel and eluted with a mixture (2:3) of benzene and petroleum ether to give 72 mg (75%) of **35**, mp 217–218 °C, after recrystallization from a mixture (2:3) of benzene and petroleum ether: IR ν_{max} (KBr) 3060 (CH), 1630 and 1600 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 255 nm (ε 41 560), 260 (26 570), 300 (27 520), 340 (2690 sh); ^1H NMR ($CDCl_3$) δ 7.0–8.8 (20 H, m, aromatic and pyrazolyl protons); ^{13}C NMR ($CDCl_3$) δ 96.98, 123.53, 124.21, 124.39, 124.69, 125.91, 126.50, 127.66, 127.74, 127.98, 128.35, 128.74, 128.83, 129.17, 129.39, 130.04, 131.65, 133.12, 152.04, 156.16; mass spectrum, *m/e* (relative intensity) 436 (M^+, 100) and other peaks.

Anal. Calcd for $C_{24}H_{16}N_2O$: C, 85.32; H, 4.59; N, 6.42. Found: C, 85.31; H, 4.22; N, 6.28.

Reaction of *erythro*-5,6-Dibenzoyl-2-phenylpyrazolo[5,1-*a*]-5,6-dihydroisoquinoline (33) with Hydrazine. A mixture of **33** (0.1 g, 0.22 mmol) and hydrazine hydrate (100%, 1 g, 20 mmol) in benzene (5 mL) was refluxed for 6 h and the water formed was removed by azeotropic distillation with benzene. The residue, after removal of the solvent was recrystallized from benzene to give 85 mg (80%) of the dihydrazone **36**, mp 195–196 °C: IR ν_{max} (KBr) 3500, 3460, 3300 and 3280 (NH), 1600 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 260 nm (ε 21 240); ^1H NMR ($CDCl_3$) δ 1.55 (4 H, s, D_2O-exchangeable, NH_2), 4.64 (1 H, d, $J_{5,6}$ = 12 Hz, H^6), 5.00 (1 H, d, $J_{5,6}$ = 12 Hz, H^5), 6.85 (1 H, s, H^1-pyrazolyl); mass spectrum, *m/e* (relative intensity) 482 (M^+, 0.2) and other peaks.

Anal. Calcd for $C_{31}H_{26}N_6$: C, 77.18; H, 5.40; N, 17.42. Found: C, 76.80; H, 5.36; N, 17.60.

Irradiation of 2-[1-(3,5-Diphenyl-4-methylpyrazolyl)]-1,4-diphenylbut-2-ene-1,4-dione (9). A solution of **9** (0.235 g, 0.5 mmol) in benzene (200 mL) was irradiated for 2 h and the product after removal of the solvent was chromatographed over silica gel. Elution with a mixture (1:1) of benzene and petroleum ether gave 58 mg (24%) of **34**, mp 174–175 °C, after recrystallization from a mixture (2:3) of benzene and petroleum ether: IR ν_{max} (KBr) 3080 (CH), 1680 (C=O) and 1600 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 246 nm (ε 30 660); ^1H NMR ($CDCl_3$) δ 2.56 (3 H, s, CH_3), 5.41 (1 H, d, $J_{5,6}$ = 3 Hz, H^6), 6.55 (1 H, d, $J_{5,6}$ = 3 Hz, H^5), 7.6 (19 H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 11.12 (CH_3), 50.10 (C-6), 62.50 (C-5), 110.64 (C-1), 124.52, 127.56, 127.70, 128.35, 128.55, 128.96, 129.33, 130.07, 133.84, 135.04, 135.95, 136.39, 152.27 (C-2), 194.39 (C=O), 196.76 (C=O); mass spectrum, *m/e* (relative intensity) 468 (M^+, 22), 450 ($M^+ - H_2O$, 6), 363 ($M^+ - COC_6H_5$, 62), 362 ($M^+ - COC_6H_5 - H$, 29) and other peaks.

Anal. Calcd for $C_{32}H_{24}N_2O_2$: C, 82.05; H, 5.12; N, 5.98. Found: C, 82.46; H, 4.87; N, 6.16.

