Photolysis of α-Aryloxy-ketones

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Irradiation of aryloxy-ketones $ArO\cdot CHR^1\cdot COR^2$ (R^1 = H, alkyl, or Ph; R^2 = alkyl or Ph) in methanol caused fission of the C–OAr bond to give a phenol (ArOH), a ketone ($R^1CH_2\cdot COR^2$), and a product of *ortho*-rearrangement which cyclised during work-up to a substituted benzofuran. The benzofurans were also synthesised by cyclisation of suitable aryloxy-ketones in polyphosphoric or sulphuric acid. In a few cases, aryloxy-ketones gave the corresponding dimethyl acetals [$ArO\cdot CHR^1\cdot C(OMe)_2R^2$] upon irradiation.

PHOTOLYSIS of α-aryloxy-acetones (II) in methanol gives the corresponding phenol (I) and dimethyl acetal (IX), and a 2-methylbenzofuran (XVI) which was formed by cyclisation of the product of *ortho*-rearrangement (XIV; R^1 = H, R^2 = Me).[1] The photoreaction was influenced by the nature of the substituents (R^3 and R^4) in the benzene ring. We have extended these investigations to a variety of ketones possessing α-aryloxy-substituents, as well as aryloxy-acetones of types not previously examined. In general, similar results were obtained, with phenols and benzofurans being formed in low yield, and a large part of the starting ketone being recovered. A further product, the ketone $R^1CH_2\cdot COR^2$ which is formed by loss of the aryloxy-substituent, was isolated after irradiation of aryloxy-ketones (V)—(VII). Dimethyl acetals were only detected after photolysis of certain of the aryloxy-acetones and butanones. The results of these photoreactions are given in Table 1.

ArOH

(I) a; Ar = *p*-methoxyphenyl
b; Ar = 3,5-xylyl
c; Ar = *p*-tolyl
d; Ar = 3,4,5-trimethoxyphenyl
e; Ar = 2,6-dimethylphenyl
f; Ar = 2,6-dimethoxyphenyl
g; Ar = 2,6-dichlorophenyl
h; Ar = phenyl
j; Ar = α-naphthyl
k; Ar = β-naphthyl

$ArO\cdot CHR^1\cdot COR^2$

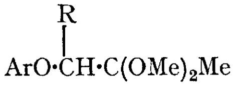
(II) R^1 = H, R^2 = Me
(III) R^1 = R^2 = $-[CH_2]_4-$
(IV) R^1 = R^2 = Me
(V) R^1 = H, R^2 = Ph
(VI) R^1 = Me, R^2 = Ph
(VII) R^1 = Ph, R^2 = Me
(VIII) R^1 = CO_2Et, R^2 = Me

$PhCO\cdot CH_2R$

(XI) R = H
(XII) R = Me

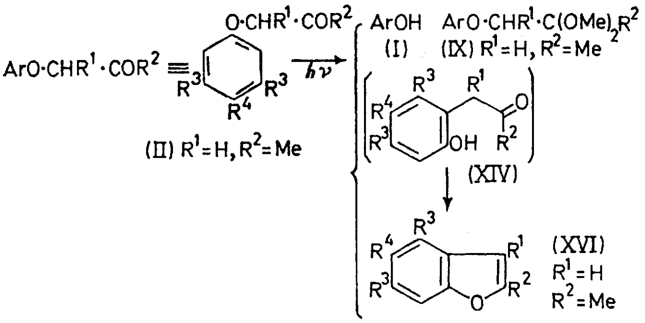
$PhCH_2Ac$

(XIII)



$ArO\cdot CH(R)\cdot C(OMe)_2Me$

(IX) R = H
(X) R = Me



The naphthoxy-acetones (IIj)[2] and (IIk)[2] behaved typically, giving the corresponding naphthol and a naphthofuran which was obtained after acid treatment of the alkali-soluble fraction of the photoproduct. No product of *para*-rearrangement [*cf.* *ortho*-rearrangement leading to benzofurans] was detected after irradiation of the 2,6-disubstituted aryloxy-acetones (IIf) and (IIg), the corresponding acetals being the only significant products.

