catalyst $[RhCl(PPh_3)_3]$ (10–15 wt %) under hydrogen. The mixture was hydrogenated overnight (24 h) at room temperature under an atmospheric pressure. The mixture was diluted with ether and passed through a short column of alumina–Celite. Removal of the solvent under reduced pressure, followed by chromatography of the residue on silica gel (hexane/EtOAc, 5:1), gave the (*Z*)-1-alkenyl sulfoxide (*Z*)-**7** in an excellent yield (see Table III).

(*Z*)-1-Pentenyl *p*-tolyl (−)-(*R*)-sulfoxide ((*R*)-(*Z*)-7a): IR 2980, 1620, 1600, 1495, 1090, 1035, 1020; ^1H NMR δ ($CDCl_3$) 1.00 (t, $J = 7$ Hz, 3 H), 1.53 (6 peaks, $J = 7$ Hz, 2 H), 2.40 (s, 3 H), 2.30–2.90 (m, 2 H), 5.90–6.40 (m, 2 H), 7.15–7.70 (AB q, $J = 8$ Hz, 4 H). Anal. Calcd for $C_{12}H_{16}OS$: C, 69.21; H, 7.74. Found: C, 69.47; H, 7.82.

(*Z*)-1-Hexenyl *p*-tolyl (−)-(*R*)-sulfoxide ((*R*)-(*Z*)-7b): IR 2980, 1620, 1600, 1495, 1090, 1035, 1020; ^1H NMR δ ($CDCl_3$) 0.93 (br t, $J = 6$ Hz, 3 H), 1.10–1.70 (m, 4 H), 2.40 (s, 3 H), 2.30–2.90 (m, 2 H), 5.95–6.40 (m, 2 H), 7.15–7.70 (AB q, $J = 8$ Hz, 4 H). Anal. Calcd for $C_{13}H_{18}OS$: C, 70.24; H, 8.16. Found: C, 69.94; H, 7.90.

(*Z*)-1-Heptenyl *p*-tolyl (−)-(*R*)-sulfoxide ((*R*)-(*Z*)-7c): IR 2980, 1620, 1600, 1495, 1090, 1035; ^1H NMR δ ($CDCl_3$) 0.90 (br t, $J = 6$ Hz, 3 H), 1.10–1.80 (m, 6 H), 2.30–2.90 (m, 2 H), 2.40 (s, 3 H), 5.95–6.40 (m, 2 H), 7.15–7.70 (AB q, $J = 8$ Hz, 4 H). Anal. Calcd for $C_{14}H_{20}OS$: C, 71.16; H, 8.53. Found: C, 71.38; H, 8.93.

(*Z*)-1-Octenyl *p*-Tolyl (−)-(*R*)-sulfoxide ((*R*)-(*Z*)-7d): IR 2980, 1620, 1600, 1495, 1090, 1035, 1020; ^1H NMR δ ($CDCl_3$) 0.91 (br t, $J = 6$ Hz, 3 H), 1.10–1.80 (m, 8 H), 2.30–2.90 (m, 2 H), 2.40 (s, 3 H), 5.95–6.40 (m, 2 H), 7.15–7.70 (AB q, $J = 8$ Hz, 4 H). Anal. Calcd for $C_{15}H_{22}OS$: C, 71.97; H, 8.86. Found: C, 72.07; H, 9.23.

(*Z*)-2-Methyl-1-hexenyl *p*-Tolyl (−)-(*R*)-Sulfoxide (12). To a solution of methylcopper(I), prepared from methyllithium (1.25 M solution, 1.6 mL, 2 mmol) and copper(I) iodide (380 mg, 2 mmol) in THF (15 mL), was added a solution of the hexynyl sulfoxide **5b** (440 mg, 2 mmol) in THF (10 mL) dropwise at −78 °C under nitrogen, and the reaction mixture was stirred for 30 min. The reaction was quenched with saturated aqueous NH_4Cl, and the product was extracted with ether. The combined organic layers were washed with water and saturated brine and evaporated to dryness. PTLC of the residue (hexane/EtOAc, 5:1) gave **12** (321 mg, 68%): IR 2960, 1620, 1600, 1490, 1085, 1035, 1015; ^1H NMR δ (CCl_4) 0.97 (br t, $J = 6$ Hz, 3 H), 1.15–1.70 (m, 4 H), 1.80 (s, 3 H), 2.50–2.75 (m, 2 H), 5.82 (s, 1 H), 7.70–7.40 (AB q, $J = 8$ Hz, 4 H). Anal. Calcd for $C_{14}H_{20}OS$: C, 71.16; H, 8.53. Found: C, 71.33; H, 8.35.

Reaction of the Ethynyl Sulfoxide 5e with Butylcopper(I). To a solution of *n*-butylcopper(I), prepared from *n*-butyllithium (1.7 M hexane solution, 0.6 mL, 1 mmol) and copper(I) iodide (190 mg, 1 mmol) in THF (5 mL), was added a solution of the ethynyl sulfoxide **5e** (142 mg, 0.86 mmol) in THF (5 mL) dropwise at −78 °C under nitrogen, and the reaction mixture was stirred for 30 min. The reaction was quenched with MeOH (10 mL) and saturated aqueous NH_4Cl, and the product was thoroughly extracted with ether. The combined extracts were washed with water and saturated brine and evaporated to dryness. PTLC of the residue (hexane/EtOAc, 5:1) gave the hexenyl sulfoxide (*R*)-(*E*)-**7b** (153 mg, 80%), identical with the sample prepared by reduction of the hexynyl sulfoxide **5b**.

***p*-Tolyl Vinyl (+)-(*R*)-Sulfoxide (6) (Improved Preparation).** To a solution of the sulfinate **2** (1.76 g, 6 mmol) in toluene (20 mL) was added a solution of vinylmagnesium bromide (1 M THF solution, 15 mL, 15 mmol) dropwise at −58 °C under nitrogen, and the reaction mixture was stirred for 10 min. The reaction was quenched with saturated aqueous NH_4Cl, and the product was extracted with a mixed solvent (ether/EtOAc/CH_2Cl_2, 2:2:1). The combined extracts were washed with saturated brine and evaporated to dryness. Chromatography of the residue on silica gel (hexane/EtOAc, 2:1) gave **6** (636 mg, 64%): $[\alpha]_D$ +413° (*c* 0.442, EtOH) [lit.[8b] $[\alpha]_D$ +386° (*c* 0.98, EtOH)]. It was reported that compound **6**, $[\alpha]_D$ +391° (*c* 1.2, acetone), was prepared in 45% yield by the reaction of **2** with vinylmagnesium bromide in ether (room temperature to reflux, 3 h).[14]

Phototransformations of Epoxyindanone Adducts. Steady-State and Laser Flash Photolysis Studies[1]

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The phototransformations of several cycloadducts of 2,3-diphenyl-2,3-epoxy-1-indanone are reported. All these substrates exhibited singlet-state-mediated transformations leading to benzoxocinones, whereas in some cases, depending on the substituents present in the alkene moiety, triplet-state-mediated reactions leading to naphthalene derivatives have also been observed. Nanosecond laser pulse excitation gave transient absorptions tentatively assigned to biradicals from Norrish type I photocleavage. In some cases, triplets acting as intermediates for di-π-methane rearrangements to naphthalene derivatives have been observed under energy-transfer sensitization.

Introduction

Phototransformations of several 1,4- and 1,2-epoxy compounds containing keto and ester substituents have already been reported.[3a–f] In a recent communication, we reported the phototransformations of few 1,4- and 1,2-epoxy compounds containing 1,2-dibenzoylalkene moieties.[3g] The photoreactions of these substrates proceed through two distinct pathways—one involving the reaction of the 1,4- or 1,2-epoxy component and the other related to the rearrangement of the 1,2-dibenzoylalkene fragment. In the present investigations we have examined the photoreactions of a few epoxyindanone adducts, **3a–e**, to study the products formed in these reactions and also to characterize the phototransients through laser flash photolysis experiments.

Results and Discussion

(1) Preparative Photochemistry and Product Identification. The starting adducts **3a–e** were prepared

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(1) Document No. NDRL-2887 from the Notre Dame Radiation Laboratory.

