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The Preparation of β-Fluoro Thioethers

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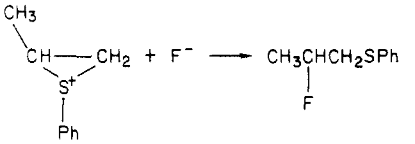
Addition of benzenesulfenyl chloride to electron-rich olefins in the presence of silver produces β-fluoro thioethers. The trans adducts could also be prepared from β-chloro thioethers and silver fluoride.

Attempts to introduce fluorine selectively into organic substrates under mild conditions led to a study of the addition of sulfenyl chlorides to alkenes in the presence of silver fluoride. Addition of benzenesulfenyl chloride to an alkene in acetonitrile in the presence of certain metal fluorides results in the formation of β-fluoro phenyl thioethers. The results, shown in Table I, indicate that the reaction is dependent on the particular metal fluoride used and that the regiochemistry is dictated by the structure of the alkene.

$$RCH{=}CH_2 + \underset{\mathbf{1}}{PhSCl} \xrightarrow[CH_3CN]{MF} \underset{\mathbf{2M}}{RCHFCH_2SPh} + \underset{\mathbf{2A}}{RCH(SPh)CH_2F} \quad (1)$$

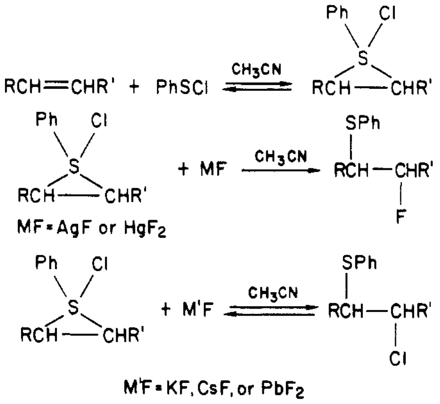
The regiochemistry of the addition of benzenesulfenyl chloride in the presence of metal fluorides is similar to that observed when methanesulfenyl chloride is added to terminal olefins.[1] In that case a high proportion of the anti-Markovnikoff adduct, with a primary chlorine, was observed for alkyl-substituted terminal alkenes. With time this adduct rearranged to the thermodynamically favored Markovnikoff adduct, with the sulfur in the primary position. Mueller and Butler[1] suggested that steric factors determine the direction of ring opening of an intermediate episulfonium ion. Since that time, the intermediacy of episulfonium ions during the addition of sulfenyl chlorides to alkenes has been questioned. During an investigation into the mechanism of sulfenyl halide addition reactions, Smit et al.[2] prepared episulfonium hexafluoroantimonates and treated them with various nucleophiles. Because the ratio of Markovnikoff (**2M**) and anti-Markovnikoff (**2A**) product differed from that observed during the alkene addition reaction, they concluded that episulfonium ions are not intermediates in the reaction. When Smit et al. treated the episulfonium ion from propene and (phenylthio)hexafluoroantimonate with fluoride ion, they found greater than 95% of the Markovnikoff adduct.[2]



(2)

After an extensive kinetic study on the addition of benzenesulfenyl chloride to a large number of alkenes under nonpolar conditions, Stirling and co-workers[3] concluded from the insensitivity of the substituent groups that there is a little charge localization on carbon in the transition state. They also noted intramolecular interaction of sulfur with heteroatom substituents on selected alkenes. These results which suggest the intermediacy of a neutral sulfurane are supported by ab initio SCF-MO calculations.[4]

Scheme I



Further support for sulfuranes comes from the isolation of the analogous selenuranes formed by reaction of the corresponding arene selenyl halides with alkenes.[5]

In a recent review the entire spectrum of intermediates ranging from free episulfonium ions to neutral sulfuranes is proposed depending upon the reaction conditions.[6] Under nonpolar conditions the absence of ionic intermediates can be inferred since solvent incorporation[7] and skeletal rearrangements[8] are not observed. Our results also suggest that the formation of the β-halo thioethers in nonpolar solvents occurs by way of intermediate halosulfuranes as shown in Scheme I.

