1720 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.41 (3 H, s), 5.37 (2 H, AB q, J = 13.9), 5.94 (1 H, d, J = 3.9), 6.00 (1 H, d, J = 3.9), 7.60–8.24 (8 H, m); UV (CHCl$_3$) λ_{max} 270 nm (ϵ 15927), 306 (13230). Anal. Calcd for $C_{22}H_{15}N_3O_7S$: C, 56.77; N, 9.03; H, 3.25. Found C, 56.53; N, 8.95; H, 3.31.

Registry No. **1a**, 86998-70-1; **1b**, 103304-84-3; **1c**, 103304-85-4; **2a**, 103365-75-9; **2b**, 103304-86-5; **2c**, 103304-87-6; **3a**, 103365-74-8; **3c**, 103304-88-7; **4a**, 91618-80-3; **4b**, 103321-10-4; **4c**, 103304-90-1; **5a**, 103304-89-8; **6a**, 91685-82-4; **6c**, 103365-73-7; **7a**, 103420-11-7; **7c**, 103365-78-2; **8a**, 103365-76-0; **8c**, 103365-77-1; **9a**, 103365-79-3; **9c**, 103365-81-7; **10a**, 103365-80-6; **10c**, 103304-91-2; **11a**, 86998-74-5; **11b**, 103304-92-3; **11c**, 103304-93-4; **12a**, 103320-89-4; **12c**, 103304-94-5.

Photochemical Transformations of 1-Imidazolyl-1,2-dibenzoylalkenes. Steady-State and Laser Flash Photolysis Investigations[1]

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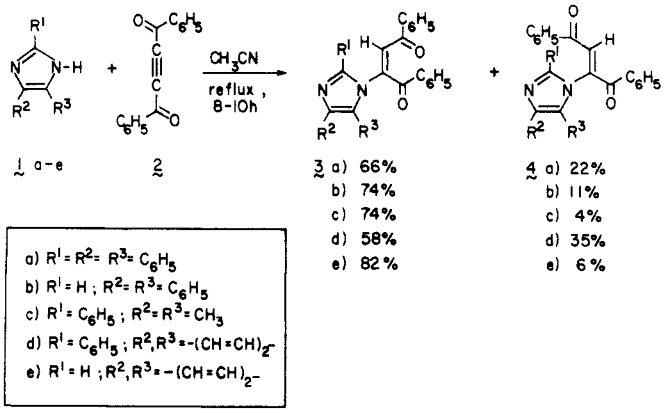
Received February 7, 1986

The photochemistry of a number of 1-imidazolyl-1,2-dibenzoylalkenes and 1-benzimidazolyl-1,2-dibenzoylalkenes has been investigated by steady-state photolysis combined with product analysis and laser flash photolysis. In several cases, the intramolecular phenyl group migration leading to ketene-mediated 3-butenoic acids and esters is observed. In addition, depending on the substituents present in the imidazolyl and benzimidazolyl groups, a variety of phototransformations occur; these include electrocyclic ring-closure reactions leading to dihydrophenanthrene and dihydroisoquinoline derivatives and photofragmentation reactions resulting in the loss of the imidazolyl moieties from the parent dibenzoylalkenes. Plausible mechanisms for these photoreactions are discussed. Laser flash photolysis in several cases gives rise to transient processes related to ketene and zwitterionic intermediates.

Photorearrangements of dibenzoylalkenes are known to give ketene-derived products and lactones, in addition to cis–trans isomerization products.[3-8] As a part of our continuing studies on the photorearrangements of 1,2-dibenzoylalkenes, we have recently examined the phototransformations of several substrates containing 1,2-dibenzoylalkene moieties such as 1,4- and 1,2-epoxy compounds,[9,10] dibenzobarrelenes,[11-13] 1-pyrazolyl-1,2-dibenzoylalkenes,[14,15] and 1-aziridinyl-1,2-dibenzoylalkenes.[16] In general, it has been observed that photorearrangements of substituted 1,2-dibenzoylalkenes strongly depend on the nature of the substitutes present in them.

Scheme I



The object of the present investigation has been to examine the phototransformations of some selected 1-imidazolyl-1,2-dibenzoylalkenes and 1-benzimidazolyl-1,2-dibenzoylalkenes, containing suitably positioned substituents which are capable of undergoing other types of photoreactions, besides the 1,2-dibenzoylalkene rearrangement. In addition, laser flash photolysis studies have

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(1) Document No. NDRL-2824 from the Notre Dame Radiation Laboratory.

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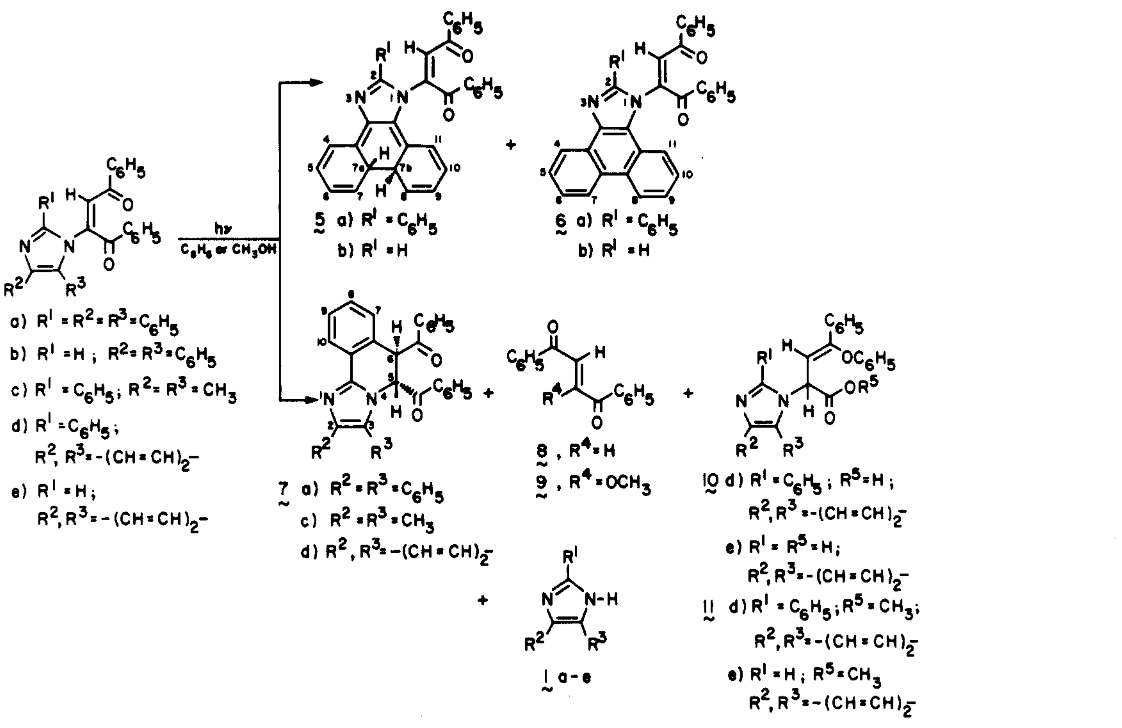
0022-3263/86/1951-3420$01.50/0

Scheme II



been carried out to characterize the transients involved in these photoreactions. The substrates that we have examined in this study include the dibenzoylethylenes **3a–e** and **4d**.

Results and Discussion

(1) Preparation of Starting Materials. The imidazolylethylenes **3a–e** and **4a–e** were prepared by refluxing equimolar amounts of the imidazole **1a–e** and dibenzoylacetylene (DBA, **2**) in acetonitrile (Scheme I). The geometry across the carbon–carbon double bond has been ascertained on the basis of their electronic spectra.[16–18] The *E* isomers **3a–e** had λ_{max} 251–271 nm (ϵ 27 820–44 240); the *Z* isomers **4a–e** absorb around 260–280 nm with higher extinction coefficients (29 800–53 000).

(2) Preparative Photochemistry and Product Identification. Irradiation of **3a** in benzene gave a mixture of the dihydroisoquinoline **7a** (18%), dihydrophenanthroimidazolyl derivative **5a** (22%), phenanthroimidazolyl derivative **6a** (20%), 2,4,5-triphenylimidazole (**1a**, 17%), and *trans*-1,2-dibenzoylethylene (**8**, 6%) (Scheme II). Similarly, the irradiation of **3a** in methanol gave a mixture of **7a** (10%), **5a** (15%), **6a** (25%), **1a** (34%), and *trans*-1-methoxy-1,2-dibenzoylethylene (**9**, 14%). The ^{1}H NMR spectrum of **5a** showed a doublet of doublets at δ 2.45 (1 H, $J_{7a,7b} = 18$ Hz, $J_{7,7a} = 4.5$ Hz), assigned to the 7a-H proton and a second doublet of doublets at δ 3.25 (1 H, $J_{7a,7b} = 18$ Hz, $J_{7b,8} = 6.5$ Hz), assigned to the $C_{7b\text{-}H}$ proton. The protons at C_7 and C_8 positions appeared as two quartets at δ 5.25 (1 H) and 6.35 (1 H), respectively, whereas the aromatic and vinylic protons appeared as a complex multiplet centered at δ 8.0 (22 H). The ^{1}H NMR spectrum of **6a** showed a multiplet spread over the region of δ 6.95–8.95, assigned to the aromatic and vinylic protons. Air-oxidation of **5a** in refluxing benzene gave a 81% yield of **6a**. The ^{1}H NMR spectrum of **7a** showed two doublets at δ 3.05 (1 H, $J = 15$ Hz) (C_6-H) and δ 4.35 (1 H, $J = 15$ Hz) (C_5-H). The relatively high coupling constant of 15 Hz ($H_{5,6}$) indicates an anti relationship of C_5- and C_6-protons in **7a**.

