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Thioxanthenylidene: A Nucleophilic Carbene[1]

Timothy B. Patrick,* Marjorie A. Dorton,[2] and James G. Dolan

Department of Chemistry, Southern Illinois University, Edwardsville, Illinois 62026

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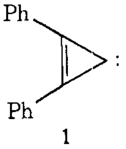
Photolysis of 9-diazothioxanthene (**8**) in tetrahydrofuran solution has been used to generate thioxanthenylidene (**7**). In the presence of cyclohexene, the primary product was the dimer thioxanthenylene. In the presence of dimethyl fumarate and dimethyl maleate, the major products were the carbene adducts **12** and **13**, respectively. The data clearly show that carbene **7** exhibits nucleophilic character. Attempts were made to generate thioxanthenylidene 10,10-dioxide, but its precursor, 9-diazothioxanthene 10,10-dioxide, gave only dimer and products from 1,3-cycloaddition reactions.

The electrophilic nature of a carbene can be attenuated by overlap of its vacant p orbital with electron-donating substituents or by incorporation of the vacant p orbital into an aromatic π system. The carbene can behave as a nucleophile if extensive stabilization of the vacant p orbital is achieved.[3]

Diphenylcyclopropylidene (**1**)[4] and cycloheptatrienylidene (**2**)[5,6] are prime examples of carbenes that exhibit nucleophilic reactions toward electron-deficient alkenes (e.g., fumaronitrile and dimethyl fumarate). In these systems, the vacant p orbital has been stabilized by incorporation into a carbocyclic aromatic π system.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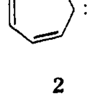
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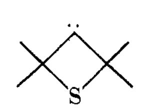
Heteroatom interactions with carbenic centers are also known. Pertinent to our work are the sulfur-containing car-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$CH_3S\ddot{C}SCH_3$
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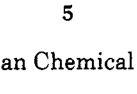
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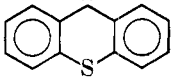
benes **3**,[7] **4**,[8,9] **5**,[10] and **6**.[11] Significant interaction between the sulfur atom and the carbenic center has been demonstrated in each of these systems. Reactions with alkenes have been reported for **3** and **4**, but nucleophilic character has been observed only for **3** in addition reactions with electron-deficient acetylenes and in a reversible Michael reaction with dimethyl fumarate.

In a study of potentially nucleophilic carbenes, we have examined the generation and chemistry of thioxanthenylidene (**7**). The carbenic center in **7** could be highly stabilized by incorporation into the heterocyclic aromatic π system (A), which is isoelectronic and anthracene.[12] Stable thioxanthenyl cations are well known.[13]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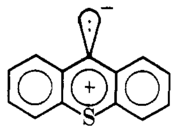

A

Recently, Durr et al.[14] have reported some preliminary work on **7**. The results of our studies on **7** and a comparison with the results of Durr et al. are the main subject of this paper.

Results and Discussion

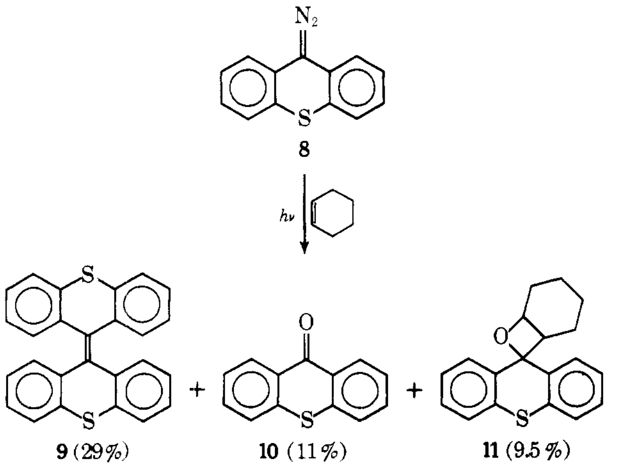
9-Diazothioxanthene (**8**)[15] was used as the precursor to **7**. Initially we attempted to prepare **8** by nitrosation of 9-acetylaminothioxanthene, but a rapid decomposition reaction prevented this from being useful for the preparation of **8**.[16] The route described by Schonberg et al.[15] was then used for the preparation of **8**.

Photolytic decomposition of **8** with a 450-W medium-pressure Hanovia lamp in Vycor tubes was used to generate **7**. In degassed cyclohexene solution, **7** decomposed in 30 min as evidenced from the measurement of nitrogen evolved and loss of the green color from **8**. The products from this reaction are shown in Scheme I.

