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Pyrylium Salts

I. Studies of 2,6-Dimethoxycarbonyl Derivatives

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2,6-Dimethoxycarbonylpyrylium perchlorate and its 4-methyl derivative have been synthesised from the respective 4H-pyrans. With amines the 4-methylpyrylium salt gives the anhydro-base while the desmethyl analogue suffers ring opening. Initial α-adduct formation was shown by NMR to take place by water addition at low temperature, and the product was rearranged to an acyclic compound on temperature increase. Alcohols are oxidised to the corresponding carbonyl compound with concurrent formation of the 4H-pyran.

Substituted pyrylium cations have been shown to be versatile synthetic intermediates.[1,2] Depending on the nature of the α- and γ-substituents the pyrylium cation will add nucleophiles in either of these positions. Most pyrylium salts carry substituents in both α- and γ-positions and often the substituents are aryl groups. Without the stabilising aryl groups the pyrylium ion can only exist in the presence of a weak nucleophilic anion such as perchlorate or fluoroborate.

Pyrylium salts without α-substituents are highly reactive towards weak nucleophiles.[3–7] We were interested in synthetically readily available pyrylium salts carrying activating substituents in the α-positions. This report deals with studies of 2,6-dicarboxylic esters which were synthesised according to Scheme 1. The choice of synthetic pathway to V was directed by the reported preparation of 2,6-dicarboxy-4H-pyran (III). Diethyl oxaloacetate was condensed with the respective aldehyde,[8,9] the condensation product (II) hydrolysed and β-decarboxylated in dilute sulphuric acid and finally cyclised to III in cold concentrated sulphuric acid.[10] The methyl ester IV was prepared by methanolysis of the acid chloride available by phosphorus pentachloride treatment of the acid. Pyrylium formation with hydride abstraction was achieved using triphenylmethyl perchlorate [11] in liquid sulphur dioxide.

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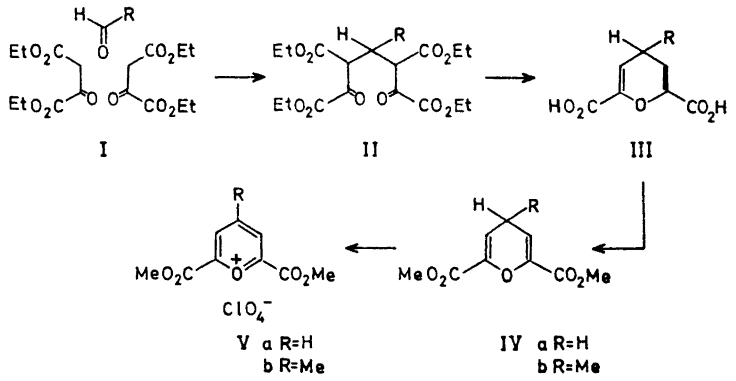
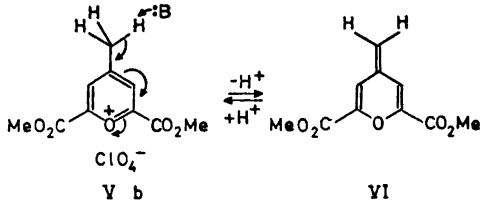


Scheme 1.

The NMR spectra of the pyrylium salts, recorded in trifluoroacetic acid (TFA), show clearly a highly electron deficient aromatic system. The methyl ester protons in V (5.7 τ) are at lower field than in the 4H-pyrans (6.0 τ). The three pyrylium protons in Va give rise to an AB_2-system (7-lines) with the γ-proton at 0.15 τ and the β-protons at 0.75 τ. The β-protons in Vb are at higher field (1.04 τ) which demonstrates the inductive contribution from the methyl group into the electron deficient nucleus which on the other side results in activation of the methyl group (6.82 τ). The 2,4,6-trimethylpyrylium cation has been reported to react with primary amines to form pyridinium derivatives.[12] In contrast, treatment of Vb with benzylamine led to anhydro-base (VI) formation. Pyridine was also a proton abstractor from Vb.