Similarly, the irradiation of **3b** in benzene gave a mixture of the dihydrophenanthroimidazolyl derivative **5b** (20%), phenanthroimidazolyl derivative **6b** (24%), 4,5-diphenylimidazole (**1b**, 35%), and *trans*-1,2-dibenzoylethylene (**8**, 12%), whereas the irradiation of **3b** in methanol yielded 16% of **5b**, 28% of **6b**, 38% of **1b**, and 17% of **9**. Likewise, the irradiation of **3c** in benzene gave a 31% yield of the dihydroisoquinoline derivative **7c**, a 47% yield of **1c**, and a 15% yield of **8**, whereas the irradiation of **3c** in methanol gave a 25% yield of **7c**, a 59% yield of **1a**, and a 23% yield of **9**.

In contrast, the irradiation of **3d** in benzene gave a mixture of the dihydroisoquinoline derivative **7d** (13%), 2-[1-(2-phenylbenzimidazolyl)]-4-phenoxy-4-phenyl-3-butenoic acid (**10d**, 9%), 2-phenylbenzimidazole (**1d**, 58%), and *trans*-1,2-dibenzoylethylene (**8**, 18%), whereas the irradiation of **3d** in methanol gave a mixture of the methyl ester **11d** (14%), **7d** (8%), **1d** (65%), and **9** (27%).

Similarly, the irradiation of **3e** in benzene, under analogous conditions, gave the acid **10e** (19%), benzimidazole (**1e**, 56%), and *trans*-1,2-dibenzoylethylene (**8**, 18%); in methanol, the methyl ester **11e**, 22%), **1e** (59%), and **9** (21%) were the products.

The structures of the butenoic acids **10d** and **10e** and the methyl butenoates **11d** and **11e** were established on the basis of spectral evidence. The ^{1}H NMR spectrum of **10d**, for example, showed a doublet at δ 5.90 (1 H, $J = 8$ Hz, D_2O-exchangeable), assigned to the methine proton and a second doublet at δ 6.45 (1 H, $J = 8$ Hz), assigned to the vinylic proton. The aromatic protons appeared as a multiplet at δ 7.10–7.65 (19 H, m), whereas the carboxylic acid proton appeared as a broad singlet at δ 7.85 (1 H, D_2O-exchangeable). The butenoic acids **10d** and **10e** were converted by treatment with diazomethane to the methyl esters **11d** (68%) and **11e** (72%), respectively.

In the (*Z*)-alkene series, irradiation of **4d** in benzene gave a 8% yield of **7d**, a 20% yield of the *E* isomer **3d**, a 14% recovery of the unchanged starting material **4d**, a 36%

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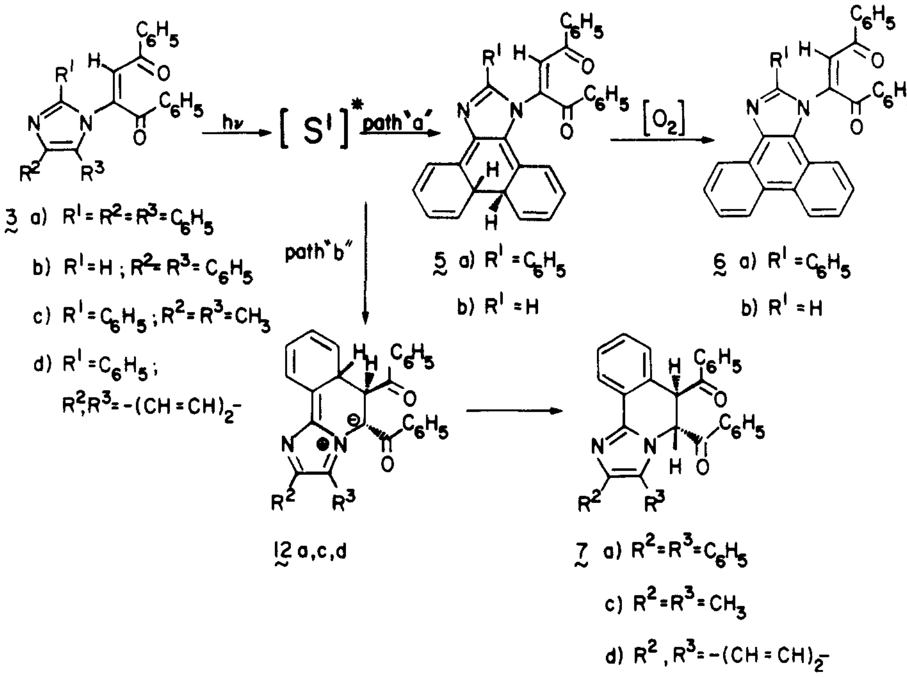
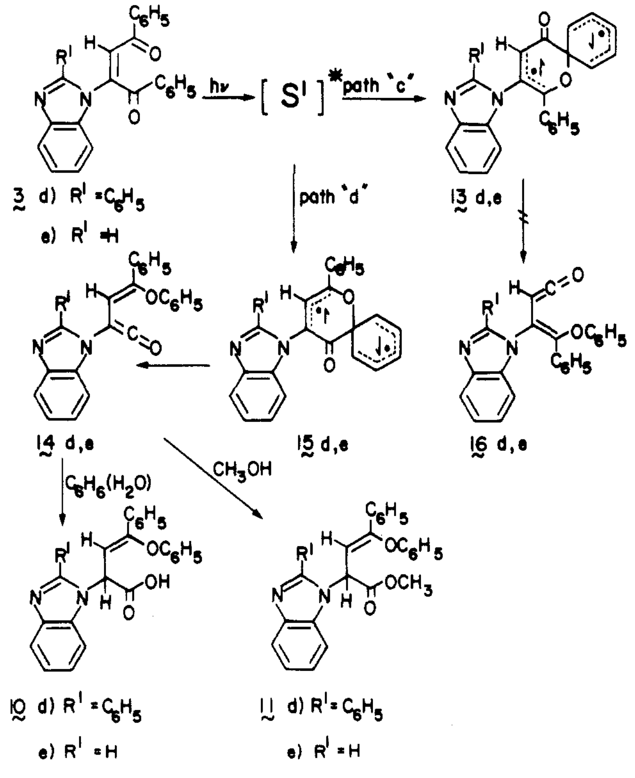
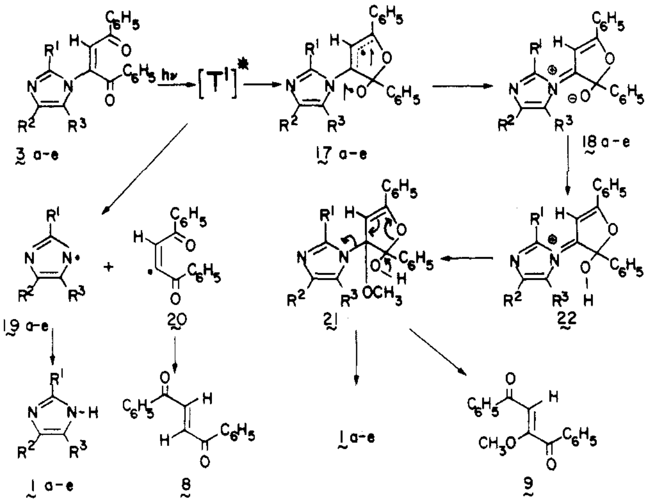
Scheme III



Scheme IV



Scheme V



yield of **1d**, and a 14% yield of **8**.

The formation of the different products in the photoreactions of 1-imidazolyl-1,2-dibenzoylalkenes **3a–e** can be understood in terms of the reaction pathways shown in Schemes III–V. It is quite evident that the photoreactions of **3a–e** are strongly dependent on the substituents present in the imidazolyl component, and several pathways leading to different products are observed in these cases. One of the photoreactions observed in the case of **3a** and **3b**, containing phenyl substituents at the C_4- and C_5-positions of the imidazolyl moiety, for example, is a singlet-state-mediated electrocyclic ring closure reaction, leading to the dihydrophenanthrene derivatives **5a** and **5b**, respectively (Scheme III, path a). Such ring closure reactions of substrates containing the *cis*-stilbene functionality, leading to dihydrophenanthrene derivatives, are well-documented in the literature.[19] The formation of the phenanthroimidazolyl-1,2-dibenzoylalkenes **6a** and **6b** in the photoreactions of **3a** and **3b**, however, could be understood in terms of the air-oxidation of the dihydrophenanthrene derivatives **5a** and **5b**, respectively, under the reaction conditions.

A second mode of reaction, observed in the case of those substrates containing a phenyl substituent in the C_2-position of the imidazolyl component, as in the case of **3a**, **3c**, and **3d** is again a singlet-state-mediated 10 or 14 electron, electrocyclic, conrotatory ring-closure reaction, involving the phenyl substituent and the 1,2-dibenzoylalkene component and leading to the zwitterionic intermediates **12a,c,d**, as shown in Scheme III (path b). Subsequent proton shifts in **12a,c,d** through a [1,4] or two successive

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[19] For some examples of the photocyclizations of stilbene derivatives, see: Stermitz, F. R. *Organic Photochemistry*; Chapman, O. L., Ed.; Marcel Dekker: New York, 1967; Vol. 1, pp 247–282.

