excellent single crystals appropriate for collecting three-dimensional X-ray data. An analytical sample had mp 124–125°; ir (CCl_4) 1734, 1325–1380, 1178, 920, 868 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (3 H, d, J = 6.5 Hz), 0.92 (3 H, s), 1.20–2.86 (11 H), 7.78 (4 H, s); mass spectrum (70 eV) m/e (rel intensity) 414 (3), 412 (3), 221 (6), 219 (6), 193 (45), 176 (24), 157 (14), 155 (14), 148 (28), 133 (12), 120 (12), 110 (100), 93 (17), 81 (41), 69 (21), 55 (21).

Anal. Calcd for $C_{18}H_{21}BrO_4S$: C, 52.31, H, 5.12. Found: C, 52.29; H, 5.21.

(1*R,3*R**,6*S**,8*R**)-8-Methoxy-1-methyltricyclo-[4.4.0.0^{3,8}]decan-2-one (IIa).** A solution of 194 mg (1.0 mmol) of Ia in 5 ml of absolute methanol saturated with hydrogen chloride was stirred overnight and worked up by quenching with saturated sodium bicarbonate solution. The ether extracts of this solution yielded an oil which GLC analysis showed to be a mixture of Ia, IIa, and several other components. The component assigned structure IIa (about 20% of the mixture) was collected by preparative GLC (4% QF-1 at 170°): ir (neat) 2930, 2855, 2820, 1730, 1460, 1325, 1135, 1115, 1100 cm^{-1}; mass spectrum (70 eV) m/e 194, 179, 95, 85, 55. The parent ion (m/e 194) exhibited isotope peaks at m/e 195 (14.5% P) and 196 (ca. 2% P); the isotopic abundance calculated for $C_{12}H_{18}O_2$ is 14.45 and 1.37%, respectively.

Acknowledgments. We thank the National Institutes of Health for their support of this work (Grant AM-10849). We also thank Dr. B. L. Barnett for his help in conducting the X-ray crystal analysis.

Registry No.—Ia, 4707-05-5; Ib, 55090-34-1; IIa, 55090-35-2; IIb, 55090-36-3; III, 55090-37-4; III brosylate, 55090-38-5; *trans*-8,8a-dimethyl-3,4,8,8a-tetrahydronaphthalene-1,6(2*H*,7*H*)-dione, 17566-22-2; *p*-bromobenzenesulfonyl chloride, 95-58-8.

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(8) All reactions were conducted under a nitrogen or argon atmosphere. Infrared spectra were recorded on a Perkin-Elmer 237B grating spectrophotometer. Proton magnetic spectra were obtained using a Varian T-60 high-resolution spectrometer. Mass spectra were obtained by Mrs. Lorraine Guile with a Hitachi RMU-6 mass spectrometer. Gas–liquid partition chromatography (GLC) was carried out using Varian Aerograph 1200 and A-90P3 instruments. Microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich.
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Synthesis and Substituent Effects in the Nuclear Magnetic Resonance and Mass Spectra of Dimethyl- and Dihaloxanthones

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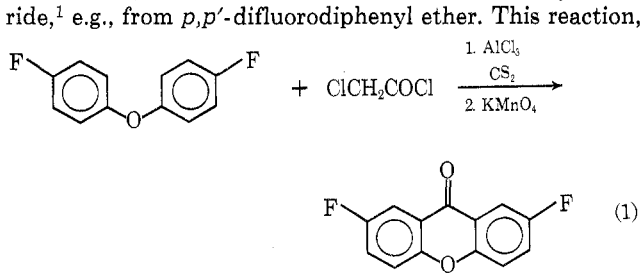
Halogen- and methyl-substituted xanthones have been prepared by three routes. The main approach has been Friedel–Crafts acylation–cyclization of aromatic ethers with oxalyl chloride or with chloroacetyl chloride followed by permanganate oxidation. The substituent shifts in the ^1H NMR spectra of the compounds studied are in good agreement with those predicted for substituted benzene derivatives. The typical electron-impact-induced CO expulsion from the molecular ion of xanthone decreases or even disappears in the halogenated derivatives owing to the competing halogen elimination.

