Pyrylium Salt Formation from Aromatic Ketones.   Part I.   Reactions of β-Methylchalcones in Non-aqueous Acidic Media

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Acetic acid solutions of 4,4'-disubstituted β-methylchalcones (substituents H, Me, MeO, Cl, or F) react in the presence of Lewis acids ($SnCl_4$, $ZnCl_2$, or $SbCl_3$) and benzoyl chloride to give the corresponding bis-2-methyl-4,6-diarylpyrylium MX_{n+2}^{2-} salts, but in the absence of benzoyl chloride bis-2,4,6-triarylpyrylium MX_{n+2}^{2-} salts are formed.   The results support the accepted mechanism for the former type of reaction; a mechanism is proposed for the latter.   Anomalous anions are formed when the substituent is the methoxy-group.
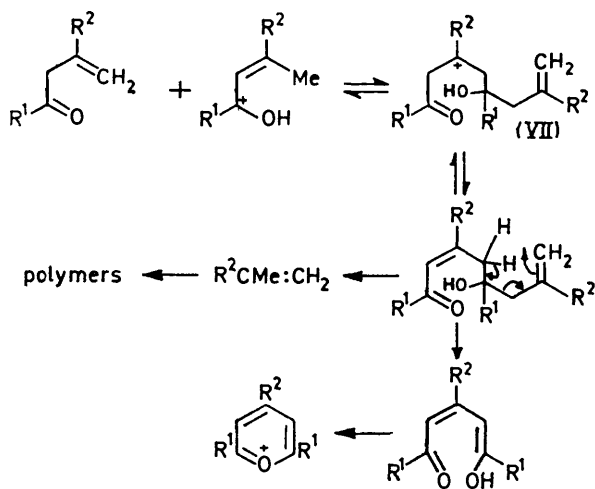
THE importance and versatility of monocyclic pyrylium salts as synthetic intermediates has been fully appreciated only in recent years; a comprehensive review of the methods available for their synthesis was published in 1969.[1]   One of these methods is the acylation of αβ-unsaturated ketones, the first reported reaction being that of β-methylchalcone (1,3-diphenylbut-2-en-1-one)

(Ia) with acetic anhydride in the presence of iron(III) chloride.[2]   As a preliminary to kinetic studies we report some preparative work using 4,4'-disubstituted β-methylchalcones (I) in acetic acid solutions containing

[1] A. T. Balaban, W. Schroth, and G. Fischer, *Adv. Heterocyclic Chem.*, 1969, **10**, 241.
[2] C. Gastaldi, *Gazzetta*, 1922, **52**, 169.

Lewis acids and both with and without added benzoyl chloride to give pyrylium salts (II) and (III).

a; R = Ph: b; R = p-MeC$_6$H$_4$: c; R = p-MeO·C$_6$H$_4$: d; R = p-ClC$_6$H$_4$: e; R = p-FC$_6$H$_4$: f; R = Me

Balaban and Nenitzescu [3] studied the acylation of mesityl oxide (1,3-dimethylbut-2-en-1-one) (If), and proposed that the βγ-isomer, isomesityl oxide (1,3-dimethylbut-3-en-1-one) (IV) was formed prior to the acylation step of the reaction. A marked improvement in the yield of pyrylium salt was obtained for this same reaction when the βγ-isomer was used as starting material,[4] and high yields of benzopyrylium salts are obtained from cyclohexenyl ketones where for conformational reasons the βγ-isomer prevails.[5] Praill and Saville [4] proposed a mechanism (Scheme 1) for the acylation of mesityl oxide (If) by acetic anhydride in perchloric acid to give 2,4,6-trimethylpyrylium perchlorate, and this is regarded as a general mechanism for the formation of pyrylium salts from αβ-unsaturated ketones by acylation under acidic conditions.

SCHEME 1

We report the reactions of 4,4'-disubstituted β-methylchalcones (Ia—c) in acetic acid solutions containing benzoyl chloride and tin(IV) chloride. In each case the cation formed is bis-2-methyl-4,6-diarylpyrylium (II) and the anion is hexachlorostannate (SnCl$_6^{2-}$), except where the substituent is methoxy, when we believe the anion to be diacetatotetrachlorostannate [SnCl$_4$-(OAc)$_2^{2-}$].

Unsubstituted β-methylchalcone (Ia) under similar reaction conditions but with zinc chloride or antimony trichloride in place of tin(IV) chloride, gives the cation

bis-2-methyl-4,6-diphenylpyrylium and the anion tetrachlorozincate (ZnCl$_4^{2-}$) or pentachloroantimonate (SbCl$_5^{2-}$), respectively.