Results

When benzenesulfenyl chloride is added to cyclohexene in acetonitrile in the presence of silver fluoride at room temperature, 1-fluoro-2-(phenylthio)cyclohexane is formed in 70% yield. None of the corresponding chloro derivative is observed in the NMR of the crude reaction product. The phenylthio and the fluorine are trans to one another as determined by NMR. From the spin-decoupled spectrum of 1-fluoro-2-(phenylthio)cyclohexane, a $^3J_{H-H}$ of 10.5 Hz is obtained for the protons on C-1 and C-2. A coupling constant of this magnitude is expected for a 1,2-diaxial proton interaction;[9] hence the PhS and F, equatorially disposed, are trans to one another. Treatment of *trans*-1-chloro-2-(phenylthio)cyclohexane with silver fluoride also results in formation of *trans*-1-fluoro-2-(phenylthio)cyclohexane.

In the reaction of 3,3-dimethyl-1-butene with benzenesulfenyl chloride in the presence of AgF at room temperature only 1-fluoro-2-(phenylthio)-3,3-dimethylbutane, the

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(7) Hogg, D. R.; Kharasch, N. *J. Am. Chem. Soc.* **1956**, *78*, 2728.

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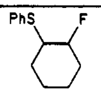
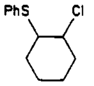
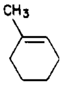
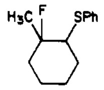
0022-3263/86/1951-1080$01.50/0

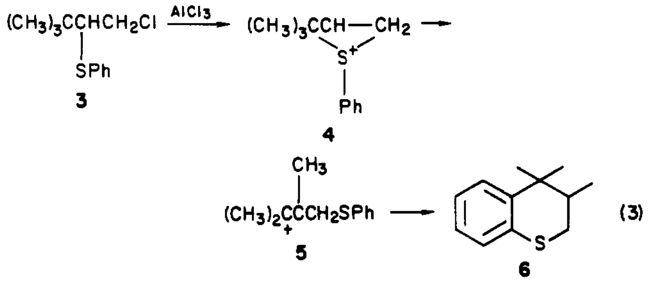
Table I. Preparation of β-Fluoro Thioethers

alkene	metal fluoride	product	yield, %	bp, °C (mmHg)
	AgF		70	115–116 (0.5)
	HgF_2		40	
	KF		*a*	*a*
	CsF		*a*	*a*
	PbF_2		*a*	*a*
$(CH_3)_3CCH{=}CH_2$	AgF	$(CH_3)_3CCH(SPh)CH_2F$	70	94–96 (0.6)
$HOC(CH_3)_2CH{=}CH_2$	AgF	$HOC(CH_3)_2CH(SPh)CH_2F$	60	*b*
$CH_3(CH_2)_7CH{=}CH_2$	AgF	$CH_3(CH_2)_7CH(SPh)CH_2F$	21	130 (0.4)
		$CH_3(CH_2)_7CH(F)CH_2SPh$	42	
$PhC(CH_3){=}CH_2$	AgF	$PhCF(CH_3)CH_2SPh$	51	oil[b]
	AgF		57	oil
$CH_2{=}CHCH_2Cl$	AgF	$FCH_2CH(SPh)CH_2Cl$	35	112 (0.3)

[a] Not determined. [b] Elemental analysis not obtained as it dehydrofluorinates.

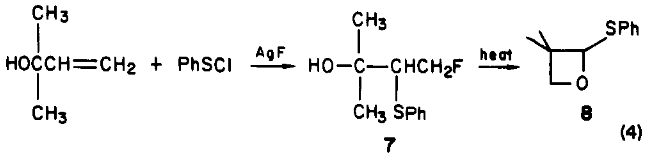
anti-Markovnikoff product, is formed. No products of rearrangement or of solvent incorporation were observed. The fluoride, unlike 1-chloro-2-(methylthio)-3,3-dimethylbutane, did not rearrange to the thermodynamically more stable isomer. Treatment of 1-chloro-2-(phenylthio)-3,3-dimethylbutane with silver fluoride under the reaction conditions produced the corresponding fluoride, as shown by NMR.

An attempt to prepare 2-chloro-1-(phenylthio)-3,3-dimethylbutane according to the literature procedure[10] resulted only in the formation of its isomer. We have been unable to effect isomerization to the Markovnikoff product. 1-Chloro-2-(phenylthio)-3,3-dimethylbutane (3) rearranged when treated with anhydrous aluminum chloride as shown in eq 3. The trimethylbenzothiane 6 was identified by NMR.