TABLE 1

Aryloxy-ketone	Reaction time (hr.)	Yield (%) [a]			
		Recovd. starting material	Phenol ArOH	Benzo[*b*]-furan	Ketone or acetal
(IIj) [b]	20	78	12(Ij)	1·6(XXIII)	
(IIk) [b]	12	87	11(Ik)	1·4(XXV)	
(IIf)	10	*ca.* 34 [d]	Trace (If) [c]		*ca.* 66(IXf) [d]
(IIg)	6	*ca.* 39 [d]	Trace (Ig) [c]		*ca.* 61(IXg) [d]
(IIIc) [b]	24	76	7(Ic)	3(XVIIIc)	
IVa)	8	76	4(Ia)	6(XVIIa)	
(IVb)	7	*ca.* 67 [d]	0·6(Ib)	0·7(XVIIb) [2·6(XIVb)] [e]	*ca.* 23(Xb) [d]
(IVe)	7·5	90	2(Ie)		
(IVh)	7·5	*ca.* 68 [d]	1·4(Ih)		*ca.* 28(Xh) [d]
(Va)	9	67	6(Ia)	1·9(XXa)	5(XI)
(Vb)	12·5	83	3(Ib)	0·7(XXb)	2(XI)
(Vc)	8	81	3(Ic)	1·7(XXc)	4(XI)
(VIa)	13·5	73	3(Ia)	0·6(XXIIa)	5(XII)
(VIb) [f]	14	70	6(Ib)	Trace (XXIIb) [c]	8(XII)
(VIIa)	8	78	3(Ia)	2(XXIa)	3·5(XIII)
(VIIb)	14	87	3(Ib)	Trace (XXIb) [c]	3(XIII)

[a] Irradiation in methanol under an atmosphere of nitrogen, with a high-pressure mercury-vapour lamp as the light source. [b] Alkali-soluble portion of the photolysis mixture was allowed to stand for 18 hr. at room-temperature in 5% methanolic hydrogen chloride before work-up. [c] Presence indicated by t.l.c. [d] Evidence for yield and structure from n.m.r. spectrum of a mixture of acetal and starting ketone. [e] Evidence for structure from i.r. and n.m.r. spectrum of a chromatographic fraction. [f] In methanol–dioxan (5 : 7).

The effect of substitution in the α-position of an aryloxy-acetone on its photochemistry was investigated by irradiating ketones (III), (IV), (VII), and (VIII). The aryloxy-ketones (V) and (VI), in which the carbonyl group is conjugated to a benzene ring, were also studied.

The cyclohexanone derivative (IIIc)[3] gave the phenol (Ic) and, after acid treatment, the cyclohexeno-benzofuran[3] (XVIIIc). No change was detected after irradiating the cyclic ketone 2-*p*-tolyloxycholestan-3-one [partial formula (XXVII)] for 17 hr.

Photolysis of each of the aryloxy-butanones (IV) yielded the corresponding phenol in low yield. Dimethyl acetals appeared to have been formed (evidence

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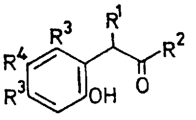
[1] M. K. M. Dirania and J. Hill, *J. Chem. Soc.* (*C*), 1968, 1311.
[2] R. Stoermer, *Annalen*, 1900, **312**, 237.
[3] S. Trippett, *J. Chem. Soc.*, 1957, 419.

from n.m.r. spectra) from the phenoxy- and 3,5-xylyloxy-butanones (IVh)[4] and (IVb)[5] respectively, similar behaviour having been noted for the corresponding *aryloxy-acetones*. When the butanone (IVb) was irradiated, the unstable product of *ortho*-rearrangement (XIVb) survived the work-up and was characterised by its i.r. and n.m.r. spectra (see Experimental section).

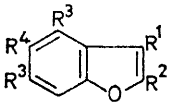
The aryloxy-ketones (V), (VI), and (VII) behaved similarly on irradiation. In all cases small amounts of the corresponding phenol (I) and the ketone $R^1CH_2{\cdot}COR^2$ were formed. Benzofurans were isolated from the alkali-soluble fraction of the photolysis mixture, indicating prior formation of a hydroxy-ketone (XIV) which cyclised during work-up. The photochemistry of ω-aryloxy-acetophenones (V) has been described,[6] but the formation of benzofurans was not reported.

The aryloxy-ketone (VIIIh),[7] which possesses an unsaturated electron-withdrawing α-substituent, was irradiated, but no change was observed.



