of 156.5–159.5 °C upon mixture with salicylic acid.

The pH 10.5 extract after evaporation yielded 191 mg (75%) of a solid that exhibited an intense blue-green fluorescence. Recrystallization from chloroform–petroleum ether afforded 100 mg of crystals, mp 153.5–155.5 °C.

For analysis the substance was recrystallized twice from chloroform–petroleum ether and dried in vacuo at 60 °C for 3 h; mp 157–157.5 °C.

Anal. Calcd for $C_{11}H_{11}ON_3$: C, 65.64; H, 5.52; N, 20.88; O, 7.95. Found: C, 65.76; H, 5.61; N, 20.88.

This product ($C_{11}H_{11}ON_3$; 100 mg, 4.7 mmol) was dissolved in 6 N HCl (20 mL) and refluxed for 48 h. The solution was then brought to pH 14 with 6 N NaOH and extracted twice with 10-mL portions of ethyl acetate. Evaporation of the ethyl acetate layer yielded 35 mg (35%) of a solid identical with **3** prepared by the reaction of 2-hydroxybenzamidine and ethyl acetoacetic ester as described in this paper. Acidification of the base layer to pH 10 and extraction with ethyl acetate followed by evaporation yielded 50 mg of the starting material.

2-Phenyl-4*H*-1,3-benzoxazin-4-one (1). The procedure described by Titherley[2] was followed: decoupled C^{13} NMR ($CDCl_3$) δ 117.0, 118.3, 127.1, 128.0, 129.0, 129.9, 134.2, 135.4, 154.9, 164.0, 166.9; ^1H NMR ($CDCl_3$) δ 7.27–7.80 (m, 5 H), 8.20 (td, 1 H), 8.38 (dd, 1 H), 8.41 (dd, 2 H).

Benzo[1,3]oxazin-2,4-dione 12. The procedure described by Kemp and Woodward[8] was followed: decoupled C^{13} NMR ($CDCl_3$) δ 1.32 (t, 3 H), 4.13 (q, 2 H), 7.30 (dd, 1 H), 7.34 (td, 1 H), 7.70 (td, 1 H), 8.08 (dd, 1 H).

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Registry No. 1, 3084-52-4; 2, 54789-69-4; 3, 76467-22-6; 4, 3605-06-9; 8, 76467-23-7; 12, 2038-01-9; 2-hydroxybenzamidine, 45744-18-1; ethyl acetoacetate, 141-97-9.

(8) Kemp, D. S.; Woodward, R. B. *Tetrahedron* **1965**, *21*, 3019.

Studies toward Practical Thioxanthene-Derived Protective Groups. 9,10-Propanothioxanthylium Salts

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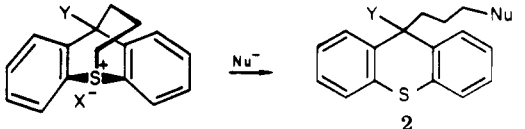
The preparation of 9,10-propanothioxanthylium salts **1** is described. The novel bridged ring system of these salts is readily cleaved by nucleophiles to yield the open-chain derivatives **2**. These readily undergo rapid solvolysis when substituted in the 9-position with an electronegative group. The potential use of a 9-oxygenated-9,10-propanothioxanthylium salt as a protective group is discussed.

Elsewhere,[2,3] we have described a general strategy for the design of new protective groups involving analogues of benzyl esters or urethanes for which an electron-withdrawing function attached to the benzyl ring can be converted selectively, under mild conditions, into a para-oriented electron-donating substituent. This conversion results in protective group removal, since the heterolytic cleavage of the benzylic C–O bond is retarded by electron-withdrawal and greatly accelerated by ortho or para electron donation.[4]

Among the reagents that can be envisaged to effect this conversion are the nucleophiles iodide and phenyl selenide ions; their high reactivity toward alkyl carbon,[5] together with their lack of basicity and inertness to the functional groups of peptides, renders them very promising candidates for orthogonal deprotection under exceptionally gentle reaction conditions that would be unlikely to damage even the most vulnerable peptide or protein.