(3)

Like 3,3-dimethyl-1-butene, 2-methyl-3-buten-2-ol formed the anti-Markovnikoff addition product as shown in eq 4. A 60% yield of 2-methyl-3-(phenylthio)-4-fluoro-2-butanol (7) was obtained from the reaction with benzenesulfenyl chloride in the presence of silver fluoride. On attempted distillation this adduct underwent the loss of HF to form oxetane 8.



(4)

Addition of benzenesulfenyl chloride to α-methylstyrene in the presence of silver fluoride led exclusively to 1-(phenylthio)-2-fluoro-2-phenylpropane. As shown by NMR this β-fluoro thioether dehydrohalogenated on standing to a mixture of 9 and 10 in a manner analogous to the chloro adduct.[3]

$$\begin{aligned} &PhC(CH_3){=}CH_2 + PhSCl \xrightarrow{AgF} PhCF(CH_3)CH_2SPh \\ &\rightarrow \underset{9}{PhC({=}CH_2)CH_2SPh} + \underset{10}{PhC(CH_3){=}CHSPh} \quad (5) \end{aligned}$$

1-Methyl-1-cyclohexene reacted with benzenesulfenyl chloride in acetonitrile in the presence of silver fluoride to provide exclusively the Markovnikoff adduct, whereas allyl chloride gave only the anti-Markovnikoff adduct. When 1-decene was used as the substrate, a 2:1 mixture of adducts was formed with the Markovnikoff product predominating. Under the reaction conditions isomerization of the anti-Markovnikoff product did not occur. Neither acrylonitrile nor 2-cyclohexen-1-one formed an adduct.

Both silver(I) fluoride and mercury(II) fluoride in acetonitrile gave rise to β-fluoro thioethers, whereas potassium, cesium, and lead(II) fluorides resulted only in the formation of β-chloro thioethers. The yield of fluorinated adduct was lower when HgF_2 was used as the fluoride source than when AgF was used. Addition of benzenesulfenyl chloride to the alkene in the presence of 18-crown-6 and KF did not lead to fluoride incorporation.

Discussion

We propose that the mechanism shown in Scheme I is operative during the addition of benzenesulfenyl halides to alkenes in nonpolar solvents. A neutral chlorosulfurane is formed reversibly. Schmid and co-workers have shown that 2-chlorocyclooctyl aryl sulfide reacts with 1-octene to form cyclooctene and 2-chlorooctyl aryl sulfide, which indicates that the overall reaction is reversible.[11] A catalytic amount of chloride ion attacks the sulfurane from the back side forming the trans adduct and generating chloride ion. This step must also be reversible. In the presence of silver fluoride, fluoride ion attacks the sulfurane generating the trans β-fluoro thioether and chloride ion which precipitates from the solution as silver chloride.

Free episulfonium ions are not involved in the reaction as evidenced by the lack of rearrangements or solvent

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incorporation from the addition of benzenesulfenyl chloride to 3,3-dimethyl-1-butene. Smit and co-workers[8] have prepared episulfonium ion **4** and find that it is stable at −20 °C but rearranges to **6** to +20 °C. We studied the addition of benzenesulfenyl chloride to 3,3-dimethyl-1-butene at room temperature and found no evidence of rearrangement. As little as 1% of **6** would have been detected in the NMR spectrum of the crude reaction mixture.

The formation of these β-fluoro thioethers from benzenesulfenyl chloride in the presence of silver fluoride is not a displacement reaction of fluoride ion on the chloro adduct. Although a primary fluoride can be prepared by a simple S_N2 displacement of chloride by fluoride, a secondary fluoride cannot be prepared in this manner. The time required for formation of the fluoride from the chloride is greater than that needed from the alkene. Further, when *trans*-1-chloro-2-(phenylthio)cyclohexane is treated with silver fluoride, the trans fluoro compound is formed, indicating assistance from the neighboring sulfur.

Stirling's group noted the order of addition of benzenesulfenyl chloride to alkenes is cyclohexene > 1-methylcyclohexene > α-methylstyrene > allyl chloride ≫ acrylonitrile. In the preparation of β-fluoro thioethers, the yield of product also decreases in this order. Electron-withdrawing groups retard formation of the intermediate so that a competitive reaction between benzenesulfenyl chloride and silver fluoride occurs. In the case of acrylonitrile, no addition product is formed.