(XIV)

(XIVb) $R^1 = R^2 = R^3 = Me$
$R^4 = H$



(XV) $R^1 = Me, R^2 = H$
(XVI) $R^1 = H, R^2 = Me$
(XVII) $R^1 = R^2 = Me$
(XVIII) $R^1 = R^2 = -[CH_2]_4-$
(XIX) $R^1 = Ph, R^2 = H$
(XX) $R^1 = H, R^2 = Ph$
(XXI) $R^1 = Ph, R^2 = Me$
(XXII) $R^1 = Me, R^2 = Ph$

a; $R^3 = H, R^4 = OMe$
b; $R^3 = Me, R^4 = H$
c; $R^3 = H, R^4 = Me$
d; $R^3 = R^4 = OMe$

From the results described above, it appears that the α-substituent in the aryloxy-ketone generally does not exert a profound influence on the photoreaction.

TABLE 2

U.v. spectra (methanol)

Aryloxy-ketone	$\lambda_{max.}$ [nm. ($\log_{10}$ ε)]
(IIj)	287 (3·79), 305 (3·53)
(IIk)	252 (3·57), 261 (3·68), 271 (3·74), 281 (3·55), 326 (3·31)
(IIf)	269 (2·81), 277·5sh (2·60)
(IIg)	272 (2·49), 279·5 (2·46)
(IIIc)	277 (3·19), 283·5 (3·09)
(IVa)	290 (3·75)
(IVb)	265 (3·22), 274 (3·17), 281·5 (3·16), 290sh (2·55)
(IVe)	271 (2·75), 274·5 (2·72)
(IVh)	267sh (2·94), 272 (3·05), 278 (2·95)
(Vb)	271sh (3·37), 280 (3·34)
(Vc)	278 (3·43), 283sh (3·42)
(VIa)	285·5 (3·23)
(VIb)	271sh (3·44), 281 (3·38)
(VIIa)	256 (3·69), 291 (3·54), 299·5sh (3·42)
(VIIb)	274 (3·26), 281 (3·27)

sh = shoulder.

All the α-aryloxy-ketones were prepared from the appropriate phenol and α-chloro- or α-bromo-ketone. U.v. spectral properties of the aryloxy-ketones are given in Table 2.

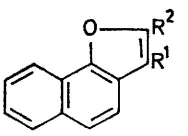
TABLE 3

N.m.r. spectra ($CDCl_3$) (τ at 60 MHz)

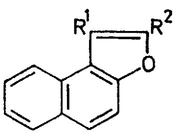
Benzofuran	2-H or 3-H	ArMe	ArOMe	ArH
(XVc)	*ca.* 2·7 [a]	7·82d, *J ca.* 1·4(3-Me); 7·57		2·5—3·1m
(XVb)	2·75q, *J ca.* 1·5	7·68d, *J ca.* 1·5(3-Me); 7·42; 7·62		2·92b, 3·22b
(XVd)	2·8q, *J ca.* 1·5	7·68d, *J ca.* 1·5	6·0, 6·12(6H)	3·22
XVIIIc)		7·62 [7—8·9m (methylene-H)]		2·6—3·5m
(XXIV)	Below 2·8 [b]	7·82d, *J ca.* 1·5		1·5—2·8m
(XXIII)	3·48q, *J ca.* 1·0	7·45d, *J ca.* 1·0		1·5—2·8m
(XXVI)	Below 2·7 [b]	7·45d, *J ca.* 1·3		1·4—2·9m
(XXV)	3·14m	7·48d, *J ca.* 1·0		1·5—2·9m
(XVIIb)		7·42, 7·62, 7·68, 7·71		2·97b, 3·23b
(XIXa)	2·3		6·25	2·2—3·25m
(XIXb)	2·63	7·62, 7·83		2·68(5H) [c] 2·87b, 3·23b
(XIXc)	2·39	7·6		2·3—3·1m
(XXa)	3·07		6·17	2—3·3m
(XXb)	3·14	7·6, 7·64		2·1—3m(5H), 2·92b, 3·22b
(XXc)	3·12	7·6		2—3·1m
(XXIa)		7·55	6·25	2·53(5H) [c], m(3H) [d]
(XXIb)		7·63, 7·75, 7·93		2·68(5H) [c], 2·9b, 3·25b
(XXIIa)		7·55	6·13	2—3·25m
(XXIIb)		7·39, 7·47, 7·62		2·1—2·9m(5H), 2·9b, 3·23b