In a preliminary communication by one of us, it was shown that the Friedel–Crafts acylation–cyclization reaction can be used to synthesize substituted xanthones (xanthen-9-ones) from aromatic ethers and chloroacetyl chloride,[1] e.g., from *p,p'*-difluorodiphenyl ether. This reaction,



(1)

which is a variation of a similar procedure using oxalyl chloride,[2–4] has also been used to prepare phenoxaphosphines[5] and phenothiaphosphines,[6] starting with phosphorus trichloride and aromatic ethers and sulfides, respectively. Whereas these earlier papers have dealt with the synthesis of substituted xanthones,[2–4] practically no comparative studies which might demonstrate the generality of this reaction have appeared. With this goal in mind, we have synthesized ten xanthone derivatives, some of which are new, and studied their properties by mass spectrometry, nuclear magnetic resonance spectrometry, and infrared absorption spectroscopy. This report provides syntheses of xanthones and some correlations of various spectral parameters with the structures of the xanthone derivatives.

Experimental Section

Melting points were taken with a Thomas-Hoover capillary apparatus and are uncorrected. Proton NMR spectra were run in $CDCl_3$ with Me_4Si and $CHCl_3$ as internal standards with a Jeol C-60 HL high-resolution spectrometer. Mass spectra were obtained with a Hitachi Perkin-Elmer RMU-6 instrument at 70 eV using the direct insertion probe and a source temperature of 150–200°. Peaks with intensities greater than 10% of the base peak are

given and isotope peaks are excluded. Infrared spectra were recorded for solutions in $CHCl_3$ with a Perkin-Elmer Infracord 137B spectrophotometer.

The syntheses and some spectral properties of **1d,g** and **2c,d,g** (vide infra) have been recently reported.[1,2] All the other aromatic ethers 1 were either commercially available (**1c,i**) or prepared by standard methods.[7,8]

Preparation of Substituted Xanthones by the Oxalyl Chloride Method. General Procedure. Oxalyl chloride (6.4 g, 0.05 mol) was added rapidly to a mechanically stirred mixture of carbon disulfide (150 ml), the substituted aromatic ether (0.05 mol), and aluminum chloride (8.6 g, 0.065 mol). The mixture was refluxed for 3 hr, oxalyl chloride (6.0 g) was again added, and the reflux was continued for 3 hr. Hydrolysis, chloroform extraction, and washing the resulting solution with 10% sodium hydroxide gave the substituted xanthone in 50–60% yield (recrystallized from ethanol). **1a** was an exception, giving only 5% yield of **2a**. The following compounds were prepared from the corresponding aromatic ethers.

3,6-Dimethylxanthone (2a) was prepared from *m*-tolyl ether, mp 167°. Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.4; H, 5.4. Found: C, 80.2; H, 5.6. Spectra: NMR ($CDCl_3$) δ 2.50 (6 H, s, Me), 7.18 (2 H, d, H-2, 7), 7.26 (2 H, d, H-4, -5, J = 1.5 Hz), 8.20 (2 H, d, H-1, -8, J = 9 Hz); mass spectrum *m/e* (rel intensity) 224 (100, M^+), 223 (15, M − H^+), 195 (23, M − CHO^+), 97 (14, M − CH_2O^{2+}).

2,7-Dimethylxanthone (2b) was prepared from *p*-tolyl ether, mp 141°. Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.4; H, 5.4. Found: C, 80.3; H, 5.3. Spectra: NMR ($CDCl_3$) δ 2.44 (6 H, s, Me), 7.28 (2 H, d, H-4, -5, J = 9 Hz), 7.48 (2 H, dd, H-3, -6, J = 9 and 2 Hz), 8.08 (2 H, m, H-1, -8); mass spectrum *m/e* (rel intensity) 224 (100, M^+), 223 (19, M − H^+), 195 (23, M − CHO^+), 181 (13, M − CO − CH_3^+).