Futher elution with benzene gave 107 mg (44%) of **22**, mp 195–196 °C, after recrystallization from a mixture (1:1) of benzene and petroleum ether: IR ν_{max} (KBr) 3060 (CH), 3000–2500 (OH, intermolecular hydrogen bonded), 1740 (C=O), 1665 and 1595 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 260 nm (ε 35 560); ^1H NMR ($CDCl_3$) δ 2.08 (3 H, s, CH_3), 6.08 (1 H, d, $J_{2,3}$ = 9 Hz, D_2O-exchangeable, methine), 6.25 (1 H, d, $J_{2,3}$ = 9 Hz, vinylic), 7.15 (21 H, m, aromatic and hydroxyl protons); ^{13}C NMR ($CDCl_3$) δ 9.97 (CH_3), 57.24 (C-2), 111.32, 112.95 (C-4′), 116.56, 122.28, 126.66, 128.22, 128.64, 128.99, 129.03, 129.32, 129.52, 130.20, 133.32, 138.81, 144.07, 150.30 (C-4), 153.30 (C-3), 156.52, 170.78 (C=O); mass spectrum, m/e (relative intensity) 468 ($M^+ - H_2O$, 31), 442 ($M^+ - CO_2$, 25), 441 ($M^+ - CO_2H$, 45), 440 ($M^+ - H_2O - CO$, 36), 393 ($M^+ - OC_6H_5$, 14), 349 ($M^+ - CO_2 - OC_6H_5$, 100) and other peaks.

Anal. Calcd for $C_{32}H_{26}N_2O_3$: C, 79.01; H, 5.34; N, 5.76. Found: C, 79.25; H, 5.00; N, 5.57.

When the irradiation of **9** was carried out in acetone under analogous conditions, a mixture of **34** (26%) and **22** (38%) was obtained.

Irradiation of a methanol solution of **9** (1.2 g, 2.2 mmol in 1000 mL) for 2 h and removal of the solvent gave a product which was recrystallized from a mixture (2:3) of benzene and petroleum ether to give 550 mg (48%) of **34**, mp 174–175 °C (mixture melting point).

The filtrate was concentrated and chromatographed over neutral alumina. Elution with a mixture (1:4) of benzene and petroleum ether gave 154 mg (12%) of **27**, mp 129–130 °C, after recrystallization from petroleum ether: IR ν_{max} (KBr) 3060, 2980, 2920 (CH), 1750 (C=O), 1660 and 1600 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 250 nm (ϵ 59 230); ^1H NMR ($CDCl_3$) δ 2.1 (3 H, s, CH_3), 3.65 (3 H, s, OCH_3), 5.8 (1 H, d, $J_{2,3} = 9$ Hz, methine), 6.05 (1 H, d, $J_{2,3} = 9$ Hz, vinylic), 7.2 (20 H, m, aromatic); mass spectrum, m/e (relative intensity) 500 (M^+, 0.5) and other peaks.

Anal. Calcd for $C_{33}H_{28}N_2O_3$: C, 79.20; H, 5.60; N, 5.60. Found: C, 79.43; H, 5.35; N, 5.35.