[a] Signal overlapped by aromatic proton multiplet. [b] Signal hidden by aromatic proton multiplet. [c] Multiplet for phenyl group appears mainly as a broad single peak. [d] 2·68d (*J* 9, 7-H), 2·93d (*J′* 2·5, 4-H), 3·13q (*J* 9, *J′* 2·5; 6-H). b = Broad signal, d = doublet, m = multiplet, q = quartet (with poor resolution), *J* in Hz.

The identities of phenols (I) and ketones $R^1CH_2{\cdot}COR^2$ formed in the above reactions were established by direct comparison with authentic samples. The n.m.r. spectra (Table 3) of the neutral products from the irradiation of naphthoxy-acetones (IIj) and (IIk) were consistent with the naphthofuran structures (XXIII)[8] and (XXV)[9] respectively, and melting points corresponding to those reported in the literature were obtained. The remainder



(XXIII) $R^1 = H, R^2 = Me$
(XXIV) $R^1 = Me, R^2 = H$



(XXV) $R^1 = H, R^2 = Me$
(XXVI) $R^1 = Me, R^2 = H$

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[4] E. Bisagni and R. Royer, *Bull. Soc. chim. France*, 1962, 925.

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[7] W. R. Boehme, *Org. Synth.*, Coll. vol. 4, 1963, 590.

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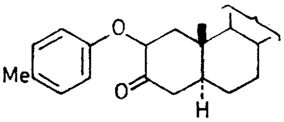
of the benzofurans, the n.m.r. spectra of which are described in Table 4, were compared with samples prepared by cyclisation of suitable aryloxy-ketones in acid. Other benzofurans, which have been included in Table 3 for comparison, were prepared similarly. Cyclisation of aryloxy-ketones in sulphuric or polyphosphoric acid has already been reported for benzofurans (XVb),[10] (XVc),[2] (XVIIa),[11] (XVIIb),[12] (XVIIIc),[3] (XIXa)[13] (XXIV),[14] and (XXVI).[2] The cyclisation of other aryloxy-ketones in polyphosphoric acid is described in Table 4.

TABLE 4

Aryloxy-ketone	Reaction time (min.)	Temp.	Benzofuran	Yield (%)
(Vb)	40	40°	(XIXb)	97
(Vc)	30	40	(XIXc) [15]	87
(Va)	30	130	(XXa) [16]	91
(Vb)	40	145	(XXb)	96
(Vc)	33	145	(XXc) [17]	98
(VIa)	30	40	(XXIa)	66
(VIb)	55	60	(XXIb) [18]	85
(VIIa)	30	50	(XXIIa)	92
(VIIb)	30	40	(XXIIb)	96

Acetals (IXf) and (IXg) were identical (comparison of the n.m.r. spectra) with the products of acetalisation of ketones (IIf) and (IIg) respectively with dimethyl sulphite. Examination of the n.m.r. spectra of the neutral photoproducts from the ketones (IVb) and (IVh) indicated that these products were mixtures of the starting ketone and corresponding dimethyl acetal [(Xb) and (Xh) respectively].



(XXVII)

The n.m.r. spectra of 2-methylbenzofurans (XVI)†, (XXIII), and (XXV) differed from those of 3-methyl isomers (XV), (XXIV), and (XXVI) in that the 3-H signal of the former occurs at higher field (above τ 3·0), the signal for the 2-H occurring below τ 2·9.

EXPERIMENTAL

The silica gel used for column chromatography was Merck Kieselgel, grade 0·05—0·20 mm. (unless otherwise stated). Light petroleum had b.p. 60—80°. Where the same compound was obtained by different routes, identity was established by comparison of the i.r. spectra.

Preparation of the Aryloxy-ketones (II)—(VII).—The following procedure was used.

The α-chloro-ketone (0·2 mole) in acetone (25 ml.) was added during 20 min. to a stirred mixture of the phenol (0·2 mole), anhydrous potassium carbonate (50 g.), potassium iodide (2 g.), and acetone (250 ml.); the mixture was then heated under reflux for 6 hr. After removal of solids and evaporation under reduced pressure, the crude product was obtained by ether extraction, excess of the phenol being removed by washing with alkali.