[1,2] sigmatropic shifts will lead to the imidazolo[2,1-*a*]-5,6-dihydroisoquinoline derivatives **7a**, **7c**, and **7d**, respectively. It may be mentioned here that similar electrocyclic ring-closure reactions have been observed earlier in the photoreactions of 5-phenyl-substituted 1-pyrazolyl-1,2-dibenzoylalkenes, leading to the corresponding pyrazolo[5,1-*a*]-5,6-dihydroisoquinoline derivatives.[14,15]

Yet another photoreaction, that has been observed only in the case of **3d** and **3e** in the present study, is the 1,2-dibenzoylalkene rearrangement,[3-8] proceeding through the ketene intermediates **14d,e** and leading to the butenoic acids **10d,e** or the butenoic esters **11d,e**, respectively, depending on the reaction conditions (Scheme IV, path d). On the basis of analogy[14,15] it is assumed that the ketene intermediates **14d,e** are formed from the singlet excited state and involving singlet diradical intermediates **15d,e**, as shown in Scheme IV (path d). It may be pointed out here that the observed regioselectivity, leading to the ketene intermediates **14d,e** (Scheme IV, path d) as against **16d,e** (Scheme IV, path c), could be understood in terms of the ground-state conformational preferences of the starting imidazolyl-1,2-dibenzoylalkenes **3d,e**. The conformers leading to the diradical intermediates **13d,e** (path c) will be less populated due to steric crowding, as compared to those leading to the diradical intermediates **15d,e** (path d) and hence the observed regioselectivity. It is not very clear why the 1,2-dibenzoylalkene rearrangement has been observed only in the case of **3d** and **3e** and not in the other substrates (**3a,b,c**) under study. Perhaps, other reactions such as the photofragmentations (Scheme V) and electrocyclic reactions (Scheme III) may be predominant in these cases. Also, steric factors, arising through phenyl or methyl substituents at C_4- and C_5-positions of the imidazolyl moiety, may be adversely affecting the 1,2-dibenzoylalkene rearrangement occurring in **3a,b,c**.

The formation of photofragmentation products such as imidazoles **1a–c** or benzimidazoles **1d,e**, *trans*-1,2-dibenzoylethylene (**8**), and *trans*-1-methoxy-1,2-dibenzoylethylene (**9**) in these reactions could be understood in terms of pathways shown in Scheme V, involving zwitterionic intermediates **18a–e**. A similar pathway has been suggested earlier for the formation of pyrazoles from 1-pyrazolyl-1,2-dibenzoylalkenes.[14] It is also possible that small amounts of **1a–e** and **8** in these reactions could arise through radical intermediates such as **19a–e** and **20** (Scheme V).

(3) Laser Flash Photolysis Studies. Preliminary studies using 337.1-nm laser excitation showed that the flash photolysis of **3a**, **3c**, and **4d** in benzene and methanol and of **3d** and **3e** in benzene led to only very weak, featureless transient absorption phenomena at 350–700 nm in the time domains 0.1–100 μs. These systems were not pursued in any more detail. In the case of **3e** in benzene (λ_{ex} = 337.1 nm), ground-state bleaching due to photochemical loss was noticed at ≤370 nm, suggesting the photoreactive nature of the compound. The laser-induced negative absorbance changes did not show any sign of recovery over the longest time scale (~100 μs).

The most prominent transient phenomena are observed in the case of **3b**. Upon 308- or 337.1-nm laser flash photolysis of **3b** in both benzene and methanol, a long-lived transient species with absorption maximum at 640 nm is formed fast within the laser pulse (Figure 1). As evident from the transient spectrum in benzene (Figure 1, part A), a second absorption band system is located at 360–390 nm; that this also belongs to the 640-nm species is suggested by the similarity of decay kinetics at the two wavelengths.

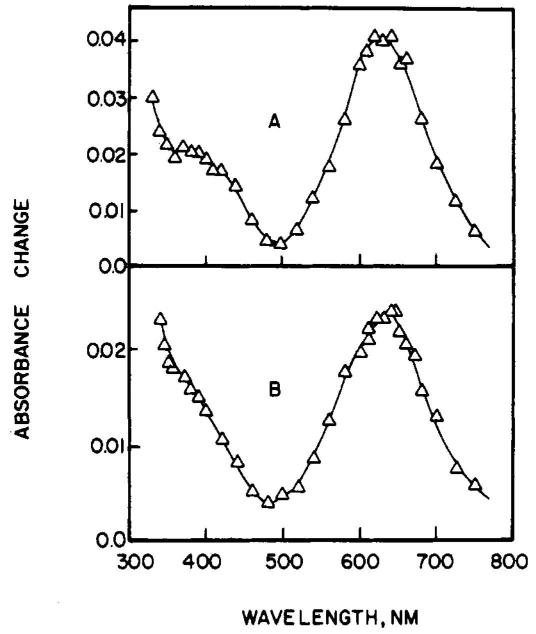


Figure 1. Transient absorption spectra observed at 2 μs following 308-nm laser flash photolysis of **3b** in (A) benzene and (B) methanol.

Table I. Lifetimes Associated with the Growth Kinetics at 360–390 nm Observed upon 337.1- or 308-nm Laser Flash Photolysis of 1-Imidazolyl-1,2-dibenzoylalkenes in Solvents Containing Methanol

	τ, μs[a]	
substrate	MeOH	MeOH + 5% H_2O + 5.6 mM TMAH[b]
3b	0.64	0.26
3d	2.9	0.20
3e	1.9	0.11

[a] ±15%. [b] TMAH = tetramethylammonium hydroxide.

A difference noticeable between benzene and methanol is that in the latter solvent a growth process occurs with a lifetime of 0.64 μs at 350–380 nm. This growth process is not observed in benzene.

The presence of oxygen (~2 mM, air-saturated solutions) does not make any difference in the yields and decay/growth kinetics of the transient absorptions photogenerated from **3b** in methanol or benzene. The decay of the 640 nm species becomes enhanced on going from benzene (τ = 80 μs) to methanol (τ = 17 μs). This species is readily quenchable by acids. For example, the bimolecular rate constants for quenching by trifluoroacetic acid (in benzene) and hydrochloric acid (in MeOH containing 5% H_2O) are 5.0×10^8 and 6.1×10^8 M^{-1} s^{-1}, respectively. The kinetic data were obtained from the linear dependence of the pseudo-first-order rate constant for 640-nm transient absorbance decay on acid concentrations. An alkali, added as tetramethylammonium hydroxide (≤6 mM) in 1:9 H_2O/MeOH (v/v), does not have any noticeable effect on the decay kinetics.

The growth of short-wavelength transient absorption (350–390 nm), observed for **3b** in methanol, is found to be common with **3d** and **3e** in the same solvent (Figure 2, parts A and B). In particular, the transient process is very prominent with **3e**. It is associated with the reaction of the alcohol with a photoproduct, as indicated by the observation of similar but slower growths of transient absorption in the case of **3e** in benzene–methanol mixtures. The transient spectrum in benzene containing 2.5 M methanol is shown in Figure 2, part C. In aqueous

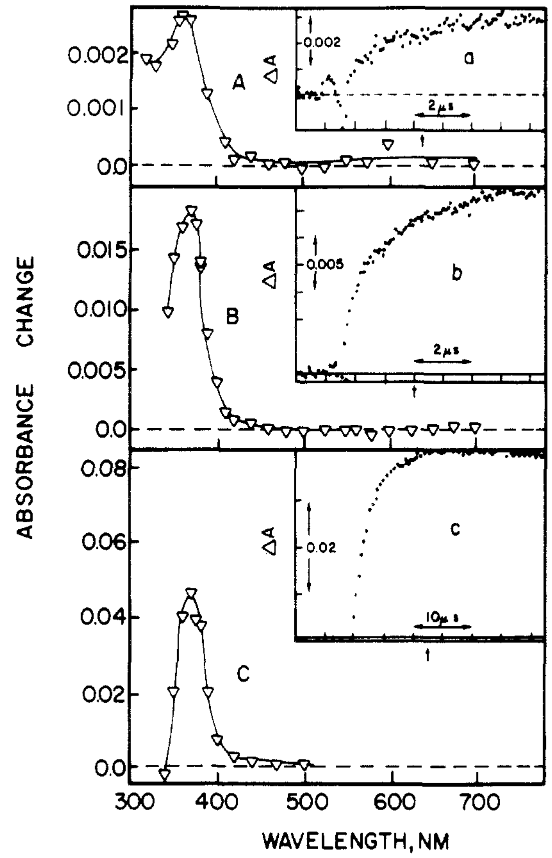


Figure 2. Transient absorption spectra observed from laser flash photolysis of (A) **3d** in methanol (λ_{ex} = 337.1 nm), (B) **3e** in methanol (λ_{ex} = 337.1 nm), and (C) **3e** in benzene + 2.5 M methanol (λ_{ex} = 308 nm). Insets: kinetic traces for growth in the respective cases at (a) 360, (b) 375, and (c) 375 nm.

methanol and in the presence of an alkali (tetramethylammonium hydroxide), the methanol-related growth kinetics become enhanced. Table I summarizes the lifetime data associated with the methanol-related processes.

Experiments were done in which biphenyl triplet was produced by pulse radiolysis[20] in benzene in the presence of **3b** and **3e** at 0.5–2 mM concentrations in order to examine if the transient phenomena observed under direct laser excitation are also obtainable under triplet sensitization. The solutions for these experiments contained 0.05 M biphenyl; at this high concentration, the latter accepted energy from the pulse-radiolytic solvent triplets[20] (benzene) and then transferred energy to the bustrates. For **3b**, concomitant with the decay of biphenyl triplet (monitored at 360 nm), we observed the growth of the 640-nm species. This is illustrated by the transient spectra and kinetic traces in Figure 3. This result established that the 640-nm species could be produced through the intermediacy of the triplet. In contrast, negative results were obtained concerning the methanol-related growth processes using **3e** as the acceptor of energy from biphenyl triplet in benzene + 5–15% methanol. That the biphenyl triplet was pulse-radiolytically produced in the presence of methanol and was quenched by **3e** was shown by the enhanced decay of its transient absorption at 360–400 nm. Thus, we conclude that the photoproduct reacting with methanol in the case of **3e** (and by analogy, **3b**,**d**) are singlet-derived. Pulse radiolysis experiments using **3b**,**c**,**e** at relatively high concentrations (~5 mM) did not furnish evidence for any long-lived substrate triplets (with τ > 100 ns). This, coupled with the fact that the formation kinetics of the 640-nm species in the case of **3b** matched very well with that of the decay of biphenyl triplet, suggested that the triplets of the dibenzoylalkenes under study are short-lived (<100 ns).

