Chemistry of 9-Diazoxanthene and 9-Xanthylidene

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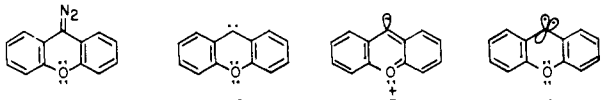
Abstract: 9-Diazoxanthene (**1**) and 9-xanthylidene (**2**) have been studied. 9-Xanthione reacts as a dipolar reagent with **1** to form bixanthylene episulfide (**5**). Dimethyl acetylenedicarboxylate and **1** give 4,5-dicarbomethoxyspiro[3*H*-pyrazole-3,9′-xanthene] (**6**); **6** decomposes to dimethyl 2*H*-benz[*e*]indeno[7,1-*bc*]pyran-1,2-dicarboxylate (**8**) or dimethyl 10b*H*-benz[*e*]-indeno[7,1-*bc*]pyran-1,2-dicarboxylate (**9**). Methyl acrylate adds to **1**, giving 5-carbomethoxyspiro[[1]pyrazoline-3,9′-xanthene] (**11**), which converts to spiro[[2]carbomethoxycyclopropane-1,9′-xanthene] (**12**) and 3-carbomethoxyspiro[2]pyrazoline-5,9′-xanthene (**13**) on heating. Ring-substituted styrenes (**14**) undergo nucleophilic dipolar addition (ρ = 0.97) of **1** to yield spiro[2-arylcyclopropane-1,9′-xanthenes] (**17**). At 25 °C **1** reacts with *cis*- and with *trans*-propenylbenzenes to give spiro[(2-methyl-*cis*-3-phenylcyclopropane)-1,9′-xanthene] (**18**) and spiro[(2-methyl-*trans*-3-phenylcyclopropane)-1,9′-xanthene] (**19**), respectively, in ≳95% stereospecificity. Cyclopentanone, cyclohexanone, ethyl phenyl ketone, 2-butanone, and phenyl acetone react at their carbonyl α positions when heated with **1** to produce 2-(9-xanthyl)cyclopentanone (**20**), 2-(9-xanthyl)cyclohexanone (**21**), 1-phenyl-2-(9-xanthyl)-1-propanone (**22**), 3-(9-xanthyl)-2-butanone (**23**), and 1-phenyl-1-(9-xanthyl)-2-propanone (**24**), respectively. Decomposition of **1** in methyl phenyl ketone leads to 1-phenyl-2-(9-xanthyl)ethanone (**25**) and 9-(2-phenyl-2-ethanoyl)-9′-bixanthyl (**26**). Insertion of **2** into cyclooctane yields 9-cyclooctylxanthene (**27**). Cumene reacts with **2** to form 9-(1-methyl-1-phenylethyl)xanthene (**28**) and bixanthyl (**29**). Toluene is converted by **2** to 9-benzylxanthene (**31**) and 9-benzyl-9-(9′-xanthyl)xanthene (**32**). The behavior of **2** in insertion into C–H of these systems is not that of a nucleophilic carbene. Diphenylmethylene (**35**) and 9-anthronylidene (**36**) abstract hydrogen more readily from toluene than does **2**; these differences are rationalizable on the basis of triplet processes. Thermolysis of **1** in cyclohexene results in C–H insertion to produce 9-(2-cyclohexenyl)xanthene (**41**); under these conditions methylenecyclohexane and 1,1-dimethoxyethylene yield dispiro[cyclohexane-1,1′-cyclopropane-2′,9″-xanthene] (**43**) and spiro[2,2-dimethoxycyclopropane-1,9′-xanthene] (**44**), respectively. Photolysis of the sodium salt (**46**) of 9-xanthone tosylhydrazone in allylbenzene results in C—H and C=C insertion to give 9-(1-phenyl-2-propenyl)xanthene (**48**) and spiro[2-benzylcyclopropane-1,9′-xanthene] (**49**). Irradiation of **46** in 3-methyl-1-butene yields 9-(1,1-dimethyl-2-propenyl)xanthene (**50**), spiro[2-(2-propyl)cyclopropane-1,9′-xanthene] (**51**), and **29**; **51** rearranges at 150 °C to 9-(3-methyl-2-butenyl)xanthene (**52**). 1,2-Dihydro-1,1-dimethyl-4-phenylnaphthalene (**53**) undergoes allylic C–H insertion with **2**, yielding 1,2-dihydro-1,1-dimethyl-2-(9-xanthyl)-4-phenylnaphthalene (**54**). Photolysis of **46** in 2,3-dimethyl-2-butene results in spiro[2,2,3,3-tetramethylcyclopropane-1,9′-xanthene] (**56**) and 9-(2,3-dimethyl-2-butenyl)xanthene (**57**). Cyclopropane **56** isomerizes at 200 °C to 2,10b-dihydro-1,1,2,2-tetramethyl-1*H*-benz[*e*]-indeno[7,1-*bc*]pyran (**58**). The behavior of **2** of note with allylic olefins is that α-C–H insertion occurs without rearrangement and there is addition to C=C bonds to give cyclopropanes. 9-Diazofluorene (**62**) and 2,3-dimethyl-2-butene photolyze to spiro[2,2,3,3-tetramethylcyclopropane-1,9′-fluorene] (**63**), 2,3-dimethyl-2-butenyl-9-fluorene (**64**), and 1,1,2-trimethyl-2-propenyl-9-fluorene (**65**). Photolysis of **46** in ring-substituted styrenes (**14**) was investigated to determine whether **2** reacts as a nucleophile or an electrophile to give cyclopropanes **17**. On the basis of the reactivities of **14** and that **2** reacts exclusively with **14** to form **17**, the addition process is that of triplet **4** rather than nucleophile **3**; alternative possibilities for formation of **17** have been considered. Photolysis of **46** in *cis*-propenylbenzene gives **18** (75–80%) and **19** (20–25%) whereas *trans*-propenylbenzene yields **19** (~95%), consistent with addition of **4** (in part) to the olefinic double bonds.

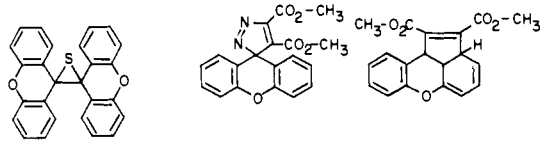
9-Diazoxanthene (**1**) and 9-xanthylidene (**2**) are of interest in synthesis and/or theory.[1-4] As a dipolar reagent, **1** undergoes addition to 1,4-quinones to give pyrazolines[1b] and is reported to be inert to styrene.[2a] Although knowledge of its behavior is limited, **2** as generated by photolysis of **1** is pre-



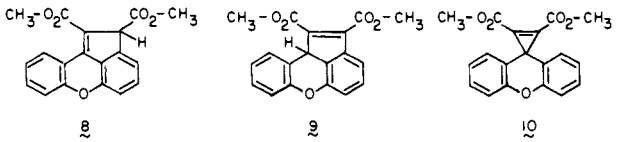
1 **2** **3** **4**

sumed to be a weak electrophile[2a-c] or a stabilized nucleophile[3] as a singlet (**3**) and/or a discriminating triplet (**4**)[2a] because it adds to styrene[2a] (see **14d**) to give spiro[(2-phenylcyclopropane)-1,9′-xanthene] (see **17d**) but fails to insert into the C—H bonds of saturated hydrocarbons[2b] or the C=C or C—H bonds of olefins.[2a,3] We now describe further the behavior of **1** and **2**. This study allows more complete definition and certain reevaluation of the chemistry of **1** and **2**.[4]

9-Diazoxanthene (**1**) is a reactive dipolar reagent. Thus **1** rapidly loses nitrogen when mixed with 9-xanthione at 20–25 °C to form bixanthylene episulfide (**5**, 86%) and adds exothermically to dimethyl acetylenedicarboxylate giving 4,5-dicarbomethoxyspiro[3*H*-pyrazole-3,9′-xanthene] (**6**, 82%). Decomposition of **6** occurs thermally or photochemically with loss of nitrogen presumably via **7** and hydrogen migration to yield a single product (57%); dimethyl 2*H*-benz[*e*]-indeno[7,1-*bc*]pyran-1,2-dicarboxylate (**8**) or its tautomer,



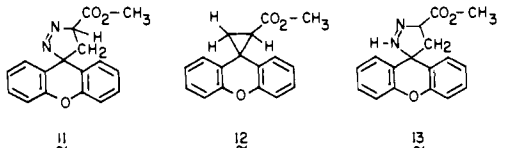
5 **6** **7**



8 **9** **10**

dimethyl 10b*H*-benz[*e*]indeno[7,1-*bc*]pyran-1,2-dicarboxylate (**9**); final structural assignment cannot yet be made.[38] There is no evidence for formation of **10** from **6**.

Methyl acrylate adds to **1** at −20° C to give 5-carbomethoxyspiro[[1]pyrazoline-3,9′-xanthene] (**11**); on warming **11** decomposes to spiro[2-carbomethoxycyclopropane-1,9′-



11 **12** **13**

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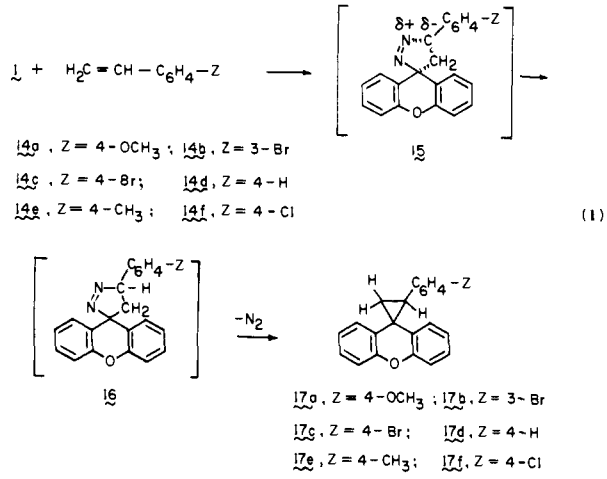
Table I. Relative Rate Constants for Dipolar Addition of 9-Diazoxanthene (**1**) to Substituted Styrenes (**14**) at 25 °C

substituent	$k_{sub}{}^a/k_{OCH_3}$	substituent	$k_{sub}{}^a/k_{OCH_3}$
4-OCH_3	1.00	4-Cl	2.74
4-CH_3	1.12[b]	4-Br	2.86
4-H	1.81	3-Br	4.62

[a] The values listed are averages of two experiments. The results from specific experiments are included in the Experimental Section. [b] This value was calculated as indicated: $k_{4\text{-}CH_3}/k_{4\text{-}OCH_3} = [(k_{4\text{-}CH_3}/k_{4\text{-}Cl})(k_{4\text{-}Cl}/k_{4\text{-}OCH_3}) + (k_{4\text{-}CH_3}/k_{4\text{-}H})(k_{4\text{-}H}/k_{4\text{-}OCH_3})]/2$.

xanthene] (**12**) and isomerizes to 3-carbomethoxyspiro[[2]-pyrazoline-5,9′-xanthene] (**13**). Methyl acrylate reacts much more rapidly with **1** than with 9-diazofluorene (see **61** and Experimental Section). The greater nucleophilic reactivity[5] of **1** presumably arises from the electron donation from its γ-pyranyl moiety into its diazo function.

Styrenes (**14**) do react rapidly (0.5–2 h, 25 °C) with **1** with evolution of nitrogen to give spiro[2-arylcyclopropane-1,9′-xanthenes] (**17**, eq 1). To determine whether **1** is behaving as a nucleophile or electrophile, its relative reactivities with electronegatively and electropositively substituted styrenes



14a, Z = 4-OCH_3; **14b**, Z = 3-Br
14c, Z = 4-Br; **14d**, Z = 4-H
14e, Z = 4-CH_3; **14f**, Z = 4-Cl

(1)

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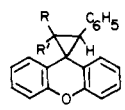
17a, Z = 4-OCH_3; **17b**, Z = 3-Br
17c, Z = 4-Br; **17d**, Z = 4-H
17e, Z = 4-CH_3; **17f**, Z = 4-Cl

(**14**) were investigated. The reactivities of **1** were determined by competition between two styrenes, each in tenfold excess; the molar product ratios are thus the reactivity ratios. The adducts, cyclopropanes **17**, are stable to workup and were analyzed by ^{1}H NMR or/and by column chromatography on silica gel.

