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(27) Transmitting wavelength limits from Hanovia 977B-1 Hg–Xe Compact arc lamp after passing through the combined Corning glass color filters CS3–72 and CS5–60.
(28) No signal was observed before the light was turned on, or when (1) nitroso-*tert*-butane (0.01 *M*) in benzene, (2) adamantanethione (0.2 *M*) and nitroso-*tert*-butane (0.01 *M*) in benzene, or (3) 2-adamantanethiol-α-d_1 (1.0 *M*) and nitroso-*tert*-butane (0.01 *M*) in benzene were irradiated with the same light source at room temperature.
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Competitive Keto–Enolate Photochemistry in the 3-Phenylisocoumaranone System[1]

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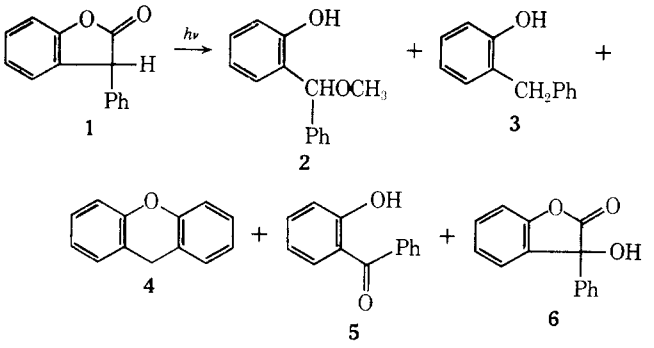
Abstract: The photochemistry of 3-phenylisocoumaranone (**1**) is markedly influenced by the tautomeric composition of the lactone in solution. Decarbonylation results from excitation of the keto tautomer using 2537-Å light. The transient *o*-quinone methide formed rapidly reacts with methanol to give *o*-hydroxybenzhydryl methyl ether (**2**). On further irradiation, **2** is converted into *o*-benzylphenol (**3**) and xanthene (**4**). Equilibrium concentrations of the enolate ion of **1** have been detected in methanol. By using 3130-Å light, the enolate ion can be selectively excited. The resulting excited state does not lose carbon monoxide but instead undergoes proton exchange with the solvent or reaction with molecular oxygen. In the presence of singlet oxygen, the ground-state enolate is also trapped to give *o*-hydroxybenzophenone (**5**) and 3-hydroxy-3-phenylisocoumaranone (**6**). The wavelength and solvent effects noted in this system suggest that certain carbonyl derivatives possess the potential for distinctive and competitive keto–enol photochemistry.

Light-induced transformations of β,γ-unsaturated lactones have been the subject of recent intensive study.[2-5] These compounds undergo a facile decarbonylation when subjected to ultraviolet excitation and produce α,β-unsaturated ketones as primary photoproducts. Similar decarbonylation processes have been observed to occur with excited lactams,[6] thiolactones,[7,8] sultones,[3] carbonates,[3] and related substituted 2-indanones.[9] Studies on the photochemical behavior of the closely related benzofuran-2-(3*H*)-one system have indicated that this lactone also undergoes a facile photodecarbonylation reaction producing an unstable *o*-quinyl methide intermediate which can be trapped by protic solvents.[3,5,10] In their examination of the photodecarbonylation reaction of unsaturated lactones,[3] Chapman and McIntosh have noted that a critical requirement for clean photochemical cleavage of the acyl–oxygen bond is the presence of a double bond adjacent to the ether oxygen. Stabilization of the incipient oxy radical was considered to be a determining factor in the photocleavage of this bond. In the absence of the double bond, the photolysis of the γ-lactone ring results in the formation of a complex mixture of photoproducts.[11] As part of a general study on the photochemical transformations of carbonyl compounds which proceed through the enol form,[12,13] we recently reported on an unusual variation to the photodecarbonylation reaction in the 3-phenylisocoumaranone (**1**) system.[10] Our observations indicated that this molecule displayed a remarkable dependence on the wavelength of excitation. The present publication describes our preliminary findings in detail and delineates the significant role played by the enolate tautomer of **1** in the overall photochemistry of this system.

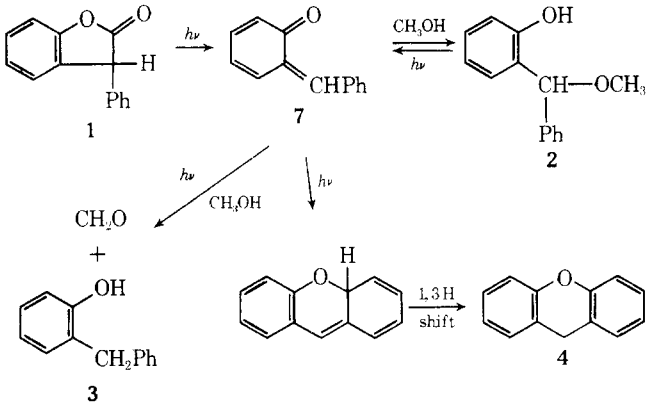
Results and Discussion

Irradiation of 3-phenylisocoumaranone[14] (**1**) in methanol with a low-pressure mercury arc (2537 Å) led to the formation of five products (**2–6**) whose relative yields varied as a function of the reaction conditions. Careful exclusion of oxygen from photolyzed solutions resulted in the formation of only *o*-hydroxybenzhydryl methyl ether (**2**), *o*-benzylphenol (**3**), and xanthene (**4**) (combined yield 44%). Irra-

diation of **1** in degassed acetonitrile (2537 Å) still resulted in the formation of xanthene. In methanol, the ratio of **2**:(**3** + **4**) decreased with irradiation time, and a control experiment revealed that photolysis of **2** led to the formation of **3** and **4**. We conclude from these experiments that both **2** and xanthene (**4**) are initially formed, but that a competing secondary photoreaction further converts **2** to both xanthene and *o*-benzylphenol.

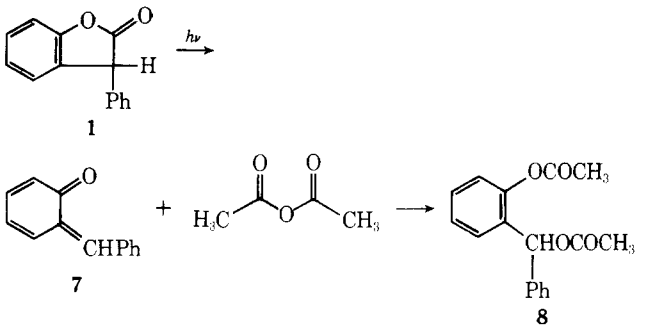


A reasonable mechanistic scheme which accounts for these observations is presented below. The initial step in-



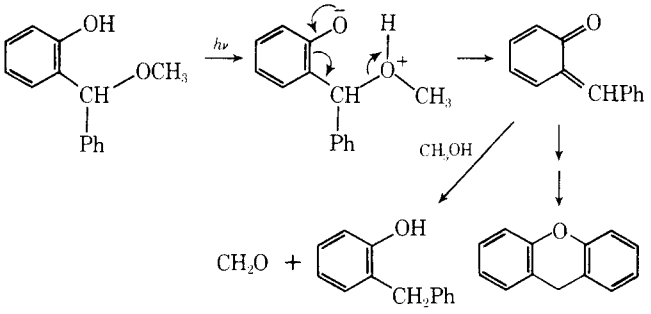
volves photochemical decarbonylation to give *o*-quinone methide **7** as a transient intermediate. When methanol is the solvent, **7** is predominantly trapped to give **2** (Φ = 0.058). This behavior is analogous to the characteristic high nucleophilic reactivity of related *o*- and *p*-quinone methides.[3,6,15-19] The formation of xanthene (Φ = 0.004) is readily explicable in terms of an electrocyclic closure of the *Z* isomer of **7** followed by a 1,3-H shift. Intramolecular pericyclic reactions of *o*-quinone methides have been reported to compete quite efficiently with the intermolecular trapping reaction in related systems,[7,20,21] thereby providing good chemical analogy for the formation of xanthene. In acetonitrile, the competitive trapping of **7** by methanol is absent, and the quantum efficiency of formation of xanthene is enhanced (Φ = 0.006). It should be noted that *o*-quinone methide **7** has two stereoisomers. Both the *Z* and *E* isomers can react with methanol to give methyl ether **2**, but only the *Z* isomer can give xanthene. The quantum yield data obtained permit an estimate that 28 times as much benzhydryl methyl ether **2** comes from the *E* as from the *Z* isomer. This assumes no solvent effect on the quantum yield of formation of xanthene.

