of Me_3SiCl (0.55 mol, 59.5 g) were premixed and added dropwise to 300 ml of vigorously stirring ice water in a 500-ml erlenmeyer flask. When complete, the solution was transferred to a separatory funnel, and the organic layer was separated, dried over Na_2SO_4, and distilled to give **2b** in 32% yield.

Reaction of Trimethylsilanol and $MeCl_2SiCH_2CHMeCH_2Cl$ (5).—Compound **5** (0.5 mol, 57 g) in 100 ml of dry THF was charged into a 250-ml flask equipped with stirrer, thermometer, and dropping funnel, and cooled to −5°. Pyridine (1 mol, 79 g) was added dropwise, keeping temperature below 0°; trimethylsilanol (1 mol, 90 g) was added dropwise to this solution, again keeping the temperature below 0°. When addition was complete, the mixture was brought to room temperature and water was stirred into the reaction mixture; the organic layer was washed three times with water and dried over Na_2SO_4. Distillation gave 32 g (20%) of **2b**. Triethylamine was substituted for pyridine and glyme for THF with no change in product yield.

Registry No.—**1a,** 1438-82-0; **1b,** 1873-88-7; **1c,** 1873-89-8; **2a,** 37611-45-3; **2b,** 37611-46-4; **2c,** 37611-47-5; **3a,** 2943-62-6; **3b,** 22407-46-1; **3c,** 17905-99-6; **4b,** 37611-51-1; **4c,** 37611-52-2; β-methallyl chloride, 563-47-3.

Acknowledgment.—We would like to thank Dr. A. Berry, University of Pennsylvania, for helpful discussions.

Synthesis, Reactivity, and Spectral Properties of 2,7-Difluoro-9-chloromethylenexanthene. Isoelectronicity with Heptafulvene Derivatives

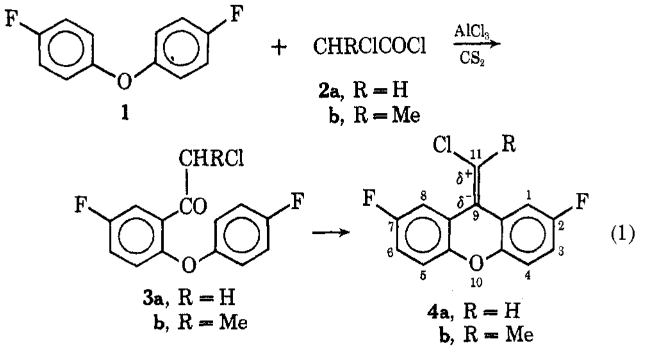
ITSHAK GRANOTH* AND ASHER KALIR

Israel Institute for Biological Research,
Tel-Aviv University Medical School, Ness-Ziona, Israel

Received July 21, 1972

The application of the Friedel–Crafts reaction for the preparation of phenoxaphosphines[1] and phenothiaphosphines[2] from aromatic ethers and sulfides, respectively, has now been extended to the xanthene system.

Synthesis, Structure, and Spectra.—2,7-Difluoro-9-chloromethylenexanthene (**4a**) was the only product isolated (in a good yield) from the reaction of **1** with **2a** (eq 1). 2-Chloroacetyl-4,4′-difluorodiphenyl ether (**3a**) was assumed as an intermediate since **2a** has been known to chloroacetylate aromatics.[3]



1

2a, R = H
b, R = Me

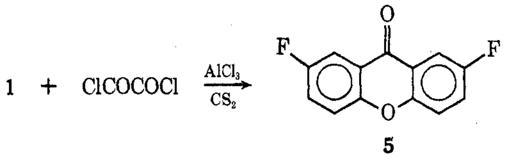
3a, R = H
b, R = Me

4a, R = H
b, R = Me

(1)

The structure of **4a** was elucidated from its spectral properties. The ir showed no carbonyl absorption and the nmr exhibited one vinylic proton and a characteristic low-field resonance at δ 8.22. The latter was a multiplet of 1 H, ortho to the fluorine (J_{HF} = 9 Hz), and further coupled with meta aromatic protons only. It was shown to be H-8 by the absence of this strong deshielding effect in other derivatives, such as **7a** and **b**, but not in **4b**. This deshielding must result from the long-range electrical effect of the chlorine atom.[4] A similar deshielding effect has been observed recently, though not confirmed, in α-chloro- and α-bromo-9-anisilidenefluorene.[5] These observations indicated the structure of **4a**, further confirmed by the analysis and the mass spectrum, which disclosed the presence of one chlorine atom and verified the molecular weight. The mass spectrum of **4a** exhibited a very intense peak corresponding to $(M - ClO)^+$. Its direct formation from the molecular ion was shown by an appropriate metastable transition. The elimination of ClO· as one entity from chlorinated aromatic ethers is known for some time.[6] However, until now the chlorine was directly attached to the aromatic ring.