The results of the reactivity study of **1** with **14** are summarized in Table I. Addition of **1** to a styrene is accelerated by electron-withdrawing and retarded by electron-donating substituents. The rate data correlate (Figure 1) with a Hammett linear free energy relationship using σ values. The ρ for reaction is +0.97 with a standard deviation of 0.051. The small positive ρ value signifies that some carbanionic character is acquired by the α carbon of a styrene in a transition state such as **15** and that **1** is functioning as a nucleophile. It is not yet known whether pyrazolines **16** are intermediates in reactions of **1** and **14**; pyrazoline **11** is indeed produced from **1** and methyl acrylate, and diazomethane reacts as a nucleophile with styrenes (ρ = 0.90 in dioxane) to give isolable pyrazolines.[6] The facts that **1** reacts at 25 °C with (1) *cis*-propenylbenzene



18, R = CH_3; R′ = H
19, R = H; R′ = CH_3

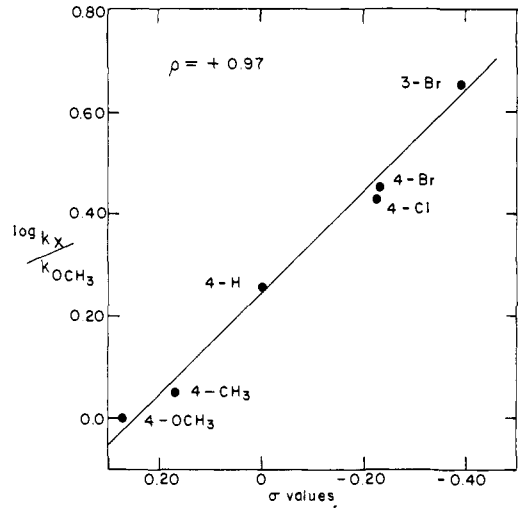
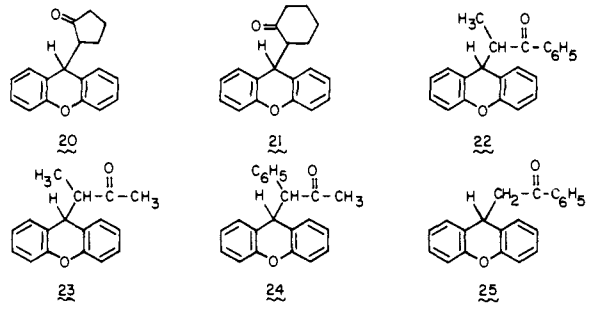


Figure 1. Log k_X/k_{OCH_3} vs. σ values for reactions of **1** with substituted styrenes (**14**).

to give spiro[(2-methyl-*cis*-3-phenylcyclopropane)-1,9′-xanthene] (**18**) and spiro[(2-methyl-*trans*-3-phenylcyclopropane)1,9′-xanthene] (**19**) in ~95/5 ratio (by ^{1}H NMR) and (2) *trans*-propenylbenzene to form **19** in >95% stereospecificity reveal the intimate nature of the dipolar addition reactions of **1** with various styrenes including loss of nitrogen.[7]

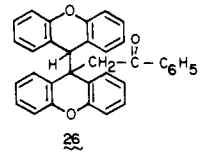
Reactions of **1** with ketones at elevated temperatures were then investigated. Addition of **1** to refluxing cyclopentanone, to cyclohexanone at 125 °C, and to ethyl phenyl ketone in refluxing benzene results in 2-(9-xanthyl)cyclopentanone (**20**, 79%), 2-(9-xanthyl)cyclohexanone (**21**, 80%), and 1-phenyl-2-(9-xanthyl)-1-propanone (**22**, 40%), respectively. 9-Diazoxanthene (**1**) reacts (~80 °C) with 2-butanone and phenyl acetone at their secondary rather than their primary α positions to give 3-(9-xanthyl)-2-butanone (**23**, 46%) and 1-phenyl-1-(9-xanthyl)-2-propanone (**24**, 76%), respectively. It is



20 **21** **22**

23 **24** **25**

not yet clear whether the above reactions occur by carbenic insertion of **2** into the ketones, by 9-xanthyl cationic processes initiated by the enols of the ketones,[8] or by more obscure mechanistic processes. Products of Wolff reactions of the ketones with **1** were not obtained. Decomposition of **1** in methyl phenyl ketone is of interest in that, along with 1-phenyl-2-(9-xanthyl)ethanone (**25**, 16%), 9-(2-phenyl-2-ethanonyl)-9′-bixanthyl (**26**, 17%) is produced. Bixanthyl **26** is presumably



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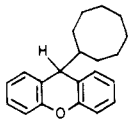
formed by insertion of **2** into **25**.

Investigations of **2** as derived thermally and photochemically from **1** were then initiated. Decomposition of **1** in cyclooctane at 145 °C results in C–H insertion to give 9-cyclooctylxanthene

(**27**, >54%). Cumene reacts with **2** at 140 °C to yield 9-(1-methyl-1-phenylethyl)xanthene (**28**, 61%), bixanthyl (**29**, 5%),



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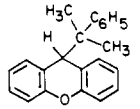

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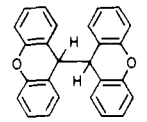

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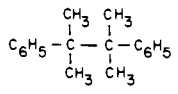
and 9-xanthone (5%);[9] bicumyl (**30**) was not detected. Toluene is converted by **2** at 110 °C to 9-benzylxanthene (**31**, 57%), 9-benzyl-9-(9′-xanthyl)xanthene (**32**, 25%), **29** (3%), 9-xanthone (4%),[9] and 9-xanthone azine (7%). Bixanthyl **32** is presumably produced by reaction of **31** and **2**. 1,2-Diphenylethane is not obtained.



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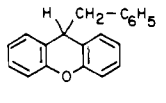

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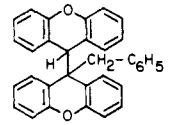

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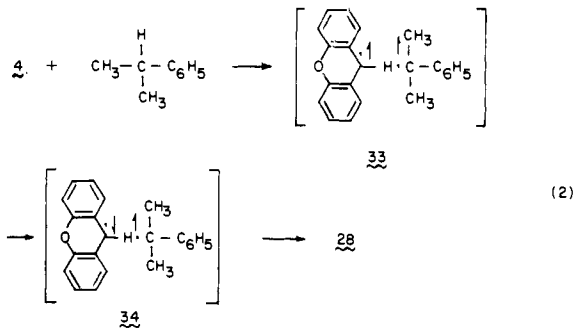
There are a number of points of note in the above experiments. First **2** is an effective and discriminating carbene in reactions with various C–H bonds. In competitive reactions of **2** at 88 °C with large excesses of cumene and toluene, the statistically corrected ratio of insertion into α-H of cumene and toluene is 15:1. Secondly, the marked ability of **2** to insert into α-H of cumene and into **31** rather than toluene is inconsistent with a carbene of considerable nucleophilicity.[10] Thirdly, formation of **29** is indicative of a triplet process, at least in part, in which **2** abstracts hydrogen to give 9-xanthyl and counterradicals. Diffusion of 9-xanthyl from its counterradical and dimerization will account for **29**. Fourthly, it is not clear whether **2** undergoes direct C–H insertion as a singlet (**3**) or/and as a triplet (**4**) by abstraction–recombination involving intimate radical pairs and spin inversion (eq 2).



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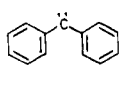
(2)

It is of interest to compare the abilities of diphenylmethylene (**35**), 9-anthronylidene (**36**), and **2** to abstract hydrogen from toluene. Reaction of **35** and toluene gives 1,1,2,2-tetraphenylethane (**37**, 35%),[11] and **36** yields 10-benzyl-9-anthrone



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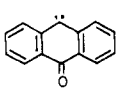

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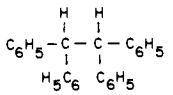

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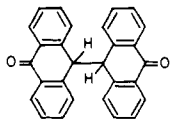
(12%) and 10,10′-bianthronyl (**38**, 56%).[12] The principal reactions of **2** and toluene, however, are insertion to yield **31** and **32**. The reasons for the differences in behavior of **35**, **36**, and **2** might be related to the ease of formation of the radicals resulting from hydrogen abstraction by the carbenes as triplets. Thus **36** yields the relatively stabilized 9-anthronyl radical (**39**) which separates from the benzyl radical and dimerizes. The conversion of **35** by toluene to the diphenylmethyl radical (**40**) and then **37** therefore parallels the behavior of **36**. Reaction



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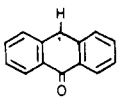

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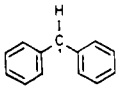

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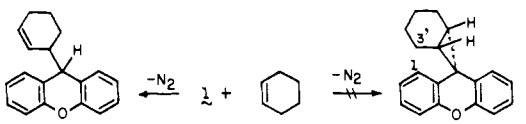
of **2** with toluene thus involves a relatively more intimate process.

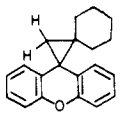
The reactions of carbene **2** with olefins which might undergo carbon hydrogen attack and/or addition to their carbon–carbon double bonds were then investigated. Thus thermolysis of **1** in cyclohexene at 78 °C results in selective C–H insertion to give 9-(2-cyclohexenyl)xanthene (**41**, 46%),[13] 9-xanthone



41 **42**

(3)

(21%), and bixanthylene (6%); **42** and isomers other than **41** were not detected. Under these conditions methylenecyclohexane and 1,1-dimethoxyethylene react with **2** to yield dispiro[cyclohexane-1,1′-cyclopropane-2′,9″-xanthene] (**43**, 71%) and spiro[2,2-dimethoxycyclopropane-1,9′-xanthene] (**44**, 40%), respectively. The inability of **2** to add to cyclohexene to form **42** is somewhat surprising and possibly stems from steric



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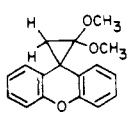

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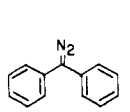
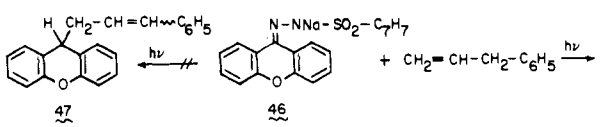


45

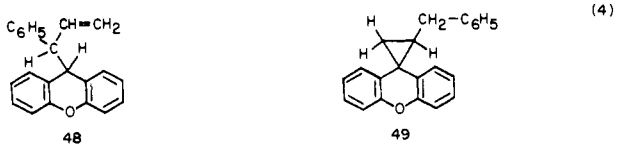
impediment in **42** at C_1-H and C_3-H. Steric restraint of addition to methylenecyclohexane is presumably less than for cyclohexene.

Certain carbenes, presumably as triplets, have the ability to abstract hydrogen from allyl positions in olefins and then allow double-bond migration or carbon-skeleton rearrangement before recombination. Thus photolysis of diphenyldiazomethane (**45**) in 3-methyl-1-butene yields 2-methyl-5,5-diphenyl-2-pentene (33%) along with 3-(diphenylmethyl)-3-methyl-1-butene (15%); 1,1-diphenyl-2-(2-propyl)cyclopropane (52%) also results from addition of **35** to the carbon–carbon double bond of 3-methyl-1-butene.[14] A study was then made of reactions of **2** with olefins which might give information with respect to the details of possible abstraction–recombination processes.

Photolysis (450-W high-pressure Hanovia mercury arc through Pyrex) of the sodium salt (**46**) of 9-xanthone tosylhydrazone in allylbenzene (eq 4) at 23 °C results in 9-(1-phenyl-2-propenyl)xanthene (**48**, 85%) and spiro[2-benzyl-



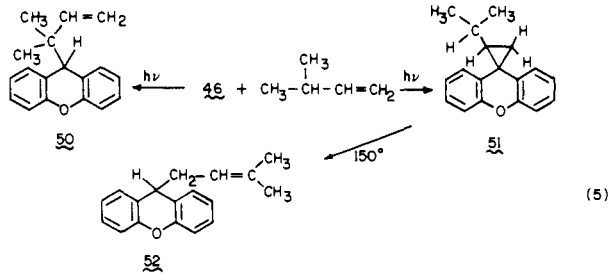
47 **46**



48 **49**

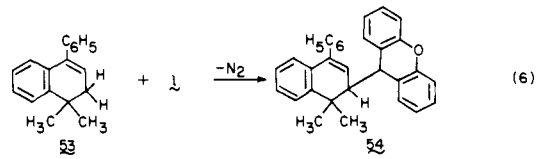
(4)

cyclopropane-1,9′-xanthene] (**49**, <15%); 9-(3-phenyl-2-propenyl)xanthenes (**47**), derived by migration of a double bond, are not formed. Irradiation of **46** in 3-methyl-1-butene at ~5 °C (eq 5) yields 9-(1,1-dimethyl-2-propenyl)xanthene



(5)

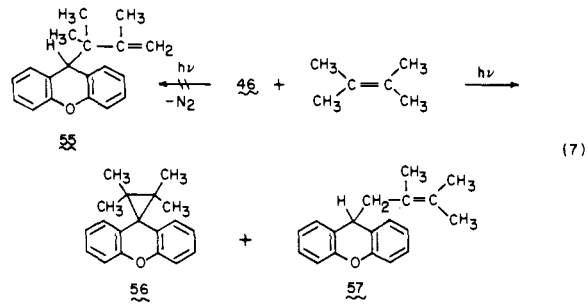
(**50**, 40%) and spiro[2-(2-propyl)cyclopropane-1,9′-xanthene] (**51**, 19%) along with **29** (4%). 9-(3-Methyl-2-butenyl)xanthene (**52**) is not obtained but is formed by GLC of **51** at 150 °C (Dow silicone 11).[15] Thus reactions of photochemically generated **2** with allylbenzene and 3-methyl-1-butene reveal that (1) insertion occurs readily on allylic C–H, (2) products derived by double bond rearrangement are not formed (as is the case with **35**), and (3) carbon–carbon double bonds undergo addition to give cyclopropanes. Further, thermal de-



(6)

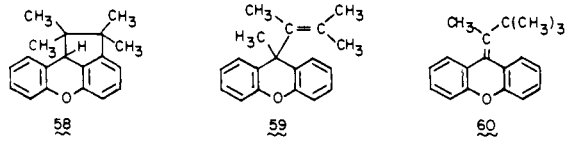
composition of **1** in 1,2-dihydro-1,1-dimethyl-4-phenylnaphthalene (**53**) gives 1,2-dihydro-1,1-dimethyl-2-(9-xanthyl)-4-phenylnaphththalene (**54**, eq 6). Insertion of **2** into allylic C–H bonds is thus highly specific and is suggestive of a singlet (**3**) process. If indeed allylic C–H insertion occurs via triplet **4**, H abstraction, spin inversion, and recombination have to be intimate (highly caged), possibly because of polar effects in radical pairs, to occur without rearrangement of the olefinic center.

