Intermolecular Hydride Transfer Reactions. I. Electrophilic Aromatic Substitution with 2,6-Dimethoxycarbonylpyrylium Cation

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The reaction of the 2,6-dimethoxycarbonylpyrylium cation with monosubstituted benzene derivatives to 4-substituted-4*H*-pyrans has been studied. Intermolecular hydride transfer between the pyrylium cation and the 4*H*-pyrans may occur, whereby the more stabilized pyrylium ion is formed.

It has previously been shown that 2,6-didimethoxycarbonylpyrylium perchlorate (*1*) reacted with carbonylactivated methyl groups to yield 4-substituted 4*H*-pyrans, and moreover that intermolecular hydride transfer between *1* and 4-alkyl substituted 4*H*-pyrans took place forming the more substituted pyrylium cations.[1]

The present work deals with the reaction of *1* with monosubstituted benzene derivatives (*2*).

Equimolecular amounts of *1* and anisole in acetonitrile solution were allowed to react for 24 h. Treatment with ether deposited a crystalline product for which elemental analysis and ^{1}H NMR data were consistent with the pyrylium salt *3* (R = OCH_3). Formation of the 4*H*-pyran *4*, which has been synthesized earlier,[2] was verified from ^{1}H NMR analysis of the concentrated etheral solution after removing of *3* (R = OCH_3). Reactions leading to *3* and *4* are depicted in Scheme 1.

It is likely that the first step of the process is an electrophilic substitution reaction to form the 4*H*-pyran *5* (R = OCH_3), which is subsequently oxidized by another molecule of *1* to yield *3* (R = OCH_3). The reduction of *1* by intermolecular hydride transfer explains the formation of *4*.

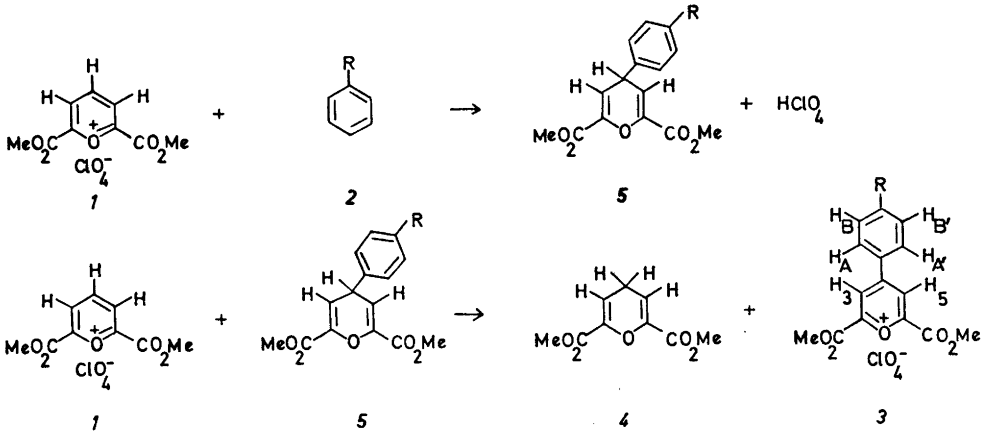
The reaction was repeated in trideuterioacetonitrile solution. The 4*H*-pyran *5* (R = OCH_3) was not formed in detectable amounts as shown by the ^{1}H NMR spectrum of the reaction mixture. The presence of nearly equimolecular amounts of unreacted anisole, the pyrylium cation *3* (R = OCH_3) and the 4*H*-pyran *4* showed that the stoichiometry of the reaction was according to the equation:

$$2(1) + (2) = (3) + (4) + HClO_4$$

The reaction between equimolecular amounts of *1* and dimethylaniline in acetonitrile solution also resulted in isolation of a salt. The product, however, was not the expected pyrylium salt *3* [R = $N(CH_3)_2$], but the hydroperchlorate of the amine *5* [R = $N(CH_3)_2$] in 85 % yield. The reaction was repeated with two molar equivalents of *1* and this yielded the pyrylium salt *3* [R = $N(CH_3)_2$] in 75 % yield and the 4*H*-pyran *4*.

The reaction of *1* with toluene (molar ratio; 2:1) in trifluoroacetic acid solution was carried out in the ^{1}H NMR sample tube. The result as shown by ^{1}H NMR spectra was analogous to that obtained in the reaction of *1* with anisole. Only formation of *3* (R = CH_3) and *4* in equal amounts and the simultaneous disappearance of *1* and toluene were observed. The pyrylium salt *3* (R = CH_3) was isolated when the reaction was quantitative.

These experiments demonstrate that the 4-unsubstituted pyrylium nucleus *1* is a very reactive cation, which readily takes part in both electrophilic aromatic substitution and hydride transfer reactions. Kinetic studies have not been carried out. The results, however, indicate that intermolecular hydride transfer is much faster than substitution in the reaction of *1* with



Scheme 1.

Table 1. The ^1H NMR spectra (δ values) of pyrylium salts *3* recorded in trifluoroacetic acid solution

R	H_3,H_5	$O-CH_3$	$H_A,H_{A'}$	$H_B,H_{B'}$	R	$J_{AB}=J_{A'B'}$ Hz
CH_3	9.23	4.30	8.38	7.68	2.65	10
OCH_3	9.00	4.27	8.50	7.38	4.17	10
$N(CH_3)_2$	8.52	4.22	8.22	7.38	3.57	10

equimolecular amounts of anisole. On the other hand, the inverse is presumably the case in the reaction of *1* with dimethyaniline. It seems likely that the explanation is an increased rate of substitution due to the dimethylamino group and furthermore a decreased rate of hydride transfer due to the formation of the hydroperchlorate of the amine *5* ([R = $N(CH_3)_2$]).