The known aryloxy-ketones (IIj),[2] (IIk),[2] and (IIIc)[3] were purified by crystallisation, and (IVh)[4] was purified by distillation under reduced pressure. The preparation of the aryloxy-ketones (IVa), (IVb), (Va—c), (VIa), (VIb), (VIIa), and (VIIb) was described recently.[5]

3,4,5-*Trimethoxyphenoxyacetone* (IId), prepared from 3,4,5-trimethoxyphenol,[19] was purified by chromatography over silica gel (Found: C, 59·7; H, 6·6. $C_{12}H_{16}O_5$ requires C, 60·0; H, 6·7%), $\nu_{max.}$ 1720 cm.$^{-1}$.

2,6-*Dimethoxyphenoxacetone* (IIf) had b.p. 124—126°/1 mm. (Found: C, 63·1; H, 6·6. $C_{11}H_{14}O_4$ requires C, 62·8; H, 6·7%), $\nu_{max.}$ 1720 cm.$^{-1}$.

2,6-*Dichlorophenoxyacetone* (IIg) had b.p. 91°/0·3 mm. (Found: C, 49·5; H, 3·9. $C_9H_8Cl_2O_2$ requires C, 49·3; H, 3·7%), $\nu_{max.}$ 1715 cm.$^{-1}$.

3-(2,6-*Xylyloxy*)*butan*-2-*one* (IVe) had b.p. 86—87°/3·5 mm. (Found: C, 75·0; H, 8·3. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·4%), $\nu_{max.}$ 1720 cm.$^{-1}$.

2-p-*Tolyloxycholestan*-3-*one* [partial formula (XXVII)].—2-α-Bromocholestan-3-one[20] (1·5 g.) was treated with *p*-cresol (0·6 g.) according to the precedure described above. The crude neutral product (0·9 g.) was chromatographed over silica gel (60 g.). Elution with benzene yielded cholestan-3-one (0·19 g.), and further elution gave 2-p-*tolyloxycholestan*-3-*one* (0·25 g.), m.p. 154° (from ether–ethanol) (Found: C, 82·7; H, 11·0. $C_{34}H_{52}O_2$ requires C, 82·8; H, 10·6%), $\nu_{max.}$ 1720 cm.$^{-1}$.

Cyclodehydration of Aryloxy-ketones in Polyphosphoric Acid.—Details are given in Table 4. The following procedure was used.

The aryloxy-ketone (1 part) was stirred vigorously with polyphosphoric acid (Albright and Wilson) (10 parts) and the mixture was then stirred well into ice-cold water. Extraction into ether yielded the crude benzofuran which was purified by crystallisation or by distillation under reduced pressure.

4,6-*Dimethyl*-3-*phenylbenzo*[b]*furan* (XIXb) had b.p. 126—127°/0·5 mm. (Found: C, 86·3; H, 6·3. $C_{16}H_{14}O$ requires C, 86·5; H, 6·3%).

4,6-*Dimethyl*-2-*phenylbenzo*[b]*furan* (XXb) had b.p. 155—156°/1·2 mm. (Found: C, 86·6; H, 6·2. $C_{16}H_{14}O$ requires C, 86·5; H, 6·3%).

5-*Methoxy*-2-*methyl*-3-*phenylbenzo*[b]*furan* (XXIa) had b.p. 206—208°/15 mm. (Found: C, 80·4; H, 5·9. $C_{16}H_{14}O_2$ requires C, 80·6; H, 5·9%).

5-*Methoxy*-3-*methyl*-2-*phenylbenzo*[b]*furan* (XXIIa) had m.p. 107—108° (from light petroleum) Found: C, 80·6; H, 5·7. $C_{16}H_{14}O_2$ requires C, 80·6; H, 5·9%).

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† N.m.r. spectra of 2-methylbenzofurans have been described previously.[1]

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[19] M. Tomita and S. Ueda, *Yakugaku Zasshi*, 1961, **81**, 724 (*Chem. Abs.*, 1961, **55**, 23,539).

[20] C. Djerassi and C. R. Scholz, *J. Amer. Chem. Soc.*, 1948, **70**, 417.