Irradiation of 2-[1-(3,5-Dimethylpyrazolyl)]-1,4-diphenylbut-2-ene-1,4-dione (10). A solution of **10** (0.16 g, 0.5 mmol) in benzene (160 mL) was irradiated for 1.25 h and the experiment was repeated several times to photolyze, in all, 1.5 g (4.55 mmol) of **10**. The combined photolysates were concentrated under vacuum and the residual solid was recrystallized from a mixture (1:1) of benzene and petroleum ether to give 1.21 g (76%) of **23**, mp 167–167.5 °C: IR ν_{max} (KBr) 3120–2500 (OH, intermolecularly hydrogen bonded), 1735 (C=O), 1650, 1600 and 1570 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 252 nm (ϵ 18 700); ^1H NMR ($CDCl_3$) δ 2.15 (3 H, s, CH_3), 2.23 (3 H, s, CH_3), 5.80 (1 H, s, $H^{4'}$-pyrazolyl proton), 5.92 (1 H, d, $J_{2,3} = 8.6$ Hz, D_2O-exchangeable, methine), 6.25 (1 H, d, $J_{2,3} = 8.6$ Hz, vinylic), 7.20 (10 H, m, aromatic), 8.20 (1 H, s (broad), D_2O-exchangeable, OH proton); ^{13}C NMR ($CDCl_3$) δ 10.78 (CH_3), 13.15 (CH_3), 56.26 (C-2), 105.71 (C-4′), 111.65, 116.36, 122.41, 126.60, 128.61, 129.20, 129.71, 133.87, 140.95, 148.84 (C-3), 153.11 (C-4), 169.93 (C=O); mass spectrum, m/e (relative intensity), 348 (M^+, 0.02), 304 ($M^+ - CO_2$, 41), 303 ($M^+ - CO_2H$, 37), 255 ($M^+ - OC_6H_5$, 94), 227 ($M^+ - CO_2 - C_6H_5$, 61), 211 ($M^+ - CO_2 - OC_6H_5$, 57), 210 ($M^+ - CO_2H - OC_6H_5$, 100), and other peaks.

Anal. Calcd for $C_{21}H_{20}N_2O_3$: C, 72.41; H, 5.74; N, 8.04. Found: C, 72.71; H, 5.70; N, 7.90.

In a repeat run, when the irradiation of **10** was carried out in acetone, a 68% yield of **23** was obtained.

In yet another run, a methanol solution of **10** (0.1 g, 0.3 mmol, 100 mL) was irradiated for 1.5 h and the photolysis was repeated several times to photolyze, in all, 2.06 g (6.0 mmol) of **10**. The combined photolysates were concentrated under vacuum and the residue was chromatographed over neutral alumina. Elution with a mixture (1:5) of benzene and petroleum ether gave 490 mg (36%) of **43**, mp 178–178.5 °C, after recrystallization from a mixture (1:1) of benzene and petroleum ether: IR ν_{max} (KBr) 3080, 3050, 2980, 2920 (CH), 1690 (C=O), 1600 and 1580 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 248 nm (ϵ 26 280); ^1H NMR ($CDCl_3$) δ 2.0 (6 H, s, CH_3), 2.1 (6 H, s, CH_3), 5.75 (2 H, s, methine), 6.00 (2 H, s, $H^{4'}$-pyrazolyl), 7.6 (10 H, m, aromatic); ^{13}C NMR ($CDCl_3$) 10.13 (CH_3), 13.55 (CH_3), 61.51 (methine), 106.07 (pyrazole C-4′), 128.40, 128.62, 133.24, 135.42, 140.75, 149.23, 192.61 (C=O); mass spectrum, m/e (relative intensity) 426 (M^+, 36), 331 ($M^+ - C_5H_7N_2$, 6), 321 ($M^+ - COC_6H_5$, 25), 293 ($M^+ - COC_6H_5 - CO$, 6) and other peaks.

Anal. Calcd for $C_{26}H_{26}N_4O_2$: C, 73.23; H, 6.10; N, 13.14. Found: C, 72.86; H, 6.23; N, 13.34.

Continued elution with a mixture (3:7) of benzene and petroleum ether gave 425 mg (19%) of **28**, mp 86–87 °C, after recrystallization from petroleum ether: IR ν_{max} (KBr) 3060, 3020, 2960 and 2920 (CH), 1735 (C=O), 1660 and 1595 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 250 nm (ϵ 22 470); ^1H NMR ($CDCl_3$) δ 2.1 (3 H, s, methyl), 2.2 (3 H, s, methyl), 3.75 (3 H, s, methoxy), 5.81 (1 H, s, $H^{4'}$-pyrazolyl), 5.91 (1 H, d, $J_{2,3} = 8.6$ Hz, D_2O-exchangeable, methine), 6.62 (1 H, d, $J_{2,3} = 8.6$ Hz), 7.25 (10 H, m, aromatic); mass spectrum, m/e (relative intensity), 362 (M^+, 0.1), 269 ($M^+ - C_6H_5$, 89), 210 ($M^+ - OC_6H_5 - CO_2CH_3$, 100) and other peaks.