Drawn by the analogy of **1** with triptycene, we were attracted to the transformation **1** → **2** as a means of realizing an iodide or phenyl selenide labile protective group. An ester of **1** (Y = $R'CO_2$) is expected to resist heterolytic C–O cleavage reactions (bridgehead tertiary alkyl) and to undergo attack by nucleophiles at acyl carbon slowly (hindered tertiary ester). However, the alkyl–sulfur bond is expected to be cleaved readily by good nucleophiles, by analogy with the reactivity of alkyldiphenylsulfonium salts. The cleaved species, **2**, is a thioxanthene that should undergo rapid solvolysis if Y is an electronegative group.



2

1a, Y = H; X = BF_4^-
b, Y = H; X = $CF_3SO_3^-$

In this paper we report the first preparation of the novel ring system of **1** together with a study of its properties. Although we do not envisage that a practical protective group can result from this study, we note that the anticipated properties of **1** and **2** have been confirmed in all respects.

Preparation of **1a** was achieved by reaction of silver tetrafluoroborate with 9-(3-iodopropyl)thioxanthene (**3**), prepared from 9-(3-chloropropyl)thioxanthene[6] and NaI.

(1) On summer leave from the College of the Holy Cross.
(2) Kemp, D. S.; Roberts, D.; Hoyng, C.; Grathan, J.; Vellaccio, F.; Reczek, J. "Proceedings of the 5th American Peptide Symposium"; Walter, R., Meienhofer, J., Eds.; Ann Arbor Science Publishers: Ann Arbor, MI, 1975; pp 295–305.
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(4) Kemp, D. S.; Hoyng, C. F. *Tetrahedron Lett.* **1975**, 4624.
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(6) Muren, J. F.; Bloom, B. M. *J. Med. Chem.* **1970**, *1*, 14.
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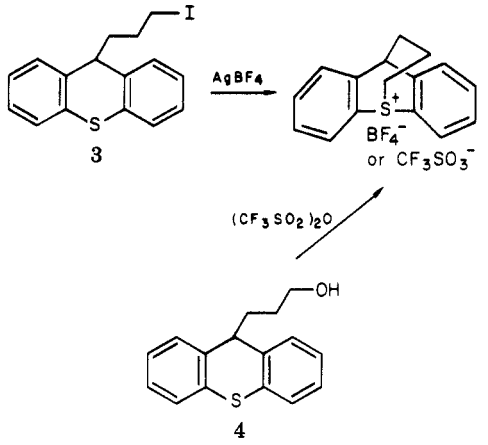
0022-3263/81/1946-1807$01.25/0

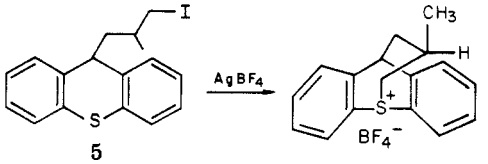
The derivative **1b** was prepared by treatment of the readily available alcohol **4** with triflic anhydride followed by ring closure.



3 4

Treatment of **1a** in acetone solution with sodium iodide results in a rapid reversion to **3**, with an approximate second-order rate constant at 25 °C of 0.4 M^{-1} min^{-1} ($t_{1/2}$ of ca. 2 min at 1 M I^-). This reactivity is in excess of that needed or desired for protective group removal, and in fact, slow ring cleavage of **1a** was also observed in acetonitrile containing benzylamine or alanine methyl ester (rate constants of ca. 2×10^{-3} M^{-1} min^{-1}).

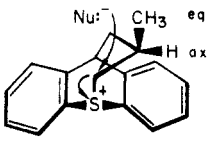
Structural modification of **1a** to retard the displacement reactions at the reactive methylene carbon was achieved by introduction of a single methyl group, creating an alkyl branch at the carbon β to the site of displacement. The required 9,10-(2-methylpropano)thioxanthylium fluoroborate (**6**) was prepared by reaction of **5** with silver fluoroborate.