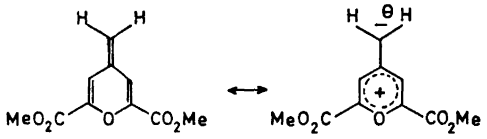
Scheme 2.

The chemical shifts in deuteriochloroform for the anhydro-base methyl ester (6.14 τ) and pyranyl (3.24 τ) protons correspond closely to those in the 4H-pyrans discussed above. Deuteriation of the 4-methyl group in Vb, as discussed below, has confirmed that the singlet at 5.20 τ is due to the terminal vinyl protons. Being an anhydro-base, VI is readily reprotonated to Vb. Thus the NMR spectrum of the latter was obtained on dissolution of the anhydro-base in TFA.

Since the 2,4,6-trimethylpyrylium cation reacts differently from Vb with primary amines it was prepared for comparative purposes. In its perchlorate salt in deuterium oxide the γ-methyl protons are exchanged rapidly, the

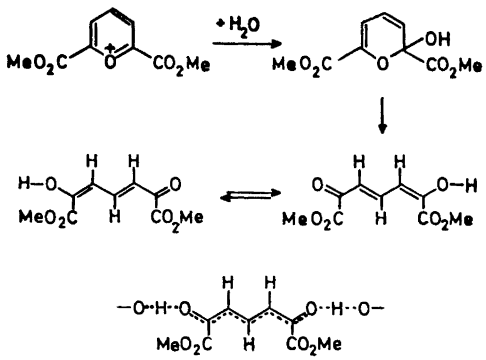
α-methyl protons more slowly.[13] For comparison of the rate of deuterium incorporation in the γ-methyl groups, NMR spectra of an equimolecular mixture of the trimethylpyrylium salt and Vb in partly deuteriated TFA were recorded after 10 and 100 min. No detectable deuteriation was seen in the trimethyl cation while the deuteriation figures for Vb were 30 and 60 % respectively, the integration standard being the non-exchangeable methyl ester protons. The signals from the β-protons and from the 4-methyl-protons in Vb are at lower field ($\Delta\nu_{4\text{-}CH_3} = 25$ cps, $\Delta\nu_{\beta\text{-}H} = 75$ cps) than in the trimethylpyrylium salt. The exchange of the α-methyl groups in the trimethylpyrylium cation with methoxycarbonyl groups (Vb) has changed the behaviour towards primary amines from that of a Lewis acid to that of a Brønsted acid.

Attempts to isolate methylene pyrans like VI have been reported unsuccessful.[13] The instability of VI was readily seen by NMR. A spectrum of VI in $CDCl_3$ recorded after 48 h at 25°C showed only polymeric product. Storage of the isolated solid also led to decomposition. The ready polymerisation is understandable in terms of the polarisability as indicated by resonance forms in Scheme 3.



Scheme 3.

Compound Va, which does not contain the acidic 4-methyl protons, reacts immediately and exothermally with primary amines. The highly coloured reaction mixture suggests ring-opening. Recyclisation to pyridinium derivatives was not achieved. With ammonium carbonate, however, pyridine-2,6-dicarboxylic acid was detected chromatographically [14] after hydrolysis. Evidence for preferential α-attack was more convincingly achieved with water as nucleophile. α-Aryl substituted pyrylium salts are relatively stable towards water while Va reacts immediately. The NMR spectrum after addition of three equivalents of water to a solution of Va in acetonitrile-d_3 at −40°C showed the methyl ester protons as two closely spaced singlets at 6.15 − 6.18 τ. The nonequivalence of the methyl groups and the ABC pattern (3.25 − 4.14 τ) for the pyranyl protons only satisfy α-substitution to a 2H-pyran. Addition of deuterium oxide instead of water gave the same spectrum. Both solutions on reaching room temperature gave the same spectrum. This spectrum was different from that at low temperature and was not changed on recooling. Addition of water to a solution of Va in acetonitrile-d_3 at room temperature gave the same spectrum. The spectrum in this case has the methyl ester protons as a singlet at 6.15 τ. The signals (7 lines) from the vinyl protons (1.97 − 3.59 τ) are interpreted to be of the AB_2 type with $\delta\nu/J_{A,B} = 5.1$ which requires the β-protons to be equivalent. In an acyclic structure this could be explained by a very rapid proton exchange between two equivalent tautomeric forms or simply due to equivalence through strong intermolecular hydrogen bonding (Scheme 4).