(2) (a) Indian Institute of Technology. (b) University of Notre Dame.

(3) (a) Payo, E.; Cortes, L.; Mantecon, J.; Rivas, C.; de Pinto, G. *Tetrahedron Lett.* **1967**, 2415–2417. (b) Prinzbach, H. *Pure Appl. Chem.* **1968**, *16*, 17–46. (c) Prinzbach, H.; Argüelles, M.; Druckrey, E. *Agnew. Chem., Int. Ed. Engl.* **1966**, *5*, 1039. (d) Prinzbach, H.; Vogel, P.; Auge, W. *Chimia* **1967**, *21*, 469–472; *Chem. Abstr.* **1968**, *68*, 104957n. (e) Prinzbach, H.; Vogel, P. *Helv. Chim. Acta* **1969**, *52*, 44–45. (f) Eberbach, W.; Argüelles, M.; Achenbach, H.; Druckery, E.; Prinzbach, H. *Helv. Chim. Acta* **1971**, *54*, 2579–2600. (g) Murty, B. A. R. C.; Kumar, C. V.; Dabral, V.; Das, P. K.; George, M. V. *J. Org. Chem.* **1984**, *49*, 4165–4171.

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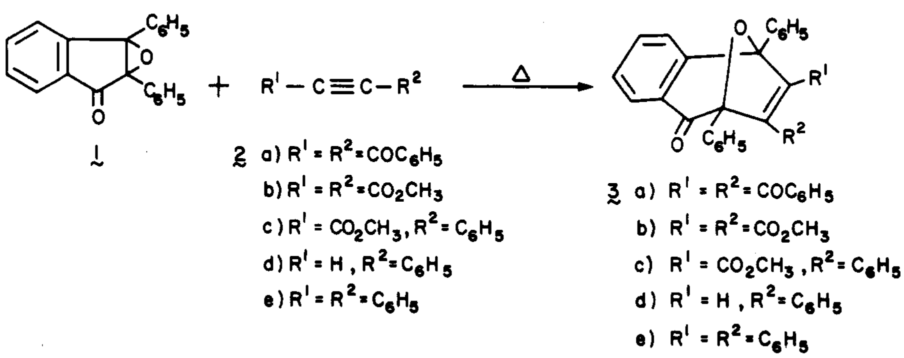
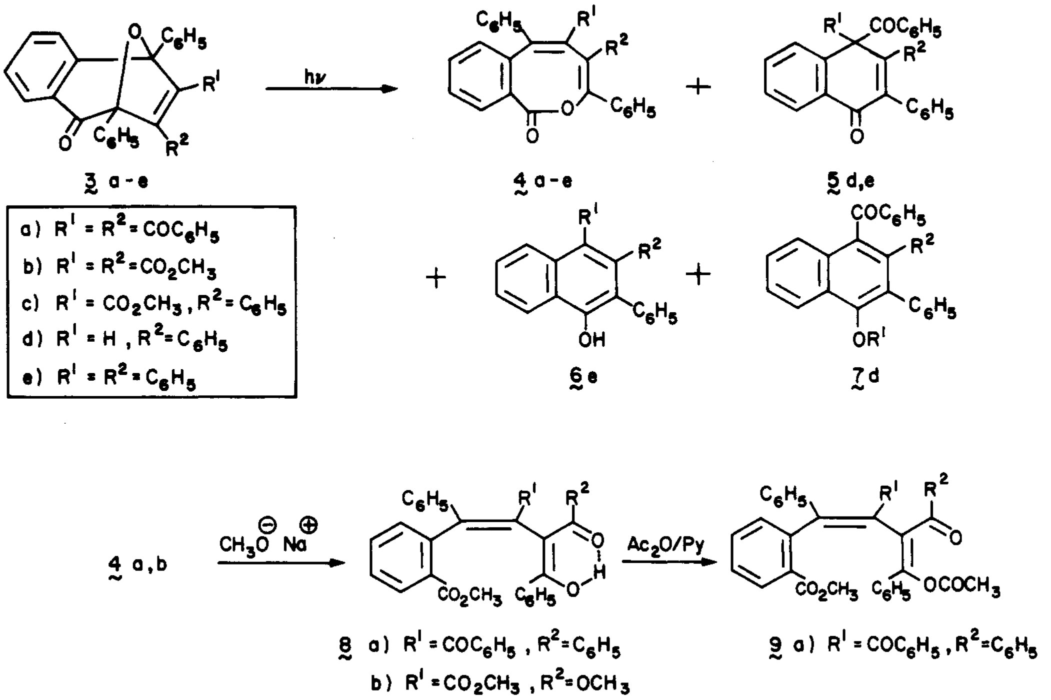
Scheme I



Scheme II



in yields ranging between 70% and 95% through the thermal addition of the carbonyl ylides formed from 2,3-diphenyl-2,3-epoxy-1-indanone (**1**) with the appropriate dipolarophiles **2a**–**e** (Scheme I). Of these, **3b**[4] and **3e**[5] were reported earlier; the structures of **3a**, **3c**, and **3d** were established on the basis of analytical results and spectral data.

Irradiation (RPR, 3000 Å, quartz) of an acetone solution of **3a** gave a 33% yield of an isomeric product, identified as 4,5-dibenzoyl-3,6-diphenyl-1*H*-2-benzoxocin-1-one (**4a**) (Scheme II). Similar results were obtained when the photolysis of **3a** was carried out in benzene or a mixture (1:9) of benzene and methanol. The structure of **4a** was established on the basis of analytical results, spectral data, and chemical evidence. Treatment of **4a** with sodium methoxide in methanol, for example, gave the enolic ester **8a** (70%), which could be acetylated, by treatment with acetic anhydride, to give **9a** (42%).

Similarly, the irradiation of **3b** in acetone, benzene, or a mixture (1:9) of benzene and methanol gave the corresponding rearranged product **4b** (60–77%). Treatment of **4b** with sodium methoxide in tetrahydrofuran gave the enolic ester **8b** (56%) (Scheme II). Likewise, the photolysis of **3c** in acetone, benzene, or a mixture (1:9) of benzene and methanol gave the corresponding benzoxocinone **4c** (55–80%).

Irradiation of **3d** in benzene gave a mixture of the benzoxocinone **4d** (43%) and 4-benzoyl-2,3-diphenyl-1-naphthol (**7d**, 17%), along with a 30% recovery of the starting material **3d**. Similarly, the irradiation of **3d** in a mixture (1:9) of benzene and methanol gave a mixture of **4d** (36%), **7d** (13%), and recovered **3d** (22%). In contrast, the irradiation of **3d** in acetone gave an 80% yield of **7d**, along with a small amount (5%) of **4d**. Interestingly, when the irradiation of **3d** was carried out in air-saturated benzene, only **4d** was isolated in a 33% yield, along with a 55% recovery of **3d**.

Irradiation of **3e** in acetone gave a mixture of the benzoxocinone **4e** (35%), 4-benzoyl-2,3,4-triphenyl-4*H*-1-naphthone (**5e**, 25%), and 2,3,4-triphenyl-1-naphthol (**6e**, 15%). Similarly, when the irradiation of **3e** was carried out in benzene or a mixture (1:9) of benzene and methanol, the products obtained were **4e** (30–33%), **5e** (5–10%), **6e** (7–25%), and recovered **3e** (15–25%). The structures of all the photoproducts were established on the basis of analytical results, spectral data, and chemical evidence. Treatment of **5e** with aluminum chloride in methylene chloride, for example, gave a 64% yield of **6e**.[6,7]