In the absence of substrate, benzenesulfenyl chloride reacts with silver fluoride and acetonitrile. The addition of benzenesulfenyl chloride to silver fluoride in acetonitrile results in the instantaneous formation of a white precipitate and a canary yellow solution. Within an hour at room temperature, the solution fades to become almost colorless. The white precipitate that forms is silver chloride, and the solution contains diphenyl disulfide. Thus, an oxidation also must be occurring. Mercury(II) fluoride is known to fluorinate acetonitrile to give various compounds containing N–F linkages;[12] however, in our reaction no N–F bonds are detected by ^{19}F NMR. Observations during the reaction lead us to postulate the intermediacy of benzenesulfenyl fluoride which fluorinates the solvent according to eq 6. On attempted isolation, the fluorinated compound decomposes.

$$\mathrm{2PhSCl + 2AgF \rightarrow 2AgCl + [2PhSF] \xrightarrow{CH_3CN} PhSSPh + [CH_3C(F){=}N{-}N{=}C(F)CH_3]} \quad (6)$$

The metal fluoride included in the reacting solution determines which halogen is incorporated. In acetonitrile, the soft Ag(I) and Hg(II) cations are solvated, and the reactivity of the fluoride is enhanced. In the case of silver fluoride, the insolubility of silver chloride in acetonitrile[13] is a driving force that pushes the reaction to completion as shown in Scheme I. When the reaction is run in THF, no organic fluoride is formed because of the insolubility of AgF in this solvent. The yield of β-fluoro thioether is low when HgF_2 is used to promote the reaction because HgF_2 is not solvated in CH_3CN as well as AgF, and also HgF_2 can fluorinate acetonitrile.[12] Since lead(II) ion is borderline and both potassium and cesium are hard cations, no complexation with acetonitrile is observed, and the salts are virtually insoluble. Therefore, no reaction involving fluoride ion occurs.

The addition reaction to form β-fluoro thioethers uses mild conditions compared with most fluorination procedures. This is particularly true for the case of tertiary fluorides that cannot be prepared by displacement reactions. We are currently investigating various methods of desulfurizing these compounds.

Experimental Section

General Data. ^{1}H NMR (90 MHz) and ^{19}F NMR (84.67 MHz) were obtained on a Varian EM-390 NMR spectrometer. Chemical shifts are reported in ppm downfield relative to internal Me_4Si for ^{1}H NMR data and to external $CFCl_3$ for ^{19}F NMR, with $CDCl_3$ as solvent in both cases. Microanalyses were performed by Atlantic Microlab Inc., Atlanta, GA. Boiling points and melting points are uncorrected. Silver fluoride was obtained from Ozark Mahonning.

General Preparation of β-Fluoro Thioethers. After acetonitrile (100 mL) and metal fluoride (0.03 mol) were stirred together for 10 min in an Erlenmeyer flask, the alkene (0.03 mol) was introduced. Then benzenesulfenyl chloride[3] (0.03 mol) was added dropwise from an addition funnel. Immediate workup showed that the reaction was complete. However, usually the mixture was stirred overnight and filtered and the solvent removed by rotary evaporation. The composition of the product mixture was then determined directly by NMR. The products were purified by distillation.

***trans*-1-Fluoro-2-(phenylthio)cyclohexane**: bp 115–116 °C (0.5 mm); ^{1}H NMR δ 1.2–2.4 (m, 8 H), 3.0–3.4 (m, 1 H, $^3J_{H-H}$ = 10.5 Hz), 4.4 (m, 1 H, $^2J_{H-F}$ = 48 Hz), 7.2–7.6 (m, 5 H); ^{19}F NMR δ −167 (m). Anal. Calcd for $C_{12}H_{15}FS$: C, 68.60; H, 7.14; S, 15.40. Found: C, 68.52; H, 6.98; S, 15.49.

Fluoro(phenylthio)decanes: bp 130 °C (0.4 mm); ^{1}H NMR δ 0.6–2.0 (m, 17 H); 7.2–7.6 (m, 5 H) [peaks also observed at δ 3.0–3.4 and 4.5 (m, 3 H) attributed to protons α to fluorine and phenylthio groups]; ^{19}F NMR δ −175, −212 (m, 2:1). Anal. Calcd for $C_{16}H_{25}FS$: C, 71.60; H, 9.30; S, 11.91. Found: C, 71.61; H, 9.42; S, 12.02.

