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Formation of Arylmethylenepyridinium Salts on Treatment of Aryl-Carbinols with Sulphonyl Chlorides in Pyridine*

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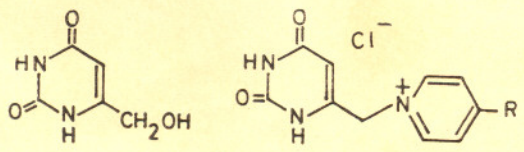
Treatment of 6-hydroxymethyluracil with mesyl chloride and of methyl 6-hydroxymethylpiperonylate with tosyl chloride in pyridine formed the corresponding arylmethylenepyridinium salts instead of the expected sulphonyl esters.

IN two independent investigations 6-mesyl-oxymethyluracil and methyl 6-tosyloxymethylpiperonylate were required and their preparation was attempted from the corresponding carbinols by treatment with the appropriate sulphonyl chloride in pyridine. The products formed, however, proved to be the corresponding pyridinium compounds and not the expected sulphonyl esters.

The known 6-hydroxymethyluracil (I)[1] was more conveniently prepared by $LiAlH_4$ reduction of *n*-butyl orotate[2] in tetrahydrofuran in 52 per cent yield; m.p. 254° (decomp.); R_f (A)†, 0·45; R_f (B), 0·42; $\lambda_{max.}$: *p*H 1, 263 mμ (ε 10800); *p*H 13, 284 mμ (ε 10280); water, 262 mμ (ε 10650).



I

II, R=H
III, R=CH_3

Treatment of an ice-cooled solution of 6-hydroxymethyluracil (284 mg., 2 mmoles) in dry pyiridine (25 ml.), with a pyridine solution (3 ml.) of mesyl chloride (284 mg., 2·5 mmoles) overnight at 0° yielded a crystalline product (251 mg., 54 per cent), which was recrystallized from methanol; m.p. 276-8° (decomp.) (Found: C, 49·73; H, 4·51; N, 17·19. $C_{10}H_{10}N_3O_2Cl$ requires C, 50·10; H, 4·17; N, 17·53%); R_f (A), 0·24; R_f (B), 0·04. $\lambda_{max.}$: *p*H 1, 259·5 mμ (ε 13790); *p*H 13, 261, 267 and 286 mμ (ε 8900, 9200 and 10140 respectively); water, 259 mμ (ε 11375).

That the product formed had the structure (II) became apparent from its elemental analysis and NMR and mass spectra. The NMR spectrum (D_2O, 60 Mcs.) signals with assignments were as follows: 1·0 τ (*m* for 2 protons) pyridinium 2-H and 6-H; 1·35 τ (*m* for 1 proton) pyridinium 4-H; 1·67 τ (*m* for 2 protons) pyridinium 3-H and 5-H; 4·21 τ (broad *s* for 2 protons) pyrimidine-6-CH_2-$N^+\lesssim$; 4·33 τ (*t*; $J = 1·0$ *cps* for 1 proton) pyrimidine 5-H. In the NMR spectrum of 6-hydroxymethyluracil, the methylene protons give rise to a doublet at 5·83 τ ($J = 1·0$ *cps*).

The mass spectrum of (II) has no molecular ion peak but shows two strong peaks at *m/e* 203 and 204, the latter being a little less abundant. The formation of these two ions can be readily visualized by the loss of HCl and of a chloride ion respectively from (II). The base peak in this spectrum is at *m/e* 78 and the other significant peaks are observed at *m/e* 159, 125, 82, 79 and 51. The known retro Diels-Alder elimination[3,4] of HNC=O from the uracil moiety of the ion of mass 203 leads to the display of a peak at *m/e* 160 which on loss of one hydrogen atom accounts for the strong peak observed at *m/e* 159. There is also a small peak at *m/e* 161 which can arise from a similar HNC=O elimination from the ion of mass 204. The ion *m/e* 125 must have arisen from the loss of the pyridine moiety from the ion of mass 204. This is supported by the presence of a metastable peak at *m/e* 76·6 and also by the presence of a strong peak at *m/e* 79. The peak at *m/e* 125 fragments further with the loss of HNC=O to yield an ion of mass 82. The loss of a hydrogen atom from the peak at 79 would account for the base peak at *m/e* 78 and

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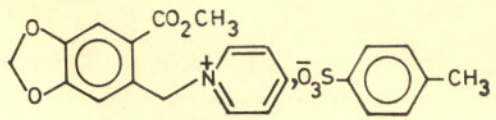
†Paper chromatography: A: descending, *n*-butanol-acetic acid-water (4:1:5); and B: ascending, *n*-butanol-water (86:14).

expulsion of HCN from this ion accounts for the strong peak at *m/e* 51. A metastable peak at *m/e* 33·3 confirms this fragmentation.