Diphenylmethylene (**35**) is reported to react with 2,3-dimethyl-2-butene to give 2,3-dimethyl-5,5-diphenyl-2-pentene (66%) and 3-(diphenylmethyl)-2,3-dimethyl-1-butene (34%); 1,1,2,2-tetramethyl-3,3-diphenylcyclopropane is presumably not formed because of steric factors.[14] A comparison of **35** and **2** and 2,3-dimethyl-2-butene has now been made. Thus photolysis of **46** in 2,3-dimethyl-2-butene (eq 7) gives



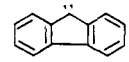
(7)

spiro[2,2,3,3-tetramethylcyclopropane-1,9′-xanthene] (**56**, 80%) and 9-(2,3-dimethyl-2-butenyl)xanthene (**57**, 20%); **55**, the product of C–H abstraction, double-bond isomerization, and recombination, is not produced. The high yield of **56**, and the lack of formation of 1,1,2,2-tetramethyl-3,3-diphenylcyclopropane from **35** and 2,3-dimethyl-2-butene, apparently indicate that **2** is much less sterically encumbered than **35** or/and reacts by a different mechanism than does **35**. Cyclopropane **56** rearranges at 200 °C to 2,10b-dihydro-1,1,2,2-tetramethyl-1*H*-benz[*e*]indeno[7,1-*bc*]pyran (**58**); the isomers

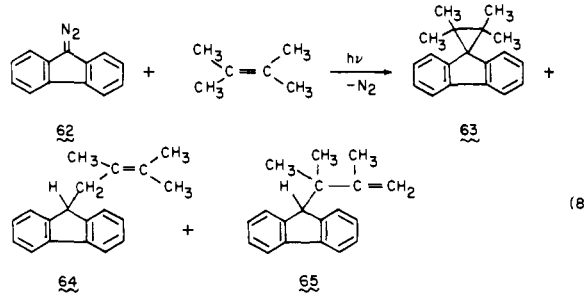


9-(1,2-dimethyl-1-propenyl)-9-methylxanthene (**59**)[16] and 9-(1,2,2-trimethylpropylidene)xanthene (**60**) are not formed.

The behavior of 9-fluorenylidene (**61**) was then compared



with **35** and **2** in reactions with 2,3-dimethyl-2-butene. Thus photolysis of 9-diazofluorene (**62**) in the olefin (eq 8) results



(8)

in addition to the double bond to form spiro[2,2,3,3-tetramethylcyclopropane-1,9′-fluorene] (**63**, 68%); C–H attack yields 2,3-dimethyl-2-butenyl-9-fluorene (**64**, 22%) and 1,1,2-trimethyl-2-propenyl-9-fluorene (**65**, 10%). The behavior of **61** is thus partly similar to **2** and **35**. Carbene **61** is more indiscriminate than **2** but allows double bond migration to give **65**.

A study was then initiated to determine whether **2** functions as a nucleophile or an electrophile in reactions with styrenes (**14**) to give cyclopropanes **17**.[17] Investigation of **2** as generated by thermolysis of **1** in **14** at 80 °C was unsatisfactory because of apparent competitive dipolar reactions as in eq 1 and the extensive conversion of **1** to 9-xanthone azine. Photolysis of **1** and **14** in ethyl ether at −30 °C stops formation of **17** by thermal dipolar addition; conversion of **1** to 9-xanthone azine is, however, still a major process. Generation of **2** was finally effected advantageously by photolysis (450-W high-pressure Hanovia mercury arc through Pyrex) of the sodium salt (**46**) of 9-xanthone tosylhydrazone suspended in mixtures of **14** in anhydrous ethyl ether at ~−25 °C. The advantages of this latter method follow: (1) **46** responds rapidly to photolysis, (2) thermal dipolar addition of **1** to **14** is insignificant at the low temperatures during the short irradiation periods (see Experimental Section), and (3) the concentration of **1** generated is small at all times and thus conversion to 9-xanthone azine is greatly reduced.

The competitive reactivities of **2** as derived from irradiation of **46** at ~−25 °C for 15–60 min were then investigated with pairs of styrenes, each in excess (10 equiv).[17] The reactivity of a styrene was determined relative to *p*-methoxystyrene (**14a**) because of the ease and efficiency of column chromatography. A mixture of spiro[2-(4-methoxyphenyl)cyclopropane-1,9′-xanthene] (**17a**) and spiro[2-phenylcyclopropane-1,9′-xanthene] (**17d**) was photolyzed in ethyl ether at 20 °C for 90 min, separated on silica gel, and isolated with little loss and minor change in the ratio of the initial materials.[18] It is concluded that photochemical alteration of the various cyclopropanes at −25 °C is insignificant.

The study of the relative reactivities of **2** with **14** is summarized in Table II. The reactivity order of a substituted styrene is *m*-Br > *p*-Br > *p*-OCH_3 > *p*-Cl > *p*-CH_3 > H. Figure 2 reveals that there is no linear free energy correlation of the relative reactivities with σ values.[19] There is also no correlation with σ^+ constants.[19] On the basis that *p*-methoxy- and *p*-methylstyrenes convert faster than styrene to cyclopropanes, it is clear, however, that **2** or its excited precursor is not behaving predominantly as a nucleophilic reactant.[10] The facts

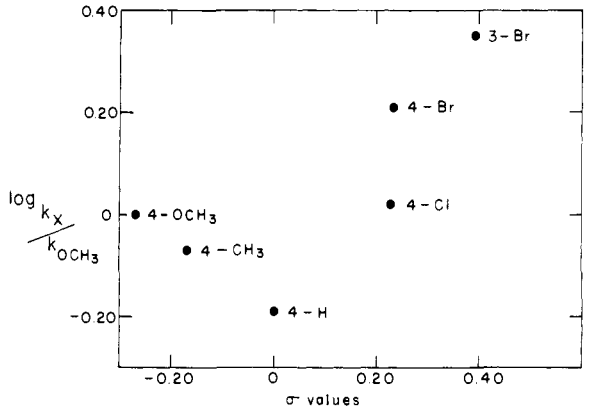
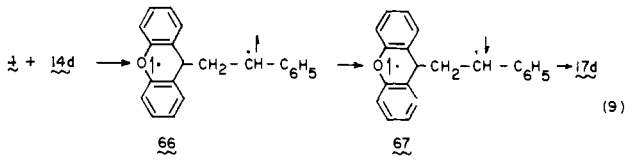


Figure 2. Log k_X/k_{OCH_3} vs. σ values for reactions of **2** with substituted styrenes (**14**).

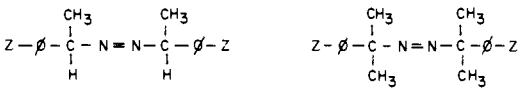
that *m*- and *p*-bromo- and *p*-chlorostyrenes react more rapidly than styrene also argue against reaction of the olefins with a simple electrophilic reagent.[17,19]

An interpretation consistent with the results, that either electron-withdrawing or electron-donating groups accelerate the reactions, is addition of **2** as a diradical (**4**) as in eq 9. This



(9)

explanation agrees with observations that both electronegative and electropositive substituents can stabilize free radical transition states of the benzyl type in which polar effects are unimportant.[20] Thus the substituent effects on the first-order thermal decomposition of 1,1′-diphenyl-1,1′-azoethanes (**68**) in cumene at 95 °C are *p*-Cl > *m*-Cl > *p*-CH_3O > *p*-CH_3 > H;[21] those for thermal decomposition of disubstituted azocumenes (**69**) in toluene at 42.8 °C are *p*-Cl > *m*-Cl > *p*-CH_3 > H.[21] Similar accelerating substituent effects have been reported for thermal decomposition of benzyl bromides to benzyl radicals and bromine atoms[22] and for rearrangement of *N*-arylidene-2,2-diphenylcyclopropylamines to 1-pyrrolines.[23]



68 **69**

There are alternate interpretations of the kinetic results of photochemical reactions of **1** with **14** to give cyclopropanes **17**. An interesting possibility is that the cyclopropanes **17** are formed by competitive addition of **2** as an electrophilic singlet and photochemically excited **1** (**1***) as a nucleophile. Thus the greater reactivities of *p*-methoxy- and *p*-methylstyrenes than styrene might arise from faster addition of **2** than **1*** whereas the enhanced reactivities of *m*- and *p*-bromo- and *p*-chlorostyrenes might stem from preferential reaction of **1***. To obtain further information with respect to the photolytic behavior of **1** with styrenes, the stereochemistries of additions to *cis*- and to *trans*-propenylbenzenes were determined. Thus photolysis of **46** at ~25 °C (2.0-2.5 h) converts *cis*-propenylbenzene stereoselectively to **18** (75-80%) and **19** (20-25%) whereas *trans*-propenylbenzene yields **19** (~95%) near stereospecifically.[24] During photolysis neither *cis*- nor *trans*-propenylbenzenes nor **18** and **19** isomerize. That **18** is not formed stereospecifically from *cis*-propenylbenzene is consistent with reaction of triplet **4**, at least in part, with the double bond of the olefin. The supposition that **2** reacts (in part) as **4** correlates also with decomposition of **1** in oxygen to give 9-xanthone.[9] It is emphasized, however, that the present experiments do not exclude addition of **2** as both **3** and **4** to the double bonds of various styrenes.[25,26]

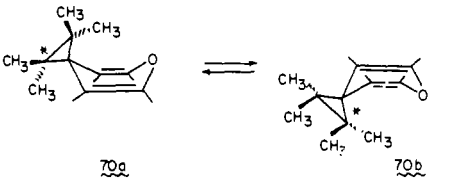
Table II. Relative Rate Constants for Addition of 9-Xanthylidene (**2**) to Substituted Styrenes (**14**)

substituent	$k_{sub}{}^a/k_{OCH_3}$	substituent	$k_{sub}{}^a/k_{OCH_3}$
4-H	0.64	4-OCH_3	1.00
4-CH_3	0.85	4-Br	1.68
4-Cl	0.97	3-Br	2.23

[a] The values are averages of two experiments. The results from individual experiments are included in the Experimental Section.

Conformational Isomerization of 56 and 51. The ^1H NMR of **56** and **51** are revealing. Cyclopropane **56** at ambient probe temperature (~30 °C) displays well-resolved aromatic splitting but the aliphatic region appears as a broad, ill-defined multiplet. Cooling **56** ($CDCl_3$, −30 °C) produces two singlets (δ 1.65 and 0.65) for the methyl groups integrating for six protons each. Heating the sample from −30 to 60 °C causes the singlets to broaden, merge, and finally sharpen to a well-defined singlet integrating for 12 protons (δ 1.2).

These phenomena are interpretable on the basis that 9*H*-xanthyl ring systems exist in boat conformation[27] which normally undergo rapid interconversion, e.g., eq 10.[28] With **56**



70a **70b**

(10)

interconversion of the two boat forms is slowed because of steric interference of the methyl groups with the aromatic hydrogens in peri positions 1 and 8. Thus at −30 °C the two boat forms are not interconverting and an equal mixture of **70a** and **70b** is present giving rise to two singlets for the methyl groups. One singlet (δ 0.65) is for the two methyl groups endo to the aromatic rings; the other (δ 1.65) is for the two methyl groups which are exo. At 60 °C interconversion of **70a** and **70b** is rapid on the ^1H NMR time scale and the methyls become equivalent, thus producing a single resonance (δ 1.2). Nonplanar conformers have been presumed to account for the ^1H NMR of spiro[2-cyanocyclopropane-1,9′-xanthene][2a] and **17d**;[2a] such conformers have been frozen out in 9-alkylidene-10,10-dimethyl-9,10-dihydroanthracenes,[29] *cis*-2,3-dimethylspiro[cyclopropane-1,3′-(dibenzo[*a*,*d*]cycloheptene)],[30] and *cis*-2,3-dimethylspiro[cyclopropane-1,9′-(tribenzo[*a*,*c*,*e*]-cycloheptene)].[30]

The ^1H NMR of **51** shows two broad peaks (δ 0.58 and 0.97) superimposed over the cyclopropyl absorption (δ 0.4-1.9). There are two possible explanations for the nonequivalence of the methyl groups. First, **51** could be undergoing restricted ring inversion similar to **56**, and/or, secondly, the methyl groups are attached to a carbon adjoining an asymmetric center.[31] A ^1H NMR temperature study of **51** shows that the methyl groups remain nonequivalent and essentially unaffected over a 250 °C temperature range (−120 °C, CS_2 to 130 °C, 1,2-dibromoethane). Thus restricted boat-boat interconversion does not account for the observed spectrum. The methyl groups are therefore nonequivalent because of molecular asymmetry.[32]

Experimental Section

9-Diazoxanthene (1).[1b,33] 9-Diazoxanthene (**1**) was prepared by oxidation of 9-xanthone hydrazone in dimethylformamide with lead tetraacetate at −78 °C according to the method of Holton.[33a] 9-

Diazoxanthene (**1**) is a blue-green solid [IR (KBr) 3.2, 4.9, 6.7, 6.9, 7.7, 7.9, 8.75, 9.2, 11.85, and 13.5 μ] which may be stored at −25 °C for several months but if left at room temperature for a few hours it converts to 9-xanthone azine. 9-Diazoxanthene is sensitive to light and to oxygen.