Dithioxanthenylene (**9**) is likely formed from the reaction between the carbene **7** and unreacted **8**.[17] The formation of thioxanthone must result from the presence of oxygen, even though the samples were rigorously degassed, while compound **11** is the Paterno–Buchi product from **10** and cyclohexene. A reaction in dihydropyran solution gave essentially the same results, but the reaction was not clean. No evidence for a cyclopropane product was obtained in either cyclohexane or dihydropyran solutions.

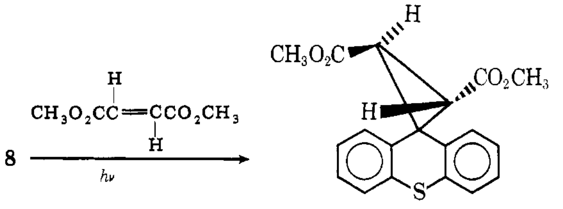
Our results on the photolysis of **8** in cyclohexene solution are very similar to the results obtained by Durr et al. for photolysis of **8** in either 2-methyl-2-butene or 2,3-dimethyl-2-butene.

Scheme I



Ample precedence is available which supports dimer formation from a carbene intermediate that most likely reacts with the diazo precursor.[5,18] Thus, the formation of carbene A is inferred from these studies.

When the photolysis was carried out (Vycor filter) in a tetrahydrofuran solution containing dimethyl fumarate, the spiro adduct **12** was obtained in 32% isolated yield. The structure of **12** stands firmly on spectral and analytical data. Furthermore, the trans stereochemistry of the adduct was firmly deduced in ^{1}H NMR experiments conducted at 220 MHz. The symmetry of the trans compound leads to equivalent 1,8-peri hydrogens whose signal appeared in the NMR spectrum as a two-proton multiplet at δ 7.49, downfield from the other aromatic protons centered at δ 7.16. Moreover, on addition of Eu(fod)$_3$, the aromatic protons shifted to a clean ABCD pattern with the correct proton integration. A product with cis stereochemistry would possess nonequivalent aromatic rings and two ABCD patterns would result. Thus, the trans configuration is established. Adduct **12** showed no tendency for rearrangement (see below).



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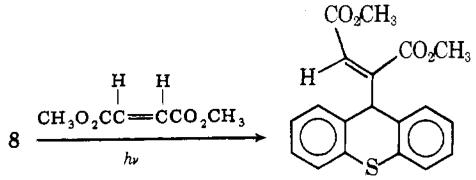
Photolysis of **8** in a tetrahydrofuran solution containing dimethyl maleate gave adduct **13** in 25% yield and thioxanthone (**10**) in 12% yield. No evidence was found for the presence of a spiro adduct in this reaction. The structure of **13** was determined from spectral and analytical data. The occurrence of a singlet at δ 4.10 for the benzylic proton established the structure as nonconjugated, and the absence of allylic coupling suggests a *Z* configuration.[20] The nonconjugated structure is reasonable on steric grounds because a conjugated system would require an unfavorable interaction between an ester function and a peri aromatic hydrogen.[21]



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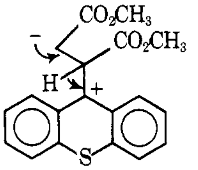

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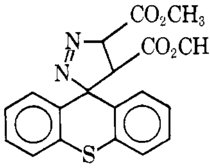


14

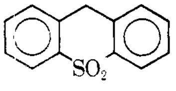
The formation of **13** can be rationalized several ways. A labile spiro adduct could have formed and undergone thermal-, photochemical-, or glass-catalyzed rearrangement. Jones has observed acid-catalyzed rearrangements of spiro adducts **1** and **2** and has noted that ether solvents facilitate thermal rearrangements of spiro adducts of **2**.[5] Another possibility is a Michael-type reaction between A and dimethyl maleate, and support for this process comes from Hartzler's work with dithiolium carbenes.[7] Structure B is a reasonable intermediate for both spiro rearrangement or Michael addition paths, and B could readily yield **13** as shown.[22]

Durr et al. observed that 8 reacted with *neat* dimethyl maleate in a 1,3-cycloaddition fashion to give pyrazoline **14.** Compound **14** was extremely stable to both heat and prolonged high-intensity photolysis and thus did not expel nitrogen. We have verified Durr's result and have also observed that 8 reacts in *tetrahydrofuran* solution with dimethyl maleate only under photolysis with expulsion of nitrogen.