2-Bromo-7-fluoroxanthone (2e) was prepared from 4-bromo-4′-fluorodiphenyl ether, mp 181°. Anal. Calcd for $C_{13}H_6BrFO_2$: C, 53.2; H, 2.1; Br, 27.3; F, 6.5. Found: C, 53.2, H, 2.2, Br, 27.0; F, 6.7. Spectra: NMR ($CDCl_3$) δ 7.40 (4 H, m, Ar), 7.93 (1 H, m, H-8), 8.38 (1 H, d, H-1, J = 2.5 Hz); mass spectrum *m/e* (rel intensity) 292 (100, M^+), 213 (19, M − Br^+), 185 (11, M − Br − CO^+), 157 (46, M − Br − CO^+), 106.5 (11, M − Br^{2+}), 78.5 (28, M − Br − $2CO^{2+}$).

2,7-Dichloroxanthone (2f) was prepared from 4,4′-dichlorodiphenyl ether, mp 219°. Anal. Calcd for $C_{13}H_6Cl_2O_2$: C, 58.9; H, 2.3; Cl, 26.8. Found: C, 59.1; H, 2.3; Cl, 26.6. Spectra: NMR ($CDCl_3$) δ 7.39 (2 H, d, H-4, -5, J = 9 Hz), 7.66 (2 H, dd, H-3, -6, J = 9 and 2 Hz), 8.23 (2 H, d, H-1, -8, J = 2 Hz); mass spectrum *m/e* (rel intensity) 264 (100, M^+), 236 (28, M − CO^+), 173 (28, M − Cl − $2CO^+$).

2-Bromo-7-chloroxanthone (2h) was prepared from 4-bromo-4′-chlorodiphenyl ether, mp 210°. Anal. Calcd for $C_{13}H_6BrClO_2$: C, 50.4; H, 1.9. Found: C, 50.7; H, 2.0. Spectra: NMR ($CDCl_3$) δ 7.34 (1 H, d, H-4), 7.40 (1 H, d, H-5), 7.66 (1 H, dd, H-6), 7.79 (1 H, dd, H-3), 8.23 (1 H, d, H-8), 8.38 (1 H, d, H-1); mass spectrum *m/e* (rel intensity) 308 (77, M^+), 173 (30, M − Br − $2CO^+$), 138 (13, M − Br − Cl − 2 CO^+).

2,7-Dibromoxanthone (2i) was prepared from 4,4′-dibromodiphenyl ether, mp 211°. Anal. Calcd for $C_{13}H_6Br_2O_2$: C, 44.1, H, 1.7; Br, 45.2. Found: C, 44.4; H, 2.0; Br, 45.2. Spectra: NMR ($CDCl_3$) δ 7.33 (2 H, d, H-4, −5, J = 9 Hz), 7.77 (2 H, dd, H-3, −6, J = 9 and 2 Hz), 8.36 (2 H, d, H-1, −8, J = 2 Hz); mass spectrum *m/e* (rel intensity) 352 (53, M^+), 273 (11, M − Br^+), 217 (28, M − Br − 2 CO^+), 138 (46, M − 2 Br − 2 CO^+), 108.5 (12, M − Br − 2 CO^{++}).

Preparation of Substituted Xanthones by the Chloroacetyl Chloride Method. General Procedure. Chloroacetyl chloride (12.4 g, 0.11 mol) was added to a mechanically stirred mixture of carbon disulfide (300 ml), the aromatic ether (0.1 mol), and aluminum chloride (20.0 g, 0.15 mol). The mixture was refluxed for 5 hr, cooled, decomposed with cold water, and extracted with chloroform. The crude substituted 9-chloromethylenexanthene (**4**) was either recrystallized and identified or dissolved in 85% aqueous pyridine, and oxidized by potassium permanganate (30 g), added portionwise. The latter mixture was heated to boiling and filtered hot. Dilution of the filtrate with water precipitated the substituted xanthone in 50–70% yield (recrystallized from ethanol). This method gave the same compounds described under the oxalyl chloride method, excluding **2a**. Examination of the NMR spectrum of the expected intermediate in an attempted synthesis of **2a** by this method showed that it was **5**.

