anthrenecarboxylate whose structure was analyzed by Mullica, Milligan, Belew, Grossie & Sappenfield (1984). Interest in stable ozonides employed in the synthesis of steroid intermediates led to the first two complete single-crystal structure analyses of such compounds (Mullica, Korp, Milligan, Belew, McAtee & Karban, 1979; Oliver, Mullica, Milligan, Karban, McAtee & Belew, 1979).

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Structures of 3-Formylthiachromen-4-one and 3-(Chloromethyl)chromen-4-one

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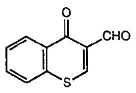
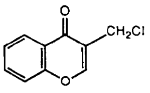
Abstract. (1) 3-Formylthiachromen-4-one, $C_{10}H_6O_2S$, $M_r = 190{\cdot}22$, monoclinic, $P2_1/c$, $a = 7{\cdot}715\,(10)$, $b = 7{\cdot}089\,(11)$, $c = 15{\cdot}64\,(4)$ Å, $\beta = 95{\cdot}43\,(16)°$, $V = 852\,(3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}484$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 3{\cdot}21$ cm^{-1}, $F(000) = 391{\cdot}6$, room temperature, final $R = 0{\cdot}0574$ for 747 independent reflections with $|F| > 3\sigma|F|$. The two six-membered rings which comprise the structure are each planar and are mutually inclined at 1°. The aldehyde group is almost coplanar with the heterocyclic ring to which it is attached [deviation of oxygen atom 0·057 (7) Å]. Bond lengths imply aromaticity confined to the benzenoid ring. (2) 3-(Chloromethyl)chromen-4-one, $C_{10}H_7ClO_2$, $M_r = 194{\cdot}62$, triclinic, $P\bar{1}$, $a = 6{\cdot}523\,(6)$, $b = 7{\cdot}044\,(5)$, $c = 10{\cdot}389\,(12)$ Å, $\alpha = 79{\cdot}49\,(7)$, $\beta = 71{\cdot}74\,(8)$, $\gamma = 75{\cdot}42\,(7)°$, $V = 435{\cdot}9\,(7)$ Å^3, $Z = 2$, $D_x = 1{\cdot}483$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 3{\cdot}93$ cm^{-1}, $F(000) = 199{\cdot}98$, room temperature, final $R = 0{\cdot}0451$ for 1164 independent reflections with $|F| > \sigma|F|$. The two six-membered rings which comprise the structure are each planar and are mutually inclined at 1°. The Cl atom is not coplanar with the heterocyclic ring to which the chloromethyl substituent is attached [deviation 1·537 (2) Å]. Bond lengths imply aromaticity confined to the benzenoid ring.

Experimental. Crystals were grown from the products obtained (Giles & Marson, 1990) by the action of dimethylformamide–phosphorus oxychloride at 373 K on the heterocyclic ketones thiachromen-4-one and chroman-4-one.



(1)



(2)

3-Formylthiachromen-4-one (1) was crystallized from propan-2-ol as light-brown plates. Diffraction intensities were measured using a crystal of dimensions 0·40 × 0·20 × 0·10 mm; X-ray data in the range $3{\cdot}5 < 2\theta < 45°$ on a Nicolet $R3$ four-circle diffractometer, ω-scan method. Cell parameters determined from 14 reflections in the range $0 < \theta < 25°$. 747 independent reflections (of 1327 measured) were corrected for Lorentz and polarization effects, and for absorption by analysis of seven azimuthal scans (min. and max. transmission coefficients 0·766 and 0·866).

The structure was solved by multiple solution direct methods and refined by blocked-cascade least squares. H atoms were detected and most were refined in riding mode; those on C(2) and C(9) were allowed free positional refinement; their isotropic thermal parameters were related to those of the supporting atom. Refinement converged at a final $R = 0{\cdot}0574$ ($wR = 0{\cdot}0461$, 124 parameters, all final shift/e.s.d = 0·00), with allowance for the thermal anisotropy of all non-H atoms. A final difference

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electron density map showed min. and max. peaks of $-0{\cdot}28$ and $+0{\cdot}26\,\text{e}\,\text{Å}^{-3}$. Scattering factors were taken from the program package *SHELXTL* (Sheldrick, 1983) as implemented on the Data General Nova 3 computer. Weighting scheme $w^{-1} = [\sigma^2(F) + 0{\cdot}00022(F)^2]$ was used in the latter stages of the refinement. Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1.* Bond lengths and bond angles with e.s.d.'s are presented in Table 2. Fig. 1 shows the molecular labelling scheme of (1).