Further support for the intermediacy of the *o*-quinone methide intermediate comes from carrying out the irradiation of **1** in the presence of acetic anhydride. The only product isolated under these conditions (Ar atmosphere, 2537 Å) was *o*-acetoxybenzhydryl acetate (**8**). In this case, the *o*-quinone methide intermediate reacts rapidly with the acetic anhydride to give acetate **8**, which is incapable of regenerating **7** on further irradiation.



The effect of added piperylene on the photodecarbonylation reaction was also examined. On the basis of the ultraviolet spectrum of piperylene, it can be shown that this diene was absorbing only a minimal portion of the incident light under the conditions employed. The results clearly indicate that the photolysis of **1** is not quenched by piperylene (E_T^{cis} = 57 kcal/mol).[22] The photolysis of **1** was likewise found not to be sensitized by benzophenone. Thus, irradiation through Pyrex of a methanol solution of **1** containing sufficient benzophenone to absorb >90% of the incident light resulted in a substantial reduction in the rate of formation of **2**. In this experiment, however, the rate of disappearance of the starting lactone was significantly increased. This might be due to the partial involvement of the lactone in the photoreduction of benzophenone. These results would tend to suggest that the photodecarbonylation reaction proceeds via the singlet state of isocoumaranone **1**.

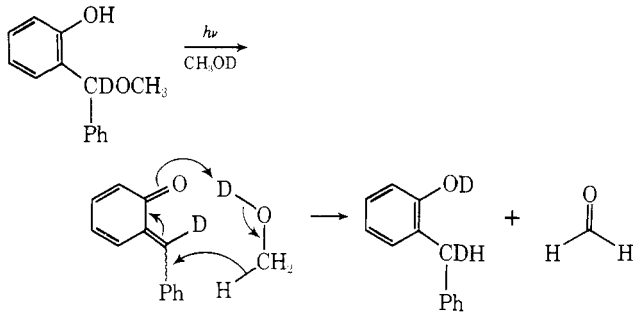
The photoconversion of benzhydryl methyl ether **2** (Φ = 0.08) into *o*-benzylphenol (Φ = 0.06) and xanthene (Φ = 0.02) also appears to involve *o*-quinone methide **7** as an intermediate. This transformation is analogous to some recent results of Schmid and coworkers[23] who found that the thermolyses of (*o*-hydroxyaryl)-2-propen-1-ols produce *o*-quinone methide intermediates by 1,4 elimination of water. The studies of Förster and Weller[24] showing enhanced acidity of phenols in the electronically excited state would tend to indicate that the phenolic moiety is essential, and that the phenolic hydrogen is transferred as a proton to the departing methoxyl group. That photochemical reactions of phenols can involve ionic intermediates has been previously demonstrated by the photochemical conversions of 2-allylphenols to 2,3-dihydrobenzofurans.[25,26]



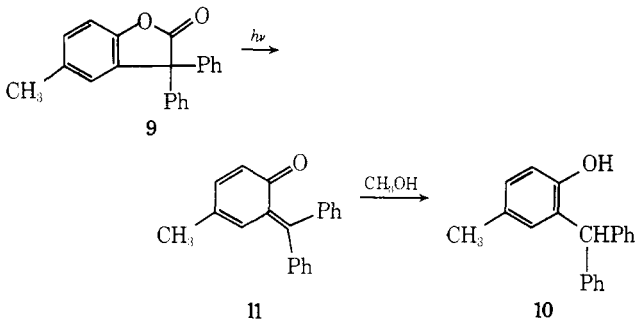
The excited state of **2** which is responsible for initiating these reactions is uncertain. The photolysis of **2** was quenched by the addition of 1,3-pentadiene, but concentrations of 0.05 *M* or higher were required. Unfortunately, at these concentrations, there existed substantial competition by the diene for the incident light under the conditions employed. Thus, it is not clear from this experiment whether singlet or triplet **2** was being quenched, particularly since quenching by high concentrations of dienes can no longer be accepted as uniquely sufficient evidence for a triplet reaction.[27]

Irradiation of a dilute solution of deuteriobenzhydryl methyl ether **2**-d_1 in deuteriomethanol gave *o*-benzylphe-

nol-d_1 as the major photoproduct. This experiment suggests that the mechanism for the reduction of the *o*-quinone methide intermediate involves initial removal of a deuterium atom from the alcohol followed by hydride ion transfer to the developing positive charge.[28]

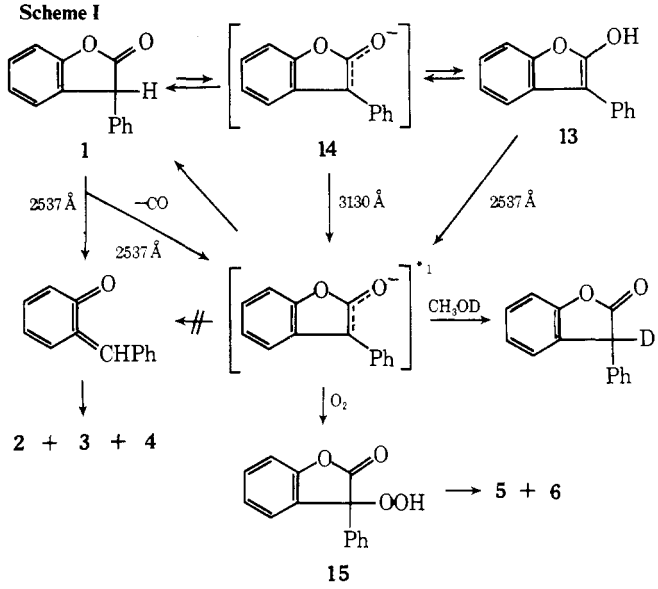


It is interesting to note that irradiation (2537 Å) of 3,3-diphenyl-5-methyl-2-benzofuranone (**9**) in methanol gave 2-hydroxy-4-methyltriphenylmethane (**10**) as the only detectable photoproduct. The formation of **10** can be viewed as arising from the photoreduction of the *o*-quinone methide intermediate (**11**). The failure of **11** to yield a benzhydryl ether can be attributed to the increased steric hindrance associated with the alcohol addition step. This is in accord with the known sensitivity of Michael additions toward steric factors.[5,29]



The nature of the photooxidation process which leads to *o*-hydroxybenzophenone (**5**) and hydroxylactone **6** is particularly interesting. We have found that trace amounts of oxygen are capable of effecting conversion of **1** to **5** and **6** with either 2537- or 3130-Å light in methanol or acetonitrile. Control experiments in the dark demonstrated that **1** is stable indefinitely in these oxygenated solvents. In the presence of added base, **5** and **6** are slowly formed from **1**. Most surprisingly, *compounds* **2**, **3**, *and* **4** *are formed only upon irradiation of* **1** *with 2537-Å light.* With 3130-Å light, **5** and **6** are the only detectable products. A clue to this seemingly anomalous behavior was obtained by examining the uv absorption spectrum of **1** in several solvents. In cyclohexane, lactone **1** shows two absorption bands with maxima at 282 and 273 nm (ϵ 1700, 1720) whereas, in acetonitrile solution, a new long-wavelength absorption band at 346 nm (ϵ 40) is also present. Similar behavior was also noted when methanol was used as the solvent [316, 278, and 272 nm (ϵ 350, 1620, 1620)]. The nature of the long-wavelength absorption of **1** in these latter two solvents was puzzling in view of the fact that the corresponding methyl enol ether (**12**) showed maxima at 265 and 223 nm in acetonitrile with no trace of the long-wavelength absorption band. This observation eliminates the likelihood that the long-wavelength absorption was due to the enol form (**13**) of lactone **1**. Furthermore, the absorption spectrum of α-hydroxylactone **6**, which provides a reasonable model for the nonenolizable lactone **1**, showed maxima at 271 and 266 nm (ϵ 1360, 1230). The possibility that the long-wavelength absorption in acetonitrile and methanol was due to the enolate anion (**14**) of **1** was confirmed when trace amounts of base were added to spectral solutions. Under these conditions, a dramatic enhancement in the intensity of the 316-nm band occurred. Zaugg[30] had previously reported that the sodium enolate of **1** gives a λ_{max} at 315 nm (ϵ 17,800) in ethanol. This maximum is in excellent agreement with our observations and suggests that, in neutral methanolic solutions, approximately 2% of the enolate anion **14** exists in equilibrium with the keto (and possibly enol) form of **1**. In acetonitrile solutions, concentrations of approximately 0.2% of **14** exist in equilibrium with **1**. Based on the above spectral data, we propose that the photooxygenation sequence of lactone **1** is controlled by the tautomeric composition of **1** in solution (see Scheme I).