2-Bromo-7-fluoro-9-chloromethylenexanthene (4 and 7, X = F; Y = Br) were prepared according to the general procedure for the chloroacetyl chloride method excluding the oxidation. The 1:1 mixture of geometrical isomers was obtained from 4-bromo-4′-fluorodiphenyl ether (**1e**), mp 112–116°. Anal. Calcd for $C_{14}H_7BrClFO$: C, 51.6; H, 2.2; F, 5.8. Found: C, 51.9; H, 2.1; F, 6.1. This isomer mixture was separated by repeated fractional crystallization from ethanol.

4, X = F; Y = Br. This was the more soluble isomer: mp 97°; NMR ($CDCl_3$) δ 6.50 (1 H, s, H-11), 7.13 (4 H, m, HAr), 7.50 (1 H, dd, H-3, J = 9 and 2 Hz), 8.55 (1 H, d, H-1, J = 2 Hz).

7, X = F; Y = Br. This high-melting isomer was the first to crystallize from the ethanol mother liquor: mp 141°; NMR ($CDCl_3$) δ 6.50 (1 H, s, H-11), 7.30 (5 H, m, HAr) 8.13 (1 H, m, H-8).

3,3′-Dimethyl-4,4′-di(chloroacetyl)diphenyl ether (5) was prepared from *m*-tolyl ether in 30% yield, as described above, excluding the oxidation, mp 113° (recrystallized from CCl_4). Anal. Calcd for $C_{18}H_{16}Cl_2O_3$: C, 61.5; H, 4.6; Cl, 20.2. Found: C, 61.3; H, 4.5; Cl, 19.9.

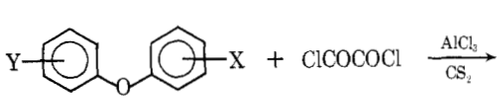
Spectra: NMR ($CDCl_3$) δ 2.54 (6 H, s, Me), 4.60 (4 H, s, $ClCH_2CO$), 6.93 (4 H, m, Ar), 7.70 (2 H, d, H-5,5′, J = 10 Hz); mass spectrum *m/e* (rel intensity) 350 (19, M^+), 301 (100, M − CH_2Cl^+), 225 (11), 224 (11, M − 2 CH_2Cl − CO^+), 126 (16, M − $2CH_2Cl^{2+}$).

2,7-Diiodoxanthone (2j). A solution of xanthone (6.2 g) in concentrated sulfuric acid (100 ml) was added gradually to a stirred mixture of iodine (20 g), potassium iodate (5.0 g), and sulfuric acid (150 ml). After 48 hr, the mixture was decomposed with crushed ice (600 g), extracted with chloroform, and washed with aqueous sodium thiosulfate, giving eventually 2.1 g of **2j**, mp 241° (ethanol). Anal. Calcd for $C_{13}H_6I_2O_2$: C, 34.8; H, 1.3; I, 56.7. Found: C, 34.9; H, 1.3; I, 57.0. Spectra: NMR ($CDCl_3$) δ 7.20 (2 H, d, H-4, −5, J = 9 Hz), 7.95 (2 H, dd, H-3, −6, J = 9 and 2.5 Hz), 8.58 (2 H, d, H-1, −8, J = 2.5 Hz); mass spectrum *m/e* (rel intensity) 448 (100, M^+), 321 (49, M − I^+), 265 (40, M − I − 2 CO^+), 224 (19, M^{2+}), 194 (13, M − 2 I^+), 166 (20, M − 2 I − CO^+), 160.5 (16, M − I^{2+}), 138 (71, M − 2 I − $2CO^+$).

Xanthone-^{18}O (2k) was prepared by the photooxidation of xanthene in the presence of 99.98% $^{18}O_2$ as previously described.[9] From its mass spectral analysis and infrared spectrum, we have determined its purity to be 95%. Sufficient quantity for NMR was not available. The mass spectrum was similar to that of xanthone except that ions containing ^{18}O were shifted by 2 mass units with respect to the parent ion peaks.