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(4) Ullman, E. F.; Milks, J. E. *J. Am. Chem. Soc.* **1964**, *86*, 3814–3819.
(5) Lown, J. W.; Matsumoto, K. *Can. J. Chem.* **1971**, *49*, 3443–3455.
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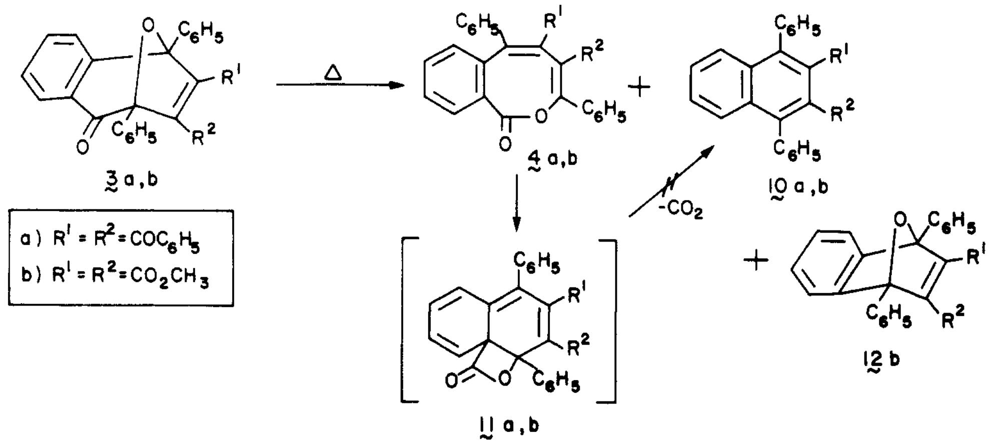
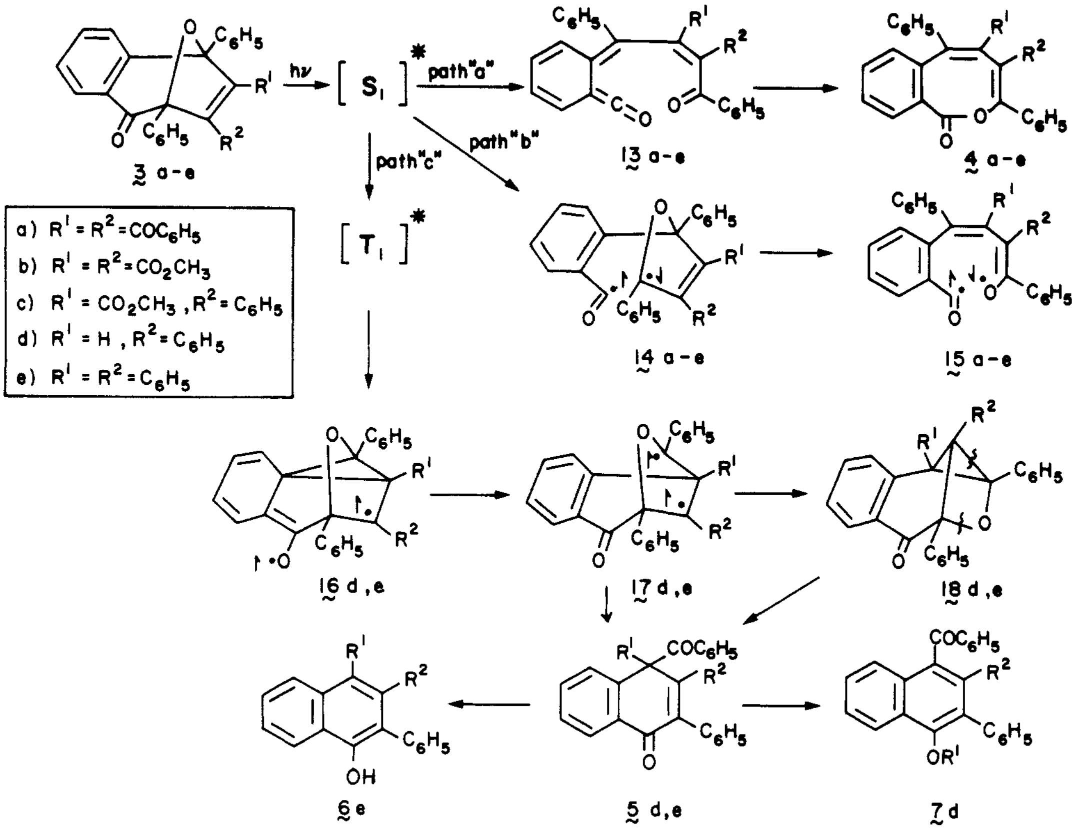
Scheme III



Scheme IV



The thermal reactions of **3a** and **3b** also gave the benzoxocinones **4a** and **4b** as the major products, respectively (Scheme III). Thus, neat heating of **3a** at ca. 300–310 °C for 3 h gave a 25% yield of **4a** and a small amount of 2,3-dibenzoyl-1,4-diphenylnaphthalene (**10a**, 5%), along with a 32% recovery of the unchanged starting material. Similarly, neat heating of **3b** at ca. 290–295 °C for 1.5 h gave a mixture of **4b** (7%), the naphthalene derivative **10b** (3%), the epoxynaphthalene **12b** (2%), and recovered starting material **3b** (52%). When **3b** was heated at ca. 290–295 °C for a longer period (3 h), the products obtained were **4b** (20%) and **10b** (35%).

The formation of the different products in the phototransformations of **3a–e** could be understood in terms of the pathways shown in Scheme IV. A priori, the benzoxocinones **4a–e** could arise through a singlet-state-mediated pathway, involving the ketene intermediate **13** (path a) or alternatively through a singlet biradical intermediate **14** (path b). The fact that no ketene-derived addition products could be isolated when the reaction of **3a–e** was carried out in a mixture of benzene and methanol would suggest that either the ketenes **13a–e** are not involved in these reactions or they undergo rapid electrocyclic ring closure to give the corresponding benzoxocinones **4a–e**. It may be pointed out in this connection that an analogous photorearrangement has been observed earlier by Padwa and Vega[8] in the transformations of the cycloadduct, derived from the reaction of 1-cyclohexyl-6-(cyclohexylimino)-1a-phenylindano[1,2-*b*]aziridine with dimethyl acetylenedicarboxylate, to give dimethyl 2-cyclohexyl-1,2-dihydro-1-(cyclohexylimino)-6-phenyl-2-benzazocine-4,5-dicarboxylate. The formation of the naphthalene de-

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(7) Obata, N.; Moritani, I. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 1975–1980.

(8) Padwa, A.; Vega, E. *J. Org. Chem.* **1975**, *40*, 175–181.

rivatives **5d,e** in the reactions of **3d,e**, however, can be explained in terms of a di-π-methane rearrangement (Zimmerman rearrangement),[9] proceeding through a triplet-state pathway, as shown in Scheme IV (path c). The triplet excited states of **3d,e** can relax to the triplet diradical intermediates **16d,e**, and later to **17d,e**, and ultimately to the tetracyclic oxetane derivatives **18d,e**. Further transformation of **18d,e** will lead to the naphthones **5d,e**. Direct conversion of **17d,e** to **5d,e** is also possible. The formation of **7d** from **5d** may be understood in terms of a simple prototropic shift, whereas **6e** from **5e** may arise through a hydrolytic cleavage. The fact that the irradiation of **3d** in acetone gives a high yield of **7d** and also that the triplet-state pathway is completely suppressed when the irradiation of **3d** is carried out in air-saturated benzene would support the triplet-state-mediated pathways shown in Scheme IV.

It is pertinent to observe that the singlet-state-mediated pathways leading to benzoxocinone derivatives **4a–c** are the exclusive pathways in the transformation of the epoxyindanone adducts **3a–c**, containing keto and ester moieties attached to the olefinic double bond. In contrast, the phototransformations of **3d** and **3e** proceed through both singlet- and triplet-state-mediated pathways. It is likely that the keto and ester groups present in the adducts **3a–c** may be facilitating the singlet diradical pathway (path b) shown in Scheme IV.