These results are in accord with the mechanism in Scheme 1, with the appearance of a methyl group at the 2-position in the pyrylium cation being explained by the rapid pre-equilibrium formation of acetyl ions by the reaction of benzoyl chloride with acetic acid, these acetyl ions then participating in the acylation step of the mechanism. A similar explanation was given by Satchell [6] for the acylation of β-naphthol by a mixture of benzoyl chloride and hydrogen chloride in acetic acid.

Pyrylium salts are formed from αβ-unsaturated ketones in acidic media in the absence of added acylating agent and Elderfield and King [7] proposed the mechanism shown in Scheme 2 for the reaction of β-methylchalcone in boron trifluoride–ether to give 2,4,6-triphenylpyrylium tetrafluoroborate. The essential features of this mechanism are the generation of the benzoyl cation as acylating agent, the active participation of the enolic form of β-methylchalcone (V) in the acylation step of the reaction, and the formation of polymers from the olefinic by-product (VI).

SCHEME 2

β-Methylchalcone and its derivatives (Ia—e) in acetic acid solution containing tin(IV) chloride but without added benzoyl chloride give a different series of pyrylium salts from those previously described. The cations have the bis-2,4,6-triarylpyrylium structure (III) and the anion is hexachlorostannate (SnCl$_6^{2-}$), except again where the substituent is methoxy, when the cation is 2,4,6-tris-p-methoxyphenylpyrylium and we believe the anion to be hydrodiacetatotetrachlorostannate [HSnCl$_4$-(OAc)$_2^-$].

The mechanism described in Scheme 2 cannot be operating under our experimental conditions since the benzoyl ions produced as intermediates would rapidly react with the reaction medium, rather than with the enolic form of the β-methylchalcone (V),[†] ive acetyl ions, which in turn would give 2-methylpy____n cations. We propose an alternative mechanism (Scheme 3) which

[3] A. T. Balaban and C. D. Nenitzescu, *Annalen*, 1959, **625**, 74.
[4] P. F. G. Praill and B. Saville, *Chem. and Ind.*, 1960, 495.
[5] G. N. Dorofeenko and V. I. Dulenko, *J. Gen. Chem.* (*U.S.S.R.*), 1962, **32**, 3378; G. N. Dorofeenko, V. I. Dulenko, and L. V. Dulenko, *ibid.*, 1964, **34**, 3155, 3637.

[6] D. P. N. Satchell, *J. Chem. Soc.*, 1960, 1752.
[7] R. C. Elderfield and T. P. King, *J. Amer. Chem. Soc.*, 1954, **76**, 5437.

involves an aldol-type condensation of αβ- and βγ-forms of the β-methylchalcones followed by an elimination reaction.

SCHEME 3

This mechanism does not require formation of a benzoyl ion and thus precludes acetylation, but it does still allow for polymer formation, which does occur to some extent in our reactions. Although dehydration of the intermediate (VII) is a possible alternative to olefinic elimination, molecular models show that the six-membered cyclic transition state of the proposed elimination step is the least sterically hindered conformation.

The microanalytical and spectroscopic (far i.r. and Mössbauer) evidence for our proposed structures for the anomalous anions $SnCl_4(OAc)_2^{2-}$ and $HSnCl_4(OAc)_2^-$ is given in the Experimental section; an explanation of their mode of formation is deferred until kinetic evidence is presented.

EXPERIMENTAL

Reagents.—Dry acetic acid was prepared by the method of Eichelberger and La Mer;[8] fractions with m.p. $>16.6°$

ampoules. Antimony trichloride (reagent grade) was purified by repeated sublimation under vacuum down a tube constricted at intervals; the end segment was finally sealed off as an ampoule. Reagent grade tin(IV) chloride was fractionally distilled from tin metal in a stream of dry nitrogen and samples (b.p. 114° at 747 mmHg) were sealed in ampoules. Reagent grade zinc chloride (fused sticks) was used without further purification.

β-Methylchalcones.—β-Methylchalcone[9] and its 4,4'-disubstituted derivatives[10] were prepared from acetophenone and the corresponding 4'-substituted acetophenones and were purified by fractional distillation in a low pressure nitrogen atmosphere. Solids were recrystallized from ethanol and ether. Purity was established by g.l.c. on a 1% SE 30 silicone gum column.