Bixanthylene Episulfide (5). 9-Xanthione was added slowly to **1** (100 mg, 0.475 mmol) in benzene (10 mL) until evolution of nitrogen ceased (5 min). Evaporation of the mixture yielded a green-white solid which on recrystallization from hexane gave **5** (161 mg, 86%) as white crystals: mp 203-204 °C; IR (KBr) 6.2, 8.0, 9.1, 9.65, 11.15, 12.8, and 13.35 μ; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 7.35-7.6 (m, 4 H) and 6.7-7.1 (m, 12 H); mass spectrum *m/e* 392 (M^+, 22%), 360 ($M^+ - 32$, 100%). Anal. ($C_{26}H_{16}O_2S$) C, H, O, S.

4,5-Dicarbomethoxyspiro[3*H*-pyrazole-3,9′-xanthene] (6). Dimethyl acetylenedicarboxylate (338 mg, 2.38 mmol) in benzene (5 mL) was slowly added to a benzene solution (20 mL) of **1** (500 mg, 2.38 mmol). The reaction was exothermic and the color changed from green to yellow. After the mixture was concentrated at reduced pressure and Skellysolve B added, yellow crystals (485 mg) of **6** were obtained. Cooling the filtrate gave additional crystals of **6** (200 mg). The total of **6** was 685 mg (82%): mp 128.5-129.5 °C dec; IR (KBr) 3.3, 5.7, 5.75, 6.1, 6.2, 6.35, 6.8, 7.0, 7.9, 8.95, 10.2, and 13.15 μ; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 6.8-7.5 (m, 6 H, aromatic), 6.55 (d, 2 H, aromatic), 4.1 (s, 3 H, OCH_3), and 3.6 (s, 3 H, OCH_3). Anal. ($C_{19}H_{14}N_2O_5$) C, H, N.

Photolysis of 6. A solution of **6** (429 mg, 2.3 mmol) in deoxygenated benzene (40 mL) was photolyzed through Pyrex with a high-pressure Hanovia lamp. After 20 min 90% of the theoretical amount of nitrogen had evolved and the photolysis was terminated. The yellow solution was concentrated and chromatographed on silica gel. Elution with benzene gave either dimethyl 2*H*-benz[*e*]indeno[7,1-*bc*]pyran-1,2-dicarboxylate (**8**) or the tautomer, dimethyl 10b*H*-benz[*e*]indeno[7,1-*bc*]pyran-1,2-dicarboxylate (**9**, 226 mg, 57%). A pure sample was obtained by recrystallization from Skellysolve B followed by an ethyl ether wash: mp 142-144 °C; IR (KBr) 3.3, 5.7, 5.8, 6.1, 6.2, 6.4, 6.9, 8.0, 8.55, 9.0, and 13.0 μ; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 9.5 (d, 1 H, J_{ab} = 8, J_{ac} = 2 Hz, aromatic), 6.9-7.6 (m, 6 H, aromatic), 4.95 (s, 1 H, methine), 3.88 (s, 3 H, OCH_3), and 3.7 (s, 3 H, OCH_3); mass spectrum *m/e* 322 (M^+, 27%), 263 (100%), and 204 (27%).

Thermolysis of **6** gave similar results, although the yield was considerably less.

Reaction of 1 and Methyl Acrylate. A cold (−78 °C) solution of methyl acrylate (5 mL) and **1** (200 mg, 0.96 mmol) in ether (10 mL) was allowed to warm slowly. At ~−20 °C, the green color of the mixture faded to pale yellow (there was no gas evolution). Upon warming (5 °C) the **11** formed, gas began to evolve slowly and continued for ~30 min at which time the solution was at room temperature. The residue upon evaporation of the solvents gave a mixture of 3′-carbomethoxyspiro[[2]pyrazoline-5,9′-xanthene] (**13**) and spiro[2-carbomethoxycyclopropane-1,9′-xanthene] (**12**) in near-quantitative yield whose ^{1}H NMR indicated it to be in a ratio of 1.65:1. Pyrazoline **13** was isolated by treating the crude residue with methylene chloride and then hexane and heating until enough methylene chloride was removed to precipitate **13**. After several recrystallizations in a similar manner an analytical sample of **11** was obtained as off-white crystals (mp 174.5-176 °C, gas evolution): IR (KBr) 2.95 (N-H), 5.85, 6.45, 8.0, 8.8, 9.6, 12.45, and 13.15 μ; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 6.9-7.6 (m, 9 H, aromatic + NH), 3.8 (s, 3 H, methoxy), and 3.35 (s, 2 H, methylene).

Cyclopropane **12** was produced in near-quantitative yield when **1** was added to hot (80 °C) methyl acrylate. Several recrystallizations from hexane gave white crystals: mp 109-110 °C; IR (KBr) 5.8, 6.85, 7.9, 8.5, 10.7, 13.3, and 13.85 μ; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 6.8-7.4 (m, 8 H, aromatic), 3.4 (s, 3 H, methoxy), and 1.8-2.6 (m, 3 H, cyclopropyl). Anal. ($C_{17}H_{14}O_3$) C, H.

Spiro[2-carbomethoxycyclopropane-1,9′-fluorene]. A solution of methyl acrylate (5 mL) and **62** (200 mg, 1.04 mmol) in ether (10 mL) was stirred at 23 °C for 30 min. Nitrogen was evolved after the first 5 min and continued for ~15 min. The yellow solution was vacuum evaporated (25 °C) and ^{1}H NMR analysis revealed nearly pure spiro[2-carbomethoxycyclopropane-1,9′-fluorene]. Recrystallization from hexane yielded white crystals: mp 98.5-99.5 °C; IR (KBr) 3.25, 3.35, 5.75, 6.95, 8.5, 10.6, 13.1, and 13.5 μ; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 6.8-7.4 (m, 8 H, aromatic), 3.55 (s, 3 H, methoxy), and 1.9-2.85 (m, 3 H, cyclopropyl). Anal. ($C_{17}H_{14}O_2$) C, H.

Preparation and Characterization of Spiro[2-arylcyclopropane-1,9′-xanthenes] (17). To **1** (100-200 mg) was added the freshly distilled substituted styrene (1-2 mL). The green solution was stored for 1-2 h, whereupon nitrogen evolved and the solution became yellow. Excess styrene was removed under reduced pressure (~0.3 mm, 40-80 °C) and the residue was chromatographed on silica gel-hexane. The following products are white or off-white crystalline solids which are not amenable to GLC analysis:

Spiro[2-(4-methoxyphenyl)cyclopropane-1,9′-xanthene] (17a): mp 98.5-99.5 °C; IR (KBr) 3.5, 6.9, 8.0, 9.65, 11.25, 11.85, and 13.3 μ; ^{1}H NMR (CCl_4, 100 MHz) δ 6.6-7.1 (m, 8 H, aromatic), 6.3-6.6 (m, 3 H, aromatic), 6.1 (d, 1 H, aromatic), 3.6 (s, 3 H, methoxy), and 1.8-2.4 (m, 3 H, cyclopropyl). Anal. ($C_{22}H_{18}O_2$) C, H.

Spiro[2-(3-bromophenyl)cyclopropane-1,9′-xanthene] (17b): mp 127.5-129 °C; IR (KBr) 6.9, 7.9, 10.65, 11.25, 12.85, and 13.25 μ; ^{1}H NMR (CCl_4, 100 MHz) δ 6.5-7.4 (m, 11 H, aromatic), 6.3 (d, 1 H, aromatic), and 1.9-2.4 (m, 3 H, cyclopropyl). Anal. ($C_{21}H_{15}BrO$) C, H.

Spiro[2-(4-bromophenyl)cyclopropane-1,9′-xanthene] (17c): mp 149.5-150 °C; IR (KBr) 3.3, 7.95, 9.3, 9.9, 11.35, 12.0, 12.4, and 13.25 μ; ^{1}H NMR ($CDCl_3$, 100 MHz) δ 6.5-7.4 (m, 11 H, aromatic), 6.3 (d, 1 H, aromatic), and 1.9-2.4 (m, 3 H, cyclopropyl). Anal. ($C_{21}H_{15}BrO$) C, H.

Spiro[2-phenylcyclopropane-1,9′-xanthene] (17d): mp 105.5-107 °C; IR (KBr) 3.2, 6.85, 7.85, 11.2, 13.1, 13.35, and 14.25 μ; ^{1}H NMR (CCl_4, 100 MHz) δ 6.3-7.1 (m, 12 H, aromatic), 6.1 (d, 1 H, aromatic), 2.3 (t, 1 H, cyclopropyl), and 2.0 (m, 2 H, cyclopropyl). Anal. ($C_{21}H_{16}O$) C, H.

Spiro[2-(4-methylphenyl)cyclopropane-1,9′-xanthene] (17e): mp 116.5-117.5 °C; IR (KBr) 3.2, 3.35, 6.9, 7.9, 9.05, 10.7, 11.25, and 13.3 μ; ^{1}H NMR (CCl_4, 100 MHz) δ 6.4-7.1 (m, 11 H, aromatic), 6.1 (d, 1 H, aromatic), 2.2 (s, 3 H, methyl), and 1.9-2.4 (m, 3 H, cyclopropyl). Anal. ($C_{22}H_{18}O$) C, H.

Spiro[2-(4-chlorophenyl)cyclopropane-1,9′-xanthene] (17f): mp 116-117 °C; IR (KBr) 6.69, 8.0, 9.05, 9.85, 11.05, 11.9, 12.35, and 13.55 μ; ^{1}H NMR (CCl_4, 100 MHz) δ 6.3-7.3 (m, 11 H, aromatic), 6.2 (d, 1 H, aromatic), and 1.8-2.4 (m, 3 H, cyclopropyl). Anal. ($C_{21}H_{15}ClO$) C, H.

Competitive Dipolar Reactivities in Reactions of 9-Diazoxanthene (1) with Styrenes (14). A. 4-Methylstyrene (14e) vs. Styrene (14d). Freshly distilled **14d** (1.037 g, 10 mmol) and **14e** (1.183 g, 10 mmol) were mixed with **1** (100 mg, 0.48 mmol) at 22-24 °C. After 1.5 h the color of the mixture had changed from green to yellow and nitrogen evolution had ceased. The excess styrenes were removed in vacuo at ~50 °C and the residue was chromatographed on silica gel using hexane as developer. Polar colored products were formed in minor quantities and adhered tightly to the silica gel column. The cyclopropane products chromatographed without complication[34] but could not be separated. The mixture of **17d** and **17e** was removed from the column and analyzed by ^{1}H NMR methods as follows. The ratio of the integrated ^{1}H NMR of the cyclopropyl and methyl regions (δ 1.9-2.4) to that of the aryl (phenyl and xanthyl) protons was obtained. This ratio was then compared to that of standard ratios obtained experimentally from known mixtures of pure samples of the respective products. The ratios of the cyclopropanes formed from **14e** and **14d** in two experiments were 0.537 and 0.585, respectively, with an average of 0.561.

B. 4-Methylstyrene (14e) vs. 4-Chlorostyrene (14f). Freshly distilled **14f** (1.381 g, 10 mmol) and **14e** (1.186 g, 10 mmol) were mixed with **1** (100 mg, 0.48 mmol) at 22-24 °C. The reaction procedure, workup, and product analysis were as in the previous experiments. The ratios of cyclopropanes (**17e** and **17f**) from **14e**/**14f** were 0.469 and 0.449, respectively (0.459 average).

C. 4-Methoxystyrene (14a) vs. Styrene (14d). To a freshly distilled mixture of **14a** (1.34 g, 10 mmol) and **14d** (1.04 g, 10 mmol) was added **1** (100 mg, 0.48 mmol). After 2 h the styrenes were removed in vacuo and ^{1}H NMR integration of the crude reaction mixture (OCH_3 singlet at δ 3.6 vs. the cyclopropyl region) revealed that the ratio of cyclopropanes (**17a** and **17d**) from **14a**/**14d** was 0.613.

In a separate experiment employing the same quantities of reactants and the conditions above, the products were separated on silica gel. Hexane eluted **17d** (62 mg, 67%) as derived from **14d**; carbon tetrachloride-hexane (50/50) eluted **17a** (34 mg, 33%) as derived from **14a**. The ratio of reactivity of **14a**:**14d** is 0.492; the average reactivity in the two experiments is 0.553.