5 6

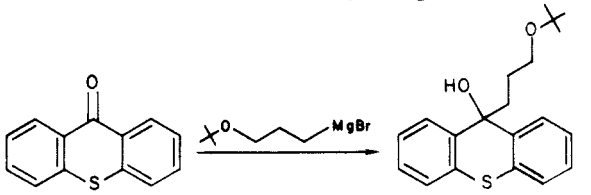
No reaction between **6** and 0.5 M benzylamine in acetonitrile could be detected even after 16 days. Sodium iodide in acetonitrile resulted in cleavage with an approximate rate constant at 25 °C of 4×10^{-3} M^{-1} min^{-1}, and tetramethylguanidinium thiophenoxide resulted in a cleavage that was complete within the time of addition to **6** in acetonitrile. In each case we observed quantitative formation of the product of nucleophilic displacement at the *S*-methylene function.

The very large rate retardation observed for the displacement by nucleophiles can be rationalized as follows. From models, the likely conformation of the propano bridge has staggered C–C bonds and positions one of the hydrogens ov C-2′ of **1a** in van der Waals contact with the π electrons of one of the phenylene functions. The methyl group of **6** is thus forced to assume an orientation that creates maximum hindrance for a displacing nucleophile as seen in **7**.



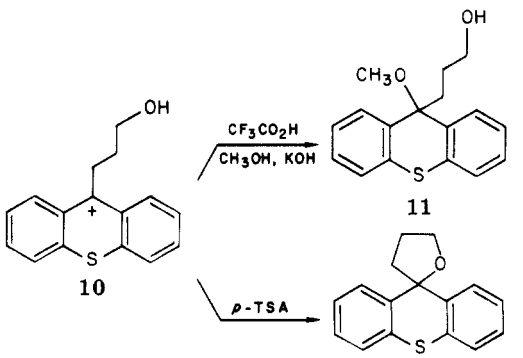
7

An entry into the desired 9-oxygenated 9-alkyl derivatives is most conveniently available from **9** which can be prepared from thioxanthone by Grignard addition.



8 9

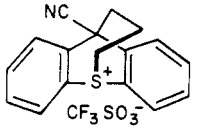
Treatment of **9** with trifluoroacetic or *p*-toluenesulfonic acid resulted in formation in solution of carbocation **10** which could be reversibly converted into ether **11** or to cyclic ether **12**. The ease of formation of **10** allows for the



10 11 12

preparation of 9-substituted thioxanthene derivatives such as **11**. However, these are difficult to obtain in pure form owing to their ready reconversion to **10** or **12**. The lability of **11** under acidic or neutral conditions provides eloquent evidence for our initial premise that species **2** would prove to be cleaved at the alkyl–oxygen bond under mild conditions; the same lability renders syntheses of species **1** (Y = OH) quite difficult.

A reddish oil which exhibited the correct ^1H NMR spectroscopic features of **1** results if **12** is treated at 0 °C with 2 equiv of triflic anhydride, stirred for 5 min at 0 °C and 5 min at 25 °C, quenched with excess *tert*-butyl alcohol in ether and repeatedly concentrated. Attempts to obtain crystalline material from this preparation have thus far failed. The sole characterized example we have thus far realized of structure **1** for which Y is an electronegative group is 9-cyano-9,10-propanothioxanthylium triflate (**13**), which has been prepared in two steps from the known 9-cyanothioxanthene.



13

Experimental Section

Unless otherwise specified, reagents and solvents were reagent grade and used without further purification. All melting points are uncorrected. The NMR spectra were recorded with a 60-MHz Varian Associate Model A-60 spectrometer. Analyses were performed by Midwest Laboratories Ltd. and Galbraith Laboratories, Inc.

