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The Chlorosilane-mediated Dimerization of Pentane-2,4-diones: a Direct Route to Pyrans

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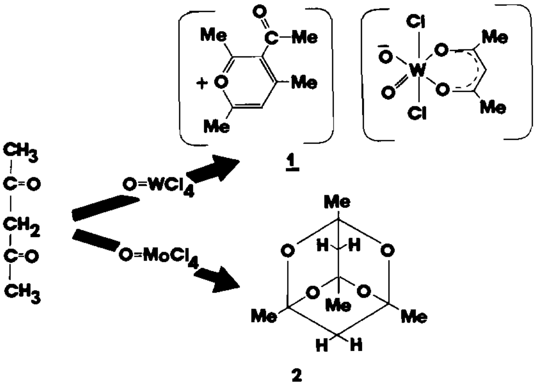
The reaction of a pentane-2,4-dionate salt with dimethyldichlorosilane yields the pyrylium salt, 2,4-dimethyl-6-(2'-hydroxy-1'-propenyl)pyrylium chloride. The trifluoromethyl analogue yields the corresponding neutral pyranylidene complex, the structure of which was established by a variety of NMR techniques. A mechanistic rationale is proposed which accounts not only for these results but also for the isomeric products obtained by reaction of acetylacetone with $MoOCl_4$ and $WOCl_4$.

Introduction

Despite early problems [1] three dimers of pentane-2,4-dione have now been isolated. In the first reported [2] successful dimerization and condensation, neat pentane-2,4-dione reacted with tungsten (VI) oxide tetrachloride to give 2,4,6-trimethyl-3-acetylpyrylium dichlorodioxo-pentane-2,4-dionatotungstate(VI), *1*. The supposedly analogous reaction with molybdenum(VI) oxide tetrachloride yielded 1,3,5,7-tetramethyl-2,4,6,8-tetraoxaadamantane, *2*.



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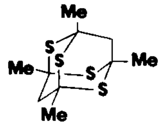
The latter reaction in many ways parallels the formation of 1,3,5,7-tetramethyl-2,4,6,8-tetrathia-adamantane, *3*, from pentane-2,4-dione, hydrogen sulphide and hydrogen chloride [3]. This process is a Lewis acid promoted cyclization, and mechanistic analogies to the $MoOCl_4$-mediated formation of the tetraoxa-adamantane *2* will become apparent.



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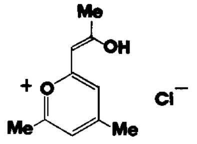
In a preliminary note, it was reported [4] that the reaction of dichlorodimethylsilane with thallium acetylacetonate yields the 6-(2'-hydroxyprop-1'-enyl)-2,4-dimethylpyrylium cation *4*, which was identified crystallographically.



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We now present ^1H, ^{13}C and ^{19}F nmr spectroscopic results on the reaction products of chlorosilanes with 2,4-pentanedionato thallium(I) and with its 1,1,1-trifluoromethyl derivative; we also propose a mechanistic rationale to account for all of these dimerisation products.

Results and Discussion

The reaction between thallium acetylacetonate and dichlorodimethylsilane did not produce the anticipated octahedral bis(acetylacetonato)dimethylsilane [5, 6] but instead yielded a yellow sublimable

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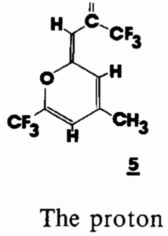
product $C_{10}H_{13}ClO_2$ (yield *ca.* 23%). The compound was identified crystallographically [4] as 6-(-2'-hydroxy-prop-1'-enyl)-2,4-dimethyl-pyrylium chloride, *4*.

The ^1H nmr spectra (35 °C) of *4* show signals at δ 8.1 and δ 6.7 (broad, ring H's), δ 2.45 and δ 2.55 (ring methyls) and δ 2.60 [CH–C(OH)–Me]. These chemical shifts are temperature dependent and are also affected by small amounts of water present in the solvent. The OH and -CH-C(OH)-resonances occur at δ 13.3 and δ 5.60 respectively at +35 °C in the 90 MHz spectrum in $CDCl_3$. Irradiation of the protons at δ 13.3 greatly diminishes the intensity of the signal at δ 5.60 (spin saturation transfer) showing the exchange of protons between the enol 'OH' and the keto 'CH_2'.

The ^{13}C spectrum (in dry $CDCl_3$) shows that the compound exists largely as the enol form. A comparison with the carbonyl and terminal methyl group chemical shifts in acetylacetone shows the keto form at 201.6 ppm and 30.6 ppm and the enol form at 191.4 and 24.7 ppm respectively. In molecule *4*, these chemical shifts occur at 186.4 and 25.1 ppm, respectively. The γ-carbon in acetylacetone is at 58.2 ppm in the keto tautomer and 100.6 ppm in the enol form; in the pyrylium salt *4* this carbon resonance is at 94.9 ppm. The infrared spectra of *4*, 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 anticipated reduction in the force constant of the O–H group *via* conjugation of the propenyl substituent with the ring.