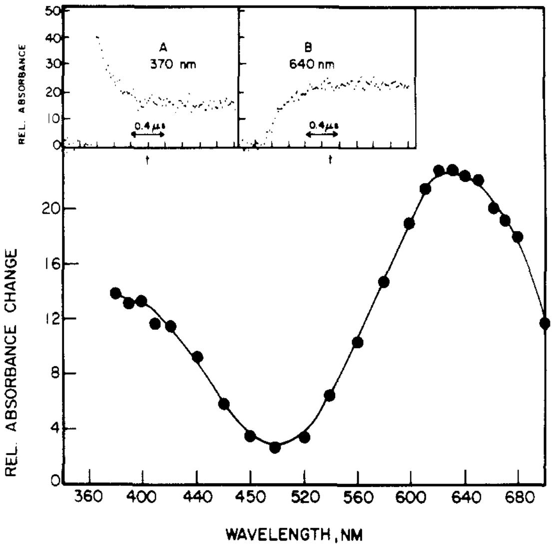
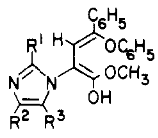


Figure 3. Transient absorption spectra at 5 μs following electron pulse irradiation of 0.05 M biphenyl in benzene containing 1.1 mM **3b**. Insets: kinetic traces showing (a) decay of biphenyl triplet at 370 nm and (b) growth of transient absorption at 640 nm.

As discussed in detail in a previous paper[14] on 1-pyrazolyl-1,2-dibenzoylalkenes, the most plausible explanation for the methanol-related growth phenomena at short wavelengths may be sought in terms of the reaction of the alcohol with the ketene **14** (Scheme IV) formed as a result of singlet-mediated, intramolecular, phenyl group migration. Thus, the primary species contributing to the plateau absorbance at 350–400 nm following the completion of growth in the presence of methanol can be the enol **23** or the enolate anion **24** depending upon the basicity of the medium. This species undergoes ketonization to the ester on a longer time scale (millisecond). Note that the methanol-related transient phenomena are the most prominent in the case of **3e**; this is also the substrate for which the phototransformation involving intramolecular phenyl group migration occurs with the highest yields (under steady-state irradiation).



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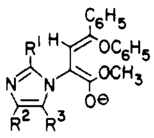

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The spectral characteristics and quenching behaviors of the 640-nm species from **3b**, and its formation via the triplet route are reminiscent of the 600/400-nm species that were commonly observed in the course of the laser flash photolysis of 1-pyrazolyl-1,2-dibenzoylalkenes.[14] In view of its quenching by acids, it appears to be a zwitterion. In our earlier paper,[14] we offered a tentative assignment in terms of the zwitterionic structure **18** (Scheme V); this, however, cannot explain why transient species with similar spectral and kinetic behaviors are not observed in the case of **3a**,**c**–**e**, although the steady-state phototransformation involving cyclization and methanol addition (Scheme V) appears to be pronounced for the latter substrates also.

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[20] (a) Bensasson, R.; Land, E. J. *Photochem. Photobiol. Rev.* **1978**, *3*, 163–191. (b) Bensasson, R.; Land, E. J. *Trans. Faraday Soc.* **1971**, *67*, 1904–1915. (c) Land, E. J. *Proc. R. Soc. London, Ser. A* **1968**, *A305*, 459–471.

Experimental Section

All melting points are uncorrected and were determined on a Mel-Temp melting point apparatus. The IR spectra were recorded on Perkin-Elmer Model 377 or 580 infrared spectrophotometers. The electronic spectra were recorded on Cary 17D or 219 spectrophotometers. ^{1}H NMR spectra were recorded on either Varian EM-390 or HA-100 NMR spectrometers, using tetramethylsilane as internal standard. The mass spectra were recorded on a Varian Mat CH7 or Hitachi RMU-6E single-focussing mass spectrometer at 70 eV. All steady-state irradiations were carried out on a Hanovia 450-W medium pressure mercury lamp in a quartz-jacketted immersion well.

Starting Materials. 2,4,5-Triphenylimidazole (**1a**),[21,22] mp 271–272 °C, 4,5-diphenylimidazole (**1b**),[23] mp 231–232 °C, 4,5-dimethyl-2-phenylimidazole (**1c**),[24] mp 142–143 °C, 2-phenylbenzimidazole (**1d**),[25] mp 289–290 °C, benzimidazole (**1e**),[26] m 171 °C, and DBA (**2**),[27,28] mp 110–111 °C, were prepared by reported procedures. Solvents for steady-state 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 (*Z*)- and (*E*)-1-Imidazolyl-1,2-dibenzoylalkenes 3a–e and 4a–e. A general procedure for the preparation of **3a–e** and **4a–e** was to reflux a mixture of the appropriate imidazole (**1a–c**) or benzimidazole (**1d**,**e**) (0.01 mol) and DBA (0.01 mol) in acetonitrile for varying periods of time. Removal of the solvent under vacuum gave a residual solid, which was chromatographed on silica gel and eluted with a mixture of benzene and petroleum ether to give the *Z* isomer first, followed by the *E* isomer. These adducts were purified, in each case, by recrystallization from suitable solvents.

(*Z*)- and (*E*)-1-(2,4,5-Triphenylimidazolyl)-1,2-dibenzoylethylene (4a and 3a). **4a** was obtained in a 22% yield (elution with a 1:3 mixture of benzene and petroleum ether and recrystallization from a 1:1 mixture of benzene and petroleum ether), mp 194–195 °C: IR $\nu_{\max}$ (KBr) 3060 and 3040 (CH), 1675 and 1660 (C=O), and 1600 (C=C) cm^{-1}; UV $\lambda_{\max}$ (methanol) 220 nm (ϵ 54 750), 278 (53 000); ^{1}H NMR (CDCl$_3$) δ 7.10–8.40 (m, vinylic and aromatic); mass spectrum, *m*/*e* (relative intensity) 530 (M$^+$, 94) 453 (M$^+$ − C$_6$H$_5$, 9), 425 (M$^+$ − COC$_6$H$_5$, 23), 424 (58), 348 (37), 320 (3), 295 (53), 105 (COC$_6$H$_5^+$, 100), 77 (C$_6$H$_5^+$, 73).

Anal. Calcd for $C_{37}H_{26}N_2O_2$: C, 83.77; H, 4.91; N, 5.28. Found: C, 84.05; H, 4.70; N, 5.51.

3a was obtained in a 66% yield (elution with a 1:2 mixture of benzene and petroleum ether and recrystallization from a 1:1 mixture of benzene and petroleum ether), mp 175 °C: IR $\nu_{\max}$ (KBr) 3065 and 3045 (CH), 1675 and 1660 (C=O), 1605 (C=C) cm^{-1}; UV $\lambda_{\max}$ (methanol) 223 nm (ϵ 47 350), 270 (46 100); ^{1}H NMR (CDCl$_3$) δ 7.15–8.45 (m, vinylic and aromatic); mass spectrum, *m*/*e* (relative intensity) 530 (M$^+$, 93), 453 (M$^+$ − C$_6$H$_5$, 8), 425 (M$^+$ − COC$_6$H$_5$, 25), 424 (46), 348 (38), 320 (3), 295 (55), 105 (COC$_6$H$_5^+$, 100), 77 (C$_6$H$_5^+$, 74).

Anal. Calcd for $C_{37}H_{26}N_2O_2$: C, 83.77; H, 4.91; N, 5.28. Found: C, 83.45; H, 4.63; N, 5.41.

(*Z*)- and (*E*)-1-(4,5-Diphenylimidazolyl)-1,2-dibenzoylethylene (4b and 3b). **4b** was obtained in a 11% yield (elution with a 1:3 mixture of benzene and petroleum ether and recrystallization from a 1:1 mixture of benzene and petroleum ether), mp 153 °C: IR $\nu_{\max}$ (KBr) 3080, 3060 and 3035 (CH), 1675 and 1660 (C=O), 1615 and 1595 (C=C) cm^{-1}; UV $\lambda_{\max}$ (methanol) 228 nm (ϵ 37 600), 270 (40 300); ^{1}H NMR (CDCl$_3$) δ 7.00–8.55 (m, vinylic and aromatic); mass spectrum, *m*/*e* (relative intensity) 454 (M$^+$, 73), 377 (M$^+$ − C$_6$H$_5$, 5), 349 (M$^+$ − COC$_6$H$_5$, 33), 248 (46), 272 (54), 219 (17), 105 (COC$_6$H$_5^+$, 100), 77 (C$_6$H$_5^+$, 79).

Anal. Calcd for $C_{31}H_{22}N_2O_2$: C, 81.94; H, 4.85; N, 6.17. Found: C, 81.63; H, 4.55; N, 6.39.

3b was obtained in a 74% yield (eltuion with a 1:2 mixture of benzene and petroleum ether and recrystallization from a 1:1 mixture of benzene an petroleum ether), mp 175 °C: IR $\nu_{\max}$ (KBr) 3080, 3065 and 3035 (CH), 1675 and 1660 (C=O), 1612 and 1595 (C=C) cm^{-1}; UV $\lambda_{\max}$ (methanol) 225 nm (ϵ 35 970), 261 (38 070); ^{1}H NMR (CDCl$_3$) δ 7.05–8.50 (m, vinylic and aromatic); mass spectrum, *m*/*e* (relative intensity) 454 (M$^+$, 73), 377 (M$^+$ − C$_6$H$_5$, 4), 349 (M$^+$ − COC$_6$H$_5$, 36), 348 (43), 272 (57), 219 (28), 105 (COC$_6$H$_5^+$, 100), and 77 (C$_6$H$_5^+$, 78).