9-(3-Iodopropyl)thioxanthene (3). A solution of 9-(3-chloropropyl)thioxanthene[6] (3.0 g, 1.1 mmol) and NaI (3.3 g, 2.2 mmol) in acetone (30 mL) was refluxed overnight. The solution containing precipitated NaCl was filtered and evaporated to yield 4.0 g (100%) of a thick, yellow oil which was used without further purification; NMR ($CDCl_3$) δ 1.7 (m, 4 H), 3.0 (t, 2 H), 3.9 (t, 1 H), 7.1 (m, 8 H).

9,10-Propanothioxanthylium Tetrafluoroborate (1a). A solution of **3** (1.5 g, 4.1 mmol) in a mixture of benzene (15 mL)

and CH_2Cl_2 (15 mL) was degassed and treated in a drybox with $AgBF_4$ (0.88 g, 4.5 mmol). As the $AgBF_4$ dissolved, a yellow precipitate appeared. After 30 min of being stirred at room temperature, the solution was filtered and evaporated to yield 1.2 g (97%) of an oily solid. Recrystallization from EtOH afforded 1.0 g (80%) of the desired product as white crystals: mp 180–190 °C dec; NMR (CD_3CN) δ 2.0 (m, 4 H), 3.5 (t, 2 H), 4.6 (t, 1 H), 7.4–8.1 (m, 8 H).

9-(3-Hydroxypropyl)thioxanthene (4). A well-stirred solution of thioxanthene (10 g, 50 mmol) in benzene (80 mL) and anhydrous ether (80 mL) under N_2 was treated with a 1.9 M solution of *n*-BuLi (10 mmol) in hexane, dropwise. After 10 min, 3-bromopropanol (7 g, 5 mmol) in anhydrous ether (50 mL) was added dropwise, but quickly. The deep red carbanion solution became clear by the end of the addition. After 2 h, 1 N HCl (100 mL) was added. The layers were separated, and the organic layer was washed twice with water, dried ($MgSO_4$), and evaporated to yield 12.2 g (95%) of a thick, yellow oil. This was used without further purification; NMR ($CDCl_3$) δ 1.2-2.0 (m, 4 H), 3.5 (t, 2 H), 4.0 (t, 1 H), 7.3 (m, 5 H).

9,10-Propanothioxanthylium Triflate (1b). To **4** (0.46 g, 1.8 mmol) in dry benzene (10 mL) under N_2 was added a 2.1 M solution of *n*-BuLi (0.86 mL) in hexane. After the mixture was stirred for 5 min, 1.1 equiv of triflic anhydride was added dropwise, in an anhydrous inert atmosphere. After 3 h at room temperature the solution was filtered and the filter cake washed with ether. The filtrate was evaporated and ether was added to the residue. Filtration yielded 0.70 g of a white, crystalline compound. Recrystallization from acetonitrile–ether afforded 0.65 g (93%) of white crystals: mp 118–122 °C; NMR (CD_3CN) δ 2.0 (m, 4 H), 3.6 (t, 2 H), 4.8 (t, 1 H), 7.5–8.4 (m, 8 H). Anal. Calcd for $C_{17}H_{15}S_2F_3O_3$: C, 52.57; H, 3.89; S, 16.51. Found: C, 52.84; H, 4.06; S, 16.13.

9-(2-Methyl-3-chloropropyl)thioxanthene. A well-stirred solution of thioxanthene (9.9 g, 50 mmol) in a mixture of dry benzene (50 mL) and anhydrous ether (50 mL) under N_2 was treated with a 1.9 M solution of *n*-BuLi (28 mL, 53 mmol) in hexane, dropwise. The resulting deep red carbanion solution was transferred to a 250-mL addition funnel with a cannula under anhydrous conditions and added under nitrogen dropwise to 1-bromo-2-methyl-3-chloropropane (47 mL) in anhydrous ether (50 mL). The solution was stirred at room temperature for 1 h and refluxed for 1 h. After cooling, the solution was filtered through a bed of Standard Super Cell and the filtrate was evaporated to yield 13 g (90%) of a yellow oil. Vacuum distillation afforded 10.5 g (73%) of a thick yellow oil: bp 141–145 °C (0.10 mm); NMR ($CDCl_3$) δ 1.1 (d, 3 H), 1.4–2.2 (m, 3 H), 3.4 (d, 2 H), 4.2 (t, 1 H), 7.3 (m, 8 H).