Anal. Calcd for $C_{22}H_{22}N_2O_3$: C, 72.92; H, 6.07; N, 7.73. Found: C, 73.04; H, 6.17; N, 7.46.

Hydrolysis of Methyl 2-[1-(3,5-Dimethylpyrazolyl)]-4-phenoxy-4-phenyl-3-butenoate (28) with Methanolic Sodium Hydroxide. A mixture of **28** (0.2 g, 0.55 mmol) and sodium hydroxide (1 g, 2.25 mmol) in methanol (10 mL) was refluxed for 0.5 h. After removal of the solvent under vacuum, the residual solid was dissolved in water and neutralized with dilute hydrochloric acid. The solid that separated out was filtered and recrystallized from a mixture (1:1) of benzene and petroleum ether to give 185 mg (96%) of the butenoic acid **23**, mp 167–167.5 °C (mixture melting point).

Reaction of 3,5-Dimethylpyrazole (4c) with 2-[1-(3,5-Dimethylpyrazolyl)]-1,4-diphenylbut-2-ene-1,4-dione (10). A mixture of the pyrazole **4c** (0.3 g, 3.1 mmol) and **10** (1.0 g, 3.03 mmol) in benzene (35 mL) was refluxed for 4 h. Removal of the solvent under vacuum gave a residual solid, which was recrystallized from a mixture (1:1) of benzene and petroleum ether to give 1.05 g (81%) of the bis(pyrazole) adduct, **43**, mp 178–178.5 °C (mixture melting point).

Irradiation of 2-[1-(3,4,5-Trimethylpyrazolyl)]-1,4-diphenylbut-2-ene-1,4-dione (11). Irradiation of a solution of **11** (1.2 g, 3.4 mmol) in benzene (1000 mL) for 2 h and workup in the usual manner gave a product, which on recrystallization from a mixture (1:1) of benzene and petroleum ether gave 850 mg (67%) of **24**, mp 175 °C: IR ν_{max} (KBr) 3080–2300 (OH, intermolecularly hydrogen bonded), 1725 (C=O), 1650 and 1595 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 255 nm (ϵ 17 330); ^1H NMR ($CDCl_3$) δ 1.82 (3 H, s, methyl), 2.06 (3 H, s, methyl), 2.17 (3 H, s, methyl), 5.87 (1 H, d, $J_{2,3} = 8.6$ Hz, D_2O-exchangeable, methine), 6.37 (1 H, d, $J_{2,3} = 8.6$ Hz, vinylic), 7.25 (10 H, m, aromatic), 8.33 (1 H, s, (broad), D_2O-exchangeable, hydroxy); mass spectrum, m/e (relative intensity) 362 (M^+, 0.2), 345 ($M^+ - OH$, 2), 318 ($M^+ - CO_2$, 40), 317 ($M^+ - CO_2H$, 41), 283 (9), 269 ($M^+ - CO_2H - OC_6H_5$, 100) and other peaks.

Anal. Calcd for $C_{22}H_{22}N_2O_3$: C, 72.79; H, 6.07; N, 7.73. Found: C, 73.18; H, 5.83; N, 7.44.

In a repeat experiment, when the irradiation of **11** was carried out in acetone, a 64% yield of **24** was obtained.

In yet another run, a solution of **11** (0.2 g, 0.55 mmol) in methanol (150 mL) was irradiated for 2.5 h and the photolysis was repeated several times to photolyze, in all, 2.0 g (0.5 mmol) of **11**. The solvent was removed under vacuum and the residue was chromatographed over neutral alumina. Elution with a mixture (1:5) of benzene and petroleum ether gave 550 mg (42%) of **44**, mp 168 °C, after recrystallization from a mixture (1:1) of benzene and petroleum ether: IR ν_{max} (KBr) 2920 and 2880 (CH), 1685 (C=O), 1590 and 1580 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 245 nm (ϵ 40 180); ^1H NMR ($CDCl_3$) δ 1.7 (6 H, s, methyl), 1.8 (6 H, s, methyl), 2.0 (6 H, s, methyl), 6.45 (2 H, s, methine), 7.5 (10 H, m, aromatic); mass spectrum, m/e (relative intensity) 454 (M^+, 83), 349 ($M^+ - COC_6H_5$, 68), 344 ($M^+ - C_6H_9N_2 - H$, 63) and other peaks.