D. 4-Methoxystyrene (14a) vs. 4-Chlorostyrene (14f). A mixture of **14a** (1.344 g, 10 mmol), **14f** (1.381 g, 10 mmol), and **1** (100 mg, 0.48

mmol) was stirred for 2 h at 22–24 °C. The styrenes were removed under vacuum (~80 °C) and the crude mixture was analyzed by integrating the ^{1}H NMR of the OCH_3 singlet at δ 3.6 relative to that of the cyclopropyl area; a ratio of reactivity of **14a** to **14f** of 0.370 was obtained. In an identical experiment quantitative separation of **17a** and **17f** was accomplished on silica gel (hexane followed by carbon tetrachloride); **17f** (78 mg, 73.5%) eluted first followed by **17a** (28 mg, 26.5%), ratio of 0.361. The average ratio of **17a**:**17f** in the two experiments is 0.366.

E. 4-Methoxystyrene (14a) vs. 3-Bromostyrene (14b). A solution of **14a** (637 mg, 4.75 mmol) and **14b** (863 mg, 4.75 mmol) was stirred with **1** (100 mg, 0.48 mmol) for 1 h. The excess styrenes were removed (0.5 mm, 80 °C) and the residue was chromatographed on silica gel. Hexane eluted **17b** (93 mg) as obtained from **14b**; **17a** (16 mg, from **14a**) was eluted with 1% ether. The ratio of product from addition to **14a** as compared to **14b** is 0.198. In a separate identical experiment a ratio of reactivity of **14a** to **14b** of 0.235 was found.

F. 4-Methoxystyrene (14a) vs. 4-Bromostyrene (14c). Reactions of **14a** (2.71 g, 20.2 mmol) and **14c** (3.70 g, 20.2 mmol) were effected with **1** (400 mg, 2.02 mmol) at 22–24 °C. After 1 h the styrenes were removed (0.5 mm, 80 °C) and the products were chromatographed (silica gel). Elution with hexane gave **17c** (352 mg) from **14c**; 0.5% ether-hexane removed **17a** (123 mg) derived from **14a**. The ratio of adduct from **14a** and **14c** is 0.408; the ratio from a similar experiment is 0.290.

2-(9-Xanthyl)cyclopentanone (20). A solution of **1** (500 mg, 2.4 mmol) in cyclopentanone (50 mL) was added dropwise to refluxing cyclopentanone (100 mL). After the cyclopentanone was evaporated, the residue was treated with hexane and filtered to yield 9-xanthone azine (33 mg, 7%). The filtrate was cooled and precipitated **20** (102 mg) as colorless crystals. The concentrated filtrate was chromatographed on silica gel employing increasing amounts of ether in hexane as solvent and gave bixanthylene (22 mg, 5%) and **20** (397 mg, total yield 79%): mp 91–92 °C; IR (KBr) 3.2, 3.3, 5.75, 6.75, 8.0, 11.25, 12.2, and 13.1 μ; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 6.8–7.9 (m, 8 H, aromatic), 4.75 (d, 1 H, 9-xanthyl), and 1.2–2.7 (m, 7 H, cyclopentyl). Anal. ($C_{18}H_{16}O_2$) C, H.

2-(9-Xanthyl)cyclohexanone (21). A solution of **1** (800 mg, 3.81 mmol) in nitrogen-purged cyclohexanone (50 mL, 0.51 mol) at 0 °C was added in 1 h to nitrogen-purged cyclohexanone at 125 °C. The yellow-orange solution was evaporated under reduced pressure and treatment with ethyl ether left a residue of 9-xanthone azine (~30 mg, 4%). The filtrate was concentrated and chromatographed on silica gel using Skellysolve B containing increasing amounts of benzene as eluent. The chromatographic products were xanthene (13 mg, 2%), bixanthylene (11 mg, 2%), **21** (851 mg, 80%), and 9-xanthone[9] (90 mg, 12%). Purification of **21** by recrystallization from Skellysolve B gave white crystals: mp 115.5–116.5 °C; IR (KBr) 3.35, 5.8, 6.3, 6.9, 8.0, 11.0, 11.25, and 12.3 μ; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 6.85–7.60 (m, 8 H, aromatic), 5.0 (d, 1 H, 9-xanthyl), and 0.9–2.15 (m, 9 H, cyclohexyl). Anal. ($C_{19}H_{18}O_2$) C, H.

1-Phenyl-2-(9-xanthyl)-1-propanone (22). To a refluxing nitrogen-purged benzene solution (150 mL) containing ethyl phenyl ketone (3 mL) was added **1** (500 mg, 2.4 mmol) in benzene (50 mL). The solution was concentrated at reduced pressure (0.5 mm) with heating. The residue, on treatment with hexane and filtration, yielded 9-xanthone azine (50 mg, 10%). Silica gel chromatography of the filtrate with increasing amounts of ether in hexane gave xanthone[9] (64 mg, 10%) and **22** (300 mg, 40%). Propanone **22** was purified via recrystallization from ethanol: mp 73–75 °C; IR (KBr) 3.2, 5.95, 6.9, 8.05, 10.3, 13.1, 13.25, and 14.1 μ; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 6.8–7.9 (m, 13 H, aromatic), 4.45 (d, 1 H, 9-xanthyl), 3.75 (m, 1 H, methine), and 1.05 (d, 3 H, methyl). Anal. ($C_{22}H_{18}O_2$) C, H.

3-(9-Xanthyl)-2-butanone (23). A mixture of **1** (500 mg, 2.4 mmol) in oxygen-free benzene (50 mL) was slowly added to an oxygen-free benzene solution (150 mL) of 2-butanone (3 mL). The mixture was evaporated at reduced pressure to leave a residue which when triturated with hexane gave 9-xanthone azine (101 mg, 21%). The filtrate was chromatographed on silica gel and developed with an ether (1–2%)-hexane mixture to yield **23** as an oil on elution: IR (NaCl) 3.35, 5.8, 8.0, 8.9, 9.0, 11.15, and 13.15 μ; ^{1}H NMR (CCl_4, 60 MHz) δ 7.1–7.6 (m, 8 H, aromatic), 4.05 (d, 1 H, 9-xanthyl), 2.45 (m, 1 H, methine), 1.7 (s, 3 H, α-CH_3), and 0.8 (d, 3 H, CH_3); mass spectrum calcd *m/e* 252.115 021 80, found 252.114 421 55.

1-Phenyl-1-(9-xanthyl)-2-propanone (24). A benzene solution (50 mL) of **1** (500 mg, 2.4 mmol) was slowly added to a refluxing oxygen-free mixture of phenylacetone (3 mL) and benzene (150 mL). After the mixture was concentrated in vacuo, the remaining oil (890 mg) was diluted with carbon tetrachloride and 9-xanthone azine (98 mg, 21%) remained. The carbon tetrachloride was removed and the residue treated with hexane, whereupon with trituration white crystals of **24** (465 mg) were isolated. The concentrated filtrate was chromatographed on silica gel using a 1–2% ether-hexane solvent system to give additional **24** (111 mg, a total yield of 76%): mp 114.5–115 °C; IR (KBr) 3.15, 5.75, 6.7, 6.8, 7.9, 9.6, 10.45, 12.9, 13.4, and 14.15 μ; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 6.5–7.5 (m, 13 H, aromatic), 4.7 (d, 1 H, 9-xanthyl), 3.8 (d, 1 H, methine), and 1.8 (s, 3 H, methyl). Anal. ($C_{22}H_{18}O_2$) C, H.

1-Phenyl-2-(9-xanthyl)ethanone (25) and 9-(2-Phenyl-2-ethanonyl)-9′-bixanthyl (26). A mixture of **1** (500 mg, 2.4 mmol) and nitrogen-purged benzene (50 mL) was added dropwise (1.5 h) to a refluxing nitrogen-purged solution of acetophenone (3 mL) in benzene (150 mL). The residue remaining, after solvent removal in vacuo, was treated with hexane and filtered to give xanthone azine (63 mg, 13%). The concentrated filtrate was chromatographed on silica gel by eluting with increasing amounts of ether in hexane to yield xanthene (22 mg, 5%), **25** (100 mg, 16%, mp 88–89 °C), acetophenone (95 mg), xanthone[9] (35 mg, 7%), and **26** (83 mg, 17%, mp 177–179 °C), respectively.

The spectral properties of **25** include IR (KBr) 5.9, 8.0, 8.2, 10.2, 13.2, and 14.65 μ; ^{1}H NMR (CCl_4, 60 MHz) δ 7.65–7.9 (m, 2 H, aromatic), 6.8–7.5 (m, 11 H, aromatic), 4.85 (t, 1 H, 9-xanthyl), and 3.3 (d, 2 H, methylene). Anal. ($C_{21}H_{16}O_2$) C, H.

The spectral properties of **26** are IR (KBr) 3.2, 5.9, 6.9, 8.0, 9.1, 10.0, 11.3, 13.3, and 14.6 μ; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 6.1–8.0 (m, 21 H, aromatic), 4.15 (s, 1 H, 9-xanthyl), and 4.05 (s, 2 H, methylene). Anal. ($C_{34}H_{24}O_3$) C, H.

9-Cyclooctylxanthene (27). Nitrogen-saturated cyclooctane (50 mL) containing **1** (500 mg, 2.38 mmol) was added (1 h) to refluxing nitrogen-purged cyclooctane (100 mL). After the cyclooctane was removed at reduced pressure, the semisolid residue was treated with Skellysolve B and filtered to leave 9-xanthone azine (~110 mg, 24%). Chromatography of the concentrated filtrate on silica gel, using increasing amounts of benzene in Skellysolve B, gave **27** (380 mg, 54%), bixanthylene (40 mg, 9%), and 9-xanthone (40 mg, 9%), respectively. Distillation (0.2 mm) of **27** yielded an analytically pure product: IR (NaCl) 3.4, 6.25, 6.35, 6.8, 6.9, 8.0, 9.0, 11.2, and 13.3 μ; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 6.8–7.35 (m, 8 H, aromatic), 3.8 (d, 1 H, 9-xanthyl), and 0.8–2.1 (m, 15 H, cyclooctyl). Anal. ($C_{21}H_{24}O$) C, H.

9-(1-Methyl-1-phenylethyl)xanthene (28). A solution of **1** (500 mg, 2.4 mmol) in cumene (50 mL) at 0 °C was dropped in 1 h into freshly distilled nitrogen-purged cumene (50 mL) at 140 °C. Upon removal of the cumene in vacuo, a residue was obtained which, when treated with Skellysolve B, precipitated 9-xanthone azine (~88 mg, 20%). Column chromatography of the concentrated filtrate on silica gel with increasing amounts of ethyl ether in Skellysolve B as developer afforded **28** (442 mg, 61%), bixanthyl (**26**, 20 mg, 5%), and 9-xanthone (45 mg, 10%). Several recrystallizations from hexane produced colorless needles of **28**: mp 87–88 °C; IR (KBr) 6.2, 6.3, 6.75, 6.9, 8.0, 8.9, 11.1, 13.2, and 14.25 μ; ^{1}H NMR (CCl_4, 60 MHz) δ 6.4–7.4 (m, 13 H, aromatic), 4.0 (s, 1 H, 9-xanthyl), and 1.2 (s, 6 H, CH_3). Anal. ($C_{22}H_{20}O$) C, H.

Reaction of 1 with Toluene. A toluene solution (50 mL) of **1** (800 mg, 3.8 mmol) at 0 °C was added in 1 h to refluxing nitrogen-purged toluene (100 mL). The yellow solution was concentrated in vacuo and chromatographed on silica gel. Elution with Skellysolve B gave 9-benzylxanthene (**31**, 621 mg, 57%), bixanthyl (**29**, ~20 mg, 3%), and 9-benzyl-9-(9′-xanthyl)xanthene (**32**, 230 mg, 25%). Methylene chloride-ethanol as eluent led to isolation of 9-xanthone (30 mg, 4%) and 9-xanthone azine (54 mg, 7%).

9-Benzylxanthene (**31**) is a white, crystalline compound which nearly melts at 71 °C, resolidifies, and then liquefies at 83–83.5 °C: IR (KBr) 3.25, 3.35, 6.2, 6.3, 6.75, 6.85, 8.0, 11.55, and 13.15 μ; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 6.6–7.4 (m, 13 H, aromatic), 4.2 (t, 1 H, 9-xanthyl), and 3.0 (d, 2 H, benzyl). Anal. ($C_{20}H_{16}O$) C, H.

Recrystallized **32** melts at 180–185 °C and thus was not analyzed. Its structural assignment is based on mass spectrum *m/e* 271 (M^+ − xanthyl, 33%), 181 (xanthyl, 100%), no parent at 452; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 6.4–7.4 (m, ~23 H, aromatic), 4.23 (s, 1 H, 9-xanthyl), and 3.75 (s, 2 H, benzyl); IR (KBr) 3.2, 3.3, 6.2, 6.3, 6.75, 6.85, 8.0, 9.1, 11.2, 13.3, and 14.3 μ.

