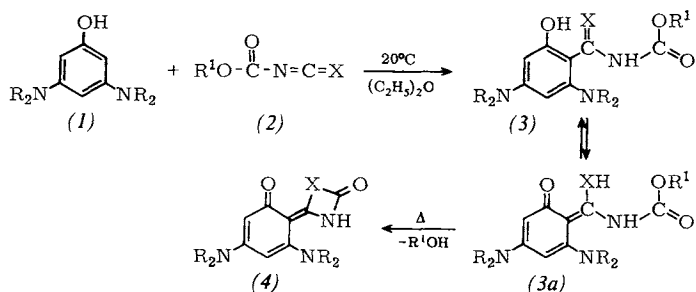


Reaction of Isocyanato- and Isothiocyanatoformates with Activated Phenols ^[1]

By F. Effenberger and R. Niess^[*]

3,5-Bis(dialkylamino)phenols (1) ^[2], which are accessible from phloroglucinol and secondary amines, contain positive electromeric substituents in *meta*-position to one another, the effect of which is markedly displayed in an increased reactivity of the ring-carbon atoms towards electrophilic reagents.

Thus they react with isocyanatoformates (2), X = O, and isothiocyanatoformates (2), X = S, even at room temperature with exclusive *C*-acylation that yields the compounds (3) and (3a), respectively. Acylation in the *para*-position could not be detected by ¹H-NMR^{*} spectroscopy.



The compounds (1) and (2) were dissolved in anhydrous ether and mixed in the molar ratio 1:1 at 20°C. After 2h at this temperature, the solution was cooled to -20°C and after *ca.* 12h the crystals that had separated were collected by filtration.

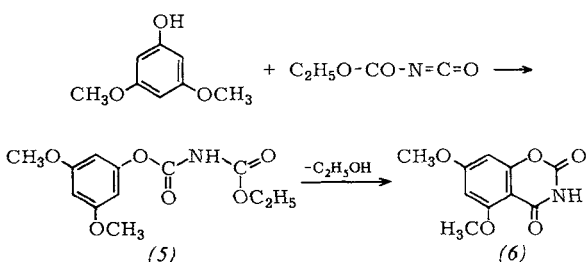
$\begin{array}{c} R \\ \diagdown \\ N- \\ \diagup \\ R \end{array}$	R ¹	X	(3a)		(4)	
			Yield (%)	M.p. (°C)	Yield (%)	M.p.
Piperidino-	CH ₃	O	77.5	156–157	94	247–248
Piperidino-	C ₂ H ₅	O	80	155–157	84.5	247–248
Piperidino-	C ₂ H ₅	S	87	ca. 148	87	220–221
Dimethyl- amino-	CH ₃	O	100	125–127	80	223–224
Dimethyl- amino-	C ₂ H ₅	S	87.5	110–111	100	221–223

Whereas the aminophenols (1) are in the benzenoid form, spectroscopic results indicate that the acylation products have the tautomeric quinonemethide structure (3a). According to the results of Gompper *et al.*^[3] quinonemethides with ω,ω -hetero-substituents are relatively stable. It is possible that hydrogen bridges contribute further to the stabilization of (3a).

Heating the acylation products (3a) above their melting points causes intramolecular removal of alcohol and formation of 1,3-oxazetidin-2-ones (4), X = O, and 1,3-thiazetidin-2-ones (4), X = S, whose structures are proved by elemental analysis, molecular-weight determination, and ¹H-NMR and UV spectra.

In contrast to the behavior of the bis(dialkylamino)phenols (1), reaction of the less activated phloroglucinol dimethyl ether with (2), X = O, R' = C₂H₅, causes exclusive O-

acylation with formation of the urethane (5), which, when heated above the melting point, also loses alcohol and gives the benzoxazine derivative (6).



Other phenols also react similarly to yield benzoxazines (6).

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