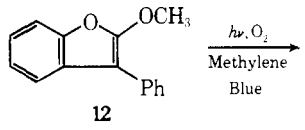
Scheme I



Excitation of the enolate ion **14** present in solution with 3130-Å light produces an excited state which is subsequently attacked by ground-state oxygen to give α-hydroperoxylactone **15.** This transient intermediate is subsequently converted to compounds **5** and **6.** Bordwell and others[31] have shown that related ketones undergo oxidative processes in the dark in the presence of base and oxygen via a similar intermediate (i.e., **15**). Support for the above rationalization was obtained by finding that irradiation of **1** in degassed CH_3OD with 3130-Å light gave only recovered starting material containing >95% deuterium incorporation. Insignificant deuterium incorporation occurred when the solution was allowed to stand at ordinary laboratory conditions.

An alternative path which could also account for the formation of the oxygenated photoproducts (**5** and **6**) derives from the reaction of the enol form of **1** (i.e., **13**) with singlet oxygen. The benzofurnanol tautomer **13** might be expected to react with singlet oxygen in an "ene" fashion[32,33] to give the hydroperoxy species **15,** or by a 2 + 2 mode to give a 1,2-dioxetane (**16**).[34,35] Either intermediate could readily be converted to **5** and **6.** The plausibility of enol **13** reacting directly with singlet oxygen to form a 1,2-dioxetane (**16**) was demonstrated by reacting the corresponding methyl enol ether **12** with photochemically generated singlet oxygen. Under these conditions, carbonate **18** was isolated in high yield. The electron-rich double bond in **12** (or **13**) is sufficiently reactive toward singlet oxygen to form the 1,2-dioxetane **19,** either directly[34] or via the intermediacy of a 1,4-addition product analogous to **17.**[35]

In this proposed scheme, lactone **1** functions both as a sensitizer and as an acceptor for singlet oxygen.[37] That singlet oxygen can effect formation of **5** and **6** was shown by



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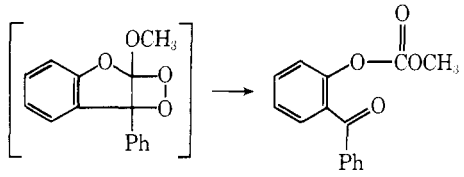
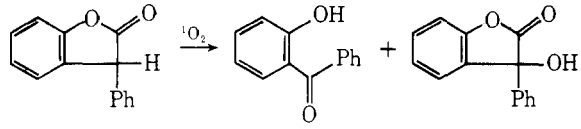


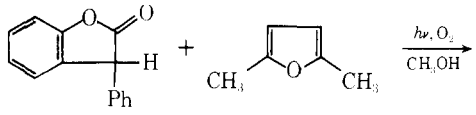
19 18

the irradiation ($h\nu > 366$ nm) of **1** in methanol with Methylene Blue or Rose Bengal as sensitizer to give **5** (49%) and **6** (6%). Furthermore, heating a degassed and sealed ampoule of **1** at 80° in a dimethyl sulfoxide–methanol mixture containing 2 equiv of 9,10-diphenylanthracene peroxide[38] also resulted in the formation of **5** (7%) and **6** (1%).

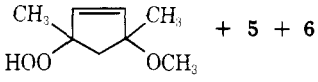


1 5 6

To determine whether **1** might serve as both a sensitizer and substrate for singlet oxygen,[37] lactone **1** was irradiated in methanol in the presence of 2,5-dimethylfuran, a good singlet oxygen trap.[39] Under these conditions, the furan was partially converted to the methoxy hydroperoxide **20**.[39] The



1



+ 5 + 6

20

formation of **5** and **6**, however, was not significantly diminished (ca. 15% reduction in overall yield of **5** + **6**) by excess (four- to sixfold) 2,5-dimethylfuran. Also, the presence of excess piperylene (0.17 *M*) did not totally suppress the photooxidation (again, ca. 15% reduction in yield of **5** + **6**). The observation that the formation of **5** and **6** is not totally suppressed by excess furan (singlet oxygen trap) or piperylene (triplet quencher) indicates that the singlet oxygen reaction cannot be the primary source of **5** and **6**. At best, it accounts for ca. 15% of product formation. Support for this supposition is provided by the observation that, in contrast to the direct irradiation oxygenations, lactone **1** is inert to photosensitized oxygenations (Rose Bengal) when the solvent used is acetonitrile, cyclohexane, or benzene. This observation would tend to support a scheme which involves reaction of the excited enolate anion (**14**) with ground-state oxygen (see Scheme I) in these solvent systems. Only in methanol does **1** exist to any appreciable extent as the enolate tautomer (ca. 2%) to allow it to react with singlet oxygen.

The failure of excess piperylene, 1,3-cyclohexadiene, or 2,5-dimethylfuran to suppress either the deuterium exchange reaction of **1** (in CH_3OD) or the oxidation reaction strongly argues for the mechanism outlined in Scheme I. From these experiments, we also conclude that it is the low-lying singlet state of **14** which is trapped by oxygen and which undergoes exchange with the protic solvent. As was pointed out earlier, a significant concentration (ca. 2%) of enolate **14** exists in equilibrium with the keto form of **1** in methanol. Irradiation of this tautomeric mixture with 3130-Å light selectively generates the electronically excited singlet state of **14** which subsequently reacts with ground-state oxygen to give **5** and **6**. When 2537-Å light is used, the keto tautomer is preferentially excited. In this case, the resulting excited state can also lose carbon monoxide and generate an *o*-quinone methide intermediate.

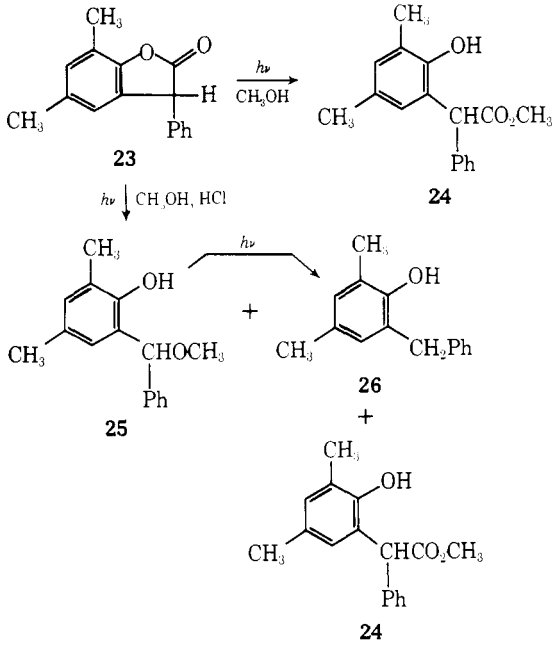
It should be pointed out that there is no spectroscopic evidence for the existence of enolate **14** in cyclohexane solutions of lactone **1**. In this solvent, **1** can be recovered unchanged after prolonged irradiation (3130 Å) in the presence of oxygen. It is especially interesting to note that when the irradiation of **1** is carried out in cyclohexane with a 2537-Å source, **5** and **6** are formed, even though the tautomeric concentration of **14** (and/or **12**) is negligible. The quantum efficiency for this reaction, however, is much less ($\Phi = 0.0005$) than that observed in methanol ($\Phi = 0.02$) or acetonitrile ($\Phi = 0.008$) using a 3130-Å source. Xanthene (**4**) and *o*-benzylphenol (**3**) were also formed when the irradiation of **1** was carried out at 2537 Å in cyclohexane in the presence of oxygen. In this case, it is tempting to speculate that photoenolization of **1** occurs on irradiation with 2537-Å light. Ample precedence for the enolization of excited carbonyl compounds can be found in the literature[40-45] and provides reasonable analog for the above suggestion.