Results and Discussion

Synthesis. The application of the Friedel–Crafts acylation–cyclization reaction for the preparation of substituted xanthones from aromatic ethers and oxalyl chloride has been briefly reported.[1–4] The main advantages of this route (eq 2) are the use of simple starting materials and easy ma-



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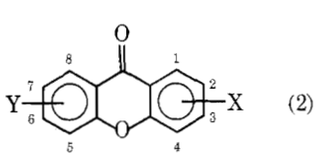
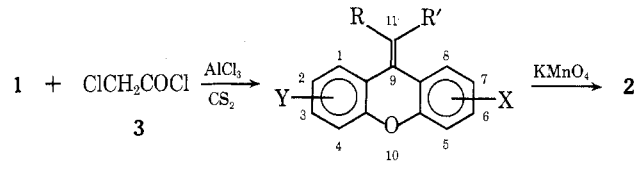


(2)

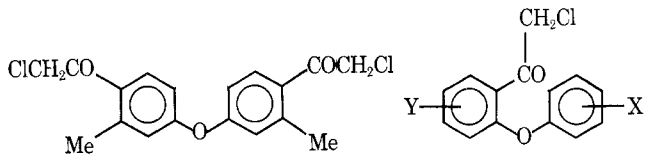
2

1a, X = 3-Me; Y = 3′-Me	2a, X = 3-Me; Y = 6-Me
b, X = 4-Me; Y = 4′-Me	b, X = 2-Me; Y = 7-Me
c, X = 4-F; Y = 4′-F	c, X = 2-F; Y = 7-F
d, X = 4-F; Y = 3′-Br	d, X = 2-F; Y = 6-Br
e, X = 4-F; Y = 4′-Br	e, X = 2-F; Y = 7-Br
f, X = 4-Cl; Y = 4′-Cl	f, X = 2-Cl; Y = 7-Cl
g, X = 4-Cl; Y = 3′-Br	g, X = 2-Cl; Y = 6-Br
h, X = 4-Br; Y = 4′-Cl	h, X = 2-Br; Y = 7-Cl
i, X = 4-Br; Y = 4′-Br	i, X = 2-Br; Y = 7-Br

nipulations. Oxalyl chloride is known to be decomposed by aluminum chloride.[10] Thus, using 50–100% excess of the former reagent is profitable in terms of yields. The 4,4′-disubstituted 1 gave ca. 50% yield of the appropriate 2. Similarly, meta-brominated 1 was well protected[2] in the para position, leading to the synthesis of **2d,g**. However, a meta methyl allowed only 5% yield of **2a**.



4, R = Cl; R′ = H
7, R = H; R′ = Cl (3)



5 6

In a preliminary communication,[1] we have described an alternative route leading to **2c**. This sequence (eq 3) has now been studied in some detail. In some cases (**2e,h**), it provided even better overall yields than those obtained by the oxalyl chloride method (eq 2). However, for the transformation **1a** → **2a**, again only 5% of **2a** was produced, while the main product of the reaction of **1a** with **3** was **5**. The structures of both **2a** and **5** have been elucidated from their ^{1}H NMR and mass spectra.

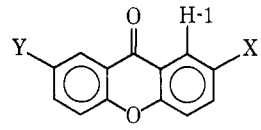
The aluminum chloride must be dry and in ca. 50% excess, or otherwise a mixture of **4** and the intermediate *ketone* **6** is obtained. In any event, the latter mixture is easily converted to **4** upon heating with phosphorus oxychloride. Best yields of **2** are achieved when the crude **4** is treated with potassium permanganate in pyridine–water. When X ≠ Y, the two geometrical isomers **4** and **7** are produced in 1:1 ratio. In the case of **1e**, the resulting isomers **4** and **7** (X = 7-F; Y = 2-Br) could not be separated by column chromatography. Repeated fractional crystallization gave eventually the pure isomers. The isomer ratio determination in the mixtures of **4** and **7** as well as monitoring isomer separation were achieved from the ^{1}H NMR spectra. This was based on the different signals of H-1 and H-8. The proton closer to the vinylic chloride is deshielded and resonates at a relatively low field. A clear separation of the signals due to the two geometrical isomers is aided by the substituent shift (vide infra). The 9-chloromethylenexanthenes (**4**) are thermally unstable (decompose at ca. 150°) and light sensitive.