Competitive Thermal Reactions of Toluene and Cumene with 9-Xanthylidene (2). 9-Diazoxanthene (**1**, 500 mg, 2.4 mmol) in nitrogen-purged benzene (50 mL) was added to a deaerated refluxing solution of benzene (100 mL) containing toluene (8.84 g, 96 mmol) and cumene (11.52 g, 96 mmol). The addition took 1.5 h and produced a yellow solution. Excess toluene and cumene were removed in vacuo (<1 mm) and the residue was analyzed via ^{1}H NMR. The statistically corrected ratio of insertion into cumene as compared to toluene is 15:1. Bicumyl (**30**) and 1,2-diphenylethane were not produced (on the basis of GLC).

9-(2-Cyclohexenyl)xanthene (41). To cyclohexene (150 mL, purified by distillation and column chromatography on Woelm neutral alumina, activity grade 1) was added **46** (2.1 g, 5.44 mmol, finely divided) and the suspension was purged with nitrogen for 15 min. After irradiation (Pyrex) with a high-pressure Hanovia lamp for 15 min the brown mixture was filtered and concentrated in vacuo to give a brown liquid (1.12 g). The filtered solid was washed with hot methylene chloride to leave 1.16 g of insoluble material (120%, calculated as sodium *p*-toluenesulfinate). Chromatography of the filtrate on silica gel gave **41** (459 mg, 32%) upon elution with hexane and **29** (40 mg, 4%) when eluted with 1% ether-hexane. 9-(2-Cyclohexenyl)xanthene (**41**) recrystallizes from hexane as white crystals; mp 97-97.5 °C; IR(KBr) 3.35, 6.2, 6.3, 6.75, 6.85, 8.0, 10.2, 11.2, and 13.3 μ; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 7.2 (broad s, 8 H, aromatic), 5.7 (s, 2 H, vinyl), 3.95 (d, 1 H, 9-xanthyl), 2.45 (m, 1 H, cyclohexenyl methine), and 1.0-2.1 (m, 6 H, cyclohexenyl). Anal. ($C_{19}H_{18}O$) C, H.

Thermal decomposition of **1** in refluxing cyclohexene produces **41** (46%), bixanthylene (6%), and 9-xanthone (21%).

Dispiro[cyclohexane-1,1′-cyclopropane-2′,9″-xanthene] (43). A mixture of **1** (850 mg, 4.05 mmol) in nitrogen-purged benzene (75 mL) was slowly added to methylenecyclohexane (2.4 g, 25 mmol) in refluxing nitrogen-purged benzene (100 mL). After refluxing for 30 min, the orange solution was evaporated in vacuo. The residue, upon treatment with hot Skellysolve B and filtration, gave xanthone azine (114 mg, 14%). The filtrate, after chromatography on silica gel using Skellysolve B as developer, yielded bixanthylene (15 mg, 2%), **43** (848 mg, 71%), and 9-xanthone (60 mg, 7%).[9] Recrystallization of **43** from hexane afforded white crystals: mp 134-135 °C; IR (KBr) 3.2, 3.35, 3.45, 6.9, 8.05, 8.2, 11.3, 12.2, and 13.3 μ; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 6.85-7.2 (m, 8 H, aromatic), 1.5 (s, 2 H, cyclopropyl), and 0.85-1.5 (m, 10 H, cyclohexyl). Anal. ($C_{20}H_{20}O$) C, H.

Spiro[2,2-dimethoxycyclopropane-1,9′-xanthene] (44). To 1,1-dimethoxyethylene (2.85 g, 32.4 mmol) in refluxing nitrogen-purged benzene (100 mL) was slowly added **1** (1.0 g, 4.8 mmol) in nitrogen-purged benzene (75 mL). After 1.5 h the solvent was removed in vacuo and hexane added to dissolve all but 9-xanthone azine (139 mg, 16%). The hexane-soluble material was chromatographed on silica gel and eluted with Skellysolve B containing increasing amounts of benzene. The chromatographic fractions consisted of crude esters (107 mg), 9-xanthone (200 mg, 25%),[9] **44** (430 mg, 40%), and unidentified products (103 mg). Spirocyclopropane **44** was recrystallized from Skellysolve B as white crystals: mp 130-131 °C; IR (KBr) 3.3, 6.2, 6.35, 6.75, 6.9, 7.95, 8.2, 8.6, 10.95, 11.25, and 13.35 μ; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 6.8-7.3 (m, 8 H, aromatic), 3.15 (s, 6 H, OCH_3), and 1.95 (s, 2 H, cyclopropyl). Anal. ($C_{17}H_{16}O_3$) C, H.

Sodium Salt (46) of 9-Xanthone *p*-Toluenesulfonylhydrazone. 9-Xanthone (20 g, 0.102 mol) was refluxed with oxalyl chloride (50 mL) containing pyridine (16 g, 0.22 mol) for 6 h. Excess oxalyl chloride was removed by codistillation with dry benzene. Upon solidification of the 9,9-dichloroxanthene it was dissolved in methylene chloride (100 mL) and added to tosylhydrazine (19 g, 0.102 mol) in methylene chloride (500 mL) in 1 h. The 9-xanthone azine precipitated (2.8 g, 7.2 mmol) was filtered and the filtrate was then neutralized with hydrochloric acid. The methylene chloride layer was washed with water, separated, dried ($MgSO_4$), and filtered. The filtrate was concentrated in vacuo and the hydrazone filtered; addition of benzene facilitated precipitation. The crude hydrazone was dissolved in hot methylene chloride and cooled, and ether was added. A slightly yellow precipitate of 9-xanthone *p*-toluenesulfonylhydrazone (21.11 g, 57%) was obtained, mp 182 °C dec (rate of heating of 10 °C/min). An analytical sample was prepared via chromatography (silica gel-benzene) as off-white crystals (mp 183-185 °C dec, 10 °C/min): IR (KBr) 3.1, 6.2, 6.9, 8.0, 8.6, 10.35, 11.15, 12.9, and 13.3 μ; ^{1}H NMR ($CDCl_3$, 100 MHz) δ 8.3 (d, 1 H, aromatic), 8.1 (d, 1 H, aromatic), 7.9 (3 H, aromatic + NH), 7.1-7.7 (m, 8 H, aromatic), and 2.4 (s, 3 H, methyl). Anal. ($C_{20}H_{16}N_2O_3S$) C, H, N, S.

The sodium salt (**46**) of 9-xanthone *p*-toluenesulfonylhydrazone was prepared by adding sodium hydride (57%, 116 mg, 2.75 mmol) to a solution of 9-xanthone *p*-toluenesulfonylhydrazone in methylene chloride (50 mL). After 4-5 h the yellow salt had precipitated and was filtered (1.05 g, 2.75 mmol, 100%). The ^{1}H NMR (Me_2SO-d_6, 100 MHz) of **46** revealed the following absorptions: δ 9.8 (d, 1 H, aromatic), 7.9 (d, 1 H, aromatic), 7.7 (d, 2 H, aromatic), 6.9-7.4 (m, 8 H, aromatic), and 2.3 (s, 3 H, methyl). The sodium salt can be stored for several days in a desiccator at room temperature without apparent decomposition. It is insoluble in a variety of organic solvents but is somewhat soluble in acetone.

Photolysis of 46 in Allylbenzene. To allylbenzene (125 mL, purified by distillation from sodium hydride and chromatography over silica gel and neutral aluminum oxide) was added **46** (1.85 g, 4.8 mmol, finely divided). The suspension was purged with nitrogen and then photolyzed for 20 min (450-W Hanovia high-pressure lamp, Pyrex) under nitrogen. The solution was filtered from its insolubles (1 g). Allylbenzene was recovered by distillation (10 mm, 70 °C bath temperature) and hexane was added to the residue. Dixanthyl ether[35] and 9-xanthene azine were filtered (140 mg), and the hexane-soluble material was chromatographed to yield an oil (897 mg) which distilled (0.03 mm, 100-110 °C bath temperature) to give 9-(1-phenyl-2-propenyl)xanthene (**48**): IR (NaCl) 3.2, 3.4, 6.75, 6.85, 7.95, 9.1, 10.05, 10.85, 13.2, and 14.3 μ; ^{1}H NMR (CCl_4, 60 MHz) δ 6.5-7.4 (m, aromatic), 5.7-6.35 (m, 1 H, vinyl), 4.7-5.15 (m, 2 H, vinyl), 4.15 (d, J_{ab} = 5.5 Hz, 1 H, 9-xanthyl), and 3.45 (d of d, J_{ab} = 5.5, J_{bx} = 9 Hz, 1 H, methine). Anal. ($C_{22}H_{18}O$) C, H.

Inspection of the ^{1}H NMR of the crude photolysate revealed that spiro[2-benzylcyclopropane-1,9′-xanthene] (**49**) might be present in at maximum 15%; **49** could not be separated, however (the product decomposes upon VPC on Dow Silicone). 9-(3-Phenyl-2-propenyl)-xanthene (**47**) could not be detected.

Photolysis of 46 in 3-Methyl-1-butene. A finely divided powder of **46** (1.94 g, 5.0 mmol) was added to a photolysis vessel containing 3-methyl-1-butene (145 mL, distilled from sodium hydride and chromatographed over aluminum oxide at 0 °C). The suspension and the Hanovia lamp (450-W, high pressure, Pyrex) were cooled with ice water and nitrogen purged the system before and during the 25-min photolysis period. After irradiation the solvent was distilled and the residue treated with ether and filtered from insoluble material (700 mg). The filtrate was chromatographed (silica gel-hexane) to give (1) a product (732 mg) whose ^{1}H NMR revealed 9-(1,1-dimethyl-2-propenyl)xanthene (**50**, 68%) and spiro[2-(2-propyl)cyclopropane-1,9′-xanthene] (**51**, 32%) to be present and (2) bixanthyl (**34**, 35 mg, 4%). The yields of **50** and **51** were 40 and 19%, respectively.

Separation of **50** and **51** was accomplished via chromatography over neutral aluminum oxide impregnated with silver nitrate. Elution of the mixture with increasing amounts of ether (0-20%) in hexane gave early fractions enriched in **51** while later fractions contained pure **50**. Recrystallization of early fractions from hexane-dry ice gave **51** as off-white crystals: mp 61-63 °C; IR (KBr) 3.35, 3.5, 6.75, 6.9, 7.3, 7.35, 7.95, 9.05, 11.3, and 13.3 μ; ^{1}H NMR (CCl_4, 60 MHz) δ 6.6-7.2 (m, 8 H, aromatic) and 0.4-1.9 (m, 10 H, cyclopropyl, methyl, and methine); mass spectrum exact mass calcd *m/e* 250.135 757, found *m/e* 250.136 105; *m/e* 250 (M^+, 41%), 235 ($M^+ - 15$, 6%), 207 ($M^+ - 43$, 100%), and 194 ($M^+ - 56$, 65%).

Recrystallization of **50** from hexane gave white crystals: mp 58-59 °C; IR (KBr) 3.35, 6.8, 6.9, 7.3, 7.35, 8.0, 10.0, 10.85, 13.1, and 13.4 μ; ^{1}H NMR (CCl_4, 60 MHz) δ 6.9-7.2 (m, 8 H, aromatic), 5.5-6.0 (m, 1 H, vinyl), 4.5-5.0 (m, 2 H, vinyl), 3.6 (s, 1 H, 9-xanthyl), and 0.85 (s, 6 H, methyl). Anal. ($C_{18}H_{18}O$) C, H.

Attempted preparative GLC separation of a portion of fraction 1 resulted in rearrangement of **51** to 9-(3-methyl-2-butenyl)xanthene (**52**): ^{1}H NMR (CCl_4, 60 MHz) δ 6.7-7.1 (m, 8 H, aromatic), 4.8 (m, 1 H, vinyl), 3.85 (t, 1 H, 9-xanthyl), 2.3 (m, 2 H, methylene), 1.6 (br s, 3 H, methyl), and 1.2 (br s, 3 H, methyl). Alkene **50** does not rearrange under the conditions nor was **52** detected in the crude reaction mixture.

1,2-Dihydro-1,1-dimethyl-4-phenylnaphthalene (53). Bromobenzene (6.59 g, 42 mmol) in absolute ether (50 mL) was added to a mixture of absolute ether (50 mL) and magnesium turnings (1.02 g, 42 mmol). After the exothermic reaction subsided, 4,4-dimethyl-1-tetralone (6.92 g, 40 mmol) was added over a 15-min period. The reaction temperature was raised to ~78 °C upon adding benzene and distilling the ether. After 1 hr at 78 °C, sulfuric acid (25%, 100 mL) was slowly added. The organic layer was washed with water, dried, and chro-

matographed on silica gel using hexane as developer to give **53** (5.45 g, 58%): IR (NaCl) 3.2, 3.3, 6.2, 6.9, 9.7, 12.25, 12.85, 13.25, and 14.3 μ; ^{1}H NMR (CCl_4, 60 MHz) δ 6.9-7.4 (m, 9 H, aromatic), 5.9 (t, 1 H, vinyl), 2.3 (d, 2 H, methylene), and 1.35 (s, 6 H, methyl). Anal. ($C_{18}H_{18}$) C, H.