A deuterium isotope effect was also noted when the α proton of lactone **1** was exchanged for deuterium. Simultaneous irradiation of solutions of **1** and **1**-d_1 in oxygenated methanol with 3130-Å light gave rise to a small but significant isotope effect ($k_H/k_D = 1.5$) for the formation of photoproducts **5** and **6**. We attribute this effect to a change in the tautomeric composition of lactone **1**-d_1 in solution. The ultraviolet spectrum of **1**-d_1 showed that the intensity of the long-wavelength component (316 nm) was reduced by ca. 30%. This would imply that the equilibrium between the keto and enolate tautomer (**14**) was shifted more toward the keto form in the deuterated system. Consequently, the quantum yield for the photooxygenation of **1** would be expected to diminish on deuterium exchange.

It is interesting at this point to compare the photochemistry of **1** with that of the previously reported parent lactone, benzofuran-2(3*H*)-one (**21**). As noted by Chapman and McIntosh,[3] **21** gives *o*-hydroxybenzyl methyl ether (**22**) upon irradiation in methanol. We have independently determined that the quantum yield for formation of **22** is 0.20 with 2537-Å light. Under optimal conditions, **1** is converted to the analogous product (i.e., **2**) with a quantum efficiency of only 0.058. The difference in quantum yields in these two systems is apparently due to a number of competing photoprocesses which deactivate the excited state(s) of **1**. In addition to the visible modes of decay which produce **2**–**4**, an "invisible" process resulting in enolization of **1** decreases the efficiency of product formation. We could find no evidence for a similar process in the photochemistry of **21** and were unable to detect any significant amount of salicylaldehyde when the irradiation of **21** was carried out in the presence of oxygen. It would appear as though the phenyl substituent not only controls the tautomeric composition of the lactone but also markedly enhances the photoenolization route. Further evidence, which tends to indicate that enolization is responsible for some of the inefficiency associated with the photochemistry of lactone **1**, was obtained by irradiating deuterated lactone **1**-d_1 (CH_3OD at 2537 Å) and measuring the quantum yield for formation of benzhydryl ether **2**. The results obtained show that the quantum yield for the formation of **2** is doubled (i.e., $\Phi = 0.12$). This observation supports the claim that enolization is a significant energy-wasting step. The presence of deuterium in the α position of **1** would be expected to minimize the enoliza-

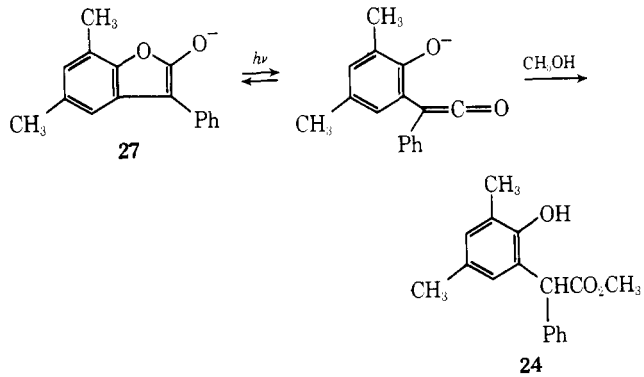
tion reaction and thereby increase the efficiency of product formation.

The photochemistry of the related benzofuranone **23** was also examined. Irradiation of 5,7-dimethyl-3-phenyl-2-benzofuranone (**23**) in methanol under an argon atmosphere using a 450-W Hanovia lamp (Pyrex filter) afforded methyl α-(2-hydroxy-3,5-dimethylphenyl)phenylacetate (**24**) as the only detectable photoproduct (85%). When the irradiation of **23** was carried out in slightly acidic methanol using a Vycor filter, a mixture of 3,5-dimethyl-2-hydroxybenzhydryl methyl ether (**25**) (10%), 2-benzyl-4,6-dimethylphenol (**26**) (28%), and methyl α-(2-hydroxy-3,5-dimethylphenyl)phenylacetate (**24**) (6%) was formed. Control experiments revealed that the photolysis of **25** led to the formation of **26,** and that uranone **23** did not react in the absence of light.

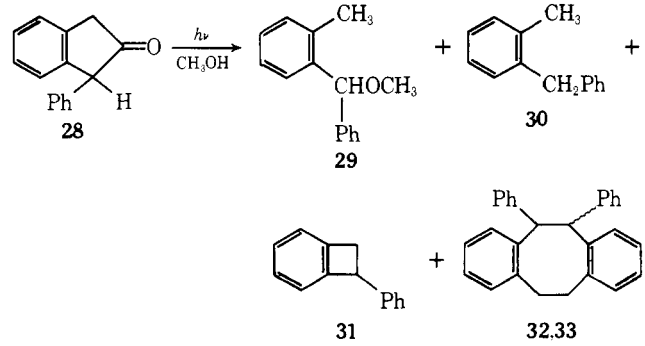


A striking feature of this system is the absence of benzhydryl ether **25** and phenol **26** in the irradiation of **23** in neutral methanol. A clue to this unusual behavior was obtained by examining the uv absorption spectrum of **23** in methanol. In this solvent, benzofuranone **23** displays absorption maxima at 315 nm (ϵ 110), 286 (1600), and 280 (1680). Addition of a slight excess of base to the spectroscopic solution caused a dramatic increase in the 315- (ϵ 22,700) and 286-nm bands (33,600). In the presence of acid, the 315-nm band disappeared. These observations suggest that the photochemistry of this system is also controlled by the tautomeric composition of the lactone in solution. Excitation of the enolate anion **27** with Pyrex-filtered light resulted in the exclusive formation of ester **24.** In this case, it is tempting to speculate that the excited enolate anion (**27**) produces a transient ketene intermediate which is subsequently trapped by the alcoholic solvent. In the presence of acid, this route is not followed, and instead the system undergoes photodecarbonylation and partial ground-state hydrolysis.[46]

In continuation of our quest for additional examples of competitive keto–enol photochemistry, we also examined the photochemical behavior of the closely related 1-phenyl-2-indanone (**28**) system in the hope that this system would also be influenced by the tautomeric composition of the ketone in solution. This expectation was not realized, however, and the photoproducts proved to be similar to those obtained from related 2-indanone systems.[21,47] Thus, irradiation of **28** in methanol with a 450-W Hanovia lamp through



Corex for 5 hr led to the formation of five products (**29–33**) whose relative yields varied as a function of the reaction conditions. The structures of the compounds were estab-



lished by comparison with authentic samples (see Experimental Section). The formation of these products can be attributed to an initial decarbonylation followed by subsequent reactions of the transient *o*-xylylene intermediate. Quinkert and coworkers have reported similar results.[48] When the irradiation of **28** was carried out in the presence of oxygen, the major products isolated were benzhydryl ether **29** (55%) and 3-phenylphthalide (**34**) (10%). This latter product apparently results from trapping of the *o*-xylylene intermediate with oxygen (i.e., Diels–Alder) followed by a subsequent oxidation. We have not been able to spectroscopically detect the enolate ion derived from **28** in reagent grade methanol. This enolate has been reported to have a high intensity maximum near 300 nm.[31] The absence of an absorption band near 300 nm could be construed to mean that the tautomeric equilibrium associated with the keto and enolate forms lies exclusively in the direction of the keto form. Alternatively, the small amount of enolate ion which is initially present may be destroyed by reaction with oxygen.[31] At any rate, the absence of the enolate ion mitigates against a wavelength effect in this system.

In conclusion, the photochemistry of certain benzofuranones appears to be markedly influenced by the tautomeric composition of the lactone in solution. The wavelength and solvent effects which we have noted suggest that tautomeric forms of certain carbonyl derivatives may yield diverse and interesting photochemistry. We are continuing to examine these effects and will report additional findings at a later date.