The ^1H NMR shift values of the pyrylium salts *3* are listed in Table 1.

The increased stabilizing effect of substituent R on the pyrylium cation through the series Me, OMe, $N(CH_3)_2$ is reflected in chemical shift positions of the heterocyclic ring protons. The upfield shifts of these protons are in agreement with a decreased positive charge of the pyrylium nucleus.

Experimental. The ^1H NMR spectra were recorded on a Varian A-60A instrument with TMS as internal standard.

*2,6-Dimethoxycarbonyl-4-*p*-methoxyphenylpyrylium perchlorate* (*3*, *R* = *OCH*$_3$). To a solution of 2,6-dimethoxycarbonylpyrylium perchlorate [2] (1.48 g, 0.005 mol) in dry acetonitrile (5 ml) was added anisole (0.540 g, 0.005 mol) at 20 °C with stirring. After 24 h anh. ether (75 ml) was added. The precipitated material was filtered off and recrystallized from acetic acid. The yield was 93 % (0.930 g), m.p. 212–215 °C (decomp.). (Found: C 47.75; H 3.84; Cl 8.76. Calc. for $C_{16}H_{15}O_{10}Cl$: C 47.71; H 3.73; Cl 8.82). ^1H NMR spectrum see Table 1. The filtrate after removal of *3* (R = OCH_3) was concentrated under reduced pressure and the residual material was redissolved in $CDCl_3$. ^1H NMR spectrum of this solution showed signals due to 2,6-dimethoxycarbonyl-4*H*-pyran (*4*) and anisole. ^1H NMR spectrum of 2,6-dimethoxycarbonyl-4*H*-pyran in $CDCl_3$ (δ): 3.05 (triplet; $2H_4$, $J_{3,4}=4$ Hz), 3.81 (singlet; OCH_3) 6.05 (triplet; H_3H_5).

*2,6-Dimethoxycarbonyl-4-*p*-dimethylaminophenyl-4H-pyran*, [*5*, *R* = *N(CH*$_3$)$_2$] *hydroperchlorate.* To a solution of 2,6-dimethoxycarbonylpyrylium perchlorate (0.60 g, 0.002 mol) dissolved in dry acetonitrile (5 ml) was added dimethylaniline (0.24 g, 0.002 mol) at 20 °C with stirring. After 24 h the title compound was filtered off (0.4 g). The filtrate was diluted with ether and additional 0.32 g was collected.

The yield was 85 % (0.720 g), m.p. 224–227 °C (decomp.) (CH_3CN). (Found: C 48.85; H 4.79; N 3.53; Cl 8.53. Calc. for $C_{17}H_{20}O_9ClN$: C 48.87; H 4.79; N 3.35; Cl 8.50). ^1H NMR spectrum in TFA (δ); 3.50 (doublet; $^+NH(CH_3)_2$, $J=5$ Hz), 4.0 (singlet; OCH_3), 4.58 (triplet; H_4, $J_{3,4}=4.0$ Hz), 6.32 (doublet; H_3H_5). The aromatic protons form an AA'BB' system centered at δ 7.67 with a small chemical shift difference between H_A and H_B.

*2,6-Dimethoxycarbonyl-4-*p*-dimethylaminophenylpyrylium perchlorate* [*3*, *R* = *N(CH*$_3$)$_2$] was prepared as *5* [R = $N(CH_3)_2$] from 0.004 mol of pyryliumsalt and 0.002 mol of dimethylaniline. The reaction mixture was left standing for one week. The yield was 75 %, m.p. 280–285 °C (decomp.). (Found: C 49.16; H 4.47; N 3.27; Cl 8.46. Calc. for $C_{17}H_{18}O_9ClN$: C 49.10; H 4.33; N 3.37; Cl 8.54). ^1H NMR spectrum see Table 1. The filtrate, after removal of the title compound, was concentrated under reduced pressure and the residual material was redissolved in $CDCl_3$. ^1H NMR spectrum of this solution showed signals due to the 2,6-dimethoxycarbonyl-4*H*-pyran (*4*).

*2,6-Dimethoxycarbonyl-4-*p*-methylphenylpyrylium perchlorate* (*3*, *R* = *CH*$_3$). 2,6-Dimethoxycarbonylpyrylium perchlorate (0.06 g, 2×10^{-4} mol) and toluene (0.01 g, 10^{-4} mol) was dissolved in trifluoroacetic acid (0.3 ml). The solution was transferred into a ^1H NMR sample tube and left standing at 20 °C. Spectra were recorded regularly and after 12 days the signals due to the added pyrylium salt were undetectable. The solution was diluted with ether and the title compound was collected by filtration: m.p. 195–197 °C (decomp.). (Found: C 49.65; H 4.01. Calc. for $C_{16}H_{15}O_9Cl$; C 49.67, H 3.88). ^1H NMR spectrum see Table 1.

1. Østensen, E. T. and Undheim, K. *Acta Chem. Scand. 27* (1973) 2184.
2. Undheim, K. and Østensen, E. T. *Acta Chem. Scand. 27* (1973) 1385.

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