The Reaction of Oximes and Phenols with Acyl Isothiocyanates; an Example of Regioselectivity

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Oximes add to acyl isothiocyanates to give intermediates which decompose by a radical-pair mechanism, whereas phenols of comparable acidity give no adducts.

It is well known that hydroxy compounds in general do not add to isothiocyanates,¹ although the analogous reactions of isocyanates are exothermic. Oximes are reported² to react with acyl isothiocyanates to give a variety of products including the parent ketone, acyl urea, and elemental sulphur, but the mechanism of the reaction is unknown.

We now find that oximes derived from aromatic ketones add rapidly and exothermically to acyl isothiocyanates to give intermediates which spontaneously rearrange in solution and decompose according to Scheme 1.



This mechanism is supported by the isolation of (5), (8), and elemental sulphur, and by strong C.I.D.N.P. ¹³C signals attributed to (2), when the reaction was carried out at elevated temperatures. A similar mechanism has been established³ for the reaction of oximes with phenyl isothiocyanate, but here the formation of the initial adduct is highly *endothermic*.

The intermediate adduct (1) from fluorenone oxime was isolated at low temperatures, by mixing the reagents in acetone at -5 °C. The structure was established by elemental analysis and ¹³C n.m.r. spectra. Absorptions, measured in CDCl₃ solutions at 0 °C were found at δ 180.8 (>C=S), 163.6 (>C=O), and 155.7 (>C=N-), in addition to aromatic absorptions over a wide range.

Phenol is reported to react slowly with phenyl isothiocyanate to give the corresponding thiocarbamate in poor yield.⁴ However, phenols with pK_a 's comparable to those of the oximes were recovered unchanged from mixtures with benzoyl isothiocyanate. If the reaction was carried out in the presence of one equivalent of triethylamine, benzoylation



Scheme 1

Scheme 2

occurred rapidly at room temperature, both with phenols and oximes.

In order to explain the remarkable difference in behaviour of oximes and phenols, we can assume a hypothetical series of processes, *for both the oximes and the phenols*, and then apply the First Law. Thus, for the addition of an oxime to benzoyl isothiocyanate see Scheme 2.

The equilibrium constant for the addition is given by the product of the above three constants $(K_{\rm H}K_1K_2)$. For two nucleophiles with identical $pK_{\rm a}$'s, $K_{\rm H}$ and K_1 are the same, and hence K_2 for the oxime must be greater than K_2 for a corresponding phenol, since only in the former case is an adduct formed.

Oximate ions are known to have abnormally high reactivity

(and hence affinity) towards carbon centres, and this defines the α -effect,⁵ the origin of which is discussed in the following communication.

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