Experimental Section[49]

3-Phenylisocoumaranone (**1**) was prepared using a modified procedure of Bistrzycki and Flatau.[14] To an ice-cooled mixture of finely pulverized phenol (26.5 g) and mandelic acid (30.45 g) was added 80 ml of a 70% sulfuric acid solution. The mixture was stirred at 0° until dissolution was nearly obtained and then heated at 115° for 45 min. The mixture was cooled to room temperature, poured onto 400 ml of an ice–water slurry, and extracted with three 100-ml portions of methylene chloride. The combined organic layers were washed with 100 ml of a saturated aqueous sodium

bicarbonate solution and dried over magnesium sulfate. Evaporation of the solvent under reduced pressure gave white crystals which were recrystallized from 95% ethanol to give 11.1 g (26%) of 3-phenylisocoumaranone (**1**): mp 113–114° (lit.[50] mp 113–114°); ir ($CHCl_3$) 5.52, 6.82, 8.89, 9.42, and 11.01 μ; uv (CH_3CN) λ_{max} 346, 278, and 272 nm (ϵ 40, 1280, and 1420); NMR (100 MHz, $CDCl_3$) δ 4.90 (s, 1 H), 7.3–7.5 (m, 9 H); *m/e* (70 eV) 211, 210, 183, 181 (base), 165, 153, 152, 151, and 77.

***o*-Hydroxybenzhydryl Methyl Ether (2).** To a stirred solution of *o*-hydroxybenzophenone (2.01 g) in absolute methanol (50 ml) at 0° was slowly added 420 mg of sodium borohydride. The mixture was stirred for 3 hr while warming to room temperature. At the end of this time, concentrated hydrochloric acid was added dropwise to make the solution strongly acidic, and the mixture was then allowed to stir overnight. The reaction mixture was then poured into 50 ml of a saturated aqueous sodium chloride solution containing sodium bicarbonate. The aqueous solution was extracted with 150 ml of chloroform, and the combined organic layers were dried over magnesium sulfate. Removal of the solvent under reduced pressure gave a pale-green oil which was sublimed at 40° (0.2 mm) to give 2.0 g (95%) of *o*-hydroxybenzhydryl methyl ether (**2**): mp 35–36°; ir (film) 3.0, 3.3, 3.42, 6.30, 6.73, 6.90, 8.08, 9.35, 10.42, 13.29, 13.70, and 14.36 μ; *m/e* (70 eV) 198 (M^+), 197, 184, 183, 165, 121, 115, 107, 106, 105, 91, 85, 83 (base), 78, and 77; NMR (100 MHz, $CDCl_3$) δ 3.46 (s, 3 H, OCH_3), 5.47 (s, 1 H), 6.8–7.5 (m, 9 H), 8.06 (s, 1 H, OH).

Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.36; H, 6.61.

3-Phenyl-3-hydroxyisocoumaranone (6). To a nitrogen-swept flask containing 462 mg of 3-phenylisocoumaranone (**1**) and 241 mg of triethylamine in 100 ml of chloroform was added a chloroform solution of bromine until a dark-red color persisted. The solution was allowed to stir for an additional 4 hr at room temperature. The solvent was then reduced to one-half of its original volume. To this solution was added 50 ml of acetone and 30 ml of an aqueous silver perchlorate solution. The mixture was stirred for an additional 30 min, and the precipitate was removed by filtration. The solvent was removed under reduced pressure, and the residue was taken up in chloroform and washed with water. The organic layer was dried over magnesium sulfate and the solvent removed in vacuo. The residue was recrystallized from hexane to give 3-phenyl-3-hydroxyisocoumaranone as a white solid: mp 102–103°; ir (KBr) 2.96, 5.60, 6.18, 6.22, 6.86, 7.19, 7.78, 8.80, 9.10, 9.29, 10.75, 11.49, 12.90, 13.11, 13.78, 14.19, and 14.40 μ; uv (CH_3CN) 271 and 266 nm (ϵ 1360 and 1230), *m/e* (70 eV) 226 (M^+), 210, 199, 198, 197 (base), 182, 181, 152, 121, 120, 105, and 93; NMR (100 MHz, $CDCl_3$) δ 3.37 (s, 1 H, disappears on addition of D_2O), 6.96–7.44 (m, 9 H).

Anal. Calcd for $C_{14}H_{10}O_3$: C, 74.33; H, 4.46. Found: C, 74.16; H, 4.46.

2-Methoxy-3-phenylbenzofuran (12) was prepared by a modification of the method of Coates and Shaw.[51] To a stirred solution of hexamethylphosphoramide (20 ml) under an argon atmosphere were added 1.01 g of 3-phenylisocoumaranone (**1**) and 169 mg of sodium hydride. After stirring for 30 min at room temperature, a mixture of 0.80 g of dimethyl sulfate in 5 ml of hexamethylphosphoramide was added, and the mixture was allowed to stir for another 6 hr. The mixture was then poured over ice-water and extracted with 100 ml of ether. The solvent was dried over magnesium sulfate and evaporated under reduced pressure. The crude residue (1.58 g) was purified using liquid–liquid partition chromatography[52] to afford 0.97 g (91%) of 2-methoxy-3-phenylbenzofuran (**12**) as a colorless oil: ir (neat) 3.25, 3.38, 6.10, 6.18, 6.64, 6.84, 6.91, 7.26, 8.25, 8.52, 9.01, 9.55, 9.69, 10.30, 10.85, 11.63, 12.68, 13.01, 13.40, and 1436 μ; NMR (100 MHz, $CDCl_3$) δ 4.09, (s, 3 H), 7.1–7.6 (m, 6 H), 7.7–7.9 (m, 3 H); *m/e* (70 eV) 224 (M^+), 212, 209 (base), 197, 181, 153, 105, and 77; uv (CH_3OH) 265 and 223 nm.

***o*-Hydroxycarbomethoxybenzophenone (18).** To a stirred solution of 1.98 g of *o*-hydroxybenzophenone in 25 ml of anhydrous pyridine at 0° was added an excess of methyl chloroformate. The mixture was allowed to stir for 12 hr at room temperature and then poured onto an ice–10% hydrochloric acid mixture. The mixture was extracted with ether, and the combined extracts were dried over magnesium sulfate. Evaporation of the solvent gave *o*-hydroxycarbomethoxybenzophenone (**18**) (2.56 g, 98%) as a colorless oil: bp 135° (0.02 mm); ir (film) 3.29, 3.38, 5.69, 6.00, 6.21, 6.30, 6.72, 6.95, 7.60, 7.90, 8.22, 8.59, 8.99, 9.39, 10.60, 11.91, 12.6, 13.2, and 14.21 μ; *m/e* (70 eV) 256 (M^+), 211, 197, 195, 181, 135, 121, 119, 117 (base); NMR ($CDCl_3$, 100 MHz) δ 3.73 (3 H, s), 7.4–8.1 (9 H, m).

Anal. Calcd for $C_{15}H_{12}O_4$: C, 70.30; H, 4.72. Found: C, 70.78; H, 4.85.

***o*-Acetoxybenzhydryl Acetate (8).** To a solution of 2.15 g of *o*-hydroxybenzophenone in 50 ml of 80% aqueous dioxane was added 0.878 g of sodium borohydride. The solution was allowed to stir overnight and then acidified with a 10% aqueous hydrochloric acid solution. After stirring for an additional 4 hr, the solution was concentrated under reduced pressure, and the residue was diluted with a saturated aqueous sodium chloride solution and extracted with ether. The ethereal extracts were dried over magnesium sulfate, and the solvent was removed under reduced pressure. The oily residue was taken up in 50 ml of acetic anhydride containing 2.0 g of sodium acetate and allowed to reflux overnight. At the end of this time, the mixture was concentrated under reduced pressure, poured over ice-water, and extracted with ether. The ethereal extracts were dried over magnesium sulfate, and the solvent was removed under reduced pressure. The oily residue obtained was purified by a short-path distillation at 130° (0.01 mm) to give 2.75 g of a colorless liquid (89%) whose spectral and analytical properties are in complete agreement with the assigned structure: ir (film) 3.21, 5.62, 6.64, 6.82, 7.24, 8.3, 9.02, 9.72, 10.12, 10.86, 12.16, 13.12, and 14.26; *m/e* (70 eV) 284 (M^+), 241, 224, 210, 209, 199, 183, 182, 181 (base), 165, 153, 152, 121, 115, 105, and 77; NMR (100 MHz, $CDCl_3$) δ 2.08 (s, 3 H), 2.14 (s, 3 H), and 6.89–7.5 (m, 10 H).