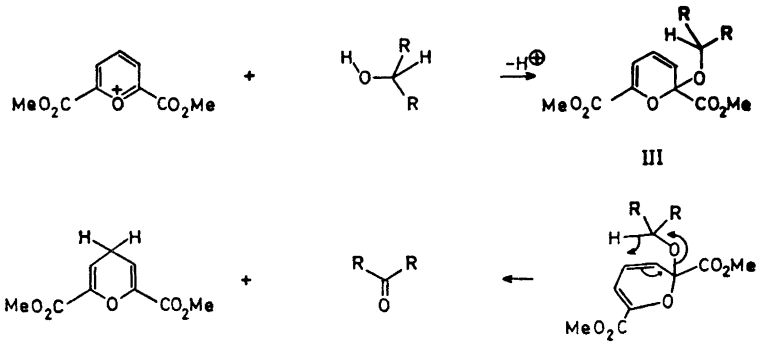


Scheme 4.

Calculations for the chemical shift of the protons in the AB_2 system give the value 3.42 τ and 2.22 τ for the β- and γ-protons, respectively, with $J_{\beta,\gamma} = 14$ cps. The coupling constant is in agreement with the *trans* arrangement of protons shown in Scheme 4.

In UV the highest wavelength-band in acetonitrile is at 335 nm (log $\varepsilon = 4.17$) which is changed to 455 nm on addition of base. The bathochromic shift is attributed to the resonance stabilised (equivalent structures) oxenol-anion.

The pyrylium salt Va is less reactive towards alcohols than towards water. The NMR spectrum of the reaction product, after heating Va in methanol for 30 min followed by evaporation, showed that 50 % of the pyrylium salt had been reduced to the 4H-pyran (IVa) with no ring-opened derivative present. For the purpose of isolation of the carbonyl compound in the reaction, IVa was heated with diphenylcarbinol in nitromethane for 30 min. Benzophenone and the 4H-pyran (IVa) were formed quantitatively. Little is known about the mechanism of this reaction. Direct hydride abstraction into the γ-pyrylium position would seem reasonable. Since water attacks in the α-



III

Scheme 5.

position, however, α-adduct formation also in this case cannot be excluded (Scheme 5). The adduct can be regarded as an allyl ether and as such could undergo a Claisen type rearrangement as indicated in Scheme 5.

EXPERIMENTAL

NMR spectra were recorded on a Varian A-60A spectrophotometer.

2,6-Dimethoxycarbonyl-4H-pyran (IVa). NMR in TFA: 6.89 τ (triplet, $2H^4$, $J_{3,4}=4.0$ cps), 3.75 τ (triplet, H^3H^5), 6.03 τ (singlet OCH_3).

2,6-Dimethoxycarbonyl-4-methyl-4H-pyran (IVb). NMR in TFA: 8.68 τ (doublet, 4-CH_3, $J_{4,CH_3}=7.0$ cps), 6.68 τ (multiplet, H^4), 3.78 τ (doublet, H^3H^5), 6.00 τ (singlet, OCH_3).