1,2-Dihydro-1,1-dimethyl-2-(9-xanthyl)-4-phenylnaphthalene (54). An oxygen-free benzene solution (50 mL) of **1** (500 mg, 2.4 mmol) was added dropwise, under nitrogen, to a refluxing solution of benzene (150 mL) and 1,2-dihydro-1,1-dimethyl-4-phenylnaphthalene (**53**, 2.09 g, 4.83 mmol). The benzene was removed in vacuo to leave an oil which deposited 9-xanthone azine (80 mg, 17%) when treated with hexane. The hexane-soluble portion was chromatographed (silica gel-hexane) to give **53** (1.67 g) followed by **54** (137 mg, 14%). Further elution produced no isomers of **54**. Recrystallization from hexane yielded white crystals of **54**: mp 169.5-171 °C; IR (KBr) 3.2, 3.35, 6.75, 8.1, 9.7, 11.05, 11.45, 13.4, and 14.2 μ; ^{1}H NMR (CCl_4, 60 MHz) δ 6.0-7.5 (m, 17 H, aromatic), 5.55 (d, 1 H, J_{ax} = 6 Hz, vinyl), 4.5 (d, 1 H, J_{xy} = 2 Hz, 9′-xanthyl), 2.45 (d, 1 H, J_{ax} = 6, J_{xy} = 2 Hz, methine), 1.9 (s, 3 H, methyl), and 1.3 (s, 3 H, methyl). Anal. ($C_{31}H_{26}O$) C, H.

Photolysis of 46 in 2,3-Dimethyl-2-butene. Salt **46** (3.9 g, 9.85 mmol, finely ground) was suspended in 2,3-dimethyl-2-butene (140 mL) which had been distilled from sodium hydride and chromatographed through alumina. The mixture was purged with nitrogen before and during photolysis through Pyrex with a 450-W Hanovia high-pressure lamp for 25 min at 18 °C. The photolysate was filtered from insoluble material (2.3 g). The filtrate was concentrated to a nonvolatile oil (1.65 g) which was chromatographed (silica gel-hexane followed by 1-3% ether). The first fraction (1.1 g) crystallized when the solvent was removed, the second fraction (124 mg) contained 1,1,2-trimethyl-2-propenyl-9-xanthyl peroxide (see below), and the third contained 9-xanthone and unidentified material.

Fraction 1 gave three peaks when analyzed by VPC on a 10 ft × $\frac{5}{8}$ in. column packed with 8% Dow Silicone grease 11 on non-acid-washed Chromosorb P. The first and principal (75%) component is spiro[2,2,3,3-tetramethylcyclopropane-1,9′-xanthane] (**56**): mp 79-80 °C; IR (KBr) 3.4, 8.1, 8.35, 10.95, 11.7, 12.35, 13.15, and 13.9 μ; ^{1}H NMR ($CDCl_3$, 60 MHz, 60 °C) δ 7.35-7.6 (m, 2 H, aromatic), 6.8-7.3 (m, 6 H, aromatic), and 1.2 (s, 12 H, CH_3); ($CDCl_3$, 60 MHz, −30 °C) δ 7.35-7.6 (m, 2 H, aromatic), 6.8-7.3 (m, 6 H, aromatic), 1.65 (s, 6 H, CH_3), and 0.65 (s, 6 H, aromatic). Anal. ($C_{19}H_{20}O$) C, H.

The second component (~20%) is 9-(2,3-dimethyl-2-butenyl)-xanthene (**57**): IR (NaCl) 3.4, 6.75, 6.85, 8.0, and 13.25 μ; ^{1}H NMR ($CDCl_3$, 100 MHz) δ 6.8-7.3 (m, 8 H, aromatic), 3.9 (t, 1 H, 9-xanthyl), 2.3 (d, 2 H, CH_2), 1.6 (s, 3 H, CH_3), 1.5 (s, 3 H, CH_3), and 1.0 (s, 3 H, CH_3). Anal. ($C_{19}H_{20}O$) C, H.

The third component, which cannot be detected in the ^{1}H NMR of the crude product and is apparently a product (5%) of rearrangement of **56** during chromatography, is 2,10b-dihydro-1,1,2,2-tetramethyl-1*H*-benz[*e*]indeno[7,1-*bc*]pyran (**58**): IR (NaCl) 3.35, 6.9, 8.0, 10.15, 11.05, 12.8, and 13.25 μ; ^{1}H NMR (CCl_4, 60 MHz) δ 6.6-7.35 (m, 7 H, aromatic), 4.1 (s, 1 H, 9-xanthyl), 1.4 (s, 3 H, CH_3), 1.1 (s, 6 H, CH_3), and 0.65 (s, 3 H, CH_3). Heating **56** does indeed effect its rearrangement to **58**. Anal. ($C_{19}H_{20}O$) C, H.

If the 2,3-dimethyl-2-butene is not purified prior to use, the major product of reaction with **2** is 1,1,2-trimethyl-2-propenyl-9-xanthyl peroxide (70%): mp 49.5-50 °C; IR (KBr) 3.3, 6.85, 7.95, 8.7, 10.6, 11.1, 11.6, 13.0, and 13.3 μ; ^{1}H NMR (CCl_4, 60 MHz) δ 7.8-8.6 (m, 8 H, aromatic), 5.85 (s, 1 H, 9-xanthyl), 4.75 (m, 2 H, vinyl), 1.65 (br s, 3 H, CH_3), and 1.1 (s, 6 H, CH_3). This product is apparently formed by reaction of **2** with 1,1,2-trimethyl-2-propenyl hydroperoxide present in the 2,3-dimethyl-2-butene. Anal. ($C_{19}H_{20}O_3$) C, H.

9-(1,2-Dimethyl-1-propenyl)-9-hydroxyxanthene. To an ether solution (50 mL) of 1,2-dimethylpropenyl bromide (2.5 g, 16.8 mmol) was added excess lithium (350 mg, 50.4 mmol) whereupon the mixture refluxed. The pale green solution was stirred for 3 h and then syringed into a suspension of 9-xanthone (3.0 g, 15.3 mmol) in ether (100 mL). The suspension dissolved and within 2 h a precipitate formed. The mixture was stirred at room temperature for 12 h and then water was added. The ether portion was washed with water, dried ($MgSO_4$), filtered, and concentrated whereupon addition of hexane left 9-xanthone (820 mg) as a precipitate. Chromatography of the hexane solution on silica gel (50% benzene-50% 30-60 °C petroleum ether) yielded 9-(1,2-dimethyl-1-propenyl)-9-hydroxyxanthene (1.729 g, 6.5 mmol, 39%). Recrystallization from hot hexane produced white crystals: mp 88.5-89.5 °C; IR (KBr) 2.8, 3.4, 8.1, 9.6, 10.1, 10.85, 11.45, and 13.2 μ; ^{1}H NMR (CCl_4, 60 MHz) δ 6.8-7.5 (m, 8 H, aromatic), 1.95 (s, 1 H, OH), 1.8 (s, 3 H, CH_3), 1.7 (s, 3 H, CH_3), and 1.4 (s, 3 H, CH_3). Anal. ($C_{18}H_{18}O_2$) C, H.

9-(1,2-Dimethyl-1-propenyl)-9-methylxanthene (59). Trimethylaluminum (752 mg, 10.5 mmol) was dissolved in benzene (25 mL, anhydrous, deoxygenated) under nitrogen. 9-(1,2-Dimethyl-1-propenyl)-9-hydroxyxanthene (490 mg, 1.84 mmol) was then added whereupon the solution warmed, evolved a gas, and turned red. The mixture was refluxed for 25 h and then worked up by adding a mixture of water, hydrochloric acid, and ether while stirring in an ice bath. The ether layer was separated, washed with water, dried ($MgSO_4$), and concentrated to a brown oil. Chromatography (silica gel-30-60 °C petroleum ether) of the residue yielded a mixture (425 mg) consisting of four components. Upon separation, the major component (66%) was shown by spectral data and combustion analysis to be **59** (280 mg, 1.06 mmol, 57.6%): IR (NaCl) 3.3, 3.4, 7.7, 8.05, 11.25, and 13.25 μ; ^{1}H NMR (CCl_4, 100 MHz) δ 6.9-7.3 (m, 8 H, aromatic), 2.1 (s, 3 H, CH_3), 1.80 (s, 3 H, CH_3), 1.6 (s, 3 H, CH_3), and 1.05 (s, 3 H, CH_3). Anal. ($C_{19}H_{20}O$) C, H.

Photolysis of 9-Diazofluorene (62) in 2,3-Dimethyl-2-butene. A solution of **62** (1.0 g, 5.2 mmol) and purified 2,3-dimethyl-2-butene (140 mL) was purged before and during photolysis (30 min, 25 °C, 450-W Hanovia lamp, Pyrex). Removal of excess 2,3-dimethyl-2-butene at 25 °C left a crude product (1.663 g) which GLC analysis revealed to contain three components (10, 22, and 68%), respectively. The residue was chromatographed (silica gel-hexane) allowing enrichment of the minor components in the first fraction. Successive fractions contained the major component pure enough to allow recrystallization. Bifluorenylidene (50 mg) was then eluted with 2% ether-hexane.

The mixture containing the two minor components was rechromatographed on neutral aluminum oxide impregnated with silver nitrate and eluted with increasing amounts of ether (0-2%) in hexane. Spiro[2,2,3,3-tetramethylcyclopropane-1,9′-fluorene] (**63**) and 2,3-dimethyl-2-butenyl-9-fluorene (**64**, the 22% component) eluted first followed by nearly pure 1,1,2-trimethyl-2-propenyl-9-fluorene (**65**, the 10% component). The mixture of **63** and **64** was now separable by GLC and gave **64** as a solid of the following properties: IR (NaCl) 3.25, 3.4, 6.95, 13.2, and 13.55 μ; ^{1}H NMR (CCl_4, 100 MHz) δ 7.6 (d, 2 H, aromatic), 7.0-7.4 (m, 6 H, aromatic), 3.9 (t, 1 H, 9-xanthyl), 2.4 (d, 2 H, CH_2), 1.9 (s, 3 H, methyl), 1.75 (s, 3 H, methyl), and 1.4 (s, 3 H, methyl). Anal. ($C_{19}H_{20}$) C, H.

Adduct **63** crystallized from ethanol as a white solid: mp 153-154 °C; IR (KBr) 3.25, 3.4, 6.9, 8.9, 10.65, 12.55, and 13.5 μ; ^{1}H NMR (CCl_4, 60 MHz) δ 7.7-7.9 (m, 2 H, aromatic), 7.1-7.5 (m, 6 H, aromatic), and 1.5 (s, 12 H, methyl). Anal. ($C_{19}H_{20}$) C, H.

Propenylfluorene **65** (<20 mg) was obtained by column chromatography: IR (NaCl) 3.35, 6.9, 7.3, 11.2, 12.95, and 13.55 μ; ^{1}H NMR (CCl_4, 60 MHz) δ 7.0-7.8 (m, aromatic), 4.8 (d, 2 H, vinyl), 4.05 (s, 1 H, 9-xanthyl), 2.1 (s, 3 H, methyl), and 0.9 (s, 6 H, methyl); mass spectrum exact mass calcd *m/e* 248.156 492 000, found *m/e* 248.156 913 42; *m/e* 248 (M^+, 19%), 168 ($M^+ - 83$, 81%), and 83 ($M^+ - 165$, 100%).

Competitive Carbenic Reactivities of Substituted Styrenes in Photochemical Decomposition of 9-Diazoxanthene (1). A. 4-Methoxystyrene (14a) vs. Styrene (14d). A suspension of **46** (2.03 g, 5.25 mmol, finely pulverized) in ethyl ether (130 mL, anhydrous) containing **13d** (5.15 g, 50 mmol) and **13a** (6.65 g, 50 mmol) was irradiated[36] for 1.25 h at −20 °C. The sodium *p*-toluenesulfinate formed was filtered (1.0 g, 107%). Upon removing the styrenes in vacuo (80 °C) and treating the concentrate with ether, an orange solid (342 mg), 9-xanthone azine, and dixanthyl ether[36] separated. The filtrate was chromatographed on silica gel employing increasing amounts of benzene in hexane as developer. The cyclopropane (**17d**, 206 mg) derived from **14d** eluted before that (**17a**, 353 mg) from **14a**. The radio of **17d**:**17c** formed is 61:39; the yield of **17a** and **17d** is ~30%. In a second experiment the ratio of **17d** and **17a** was identical.

B. 4-Methoxystyrene (14a) vs. 4-Chlorostyrene (14f). The photolysis apparatus was as previously described[36] except that ethyl ether (−78 °C) was used to cool the lamp.

The sodium salt (**46**) of 9-xanthone tosylhydrazone (2.1 g, 5.45 mmol, finely divided) was suspended in an ether solution (130 mL) of **14f** (6.9 g, 50 mmol) and **14a** (6.65 g, 50 mmol) and photolyzed for 1.25 h. The temperature at the end of the photolysis was −36 °C. The yellow solution was filtered to remove sodium *p*-toluenesulfinate and

the styrenes were removed under reduced pressure (80 °C). Treatment of the remaining oil with ether left a mixture (250 mg) of dixanthyl ether and 9-xanthone azine. The ether-soluble portion of the residue was chromatographed on silica gel using hexane to elute **17f** (237 mg) followed by carbon tetrachloride to remove **17a** (212 mg). The molar reactivity ratio of **14f:14a** in reaction of 9-xanthylidene (**2**) is 52.5:47.5. Repetition of the above experiment produced a reactivity ratio of 46:54 and a 37.5% yield of cyclopropanes. The components of the latter experiment were a little more difficult to purify than those of the first. The values of the ratios from the two experiments were averaged.