The formation of the benzoxocinones **4a** and **4b** from **3a** and **3b**, respectively, under thermal conditions may proceed from vibrationally excited states through a direct pathway (Scheme III) or may involve diradical intermediates such as **14** (Scheme IV). It may be mentioned in this connection that a direct pathway has been suggested for the thermal transformation of analogous cycloadducts derived from the reaction of an aziridine derivative with dimethyl acetylenedicarboxylate (DMAD)[10] and 1-oxo-3-phenylphthalazinium with DMAD[11] to the corresponding benzazocine and benzodiazocine derivatives, respectively. The formation of small amounts of the epoxynaphthalene **12b** from **3b** may proceed through the decarbonylation of the diradical intermediate **14**, followed by recombination, whereas **10b** in this reaction may arise through the deoxygenation of **12b**. In support of this view, we have shown that neat heating of **12b** at ca. 290–295 °C for 2 h gives a 56% yield of **10b**. Similar deoxygenation reactions of 1,4-epoxy compounds have been reported earlier.[12] An alternative pathway for the formation of **10a,b** from **3a,b** would be through the decarboxylation of the tricyclic intermediate **11a,b**, formed through an electrocyclic ring closure of **4a,b** (Scheme III). However, our attempts to bring about the decarboxylation of **4a,b** on heating have not been successful.

(2) Laser Flash Photolysis. In order to obtain information on the photointermediates, namely, triplets, biradicals, and ketenes, that can plausibly be involved in the observed phototransformations (see Scheme IV), the substrates **3a–e** were subjected to laser flash photolysis investigations in benzene and methanol solutions at room temperature. Upon 337.1-nm laser pulse excitation, deaerated benzene solutions of **3a–e** give rise to weak absorbance changes[13] at 350–500 nm (see Figure 1) which show very little or no decay on the longest time scale (~100 μs) used in our experiments. Oxygen (~2 mM) does not affect the yields or decay kinetics of the long-lived photoproducts. The insensitivity of decay toward oxygen as well as ferrocene (5 mM) rules out assignments of the long-lived absorbance changes in terms of triplets of the substrates. On adding methanol (up to 8 M) to benzene solutions the decay of the photoproducts remains practically unchanged. This coupled with the fact that products assignable to the trapping of ketene **13** by methanol are not obtained in the course of steady-state photolysis of **3a–e** in methanol–benzene mixtures suggests that the laser-induced long-lived absorbance changes cannot possibly be due to the ketene intermediates **13a–e** (Scheme IV). Thus we are left with assignments in terms of the biradicals **14**, **15**, **16**, or **17** and/or the final products benzoxocinones **4a–e**. The involvement of biradicals **16** or **17** can be ruled out in the case of **3a–c** because photoproducts mediated through them are not isolated from the photolysates of these substrates. Also, the ground-state absorption spectra of benzoxocinones **4a–e** indicate that they do not absorb significantly at wavelengths longer than 400 nm. Based on the facts that the benzoxocinone formation is the major phototransformation observed with all of the substrates **3a–e** and that the absorbance changes caused by laser pulse excitation extend well beyond 400 nm (Figure 1), it seems plausible that the latter are, at least in part, due to the biradicals **14** or **15**. Since we have not explored the decay behavior of the laser-induced absorptions on time scales longer than microsecond and since there is a possibility that some minor photoproducts have remained undetected in the course of isolation and analysis, the biradical assignment is to be considered tentative.

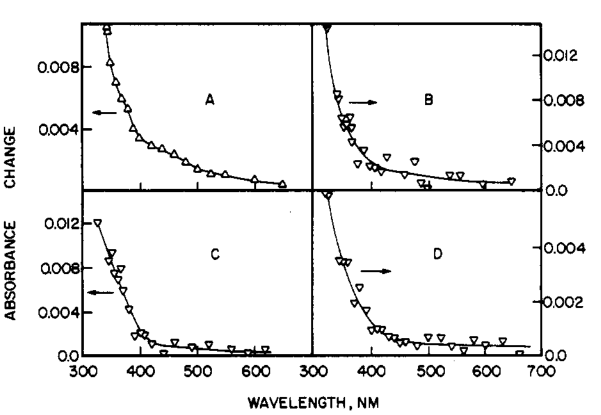

Figure 1. Absorbance changes at 5–10 μs following 337.1-nm laser flash photolysis of (A) **3a**, (B) **3c**, (C) **3d**, and (D) **3e** in deaerated benzene. Ground-state absorbances of the substrates at 337.1 nm were 0.5–1.0 (in 2-mm cells).

In order to see if triplets capable of transferring energy to 1-methylnaphthalene (MN) are produced as a result of photoexcitation of **3a–e**, these were flash-photolyzed at 337.1 nm in benzene solutions in the presence of high

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[10] Padwa, A.; Sackman, P.; Shefter, E.; Vega, E. *J. Chem. Soc., Chem. Commun.* **1972**, 680–681.

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[12] Beringer, F. M.; Huang, S. J. *J. Org. Chem.* **1964**, *29*, 445–448.

[13] Occasionally, we have observed a weakly absorbing transient (λ_{max} 490 nm, τ ~10 μs) to be produced upon 337.1- or 355-nm laser flash photolysis of **3a** in benzene. The decay of this transient is enhanced in the presence of oxygen ($k_q = 1.2 \times 10^9$ M^{-1} s^{-1}) and ferrocene ($k_q = 3 \times 10^9$ M^{-1} s^{-1}). Since a species with similar transient spectral behavior is not observed under triplet sensitization by benzophenone or *p*-methoxyacetophenone, an assignment of the 490-nm species in terms of the triplet of **3a** appears untenable. On the other hand, 337.1-nm laser flash photolysis of the benzoxocinone derivative **4a** in benzene results in strong absorption signals due to its triplet (λ_{max} 490 nm) with decay and quenching behaviors similar to those of the transient species seen in the direct excitation of **3a**. It is likely that the triplet of the photoproduct **4a** is formed as a result of its formation from **3a** and its excitation in the same laser pulse.

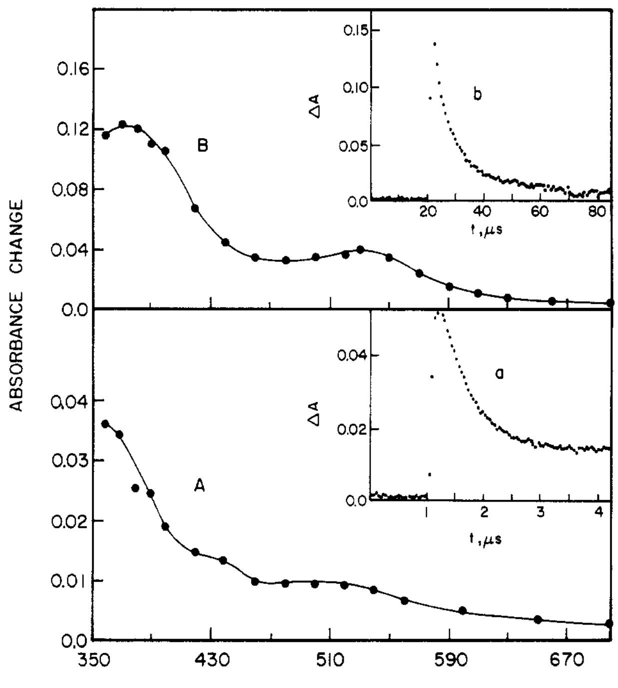

Figure 2. Transient absorption at 1 μs following 337.1-nm laser flash photolysis of benzophenone in the presence of (A) 1.3 mM **3c** and (B) 1.1 mM **3e**, in degassed benzene. Insets: kinetic traces showing the decay of triplet-derived transients at 370 nm in the case of (a) **3c** and (b) **3e** (substrate concentration = 5 mM for both).

concentrations of MN. In the case of **3a** and **3d**, no significant transient absorption that could be attributed to energy-transfer-derived MN triplet ($\lambda_{max}{}^{T}$ = 425 nm) was observed at the highest [MN] (0.6 M). For **3b–d**, small but nonnegligible absorptions due to ^{3}MN* were noted at high [MN] (0.2–0.6 M). The intercept-to-slope ratios of the plots of reciprocal of transient absorbances (end-of-pulse) due to ^{3}MN* against 1/[MN] were 2, 7, and 2 M^{-1} for **3b**, **3c**, and **3d**, respectively. These represent $k_q{}^T\tau_T$ values, where $k_q{}^T$ is the bimolecular rate constant for energy transfer from a donor triplet state of lifetime τ_T. The low $k_q{}^T\tau_T$ values suggest that the donor triplets are short-lived ($\tau_T \leq 1$ ns if the energy transfer is diffusion-controlled, e.g., from a carbonyl-like triplet) and/or the energy-transfer process is slow.