Anal. Calcd for $C_{17}H_{16}O_4$: C, 71.82; H, 5.67. Found: C, 72.13; H, 5.62.

Irradiation of 3-Phenylisocoumaranone (1) in Methanol with 2537-Å Light. A nondeaerated solution of 3-phenylisocoumaranone (**1**) (103 mg) in 100 ml of methanol was irradiated with a 2537-Å low-pressure mercury arc or with a 450-W Hanovia mercury arc lamp equipped with a Corex filter. The progress of the photoreaction was followed by vapor-phase chromatography with a 6 ft × 0.25 in. copper column packed with 10% FS-1265 on Diatoport S at a flow rate of 60 cm^3/min and at a temperature of 210°. The solvent was removed on a rotatory evaporator, and the remaining oil was subjected to either preparative VPC or thick-layer chromatography. Spectroscopic (NMR) and vapor-phase chromatography indicated that the mixture contained *o*-hydroxybenzhydryl methyl ether (**2**) (30%), xanthene (**4**) (3%), *o*-benzylphenol (**3**) (11%), *o*-hydroxybenzophenone (**5**) (14%), and 3-phenyl-3-hydroxyisocoumaranone (**6**) (5%). These compounds were identified by comparison with authentic samples. Under identical conditions, irradiation of 3-phenylisocoumaranone (**1**) containing 0.1 *M cis*-piperylene gave a mixture of the above products, 29% **2**, **4** (3%), 10.5% **3**, 7.5% of **5**, and a trace of **6**.

Irradiation of *o*-Hydroxybenzhydryl Methyl Ether (2) in Methanol. A Quartz tube containing 5 ml of a 0.024 *M* solution of *o*-hydroxybenzhydryl methyl ether was degassed by four freeze–pump–thaw cycles and sealed under vacuum. The sample was irradiated for 120 min with five 2537-Å lamps in a Rayonet reactor and analyzed by vapor-phase chromatography as well as by NMR analysis. The three products present were identified as recovered starting material (46.1%), xanthene (3%), and *o*-benzylphenol (**3**) (28%).

Irradiation of 3-Phenylisocoumaranone (1) in Methanol with 3130-Å Light. A 54-mg sample of 3-phenylisocoumaranone (**1**) in 6 ml of methanol was irradiated in a Pyrex test tube for 18 hr using 3130-Å filtered light. Analysis of the mixture using vapor-phase chromatography and NMR indicated the presence of only *o*-hydroxybenzophenone (**5**) and 3-phenyl-3-hydroxyisocoumaranone (**6**). Combined VPC and NMR analysis revealed no detectable quantities of *o*-hydroxybenzhydryl methyl ether (**2**), xanthene (**4**), or *o*-benzylphenol (**3**).

In another experiment, a sample of 3-phenylisocoumaranone (**1**) (24 mg) in 5 ml of methanol-*O*-*d* was placed in a Pyrex tube and degassed with four freeze–pump–thaw cycles before sealing under vacuum. The tube was irradiated with 3130-Å light for 64 hr. The only detectable product in the vapor-phase chromatogram was recovered starting material. The recovered starting material was isolated by preparative VPC and analyzed by high resolution mass

spectrometry for deuterium incorporation. The data obtained indicated that starting material had incorporated more than 90% deuterium in the 3 position of the benzofuranone ring.

Rose Bengal-Sensitized Oxygenation of 3-Phenylisocoumaranone. A solution of 3-phenylisocoumaranone (**1**) (118 mg) in 100 ml of methanol containing 5 mg of Rose Bengal was purged with oxygen and then irradiated for 1 hr with a 450-W Hanovia lamp fitted with a uranium glass filter (cutoff <366 nm). The solution was concentrated under reduced pressure and analyzed by vapor-phase chromatography as well as by NMR. The photolysate was shown to contain only *o*-hydroxybenzophenone (**5**) and 3-phenyl-3-hydroxyisocoumaranone (**6**).

In a similar experiment, Methylene Blue-sensitized oxygenation of **1** in methanol similarly afforded **5** and **6** as the only two photoproducts.

Thermal Decomposition of 9,10-Diphenylanthracene Peroxide in the Presence of 3-Phenylisocoumaranone (1). A solution of 3-phenylisocoumaranone (**1**) (66 mg) and the endo peroxide of 9,10-diphenylanthracene[38] (174 mg) in 10 ml of dimethyl sulfoxide was rigorously degassed using five freeze–pump–thaw cycles and sealed under vacuum. The reaction mixture was placed in an oil bath held at 82° for 44 hr. Analysis of the reaction mixture by VPC and NMR indicated the presence of only recovered starting material, *o*-hydroxybenzophenone and 3-phenyl-3-hydroxyisocoumaranone. A control experiment indicated that **1** was unreactive in dimethyl sulfoxide in the absence of 9,10-diphenylanthracene peroxide at 80°.

Rose Bengal-Sensitized Oxygenation of 2-Methoxy-3-phenylbenzofuran (12). A solution of 2-methoxy-3-phenylbenzofuran (**12**) (234 mg) in 100 ml of methanol containing a trace of Rose Bengal was purged with oxygen and irradiated for 62 min with a 450-W Hanovia medium-pressure arc fitted with a uranium glass filter. The solution was concentrated under reduced pressure and analyzed by VPC and NMR analysis. In addition to starting material, the two major components were identified as *o*-hydroxybenzophenone (13%) and *o*-hydroxycarbomethoxybenzophenone (**18**) (49%). In a similar experiment, Rose Bengal-sensitized oxygenation of the benzofuran methyl ether **12** (209 mg) in 90 ml of *tert*-butyl alcohol–10 ml of acetonitrile for 60 min afforded a reaction mixture which contained *o*-hydroxybenzophenone (12%), *o*-hydroxycarbomethoxybenzophenone (**18**) (50%), and recovered starting material.

Irradiation of 3-Phenyl-3-hydroxyisocoumaranone in Acetonitrile. A Quartz tube containing 43 mg of 3-phenyl-3-hydroxyisocoumaranone in 5.5 ml of acetonitrile was irradiated with a 2537-Å source in a Rayonet reactor for 12 hr. The solvent was removed under reduced pressure, and the mixture was analyzed by vapor-phase chromatography. The only product, besides recovered starting material, was identified as *o*-hydroxybenzophenone (95%).

Irradiation of 3-Phenylisocoumaranone in Acetic Anhydride. A solution of 255 mg of 3-phenylisocoumaranone in 100 ml of acetic anhydride was thoroughly deaerated with argon and then irradiated with a 450-W Hanovia lamp (Corex filter) for 12 hr. The solvent was removed under reduced pressure, and the mixture was analyzed by VPC and NMR. The major volatile product (77%) of the reaction was a colorless liquid whose structure was elucidated as *o*-acetoxybenzhydryl acetate (**8**) by comparison with an independently synthesized sample.