Anal. Calcd for $C_{31}H_{22}N_2O_2$: C, 81.94; H, 4.85; N, 6.17. Found: C, 82.15; H, 5.05; N, 6.32.

(*Z*)- and (*E*)-1-(4,5-Dimethyl-2-phenylimidazolyl)-1,2-dibenzoylethylene (4c and 3c). **4c** was obtained in a 4% yield (elution with a 1:2 mixture of benzene and petroleum ether and recrystallization from a 1:1 mixture of methylene chloride and petroleum ether), mp 188 °C: IR $\nu_{\max}$ (KBr) 3090, 3065, 3045, 2975 and 2875 (CH), 1670 and 1660 (C=O), 1610 (C=C) cm^{-1}; UV $\lambda_{\max}$ (methanol) 218 nm (ϵ 27 350), 272 (46 130); ^{1}H NMR (CDCl$_3$) δ 1.95 (3 H, s, CH$_3$), 2.45 (3 H, s, CH$_3$), 7.05–8.35 (16 H, m, vinylic and aromatic).

Anal. Calcd for $C_{27}H_{22}N_2O_2$: C, 79.80; H, 5.42; N, 6.90. Found: C, 80.11; H, 5.68; N, 7.15.

3c was obtained in a 74% yield (elution with a 1:1 mixture of benzene and petroleum ether and recrystallization from a 1:1 mixture of methylene chloride and petroleum ether), mp 173–174 °C: IR $\nu_{\max}$ (KBr) 3085, 3065, 3040, 2975 and 2880 (CH), 1670 and 1660 (C=O), 1608 (C=C) cm^{-1}; UV $\lambda_{\max}$ (methanol) 215 nm (ϵ 22 960), 263 (44 240); ^{1}H NMR (CDCl$_3$) δ 1.85 (3 H, s, CH$_3$), 2.35 (3 H, s, CH$_3$), 7.05–8.40 (16 H, m, vinylic and aromatic); mass spectrum, *m*/*e* (relative intensity) 406 (M$^+$, 83), 329 (M$^+$ − C$_6$H$_5$, 5), 301 (M$^+$ − COC$_6$H$_5$, 23), 300 (36), 224 (38), 171 (11), 105 (COC$_6$H$_5^+$, 100), 77 (C$_6$H$_5^+$, 75).

Anal. Calcd for $C_{27}H_{22}N_2O_2$: C, 79.80; H, 5.42; N, 6.90. Found: C, 79.55; H, 5.28; N, 7.19.

(*Z*)- and (*E*)-1-(2-Phenylbenzimidazolyl)-1,2-dibenzoylethylene (4d and 3d). **4d** was obtained in a 35% yield (elution with a 1:4 mixture of benzene and petroleum ether and recrystallization from a 1:1 mixture of benzene and petroleum ether), mp 170 °C: IR $\nu_{\max}$ (KBr) 3090, 3060 and 3035 (CH), 1660 and 1650 (C=O), 1605 (C=C) cm^{-1}; UV $\lambda_{\max}$ (methanol) 219 nm (ϵ 37 830), 239 (31 480), 280 (35 900); ^{1}H NMR (CDCl$_3$) δ 6.90–8.80 (m, vinylic and aromatic); mass spectrum, *m*/*e* (relative intensity) 428 (M$^+$, 98), 351 (M$^+$ − C$_6$H$_5$, 7), 323 (M$^+$ − COC$_6$H$_5$, 31), 322 (49), 246 (21), 218 (3), 193 (9), 105 (COC$_6$H$_5^+$, 100), 77 (C$_6$H$_5^+$, 76).

Anal. Calcd for $C_{29}H_{20}N_2O_2$: C, 81.31; H, 4.67; N, 6.54. Found: C, 81.56; H, 4.71; N, 6.38.

3d was obtained in a 58% yield (elution with a 1:2 mixture of benzene and petroleum ether and recrystallization from a 1:1 mixture of benzene and petroleum ether), mp 197–198 °C: IR $\nu_{\max}$ (KBr) 3085, 3065 and 3040 (CH), 1665 and 1655 (C=O), 1610 (C=C) cm^{-1}; UV $\lambda_{\max}$ (methanol) 220 nm (ϵ 35 100), 237 (31 030), 271 (32 740); ^{1}H NMR (CDCl$_3$) δ 6.90–8.80 (m, vinylic and aromatic); mass spectrum, *m*/*e* (relative intensity) 428 (M$^+$, 96), 351 (M$^+$ − C$_6$H$_5$, 8), 323 (M$^+$ − COC$_6$H$_5$, 33), 322 (50), 246 (21), 218 (3), 193 (9), 105 (COC$_6$H$_5^+$, 100), 77 (C$_6$H$_5^+$, 79).

Anal. Calcd for $C_{29}H_{20}N_2O_2$: C, 81.31; H, 4.67; N, 6.54. Found: C, 81.60; H, 4.38; N, 6.33.

(*Z*)- and (*E*)-1-Benzimidazolyl-1,2-dibenzoylethylene (4e and 3e). **4e** was obtained in a 6% yield (elution with a 1:4 mixture of benzene and petroleum ether and recrystallization from a 1:1 mixture of benzene and petroleum ether), mp 161–162 °C: IR $\nu_{\max}$ (KBr) 3085, 3065 (CH), 1665 and 1655 (C=O), 1615 (C=C) cm^{-1}; UV $\lambda_{\max}$ (methanol) 220 nm (ϵ 24 120), 260 (29 800), 323 (8800); ^{1}H NMR (CDCl$_3$) δ 7.00–8.60 (m, vinylic and aromatic).

Anal. Calcd for $C_{23}H_{16}N_2O_2$: C, 78.41; H, 4.55; N, 7.95. Found: C, 78.66; H, 4.31; N, 8.17.

3e was obtained in a 82% yield (elution with a 1:2 mixture of benzene and petroleum ether and recrystallization from a 1:1 mixture of benzene and petroleum ether), mp 146 °C: IR $\nu_{\max}$ (KBr) 3080 and 3065 (CH), 1665 and 1655 (C=O), 1610 (C=C) cm^{-1}; UV $\lambda_{\max}$ (methanol) 218 nm (ϵ 22 180), 251 (27 820), 314 (8130); mass spectrum, *m*/*e* (relative intensity) 352 (M$^+$, 100),

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275 ($M^+ - C_6H_5$, 6), 247 ($M^+ - COC_6H_5$, 19), 246 (53), 170 (23), 118 (71), 105 ($COC_6H_5^+$, 105), 77 ($C_6H_5^+$, 78).

Anal. Calcd for $C_{23}H_{16}N_2O_2$: C, 78.41; H, 4.55; N, 7.95. Found: C, 78.42; H, 4.80; N, 7.68.

Irradiation of (*E*)-1-(2,4,5-Triphenylimidazolyl)-1,2-dibenzoylethylene (3a) in Benzene. A benzene solution of **3a** (500 mg, 0.943 mmol in 500 mL) was purged with nitrogen and irradiated for 1.5 h. Removal of the solvent under vacuum gave a residual solid, which was chromatographed over silica gel. Elution with petroleum ether gave 15 mg (6%) of *trans*-1,2-dibenzoylethylene (**8**), mp 109 °C (mixture melting point), after recrystallization from methanol.

Subsequent elution of the column with a mixture (1:4) of benzene and petroleum ether gave 90 mg (18%) of *threo*-5,6-dibenzoyl-5,6-dihydro-2,3-diphenylimidazolo[2,1-*a*]isoquinoline (**7a**), mp 218–218 °C, after recrystallization from a mixture (1:1) of benzene and petroleum ether: IR ν_{max} (KBr) 3075, 3035, 2960 and 2898 (CH), 1682 and 1675 (C=O), 1600 and 1590 (C=C) cm^{-1}; UV λ_{max} (methanol) 220 nm (ϵ 14 450), 249 (14 800); ^{1}H NMR ($CDCl_3$) δ 3.05 (1 H, d, J = 15 Hz, C_6-H), 4.35 (1 H, d, J = 15 Hz, C_5-H), 7.00–8.15 (24 H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 50.13 (C_6), 62.81 (C_5), 118.21, 120.73, 121.22, 122.35, 122.73, 122.99, 123.12, 123.61, 125.37, 125.49, 125.84, 126.23, 126.34, 127.54, 127.67, 128.71, 128.83, 128.91, 129.15, 129.37, 130.74, 132.33, 138.75, 155.77, 192.3 (C=O), 193.47 (C=O); mass spectrum, *m/e* (relative intensity) 530 (M^+, 3), 453 ($M^+ - C_6H_5$, 7), 425 ($M^+ - COC_6H_5$, 53), 424 ($M^+ - COC_6H_5 - H$, 55), 320 ($M^+ - 2COC_6H_5$, 31), 294 (7), 105 ($COC_6H_5^+$, 105).

Anal. Calcd for $C_{37}H_{26}N_2O_2$: C, 83.77; H, 4.91; N, 5.28. Found: C, 84.08; H, 4.74; N, 5.45.