Several experiments were done in which benzophenone or *p*-methoxyacetophenone were preferentially excited by laser pulses (λ_{ex} = 337.1 or 355 nm) in the presence of 0.5–2 mM **3a–d** in benzene. In these experiments, the aromatic ketones were meant to act as donors of triplet excitation to the substrates. Their ground-state absorbances at the laser wavelengths were kept high (2.0–3.0 in 2-mm cells) and the fractions of laser photons absorbed by the substrates (acceptors) were usually small (≤ 10%). The bimolecular rate constants for benzophenone triplet quenching by **3a–e** were 1.5–3.5 × 10^9 M^{-1} s^{-1} in benzene. Only in the case of **3c** and **3e** did we observe fairly long-lived transients produced via the route of triplet excitation transfer. The absorption spectra of these transients are shown in Figure 2. While in the case of **3e** two maxima (370 and 530 nm) are clearly discernible in the spectral region >360 nm, the transient from **3c** displays its major maximum at >360 nm.[14] The triplet-mediated transient from **3c** decays by first-order kinetics with a lifetime of 540 ns (measured at 5 mM [**3c**], see inset a of Figure 2). The decay of the 370/530 nm transient derived from **3e** is complex and takes place on a longer time scale ($\tau_{1/2} \sim$ 11 μs, see inset b of Figure 2).

Oxygen and ferrocene readily enhance the decay of the triplet-sensitized transients in the case of **3c** and **3e**. The rate constants for quenching by oxygen are 7.8 × 10^8 and 1.6 × 10^9 M^{-1} s^{-1} in the case of **3c** and **3e**, respectively. This quenching behavior suggests a triplet assignment in both cases. However, we find it interesting that the triplet of **3e** is only poorly quenched by ferrocene. In the absence of geometric relaxation or intramolecular interaction, the energy of the lowest triplet of **3e** should be comparable to that of *cis*-stilbene ($E_T \cong$ 57 kcal mol^{-1})[15] and energy transfer from it to ferrocene ($E_T \cong$ 40 kcal mol^{-1})[16] should be highly exothermic. Although the *cis*-stilbene moiety of **3e** has a scope for undergoing partial distortion in the triplet state, that this distortion is not pronounced is indicated by the long lifetime of the observed triplet. It is plausible that the intramolecular interaction of the *cis*-stilbene moiety with the aromatic carbonyl chromophore, expressed in terms of the diradical structures **16** and **17**, results in substantial lowering of the triplet energy. Alternatively, the triplet is in fast equilibrium with the diradicals, the latter being nonquenchable by ferrocene. Similar triplet-quenching behaviors have been noted[17] by us for several dibenzobarrelene systems that undergo triplet-mediated di-π-methane rearrangements to dibenzosemibullvalenes.

While the lack of observation of a triplet on our time scale in the case of **3b** and **3d** can be understood in terms of short lifetimes and/or weak absorptions at >360 nm, the same in the case of **3a** is surprising. It appears that the lowest triplet of **3a** is short-lived (<100 ns)[18] because of intramolecular photochemistry (absorbance changes due to long-lived photoproducts, similar to those produced under direct laser excitation, are also observed under triplet sensitization). By the same token, although the molecule has the dibenzoylalkene moiety locked in a cis geometry, it does not undergo the well-known intramolecular phenyl group migration.[19] Besides the lack of isolation of 2-butenoic acid/ester derivatives from the steady-state photolysis of **3a**, we do not observe, in the laser flash photolysis of **3a** in alcohol-containing solvents, the growth of transient absorptions assignable to the addition of alcohols to ketene intermediates. The latter is a characteristic behavior[20] of *cis*-1,2-dibenzoylalkene systems that undergo the rearrangement (singlet-mediated) with high yields. Again, the absence of this reaction in the case of **3a** is indicative of its unfavorable competition with fast photophysicochemical pathways (i.e., paths a–c in Scheme IV).

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(14) The short-wavelength region (<360 nm) remains inaccessible in these experiments because of high ground-state absorbances of the aromatic ketone donors.

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(18) Search for a short-lived triplet is made difficult by the fact that the triplet energy transfer from aromatic ketone triplets to **3a** could not be made fast by using high [**3a**], because of the screening of laser photons by the substrate at high concentrations. Attempts to observe the triplet of **3a** by energy transfer from pulse-radiolytic biphenyl triplet to **3a** in benzene also gave negative results.

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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 spectrometers. 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 in a Srinivasan-Griffin-Rayonet photochemical reactor (RPR 2537 or 3000 Å) in quartz tubes.

Starting Materials. Dibenzoylacetylene (DBA, **2a**),[21,22] mp 110–111 °C, dimethyl acetylenedicarboxylate (DMAD, **2b**),[23] bp 95–98 °C (19 mm), methyl phenylpropiolate (**2c**),[24] bp 70–75 °C (20 mm), phenylacetylene (**2d**),[25] bp 82–83 °C (80 nm), diphenylacetylene (**2e**),[26] mp 59–60 °C, 2,3-diphenyl-2,3-epoxy-1-indanone (1),[27] mp 140 °C, and the epoxyindanone adducts **3b**,[4] mp 168–169 °C, and **3e**,[5] mp 170–171 °C, were prepared by reported procedures. Solvents for steady-state photolysis experiments were purified and distilled before use. Aldrich Gold-Label solvents were used for laser studies. Petroleum ether used was the fraction with bp 60–80 °C.

Preparation of the Epoxyindanone Adducts 3a, 3c, and 3d. A general procedure was to reflux a mixture of 1 (10 mmol) and the appropriate dipolarophile (**2a**, **2c**, and **2d**, 10 mmol) in *o*-dichlorobenzene (10 mL, bp 175–178 °C) for 30 min. Removal of the solvent under vacuum and recrystallization of the residual solid from a mixture (1:9) of benzene and petroleum ether gave the corresponding adducts.

Compound **3a** (92%): mp 205–206 °C; IR ν_{max} (KBr) 3060 and 3040 (CH), 1720 and 1665 (C=O), 1600 (C=C) cm^{-1}; UV λ_{max} (methanol) 260 nm (ϵ 26 000), and 295 (3000, sh); ^{1}H NMR (CDCl$_3$) δ 6.9–8.31 (m, Ar).

Anal. Calcd for $C_{37}H_{24}O_4$: C, 83.46; H, 4.51. Found: C, 83.14; H, 4.32.

Compound **3c** (86%): mp 183–184 °C; IR ν_{max} (KBr) 3040, 3020, 2940, and 2900 (CH), 1718 and 1710 (C=O), 1590 (C=C) cm^{-1}; UV λ_{max} (methanol) 252 nm (ϵ 27 500), and 305 (5200); ^{1}H NMR (CDCl$_3$) δ 3.49 (3 H, s, methoxy), and 6.8–7.71 (19 H, m, Ar).

Anal. Calcd for $C_{31}H_{22}O_4$: C, 81.22; H, 4.80. Found: C, 81.49; H, 4.65.

Compound **3d** (82%): mp 220–222 °C; IR ν_{max} (KBr) 3045, 3020, and 2920 (CH), 1698 (C=O), 1590 (C=C) cm^{-1}; UV λ_{max} (methanol) 248 nm (ϵ 49 000), and 290 (11 000); ^{1}H NMR (CDCl$_3$) δ 6.52–8.1 (m, Ar and vinylic).

Anal. Calcd for $C_{29}H_{20}O_2$: C, 87.0; H, 5.0. Found: C, 86.83; H, 4.76.