3-(Chloromethyl)chromen-4-one (2) was crystallized from propan-2-ol as light-brown needles. Diffraction intensities were measured using a crystal of dimensions $0{\cdot}30 \times 0{\cdot}15 \times 0{\cdot}10$ mm; room-temperature X-ray data were collected in the range $3{\cdot}5 < 2\theta < 50°$ on a Nicolet *R*3 four-circle diffractometer (Mo $K\alpha$ radiation) using the ω-scan method. The 1164 independent reflections (of 1550 measured) were corrected for Lorentz and polarization effects, and for absorption by analysis of 7 azimuthal scans (min. and max. transmission coefficients 0·867 and 0·942).

The structure was solved by multiple solution direct methods and refined by blocked-cascade least squares. H atoms were detected and refined; their isotropic thermal parameters were related to those of the supporting atom. Refinement converged at a final $R = 0{\cdot}0451$ ($wR = 0{\cdot}0428$, 139 parameters, max. shift/e.s.d. = 0·001), with allowance for the thermal anisotropy of all non-H atoms, $w^{-1} = [\sigma^2(F) + 0{\cdot}00028(F)^2]$. A final difference electron density map showed min. and max. peaks of $-0{\cdot}24$ and $+0{\cdot}18\,\text{e}\,\text{Å}^{-3}$. Atomic scattering factors and software are as described above. Atomic coordinates and equivalent isotropic thermal parameters are given in Table 3. Bond lengths and bond angles with e.s.d.'s are presented in Table 4. Fig. 2 shows the molecular labelling scheme of (2).

Related literature. A preparation of (1) unrelated to that involving Vilsmeier reagents has been reported by Nakazumi, Endo, Sonoda & Kitao (1985). Dean & Murray (1975) reported the preparation of (2) by an unrelated route.

Table 1. *Positional parameters* ($\times 10^4$) *and equivalent isotropic temperature factors* ($\text{Å}^2 \times 10^3$) *for* (1)

	x	y	z	U_{eq}
S(1)	1334 (2)	−1323 (2)	1578 (1)	62 (1)*
O(4)	3381 (4)	960 (5)	−789 (2)	63 (1)*
O(9)	1112 (5)	−4164 (5)	−1033 (2)	73 (2)*
C(2)	1286 (7)	−2267 (8)	569 (3)	52 (2)*
C(3)	1929 (6)	−1501 (7)	−136 (3)	44 (2)*
C(4)	2793 (6)	329 (7)	−131 (3)	44 (2)*
C(4a)	2981 (6)	1464 (7)	678 (3)	42 (2)*
C(5)	3805 (6)	3211 (7)	668 (3)	51 (2)*
C(6)	4095 (6)	4312 (7)	1397 (3)	56 (2)*
C(7)	3529 (7)	3665 (8)	2169 (3)	58 (2)*
C(8)	2691 (7)	1965 (8)	2204 (3)	54 (2)*
C(8a)	2409 (6)	827 (7)	1466 (3)	44 (2)*
C(9)	1727 (7)	−2603 (9)	−948 (3)	60 (2)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Bond lengths* (Å) *and bond angles* (°) *for* (1)

S(1)—C(8a)	1·752 (6)	S(1)—C(2)	1·712 (6)
O(4)—C(4)	1·247 (7)	O(9)—C(9)	1·207 (7)
C(2)—C(3)	1·363 (7)	C(3)—C(4)	1·457 (7)
C(3)—C(9)	1·487 (8)	C(4)—C(4a)	1·495 (7)
C(4a)—C(5)	1·392 (8)	C(4a)—C(8a)	1·422 (7)
C(5)—C(6)	1·383 (8)	C(6)—C(7)	1·400 (8)
C(7)—C(8)	1·371 (8)	C(8a)—C(8)	1·408 (7)