The characteristic uv band of **4a** in EtOH appeared at 338 nm and was not shifted in cyclohexane. This, and the absence of the 338-nm band in the xanthene itself, suggested that the latter band is due to the $\pi \rightarrow \pi^*$ transition connected with the extended conjugation in 9-methylenexanthene derivatives as compared with xanthene. The methylenexanthene skeleton of **4a** was established by its oxidation with potassium permanganate to 2,7-difluoroxanthen-9-one (**5**). This compound was identical with a sample prepared as in eq 2.[7] Decarbonylation of oxalyl chloride during Friedel–Crafts reactions with aluminum chloride is well known.[8] Thus, two one-step syntheses of 2,7-difluoroxanthene derivatives were achieved.



5

(2)

The reaction described by eq 1 was markedly influenced by the substituent R. When R = H, the intermediate **3a** was very reactive, not allowing its isolation under the reaction conditions. When R = Me, **3b** was not cyclized by aluminum chloride in boiling carbon disulfide, thus enabling its isolation and characterization by nmr. (See Experimental Section.) Crude **3b** gave eventually **4b** upon heating on a water bath with little methanol and a trace of hydrochloric acid. However, no **4** (R = C_6H_5) was isolated from the reaction of **1** and **2** (R = C_6H_5), which yielded unidentified oil.[9] The introduction of an α-methyl group in **4a**,

---

[1] J. B. Levy, G. W. Whitehead, and I. Granoth, *Israel J. Chem.*, **10**, 27 (1972), and references cited therein.

[2] I. Granoth, A. Kalir, Z. Pelah, and E. D. Bergmann, *Tetrahedron*, **25**, 3919 (1969).

[3] F. Tutin, *J. Chem. Soc.*, **97**, 2495 (1910).

[4] R. F. Zürcher in "Nuclear Magnetic Resonance in Chemistry," B. Pesce, Ed., Academic Press, New York, N. Y., 1965, p 45.

[5] Z. Rappoport and A. Gal, *J. Org. Chem.*, **37**, 1174 (1972).

[6] I. Granoth and J. B. Levy, *J. Chem. Soc. B*, 2391 (1971).

[7] J. W. Cusic and R. A. Robinson, U. S. Patent 2,776,299 (1957); *Chem. Abstr.*, **51**, 8146 (1957).

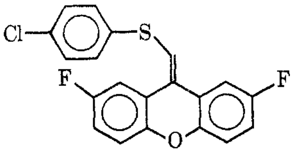
[8] P. E. Sokol, *Org. Syn.*, **44**, 69 (1964).

[9] A study of the scope and mechanisms of the reactions outlined by eq 1 and 3 is now in progress, including reactions of other aromatics with various α-substituted acid halides.

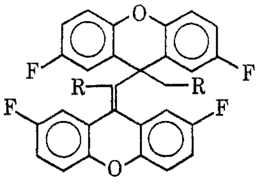
e.g., **4b**, produced a hypsochromic shift of the characteristic uv band by 16 nm to 322 nm.

Reactivity.—**4a** was inert toward sodium ethoxide in boiling ethanol, but with sodium *p*-chlorothiophenoxide under the same conditions gave **6**. Nucleophiles such as dibenzylamine (in boiling toluene) and methylmagnesium iodide (in ether) did not react with **4a**, which was recovered unchanged.

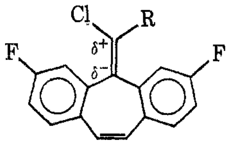
The compounds **4a** and **b** are isoelectronic[10] with the unknown heptafulvenes **8**.[11] Ordinary heptafulvenes have a polar exocyclic double bond, the terminal carbon being negative.[11] In the fulvenes,[11] and in those heptafulvenes bearing an electronegative substituent on the terminal carbon,[12] the exocyclic double bond is also polar, but the terminal carbon is positive. We suggest that, similarly to the latter, the terminal carbon of the exocyclic double bond in **4a** and **b** is positive. This would explain the formation of **7a** and **b** as the sole products of the $LiAlH_4$ reduction of **4a** and **b**.



