THE REACTION OF 2,4,6-TRIARYLPYRYLIUM CATIONS WITH METHOXIDE-ION[1]

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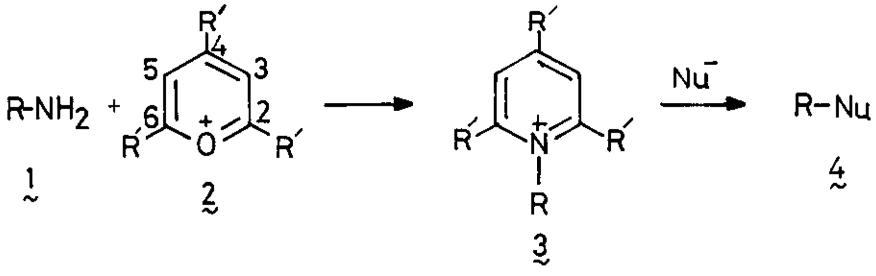
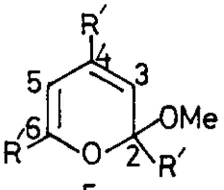
Abstract - The title reaction is shown by ^{13}C nmr to give 2-methoxy[2H]pyrans: no evidence was found for 4-adducts or ring opened compounds.

Extensive work in our laboratory[4] has demonstrated the synthetic potential of the transformation of primary amines to other functional groups. This has been accomplished by reacting the amine 1 with a pyrylium salt (2) to produce a pyridinium salt (3) followed by nucleophilic displacement to give the desired product (4). Investigations of the first step in which the amine is converted into the pyridinium salt 3 have revealed complex kinetics and equilibria[5], and we therefore studied this step using methoxide ion as the nucleophile because conversion of an intermediate to the pyridinium salt 3 is not possible, thereby simplifying the system under study.

The reaction of the pyrylium salt 2 with methoxide ion was followed by ^{13}C nmr in DMSO-d_6 solution[6]. A number of products of this reaction are possible. There are the 2- and/or 4-adducts (5 and 6), of which the 2-adduct could exist in the ring-opened valence bond isomer 7. Positive identification of the actual product requires assignment of all the peaks in the ^{13}C spectra, and as an aid to this assignment we synthesized the tris-p-fluorophenyl (2c) and p-tolyl analogues (2b).

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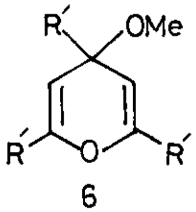
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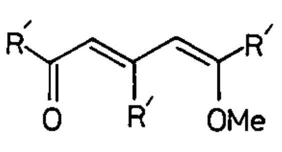
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a R' = C_6H_5
b R' = C_6H_4Me-p
c R' = C_6H_4F-p

Chemical Shift Assignments for the Pyrylium Cations (Table 1). The pyrylium ring carbon signals are identified by their multiplicity in the off resonance decoupled (ORD) spectra, and their intensities. The 2,6- and 4-carbons are deshielded as expected by conjugation with the electron deficient oxygen. In the fluorine compound 2c, the characteristic distance dependent C-F couplings make assignment of the phenyl ring carbons straightforward. The phenyl ring shifts in the methyl (2b) and hydrogen (2a) compounds were then assigned on substituent chemical shift considerations. As substituent chemical shifts depend on the electronic environment, the corresponding substituent shifts in the para-nitro compounds were chosen as a model. The use of the substituent shifts of Table 2, and the relative intensities allows the complete assignment for 2a and 2b. The shifts of the para carbons in the phenyl rings are deshielded (135.1 and 135.2) reflecting conjugation with the electron deficient pyrylium ring. The ipso carbon signals are extremely narrow and therefore of large height. Our assignment differs from that of Balaban and Wray[7]; however their spectrum refers to trifluoroacetic acid/dichloromethane solvent.

The Methoxide Adducts. Methanolic sodium methoxide (0.3M) was obtained by dissolving sodium metal in absolute methanol under nitrogen[8]. Addition of this solution to the pyrylium salts 2a,b,c in DMSO-d_6 resulted in immediate and complete formation of adducts as shown by ^{13}C nmr spectra. Analysis of these spectra clearly shows that addition to the 2-position is involved to give 5a,b,c.

Although the low symmetry of the adducts 5a,b,c precludes unique assignment of all the phenyl ring carbons, the fluoro compound 5c again provides the key to a reasonable analysis. In 5c the C-F couplings distinguish the phenyl from the pyran ring carbons. The shifts of the latter are essentially independent of the phenyl substituent, and therefore are easily identified. The 2-, 4-, and 6-carbons were identified from the ORD spectra and the assignments made from shift comparisons with the cationic spectra. Ring carbon-5 has been assigned upfield of C-3 because of its greater conjugation with the oxygen.

The fluorine couplings in 5c allow the identification of the phenyl ring carbons and assignments of each shift to a position in the phenyl ring, however the assignment to the individual phenyl ring is not possible. The use of substituent chemical shifts for the monosubstituted benzenes (Table 2) then identifies the phenyl carbon shifts for 5a and 5b.

The lack of symmetry in the ^{13}C spectra of all the adducts, and especially the three distinct ipso- and para-shifts positively identifies these compounds as the 2-adducts: no evidence for any 4-adduct (6) or ring-opened form (7) was found.

EXPERIMENTAL

The tetrafluoroborates 2a,c were prepared according to the literature procedure[9] and vacuum dried before use. The p-tolyl perchlorate was prepared by Miss Z. Zakaria[10], mp 310°C dec. The p-fluoro tetrafluoroborate was prepared in 37% yield and was recrystallized from acetone to give yellow prisms, mp 244-246°C (Found: C, 61.4; H, 3.2. $C_{23}H_{14}BF_7O$ requires: C, 61.4; H, 3.1%).