2,6-Dimethoxycarbonylpyrylium perchlorate (Va). 2,6-Dimethoxycarbonyl-4H-pyran (6.93 g, 0.035 mol) was dissolved in dry, liquid sulphur dioxide (100 ml) at −30°C and triphenylmethyl perchlorate (11.65 g, 0.034 mol) added with stirring under anhydrous conditions. The reaction mixture was then left by itself until the sulphur dioxide had evaporated. The residue was triturated with anhydrous ether (250 ml) under stirring for about 10 min and most of the ether sucked out. The process was repeated three times more with fresh ether before the solid was isolated by filtration. The product is very hygroscopic and is decomposed by the moisture in the atmosphere and should be kept in a tight bottle in a refrigerator; yield 9.00 g (90 %), m.p. 146 – 148°C (decomp.). (Found: C 36.34; H 3.18; Cl 11.84. Calc. for $C_9H_9ClO_5$: C 36.42; H 3.03; Cl 11.95.) NMR in TFA: 5.69 (singlet, OCH_3). The pyrylium protons give a 7 line spectrum. Calculated for $AB_2(\delta\nu/J_{AB}=4.4)$ gave: 0.75 τ (H^3H^5), 0.15 τ (H^4, $J_{3,4}=8.1$ cps).

2,6-Dimethoxycarbonyl-4-methylpyrylium perchlorate (Vb) was prepared as above from 2,6-dimethoxycarbonyl-4-methyl-4H-pyran in 78 % yield, m.p. 135°C (decomp.). (Found: C 39.61; H 4.36; Cl 10.85. Calc. for $C_{10}H_{11}ClO_5$: C 38.65; H 3.54; Cl 11.4.) NMR in TFA: 6.82 τ (singlet, 4-CH_3), 1.04 τ (singlet, H^3H^5) 5.71 τ (singlet, OCH_3).

2,6-Dimethoxycarbonyl-4-methylenepyran (VI). 2,6-Dimethoxycarbonyl-4-methylpyrylium perchlorate (1.55 g, 0.005 mol) was suspended in anhydrous ether (300 ml) and a solution of pyridine (0.39 g, 0.005 mol) in ether (25 ml) was added dropwise with vigorous stirring. The reaction was stirred in the cold overnight, the pyridinium salt removed by filtration and the filtrate evaporated; yield 0.8 g (76 %). The compound is unstable and did not have a sharp melting point. Molecular weight determined by mass spectrometry: 210.0533. Calc. for $C_{10}H_{10}O_5$: 210.0528. NMR in $CDCl_3$: 5.20 τ (singlet, 4-CH_2), 3.24 τ (singlet, H^3H^5), 6.14 τ (singlet, OCH_3).

REFERENCES

1. Dimroth, K. and Wolf, K. H. *Newer Methods of Preparative Organic Chemistry*, Academic, New York 1964, Vol. 3, p. 357.
2. Balaban, A. T., Schroth, W. and Fischer, G. *Advan. Heterocycl. Chem.* **10** (1969) 241.
3. Købrich, G. *Annalen* **648** (1961) 114.
4. Degani, I. and Vincenzi, C. *Boll. Sci. Fac. Chim. Ind. Bologna* **25** (1967) 51.
5. Klages, F. and Träger, H. *Chem. Ber.* **86** (1953) 1327.
6. Balaban, A. T. and Nenitzescu, C. D. *Izv. Akad. Nauk. SSSR* **11** (1960) 2064.
7. Degani, I., Fochi, R. and Vincenzi, G. *Gazz. Chim. Ital.* **94** (1964) 203.
8. Cope, A. and Fournier, A. *J. Am. Chem. Soc.* **79** (1957) 3896.
9. Gault, H. *Bull. Soc. Chim. France* **1907** 21, 40.
10. Blaise, E. E. and Gault, H. *Bull. Soc. Chim. France* **1907** 129.
11. Dauben, H. I. and Honnen, L. *J. Org. Chem.* **25** (1960) 1442.
12. Toma, C. and Balaban, A. T. *Tetrahedron Suppl.* **7** (1966) 9.
13. Gârd, E., Stanoiu, I. and Balaban, A. T. *Rev. Roum. Chim.* **14** (1969) 247.
14. Tallent, W. H. and Horning, E. C. *J. Am. Chem. Soc.* **78** (1956) 4467.

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