1-Fluoro-2-(phenylthio)-3,3-dimethylbutane: bp 94–96 °C (0.6mm); ^{1}H NMR δ 1.0–1.2 (s, 9 H), 3.05 (6 lines, 1 H), 4.6 (6 lines, 2 H), 7.2–7.6 (m, 5 H); ^{19}F NMR −208 (m, J_{HF} = 48 Hz). Anal. Calcd for $C_{12}H_{17}FS$: C, 67.90; H, 8.01; S, 15.09. Found: C, 67.97: H, 8.08; S, 14.96.

2-Methyl-3-(phenylthio)-4-fluoro-2-butanol (7): oil; ^{1}H NMR δ 1.31–1.39 (d, 6 H), 2.51–2.61 (s, 1 H), 3.26 (6 lines, dt, 1 H), 4.62 (6 lines, 2 H, $^2J_{HF}$ = 48 Hz), 7.13–7.52 (m, 5 H); ^{19}F NMR −211 (dt). Attempted distillation at 140 °C (3 mm) gave **8**: oil, ^{1}H NMR δ 1.06 (s, 3 H, 1.35 (s, 3 H), 2.8–3.2 (m, 3 H), 7.2–7.5 (m, 5 H). Anal. Calcd for $C_{11}H_{14}OS$: C, 67.94; H, 7.26; S, 16.50. Found: C, 67.94; H, 7.27; S, 16.46.

1-(Phenylthio)-2-fluoro-2-phenylpropane: oil; ^{1}H NMR δ 1.75 (d, 3 H, $^3J_{H-F}$ = 24 Hz), 3.28, 3.31, and 3.52 (3 s, 2 H), 7.07–8.52 (m, 10 H); ^{19}F NMR δ −142(m). On standing, dehydrofluorination occurs to give a mixture of **9** and **10** (30:70) as determined by ^{1}H NMR. **9**: ^{1}H NMR δ 3.85, 5.10, 5.30, 7.08–7.53;[14] **10**: ^{1}H NMR δ 1.55, 7.08–7.53.

1-Fluoro-1-methyl-2-(phenylthio)cyclohexane: oil; ^{1}H NMR δ 1.2–2.2 (m, 11 H), 3.31 (m, 1 H), 7.1–7.6 (m, 5 H); ^{19}F NMR δ −133. Anal. Calcd for $C_{13}H_{17}FS$: C, 69.60; H, 7.64; S, 14.29. Found: C, 69.35; H, 7.55; S, 14.42.

1-Fluoro-2-(phenylthio)-3-chloropropane: bp 112–113 °C (0.3 mm); ^{1}H NMR 3.32–3.78 (m, 2 H), 3.8–3.96 (d, 1 H), 4.4–4.93 (dd, 2 H, $^2J_{H-F}$ = 45 Hz), 7.17–7.6 (m, 5 H); ^{19}F NMR δ −220 (m). Anal. Calcd for $C_9H_{10}ClFS$: C, 52.80; H, 4.80; S, 15.69. Found: C, 52.71; H, 4.90; S, 15.65.

Fluorination of β-Chloro(phenylthio)alkanes. To a solution of AgF in CH_3CN, an equimolar portion of chloride was added. After the mixture was stirred overnight, the solid was filtered off and the solvent removed to provide the fluoride. On immediate workup of the reaction after mixing, β-chloro thioether was present.

Isomerization of 3 with $AlCl_3$. To 1-chloro-2-(phenylthio)-3,3-dimethylbutane[8] (1.2 g, 5.3 mmol) in 2 mL of CH_2Cl_2

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anhydrous $AlCl_3$ (0.5 g, 3.8 mmol) was added. The solution which stirred overnight at 0 °C turned wine red. The CH_2Cl_2 solution was extracted with cold water; removal of solvent gave **6**, an oil: ^1H NMR δ 0.98 (d, 3 H, J = 6 Hz), 1.29 (s, 3 H), 1.35 (s, 3 H), 2.0 (m, 1 H), 2.70 (dd, 1 H, J_{AB} = 6 Hz, J_{AC} = 14 Hz), 3.35 (dd, 1 H, J_{BA} = 5 Hz, J_{BC} = 14 Hz), 6.96–7.59 (m, 4 H).

Reaction of AgF with Benzenesulfenyl Chloride. To 0.88 g of AgF (6.9 mmol) in acetonitrile (4.0 mL) under nitrogen was added 1.00 g of benzenesulfenyl chloride (6.9 mmol) with stirring. A precipitate formed, and the solution turned canary yellow. After 1 h, the solution was almost colorless. Silver chloride (0.81 g, 82%) was recovered by filtration. ^{19}F NMR of the remaining solution showed a multiplet at δ −173. On attempted distillation the signal disappeared. Diphenyl disulfide (0.73 g, 95%) was recovered after removal of solvent.