C(2)—S(1)—C(8a)	102·5 (3)	S(1)—C(2)—C(3)	127·7 (4)
C(2)—C(3)—C(4)	123·4 (4)	C(4)—C(3)—C(9)	118·9 (4)
C(2)—C(3)—C(9)	117·7 (5)	O(4)—C(4)—C(4a)	119·4 (4)
O(4)—C(4)—C(3)	121·1 (4)	C(3)—C(4)—C(4a)	119·4 (4)
C(5)—C(4a)—C(8a)	118·2 (4)	C(4)—C(4a)—C(8a)	123·3 (4)
C(4)—C(4a)—C(5)	118·5 (4)	C(4a)—C(5)—C(6)	122·1 (5)
C(5)—C(6)—C(7)	119·2 (5)	C(6)—C(7)—C(8)	120·6 (5)
C(7)—C(8)—C(8a)	120·5 (5)	S(1)—C(8a)—C(8)	117·0 (4)
S(1)—C(8a)—C(4a)	123·5 (4)	C(4a)—C(8a)—C(8)	119·5 (5)
O(9)—C(9)—C(3)	125·8 (5)		

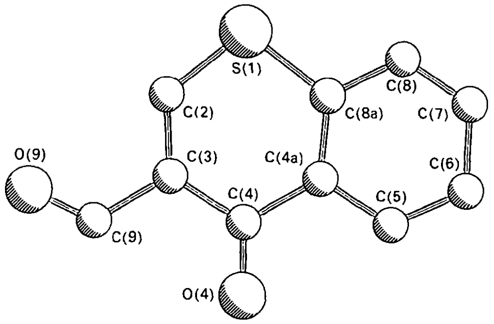

Fig. 1. Drawing showing the atom-numbering scheme of (1).

Generation of compounds containing the functional groups present in (1) and (2) from a Vilsmeier reagent is without precedent. The structure determinations of (1) and (2) provide unequivocal evidence for the formation of products other than β-chlorovinyladehydes from reactions involving dimethylformamide–phosphorus oxychloride at elevated temperatures. These structure determinations in conjunction with other experimental data (Giles & Marson, 1990) provide verification of the work of Nakazumi, Endo, Sonoda & Kitao (1985), while casting doubt upon the preparation of (1) claimed by Chen & Reynolds (1979).

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and geometrical data of H atoms of (1) and (2) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53786 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Positional parameters* (× 10^4) *and equivalent isotropic temperature factors* (Å^2 × 10^3) *for* (2)

	x	y	z	U_{eq}
Cl(1)	−2188 (1)	−1347 (1)	5317 (1)	68 (1)*
O(1)	−3598 (3)	−2000 (3)	1111 (2)	48 (1)*
O(4)	1553 (3)	−3687 (3)	2810 (2)	59 (1)*
C(2)	−3901 (4)	−2333 (4)	2478 (3)	45 (1)*
C(3)	−2298 (4)	−2863 (4)	3102 (2)	39 (1)*
C(4)	10 (4)	−3153 (4)	2291 (3)	41 (1)*
C(4a)	347 (4)	−2797 (3)	805 (2)	36 (1)*
C(5)	2463 (4)	−3019 (4)	−122 (3)	46 (1)*
C(6)	2736 (5)	−2713 (4)	−1502 (3)	55 (1)*
C(7)	896 (6)	−2167 (4)	−1999 (3)	57 (1)*
C(8)	−1194 (5)	−1927 (4)	−1125 (3)	50 (1)*
C(8a)	−1454 (4)	−2242 (4)	272 (2)	40 (1)*
C(9)	−2879 (5)	−3201 (5)	4626 (3)	51 (1)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

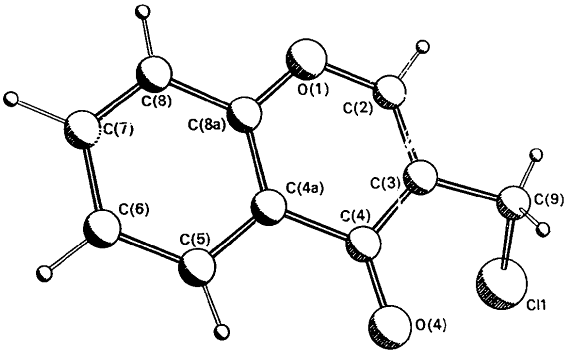

Fig. 2. Drawing showing the atom-numbering scheme of (2).