The m.p.s or b.p.s of β-methylchalcone (Ia),[10] 150° at 0.5 mmHg; β,4,4'-trimethylchalcone (Ib),[11] 57—58°; and 4,4'-dichloro-β-methylchalcone (Id),[11] 79—80° agrees well with the literature data and analyses were satisfactory. 4,4'-*Dimethoxy-β-methylchalcone* (Ic) was a yellow solid, m.p. 84—85° (Found: C, 76·4; H, 6·5. $C_{18}H_{18}O_3$ requires C, 76·6; H, 6·4%). 4,4'-*Difluoro-β-methylchalcone* (Ie) was a pale yellow solid, m.p. 46—47° (Found: C, 74·0; H, 4·7. $C_{16}H_{12}F_2O$ requires C, 74·4; H, 4·7%).

Pyrylium Salts.—The chalcone (I) was added to an acetic acid solution (50 ml) of Lewis acid (MX_n) and benzoyl chloride and the mixture was kept at 50° for a time (t). The solution was then poured into ether (1 l) at 0° and the solid formed was purified by repeated dissolution in acetone followed by precipitation with ether.

U.v. spectra were determined for solutions in acetic acid solution with a Unicam SP 800B spectrophotometer, uncorrected fluorescence spectra for solutions in acetone with an Amino–Bowman spectrofluorimeter, and i.r. spectra for potassium bromide discs (1—25μ) with a Grubb–Parson Spectromaster. Far i.r. spectra for polythene wax discs (40—400 cm⁻¹), obtained with an R.I.I.C. interferometer, and Mössbauer spectra for samples held between aluminium foil at 77 K were determined by the Physico-chemical Measurements Unit, Harwell. Satisfactory analyses were obtained for all pyrylium salts except (IIIb, d, and e). In these cases the possibility of contamination by the analogous series (II) compounds was discounted on spectroscopic grounds (u.v.).

Preparation of pyrylium salts

Substrate (mol)	MX_n (mol)	PhCOCl (mol)	t	Yield (%)	Product Cation	Product Anion
(Ia) (0·44)	$SnCl_4$ (1·5)	0·25	60 h	10	(IIa)	$SnCl_6^{2-}$
(Ib) (0·38)	$SnCl_4$ (1·0)	0·30	60 h	14	(IIb)	$SnCl_6^{2-}$
(Ic) (0·20)	$SnCl_4$ (0·65)	0·16	60 h	15	(IIc)	$SnCl_4(OAc)_2^{2-}$
(Id) (0·20)	$SnCl_4$ (0·89)	0·58	60 h	39	(IId)	$SnCl_6^{2-}$
(Ie) (0·10)	$SnCl_4$ (0·85)	0·51	60 h	85	(IIe)	$SnCl_6^{2-}$
(Ia) (0·26)	$ZnCl_2$ (0·70)	0·70	60 h	24	(IIa)	$ZnCl_4^{2-}$
(Ia) (0·28)	$SbCl_3$ (1·1)	0·30	1 week	4	(IIa)	$SbCl_5^{2-}$
(Ia) (0·46)	$SnCl_4$ (1·0)		60 h	15	(IIIa)	$SnCl_6^{2-}$
(Ib) (0·26)	$SnCl_4$ (1·0)		3 days	6	(IIIb)	$SnCl_6^{2-}$
(Ic) (0·14)	$SnCl_4$ (1·8)		3 days	11	†	†
(Id) (0·20)	$SnCl_4$ (0·96)		1 week	3	(IIId)	$SnCl_6^{2-}$
(Ie) (0·08)	$SnCl_4$ (1·0)		1 week	30	(IIIe)	$SnCl_6^{2-}$

† Salt formed 2,4,6-tris-*p*-methoxyphenylpyrylium $HSnCl_4(OAc)_2^-$.

were used. Benzoyl chloride (reagent grade) was fractionally distilled under reduced pressure in a stream of dry nitrogen and fractions (b.p. 56° at 4 mmHg) were sealed in

Bis-2-methyl-4,6-diphenylpyrylium hexachlorostannate (IIa; $SnCl_6^{2-}$) was a yellow fluorescent solid, m.p. 248—

[8] W. C. Eichelberger and V. K. La Mer, *J. Amer. Chem. Soc.,* 1933, **55**, 3633.

[9] W. Wayne and H. Adkins, *Org. Synth.,* 1941, **21**, 39.
[10] J. Guthrie and N. Rabjohn, *J. Org. Chem.,* 1957, **22**, 176.
[11] R. Carrie and J-C. Rochard, *Compt. rend.,* 1963, 2849.