Further elution of the column with a mixture (1:1) of benzene and petroleum ether gave 110 mg (22%) of **5a**, mp 227–228 °C, after recrystallization from a mixture (1:1) of methylene chloride and petroleum ether: IR ν_{max} (KBr) 3078, 3035, 2975 and 2895 (CH), 1665 and 1655 (C=O), 1600 and 1590 (C=C) cm^{-1}; UV λ_{max} (methanol) 236 nm (ϵ 29 800), 290 (16 000), 314 (19 000); ^{1}H NMR ($CDCl_3$) δ 2.45 (1 H, dd, $J_{7a,7b}$ = 18 Hz, $J_{7,7a}$ = 4.5 Hz, C_{7a}-H), 3.25 (1 H, dd; $J_{7a,7b}$ = 18 Hz, $J_{7b,8}$ = 6.5 Hz, C_8-H), 5.15 (1 H, q, C_7-H), 6.65 (1 H, q, C_8-H) 7.10–8.90 (22 H, m, vinylic and aromatic protons); mass spectrum, *m/e* (relative intensity) 530 (M^+, 3) 528 ($M^+ - 2$ H, 100), 453 ($M^+ - C_6H_5$, 9), 451 ($M^+ - C_6H_5 - 2$ H, 41), 425 ($M^+ - COC_6H_5$, 4), 423 ($M^+ - COC_6H_5 - 2$ H, 38), 422 (45), 320 (4), 318 (12), 293 (53), 216 (10), 105 ($COC_6H_5^+$, 89).

Anal. Calcd for $C_{37}H_{26}N_2O_2$: C, 83.77; H, 4.91; N, 5.28. Found: C, 83.49; H, 4.63; N, 5.47.

Subsequent elution of the column with a mixture (4:1) of benzene and petroleum ether gave 100 mg (20%) of **6a**, mp 258–259 °C, after recrystallization from a mixture (1:1) of methylene chloride and petroleum ether: IR ν_{max} (KBr) 3075 and 3035 (CH), 1670 and 1660 (C=O), 1610 and 1590 (C=C) cm^{-1}; UV λ_{max} (methanol) 223 nm (ϵ 30 990), 254 (54 790); ^{1}H NMR ($CDCl_3$) δ 6.95–8.95 (m, vinylic and aromatic protons); ^{13}C NMR ($CDCl_3$) δ 114.34, 115.21, 118.15, 118.99, 119.21, 119.67, 120.37, 120.63, 123.25, 123.68, 124.12, 124.26, 124.64, 124.85, 125.27, 126.18, 126.38, 132.33, 132.98, 133.46, 134.35, 142.18, 143.17, 154.53, 156.78, 157.85, 158.35, 193.20 (C=O), 194.18 (C=O); mass spectrum, *m/e* (relative intensity) 528 (M^+, 100), 451 ($M^+ - C_6H_5$, 37), 423 ($M^+ - COC_6H_5$, 33), 422 (44), 346 (3), 318 (11), 293 (55), 216 (11), 105 ($COC_6H_5^+$, 91).

Anal. Calcd for $C_{37}H_{24}N_2O_2$: C, 84.09; H, 4.55; N, 5.30. Found: C, 84.23; H, 4.41; N, 5.51.

The column was finally eluted with benzene to give 50 mg (17%) of 2,4,5-triphenylimidazole (**1a**), mp 271–272 °C (mixture melting point), after recrystallization from 50% acetic acid.

Irradiation of 3a in Air-Saturated Benzene. A solution of **3a** in benzene (500 mg, 0.943 mmol in 500 mL) was saturated with air and irradiated for 1.5 h. Workup as in the earlier case by removal of the solvent under vacuum and chromatographing the residue over silica gel gave 25 mg (11%) of **8** (elution with petroleum ether), mp 109 °C (mixture melting point), 50 mg (10%) of **7a** (elution with a 1:4 mixture of benzene and petroleum ether and recrystallization from a 1:1 mixture of benzene and petroleum ether), mp 217–218 °C (mixture melting point), 150 mg (31%) of **6a** (elution with benzene and recrystallization from a 1:1 mixture of methylene chloride and petroleum ether), mp 258–259 °C (mixture melting point), and 100 mg (34%) of **1a** (elution with a 9:1 mixture of benzene and ethyl acetate and recrystallization from 50% acetic acid), mp 271–272 °C (mixture melting point).

Irradiation of 3a in Methanol. A methanol solution of **3a** (500 mg, 0.943 mmol in 500 mL) was irradiated for 1.5 h and worked up as in the earlier cases to give 35 mg (14%) of *trans*-1-methoxy-1,2-dibenzoylethylene (**9**) (elution of the silica gel column with petroleum ether and recrystallization from methanol), mp 108 °C (mixture melting point), 50 mg (10%) of **7a** (elution with a 1:4 mixture of benzene and petroleum ether and recrystallization from a 1:1 mixture of benzene and petroleum ether), mp 217–218 °C (mixture melting point), 75 mg (15%) of **5a** (elution with a 1:1 mixture of benzene and petroleum ether and recrystallization from a 1:1 mixture of methylene chloride and petroleum ether), mp 227–228 °C (mixture melting point), 120 mg (25%) of **6a** (elution of a 4:1 mixture of benzene and petroleum ether and recrystallization from a 1:1 mixture of methylene chloride and petroleum ether), and 100 mg (34%) of **1a** (elution with a 9:1 mixture of benzene and ethyl acetate and recrystallization from 50% acetic acid), mp 271–272 °C (mixture melting point).

Air-Oxidation of 5a to 6a. A solution of **5a** (50 mg, 0.094 mmol) in benzene (40 mL) was refluxed under air-saturation for 40 h. Removal of the solvent under vacuum gave a residual solid, which was recrystallized from a mixture (1:1) of methylene chloride and petroleum ether to give 40 mg (81%) of **6a**, mp 258–259 °C (mixture melting point).

Irradiation of (*E*)-1-(4,5-Diphenylimidazolyl)-1,2-dibenzoylethylene (3b) in Benzene. A solution of **3b** (500 mg, 1.13 mmol) in benzene (50 mL) was purged with nitrogen for 15 min and irradiated for 1.5 h. Removal of the solvent under vacuum gave a residual solid, which was chromatographed over silica gel. Elution with petroleum ether gave 30 mg (12%) of **8**, mp 109 °C (mixture melting point), after recrystallization from methanol.

Further elution with a mixture (1:1) of benzene and petroleum ether gave 100 mg (20%) of **5b**, mp 223 °C, after recrystallization from a mixture (1:1) of methylene chloride and petroleum ether: IR ν_{max} (KBr) 3075, 3035, 2980 and 2875 (CH), 1675 and 1660 (C=O), 1605 and 1590 (C=C) cm^{-1}; UV λ_{max} (methanol) 239 nm (ϵ 36 970), 268 (39 500), 312 (17 350); ^{1}H NMR ($CDCl_3$) δ 2.35 (1 H, dd, $J_{7a,7b}$ = 18 Hz, $J_{7,7a}$ = 4.5 Hz, C_{7a}-H), 3.20 (1 H, dd, $J_{7a,7b}$ = 18 Hz, $J_{7b,8}$ = 6.5 Hz, C_8-H), 5.05 (1 H, q, C_7-H), 6.50 (1 H, q, C_8-H), 6.90–8.65 (18 H, m, vinylic and aromatic); mass spectrum, *m/e* (relative intensity), 454 (M^+, 12), 452 ($M^+ - 2H$, 84), 375 ($M^+ - C_6H_5 - 2H$, 35), 349 ($M^+ - COC_6H_5$, 3), 347 (17), 346 (23), 242 (9), 220 (4), 218 (19), 105 ($COC_6H_5^+$, 100), 77 ($C_6H_5^+$, 89).

Anal. Calcd for $C_{31}H_{22}N_2O_2$: C, 81.94; H, 4.85; N, 6.17. Found: C, 81.76; H, 4.71; N, 6.34.

Subsequent elution with a mixture (2:1) of benzene and petroleum ether gave 120 mg (24%) of **6b**, mp 254 °C, after recrystallization from a mixture (1:1) of methylene chloride and petroleum ether: IR ν_{max} (KBr) 3080 and 3030 (CH), 1670 and 1660 (C=O), 1600 and 1590 (C=C) cm^{-1}; UV λ_{max} (methanol) 226 nm (ϵ 32 370), 270 (41 230); ^{1}H NMR ($CDCl_3$) δ 6.95–8.68 (m, vinylic and aromatic); ^{13}C NMR ($CDCl_3$) δ 113.75, 114.23, 121.34, 122.33, 122.58, 122.76, 124.54, 125.86, 126.08, 126.73, 126.95, 128.34, 128.58, 129.56, 130.37, 132.39, 145.62, 151.35, 153.56, 192.47 (C=O), 193.84 (C=O); mass spectrum, *m/e* (relative intensity) 452 (M^+, 85), 375 ($M^+ - C_6H_5$, 33), 347 ($M^+ - COC_6H_5$, 17), 346 ($M^+ - COC_6H_5 - H$, 47), 242 (11), 278 (21), 105 ($COC_6H_5^+$, 100), 77 ($C_6H_5^+$, 83).

Anal. Calcd for $C_{31}H_{20}N_2O_2$: C, 82.30; H, 4.42; N, 6.19. Found: C, 82.43; H, 4.27; N, 6.34.

Further elution of the column with benzene gave 110 mg (35%) of **1b**, mp 231 °C (mixture melting point), after recrystallization from methanol.

Irradiation of 3b in Methanol. Irradiation of a methanol solution of **3b** (500 mg, 1.13 mmol in 500 mL) for 1.5 h and workup as in the earlier case gave 50 mg (17%) of **9**, mp 108 °C (mixture melting point), 80 mg (16%) of **5b**, mp 223 °C (mixture melting point), 140 mg (28%) of **6b**, mp 254 °C (mixture melting point), and 120 mg (41%) of **1b**, mp 231 °C (mixture melting point).

Air-Oxidation of 5b to 6b. A benzene solution of **5b** (50 mg, 0.113 mmol in 50 mL) was refluxed under air-saturation for 40 h. Removal of the solvent under vacuum and recrystallization of the residual solid from a mixture (1:1) of methylene chloride and petroleum ether gave 35 mg (76%) of **6b**, mp 254 °C (mixture melting point).