One of the desired xanthones, i.e., **2j** (X = 2-I; Y = 7-I), has been prepared from xanthone by direct iodination in sulfuric acid in the presence of potassium iodate. In addition to the expected melting point, as reported[11] for a sample prepared by a multistep procedure, the structure of **2j** has been established from its mass spectrum and the ^{1}H NMR spectrum, typical of 2,7-disubstituted xanthones.

^{1}H NMR Spectra. The ^{1}H NMR spectra of the substituted xanthones have been used to characterize these compounds and to determine the substitution pattern for **2a** and **2j** in particular (Table I). H-1 and H-8 resonate at a relatively low field owing to the typical deshielding effect by the ortho cyclic carbonyl function.[12] The series of 2,7-disubstituted xanthones enables one to verify the validity and accuracy of predicted[13] substituent shielding effects in benzene derivatives for this ring system. Predicted and observed substituent shifts along with the chemical shift of H-1 (or H-8) in the substituted xanthones are given in Table I. The shielding constant of H-2 on H-1 in xanthone is taken as 0.00 ppm, and those of the other functional groups as additive.

Indeed, there seems to be a very good agreement between the calculated and actual substituent shifts. This verification suggests that this technique may be useful[14] in the structural analysis of other complex aromatic systems justifying the current interest in the tool.[15,16] In addition to the expected chemical shifts of H-1,8 in the ^{1}H NMR spectra of **2a** and **2j**, the substituents' positions have been further confirmed from the lines' shapes and integration of the NMR signals, (see Experimental Section).

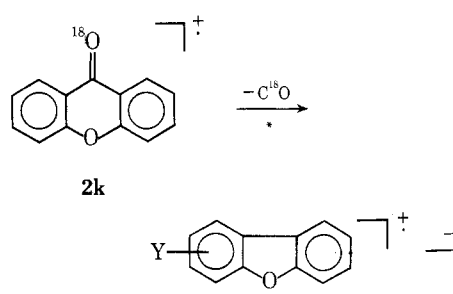
Table I
Substituent Effects on the Chemical Shift of H-1 in Xanthones



Substituent X	Y	δH-1, ppm	Substituent shift constant, ppm: Observed	Predicted[8]
H	H	8.25	0.00	0.00
Me	Me	8.08	0.17	0.17
F	F	7.92	0.33	0.30
F	Br	7.93	0.32	0.30
Cl	Cl	8.23	0.02	−0.02[a]
Cl	Br	8.23	0.02	−0.02
Br	F	8.39	−0.14	−0.22
Br	Cl	8.39	−0.14	−0.22
Br	Br	8.36	−0.11	−0.22
I	I	8.58	−0.33	−0.40
3-Me[b]	6-Me	8.20	0.05	0.09

[a] Negative sign denotes downfield shift. [b] In 3,6-dimethylxanthone.

Mass Spectra. The electron-impact-induced decomposition of xanthone has been reported,[17] and the influence of hydroxy and methoxy substituents on the fragmentation patterns has been studied in detail.[18] The main reactions of xanthone in the mass spectrometer are the successive eliminations of two molecules of CO. By ^{18}O labeling of the carbonyl in xanthone, we have now confirmed that the first lost molecule of CO is totally derived from the carbonyl function (eq 4), as suggested intuitively earlier.[18] Further-



2k

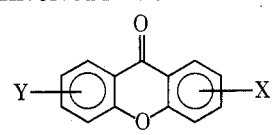
(4)

more, the ion at *m/e* 92, though not abundant, is completely shifted to *m/e* 94 after incorporation of ^{18}O into the carbonyl group of xanthone. This ion must be $C_6H_4O^{\cdot+}$. It is probably formed by a minor, but specific, rearrangement involving the carbonyl oxygen in a portion of the molecular ions which do not lose CO.