Irradiation of 3,3-Diphenyl-5-methyl-2-benzofuranone (9) in Methanol. 3,3-Diphenyl-5-methyl-2-benzofuranone (**9**), mp 128–129°, was prepared according to the procedure of Bistrzycki and Nowakowsk.[53] A solution containing 150 mg of **9** in 150 ml of methanol was irradiated with a Hanovia 450-W mercury lamp through a Corex filter under a nitrogen atmosphere for 3 hr. The solvent was removed under reduced pressure, and the residual oil obtained was chromatographed on a thick-layer plate using a 1:1 benzene–chloroform mixture as the eluent. The fastest moving band ($R_f \sim 0.6$) was unreacted starting material. The second band isolated from the thick-layer plate was recrystallized from hexane to give 2-hydroxy-4-methyltriphenylmethane (**10**) as colorless prisms: mp 131–133°; NMR ($CDCl_3$) τ 7.83 (s, 3 H), 5.5 (broad s, 1 H), 4.29 (s, 1 H), 2.5–3.5 (m, 13 H); ir (KBr) 2.87, 6.30, 6.70, 6.95, 7.60, 8.0, 8.50, 9.21, 9.31, 12.35, 13.40, 13.60, 14.05, and 14.39 μ. The structure of **10** was verified by comparison with an authentic sample of 3-hydroxy-4-methyltriphenylmethane synthesized by the procedure of Busch and Knoll.[54]

Preparation of 5,7-Dimethyl-3-phenyl-2-benzofuranone (23). 5,7-Dimethyl-3-phenyl-2-benzofuranone (**23**) was prepared by heating a mixture of 2,4-dimethylphenol (36.6 g), mandelic acid (30.4 g), and 80 ml of an 80% sulfuric acid solution at 100° for 17 min. The mixture was cooled, poured onto 500 ml of crushed ice and extracted with 250 ml of methylene chloride. The combined organic layers were washed with water, followed by a saturated aqueous sodium chloride solution, and then dried over anhydrous magnesium sulfate. Removal of the solvent left a viscous oil which was chromatographed on a silica gel column using 5% ethyl acetate in hexane as the eluent. The initial fractions contained 6 g (13%) of 5,7-dimethyl-3-phenyl-2-benzofuranone. Recrystallization from ethanol gave a white crystalline solid: mp 70–71°; ir (KBr) 3.40, 5.51, 6.10, 6.77, 6.88, 8.15, 8.72, 9.19, 9.63, 10.30, 10.87, 12.14, 12.50, 12.70, 13.60, and 14.31 μ; uv (methanol) 314, 286, and 280 nm (ϵ 290, 1600, and 1700); NMR ($CDCl_3$) τ 7.80 (s, 3 H), 7.74, (s, 3 H), 5.26 (s, 1 H), 3.24 (s, 1 H), 3.08 (s, 1 H), and 2.60–2.90 (m, 5 H).

Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found: C, 80.44; H, 6.06.

Irradiation of 5,7-Dimethyl-3-phenyl-2-benzofuranone in Methanol. A solution containing 200 mg of **23** in 150 ml of methanol was irradiated with a 450-W Hanovia lamp through a Pyrex filter sleeve under an argon atmosphere for 1 hr. The solvent was removed under reduced pressure, and the residual oil that remained was chromatographed on a thick-layer plate using a 1:1 benzene–pentane mixture as the eluent. The only product isolated from the thick-layer plate (180 mg) was identified as methyl α-(2-hydroxy-3,5-dimethylphenyl)phenylacetate (**24**): mp 110–111°; ir (KBr) 2.90, 5.82, 6.25, 6.78, 6.91, 7.00, 8.2 1, 8.32, 8.93, 10.51, 11.55, 12.11, 13.55, 13.85, and 14.30 μ; NMR ($CDCl_3$) τ 7.84 (s, 3 H), 7.81 (s, 3 H), 6.26 (s, 3 H), 4.91 (s, 1 H), 2.7–3.2 (m, 8 H).

Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.73. Found: C, 75.73; H, 6.77.

An authentic sample of **24** was independently prepared by refluxing 500 mg of 6,7-dimethyl-3-phenyl-2-benzofuranone (**23**) in 80 ml of methanol which contained 0.2 ml of concentrated hydrochloric acid for 36 hr. Removal of the solvent under reduced pressure gave an oil which was taken up in chloroform and subsequently washed with a 5% sodium bicarbonate solution. The organic layer was dried over magnesium sulfate and the solvent removed under reduced pressure to give 350 mg of **24**, mp 110–111°. This material was identical in every respect with the solid isolated from the irradiation of **23**. A control experiment in the dark (with or without added base) showed that 5,7-dimethyl-3-phenyl-2-benzofuranone could be recovered unchanged from a neutral methanolic solution.

When the irradiation of 5,7-dimethyl-3-phenyl-2-benzofuranone (200 mg) was carried out in a methanol solution which contained 1 drop of concentrated hydrochloric acid for 3 hr, the yield of **24** dropped significantly (ca. 13 mg) as judged by NMR analysis of the crude photolysate. Removal of the solvent under reduced pressure left an oil which was taken up in chloroform and then washed with a 5% sodium bicarbonate solution. The organic layer was dried over magnesium sulfate and the oil obtained on removal of the solvent was chromatographed on a thick-layer plate using benzene–pentane (1:1) as the eluent. The first band isolated amounted to 20 mg (10%) and was recrystallized from pentane to give 3,5-dimethyl-2-hydroxybenzhydryl methyl ether (**25**) as a crystalline solid: mp 61–62°; ir (KBr) 3.00, 3.40, 6.20, 6.71, 6.89, 8.10, 8.63, 9.40, 9.73, 10.20, 11.38, 11.68, 12.90, 13.27, 14.10, 14.40 μ; uv (methanol) 283 nm (ϵ 2500); NMR ($CDCl_3$); τ 7.77 (s, 6 H), 6.54 (s, 3 H), 4.65 (s, 1 H), 3.47 (d, 1 H, J = 2.0 Hz), 3.11 (d, 1 H, J = 2.0 Hz), 2.70 (s, 5 H), 2.12 (s, 1 H).

Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.30; H, 7.36.

An authentic sample of **25** was prepared by heating 1.2 g of 3,5-dimethyl-2-hydroxybenzhydrol[55] in 20 ml of methanol which contained 0.2 ml of concentrated hydrochloric acid for 1.5 hr. A mixture melting point of the two samples was undepressed.

The second band isolated from the thick-layer plate was unreacted starting material (48 mg, 24%). The third component isolated from the thick-layer plate ($R_f \sim 0.4$) was a crystalline solid (46 mg, 28%), mp 63–64°, whose structure was assigned as 2-benzyl-4,6-dimethylphenol (**26**) on the basis of the following data: ir (KBr) 2.98, 3.35, 3.45, 6.24, 6.78, 6.92, 7.55, 8.33, 8.76, 9.30,

9.70, 10.29, 10.53, 11.00, 11.62, 13.70, and 14.49 μ; uv (methanol) 282 nm (ε 2100); NMR ($CDCl_3$) τ 7.88 (s, 3 H), 7.84 (s, 3 H), 6.14 (s, 2 H), 5.70 (broad s, 1 H), 3.32 (s, 2 H), 2.93 (s, 5 H).

Anal. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 84.85; H, 7.58.

An authentic sample of 2-benzyl-4,6-dimethylphenol (**26**) was independently prepared by heating a mixture of 8.5 g of 2,4-dimethylphenol, 2.5 g of benzyl chloride, and 0.02 g of zinc chloride at 95° for 3 hr. Fractional distillation of the residue afforded 2-benzyl-4,6-dimethylphenol [(6.0 g), bp 49–50° (0.4 mm)]. A mixture melting point of the two samples was undepressed at 63–64°.

The last band isolated from the thick-layer plate contained 13 mg of methyl α-(2-hydroxy-3,5-dimethylphenyl)phenylacetate (**24**). When the irradiation of **23** was carried out in acidic methanol for 5.5 hr, the yield of 2-benzyl-4,6-dimethylphenol (**26**) increased to 44%, while the yield of 3,5-dimethyl-2-hydroxybenzhydryl methyl ether (**25**) dropped to less than 5%. That phenol **26** was derived from methyl ether **25** was established by irradiating 100 mg of **25** in 150 ml of methanol for 1 hr using a 450-W Hanovia lamp. Evaporation of the solvent left an oil which contained 2-benzyl-4,6-dimethylphenol (**26**) as the major product.