Table 1: ^{13}C Nmr chemical shifts of pyrylium salts and methoxide ion adducts in DMSO-d_6(0,3M)

Cpd.	2a (H)	2b (Me)[a]		2c (F)			5a (H)	5b (Me)[b]		5c (F)		
Carb	δ[c]	δ	SCS[d]	δ	SCS	J[e]	δ	δ	SCS	δ	SCS	J
2	170.0	168.8	-1.2	168.9	-1.1	0	102.2	102.2	0.0	102.1	-0.1	0
3	115.1	112.7	-2.4	114.5	-0.6	0	114.6	113.8	-0.8	114.0	-0.5	0
4	165.1	163.5	-1.6	163.7	-1.4	0	135.7	135.4	-0.3	134.9	-0.8	0
5	115.1	112.7	-2.4	114.5	-0.6	0	96.9	96.2	-0.7	96.7	-0.2	0
6	170.0	168.8	-1.2	168.9	-1.1	0	151.7	151.7	0.0	150.9	-0.8	0
2-i	129.0	126.0	-3.0	125.7	-3.3	2.4	133.8[f]	131.2	-2.6	130.2	-3.6	2.4
2-o	128.8	128.4	-0.4	132.0	3.2	9.8	125.1[f]	125.0	-0.1	127.4	2.3	8.5
2-m	129.9	130.4	0.5	117.3	-12.6	22.0	128.7[f]	129.2	0.5	115.4	-13.3	22.0
2-p	135.1	146.2	11.1	166.1	31.0	256.0	128.4[f]	137.7	9.3	162.3	33.9	245.3
4-i	132.4	129.1	-3.3	128.9	-3.5	2.4	137.5[f]	134.7	-2.8	133.7	-3.8	2.4
4-o	130.0	129.9	-0.1	133.3	3.3	8.5	126.2[f]	126.1	-0.1	128.4	2.2	8.5
4-m	129.9	130.4	0.5	117.3	-12.6	22.0	129.0[f]	129.5	0.5	115.7	-13.3	22.0
4-p	135.2	146.9	11.7	166.6	31.4	256.0	129.0[f]	138.0	9.0	162.7	33.7	245.4
6-i	129.0	126.0	-3.0	125.7	-3.3	2.4	142.4[f]	139.7	-2.7	138.7	-3.7	2.4
6-o	128.8	128.4	-0.4	132.0	3.2	9.8	126.2[f]	126.0	-0.2	128.4	2.2	8.5
6-m	129.9	130.4	0.5	117.3	-12.6	22.0	129.0[f]	129.5	0.5	115.9	-13.1	22.0
6-p	135.1	146.2	11.1	166.1	31.0	256.0	129.5[f]	139.1	9.6	163.1	33.6	246.6
OMe	-	-	-	-	-	-	49.5	49.3	-0.2	49.5	0.0	0

a) Methyl carbon shift is 21.5 ppm. b) Methyl shifts are 21.0(2), 20.9(4,6). c) Chemical shift in ppm relative to TMS, calculated by adding 39.6 ppm to the shift relative to the centre peak of DMSO-d_6; see G.C. Levy and J.D. Cargioli, J. Magn. Res., 1972, 6, 143. d) Substituent chemical shift resulting from the replacement of H by the para-substituent. e) Carbon-fluorine coupling constant in Hz, accurate to 1.2 Hz. f) Alternative assignments for all the methoxide ion adducts.

Table 2: Substituent chemical shifts in 1-X,4-Y disubstituted benzenes in $CDCl_3$ [a]

		Y = H				Y = NO_2			
X	Carbon	1	2	3	4	1	2	3	4
F		34.5	-13.0	1.3	-4.4	31.7	-12.8	2.8	-3.8
Me		9.5	0.7	-0.1	-3.1	11.4	0.5	0.1	-2.1

a) J. Bromilow, R.T.C. Brownlee, D.J. Craik, M. Sadek, V.O. Lopez and R.W. Taft, unpublished results.

Spectroscopic Measurements. The spectra were recorded at room temperature on a JEOL FX-100 Spectrometer at 25.05 MHz. Typical conditions were: 5 KHz width; 8K data (resolution 0.05 ppm); pulse width 5 μsec (30^{o}) with a repetition time of 1 sec. Solutions were about 0.3M in DMSO-d_6 which was also used as the internal standard.

FOOTNOTES AND REFERENCES

1. Heterocycles in Organic Synthesis Part 37. For Part 36 see A.R. Katritzky and S.S. Thind, in preparation.
2. Permanent address: Dept. of Chemistry, La Trobe University, Bundoora, Victoria, Australia.
3. Permanent address: Istituto Di Chimica, Universita di Catania, Viale A. Doria, 8, 95125 Catania, Italy.
4. Much of this work is as yet unpublished, but see inter alia, A.R. Katritzky, U. Gruntz, N. Mongelli, and M.C. Rezende, J.C.S. Chem. Comm., 1978, 133. N.F. Eweiss, A.R. Katritzky, P.-L. Nie, and C.A. Ramsden, Synthesis, 1977, 634. U. Gruntz, A.R. Katritzky, D.H. Kenny, M.C. Rezende, and H. Sheikh, J.C.S. Chem. Comm., 1977, 701.
5. Unpublished work with Ch. Sana-Ullah.
6. Cognate work on following this reaction has been carried out by G. Doddi, G. Illuminati, and F. Stegel. We thank Prof. Illuminati and Dr. Stegel for comments and discussions (cf. also S. Bersani, G. Doddi, S. Fornarini, and F. Stegel, J. Org. Chem., 1978, **43**, 4112).
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