Irradiation of 3a. A solution of **3a** (270 mg, 0.51 mmol) in acetone (300 mL) was irradiated for 1.5 h (RPR, 3000 Å). On removal of the solvent under vacuum, the residue was chromatographed over silica gel. Elution with a mixture (3:2) of benzene and petroleum ether gave 150 mg (55%) of the recovered starting material **3a**, mmp 205–206 °C. Further elution with a mixture (1:9) of ethyl acetate and benzene gave 90 mg (33%) of **4a**, mp 139–140 °C, after recrystallization from a mixture (3:7) of benzene and petroleum ether: IR ν_{max} (KBr) 3085, 3060, and 3020 (CH), 1730, 1670, and 1645 (C=O), 1625 and 1600 (C=C) cm^{-1}; UV λ_{max} (methanol) 245 nm (ϵ 47 000), 285 (16 000), and 312 (8800 sh); ^{1}H NMR (CDCl$_3$) δ 6.8–8.2 (m, Ar); ^{13}C NMR (CDCl$_3$) δ 123.85, 125.74, 126.88, 128.03, 128.59, 129.27, 129.70, 130.29, 131.63, 132.71, 135.31, 137.02, 137.83, 152.74, 190.75 (C=O), 195.20 (C=O), 196.86 (C=O); mass spectrum, *m*/*e* (relative intensity) 532 (M$^+$, 4), 427 (M$^+$ – COC$_6$H$_5$, 2), 411 (M$^+$ – CO$_2$ – C$_6$H$_5$, 3), 306 (M$^+$ – CO$_2$ – C$_6$H$_5$ – COC$_6$H$_5$, 1), 105 (COC$_6$H$_5^+$, 100) and other peaks.

Anal. Calcd for $C_{37}H_{24}O_4$: C, 83.46; H, 4.51. Found: C, 83.18; H, 4.52.

Irradiation of **3a** in benzene, under analogous conditions, gave **4a** (19%) and recovered starting material (**3a**, 70%), whereas irradiation in a mixture (1:9) of benzene and methanol gave a 30% yield of **4a**, along with recovered starting material (**3a**, 60%).

Treatment of 4a with Sodium Methoxide. A mixture of **4a** (100 mg, 0.19 mmol) and sodium methoxide (10 mg, 0.43 mmol) in methanol (10 mL) was stirred at room temperature (~25 °C) for 12 h and later neutralized with 5% hydrochloric acid. Extraction with ether and removal of the solvent under vacuum gave a solid which was recrystallized from a mixture (1:9) of benzene and petroleum ether to give **8a** (75 mg, 70%), mp 175–176 °C: IR ν_{max} (KBr) 3420 (OH, intramolecularly hydrogen bonded), 3060, 2965, and 2940 (CH), 1725, 1650, and 1645 (C=O), 1590 (C=C) cm^{-1}; UV λ_{max} (methanol) 253 nm (ϵ 24 000), 285 (14 000), and 365 (11 800); ^{1}H NMR (CDCl$_3$) δ 3.45 (3 H, s, methoxy), 6.6–7.81 (24 H, m, Ar), 17.35 (1 H, s, enolic OH, D$_2$O-exchangeable); mass spectrum, *m*/*e* (relative intensity) 564 (M$^+$, 16), 533 (M$^+$ – OCH$_3$, 2), 505 (M$^+$ – CO$_2$CH$_3$, 1), 459 (M$^+$ – COC$_6$H$_5$, 3), 428 (M$^+$ – OCH$_3$ –COC$_6$H$_5$, 3), 295 (M$^+$ – CO$_2$CH$_3$ – 2COC$_6$H$_5$, 2), 105 (COC$_6$H$_5^+$, 100), and other peaks.

Anal. Calcd for $C_{38}H_{28}O_5$: C, 80.85; H, 4.96. Found: C, 80.57; H, 5.13.

Acetylation of 8a. A mixture of **8a** (100 mg, 0.18 mmol), acetic anhydride (2 mL), and pyridine (2 mL) in dry benzene (10 mL) was stirred for 3 h and poured onto crushed ice. The organic layer was washed with water, dried over sodium sulfate, and removed the solvent under vacuum to give a solid, which was recrystallized from a mixture (1:4) of benzene and petroleum ether to give 45 mg (42%) of **9a**, mp 186–188 °C: IR ν_{max} (KBr) 3060, 3025, 2980, 2925, and 2860 (CH), 1765, 1730, and 1665 (C=O), 1600 and 1585 (C=C) cm^{-1}; UV λ_{max} (methanol) 238 nm (ϵ 52 000, sh), 253 (46 000), 262 (51 000), and 280 (48 000); ^{1}H NMR (CDCl$_3$) δ 2.11 (3 H, s, methyl), 3.62 (3 H, s, methoxy), and 6.9–7.71 (24 H, m, Ar).

Anal. Calcd for $C_{40}H_{30}O_6$: C, 79.20; H, 4.95. Found: C, 78.95; H, 4.67.

Irradiation of 3b. A solution of **3b** (220 mg, 0.5 mmol) in acetone (200 mL) was irradiated for 2.5 h (RPR, 2537 Å) and the solvent was removed to give a residual solid, which was chromatographed over silica gel. Elution with a mixture (1:9) of ethyl acetate and benzene gave 155 mg (70%) of **4b**, mp 178–179 °C, after recrystallization from a mixture (3:7) of benzene and petroleum ether: IR ν_{max} (KBr) 3040, 3015, 2980, and 2925 (CH), 1732, 1715, and 1700 (C=O), 1625 and 1585 (C=C) cm^{-1}; UV λ_{max} (methanol) 240 nm (ϵ 32 000), 280 (16 500), and 285 (16 000); ^{1}H NMR (CDCl$_3$) δ 3.18 (3 H, s, methoxy), 3.75 (3 H, s, methoxy), 7.15–8.10 (14 H, m, Ar); ^{13}C NMR (CDCl$_3$) δ 51.28 (OCH$_3$), 51.90 (OCH$_3$), 124.69, 126.71, 127.27, 127.92, 128.95, 129.66, 131.08, 136.02, 136.54, 137.41, 151.73, 163.87 (C=O), 166.97 (C=O), and 207.05 (C=O); mass spectrum, *m*/*e* (relative intensity) 440 (M$^+$, 35), 409 (M$^+$ – OCH$_3$, 11), 381 (M$^+$ – CO$_2$CH$_3$, 10), 350 (M$^+$ – CO$_2$CH$_3$ –OCH$_3$, 4), 322 (M$^+$ – 2CO$_2$CH$_3$, 2), 105 (COC$_6$H$_5^+$, 100), and other peaks.

Anal. Calcd for $C_{27}H_{20}O_6$: C, 73.63; H, 4.55. Found: C, 73.31; H, 4.56.

Upon irradiation of **3b** in benzene and in a mixture (1:9) of benzene and methanol, **4b** was obtained in 60% and 66% yields, respectively.

Treatment of 4b with Sodium Methoxide. A mixture of **4b** (100 mg, 0.23 mmol) and sodium methoxide (25 mg, 0.46 mmol) in tetrahydrofuran (10 mL) was stirred at room temperature (~25 °C) for 1 h and later neutralized with 5% hydrochloric acid. Extraction with ether and removal of the solvent under vacuum gave 60 mg (56%) of **8b**, mp 160–162 °C, after recrystallization from a mixture (1:9) of benzene and petroleum ether: IR ν_{max} (KBr) 3415, (OH, intramolecularly hydrogen bonded), 3080, 3060, 3020, 2945, and 2885 (CH), 1725, 1700, and 1645 (C=O), 1595 and 1570 (C=C) cm^{-1}; UV λ_{max} (methanol) 241 nm (ϵ 16 500), 250 (14 200), 255 (12 000), and 310 (9500); ^{1}H NMR (CHCl$_3$) δ 3.30 (3 H, s, methoxy), 3.62 (3 H, s, methoxy), 3.71 (3 H, s, methoxy), 6.75–7.82 (14 H, m, Ar), and 12.90 (1 H, s, enolic OH, D$_2$O-exchangeable).

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Anal. Calcd for $C_{28}H_{24}O_7$: C, 71.18; H, 5.08. Found: C, 71.29; H, 4.82.