Irradiation of (*E*)-1-(4,5-Dimethyl-2-phenylimidazolyl)-1,2-dibenzoylethylene (3c) in Benzene. A solution of **3c** (500 mg, 1.23 mmol) in benzene (500 mL) was irradiated for 1 h. The irradiation was repeated again to photolyze, in all, 2.0 g of **3c**. Removal of the solvent under vacuum from the combined photolysates gave a residual solid, which was chromatographed over silica gel. Elution with petroleum ether gave 45 mg (15%) of **8**, mp 109 °C (mixture melting point), after recrystallization from methanol.

Further elution with a mixture (1:3) of benzene and petroleum ether gave 310 mg (31%) of **7c**, mp 163–164 °C, after recrystallization from a mixture (1:1) of benzene and petroleum ether: IR ν_{max} (KBr) 3085, 3040, 2965 and 2870 (CH), 1670 and 1655 (C=O), 1610 and 1590 (C=C) cm^{-1}; UV λ_{max} (methanol) 223 nm (ϵ 27380), 256 (39730); ^{1}H NMR (CDCl$_3$) δ 2.05 (3 H, s, CH$_3$), 2.45 (3 H, s, CH$_3$), 2.90 (1 H, d, J = 15 Hz, C$_6$-H), 4.20 (1 H, d, J = 15 Hz, C$_5$-H), 7.10–8.25 (14 H, m, aromatic); ^{13}C NMR (CDCl$_3$) δ 23.27, 27.31, 55.38, 62.78, 122.28, 124.74, 128.22, 128.38, 128.85, 129.44, 130.73, 132.71, 133.58, 135.63, 136.44, 145.60, 152.27, 192.35 (C=O), 193.77 (C=O); mass spectrum, *m/e* (relative intensity) 406 (M$^+$, 7), 404 (M$^+$ – H$_2$, 4), 329 (M$^+$ – C$_6$H$_5$, 27), 301 (M$^+$ – COC$_6$H$_5$, 19), 300 (M$^+$ – COC$_6$H$_5$ – H, 48), 296 (8), 171 (37), 105 (COC$_6$H$_5^+$, 100), 77 (C$_6$H$_5^+$, 92).

Anal. Calcd for $C_{27}H_{22}N_2O_2$: C, 79.80; H, 5.42; N, 6.90. Found: C, 80.11; H, 5.35; N, 6.78.

Subsequent elution of the column with benzene gave 200 mg (47%) of **1c**, mp 141–142 °C, after recrystallization from methanol.

Irradiation of 3c in Methanol. A methanol solution of **3c** (200 mg, 0.49 mmol in 200 mL) was irradiated for 1 h and worked up as in the earlier case to give 75 mg (23%) of **9**, mp 109 °C (mixture melting point) (after recrystallization from methanol), 50 mg (25%) of **7c** (elution with a 1:3 mixture of benzene and petroleum ether and recrystallization from a 1:1 mixture of benzene and petroleum ether), mp 163–164 °C (mixture melting point), and 50 mg (59%) of **1c**, mp 141–142 °C (mixture melting point).

Irradiation of (*E*)-1-(2-Phenylbenzimidazolyl)-1,2-dibenzoylethylene (3d) in Benzene. A solution of **3d** (500 mg, 1.167 mmol) in benzene (500 mL) was irradiated for 1 h. Removal of the solvent under vacuum gave a residual solid, which was chromatographed over silica gel. Elution with petroleum ether gave 50 mg (18%) of **8**, mp 109 °C (mixture melting point) after recrystallization from methanol.

Further elution of the column with a mixture (1:3) of benzene and petroleum ether gave 65 mg (13) of **7d**, mp 206 °C, after recrystallization from a mixture (1:1) of benzene and petroleum ether: IR ν_{max} (KBr) 3087, 3035, 2975 and 2860 (CH), 1670 and 1660 (C=O), 1600 and 1590 (C=C) cm^{-1}; UV λ_{max} (methanol) 220 nm (ϵ 39780), 260 (30360); ^{1}H NMR (CDCl$_3$) δ 3.35 (1 H, d, J = 16 Hz, C$_6$-H), 4.70 (1 H, d, J = 16 Hz, C$_5$-H), and 7.05–8.85 (18 H, m, aromatic); ^{13}C NMR (CDCl$_3$) δ 58.34, 63.84, 110.69, 111.54, 120.84, 121.78, 124.06, 124.42, 128.47, 128.56, 128.67, 129.54, 129.67, 129.93, 130.36, 131.15, 133.55, 135.50, 136.77, 148.20, 192.35 (C=O), 194.12 (C=O); mass spectrum, *m/e* (relative intensity) 428 (M$^+$, 17), 426 (M$^+$ – H$_2$, 3), 351 (M$^+$ – C$_6$H$_5$, 15) 349 (M$^+$ – C$_6$H$_5$ – 2 H, 38), 323 (M$^+$ – COC$_6$H$_5$, 11), 322 (42), 218 (17), 105 (COC$_6$H$_5^+$, 100), 77 (C$_6$H$_5^+$, 83).

Anal. Calcd for $C_{29}H_{20}N_2O_2$: C, 81.31; H, 4.67; N, 6.54. Found: C, 81.64; H, 4.51; N, 6.60.

Further elution of the column with benzene gave 115 mg (58%) of **1d**, mp 288–289 °C (mixture melting point), after recrystallization from 75% ethanol.

Subsequent elution of the column with a mixture (4:1) of benzene and ethyl acetate gave 50 mg (9%) of 2-[1-(2-phenylbenzimidazolyl)]-4-phenoxy-4-phenyl-3-butenoic acid (**10d**), mp 270–271 °C, after recrystallization from a 1:1 mixture of ethyl acetate and benzene: IR ν_{max} (KBr) 3060 and 3025 (CH), 3000–2500 (OH), 1742 (C=O), 1635 and 1590 (C=C) cm^{-1}; UV λ_{max} (methanol) 253 nm (ϵ 48730); ^{1}H NMR (CDCl$_3$) δ 5.90 (1 H, d, J = 8 Hz, D$_2$O-exchangeable, methine proton), 6.45 (1 H, d, J = 8 Hz, vinylic), 7.10–7.65 (19 H, m, aromatic), 7.85 (1 H, br s, D$_2$O-exchangeable, OH); mass spectrum, *m/e* (relative intensity) 446 (M$^+$, 2), 429 (M$^+$ – OH, 100), 428 (M$^+$ – H$_2$O, 13), 401 (M$^+$ – CO$_2$H, 34), 308 (73), 194 (87), 93 (49).

Anal. Calcd for $C_{29}H_{22}N_2O_3$: C, 78.03; H, 4.91; N, 6.28. Found: C, 78.31; H, 4.78; N, 6.12.

Irradiation of 3d in Methanol. A solution of **3d** (500 mg, 1.167 mmol) in methanol (500 mL) was irradiated for 1 h and worked up by removing the solvent under vacuum and chromatographic separation of the residual solid over silica gel. Elution with a mixture (1:9) of benzene and petroleum ether gave 85 mg (27%) of **9**, mp 108 °C (mixture melting point), after recrystallization from methanol.

Further elution of the column with a 1:4 mixture of benzene and petroleum ether gave 80 mg (14%) of methyl 2-[1-(2-phenylbenzimidazolyl)]-4-phenoxy-4-phenyl-3-butenoate (**11d**), mp 158 °C, after recrystallization from cyclohexane: IR ν_{max} (KBr) 3075, 3025, 2978 and 2840 (CH), 1745 (C=O), 1638 and 1595 (C=C) cm^{-1}; UV λ_{max} (methanol) 248 nm (ϵ 50780); ^{1}H NMR (CDCl$_3$) δ 3.75 (3 H, s, OCH$_3$), 5.80 (1 H, d, J = 8 Hz, D$_2$O-exchangeable, methine proton), 6.35 (1 H, d, J = 8 Hz, vinylic), and 7.10–7.65 (19 H, m, aromatic); mass spectrum, *m/e* (relative intensity) 460 (M$^+$, 2), 445 (M$^+$ – CH$_3$, 3), 430 (49), 429 (M$^+$ – OCH$_3$, 100), 428 (M$^+$ – CH$_3$OH, 36), 367 (11), 336 (11), 194 (88), 93 (50).

Anal. Calcd for $C_{30}H_{24}N_2O_3$: C, 78.26; H, 5.22; N, 6.09. Found: C, 78.38; H, 5.34; N, 5.89.

Subsequent elution of the column with a mixture (1:3) of benzene and petroleum ether gave 40 mg (8%) of **7d**, mp 206 °C (mixture melting point), after recrystallization from a mixture (1:1) of benzene and petroleum ether.

Continued elution of the column with benzene gave 135 mg (65%) of **1d**, mp 288–289 °C (mixture melting point), after recrystallization from ethanol.

Reaction of 2-[1-(2-Phenylbenzimidazolyl)]-4-phenoxy-4-phenyl-3-butenoic Acid (10d) with Diazomethane. To a stirred solution of **10d** (50 mg, 0.11 mmol) in ether (5 mL) was added an ether solution of diazomethane (1 mL, 5%) at 0 °C, and the stirring was continued for 1 h. Removal of the solvent under vacuum and recrystallization of the product from cyclohexane gave 35 mg (68%) of **11d**, mp 156–157 °C (mixture melting point).