253° (decomp.) (Found: C, 52·0; H, 3·6. $C_{36}H_{30}Cl_6O_2Sn$ requires C, 52·3; H, 3·7%); $\lambda_{max.}$ 254, 340, and 372 nm (lit.,[12] for anion ClO_4^- in $HClO_4$ solution 254, 338, and 374 nm); fluorescence $\lambda_{max.}$ excit. ca. 350sh and 370 nm, $\lambda_{max.}$ emiss. 448 nm; i.r. agreed with that of the corresponding perchlorate;[13] far i.r. $\nu_{max.}$ 164, 290, and 306 cm^{-1} (lit.,[14] $SnCl_6^{2-}$ in pyridinium salt 280 and 310 cm^{-1}; lit.,[15] in tetra-ethylammonium salt [15] 161, 276, 310sh, and 318 cm^{-1}).

Bis-2-methyl-4,6-di-p-tolylpyrylium hexachlorostannate (IIb; $SnCl_6^{2-}$) was a green fluorescent solid, m.p. 248—256° (decomp.) (Found: C, 54·1; H, 4·5; Cl, 23·5. $C_{40}H_{38}Cl_6O_2Sn$ requires C, 54·5; H, 4·3; Cl, 24·1%); $\lambda_{max.}$ 261, 353, and 392 nm; fluorescence $\lambda_{max.}$ excit. 350sh and 388 nm, $\lambda_{max.}$ emiss. 465 nm.

Bis-2-methyl-4,6-bis-p-methoxyphenylpyrylium diacetato-tetrachlorostannate [IIc; $SnCl_4(OAc)_2^{2-}$] was a brown fluorescent solid, m.p. 275—278° (decomp.) (Found: C, 53·0; H, 4·2. $C_{48}H_{50}Cl_4O_{14}Sn$ requires C, 53·1; H, 4·5%); $\lambda_{max.}$ 273, 378, and 420 nm; fluorescence $\lambda_{max.}$ excit. 410 and 460 nm, $\lambda_{max.}$ emiss. 523 nm; far i.r. $\nu_{max.}$ 164, 288, and 310sh cm^{-1}, Mössbauer δ 1·1 mm s^{-1}; *picrate*, red solid, m.p. 201—203° (Found: C, 58·0; H, 4·1; N, 7·7. $C_{26}H_{21}N_3O_{10}$ requires C, 58·3; H, 4·0; N, 7·9%). This picrate analysis is conclusive for the cation structure and we believe that the anion suggested is the most likely in view of the far i.r. and Mössbauer evidence.

Bis-2-methyl-4,6-bis-p-chlorophenylpyrylium hexachlorostannate (IId; $SnCl_6^{2-}$) was a yellow fluorescent solid, m.p. 249—252° (decomp.) (Found: C, 44·9; H, 3·2; Cl, 41·1. $C_{36}H_{26}Cl_{10}O_2Sn$ requires C, 44·9; H, 2·7; Cl, 36·8%), $\lambda_{max.}$ 262, 348, and 353 nm; fluorescence $\lambda_{max.}$ excit. 350sh and 380 nm, $\lambda_{max.}$ emiss. 464 nm.

Bis-2-methyl-4,6-bis-p-fluorophenylpyrylium hexachlorostannate (IIe; $SnCl_6^{2-}$) was a yellow fluorescent solid, m.p. 254—258° (decomp.) (Found: C, 47·9; H, 3·3. $C_{36}H_{26}Cl_6F_4O_2Sn$ requires C, 48·2; H, 2·9%); $\lambda_{max.}$ 257, 342, and 376 nm; fluorescence $\lambda_{max.}$ excit. 350 and 370 nm, $\lambda_{max.}$ emiss. 452 nm.

Bis-2-methyl-4,6-diphenylpyrylium tetrachlorozincate (IIa; $ZnCl_4^{2-}$). In this case a precipitate formed in the system before addition to ether. This precipitate was purified as described previously, giving a yellow fluorescent solid, m.p. 225—227° (decomp.) (Found: C, 60·7; H, 4·4; Cl, 20·0. $C_{36}H_{30}Cl_4O_2Zn$ requires C, 61·6; H, 4·3; Cl, 20·2%); u.v. and i.r. spectra identical with those for bis-2-methyl-4,6-di-phenylpyrylium hexachlorostannate (IIa; $SnCl_6^{2-}$); far i.r. $\nu_{max.}$ 132, 224, 271, and 286 cm^{-1} (lit.,[16] $\nu_{max.}$ for Me_4N^+ $ZnCl_4^{2-}$, 271 cm^{-1}). The remaining solution was treated by the general method and gave a yellow solid with $\lambda_{max.}$ 254 and 278 nm (lit.,[12] for bis-2,4,6-triphenylpyrylium cation, 278 nm), thought to be a mixture of (IIa; $ZnCl_4^{2-}$) and bis-2,4,6-triphenylpyrylium tetrachlorozincate (IIIa; $ZnCl_4^{2-}$).