Irradiation of 3c. A solution of **3c** (230 mg, 0.5 mmol) in acetone (200 mL) was irradiated for 3.5 h (RPR, 2537 Å). On removal of the solvent, the residue was chromatographed over silica gel. Elution with benzene gave 185 mg (80%) of **4c**, mp 174–176 °C, after recrystallization from a mixture (1:9) of benzene and petroleum ether: IR ν_{max} (KBr) 3040, 3020, 2940, and 2910 (CH), 1720 and 1700 (C=O), 1590 (C=C) cm^{-1}; UV λ_{max} (methanol) 242 nm (ϵ 58 000), 275 (31 000), and 320 (5700, sh); ^{1}H NMR ($CDCl_3$) δ 3.1 (3 H, s, methoxy), 7.15–7.95 (19 H, m, Ar); mass spectrum, *m/e* (relative intensity) 458 (M^+, 4), 457 ($M^+ - H$, 10), 399 ($M^+ - CO_2CH_3$, 1), 322 ($M^+ - CO_2CH_3 - C_6H_5$, 5), 105 ($COC_6H_5^+$, 100), and other peaks.

Anal. Calcd for $C_{31}H_{22}O_4$: C, 81.22; H, 4.80. Found: C, 80.91; H, 4.63.

Irradiation of **3c** in benzene, under analogous conditions, gave a 62% yield of **4c**, along with a 15% recovery of the unchanged starting material (**3c**). Upon irradiation of **3c** in a mixture (1:9) of benzene and methanol, a mixture of **4c** (55%) and recovered **3c** (18%) was obtained.

Irradiation of 3d. Irradiation of **3d** (1.0 g, 2.5 mmol) in benzene (1 L) for 3 h and removal of the solvent under vacuum gave a residual solid, which was chromatographed over silica gel. Elution with a mixture (3:7) of benzene and petroleum ether gave 300 mg (30%) of recovered starting material **3d**, mmp 220–222 °C, after recrystallization from a mixture (1:4) of benzene and petroleum ether. Further elution with a mixture (1:1) of benzene and petroleum ether gave 160 mg (16%) of **7**, mp 118–120 °C, after recrystallization from a mixture (1:9) of methylene chloride and petroleum ether: IR ν_{max} (KBr) 3600 (OH), 3400 (OH, hydrogen bonded), 3060 and 2920 (CH), 1648 (C=O), 1590, and 1580 (C=C) cm^{-1}; UV λ_{max} (methanol) 245 nm (ϵ 65 000), and 325 (7500); ^{1}H NMR ($CDCl_3$) δ 5.75 (1 H, s, OH, D_2O-exchangeable), 6.72–7.52 (19 H, m, Ar); mass spectrum, *m/e* (relative intensity) 400 (M^+, 100), 327 ($M^+ - C_6H_5$, 85), 295 ($M^+ - COC_6H_5$, 1), 105 ($COC_6H_5^+$, 61), and other peaks.

Anal. Calcd for $C_{29}H_{20}O_2$: C, 87.00, H, 5.00. Found: C, 86.79; H, 4.75.

Further elution of the column with a mixture (1:9) of ethyl acetate and benzene gave 430 mg (43%) of **4d**, mp 192–193 °C, after recrystallization from a mixture (1:9) of benzene and petroleum ether: IR ν_{max} (KBr) 3060, 3020, and 2920 (CH), 1718 (C=O), 1665 and 1600 (C=C) cm^{-1}; UV λ_{max} (methanol) 250 nm (ϵ 29 000), and 315 (3000); ^{1}H NMR ($CDCl_3$) δ 7.05–7.75 (m, Ar and vinylic); mass spectrum, *m/e* (relative intensity) 400 (M^+, 9), 323 ($M^+ - C_6H_5$, 2), 295 ($M^+ - COC_6H_5$, 3), 267 ($M^+ - COC_6H_5$, $- CO_2$, 2), 105 ($COC_6H_5^+$, 100) and other peaks.

Anal. Calcd for $C_{29}H_{20}O_2$: C, 87.00; H, 5.00. Found: C, 86.91; H, 4.93.

In a repeat run, **3d** was irradiated in acetone for 3 h, under analogous conditions. The residual solid, obtained after removal of the solvent, was chromatographed over silica gel. Elution with a mixture (1:1) of benzene and petroleum ether gave **7d** (80%), mmp 118–120 °C, after recrystallization from a mixture (1:9) of benzene and petroleum ether. Further elution of the column with a mixture (1:9) of ethyl acetate and benzene gave **4d** (5%), mmp 192–193 °C, after recrystallization from a mixture (3:7) of benzene and petroleum ether.

In repeat experiments, **3d** was photolyzed in different solvents and conditions and the yield of products, under similar workup procedure, are indicated in parentheses; mixture (1:9) of benzene and methanol (**4d**, 36%; **7d**, 13%; **3d**, 22% (recovery)) and benzene saturated with oxygen (**4d**, 33%; **3d**, 55% (recovery)).

Irradiation of 3e. A solution of **3e** (250 mg, 0.53 mmol) in acetone (300 mL) was irradiated for 2.5 h (RPR, 3000 Å) and the irradiation was repated several times to photolyze, in all, 1.0 g (2.1 mmol) of **3e**. Removal of the solvent from the combined photolysates gave a residual solid, which was chromatographed over silica gel. Elution with a mixture (1:9) of benzene and petroleum ether gave 150 mg (15%) of 2,3,4-triphenyl-1-naphthol (**6e**), mp 160–161 °C, after recrystallization from a mixture (1:9) of benzene and petroleum ether (lit.[7] mp 161–162 °C). Further elution of the column with a mixture (1:1) of benzene and petroleum ether gave 250 mg (25%) of 4-benzoyl-2,3,4-triphenyl-4*H*-1-naphthone (**5e**), mp 164–166 °C, after recrystallization from a mixture (1:9) of benzene and petroleum ether: IR ν_{max} (KBr) 3060 and 3020 (CH), 1670 and 1648 (C=O), 1595 and 1575 (C=C) cm^{-1}; UV $\lambda_{ma}x$ (methanol 253 nm (ϵ 31 500), and 309 (8000); ^{1}H NMR ($CDCl_3$) δ 6.51–7.70 (m, Ar); mass spectrum, *m/e* (relative intensity) 476 (M^+, 10), 371 ($M^+ - COC_6H_5$, 4), 343 ($M^+ - COC_6H_5$, $- CO$, 2), 294 ($M^+ - COC_6H_5 - C_6H_5$, 2), 105 ($COC_6H_5^+$, 100), and other peaks.

Anal. Calcd for $C_{35}H_{24}O_2$: C, 88.23; H, 5.04. Found: C, 87.96; H, 5.32.

Further elution of the column with a mixture (1:9) of ethyl acetate and benzene gave 350 mg (35%) of **4e**, mp 210–212 °C, after recrystallization from a mixture (3:7) of benzene and petroleum ether: IR ν_{max} (KBr) 3060, 3020, and 2980 (CH), 1720 (C=O), 1670, 1600, and 1580 (C=C) cm^{-1}; UV λ_{max} (methanol) 249 nm (ϵ 31 000), and 300 (10 000); ^{1}H NMR ($CDCl_3$) δ 6.45–7.91 (m, Ar); ^{13}C NMR ($CDCl_3$) δ 123.71, 126.45, 126.84, 127.24, 127.69, 127.88, 128.03, 128.29, 128.47, 128.63, 131.14, 131.91, 132.26, 132.39, 132.52, 132.81, 132.87, 133.67, 134.63, 137.74, 197.70 (C=O); mass spectrum, *m/e* (relative intensity) 476 (M^+, 13), 371 ($M^+ - COC_6H_5$, 3), 294 ($M^+ - COC_6H_5 - C_6H_5$, 1), 105 ($COC_6H_5^+$, 100), and other peaks.

Anal. Calcd for $C_{35}H_{24}O_2$: C, 88.23; H, 5.04. Found: C, 88.02; H, 5.31.

In repeat experiments, **3e** was irradiated in different solvents under analogous conditions and the yields of products under similar workup conditions are indicated in parentheses: benzene (**4e**, 30%; **5e**, 10%; **6e**, 7%; and **3e**, 25% (recovery)) and mixture (1:9) of benzene and methanol (**4e**, 33%; **5e**, 5%; **6e**, 25%; and **3e**, 15% (recovery)).