Irradiation of 1-Phenyl-2-indanone in Methanol under a Nitrogen Atmosphere. 1-Phenyl-2-indanone (**28**) was prepared by the method of Smith and Wilson.[57] Several recrystallizations from hexane gave large prisms: mp 47–48° (lit.[57] 51–53°); ir (KBr) 5.73 μ; NMR ($CDCl_3$) τ 6.46 (s, 2 H), 5.42 (s, 1 H), and 2.1–2.6 (m, 9 H). A solution containing 208 mg of 1-phenyl-2-indanone in 550 ml of absolute methanol was irradiated through a Corex filter sleeve with a 450-W Hanovia lamp under a nitrogen atmosphere for 4 hr. Evaporation of the solvent under reduced pressure left a yellow oil which was dissolved in chloroform and separated into a mixture of components by chromatography using a thick-layer silica gel plate with a 25% chloroform–hexane mixture as the eluent. Five components were isolated from the thick-layer plate and were identified as 7-phenylbicyclo[4.2.0]octa-1,3,5-triene (**31**) (6%), phenyl-*o*-tolylmethane (**30**) (11%), *cis*- and *trans*-5,6-diphenyl-*sym*-dibenzocyclooctane (**32,33**) (21%), and α-methyoxyphenyl-*o*-tolylmethane (**29**) (41%). 7-Phenylbicyclo[4.2.0]octa-1,3,5-triene (**31**) was assigned on the basis of its characteristic NMR spectrum: ($CDCl_3$) τ 7.0 (dd, 1 H, J = 5.0 and 3.0 Hz), 6.4 (dd, 1 H, J = 5.0 and 3.0 Hz), 5.4 (dd, 1 H, J = 5.0 and 3.0 Hz), 2.8–2.9 (m, 9 H). Phenyl-*o*-tolylmethane (**30**) was identified by comparison of its NMR, ir, and GLPC retention time with an authentic sample prepared by the Wolff–Kishner reduction of *o*-methylbenzophenone. The mixture of diastereoisomeric 5,6-diphenyl-*sym*-dibenzocyclooctanes (**32,33**) isomer A [mp 205–206°; NMR ($CDCl_3$) τ 7.0 (s, 4 H), 4.8 (s, 2 H), 2.6–2.9 (m, 18 H); *m/e* 360 (M^+)] and isomer B [mp 172–173°; NMR ($CDCl_3$) τ 6.8 (s, 4 H), 4.8 (s, 2 H), 2.6–3.1 (m, 18 H); *m/e* 360 (M^+)] had previously been reported to be formed from the irradiation of **28** by Quinkert and coworkers.[48] α-Methoxyphenyl-*o*-tolylmethane (**29**) was identified on the basis of its characteristic NMR spectrum: ($CDCl_3$) τ 7.77 (s, 3 H), 6.60 (s, 3 H), 4.60 (s, 1 H), 2.5–2.9 (m, 9 H); *m/e* 212 (M^+). An authentic sample of **29** was independently prepared from 2-methylbenzhydrol[58] by refluxing this alcohol in absolute methanol which contained several drops of concentrated hydrochloric acid. The oil obtained was identical with **29** as judged by NMR, ir, and GLPC retention times.

Irradiation of 1-Phenyl-2-indanone in Methanol under an Oxygen Atmosphere. A solution containing 1-phenyl-2-indanone (208 mg) in 550 ml of absolute methanol was saturated with oxygen and then irradiated through a Corex filter sleeve using a 450-W Hanovia lamp for 5 hr. The solvent was removed under reduced pressure, and the residual oil was dissolved in chloroform and separated into two major components by thick-layer chromatography using a 25% chloroform–hexane mixture as the eluent. The fastest moving component was identified as α-methoxyphenyl-*o*-tolylmethane (**29**) (54%) by comparison of NMR and ir spectra with an authentic sample. The slower moving component was identified as 3-phenylphthalide (**34**) (10%) on the basis of the following data: mp 112–113° (lit.[59] 114–115°); ir (KBr) 5.73 μ; NMR ($CDCl_3$) 3.6 (s, 1 H), 2.0–2.8 (m, 9 H); *m/e* 219 (M^+). An authentic sample of 3-phenylphthalide (**34**) was prepared by treating *o*-benzoylbenzoic acid with zinc in acetic acid.[59]

Quantum-Yield Determinations. Quantitative measurements were made on a rotating assembly with a series of low-pressure 2537- or 3130-Å lamps in a Rayonet reactor. Samples in 13-mm Pyrex or quartz ampoules were placed in holders on the assembly approximately 6 cm from the light source. All studies were made at room temperature. Samples were degassed to 10^{-4} mm in several freeze–pump–thaw cycles and then sealed. Cyclopentanone[60] solutions were used as the chemical actinometer (a quantum yield of 0.38 was used). After irradiation, the degree of reaction was determined by quantitative NMR or vapor-phase chromatography. The conversions were run to 10% or less.

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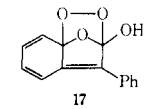

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Electrophilic Reactions at Multiple Bonds. III.[1a] Addition of Fluorosulfuric Acid to Alkynes. Intermediacy of Open-Chain and Hydrogen-Bridged Vinyl Cations

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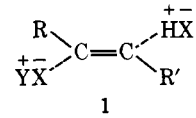
Abstract: The addition of FSO_3H to a series of alkynes has been studied in SO_2ClF at −120° or SO_2 at −78°. The reactions proceed instantaneously and quantitatively, forming alkenyl (vinyl) fluorosulfates as the primary reaction products. Terminal alkynes, as shown by FSO_3D addition, undergo syn:anti addition in the ratio 4.0:1, the highest ratio yet observed for protic acid addition to such systems. 2-Butyne undergoes predominant anti addition (anti:syn = 6.75:1), while 3-hexyne reacts nonstereospecifically (anti:syn = 9.5:10.0) with FSO_3H, but in the presence of a mole equivalent of pyridinium fluorosulfate it adds anti:syn = 3.0:2.0. 2-Butyne also forms approximately 10% of the 1,2,3,4-tetramethylcyclobutenyl cation, while 1-phenylpropyne forms the 2,4-dimethyl-1,3-diphenylcyclobutenyl cation as the exclusive product. After the initial proton addition, terminal alkynes subsequently react via an open vinyl cation–fluorosulfate ion pair, and aryl-substituted alkynes react by free, open vinyl cations following escape from the ion pair. The data for the addition to 3-hexyne, 2-butyne, and 1,4-dichloro-2-butyne are consistent with the initial formation of hydrogen-bridged vinyl cations which then react competitively via the hydrogen bridge and subsequently formed open vinyl cations.

Electrophilic addition reactions of alkynes have received particular attention during the last decade and have been the subject of several reviews.[2-4] In spite of the volume of experimental data, the mechanistic aspects of these reactions are still not fully understood.[2-4]

The principle question of mechanistic interest concerns the factors which determine the molecularity of the reactions and the nature of the intermediates which are involved. Much of the experimental evidence indicates that bimolecular (AdE2) reactions are occurring via rate-determining addition of the electrophile, although work by Fahey and coworkers[2,5] has suggested that termolecular (AdE3) reactions involving the transition state **1** are important under some conditions. The intermediates from the AdE2 reactions are vinyl cations, which can be either open (**2**) or bridged, i.e., σ bridged (**3**) or π bridged (**4**), the type of bonding being dependent upon the nature of X. Vinyl cations are also intermediates in the solvolysis of vinyl halides, esters, and related systems and have also been extensively reviewed.[2,3,6,7]



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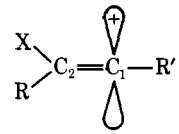

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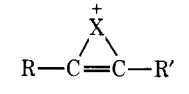

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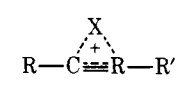

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Yates[8] has critically examined the question of open vs. bridged vinyl cations in electrophilic reactions of alkynes and has concluded that "studies of product stereochemistry indicate that phenyl substitution (i.e., R′ = Ph in **2–4**) leads to open intermediates (i.e., **2**), except for sulfenyl halide additions, whereas exclusive alkyl substitution (R, R′ = alkyl) leads to bridged ions (**3, 4**) except for proton addition".[8] Modena and Melloni[9-11] have examined the selectivity of nucleophilic attack on open vinyl cations (i.e., syn or anti to X in **2**) and have demonstrated the expected sensitivity to attack at C_1 due to the size and electronic character of R and X.

The addition of protic acids is the least understood of all the electrophilic reactions of alkynes. Stang[3] has concluded that "the exact behavior and mechanism of electrophilic additions (of acids) to alkynes is clearly strongly dependent upon the reaction conditions. In a highly polar and strongly acidic but weakly nucleophilic solvent such as trifluoroacetic acid, addition via a vinyl cation intermediate is favored