Although the gross structure of the product from $SiCl_4$ and $Tl[CF_3COCHCOCH_3]$ was similar to *4*, the relative positions of the methyl and trifluoromethyl groups in the pyran ring were not readily apparent; in order to distinguish between the isomers *5* or *6*, a series of nmr experiments was performed.



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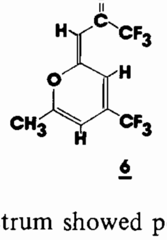

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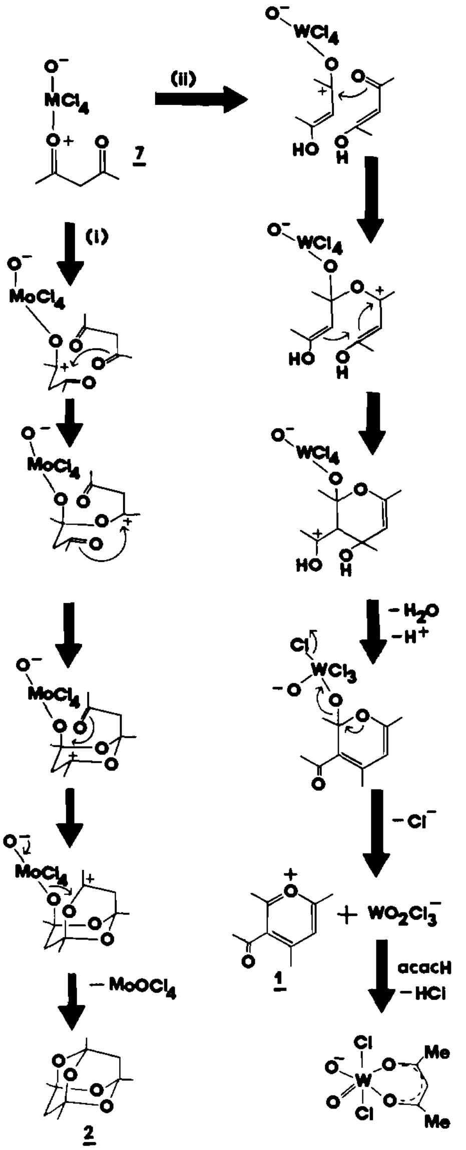
The proton nmr spectrum showed peaks at δ 8.1, 6.5 and 5.9 each representing a single proton, and a CH_3 absorption at δ 2.3. Irradiation of the CH_3 group considerably sharpened the other three proton signals, whilst decoupling of the ring CF_3 group removed coupling from the protons at 8.1 and 6.5 ppm only. Simultaneous irradiation of the ring CF_3 and CH_3 groups produced sharp doublets ($^4J_{HH}$ = 1.5 Hz) at 6.5 and 8.1 ppm showing that these were the ring protons. The proton at 5.9 ppm remains coupled to the acyl trifluoromethyl group.

The ambiguity as to the relative positions of the ring CF_3 and CH_3 groups was clearly resolved by Nuclear Overhauser Effect measurements. Irradiation of the ring methyl group enhanced the protons at 6.5 and 8.1 ppm by 14% and 21% respectively. Heteronuclear N.O.E. measurement showed an enhancement of 19% for the protons at 6.5 ppm on irradiation of the lowest field fluorine resonance; no enhancement was observed for the proton at 8.1 ppm. It is clear from these results that *5* is the correct structure. The modest enhancement of the δ 8.1 peak when the exocyclic CF_3 was irradiated supports the contention that these nuclei are proximate to each other as shown in *5*.

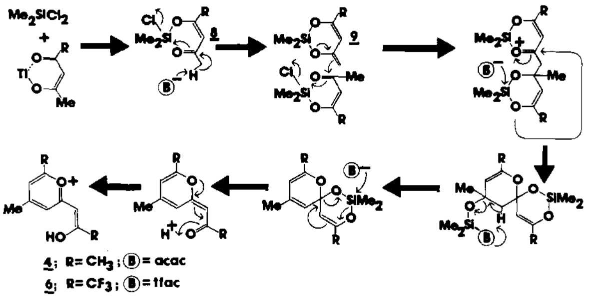
The carbon-13 spectrum showed the presence of two CF_3 groups at 117.1 ($^1J_{CF}$ = 290.8 Hz) and 118.3 ppm ($^1J_{CF}$ = 272.1 Hz); a long range coupling ($^4J_{CF}$ = 3 Hz) was observed at the carbon bearing the proton at δ 6.5, again confirming structure *5*. The remaining chemical shifts and coupling constants were consistent with this structure for the molecule.