Bis-2-methyl-4,6-diphenylpyrylium pentachloroantimonate (IIa; $SbCl_5^{2-}$) was a yellow fluorescent solid, m.p. 170—172° (decomp.) (Found: C, 52·9; H, 3·7; Cl, 22·4. $C_{36}H_{30}Cl_5O_2Sb$ requires C, 54·3; H, 3·3; Cl, 22·5%); u.v. and

i.r. spectra identical with those for bis-2-methyl-4,6-di-phenylpyrylium hexachlorostannate (IIa; $SnCl_6^{2-}$); far i.r. $\nu_{max.}$ 114, 178s, 246, 286, and 332 cm^{-1} (lit.,[17] for $SbCl_6^{3-}$ 178 cm^{-1}; lit.,[18] for $SbCl_5^{2-}$ 72sh, 158s, 195s, 260, 297s, 315s, and 340sh cm^{-1}). Allowing for wavelength shifts due to difference in cations the far i.r. evidence favours the presence of the $SbCl_5^{2-}$ ion, and since this is compatible with the analytical data we prefer this structure.

Bis-2,4,6-triphenylpyrylium hexachlorostannate (IIIa; $SnCl_6^{2-}$) was a yellow fluorescent solid, m.p. 304—307° (decomp.) (lit.,[19] 290—298°) (Found: C, 58·3; H, 3·7. Calc. for $C_{46}H_{34}Cl_6O_2Sn$: C, 58·2; H, 3·6%), $\lambda_{max.}$ 277, 361, and 408 nm (lit.,[12] for corresponding perchlorate 278, 361, and 408 nm); fluorescence $\lambda_{max.}$ excit. 355 and 402 nm, $\lambda_{max.}$ emiss. 468 nm; i.r. spectrum agreed with that for corresponding perchlorate.[13]

Bis-2,4,6-tri-p-tolylpyrylium hexachlorostannate (IIIb; $SnCl_6^{2-}$) was a yellow fluorescent solid, m.p. 260—266° (decomp.) (Found: C, 59·1; H, 4·8. $C_{52}H_{46}Cl_6O_2Sn$ requires C, 60·4; H, 4·5%); $\lambda_{max.}$ 288, 381, and 424 nm, fluorescence $\lambda_{max.}$ excit. 375 and 420 nm, $\lambda_{max.}$ emiss. 490 nm.

2,4,6-Tris-p-methoxyphenylpyrylium hydrodiacetatotetra-chlorostannate (see footnote to Table) was a brick-red solid, m.p. 278—280° (decomp.) (Found: C, 45·4; H, 4·0; Cl, 18·4. $C_{30}H_{30}Cl_4O_8Sn$ requires C, 46·3; H, 3·9; Cl, 18·2%); far i.r. $\nu_{max.}$ 160, 288, 316, and 322sh cm^{-1}; Mössbauer δ 1·1 mm s^{-1}; *picrate*, red solid, m.p. 283—285° (lit.,[20] 283—284°; lit.,[21] 276—283°) (Found: C, 61·1; H, 4·1; N, 6·6. Calc. for $C_{32}H_{25}N_3O_{11}$: C, 61·2; H, 4·0; N, 6·7%). The picrate analysis confirms the structure of the cation and the Mössbauer and i.r. evidence indicates that the anion contains six-co-ordinated tin but not $SnCl_6^{2-}$. We suggest that the structure given is the most likely one.

Bis-2,4,6-tris-p-chlorophenylpyrylium hexachlorostannate (IIId; $SnCl_6^{2-}$) was a yellow fluorescent solid, m.p. 320—325° (decomp.) (Found: C, 46·8; H, 3·3. $C_{46}H_{28}Cl_6O_2Sn$ requires C, 47·8; H, 2·4%); $\lambda_{max.}$ 260, 350sh, 381, and 430sh nm; fluorescence $\lambda_{max.}$ excit. 370 and 415 nm, $\lambda_{max.}$ emiss. 488 nm.

Bis-2,4,6-tris-p-fluorophenylpyrylium hexachlorostannate (IIIe; $SnCl_6^{2-}$) was a yellow fluorescent solid, m.p. 254—258° (decomp.) (Found: C, 49·2; H, 2·9. $C_{46}H_{28}Cl_6F_6O_2Sn$ requires C, 52·2; H, 2·7%); $\lambda_{max.}$ 255, 280, 340sh, 367, and 415sh nm; fluorescence $\lambda_{max.}$ excit. 360 and 400 nm, $\lambda_{max.}$ emiss. 475 nm.

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