Novel Dimer of Pentane-2,4-dione. The Crystal and Molecular Structure of the Cation $(C_{10}H_{13}O_2)^+$

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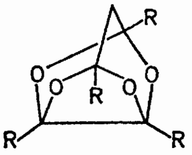
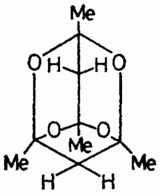
Summary Reaction of a pentane-2,4-dionate salt with dimethyldichlorosilane yields a bright yellow compound; *X*-ray structure analysis reveals it to be the novel substituted pyrylium species, 6-(2-hydroxy-prop-1-enyl)-2,4-dimethylpyrylium chloride (III).

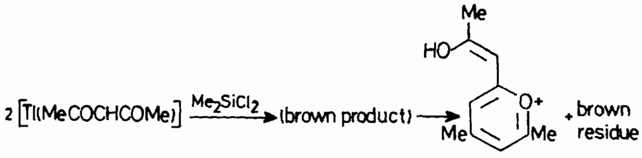
Until recently, attempts to dimerize 1,2- or 1,3-diketones have been unsuccessful,[1] Acid-catalysed reactions of 1,2-diketones with 1,3-diketones have led to some unique compounds *e.g.* the 2,4,6,8-tetraoxatricyclo[3,3,1,$0^{3,7}$]-nonanes (I). Further, treatment[2] of pentane-2,4-dione (neat) with $[MoOCl_4]$ produces the tetraoxa-adamantane (II) formed by the dimerization of two molecules of the 1,3-diketone, while reaction with $[WOCl_4]$ yields the cationic species 2,4,6-trimethyl-3-acetylpyrylium.[2] In contrast, reaction of $[MoOCl_4]$ and $[WOCl_4]$ with pentane-2,4-dione in solution has produced the neutral diketone adduct,



(I)



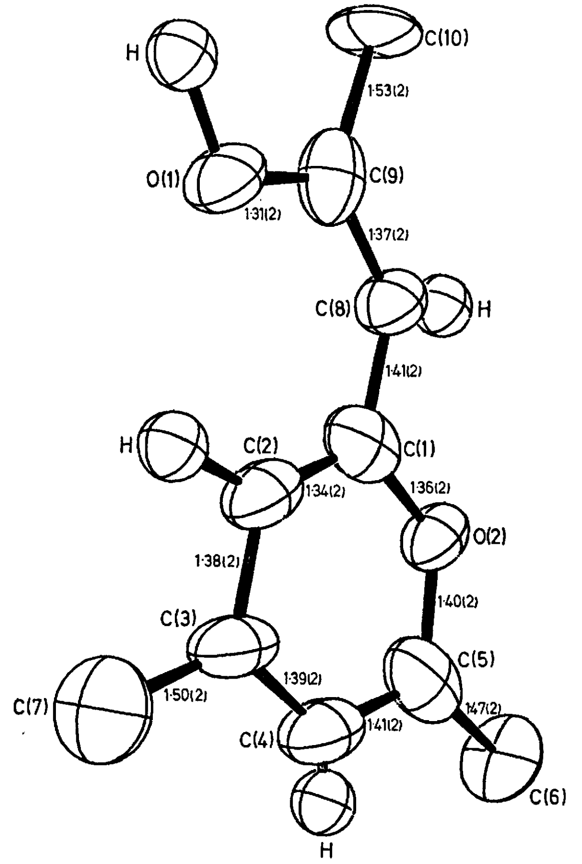
(II)



(III)

Scheme

[$MoOCl_3(C_5H_8O_2)$],[3] and the pentane-2,4-dionate complex, [$WOCl_3(C_5H_7O_2)$],[4] respectively. The recent study of Drew, *et al.*[2] prompts us to report our findings on the reaction between [Tl(MeCOCHCOMe)] and Me_2SiCl_2 according to the Scheme. Addition of Tl(MeCOCHCOMe) (24·1 mmol) to a stirred solution of Me_2SiCl_2 (14·6 mmol; 20% excess) in anhydrous CH_2Cl_2 (75 ml) produces a red mixture. Filtration and concentration of the filtrate followed by addition of dry hexane yields, on cooling, a brown product. Sublimation of this product gives a yellow sublimate, m.p. 153—154° (decomp.), giving analytical data in accordance with the formula $C_{10}H_{13}ClO_2$ (yield *ca.* 10%,† *M* 190 in $CHCl_3$; calc. 200). We assign structure (III) to this product, and we believe it may be formed following formation of a 1,5-ene dione condensation species followed by dehydration of the latter.[5]



Figure

With difficulty, crystals were obtained from dry CH_2Cl_2 solution, and, although small, were used for the *X*-ray diffraction study. Space group $P2_1/m$; $a = 8{\cdot}307(8)$, $b = 6{\cdot}770(7)$, $c = 9{\cdot}667(8)$ Å, $\beta = 106{\cdot}96(4)$, Z for [$C_{10}H_{13}O_2$]Cl = 2. Diffraction data were collected on a Picker-Nuclear automated *X*-ray diffractometer. The structure was solved by direct methods in two-dimensional projection (down *b*) using 41 reflections. Using the 883 reflections with $I > 3\sigma(I)$, full-matrix least-squares refinement of all non-hydrogen atoms with anisotropic thermal parameters and all non-methyl hydrogens with isotropic thermal parameters reduced the conventional *R* factor to 9·3%. Attempts to refine in space group $P2_1$ did not reduce the *R* factor; the rather high value is probably attributable to the weakness of the diffraction intensities.

The crystallographically required planar molecular geometry of the cation [$C_{10}H_{13}O_2$]$^+$ is illustrated in the Figure; the counterion Cl^- has been omitted. Anisotropic motion appears normal, further supporting the assignment of $P2_1/m$ as the appropriate space group. Carbon–carbon and carbon–oxygen bond distances in the pyrylium ring are similar to those reported by Drew, *et al.*[2], and are intermediate between bond lengths[6] for single [C–C, 1·541(3) and C–O, 1·43(1) Å] and double bonds [C=C, 1·337(6) and C=O, 1·23(1) Å]. Such rings are isoelectronic with benzene and are therefore expected to show aromatic character.[5] Bond lengths C(1)–C(8), C(8)–C(9), and C(9)–O(1) also possess partial double-bond character, indicative of extensive conjugation of the propenyl fragment with the pyrylium ring.

The ^1H n.m.r. spectra ($CDCl_3$; Me_4Si; Varian A-60A) of (III) show signals at δ 8·10 and 6·87 (br, Ph), 2·61 and 2·49 (ring Me), and 2·58 [CHC(OH)*Me*]. The OH and –*CH*C(OH)– resonances were not observed in the room-temperature spectra probably owing to a fast keto–enol tautomeric exchange process. At −44·8 °C, the –*CH*C(OH)– signal occurs at δ 5·62, while the OH proton is observed at δ 15·0. The i.r. spectra of (III) (Nujol; KBr windows), unlike that of pentane-2,4-dione, show a very broad band at *ca.* 2400 cm^{-1} and a weak broad band at *ca.* 1770 cm^{-1}. The latter band is tentatively assigned to the ring C–O stretching vibration in keeping with earlier results[7] on pyrylium perchlorates; the band at 2400 cm^{-1} is tentatively ascribed to O–H stretching. Such a low frequency is not unexpected in view of the expected reduction in the force constant of the O–H group *via* conjugation of the propenyl substituent with the ring.

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† Reaction conditions are being optimized to increase this rather low yield.

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