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Reactions of Sulphonyl Chloride-NN-Dimethylformamide Complexes

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THE interaction of NN-dimethylformamide (DMF) with thionyl chloride, phosphorus oxychloride, phosgene, carbonyl fluoride, and carboxylic acid halides has been extensively investigated.1-5 Reactions of complex (I), formed from DMF and arylsulphonyl chlorides, 1 have received almost no attention and are the subject of this communication.

Complex (I) is found to be an excellent formylating agent for certain alcohols; thus, testosterone and toluene-p-sulphonyl chloride in DMF give 79% of testosterone O-formate.6 In a similar

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manner yohimbine gives 59% of yohimbine O-formate7 (m.p. 127-132°), identical with the product obtained in 66% yield from yohimbine and chloromethylenedimethylammonium chloride.2,4 The reaction is thought to proceed by nucleophilic attack of the alcohol on the iminium salt (I) to yield intermediate (II)8 which is hydrolysed to an O-formate (III) during hydrolytic work-up.

With p-nitrobenzyl alcohol and with picric acid the reaction takes a different course since p-nitrobenzyl chloride (95%) and picryl chloride (97%) are obtained. These products (IV) result from attack by chloride on C of (II).

Treatment of 4-methyl-6-phenyl-s-triazin-2-one9 (V) with complex (I; $Ar = p - Me - C_6H_4$), from toluene-p-sulphonyl chloride and DMF, gives 4-(2-dimethylaminovinyl)-6-phenyl-s-triazin-2-one (VI),7 m.p. 174-175° dec. In the p.m.r. spectrum¹⁰ the olefinic protons are observed as a pair of doublets centred at $\delta 4.94$ and $\delta 8.34$ with I=13c./sec., thus confirming the structural assignment (VI).

Reaction of arylsulphonyl chlorides in DMF with arylamines is found to produce sulphonanilides and/or formamidines.11 In general, reaction of benzenesulphonyl chloride in DMF with weakly basic arylamines (p $K_a < 3.5$) gives mainly formamidines (as salts VIII) whereas more strongly basic arylamines (p $K_a > 3.5$) gives either sulphonanilides (VII) or formamidine salts (VIII) or mixtures of (VII) and (VIII) depending upon reaction conditions.

Arylsulphonyl chlorides having electron-withdrawing groups such as nitro at ortho- and parapositions give increased amounts of formamidines. For example, benzenesulphonyl chloride (1 mole) and p-chloroaniline (2 moles) in DMF produce 89% of sulphonanilide (VII) (R = Ph, Ar = p-Cl- C_6H_4)¹² and 6% of formamidine salt (VIII) (Ar = $p\text{-Cl-C}_6H_4$, R = Ph) (m.p. 188—190°)⁷ while 2,6-dichloro-4-nitrobenzenesulphonyl chloride (1 mole) and p-chloroaniline (2 moles) afford 85% of formamidine salt (VIII) (Ar = p-Cl-C₆H₄, R = 2,6-Cl₂-4-NO₂-C₆H₂) (m.p. 210—217°).

$$Me_2\overset{\dagger}{N}=CHOSO_2R$$
 Cl^-+ArNH_2

$$\downarrow$$
 $RSO_2NH\cdot Ar + Me_2\overset{\dagger}{N}=CH\cdot NH\cdot Ar RSO_2O^ (VII)$ $(VIII)$

The aniline/sulphonyl chloride ratio is an important factor in these reactions. Thus, as contrasted with the results obtained with the 2/1ratio above, a p-chloroaniline/benzenesulphonyl chloride ratio of 0.25 produces 80% of formamidine salt (VIII) (Ar = p-Cl-C₆H₄, R = Ph). Similar results are observed with methanesulphonyl chloride: p-chloroaniline (2 moles) and methanesulphonyl chloride (1 mole) in DMF give 73% of sulphonanilide (VII) (R = Me, Ar = p-Cl-C₆H₄)¹³ while, with 1 mole of p-chloroaniline, a mixture of 22% of sulphonanilide (VII) (R = Me, Ar = p- $Cl-C_6H_4$) and 50% of formamidine (VIII) (Ar = p-Cl-C₆H₄)¹⁴ is obtained. Decreasing the amount of p-chloroaniline to 0.65 mole results in production of 71% of formamidine.

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⁷ Satisfactory elemental analyses were obtained for all new compounds.

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10 Determined in deuterated dimethyl sulphoxide with a Varian Model A-60 spectrometer; chemical shifts (δ) are given in p.p.m. from tetramethylsilane as internal standard.

¹¹ For the formation of formamidines from the complex of benzoyl bromide and DMF see ref. 3.

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