6

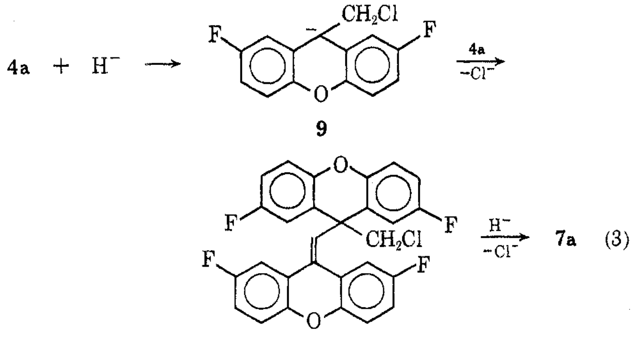


7a, R = H
b, R = Me



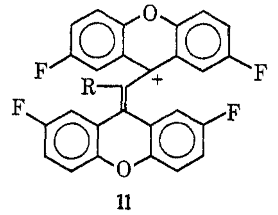
8

A vinylic chlorine is known[13] not to be hydrogenolyzed by $LiAlH_4$ under our reaction conditions. Taking into account that the reaction of **4a** with $LiAlH_4$ was exothermal, we assumed that the latter reaction proceeded as in eq 3.

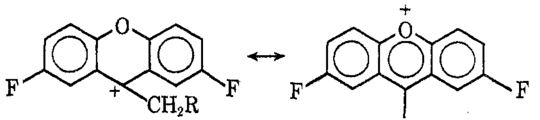


The hydride addition to **4a** is not unusual, but the nucleophilic attack of the hindered carbanion **9** on **4a** seems to be quite remarkable. The final hydrogenolysis of the chlorine in **10** could be expected, once **10** was obtained in the presence of $LiAlH_4$. The structures of **7a** and **b** were deduced from their nmr and mass spectra. (See also Experimental Section).

The only intense peaks in the mass spectra of **7a** and **7b** were $M\cdot^+$, $M - RCH_2^+$ (**11**), and **12**. This is attributed to the high stability of the ions **11** and **12**, which may be stabilized by resonance with, *e.g.*, **13**. Another characteristic ion in the latter two spectra was **14** (*m/e* 217), which is typical of xanthene derivatives.

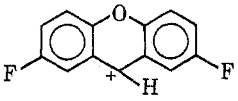


11



12a, R = H
b, R = Me

13



14

The nmr spectrum of **7b** displayed, *inter alia*, δ 0.47 (3 H, t, aliphatic Me) and 5.95 (1 H, dd, H-1). The latter was assigned to H-1 since it showed $J_{HF} = 9$ Hz and further coupling with a meta proton. These are considerable shielding effects of H-1 and the aliphatic Me which are brought toward the influence of the diamagnetic-ring current,[14] owing to the crowding near the ethyl substituent in **7b**. The uv spectrum of **7b** showed a blue shift of 29 nm, as compared with **7a**. Assuming that the α-Me in **7b** contributed a shift of 16 nm (as in **4b** above), it might be concluded that the additional 13-nm shift was due to the increased distortion of coplanarity of the two aromatic systems in **7b**, resulting from the crowding in this compound.

Experimental Section

Melting points are uncorrected. Proton nmr spectra were recorded in $CDCl_3$ with a JEOL 60 HL instrument, and are given in δ units downfield from internal TMS. Mass spectra were obtained with a Hitachi Perkin-Elmer RMU6 mass spectrometer at 70 eV using the direct insertion probe, and source temperature 150–200°. Peaks of intensity greater than 20% of the base peak are given and isotope peaks are excluded. The uv spectra were measured on a Bausch & Lomb 505 spectrometer.