Treatment of 6-hydroxymethyluracil with mesyl chloride in γ-picoline instead of pyridine led to the formation of the corresponding 4-methylpyridinium compound; m.p. 280-82° (decomp.) (Found: C, 48·97; H, 5·42; N, 15·67. $C_{11}H_{12}N_3O_2Cl.H_2O$ requires C, 48·61; H, 5·15; N, 15·46%); R_f (A), 0·30; R_f (B), 0·09; $\lambda_{max.}$: *p*H 1, 257 (ε 13260); *p*H 13, 256, 263, 285 mμ (ε 6059, 6200 and 7852 respectively). NMR: 1·27 τ (*d*; $J = 7·0$ *cps* for 2 protons) pyridinium 2-H and 6-H; 1·93 τ (*d*; $J = 7·0$ *cps* for 2 protons) pyridinium 3-H and 5-H; 4·31 τ (*s*, broad for 2 protons) pyrimidine-6-CH_2-$N^+\lesssim$; 4·40 τ (*t*; $J = 1·0$ *cps* for 1 proton) pyrimidine 5-H; 7·25 τ (*s* for 3 protons) 4-CH_3 on pyridine.

Methyl 6-hydroxymethylpiperonylate was obtained by the treatment of a solution of 6-hydroxymethylpiperonylic acid[5], in THF with an ethereal diazomethane solution and crystallized from benzene-hexane; m.p. 78-79° (Found: C, 57·21; H, 4·77. $C_{10}H_{10}O_5$ requires C, 57·10; H, 4·76%).

A solution of methyl 6-hydroxymethylpiperonylate and tosyl chloride (molar equivalents) in pyridine was stirred at 15° for 12 hr. Pyridine was removed under reduced pressure and the water soluble product obtained crystallized from methanol-ether; m.p. 161° (Found: C, 59·88; H, 4·89; N, 3·30. $C_{23}H_{21}NO_7S$ requires C, 59·5; H, 4·70; N, 3·10%). $\nu_{max.}$ (KBr): 1725 cm.$^{-1}$ (aromatic ester C=O); 1640 cm.$^{-1}$ (C=N); 1200, 1150, 1020 and 675 cm.$^{-1}$ (sulphonate salt). NMR ($CDCl_3$, 60 Mcs.); 0·90 τ (*m* for 2 protons) pyridinium 2-H and 6-H; 1·25 τ (*m* for 1 proton) pyridinium 4-H; 1·55 τ (*m* for 2 protons) pyridinium 3-H and 5-H; 2·31 τ (*m* for 6 protons) aromatic protons of piperonyl and *p*-tolyl groups; 3·75 τ



IV

(*s*, broad for 2 protons) Ph-CH_2-$N^+\lesssim$; 3·93 τ (*s* for 2 protons) O-CH_2-O; 7·7 τ (*s* for 3 protons) Ph-CH_3. The compound could, therefore, be assigned the structure 6-methoxycarbonyl-3,4-methylenedioxybenzylpyridinium *p*-toluene sulphonate (IV).

The formation of the pyridinium salts (II)-(IV) can be rationalized by the nucleophilic attack of the pyridine nitrogen on the aryl methylene carbon of the initially formed sulphonyl esters. The instability of these sulphonyl esters could possibly be attributed to the formation of resonance stabilized benzylic carbonium ions, which could then undergo S_N1 attack. It is pertinent to point out that benzyl alcohol has also been reported[6] to give a water soluble product on treatment with tosyl chloride and pyridine but no analytical data for this compound were given. On the basis of the present work it would appear that their product was also a benzylpyridinium salt.

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