The halogenated xanthones allowed the examination of the gas-phase simple bond (C–halogen) cleavage vs. the competing rearrangement reaction, namely the CO expulsion, both from the molecular and from M − CO$^{\cdot+}$ ions. The relative intensities of the relevant ions are shown in Table II.

Generally, the halogenated xanthones show similar fragmentation patterns, while the dimethyl derivatives behave

Table II
Relative Intensities[a] of the Ions Involved in CO Elimination in the 70 eV Mass Spectra of A



A

X	Y	M − CO	M − Y	M − YCO[b]	M − 2 CO	M − Y − 2 CO[b]	M − Y − X	M − YCO − X[b]	M − YCO − XCO[b]
H	H	50	4		7	40			
2-F	7-F	40			7	5			
2-Cl	7-Cl	28	4	3	3	15			
2-Cl	7-Br	10	6	4		20			
2-Cl	6-Br	13	3	6		20			
2-F	7-Br	15	9	6		23			
2-F	6-Br	15	5	9		24			
2-Br	7-Br	8	11	5		28			23
2-I	7-I		49	9		40	13	20	71
2-Me	7-Me	5	7	13		3			
3-Me	6-Me	9	5	9		5			

[a] Isotopic ions are included in the calculation of the relative intensities to enable comparison with xanthones having negligible isotopic ions. [b] The loss of YCO as one entity in the mass spectral fragmentations of oxygen heterocycles where Y = H^{18}, Cl^{19} has been established. Here, both the one-step and two-step reactions are included, since they are indistinguishable.

somewhat differently. The three pairs of isomeric xanthones studied exhibit practically indistinguishable spectra within each pair. Thus, mass spectrometry is not very useful for structure elucidation of the positional isomers studied.

The competing C–Y bond cleavage and CO expulsion in the molecular ions of the halogenated xanthones depend on the C–Y bond energy. The stronger this bond, the higher is the ratio M − CO/M − Y. Thus, no fluorine elimination is observed from a fluorinated xanthone, while CO loss from the molecular ion of **2j** is entirely quenched by the energetically more favorable C–I bond rupture. A similar trend is found for M − CO − YCO^+ ions where Y elimination after successive loss of two CO molecules is also competing with the expulsion of a hydrogen atom. It has been established that rearrangement reactions are relatively low energy processes,[19] as compared with direct bond cleavages. However, it should be noted that a simple weak bond cleavage, such as the C–I bond, may be favored over a competing rearrangement. The labile nature of the C–I bond is further demonstrated by the observation that photolysis of **2j** in isooctane leads to the formation of I_2 and another product whose identity was not determined.[20]

Summary. Ten dimethyl- or dihaloxanthone derivatives have been synthesized mainly by the acylation–cyclization of aromatic ethers with oxalyl- or chloroacetyl chloride in the presence of aluminum chloride, followed by permanganate oxidation in the latter route. The yields are typically in the range of 50–70%. The mass spectral data show that loss of CO is an important process except when elimination of the higher atomic weight halogen atoms can effectively compete with the latter process. The ^1H NMR spectra of the xanthones can readily be predicted on the basis of the substituent shift constants reported for benzene derivatives.

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Registry No.—**1a,** 19814-71-2; **1b,** 1579-40-4; **1c,** 330-93-8; **1d,** 50904-38-6; **1e,** 55102-99-3; **1f,** 2444-89-5; **1g,** 6842-61-1; **1h,** 30427-95-3; **1i,** 2050-47-7; **2a,** 19814-69-8; **2b,** 7573-15-1; **2c,** 37611-32-8; **2d,** 50904-46-6; **2e,** 55103-00-9; **2f,** 55103-01-0; **2g,** 50904-47-7; **2h,** 55103-02-1; **2i,** 40102-85-0; **2j,** 55103-03-2; **2**(X = Y = H), 90-47-1; **3,** 79-04-9; **4**(X = 7-F; Y = 2-Br), 55124-07-7; **5,** 55103-04-3; **7**(X = 7-F; Y = 2-Br), 55103-05-4; oxalyl chloride, 79-37-8.

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