Anal. Calcd for $C_{28}H_{30}N_4O_2$: C, 74.00; H, 6.60; N, 12.33. Found: C, 74.35; H, 6.84; N, 12.00.

Continued elution with a mixture (3:7) of benzene and petroleum ether gave 850 mg (38%) of **29**, mp 97–97.5 °C, after recrystallization from petroleum ether: IR ν_{max} (KBr) 3080, 3020, 2960 and 2920 (CH), 1735 (C=O), 1660 and 1590 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 248 nm (ϵ 15 720); ^1H NMR ($CDCl_3$) δ 1.9 (3 H, s, methyl), 2.0 (3 H, s, methyl), 2.15 (3 H, s, methyl), 3.75 (3 H, s, methoxy), 5.87 (1 H, d, $J_{2,3} = 9$ Hz, D_2O-exchangeable, methine), 6.62 (1 H, d, $J_{2,3} = 9$ Hz, vinylic), 7.5 (10 H, m, aromatic); mass spectrum, m/e (relative intensity) 317 ($M^+ - CO_2CH_3$, 5), 283 ($M^+ - OC_6H_5$, 90), 224 ($M^+ - OC_6H_5 - CO_2CH_3$, 100) and other peaks.

Anal. Calcd for $C_{23}H_{24}N_2O_3$: C, 73.40; H, 6.38; N, 7.44. Found: C, 73.77; H, 6.00; N, 7.26.

Reaction of 3,4,5-Trimethylpyrazole (4d) with 2-[1-(3,4,5-Trimethylpyrazolyl)]-1,4-diphenylbut-2-ene-1,4-dione (11). A mixture of **4d** (0.33 g, 3 mmol) and **11** (1.0 g, 3 mmol) in benzene (40 mL) was refluxed for 4 h. Removal of the solvent under reduced pressure gave a residual solid, which was recrystallized from a mixture (1:1) of benzene and petroleum ether to give 985 mg (74%) of **20**, mp 168 °C (mixture melting point).

Irradiation of 2-[1-(5-Methyl-3-phenylpyrazolyl)]-1,4-diphenylbut-2-ene-1,4-dione (12). A solution of **12** (0.1 g, 0.26 mmol) in benzene (100 mL) was irradiated for 2 h and the photolysis was repeated several times to photolyze, in all, 1.0 g (2.6 mmol) of **12**. The residual solid, after removal of the solvent, was recrystallized from a mixture (1:1) of benzene and petroleum ether to give 650 mg (62%) of **25**, mp 169–170 °C: IR ν_{max} (KBr) 3100–2400 (OH, intermolecularly hydrogen bonded), 1745 (C═O), 1660, 1600 and 1550 (C═C) cm^{-1}; UV λ_{max} (CH_3OH) 255 nm (ϵ 29 390); ^1H NMR ($CDCl_3$) δ 2.3 (3 H, s, methyl), 6.15 (1 H, d, $J_{2,3}$ = 9 Hz, D_2O-exchangeable, methine), 6.4 (1 H, d, $J_{2,3}$ = 9 Hz, vinylic), 6.45 (1 H, s, $H^{4'}$-pyrazolyl), 7.5 (15 H, m, aromatic), 8.25 (1 H, s (broad), D_2O-exchangeable, hydroxy); ^{13}C NMR ($CDCl_3$) δ 10.84 (CH_3), 56.42 (CH), 102.70 (C-4′), 111.64, 116.14, 122.24, 125.76, 126.43, 127.70, 127.52, 128.49, 129.10, 129.65, 133.78, 134.03, 140.54 (C-4′), 150.94 (C-3′), 152.52 (C-3), 156.80 (C-4), 170.43 (C═O); mass spectrum, *m/e* (relative intensity) 393 ($M^+ - OH$, 9), 392 ($M^+ - H_2O$, 10), 366 ($M^+ - CO_2$, 31), 365 ($M^+ - CO_2H$, 30), 317 ($M^+ - OC_6H_5$, 69), 289 ($M^+ - CO_2 - C_6H_5$, 25), 273 ($M^+ - OC_6H_5 - CO_2$, 100), 272 ($M^+ - OC_6H_5 - CO_2H$, 57) and other peaks.