In the light of these results it is necessary to propose a mechanistic rationale to account for the different dimerisation and condensation products obtained with different reagents. In the original work of Drew *et al.* [2] the role of $MOCl_4$ (M = Mo, W) is clearly that of a Lewis acid. Complexation by acetylacetone to give *7* induces an electrophilic site which is attacked by a ketonic oxygen of the second acetylacetone molecule. The cyclizations (always involving sterically favored chair-like 6-membered rings) now proceed according to pathways (i) or (ii) [in Scheme 1] which are adopted by Mo and W respectively. The pyrylium ion route may be more favored for W because of the concomitant formation of the second strong W=O bond. It has been suggested [8] that it is merely the HCl generated by hydrolysis of the $MOCl_4$ which acts as the Lewis acid catalyst. However, this is at odds with the work of Johnson [1] who was unable to condense together two acetylacetone molecules in the absence of a metal center. Furthermore, it has been reported that cation *1* is also generated when 2,4-pentanedione reacts with $PtCl_4$ [9]. It therefore seems mandatory to invoke participation of the transition metal center as the original site of Lewis acid activity, as indicated in Scheme 1.

In contrast, the silicon promoted dimerization presumably proceeds via the dimethylsilylacetylacetonate *8*. This molecule now suffers proton abstraction by the excess Tlacac to produce *9* which possesses a carbon-based nucleophilic centre; subsequent coupling of the acetylacetonate moieties, as in Scheme 2 eventually leads to a pyrylium salt



Scheme 1.



Scheme 2.

isomeric with the one obtained from the $WOCl_4$-mediated process. This mechanism also accounts for the formation of the neutral pyran *5* in which the proximity of the highly electronegative trifluoromethyl group reduces the basicity of the ring oxygen and vitiates the formation of the corresponding pyrylium salt. We note that the position of the CF_3 group which ends up next to the ring oxygen is governed by the site of attack on *8* by the nucleophilic double bond of *9*. Apparently the $Me_2Si(Cl)$-tfac, *8*, is preferentially bonded via the oxygen proximate to the CF_3 group in the original $CF_3CO\overset{-}{C}HCOCH_3$; this sets up the observed regiospecificity.

In conclusion, the use of chlorosilanes as templates for the formation of specifically substituted pyrans or pyrylium salts holds promise of great synthetic utility.

Experimental

NMR spectra were obtained using a Bruker WH90 spectrometer operating at 90 MHz and 22.62 MHz for ^1H and ^{13}C respectively. Homonuclear triple irradiation experiments and homonuclear NOE measurements were performed on a Varian HA100 spectrometer. The simultaneous homo- and heteronuclear decoupling experiments were performed on a Varian DP60 spectrometer as were the heteronuclear NOE measurements. Infrared spectra were run on a PE-457 grating spectrometer; samples were Nujol mulls made up under nitrogen in a glove bag. Mass spectra were recorded with a Hitachi-Perkin Elmer RMU-6E mass spectrometer. Appropriate samples were prepared just prior to determination of spectra.

Preparation of 2,4-dimethyl-6-(2'-hydroxy-1'-propenyl)pyrylium Chloride

In a 50 ml Erlenmayer flask, fitted with a side-arm, dimethyldichlorosilane (2.00 ml, 0.0166 mol) was mixed with 25 ml of dry dichloromethane. To this solution was added the thallium salt of 2,4-pentanedione (3.00 g, 0.00988 mol). Almost instantly, a dark-red solution with a white precipitate formed. The stoppered flask was removed from the glovebag, and the mixture was stirred for 1 hr at ambient temperature. A medium-porosity filtered funnel was utilized in the removal of the white precipitate (TlCl). The volume of the dark-red filtrate was reduced *via* a rotary evaporator to approximately 10 ml. Dry hexane (10 ml) was added to precipitate the required crude product. The flask was placed in a freezer (−4°) for 1 hr to complete precipitation. An orange solid was isolated by filtration on a fine-porosity filter funnel, and the solid was dried *in vacuo* for not more than 30 min. The solid was sublimed at 90° under a continuous vacuum. The required yellow product was washed from the cold-finger with dry dichloromethane, and subsequently recovered by precipitation with hexane. The bright yellow solid was dried *in vacuo* for 15 min. Yield 0.23 g (23% of theoretical). Mp 155–156° (dec). Because of the photosensitivity and thermal decomposition of this compound, no consistent elemental analyses were obtained. Rather, the purity of the compound was ascertained from NMR, infrared and mass spectra. The molecular ion $C_{10}H_{13}O_2^+$ occurs at m/z 165; HCl is observed at m/z 36 and 38 in appropriate isotopic intensities.

Preparation of 6-trifluoromethyl-4-methyl-2-trifluoroacetyl-pyranylidene

To a solution of 1,1,1-trifluoro-2,4-pentanedione (3.77 g, 0.0245 mol) and 20 ml of dichloromethane in a 50 ml round-bottomed flask was added silicon tetrachloride (1.40 g, 0.0122 mol). Refluxing for 5 hr resulted in a dark-red solution. The solvent was removed and the remaining dark-red oil was fractionated at a temperature of 30° and under a continuous vacuum. Bright yellow crystals were obtained in a yield of 0.55 g (16.5% of theoretical). Mp 45–46 °C. The purity of this compound was also ascertained from NMR, infrared and mass spectral studies. The molecular ion $C_{10}H_6F_6O_2^+$ is found at m/z 272.

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