A kinetic study showed that the rate of nitrogen evolution in the photolytic reaction of 8 with either dimethyl maleate or dimethyl fumarate in tetrahydrofuran solution was independent of the acceptor alkene concentration. A rate constant of $4.90 \pm 0.1 \times 10^{-2}\ \mathrm{s}^{-1}$ for ratios of alkene to 8 ranging from 1:1 to 6:1 was obtained. These results, coupled with the observation of Durr et al. that the pyrazoline 14 is exceptionally stable to photolytic decomposition, indicate that a pyrazoline intermediate is not involved in our reaction. Moreover, the observation of dimer **9**, spiro **12**, and adduct **13** strongly suggests that carbene A is the prevailing intermediate in these reactions and that the carbene exhibits nucleophilic character.

Attempts were made to study the chemistry of thioxanthenylidene 10,10-dioxide (**15**) with the rationale that the sulfur electrons would be held in the sulfone function and therefore be unavailable for stabilization of the carbenic center. This would give an electrophilic carbene.

The photolysis of 9-diazothioxanthene 10,10-dioxide (**16**)[23] was investigated as a route to **15.** When the photolysis was conducted in cyclohexene solution, the only product observed was the dimer 17 (Scheme II). The major reaction of 16 with electron-deficient alkenes was a facile room temperature 1,3-cycloaddition reaction. The pyrazoline products **18** and **19,** formed from reaction of **16** with methyl vinyl ketone (MVK) and benzyne, respectively, were characterized by spectral and analytical data. These pyrazolines were stable to photolysis but decomposed on melting. Thus, carbene formation from **15** is indicated only in the formation of dimer **17.**[17] No conclusions about its electronic character can be deduced from these results.



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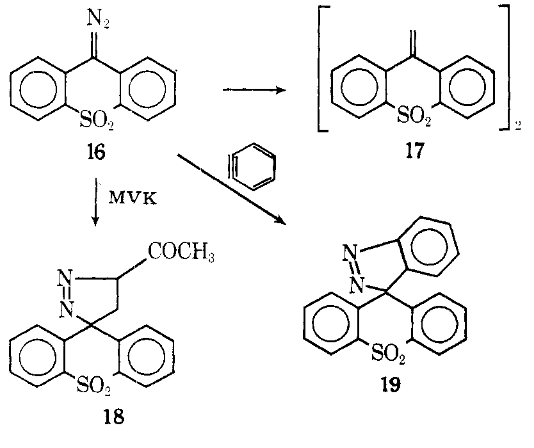
Experimental Section

General. All temperature readings are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Infrared spectra were recorded with a Perkin-Elmer 337 grating spectrophotometer or a Beckman Model IR-33 spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Varian T-60 spectrometer with tetramethylsilane (δ 0.0) as an internal standard. Mass spectra were obtained with a Varian MAT-111 spectrometer at 80 eV.

Scheme II



Analytical thin-layer chromatography (TLC) was accomplished on 20 × 75 mm slides coated with Malinkcrodt Silicar silica gel G at 300-μm thickness.

All photolyses were performed on degassed samples contained in closed Vycor tubes. The light source was a Hanovia 450-W medium-pressure mercury arc immersion lamp. Tetrahydrofuran was dried by distillation from lithium aluminum hydride.

Reaction mixtures were separated by column chromatography with Fisher Alumina Absorption (80–200 mesh). Chromatographic solvents were distilled before use.

Photolysis of 9-Diazothioxanthene in Cyclohexene. 9-Diazothioxanthene[15] (0.11 g, 0.5 mmol) was dissolved in 3 mL of pure cyclohexene, and the mixture was degassed in three freeze–thaw cycles. The green solution was irradiated for 50 min to give a clear yellow liquid containing a yellow precipitate.

The precipitate was identified as dithioxanthenylene (**9**): 28 mg (29%); mp 355–370 °C dec (lit.[15] decomposes above 350 °C). Anal. Calcd for $C_{26}H_{18}S$: C, 79.18; H, 4.57; S, 16.24. Found: C, 79.23; H, 4.46; S, 16.41.

Chromatography of the concentrated liquid (12-mL aliquots) gave two major components. The first component (fractions 9–11; benzene/hexane) was identified as 2,3-tetramethylenespiro[oxetane-4,9′-thioxanthene] (**11**) as a slightly yellow solid: 14 mg (9.5%); mp 190–191 °C; IR (KBr) 3090, 2950, 920 (s), 745 (s) cm^{-1}; NMR (CDCl$_3$) δ 0.9–2.2 (10 H, aliphatic), 6.90–7.50 (8 H, aromatic); MS *m/e* 294 (P), 278, 216 (base). Anal. Calcd for $C_{19}H_{18}OS$: C, 77.55; H, 6.12; S, 10.88. Found: C, 77.30; H, 6.26; S, 10.89.

The second component (fractions 13 and 14; benzene) was identified as thioxanthone (**10**): 12 mg (11%); mp 207–208 °C. The spectral properties were identical with those of an authentic sample.