9-(2-Methyl-3-iodopropyl)thioxanthene (5). A solution of 9-(2-methyl-3-chloropropyl)thioxanthene (2.0 g, 6.9 mmol) and NaI (11.0 g, 74 mmol) in acetone (25 mL) was refluxed for 51 h. Filtration yielded NaCl (0.35 g). The filtrate was evaporated to yield 2.5 g (96%) of an oil which crystallized. Recrystallization from EtOH afforded 2.0 g (77%) of white needles: mp 70–73 °C; NMR ($CDCl_3$) δ 1.0–2.0 (m, 6 H), 3.2 (d, 2 H), 4.1 (t, 1 H), 7.3 (m, 8 H).

9,10-(2-Methylpropano)thioxanthylium Tetrafluoroborate (6). A solution of **5** (4.0 g, 11 mmol) in dry benzene (10 mL) and dry CH_2Cl_2 (10 mL) was degassed, protected from light, and treated in a drybox with $AgBF_4$ (2.3 g, 12 mmol). The solution (under an inert atmosphere) was taken out of the drybox immediately and cooled to 0 °C. After 3 h at 0 °C, it was stirred for 1 h at room temperature. The orange solution containing a yellow precipitate was then filtered through a bed of Standard Super Cell and the filtrate was evaporated to yield an oil. CH_3CN was added, the solution was again filtered through a bed of Standard Super Cell, and the filtrate was concentrated to yield an oil. Trituration with ether–EtOH followed by filtration yielded 2.1 g (59%) of a yellow powder containing some silver salts. Recrystallization from EtOH (hot filtration) afforded 1.1 g (30%) of white needles: mp 193–196 °C; NMR[8] (CD_3CN) δ 0.9 (d, 3 H), 1.6 (m, 2 H), 2.4 (d, 1 H), 3.0 (m, 1 H), 3.8 (d with additional fine splitting, 1 H), 4.7 (d, 1 H), 7.7 (m, 6 H), 8.0 (m, 2 H); UV (EtOH) 270 mm (2400). Anal. Calcd for $C_{17}H_{17}BF_4S$: C, 60.02; H, 5.04; S, 9.43. Found: C, 60.27; H, 5.26; S, 9.23.

Reactions of Benzylamine, Alanine Methyl Ester, Sodium Iodide, and Thiophenoxide with 1a and 6. The thioxanthylium salt was weighed directly in an NMR tube and dissolved in a measured volume of CD_3CN. At the NMR spectrometer, 1 or 2 equiv of the nucleophile was added. After the tube was briefly shaken, the NMR spectrum was taken at intervals appropriate for following the reaction. The rate of cleavage could be determined by observing the upfield peak shift of the methine proton with time. In the reaction with NaI, a final spectrum was obtained which was superimposable with the respective iodides (**3** and **5**) prepared as described previously. The reactions with benzylamine, alanine methyl ester, and thiophenoxide gave spectra with the predicted chemical shifts.