Anal. Calcd for $C_{26}H_{22}N_2O_3$: C, 76.09; H, 5.36; N, 6.83. Found: C, 75.90; H, 5.00; N, 7.00.

In a separate experiment, when a solution of **12** in acetone was irradiated under analogous conditions, a 64% yield of **25** was obtained.

In yet another run, a solution of **12** (0.2 g, 0.5 mmol) in methanol (150 mL) was photolyzed for 2 h and the photolysis was repeated several times to photolyze, in all, 1.0 g (2.55 mmol) of **12**. The residual solid, after removal of the solvent was chromatographed over silica gel. Elution with a mixture (2:3) of benzene and petroleum ether gave 476 mg (44%) of **30**, mp 126–127 °C: IR ν_{max} (KBr) 3070, 3050, 2980, and 2930 (CH), 1750 (C═O), 1660 and 1600 (C═C) cm^{-1}; UV λ_{max} (CH_3OH) 245 nm (ϵ 16 750); ^1H NMR ($CDCl_3$) δ 2.1 (3 H, s, methyl), 3.6 (3 H, s, methoxy), 5.5 (1 H, d, $J_{2,3}$ = 9 Hz, D_2O-exchangeable, methine), 6.0 (1 H, s, $H^{4'}$-pyrazolyl), 7.30 (16 H, m, aromatic and vinylic); mass spectrum, 365 ($M^+ - CO_2CH_3$, 4), 347 ($M^+ - C_6H_5$, 0.5), 288 ($M^+ - C_6H_5 - CO_2CH_3$, 16) and other peaks.

Anal. Calcd for $C_{27}H_{24}N_2O_3$: C, 76.41; H, 5.66; N, 6.60. Found: C, 76.80; H, 5.79; N, 6.22.

Further elution with a mixture (1:1) of benzene and petroleum ether gave 112 mg (11%) of the unchanged starting material (**12**), mp 164 °C (mixture melting point), after recrystallization from benzene.

Irradiation of Dimethyl 2-[1-(3,4,5-Trimethylpyrazolyl)]fumarate (14). A solution of **14** (0.21 g, 0.8 mmol) in benzene (200 mL) was irradiated for 2.5 h. The experiment was repeated several times to photolyze, in all, 2.1 g (8 mmol) of **14**. Removal of the solvent gave a solid, which was chromatographed over neutral alumina. Elution with a mixture (1:4) of benzene and petroleum ether gave 200 mg (14%) of **45**,[13] mp 193 °C, after recrystallization from a mixture (1:1) of benzene and petroleum ether: IR ν_{max} (KBr) 2960 and 2920 (CH), 1750 (C═O), 1590 (C═C) cm^{-1}; UV λ_{max} (CH_3OH) 235 nm (ϵ 9800); ^1H NMR ($CDCl_3$) δ 1.9 (6 H, s, methyl), 2.12 (6 H, s, methyl), 2.35 (6 H, s, methyl), 3.55 (6 H, s, methoxyl), 5.91 (2 H, s, methine); ^{13}C NMR ($CDCl_3$) δ 8.16, 9.50, 12.10, 52.52, 58.72, 111.93, 137.68, 148.26, 167.55; mass spectrum, *m/e* (relative intensity) 362 (M^+, 25) and other peaks.

Anal. Calcd for $C_{18}H_{26}N_4O_4$: C, 59.66; H, 7.18; N, 15.47. Found: C, 60.00; H, 6.89; N, 15.50.

Continued elution with a mixture (1:1) of benzene and petroleum ether gave 890 mg (43%) of the unchanged starting material (**14**), mp 96 °C (mixture melting point), after recrystallization from a mixture (1:1) of benzene and petroleum ether.