Photolysis of 9-Diazothioxanthene in the Presence of Dimethyl Fumarate. A degassed solution of 8 (0.18 g, 0.8 mmol), dimethyl fumarate (0.13 g, 0.9 mmol) and tetrahydrofuran (3 mL) was subjected to photolysis for 10 min. The concentrated reaction mixture was chromatographed (CHCl$_3$) to give 86 mg (32%) of *trans*-1,2-dicarbomethoxyspiro[cyclopropane-3,9′-thioxanthene] (**12**): mp 141–143 °C (hexane); IR (KBr) 1710 (C=O), 1160 (C–O), 750 cm^{-1}; NMR (CDCl$_3$, 220 MHz) δ 3.11 (s, 2 H, cyclopropyl), 3.61 (s, 6 H, CH$_3$), 7.16 (m, 6 H, aromatic), 7.46 (m, 2 H, aromatic); MS *m/e* 340 (P), 280 (base). Anal. Calcd for $C_{19}H_{16}O_4S$: C, 67.06; H, 4.71; S, 9.41. Found: C, 67.23; H, 4.76; S, 9.14.

Photolysis of 9-Diazothioxanthene in the Presence of Dimethyl Maleate. A degassed solution of 8 (0.18 g, 0.8 mmol), dimethyl maleate (0.13 g, 0.9 mmol), and tetrahydrofuran (3 mL) was subjected to photolysis for 10 min. The concentrated solution was chromatographed (15-mL fractions) to give two compounds.

The first component (benzene) was identified as thioxanthone (22 mg, 13%) by comparison with an authentic sample (melting point, IR, and NMR).

The second component (ethyl acetate) was identified as dimethyl (9-thioxanthenyl)maleate (**13**): 40 mg (15%); mp 129–131 °C; IR (KBr) 1745 (C=O), 1560 (C=C), 1215, 1170, 1115 (C–O), 750 cm^{-1}; NMR (CDCl$_3$) δ 3.20 (s, 3 H, CH$_3$), 3.80 (s, 3 H, CH$_3$), 9.10 (s, 1 H, CH), 7.19–8.0 (m, 9 H, aromatic and alkene); MS (20 eV) *m/e* 340 (P), 212 (base). Anal. Calcd for $C_{19}H_{16}O_4S$: C, 67.06; H, 4.71; S, 9.41. Found: C, 66.93; H, 4.55; S, 9.44.

Rate of Photolytic Decomposition of 9-Diazothioxanthene in Dimethyl Fumarate and Dimethyl Maleate. A solution of 8 (123 mg, 0.55 mmol) in 3 mL of tetrahydrofuran and dimethyl fumarate or dimethyl maleate (1–6 equiv) was placed in a Vycor tube fitted with a rubber septum and a gas exit valve. The mixture was photolyzed (28 °C), and nitrogen evolution was monitored by collection over water in a buret. Plots of nitrogen concentration (corrected for water vapor) vs. time followed first-order kinetics, and thus the reaction was independent of alkene concentration. Nitrogen evolution rate was also independent of the concentration of a mixture of dimethyl maleate and dimethyl fumarate (5:1 equiv).

Photolysis of 9-Diazothioxanthene 10,10-Dioxide in Cyclohexene. A solution of **16** (0.9 g, 3.7 mmol) in 220 mL of cyclohexene was subjected to photolysis for 30 min, during which time the red color of **16** completely disappeared. A yellow precipitate of analytically pure di-9,9′-thioxanthene 10,10-dioxide (**17**) was recovered by filtration: 0.76 g (90%); mp 383–385 °C (lit.[24] mp 380 °C). Anal. Calcd for $C_{26}H_{16}O_4S_2$: C, 68.42; H, 3.51; S, 14.03. Found: C, 68.11; H, 3.77; S, 13.79.

Reaction of 9-Diazothioxanthene 10,10-Dioxide with Methyl Vinyl Ketone. To 0.9 g (3.7 mmol) of **16** in 50 mL of benzene was added 1 mL of methyl vinyl ketone. The red color of the diazo compound faded rapidly, and the resulting yellow solution was concentrated to a yellow solid. Recrystallization from cyclohexane/ether gave

0.48 g (40%) of **18** as yellow crystals: mp 149–150 °C; IR (KBr) 1710 (C=O), 1300, 1170, 830, 770, 755, 730 (aromatic) cm^{-1}; NMR ($CDCl_3$) δ 2.21 (s, 3 H, CH_3), 2.2–2.8 (m, 3 H, aliphatic), 7.4–8.5 (complex, 8 H, aromatic). Anal. Calcd for $C_{17}H_{14}N_2O_3S$: C, 62.58; H, 4.29; S, 9.82. Found: C, 62.59; H, 4.60; S, 9.94.