C. 4-Methoxystyrene (14a) vs. 3-Bromostyrene (14b). To **14a** (6.97 g, 52 mmol) and **14b** (9.52 g, 52 mmol) in absolute ether (130 mL) was added **46** (2.0 g, 5.17 mmol, finely divided). The suspension was irradiated for 30 min (as in system A above) and then filtered to remove insoluble material (960 mg). The filtrate was concentrated and the styrenes were removed by vacuum evaporation (0.2 mm, 55 °C). The crude photolysate was chromatographed on silica gel using hexane and then carbon tetrachloride as developers. Spiro[2-(3-bromophenyl)cyclopropane-1,9′-xanthene] (**17b**, 590 mg) eluted first followed by **17a** (210 mg). The yield of **17a** and **17b** was 44.5%; the molar reactivity ratio of **14a:14b** is 29.5:70.5. A second experiment was conducted using the same ratio of reactants as above; the amount of absolute ether used was 200 mL and the irradiation was for 75 min. A ratio of **17a:17b** of 32.5:67.5 and a yield of 47% were obtained.

D. 4-Methoxystyrene (14a) vs. 4-Bromostyrene (14c). A mixture of **14c** (10.06 g, 55 mmol), **14a** (7.37 g, 55 mmol), ethyl ether (125 mL, anhydrous), and **46** (2.05 g, 5.3 mmol, finely divided) was photolyzed for 30 min. The internal temperature at the end of the irradiation was −18 °C. The suspension was filtered free of insolubles (1.21 g, 128%, based on sodium *p*-toluenesulfinate). The ether and excess styrenes were removed in vacuo and the residue treated with ether. The ether-insoluble material (165 mg, dixanthyl ether and 9-xanthone azine) was filtered and the filtrate concentrated and chromatographed (silica gel-hexane followed by carbon tetrachloride). Hexane removed **17c** (341 mg) derived from **14c**; carbon tetrachloride eluted **17a** (147 mg) obtained from **14a**. The ratio of **17a:17c** produced is 33:67 and the yield of **17a** and **17c** is 27%. In a similar experiment the photolysis was run for 75 min and a 43:57 ratio (26%) was obtained.

E. 4-Methoxystyrene (14a) vs. 4-Methylstyrene (14e). To a solution of **14a** (6.7 g, 50 mmol) and **14e** (5.9 g, 50 mmol) in ethyl ether (200 mL, anhydrous) was added **46** (1.92 g, 4.97 mmol). The mixture was irradiated for 45 min at −30 °C and filtered free of insolubles (900 mg). The excess styrenes were removed in vacuo (80 °C) and the residue was chromatographed on silica gel with benzene (0-40%) in hexane. Cyclopropane **17e** (360 mg, from **14e**) eluted first followed by bixanthyl (**29**, 23 mg, 6%) and finally cyclopropane **17a** (447 mg, from **12a**). The reactivity ratio of **14a:14e** is 54:46 and the yield is 52%. Repetition of the above experiment with similar quantities and conditions led to an identical reactivity ratio and a 42% yield.

Reactivity of 1 with *p*-Bromostyrene (14c) at −25 °C. An ethyl ether solution (30 mL) of **1** (217 mg, 1.1 mmol) and **14c** (2.01 g, 11 mmol) was kept at −25 °C for 1.5 h. Neither nitrogen evolution nor diazo discoloration (green) occurred. Unreacted **1** was rapidly decomposed (−25 °C) upon addition of sulfur dioxide (spiro[2-(4-bromophenyl)-cyclopropane-1,9′-xanthene] (**17c**) is unaffected by sulfur dioxide). The mixture was evaporated in vacuo (0.1 mm, 50 °C) and its ^{1}H NMR spectrum revealed no cyclopropyl products. Likewise, chromatography (silica gel-1% ether/petroleum ether, 30-60 °C) of the mixture gave no indication of a reaction between **1** and **14c** under these conditions.

Synthesis of Spiro[(2-methyl-*cis*-3-phenylcyclopropane)-1,9′-xanthene] (18). A solution of **1** (620 mg, 3.0 mmol) in freshly distilled *cis*-propenylbenzene (20 g) at 0 °C was dropped into *cis*-propenylbenzene (7 g) at 100 °C in 0.5 h. After the excess *cis*-propenylbenzene had been removed by distillation (34 °C, mm), the hexane-soluble part of the residue was chromatographed on silica gel-hexane to give **18** (290 mg, 32%) as a yellow solid. Several recrystallizations from hexane gave **18**[37] as off-white crystals: mp 129-130 °C; IR (KBr) 3.25, 3.3, 3.4, 6.25, 6.7, 6.9, 7.6, 7.9, 8.2, 11.05, 13.2, 13.5, and 14.1 μ; ^{1}H NMR (CCl_4, 90 MHz) δ 6.82-7.15 (m, 11 H, aromatic), 6.45 (m, 1 H, aromatic), 5.94 (d, 1 H, aromatic), 3.14 (d, 1 H, J = 9.7 Hz, cyclopropyl), 1.70 (m, 1 H, cyclopropyl), and 1.23 (d, 3 H, J = 6.6 Hz, methyl); mass spectrum for $C_{22}H_{18}O$, exact mass calcd *m/e* 298.135 756 9, found *m/e* 298.136 707 3; *m/e* 298 (M^+, 97%), 283 (M − 15, 100%), 118 (M − 117, 30%).

Synthesis of Spiro[(2-methyl-*trans*-3-phenylcyclopropane)-1,9′-xanthene] (19). Reaction of **1** with *trans*-propenylbenzene, conducted as previously for **1** and *cis*-propenylbenzene, gave **19**[37] as a glassy solid (317 mg, 35%): IR (KBr) 3.25, 3.3, 3.4, 6.25, 6.7, 6.9, 7.6, 7.9, 8.25, 11.05, 12.65, 13.3, and 14.3 μ; ^{1}H NMR (CCl_4, 90 MHz) δ 6.82-7.20 (m, 11 H, aromatic), 6.41 (m, 1 H, aromatic), 5.98 (d, 1 H, aromatic), 2.97 (d, 1 H, J = 8.0 Hz, cyclopropyl), 1.71 (m, 1 H, cyclopropyl), and 1.23 (d, 3 H, methyl); mass spectrum for $C_{22}H_{18}O$, exact mass calcd *m/e* 298.135 756 9, found *m/e* 298.136 471 3; *m/e* 298 (M^+, 90%), 283 (M − 15, 100%), 181 (M − 117, 25%).

Reaction of 1 and *cis*-propenylbenzene at 25 °C. Freshly distilled *cis*-propenylbenzene (6.3-9.0 g) was added to **1** (200-327 mg) at ~25 °C. The green solution was stirred until it became yellow (2-5 h); gas was evolved during these periods. Excess *cis*-propenylbenzene was removed under reduced pressure and the hexane-soluble residue was chromatographed on silica gel-hexane to give a mixture of **18** and **19**.[37] The ratios of **18:19** were 95:5 as determined by the integrated ^{1}H NMR of the benzylic proton regions (δ 3.2-2.8); the protons appear as two sets of distinguishable doublets.

Reaction of 1 and *trans*-Propenylbenzene at 25 °C. Reaction of **1** and *trans*-propenylbenzene at ~25 °C and isolation of products were effected as described previously for **1** and *cis*-propenylbenzene. ^{1}H NMR analysis revealed formation of **19** with no detectable amount of **18**.[37]

Photolysis of 46 in *cis*-Propenylbenzene. A suspension of **46** (1.25 g, 3.2 mmol) in ethyl ether (20 mL, anhydrous) and *cis*-propenylbenzene (12.5 g, freshly distilled from sodium hydride) in a Pyrex test tube (nitrogen purged, serum stopper sealed) was irradiated for 2.5 h at ~25 °C with a 450-W Hanovia medium-pressure lamp. The sodium *p*-toluenesulfinate formed was filtered and the *cis*-propenylbenzene was removed in vacuo. The residue (0.56 g), on chromatography on silica gel-hexane, gave a mixture of **18** and **19** (0.27 g, 28%): ^{1}H NMR analysis indicated a ratio of 80:20.[37] In a second experiment **18** and **19** were formed in 75:25 ratio.

Photolysis of 46 in *trans*-Propenylbenzene. Photolyses of **46** in *trans*-propenylbenzene conducted as described for **46** and *cis*-propenylbenzene gave **18** and **19** in 5:95 ratios.[37]

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(8) The 9-xanthyl cation might give **20-25** by (1) addition to the β carbon of the ketone enols with proton loss and/or (2) reaction with oxygen of the ketones and/or their enols, loss of a proton, and rearrangement of intermediate vinyl 9-xanthyl ethers.
(9) Carbene **2** reacts readily with oxygen to produce 9-xanthone. All thermal decompositions of **1** were conducted in a nitrogen atmosphere; however, no attempt was made to exclude oxygen rigorously.
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(16) Alkene **59** was prepared by treating 9-xanthone with 1,2-dimethyl-1-propenyllithium to form 9-(1,2-dimethyl-1-propenyl)-9-hydroxyxanthene (39%); the latter compound reacts with trimethylaluminum to give **59** (58%) (see Experimental Section).
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(24) (a) Photolysis of **1** in *cis*-propenylbenzene at −78 °C in ethyl ether gives 9-xanthone azine as the principal product. (b) Cyclopropanes **18** and **19** were analyzed by ^{1}H NMR methods; because of the limitations of the ^{1}H NMR method, small amounts of **18** or **19** in admixture with its geometric isomer could not be determined.
(25) (a) Diarylcarbenes such as diphenylmethylene and **61** show reactions in mixed singlet and triplet states. Styrenes, however, are excellent triplet scavengers and may siphon off **4** much faster than **3**. (b) Reference 10a, pp 73–84. (c) G. Cauquis and G. Reverdy, *Tetrahedron Lett.*, 3491 (1972).
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(37) (a) The stereochemical assignments of **18** and **19** were made in accord with the general observation that for cyclopropanes cis is larger than trans *vicinal* coupling,[37b-d] and in agreement with the Karplus rule which predicts J_{trans} never to be larger than J_{cis} for any given pair of cyclopropane isomers.[37e,f] (b) H. M. Hutton and T. Schaefer, *Can. J. Chem.*, **40**, 875 (1962). (c) D. J. Patel, M. E. H. Howden, and J. D. Roberts, *J. Am. Chem. Soc.*, **85**, 3218 (1963). (d) G. L. Closs and R. A. Moss, *ibid.*, **86**, 4042 (1964). (e) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959). (f) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed., Pergamon Press, Oxford, 1969, pp 286–287.
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Solvent Nucleophilicity. A Scale Based on Triethyloxonium Ion Solvolysis[1]

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Abstract: First-order rate coefficients have been obtained for the solvolysis of triethyloxonium hexafluorophosphate in a variety of organic and aqueous-organic solvents. These have been used to set up a scale of solvent nucleophilicities based upon the four-parameter (two-term) Grunwald-Winstein equation. The required corrections for variation in solvent influence upon the leaving group were estimated from data available for *tert*-butyldimethylsulfonium ion solvolysis. A previously established scale, based upon methyl *p*-toluenesulfonate solvolysis, can be brought into good agreement with this scale if a revised value is used for methyl *p*-toluenesulfonate sensitivity to the electrophilic influence of the solvent. The scale is applied to previously studied solvolyses of alkyl *p*-toluenesulfonates and chlorides.

Determination of solvent nucleophilicities is complicated by concurrent solvent influence upon the leaving group. Previous attempts to establish a nucleophilicity scale for solvolytic reactions have used data from initially neutral substrates;[2,3] to a first approximation, the overall influence of the solvent could be considered as a nucleophilic push at the α carbon and an electrophilic pull at the leaving group. Two-term (four-parameter) equations have been proposed[2,4] for the combination of these two effects within a linear free energy relationship. Subsequent work[3,5-8] has favored the earlier formulation,[4] expressed in the equation

$$\log (k/k_0) = lN + mY \qquad (1)$$

In eq 1, k represents the specific rate in a given solvent, k_0 the specific rate in 80% ethanol, and, for a given substrate, l and m represent the sensitivities of the solvolysis to N and Y, the solvent nucleophilicity and the solvent ionizing power. The equation was developed as an extension of the more familiar one-term (two-parameter) Grunwald-Winstein equation[9] (eq 2) from S_N1 to S_N2 solvolyses.

$$\log (k/k_0) = m'Y \qquad (2)$$

Peterson and Waller[5] attempted to overcome the problem of variable influence upon the leaving group by studying nucleophilicities toward cyclic halonium ions in a large excess of liquid sulfur dioxide. Because the carboxylic acids studied have similar dimer $\rightleftharpoons$ monomer equilibrium constants[10] (favoring the dimer), the observed three-halves-order kinetics could be approximately related to the relative nucleophilicities of individual solute molecules. For alcohols, which show complex aggregation behavior in relatively low polarity solvents,[11] the more complex kinetic patterns could not readily

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