3,4,6-*Trimethyl-2-phenylbenzo*[b]*furan* (XXIIb) had m.p. 62—63° (from methanol) (Found: C, 86·2; H, 6·6. $C_{17}H_{14}O$ requires C, 86·4; H, 6·8%).

4,5,6-*Trimethoxy-3-methylbenzo*[b]*furan* (XVd).—3,4,5-Trimethoxyphenoxyacetone (0·4 g.) was stirred with conc. sulphuric acid (4 ml.) for 4 min. at 0°. The mixture was stirred with ice–water and the product was extracted into ether to yield a mixture of the ketone (IId) and the benzofuran (XVd). Chromatography over silica gel (Hopkin and Williams M. F. C.) (25 g.), and elution with benzene–ethyl acetate (10 : 1), gave 4,5,6-*trimethoxy-3-methylbenzo*[b]*furan* (0·07 g.) (Found: C, 64·7; H, 6·2. $C_{12}H_{14}O_4$ requires C, 64·9; H, 6·3%).

Irradiation of Aryloxy-ketones (*See Table* 1).—A stirred 2·5% solution of the ketone in methanol (distilled from potassium carbonate) under nitrogen was irradiated at room temperature. The light source, a high-pressure mercury-vapour lamp (type Q 81, Quarzlampen GMBH, Hanau), was centrally situated in a water-cooled quartz cold-finger. After irradiation, the solution was evaporated and the products were separated into neutral and alkali-soluble fractions. Column chromatography was used for further separation and, in some cases, for purification of phenols (elution with benzene–light petroleum, benzene, or benzene–ethyl acetate).

Benzofurans (XVIIa), (XXa—c), (XXIa), and (XXIIa), and hydroxy-ketone (XIVb) were obtained after acidification and subsequent chromatography of the alkali-soluble fraction. Benzofuran (XVIIIc) was obtained after treatment of an alkali-soluble product from ketone (IIIc) with 5% methanolic hydrogen chloride.

Irradiation of 3-(3,5-xylyloxy)butan-2-one (IVb) gave, in addition to 3,5-xylenol (Ib), benzofuran (XVIIb), and acetal (Xb), an unstable material the spectral characteristics of which were consistent with the structure 3-(2-hydroxy-4,6-dimethylphenyl)butan-2-one (XIVb); $\nu_{max.}$ 1695 and 3345 cm.$^{-1}$; τ ($CDCl_3$) 3·42 (2 ArH), 4·0 (OH), 6·15 (q, *J* 7 Hz, CH), 7·8 (2 ArMe), 8·01 (Me), and 8·66 (d, *J* 7 Hz, Me).

The n.m.r. spectra of the neutral fractions from the irradiation of the aryloxy-butanones (IVb) and (IVh) showed the expected signals for the ketones together with the following signals for the corresponding acetals (Xb) and (Xh) respectively.

Acetal (Xb): τ 6·73 (OMe), 6·82 (OMe), 8·72 (d, and *J* 6·5 Hz, Me).

Acetal (Xh): τ 6·73 (OMe), 6·82 (OMe), 8·58 (Me,) and 8·71 (d, *J* 6·5 Hz, Me).

The signals for the remaining groups in each acetal coincided with signals for the corresponding ketones.

Acetalisation of the Aryloxy-acetones (IIf) *and* (IIg).—The dimethyl acetals (IXf) and IXg) were prepared from ketones (IIf) and (IIg) respectively by treatment with dimethyl sulphite according to the method already described for dimethyl acetals of other aryloxy-acetones.[1]

Dimethyl acetal (IXf) (82%) had b.p. 110—111°/0·3 mm. (Found: C, 60·3; H, 7·7. $C_{13}H_{20}O_5$ requires C, 60·9; H, 7·9%); τ ($CDCl_3$) 2·9—3·6 (m, ArH), 6·23 (2 ArOMe), 6·1 (CH_2), 6·72 (acetal OMe), and 8·44 (Me).

Dimethyl acetal (IXg) (77%) had b.p. 99—102/0·3 mm. (Found: C, 50·1; H, 5·4. $C_{11}H_{14}Cl_2O_3$ requires C, 49·8; H, 5·3%); τ ($CDCl_3$) 2·6—3·2 (m, ArH), 6·02 (CH_2), 6·67 (acetal OMe), and 8·37 (Me).

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