BENZOYLATION AND p-CHLOROBENZOYLATION OF DIBENZOTHIOPHENE

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The benzoylation and p-chlorobenzoylation of dibenzothiophene in the presence of small amounts of $FeCl_3$ and its complex with nitromethane, $ZnCl_2$, and iron acetylacetonate lead to the corresponding 3-acyldibenzothiophenes in good yields.

The acetylation [1, 2] and p-chlorobenzoylation [3] of dibenzothiophene in the presence of large amounts of $AlCl_3$ have been previously described. No data on the benzoylation of dibenzothiophene are available in the literature. The use of a large amount of catalyst leads to resinification of the reaction products and markedly hinders their isolation. However, it is known that the acetylation and benzoylation of carbazole [4] and dibenzofuran [5] in the presence of small amounts of catalysts ($1 \cdot 10^{-3}$ mole of $FeCl_3$ with CH_3NO_2, $FeCl_3$, and $ZnCl_2$) and iron acetylacetonate leads to the corresponding ketones in high yields (60-80%); in this case, in addition to the economical use of the catalyst, the isolation of the ketones is facilitated.

We investigated the benzoylation and p-chlorobenzoylation of dibenzothiophene in the presence of small amounts of Lewis acids under the conditions used for the benzoylation of dibenzofuran [5]; high yields of the ketones (67-76%) were obtained in the case of benzoylation, and lower yields (51-77%) were obtained in the case of p-chlorobenzoylation. As in the case of the reactions in [5], the $FeCl_3$ complex with nitromethane was found to be the best catalyst in these reactions. 3,6-Dibenzoylbenzothiophene was obtained in 62-65% yield in the benzoylation of 3-benzoyldibenzothiophene. In the case of p-chlorobenzoylation we were unable to isolate the corresponding diketone despite variation of the reaction conditions.

EXPERIMENTAL

The individuality of the compounds was determined by thin-layer chromatography (TLC) on Al_2O_3 (activity II) in a chloroform–hexane system (4:1). The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer. The mass spectra were obtained with an MKh-1303 mass spectrometer at an ionizing-electron energy of 50 eV and an ionization-chamber and input-system temperature of 125-150°C.

The acylation reactions were carried out by heating a mixture of 1.84 g (0.01 mole) of dibenzothiophene, 0.01 mole of the acid chloride, and 0.02 g of the catalyst (in the case of the nitromethane complex the indicated amount of $FeCl_3$ was dissolved in 1 ml of nitromethane). In the reactions catalyzed by $FeCl_3 \cdot CH_3NO_2$ heating was carried out for 3 h while the temperature was gradually raised from 100 to 155°C; in the remaining cases the mixtures were heated

TABLE 1. Yields of 3-Acyldibenzothiophenes as a Function of the Nature of the Acid Chloride and Catalyst

Acylating agent	Yield, %					
	3-acyldibenzothiophenes				3,6-dibenzoyldibenzothiophene	
	$FeCl_3 \cdot CH_3NO_2$	$FeCl_3$	$ZnCl_2$	iron acetylacetonate	$FeCl_3$	$ZnCl_2$
C_6H_5COCl	76	75	72	67	65	62
p-ClC_6H_4COCl	77	53	51	51		

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at 170-180°C for 1 h. The reaction mixtures were then dissolved in benzene, and the solutions were washed successively with 10% alkali solution and water and dried over calcium chloride. The benzene solution was passed through a column filled with 90 g of Al_2O_3 (elution with benzene), the benzene was removed from the eluate by distillation, and the residue was recrystallized. The yields of the ketones are presented in Table 1. The reaction of 3-benzoyldibenzothiophene [3.6 g (0.0125 mole)] with benzoyl chloride [1.75 g (0.0125 mole)] was carried out similarly in the presence of 0.02 g of $FeCl_3$ or $ZnCl_2$, and the diketone was purified as described above.

3-Benzoyldibenzothiophene. This compound was purified by successive recrystallization from benzene—alcohol and glacial acetic acid and had mp 149°C, M^+ 288 (by mass spectrometry), and R_f 0.87. Found, %: C 78.9; H 4.2; S 11.0. $C_{19}H_{12}OS$. Calculated, %: C 79.1; H 4.2; S 11.1. IR spectrum: 1655 (C=O), 700-800 (C-S bonds), 957 (C=C bonds in a heterocyclic compound), and 829 cm^{-1} (1,2- and 1,2,4-substituted aromatic compounds).

3-(p-Chlorobenzoyl)dibenzothiophene. This compound was recrystallized from glacial acetic acid and had mp 118°C, M^+ 322 (by mass spectrometry), and R_f 0.51. IR spectrum: 1665 (C=O), 700-800 (C-S bonds), 950 (C=C bonds in a heterocyclic compound), and 822 cm^{-1} (1,2- and 1,2,4-substituted aromatic compounds). According to the data in [3], this compound has mp 114-116°C.

3,6-Dibenzoyldibenzothiophene. This compound was purified by successive recrystallization from benzene—alcohol and glacial acetic acid and had mp 172°C, M^+ 392 (by mass spectrometry), and R_f 0.13. Found, %: C 79.2; H 3.6; S 8.2. $C_{26}H_{16}O_2S$. Calculated, %: C 79.5; H 4.1; S 8.2. IR spectrum: 1657 (C=O), 700-800 (C-S bonds), 960 (C=C bonds in a heterocyclic compound), and 829 cm^{-1} (1,2- and 1,2,4-substituted aromatic compounds).

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CONVERSION OF 2-ACETAMIDO-1-THIOCHROMONE TO THE CORRESPONDING 4-CHLORO AND 4-AMINO DERIVATIVES

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2-Acetimido-4-chloro-2H-1-thiochromene, in which the chlorine atom is exchanged by hydroxy and amino groups, was synthesized by the action of phosphorus oxychloride on 2-acetamido-1-thiochromone. It was established on the basis of the IR, UV, PMR, and mass spectra that the product of the reaction of this compound with aniline has the 2-acetamido-1-thiochromene structure.

It has been previously established that 2-aminochromones [1], 2-aminothiochromones [2], and their N-acyl derivatives [2, 3] exist in the aminochromone tautomeric form and that the introduction of the strong electron-acceptor trichloroacetylene does not shift the equilibrium to favor the 4-hydroxycoumarin form, in contrast to some other systems with a smaller difference in the energies of the two tautomeric forms (for example, see [4]). In conformity with the general position regarding the dependence of tautomeric equilibria on the acidities of the tautomeric forms [5] it might have been expected that replacement of the oxygen atom of the pyrone carbonyl group by the more basic imino group would promote a shift of the equilibrium to favor the formation of the 2-imino-4-amino form.

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