9-Cyano-9-(3-hydroxypropyl)thioxanthene. To a stirred solution of 9-cyanothioxanthene[7] (2.0 g, 9 mmol) in dry DMF (10 mL) under N_2 at 0 °C was added 50% NaH in oil (1.2 g, 18 mmol). After bubbling ceased, 3-bromo-1-propanol (1.4 g, 9 mmol) was added dropwise to the red solution. The mixture was stirred at room temperature for 10 min and at 40 °C for 15 min. After dilution with two volumes of water, the products were extracted into EtOAc. The EtOAc extracts were washed once with 1 N HCl, once with 1 N NaOH, and three times with water, dried ($MgSO_4$), and evaporated to yield an oil. After three washings with hexane, 2.0 g (80%) of the 9-cyano-9-(3-hydroxypropyl)thioxanthene containing a small amount of 3-bromo-1-propanol was obtained as an oil; NMR ($CDCl_3$) δ 1.6 (m, 2 H), 2.1 (m, 2 H), 3.4 (t, 2 H), 7.3 (m, 6 H), 7.8 (m, 2 H).

9-Cyano-9,10-propanothioxanthylium Triflate (13). To 9-cyano-9-(3-hydroxypropyl)thioxanthene (1.0 g, 3.6 mmol) in dry benzene (10 mL) was added at 10 °C a 2.1 M *n*-BuLi–hexane solution (1.7 mL, 3.6 mmol). After the mixture was stirred for 5 min, triflic anhydride (0.62 mL, 3.6 mmol) was added. A red color eveloped and a small amount of red oil was deposited on the sides of the flask. After 2 h, the solution was concentrated and the residual red oil was dissolved in a minimal amount of CH_3CN. Ether was then added dropwise until the solution became cloudy. After the mixture cooled to 0 °C, a crystalline precipitate appeared. Filtration yielded 0.5 g (34%) of white crystals. Recrystallization from EtOH–ether afforded 0.3 g (20%) of the triflate salt: mp 175–190 °C; NMR (CD_3CN) δ 2.0 (m, 2 H), 2.6 (t, 2 H), 3.6 (t, 2 H), 7.6–8.3 (m, 8 H).

9-Hydroxy-9-(3-*tert*-butoxypropyl)thioxanthene (9). A solution of 3-*tert*-butoxy-1-propyl bromide (13.8 g, 71 mmol) in anhydrous ether (100 mL) was added dropwise to a suspension of magnesium turnings (1.7 g, 75 mmol) in anhydrous ether (10 mL) containing 2 drops of 1,2-dibromoethane under N_2. After the addition of approximately 1 mL of the solution, the ether was gently refluxed to initiate the reaction. The ether continued to reflux and the magnesium dissolved without any further application of outside heat for the continuation of the addition of the halide solution. After the addition, the solution was refluxed for 1 h and thioxanthen-9-one (5.5 g, 26 mmol) was added in portions over a 30-min period. A white, thick precipitate formed during the addition. After a continued reflux for 1.5 h, 3 N NH_4Cl (100 mL) solution was slowly added dropwise. To the resulting solidified solution were added EtOAc (100 mL) and water (100 mL) and the mixture was stirred until homogeneous. The layers were separated and the EtOAc layer was washed twice with water, dried (Na_2SO_4), and evaporated to yield 8.6 g (100%) of a white solid. Recrystallization from EtOH afforded 7.0 g (80%) of white crystals: mp 139–143 °C; IR ($CDCl_3$) 3300 cm^{-1}; NMR ($CDCl_3$) δ 1.3 (s, 9 H), 2.0 (m, 2 H), 3.3 (t, 2 H), 6.1 (exchangeable s, 1 H), 7.3 (m, 6 H), 8.0 (m, 2 H). Anal. Calcd for $C_{20}H_{24}SO_2$: C, 73.13; H, 7.36; S, 9.76. Found: C, 72.98; H, 7.41; S, 9.78.

Addition of a small amount of *p*-TSA converts the alcohol to the eliminated product, 9-(3-*tert*-butoxy-1-propylene)thioxanthene; NMR ($CDCl_3$) δ 1.3 (s, 9 H) 2.7 (m, 2 H), 3.5 (t, 2 H), 5.9 (t, 1 H), 7.3 (m, 8 H).