2,7-Difluoro-9-chloromethylenexanthene (**4a**).—Chloroacetyl chloride (12.4 g, 0.11 mol) was added rapidly to a mechanically stirred mixture of carbon disulfide (300 ml), 4,4′-difluorodiphenyl ether (**1**) (20.6 g, 0.1 mol), and aluminum chloride (17.3 g, 0.13 mol). The mixture was refluxed for 5 hr and cooled, and the solvent was decanted. The solid residue was decomposed with ice-water and extracted with chloroform, affording the

---

[10] For a recent improvement of the basic isoelectronic principle, see J. F. Liebman, *J. Chem. Educ.*, **48**, 188 (1971). One of the authors (I. G.) and J. F. Liebman are currently investigating further modifications of the isoelectronic principle.

[11] E. D. Bergmann, *Chem. Rev.*, **68**, 41 (1968).

[12] T. Asao, N. Morita, and Y. Kitahara, *J. Amer. Chem. Soc.*, **94**, 3655 (1972).

[13] N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience, New York, N. Y., 1956, p 902.

[14] L. M. Jackman and S. Sternhell, "Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Elmsford, N. Y., 1969 p, 94.

crude product after evaporation. Crystallization from ethyl acetate–ethanol gave 15.8 g (60%) of **4a**, mp 147°.

Anal. Calcd for $C_{14}H_7ClF_2O$: C, 63.5; H, 2.6; Cl, 13.4. Found: C, 63.7; H, 2.4; Cl, 13.4. Spectra: nmr ($CDCl_3$) δ 6.54 (1 H, s, H-α), 7.15 (5 H, m, Ar), 8.22 (1 H, m, H-8); mass spectrum *m/e* (rel intensity) 264 (100, $M\cdot^+$), 201 (51, M − $CClO^+$); λ_{max} (EtOH) 240 nm (sh, ϵ 10,900), 258 (sh, 5100), 290 (sh, 3200), 338 (8400).

α-Chloro-2,7-difluoro-9-ethylidenexanthene (4b).—α-Chloropropionyl chloride (13.9 g, 0.11 mol), **1** (20.6 g, 0.1 mol), and aluminum chloride (17.3 g, 0.13 mol) were refluxed for 5 hr in carbon disulfide (300 ml) with agitation. Decantation of the solvent, hydrolysis, and chloroform extraction gave an impure oil, shown by nmr to contain mainly **3b**, nmr δ 1.37 (3 H, d, Me), 4.23 (1 H, q, CHCl), 6.92 (7 H, m, Ar). The above oil and 100 ml of methanol were refluxed for 10 min and heated in a rotovaporator for 1 hr on a steam bath. The residue solidified upon trituration with hexane, and was crystallized from cyclohexane giving 4.5 g (16%) of **4b**, mp 162°.

Anal. Calcd for $C_{15}H_9ClF_2O$: C, 64.6; H, 2.8; Cl, 12.7; F, 13.6. Found: C, 64.2; H, 3.1; Cl, 13.1; F, 13.7. Spectra: nmr ($CDCl_3$) δ 2.55 (3 H, s, Me), 7.16 (5 H, m, Ar), 7.86 (1 H, m, H-8); mass spectrum *m/e* (rel intensity) 278 (100, $M\cdot^+$), 243 (58, M − $Cl\cdot^+$), 242 (45, M − $HCl\cdot^+$), 241 (74, M − H_2Cl^+), 214 (22, M − $CHClO^+$); λ_{max} (EtOH) 238 nm (sh, ϵ 10,100), 253 (sh, 8800), 288 (3200), 322 (9100).

2,7-Difluoroxanthen-9-one (5). A.—Potassium permanganate (8 g) was added in four portions during 10 min to a stirred solution of **4a** (5.3 g, 0.02 mol) in 85% aqueous pyridine (100 ml). When the exothermal reaction slowed down, the mixture was heated to the boiling point and filtered hot. Dilution of the filtrate with water precipitated **5**, which was collected and crystallized from ethanol, giving 3.0 g (65%), mp 170°.

Anal. Calcd for $C_{13}H_6F_2O_2$: C, 67.2; H, 2.6; F, 16.4. Found: C, 67.2; H, 2.7; F, 16.7. Spectra: nmr ($CDCl_3$) δ 7.45 (4 H, m, Ar), 7.83 (2 H, m, H-1, 8, J_{HF} = 9 Hz); mass spectrum *m/e* (rel intensity) 232 (100, $M\cdot^+$), 204 (40, M − $CO\cdot^+$), 176 (28, M − $2CO\cdot^+$); λ_{max} (EtOH) 230 nm (ϵ 39,400), 257 (sh, 14,900), 294 (5500), 355 (9100).