Irradiation of (*Z*)-1-(2-Phenylbenzimidazolyl)-1,2-dibenzoylethylene (4d) in Benzene. A solution of **4d** (500 mg, 1.167 mmol) in benzene (50 mL) was irradiated for 1 h and worked up in the usual manner by removal of the solvent under vacuum and chromatographic separation of the residual product mixture over silica gel to give 40 mg (14%) of **8**, mp 109 °C (mixture melting point) (elution with petroleum ether and recrystallization from methanol), 40 mg (8%) of **7d**, mp 206 °C (mixture melting point) (elution with a 1:4 mixture of benzene and petroleum ether and recrystallization from a 1:1 mixture of benzene and petroleum ether), 70 mg (14%) of the unchanged starting material (**4d**), mp 170 °C (mixture melting point) (elution with a 1:3 mixture of benzene and petroleum ether and recrystallization from methanol), 100 mg (20%) of the *E* isomer, **3d**, mp 197–198 °C (mixture melting point) (elution with a mixture (1:2) of benzene and petroleum ether and recrystallization from methanol), and 70 mg (33%) of **1d**, mp 288–289 °C (mixture melting point) (elution with benzene and recrystallization from 75% ethanol).

Irradiation of (*E*)-1-Benzimidazolyl-1,2-dibenzoylethylene (3e) in Benzene. A solution of **3e** (500 mg, 1.42 mmol) in benzene (500 mL) was irradiated for 1 h and worked up by removing the solvent under vacuum and chromatographic separation of the product mixture over silica gel. Elution with petroleum ether gave 60 mg (18%) of **8**, mp 109 °C (mixture melting point), after recrystallization from methanol.

Further elution with benzene gave 60 mg (56%) of **1e**, mp 172 °C (mixture melting point), after recrystallization from ethanol.

Subsequent elution of the column with a mixture (4:1) of benzene and ethyl acetate gave 100 mg (19%) of 2-benzimidazolyl-4-phenoxy-4-phenyl-3-butenoic acid (**10e**), mp 264–265 °C, after recrystallization from a mixture (1:1) of benzene and ethyl acetate: IR ν_{max} (KBr) 3080 and 3030 (CH), 3000–2500 (OH), 1645 (C=O), 1630 and 1590 (C=C) cm^{-1}; UV λ_{max} (methanol) 256 nm (ϵ 38760); ^{1}H NMR (CDCl$_3$) δ 5.45 (1 H, d, J = 9 Hz, D$_2$O-exchangeable, methine proton), 6.35 (1 H, d, J = 9 Hz, vinylic), 7.0–7.55 (15 H, m, aromatic), 7.85 (1 H, s, D$_2$O-exchangeable, OH); mass spectrum, *m/e* (relative intensity) 370 (M$^+$, 3), 353 (M$^+$ – OH, 100), 352 (M$^+$ – H$_2$O, 23), 325 (M$^+$ – CO$_2$H, 34), 117 (88), 93 (73).

Anal. Calcd for $C_{23}H_{18}N_2O_3$: C, 74.59; H, 4.86; N, 7.57. Found: C, 74.37; H, 4.66; N, 7.69.

Irradiation of 3e in Methanol. A methanol solution of **3e** (500 mg, 1.42 mmol in 500 mL) was irradiated for 1 h and worked up by removal of the solvent under vacuum and chromatographic separation of the residual solid on silica gel. Elution with a mixture (1:9) of benzene and petroleum ether gave 80 mg (21%) of **9**, mp 108 °C (mixture melting point), after recrystallization from methanol.

Further elution with a mixture (1:3) of benzene and petroleum ether gave 125 mg (22%) of methyl 2-(1-benzimidazolyl)-4-phenoxy-4-phenyl-3-butenoate (**11e**), mp 116 °C, after recrystallization from cyclohexane: IR ν_{max} (KBr) 3075, 3030, 2965 and 2850 (CH), 1745 (C=O), 1635 and 1595 (C=C) cm^{-1}; UV λ_{max} (methanol) 246 nm (ϵ 47 570); ^1H NMR ($CDCl_3$) δ 3.70 (3 H, s, OCH_3), 5.40 (1 H, d, J = 9 Hz, D_2O-exchangeable, methine proton), 6.30 (1 H, d, J = 9 Hz, vinylic), 7.05–7.55 (15 H, m, aromatic); mass spectrum, m/e (relative intensity) 384 (M^+, 3), 369 ($M^+ - CH_3$, 8), 354 (77), 353 ($M^+ - OCH_3$, 100), 352 ($M^+ - CH_3OH$, 33), 325 (5), 291 (7), 260 (21), 117 (89), 93 (78).

Anal. Calcd for $C_{24}H_{20}N_2O_3$: C, 75.00; H, 5.21; N, 7.29. Found: C, 75.23; H, 5.34; N, 7.18.

Continued elution of the silica gel column with benzene gave 100 mg (59%) of **1e**, mp 172 °C (mixture melting point), after recrystallization from ethanol.

Reaction of 2-(1-Benzimidazolyl)-4-phenoxy-4-phenyl-3-butenoic Acid (10e) with Diazomethane. To a stirred solution of **10e** in ether (40 mg, 0.12 mmol in 5 mL) was added an ether solution of diazomethane (1 mL, 5%) at 0 °C, and the stirring was continued for an additional hour. Removal of the solvent under vacuum and recrystallization of the product from cyclohexane gave 30 mg (72%) of **11e**, mp 116 °C (mixture melting point).

Laser Flash Photolysis. Pulse excitation was carried out at 337.1 nm (2–3 mJ, ~8 ns), employing a UV 400 Molectron nitrogen laser or at 308 and 248 nm (≤40 mJ, defocused, ~20 ns) employing a Lambda-Physik MSC 101 excimer laser. The transient phenomena were studied by using a kinetic spectrometer, described elsewhere.[29] The solvents employed were benzene and methanol, and unless oxygen effects were meant to be studied, the solutions were deoxygenated by purging with argon or nitrogen. In experiments where a large number of laser shots were necessary, e.g., for wavelength-by-wavelength measurements of transient absorption spectra, a flow system was used in which the solutions for photolysis was allowed to drain from a reservoir through a cell.

Pulse Radiolysis. The pulse radiolysis experiments were performed, employing 7-MeV electron pulses (5 ns) from the Notre Dame ARCO-LP-7 linear accelerator in the computer controlled apparatus, described elsewhere.[30]

Acknowledgment. We thank the Department of Science and Technology, Government of India, Indian Institute of Technology, Kanpur, and the Office of Basic Energy Sciences of the U.S. Department of Energy for financial support of this work.

Registry No. **1a**, 484-47-9; **1b**, 668-94-0; **1c**, 13682-20-7; **1d**, 716-79-0; **1e**, 51-17-2; **2**, 1087-09-8; **3a**, 103456-86-6; **3b**, 103456-87-7; **3c**, 103456-88-8; **3d**, 103456-89-9; **3e**, 103456-90-2; **4a**, 103456-91-3; **4b**, 103456-92-4; **4c**, 103456-93-5; **4d**, 103456-94-6; **4e**, 103456-95-7; **5a**, 103456-96-8; **5b**, 103456-99-1; **6a**, 103477-28-7; **6b**, 103457-00-7; **7a**, 103456-97-9; **7c**, 103457-01-8; **7d**, 103457-02-9; **8**, 959-28-4; **9**, 103456-98-0; **10d**, 103457-03-0; **10e**, 103457-05-2; **11d**, 103457-04-1; **11e**, 103457-06-3.

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Synthesis and Reactions of 3-Mercaptocyclobutanol and Derivatives. Preparation of a 2,4-Dithiabicyclo[3.1.1]heptane

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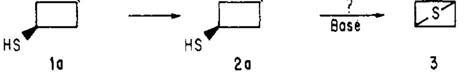
Received April 7, 1986

Reaction of the lithio derivative of 2-[(bis(trimethylsilyl)methyl)thio]tetrahydropyran (**4**) with epichlorohydrin gave both isomers of 3-[(2-tetrahydropyranyl)thio]-3-(trimethylsilyl)-1-(trimethylsiloxy)cyclobutane (**5**). The latter compound upon treatment with potassium carbonate in methanol gave 3-[(2-tetrahydropyranyl)thio]-3-(trimethylsilyl)cyclobutanol (**6**) while treatment with tetrabutylammonium fluoride gave *trans*- and *cis*-3-[(2-tetrahydropyranyl)thio]cyclobutanol (**7a,b**). Treatment of the latter compound with mercuric chloride in aqueous acetonitrile gave *trans*- and *cis*-3-mercaptocyclobutanol (**1a,b**), which could be oxidized to bis(3-hydroxycyclobutyl) disulfide (**11**) or could be converted by sequential acetylation and tosylation to *trans*- and *cis*-(acetylthio)cyclobutanol (**9a,b**) and *trans*- and *cis*-3-(acetylthio)cyclobutyl tosylate (**10a,b**), respectively. Compound **7a,b** could also be converted to *trans*- and *cis*-3-[(2-tetrahydropyranyl)thio]cyclobutyl tosylate (**8a,b**). X-ray crystallography of the minor isomer **8b** established the ring stereochemistry as cis, thereby establishing that the major isomers in these series of compounds have trans stereochemistry. NMR spectroscopy was also employed to determine stereochemistry of the various isomeric 1,3-disubstituted cyclobutanes. Treatment of **8a** with mercuric chloride gave *trans*-3-mercaptocyclobutyl tosylate (**2a**). This upon treatment with base gave a mixture of 3-allyl-2,4-dithiabicyclo[3.1.1]heptane (**15**) and (*Z*)-3-methyl-2,6-dithiabicyclo[5.1.1]non-4-ene (**16**). The structure of **15** was established by 2D NMR analysis as well as by hydrolysis to *cis*-1,3-cyclobutanedithiol. A mechanism is proposed for conversion of **2a** to **15** based on deuterium labeling studies.

2-Thiabicyclo[1.1.1]pentane (**3**) is a novel strained heterocycle that has thus far eluded synthesis.[1] Nucleophilic ring closure of a derivative of *trans*-3-mercaptocyclobutanol (**1a**) such as *trans*-3-mercaptocyclobutyl tosylate (**2a**) (eq 1) would represent a direct approach to **3**



(1)

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† Fellow of the John Simon Guggenheim Memorial Foundation, 1984–1985.

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