Irradiation of 2-[1-(3,5-Diphenylpyrazolyl)]-1,4-diphenylbutane-1,4-dione (16). A solution of **16** (230 mg, 0.5 mmol) in benzene (200 mL) was irradiated for 1 h. Removal of the solvent under vacuum gave a residue, which was chromatographed over silica gel. Elution with a mixture (1:4) of benzene and petroleum ether gave 45 mg (20%) of the unchanged starting material (**16**), mp 153 °C (mixture melting point), after recrystallization from a mixture (1:1) of benzene and petroleum ether.

Further elution with a mixture (1:1) of benzene and petroleum ether gave 63 mg (55%) of DBE (**15**), mp 135 °C (mixture melting point), after recrystallization from methanol.

Continued elution with benzene gave 60 mg (54%) of **4a**, mp 197 °C (mixture melting point), after recrystallization from benzene.

In a repeat run, a solution of **16** (0.23 g, 0.5 mmol) in acetone (200 mL) was irradiated for 1 h under analogous conditions and the photolyzate was worked up as in the earlier case to give 48 mg (21%) of the unchanged starting material, mp 153 °C (mixture melting point), 62 mg (52%) of DBE (**15**), mp 135 °C (mixture melting point), and **4a** (60 mg, 54%), mp 197 °C (mixture melting point).

In yet another run, a methanol solution of **16** (0.2 g, 0.5 mmol, 150 mL) was irradiated for 1 h. Workup of the reaction mixture as in the earlier case gave 60 mg (26%) of the unchanged starting material, mp 153 °C (mixture melting point), 65 mg (55%) of DBE (**15**), mp 135 °C (mixture melting point), and 55 mg (50%) of 3,5-diphenylpyrazole (**4a**), mp 197 °C (mixture melting point).

Laser Flash Photolysis. Pulse excitation was carried out at 337.1 nm (2–3 mJ, ~8 ns, UV 400 Molectron nitrogen laser). The transient phenomena were observed in 3 × 7 mm quartz cells with kinetic spectrometer, described elsewhere.[29] Unless otherwise mentioned, the solutions used in all experiments were deaerated by purging with oxygen-free argon.

Quantum Yields. For photochemical quantum yield measurements, the excitation source was a medium-pressure mercury lamp (B&L SP-200) coupled with a B&L monochromator (33-86-07) and a Corning filter (CS 0-54). Irradiation was carried out at 366 nm in solutions contained in 1 × 1 cm quartz cells and magnetically stirred during the experiment. The photochemical loss measured from the decrease in absorbance due to the substrates was kept below 10%. Ferrioxalate actinometry was performed according to the procedure described by Parker.[30]

Pulse Radiolysis. The computer controlled pulse radiolysis apparatus, which allows determination of transient spectra at various times after the pulse and kinetic measurements of the spectral changes have been described earlier.[31]

γ-Radiolysis. The ^{60}Co source used for steady-state γ-irradiation was Model GC 220 and the dose rate estimated by Fricke dosimeter[32] at the location in the radiation source, where the sample was placed, was 0.2 Mrad h^{-1} in March, 1983.

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Registry No. **4a**, 1145-01-3; **4b**, 17953-46-7; **4c**, 67-51-6; **4d**, 5519-42-6; **4e**, 56426-41-6; **5**, 1087-09-8; **6**, 762-42-5; **8**, 92670-69-4; **9**, 92670-70-7; **10**, 92670-71-8; **11**, 92670-67-2; **12**, 92670-68-3; 14, 92670-72-9; **15**, 959-27-3; **16**, 92670-73-0; **20** (R^1, R^2, R^3 = CH_3), 92670-90-1; **21**, 92670-74-1; **22**, 92670-75-2; **23**, 92670-76-3; **24**, 92670-77-4; **25**, 92670-78-5; **26**, 92670-79-6; **27**, 92670-80-9; **28**, 92670-81-0; **29**, 92670-82-1; **30**, 92670-83-2; **33**, 92694-72-9; **34**, 92670-84-3; **35**, 92670-85-4; **36**, 92670-86-5; **43**, 92670-88-7; **44**, 92670-89-8; **45**, 92670-87-6; O_2, 7782-44-7; CH_3OH, 67-56-1; H_2NNH_2, 302-01-2; biphenyl, 92-52-4.

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