Conversion of 5e to 6e. A mixture of **5e** (50 mg, 0.11 mmol) and anhydrous aluminum chloride (50 mg, 0.37 mmol) in methylene chloride (15 mL) was stirred at room temperature for 5 h. The reaction mixture was treated with ice-cold water and extracted with ether. Removal of the solvent under vacuum gave a residual solid, which was recrystallized from a mixture (1:9) of benzene and petroleum ether to give 25 mg (64%) of **6e**, mmp 160–161 °C.

Thermolysis of 3a. A sample of **3a** (2.0 g, 3.8 mmol) was heated at ca. 300–310 °C for 3 h in a sealed tube and the mixture was chromatographed over silica gel. Elution with a mixture (3:7) of benzene and petroleum ether gave 640 mg (32%) of the unchanged starting material (**3a**), mmp 205–206 °C. Further elution with a mixture (1:1) of benzene and petroleum ether gave 75 mg (4%) of **10a**, mmp 184–185 °C (lit.[28] mmp 185–186 °C), after recrystallization from a mixture (1:9) of methylene chloride and petroleum ether. Subsequent elution of the column with a mixture (1:9) of ethyl acetate and benzene gave 500 mg (25%) of **4a**, mmp 139–140 °C, after recrystallization from a mixture (1:9) of benzene and petroleum ether.

In a repeat run, an attempted thermolysis of **3a** (150 mg, 0.28 mmol) by refluxing in diphenyl ether (10 mL) for 10 h and workup in the usual manner resulted in the recovery of 140 mg (93%) of the unchanged starting material **3a**, mmp 205–206 °C.

Thermolysis of 3b. A sample of **3b** (2.0 g, 4.5 mmol) was heated at ca. 290–295 °C for 1.5 h in a sealed tube and the reaction mixture was chromatographed over silica gel. Elution with a mixture (1:4) of benzene and petroleum ether gave 38 mg (2%) of **12b**, mmp 158–160 °C (lit.[6] mmp 158–160 °C), after recrystallization from a mixture (1:9) of benzene and petroleum ether. Further elution with a mixture (3:7) of benzene and petroleum ether gave 55 mg (3%) of **10b**, mmp 228–229 °C (lit.[29] mmp 228–229 °C), after recrystallization from a mixture (1:9) of methylene chloride and petroleum ether. Subsequent elution with a mixture (1:1) of benzene and petroleum ether gave 1.04 g (52%) of the unchanged starting material (**3b**), mmp 169–170 °C), after recrystallization from a mixture (3:7) of benzene and petroleum ether. Further elution of the column with a mixture (1:9) of ethyl acetate and benzene gave 140 mg (7%) of **4b**, mmp 178–179 °C), after recrystallization from a mixture (1:9) of benzene and petroleum ether.

In a repeat experiment, **3b** (2.0 g, 4.5 mmol) was heated at ca. 290–300 °C for 3 h in a sealed tube and worked up as in the earlier

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case to give a mixture of 630 mg (35%) of **10b** and 400 mg (20%) of **4b**.

In an attempted thermolysis, a solution of **3b** (150 mg, 0.34 mmol) in diphenyl ether (10 mL) was refluxed for 15 h and worked up in the usual manner to give 1.45 g (96%) of the recovered starting material **3b**.

Thermolysis of 12b. A sample of **12b** (150 mg, 0.36 mmol) was heated in a sealed tube at ca. 290–295 °C for 2 h. The mixture was chromatographed over silica gel. Elution with a mixture (1:1) of benzene and petroleum ether gave 80 mg (56%) of **10b**, mmp 228–229 °C, after recrystallization from a mixture (1:9) of methylene dichloride and petroleum ether.

Attempted Thermolysis of 4a. Refluxing a solution of **4a** (100 mg, 0.188 mmol) in diphenyl ether (10 mL) for 20 h and workup in the usual manner gave 90 mg (90%) of the unchanged starting material (**4a**), mmp 139–140 °C.

In a repeat experiment, **4a** (0.5 g, 0.94 mmol) was heated at ca. 300–310 °C for 1.5 h and worked up in the usual manner to give 150 mg (30%) of the recovered starting material **4a**, mmp 139–140 °C. No other product could be isolated from this reaction.

Attempted Thermolysis of 4b. A solution of **3b** (150 mg, 0.34 mmol) in diphenyl ether (10 mL) was refluxed for 15 h and worked up in the usual manner to give 140 mg (93%) of the unchanged starting material **4b**, mmp 178–179 °C.

In a repeat experiment, **4b** (440 mg, 1 mmol) was heated in a sealed tube at ca. 295–300 °C for 1 h and worked up by chromatographing over silica gel and elution with a mixture (1:9) of ethyl acetate and benzene to give 200 mg (45%) of the unchanged starting material **4b**, mmp 178–179 °C.

Laser Flash Photolysis. For laser flash photolysis, use was made of pulsed outputs from a UV-400 Molectron nitrogen (337.1 nm, 2–3 mJ, ~8 ns) or a Quanta-Ray DCR-1 Nd-YAG (third harmonic, 355 nm, ~6 ns). The laser intensities were attenuated and kept in the range 2–10 mJ/pulse. The details of the kinetic spectrophotometer and data collecting system are described in earlier publications[30,31] from the Radiation Laboratory. For transient spectra, a flow cell was used. For kinetics, static cells (path lengths 1–3 mm) containing 1–2 mL of the solutions for photolysis were used. Unless the effect of oxygen was meant to be studied, the solutions were deaerated by saturating with high-purity argon.

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Cyclization Reactions through the $S_{RN}1$ Mechanism. Reactions of *o*-Dihaloaromatic Compounds with Dithiolate Ions

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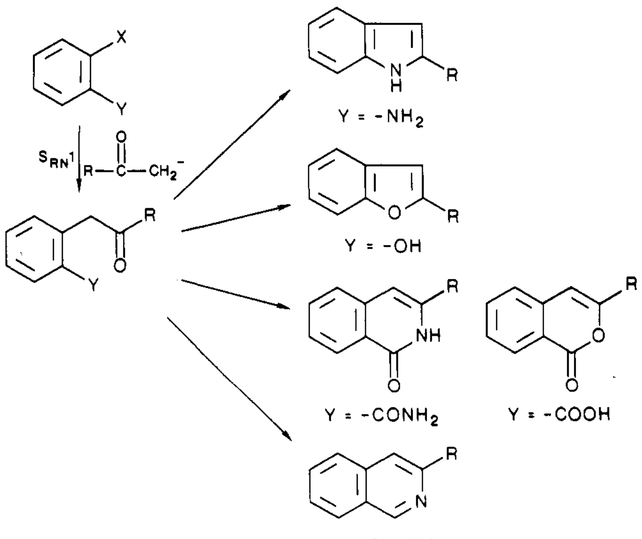
In the present paper we report the reactions of *o*-dihaloaromatic compounds with dithiolate ions as new cyclization reactions occurring by the $S_{RN}1$ mechanism. *o*-Diiodo- and *o*-bromochlorobenzene react under photostimulation with 3,4-toluenedithiolate ion to give good yields (≈60%) of the cyclic disubstituted compound 2-methylthianthrene. The reaction occurs to a lesser extent (≈20%) when the substrate was 1-bromo-2-iodonaphthalene. 2,3-Dichloroquinoxaline reacts with the same nucleophile in the dark or in the presence of radical traps to give a 100% yield of the cyclic disubstituted compound. The reaction of *o*-diiodobenzene with 1,2-ethanedithiolate gave a low yield of the cyclic compound benzo-1,4-dithiane. This decrease was explained in terms of fragmentation reactions of the proposed radical anions intermediates.

The synthetic scope of the radical nucleophilic substitution reaction ($S_{RN}1$) is broad and widely known.[1]

The fact that the mechanism produces a regiospecific substitution of the leaving group has been extensively used as a synthetic route to heterocyclic ring systems. Treatment of enolate anions derived from ketones or aldehydes with aryl halides bearing a function adjacent to the leaving group led to the $S_{RN}1$ substitution product which can undergo a spontaneous cyclization to give indoles,[2,3] azaindoles,[3,4] benzofurans,[5] isocarbostyrils,[6,7] isocumarones,[6] and isoquinolines[8] (Scheme I).

Scheme I



Another route to cyclization reactions through the $S_{RN}1$ mechanism has been the intramolecular photosubstitution

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