B.—**1** (10.3 g, 0.05 mol), aluminum chloride (10.0 g, 0.075 mol), oxalyl chloride (9.5 g, 0.075 mol), and carbon disulfide (150 ml) were refluxed for 7 hr, cooled, and treated with ice water. The organic layer was evaporated and the residue gave 4.1 g (35%) of **5** upon crystallization from ethanol, mp and mmp 170°. This sample was identical with the one obtained by method A.

α-*p*-Chlorophenylthio-2,7-difluoro-9-methylenexanthene (6).—Sodium hydride (0.12 g, 5 mmol), *p*-chlorothiophenol (0.73 g, 5 mmol), and **4a** (1.32 g, 5 mmol) were added in turn to absolute ethanol (100 ml) and the mixture was refluxed for 5 hr. The yellow precipitate (**6**) was filtered and crystallized from ethanol, giving 1.7 g (91%), mp 156°.

Anal. Calcd for $C_{20}H_{11}ClF_2OS$: C, 64.4; H, 3.0; Cl, 9.5; F, 10.2; S, 8.6. Found: C, 64.1; H, 2.8; Cl, 10.0; F, 10.4; S, 9.0. Spectra: nmr ($CDCl_3$) δ 6.61 (1 H, s, H-α), 7.15 (5 H, m, Ar), 7.43 (4 H, s, Ar S), 7.66 (1 H, m, H-8); λ_{max} (dioxane) 255 nm (ϵ 9100), 295 (10,100), 368 (21,700).

2,7-Difluoro-9-(2′,7′-difluoro-9′-methyl)xanthylmethylenexanthene (7a).—Lithium aluminum hydride (1.1 g, 0.03 mol) was added to a solution of **4a** (5.3 g, 0.02 mol) in dry THF (100 ml). The mixture was refluxed for 1 hr, cooled, and decomposed with 5 ml of dilute hydrochloric acid. The organic layer was evaporated and the residue was crystallized from ethanol, thus giving 3.0 g (65%) of **7a**, mp 165°.

Anal. Calcd for $C_{28}H_{16}F_4O_2$: C, 73.0; H, 3.5; F, 16.5. Found: C, 73.1; H, 3.5; F, 17.1. Spectra: nmr ($CDCl_3$) δ 1.70 (3 H, s, Me), 6.17 (1 H, s, H-α), 6.07–7.20 (12 H, m, Ar); mass spectrum *m/e* (rel intensity) 460 (30, $M\cdot^+$), 445 (100, M − Me^+), 231 (42, **12a**); λ_{max} (EtOH) 240 nm (sh, ϵ 23,700); 260 (sh, 10,300), 291 (8500), 336 (11,900).

2,7-Difluoro-α-9-(2′,7′-difluoro-9′-ethyl)xanthylethylidenexanthene (7b).—The procedure for **7a** was repeated with $LiAlH_4$ (0.38 g, 10 mmol), **4b** (1.4 g, 5 mmol), and THF (50 ml). Trituration with ethanol yielded 0.3 g of **4b** (recovered from the ethanol), and 0.4 g (42%) of **7b**, mp 247°.

Anal. Calcd for $C_{30}H_{20}F_4O_2$: C, 73.8; H, 4.1; F, 15.6. Found: C, 73.5; H, 4.2; F, 15.7. Spectra: nmr ($CDCl_3$) δ 0.47 (3 H, t, $MeCH_2$), 2.06 (2 H, q, CH_2), 2.59 (3 H, s, Me-α), 5.95 (1 H, dd, H-1, J_{HF} = 10 Hz), 7.00 (11 H, m, Ar); mass spectrum *m/e* (rel intensity) 488 (7, $M\cdot^+$), 459 (20, M − Et^+), 245 (100, **12b**); λ_{max} (EtOH) 248 nm (ϵ 18,900), 288 (7900), 307 (12,300).

Registry No.—**1**, 330-938; **4a**, 37611-30-6; **4b**, 37611-31-7; **5**, 37611-32-8; **6**, 37611-33-9; **7a**, 37735-74-3; **7b**, 37611-34-0; chloroacetyl chloride, 79-04-9; α-chloropropionyl chloride, 7623-09-8.