Thioxanthenespiro-2′-(tetrahydrofuran) (12). A solution of **9** (1.3 g, 4.0 mmol) and *p*-TSA (40 mg) in benzene (30 mL) was refluxed for 16 h. The solution was then vigorously stirred while a 5% $NaHCO_3$ solution (20 mL) was added. The layers were then separated and the base layer was washed once with benzene. The

(8) The ^1H NMR spectrum is complicated because the methyl group in the propyl ring bridge hinders the flipping of the propyl grouping, thereby rendering the protons on the bridge unequivalent.

benzene layers were combined, dried (Na_2SO_4), and evaporated to yield 0.9 g (90%) of a yellow oil which slowly crystallized. Recrystallization from EtOAc–cyclohexane afforded 8.0 g (80%) of white crystals: mp 71–75 °C; NMR ($CDCl_3$) δ 2.0 (m, 4 H), 4.3 (t, 2 H), 7.0–7.8 (m, 8 H). Anal. Calcd for $C_{16}H_{14}OS$: C, 75.56; H, 5.55; S, 12.64. Found: C, 75.34; H, 5.51; S, 12.64.

9-Methoxy-9-(3-hydroxypropyl)thioxanthene (11). A solution of **9** (0.20 g, 0.6 mmol) in TFA (1 mL) was stirred at room temperature. The solution was deep red. After 2 h, MeOH (10 mL) was added and the resulting pale yellow solution was immediately added to vigorously stirred MeOH (30 mL) containing KOH (1.2 g). After 1 h of stirring, the volume of solution was evaporated to ca. 5 mL and Et_2O (20 mL) was added. The ether solution was washed twice with water, dried ($NaSO_4$), and evaporated to yield 0.15 g (88%) of a thick, yellow oil which by NMR was 85% of the desired **11**; NMR ($CDCl_3$) δ 1.4 (m, 2 H), 1.9 (m, 2 H), 2.4 (br exchangeable s, 1 H), 3.0 (s, 3 H), 3.3 (t, 2 H), 7.1–7.7 (m, 8 H). Addition of a small amount of *p*-TSA to the NMR tube converts the methyl ether to **12**.

Acknowledgment. Financial support from the National Institutes of Health (GM 13453-15) is gratefully acknowledged.

Registry No. 1a, 76583-73-8; **1b**, 76583-74-9; **3**, 76583-75-0; **4**, 76583-76-1; **5**, 76583-77-2; **6**, 76583-79-4; **8**, 492-22-8; **9**, 76583-80-7; **11**, 76583-81-8; **12**, 76583-82-9; **13**, 76583-87-4; 9-(3-chloropropyl)-thioxanthene, 25559-90-4; thioxanthene, 261-31-4; 3-bromopropanol, 627-18-9; 9-(2-methyl-3-chloropropyl)thioxanthene, 76583-83-0; 1-bromo-2-methyl-3-chloropropane, 6974-77-2; 9-cyano-9-(3-hydroxypropyl)thioxanthene, 76583-84-1; 9-cyanothioxanthene, 25559-83-5; 3-*tert*-butoxy-1-propyl bromide, 30418-76-9; 9-(3-*tert*-butoxy-1-propylene)thioxanthene, 76583-85-2.

Regiospecific Reactions of Some Vinylogous Ketene Acetals with Haloquinones and Their Regioselective Formation by Dienolization

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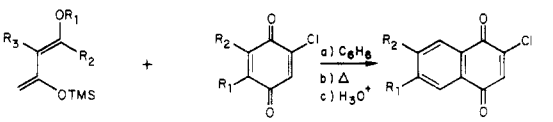
Regiospecific reactions of simple 1,3-bis(trimethylsiloxy)-1,3-butadienes with 2,5- and 2,6-dichlorobenzoquinones gave chloronaphthoquinones which, by applying the appropriate vinylketene acetal, provided various monomethyl ethers of isomeric polyhydroxyanthraquinones. The first total synthesis of macrosporin (**27**) was obtained in this way and the proposed structure for "cajaquinone" (**28**) found to be incorrect. Simple syntheses of 2-hydroxy-3-methylanthraquinone (**16**), phomarin (**19**), soranjidiol (**22**) and other naturally occurring quinones are also described. The dienolization of 1-methoxy-2,4-pentanedione in the presence of chlorotrimethylsilane gave either 1- or 5-methoxy-2,4-bis(trimethylsiloxy)-1,3-pentadiene, depending upon the reaction conditions. Both dienes react with haloquinones, giving regiospecific products, e.g., tetra-*O*-methylerythrolaccin (**35**).

