Reaction of Isocyanato- and Isothiocyanato-formates with Activated Phenols

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3,5-Bis(dialkylamino)phenols (I), 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 $^1$H-NMR spectroscopy.

The compounds (I) 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.
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.[31] quinonemethides with \(\omega,\omega\)-hetero-substituents are relatively stable. It is possible that hydrogen bridges contribute further to the stabilization of (3a).

Hecting 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), \(X = O\), \(R' = C_2H_5\), 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).

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\begin{align*}
\text{OH} & \quad + \quad \text{C}_3\text{H}_5\text{O} \cdot \text{CO} \cdot \text{N} \cdot \text{C}=\text{O} \\
\text{CH}_3 & \quad \text{O} \quad \text{CH}_3 & \rightarrow \\
\text{CH}_3 & \quad \text{O} \quad \text{NH}_2 & \quad \text{OC}_3\text{H}_5 \\
\text{O} & \quad \text{OC}_3\text{H}_5 & \rightarrow \\
\text{CH}_3 & \quad \text{O} \quad \text{NH}_2 & \quad \text{H}_2\text{CO} \\
& \quad \text{OC}_3\text{H}_5 & \\
\end{align*}
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(5)

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

Received: March 23rd, 1967

German version: Angew. Chem. 79, 474 (1967)

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[1] We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for support of this work.