Acknowledgment. We thank Dan Woodard for technical assistance.

Registry No. **3**, 57187-86-7; **6**, 54442-00-1; **8**, 100655-83-2; **9**, 84538-93-2; **10**, 36219-91-7; AgF, 7775-41-9; HgF_2, 7783-39-3; $FCH_2CH(SPh)CH_2Cl$, 100655-81-0; $CH_3(CH_2)_7CH(F)CH_2SPh$, 100655-82-1; $(CH_3)_3CCH(SPh)CH_2F$, 100655-76-3; $HO(CH_2)_2CH(SPh)CH_2F$, 100655-77-4; $CH_3(CH_2)_7CH(SPh)CH_2F$, 100655-78-5; $PhCF(CH_3)CH_2SPh$, 100655-79-6; $(CH_3)_3CCH{=}CH_2$, 558-37-2; $HOC(CH_3)_2CH{=}CH_2$, 115-18-4; $CH_3(CH_2)_7CH{=}CH_2$, 872-05-9; $PhC(CH_3){=}CH_2$, 98-83-9; $CH_2{=}CHCH_2Cl$, 107-05-1; cyclohexene, 110-83-8; 1-methylcyclohexene, 591-49-1; benzenesulfenyl chloride, 931-59-9; diphenyl disulfide, 882-33-7; 1-(phenylthio)-2-fluorocyclohexane, 97231-52-2; 2-methyl-2-fluoro-1-(phenylthio)cyclohexane, 100655-80-9.

Preparations and Reactions of 10-(Halomethylene)anthrones

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(Halomethylene)anthrones **3** and **4** were prepared by the simple method from 10-methylene- and 10-benzylideneanthrones. The reaction of **3** with azide ion gave 10-(azidomethylene)anthrone **5a**, which afforded **16** and/or **17** by photolysis and thermolysis, while similar treatment of **4** led to spiro[anthroneazirine] **19**. The reaction of **3** and **4** with cyanide ion gave the corresponding 10-(cyanomethylene)anthrones **5b** and **6b**. (Halomethylene)anthrone **3** reacted with methoxide ion, hydroxide ion, and aniline to give **5c**, **5d**, and **5e**, respectively.

Methyleneanthrones are members of a class of compounds which are called "quinone methides", that is, compounds in which one carbonyl oxygen atom of a quinone is replaced by a methylene (or substituted methylene) group. This system is unstable and is subject to ionic addition and cycloaddition reactions because of the strong driving force for reaction supplied by aromatization of the product.[1] However, 10-methyleneanthrones, e.g., **1** and **2**, are stable and show no tendency toward spontaneous aromatization. The low probability of the central ring becoming aromatic makes their quinone methide character weak. Since the ethylenic bond is comparatively isolated from the carbonyl group in the molecule, these compounds behave as a quinone methide as well as an olefin.[1]

The chemistry of methyleneanthrones having an unsubstituted and aryl-substituted exomethylene group has been widely studied. They are useful starting or intermediate materials for a number of syntheses including the preparation of fused polycyclic compounds,[1a,c] 9,10-disubstituted anthracenes whose substituents are functionalized,[1a,2] and spiroanthronyl-substituted compounds which contain an anthrone (quinonoid) moiety and a carbocycle or heterocycle in spiroconfiguration.[2b–f,3] On the other hand, methyleneanthrones whose exomethylene is substituted by a group other than an aryl have received less attention, though some of their unique properties were known as described below. 10-(Hydroxymethylene)anthrone, prepared by the treatment of spiro[anthrone-10,2′-oxirane] with boron trifluoride etherate, is in tautomeric equilibrium in solution with 10-formylanthrone and 10-formyl-9-hydroxyanthracene. Also it has been converted into α-chloro-, α-methoxy-, and α-benzoyloxy-substituted methyleneanthrones.[2b–d] The solvolysis reaction via intermediate vinyl cations of 10-(α-bromoarylidene)anthrones, which are prepared by dehydrobromination of 10-arylideneanthrone dibromides, has been studied.[4] The present paper is concerned with the syntheses and reactions of α-substituted 10-methylene-

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