Table 4. *Bond lengths* (Å) *and bond angles* (°) *for* (2)

Cl(1)—C(9)	1·807 (4)	O(1)—C(2)	1·355 (3)
O(1)—C(8a)	1·384 (3)	O(4)—C(4)	1·234 (4)
C(2)—C(3)	1·339 (5)	C(3)—C(4)	1·460 (3)
C(3)—C(9)	1·496 (4)	C(4)—C(4a)	1·472 (4)
C(4a)—C(5)	1·404 (4)	C(4a)—C(8a)	1·392 (4)
C(5)—C(6)	1·371 (4)	C(6)—C(7)	1·392 (6)
C(7)—C(8)	1·369 (4)	C(8)—(C8a)	1·390 (4)
C(2)—O(1)—C(8a)	117·9 (2)	O(1)—C(2)—C(3)	125·7 (2)
C(9)—C(3)—C(4)	120·3 (3)	C(9)—C(3)—C(2)	119·9 (2)
C(2)—C(3)—C(4)	119·8 (2)	O(4)—C(4)—C(3)	122·6 (2)
O(4)—C(4)—C(4a)	122·7 (2)	C(3)—C(4)—C(4a)	114·7 (2)
C(4)—C(4a)—C(5)	122·0 (3)	C(4)—C(4a)—C(8a)	120·4 (2)
C(5)—C(4a)—C(8a)	117·6 (2)	C(4a)—C(5)—C(6)	121·0 (3)
C(5)—C(6)—C(7)	119·9 (3)	C(6)—C(7)—C(8)	120·8 (3)
C(7)—C(8)—C(8a)	118·9 (3)	O(1)—C(8a)—C(4a)	121·5 (2)
O(1)—C(8a)—C(8)	116·7 (3)	C(4a)—C(8a)—C(8)	121·9 (2)
Cl(1)—C(9)—C(3)	111·4 (2)		

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Structure of 5-Bromouridine: a Redetermination

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Abstract. $C_9H_{11}BrN_2O_6$, $M_r = 323{\cdot}10$, monoclinic, $P2_1$, $a = 7{\cdot}722$ (6), $b = 5{\cdot}809$ (1), $c = 13{\cdot}259$ (1) Å, $\beta = 101{\cdot}17$ (7)°, $V = 583{\cdot}6$ (2) Å^3, $Z = 2$, $D_x = 1{\cdot}839$ g cm^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 50{\cdot}84$ cm^{-1}, $F(000) = 324$, $T = 296$ K, $R = 0{\cdot}043$, $wR = 0{\cdot}063$ for 1290 independent reflections with $I > 3\sigma(I)$. The precision of this structure is improved (averaged coordinate e.s.d.'s are smaller by a factor of three) by comparison with the previous report [$R = 0{\cdot}074$, for 1312 reflections; Iball, Morgan & Wilson (1966). *Proc. R. Soc. London*, **295**, 320–333]. This study is a pre-requisite for using the sample as a test case for anomalous-dispersion studies at a synchrotron.

Experimental. 5-Bromouridine was obtained from Aldrich Chemical Co. Thin colourless plates, typically 1·5 × 0·5 × 0·1 mm, grown from aqueous solution by slow evaporation at room temperature. Sample glued on a glass fibre for data collection. Space group determined from systematic absences, $0k0$: $k = 2n$, Rigaku AFC5 diffractometer on an Ru200 rotating anode, graphite monochromator, Cu $K\alpha$ radiation, 50 kV 180 mA, 23 reflections (77 <

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