Reaction of 9-Diazothioxanthene 10,10-Dioxide with Benzyne. To a solution of 2.6 g (0.01 mol) of **16** and 1.35 g (0.012 mol) of iosamyl nitrite in 50 mL of methylene chloride heated at reflux was added 1.4 g (0.11 mol) of anthranilic acid in 12 mL of acetone over a period of 1.5 h. The solvent was removed to give 2.87 g of a dark residue. The residue was washed with ethanol and recrystallized from acetonitrile to give 2.85 g (86%) of **19** as orange-red crystals: mp 195–197 °C; IR (KBr) 1600 (w), 1480, 1300, 1170, 750 (aromatic) cm^{-1}; NMR ($CDCl_3$) δ 6.8, 7.75, 8.63 (complex aromatic pattern). Anal. Calcd for $C_{19}H_{12}N_2O_2S$: C, 68.67; H, 3.61; N, 8.43; S, 9.64. Found: C, 68.58; H, 3.55; N, 8.50; S, 9.61.

Test for Dark Reactions. Solutions of 8 in tetrahydrofuran and dimethyl fumarate or dimethyl maleate were degassed and allowed to stand in the absence of light. The solutions were monitored by NMR spectroscopy at 5-min intervals for 2 h. No evidence of any reaction was observed.

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Registry No.—**7**, 66688-04-8; **8**, 23619-77-4; **9**, 27090-16-0; **10**, 492-22-8; **11**, 66688-13-9; **12**, 66688-03-7; **13**, 66688-12-8; **16**, 3166-17-4; **17**, 66688-14-0; **18**, 66719-15-1; **19**, 66688-15-1; cyclohexene, 110-83-8; dimethyl fumarate, 624-49-7; dimethyl maleate, 624-48-6; MVK, 78-94-4; benzyne, 462-80-6.

References and Notes

(1) Presented in part at the 13th Midwest Regional American Chemical Society Meeting, Nov. 3, 1977, Rolla, Mo., Abstract No. 517.

(2) Taken in part from the M.S. Thesis of M.A.D., Southern Illinois University, 1976.

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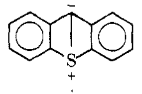

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Reactions of Esters with Phosphorus Ylides. 2.[1] Mechanistic Aspects

Arnold P. Uijttewaal, Froukje L. Jonkers, and Arne van der Gen*

Department of Organic Chemistry, University of Leiden, P.O. Box 9502, 2300 RA Leiden, The Netherlands

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Esters can be directly converted into branched alkenes by reaction with an excess of a nonstabilized phosphorus ylide, $(C_6H_5)_3P^+{-}^-CHR_3$, in polar aprotic solvents or under "salt-free" conditions (Scheme I, reaction path c). On the basis of labeling experiments and the isolation of a reaction intermediate and side products, a mechanism for this conversion is proposed (Scheme II). The rate-determining step appears to be attack of the ylide carbanion on the ester carbonyl to give an alkoxybetaine **22.** This betaine rearranges to a pentacoordinate phosphorus intermediate (**23**) which, after pseudorotation, undergoes attack by a nucleophile, e.g., a second molecule of ylide to form a new phosphonium salt, triphenylphosphine oxide, and an enolate anion. After protonation of this enolate to the corresponding ketone, reaction with a third molecule of ylide provides the final product. The relation of this reaction sequence to the other known reactivities that esters can show toward phosphorus ylides is discussed.

Reaction of esters with phosphorus ylides may result in the formation of several types of products, as depicted in Scheme I. Reaction path a was first discovered by Wittig and Schöllkopf[2] when ethyl benzoate was allowed to react with methylenetriphenylphosphorane, prepared by reacting the corresponding phosphonium bromide with phenyllithium in ether. The reaction sequence can be depicted as shown, starting with nucleophilic attack of the ylide on the ester carbonyl group to form the alkoxybetaine **1.** Loss of alkoxide ion from this betaine leads to the formation of an acylated phosphonium salt **2.** Bestmann and Arnason[3] have shown that this phosphonium salt rapidly loses a proton to a second molecule of ylide or alkoxide ion to form the acylated phosphorane **3.** Several investigators have improved this reaction by using acyl derivatives with a different leaving group (e.g., phenyl esters, phenyl thioesters[3] and imidazolides[4,5]). The phosphoranes **3** can be hydrolyzed to the corresponding ke-

Scheme I. Products from the Reaction of Esters with Phosphorus Ylides[*]