Vinylogous ketene acetals (1,3-dioxygenated butadienes) have been shown to be useful partners in cycloaddition reactions with quinones[1a-m] and on occasion to provide effective regiochemical control of this process.[1d,f,i-k] Juglone (5-hydroxynaphthoquinone) and its derivatives in particular give regiospecific products,[1d,k] but the orientation of addition induced by halogen substituents has been observed only in the case of hindered reagents such as 2,4-dioxygenated pentadienes[1i] (**3**, **4**).

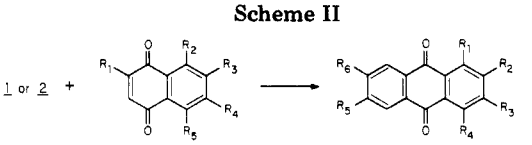
It has now been established that simple 1,3-bis(trimethylsiloxy)-1,3-butadienes (**1**, **2**) give analogous results with 2,5- and 2,6-dichlorobenzoquinones (**5**, **6**), providing chloronaphthoquinones as convenient intermediates for a second regiospecific annulation with other dienes such as vinylketene acetals (**23**, **26**). They also react directly with halonaphthoquinones to give various naturally occurring anthraquinones.

Scheme I



1 R_1 = TMS, R_2 = R_3 = H
2 R_1 = TMS, R_2 = H, R_3 = CH_3
3 R_1 = R_2 = CH_3, R_3 = H
4 R_1 = R_2 = CH_3, R_3 = CO_2CH_3
5 R_1 = Cl, R_2 = H
6 R_1 = H, R_2 = Cl
7 R_1 = H, R_2 = OH
8 R_1 = OH, R_2 = H
9 R_1 = CH_3, R_2 = OH
10 R_1 = OH, R_2 = CH_3

Scheme II



11 R_1 = Cl, R_2 = R_3 = R_4 = R_5 = H
12 R_1 = Cl, R_2 = OH, R_3 = R_4 = R_5 = H
13 R_1 = Cl, R_2 = OH, R_3 = R_5 = H, R_4 = CH_3
14 R_1 = Br, R_2 = OH, R_3 = CH_3, R_4 = H, R_5 = Cl
15 R_1 = R_2 = R_3 = R_4 = R_6 = H, R_5 = OH
16 R_1 = R_2 = R_3 = R_4 = H, R_5 = OH, R_6 = CH_3
17 R_1 = R_2 = R_3 = R_4 = H, R_5 = OCH_3, R_6 = CH_3
18 R_1 = R_5 = OH, R_2 = R_3 = R_4 = R_6 = H
19 R_1 = R_5 = OH, R_2 = R_4 = R_6 = H, R_3 = CH_3
20 R_1 = OH, R_2 = R_4 = R_6 = H, R_3 = CH_3, R_5 = OCH_3
21 R_1 = R_5 = OH, R_2 = CH_3, R_3 = R_6 = H, R_4 = Cl
22 R_1 = R_5 = OH, R_2 = CH_3, R_3 = R_4 = R_6 = H

The usual procedures used in combining ketene or vinylketene acetals with benzoquinones gave unsatisfactory results. An adduct formed in THF at −60 °C between diene **1** and quinone **6** was aromatized by being refluxed in methanol and gave a 14% yield of 2-chloro-6-meth-

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