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## ACYLATION OF DIBENZOFURAN WITH p-SUBSTITUTED

## BENZOYL CHLORIDES

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It is shown that benzoylation and p-chloro- and p-nitrobenzoylation of dibenzofuran in the presence of small amounts of  $FeCl_3$ , the  $FeCl_3 \cdot CH_3NO_2$  complex,  $ZnCl_2$ , and acetylaceto-natoiron lead to the production of the corresponding 3-acyldibenzofurans in high yields.

Reactions involving the acylation of heterocyclic compounds, particularly dibenzofuran, in the presence of  $AlCl_3$  require the consumption of large amounts of the catalyst [1-4]. The use of 1.5 moles of anhydrous alu-

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	Yields of 3-acyldibenzofurans, %			
Acylating agent	FeCl <sub>3</sub> - CH <sub>3</sub> NO <sub>2</sub>	FeCl₃	ZnCl <sub>2</sub>	acetylace- tonateiron
C <sub>6</sub> H <sub>5</sub> COCl <i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> COCl <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> COCl	77 80 77	75 78 52	75 72 55	68 81 54

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

minum chloride leads to resinification of the products and markedly hinders their isolation. In addition, it is known that acetylation and benzoylation of carbazole [5] in the presence of small amounts of catalysts  $(1 \cdot 10^{-3} \text{ mole of FeCl}_3)$  give the corresponding ketone in 60 to 70% yield.

When small amounts of the catalyst are used, not only is economy realized, but the isolation of the product is markedly facilitated.

We have found that the reaction of dibenzofuran with benzoyl and p-chlor- and p-nitrobenzoyl chlorides proceeds readily in the presence of small amounts of Lewis acids at high temperatures to give 3-acyldibenzofurans in yields that exceed those obtained in the presence of  $AlCl_3$ . Moreover, the highest yields of ketones (72-81%) were obtained in the case of p-nitrobenzoylation, and the lowest yields (52-77%) were obtained in the case of p-chlorobenzoylation. The best catalyst in these reactions was found to be the  $FeCl_3 \cdot nitromethane$ complex.

It has been previously shown [6] that very small amounts of acetylacetonatoiron readily catalyze the benzoylation of carbazole. In the case of acylation of dibenzofuran this catalyst gives almost the same yields of ketones as in the reactions with anhydrous ferric chloride and zinc chloride.

It was of interest to find conditions for the preparation of diacyl derivatives of dibenzofuran. It is known [7] that a second benzoyl group can be relatively easily introduced in an aromatic ring in the presence of small amounts of  $FeCl_3$ .

Benzoylation of 3-benzoyldibenzofuran by this method gave 3,6-dibenzoyldibenzofuran in 60% yield. In the remaining cases - p-nitro- and p-chlorobenzoylation of the corresponding monoketones - we were unable to obtain diketones despite variation of the reaction conditions.

## EXPERIMENTAL

The individuality of the compounds was determined by thin-layer chromatography (TLC) on  $Al_2O_3$  (activity I) in a chloroform-hexane system (4:1). The IR spectra of the compounds were recorded with a UR-20 spectrometer. The mass spectra were recorded with an MKh-1303 spectrometer.

The acylation reactions were carried out by heating a mixture of 1.68 g (0.01 mole) of dibenzofuran, 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<sub>3</sub> 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 gradually raising the temperature from 100 to 155°; in the remaining cases the mixtures were heated at 170-180°. The reaction mixtures were subsequently dissolved in benzene, and the benzene solution was washed with 10% alkali solution and water and dried over calcium chloride. It was then passed through a column filled with 80 g of  $Al_2O_3$ , 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-benzoyl-dibenzofuran [6,8 g (0.025 mole)] with benzoyl chloride [3.5 g (0.025 mole)] in the presence of 0.05 g of FeCl<sub>3</sub> or ZnCl<sub>2</sub> was carried out similarly. The product was purified as described above.

3-Benzoyldibenzofuran. The product ketone was purified by successive recrystallization from benzenealcohol and acetic acid to give a product with mp 134° and M 272 (by mass spectrometry). The oxime had mp 152-153° and Rf 0.83. IR spectrum: 1667 (C=O); 712 and 718 cm<sup>-1</sup> (monosubstituted benzene ring) (according to the data in [1, 2], the ketone has mp 137-138°, and its oxime has mp 152-153°).

<u>3-(p-Nitrobenzoyl)dibenzofuran</u>. The ketone was recrystallized successively from alcohol-chloroform (1:2) and glacial acetic acid and had mp 201°, M 317 (by mass spectrometry), and  $R_f$  0.87. IR spectrum: 1670 (C=O); 1525 and 1354 (NO<sub>2</sub>) (according to the data in [8], the ketone has mp 203°).

<u>3-(p-Chlorobenzoyl)dibenzofuran.</u> The ketone was purified by recrystallization from glacial acetic acid or alcohol to give a product with mp 153°, M 306 (by mass spectrometry), and  $R_f$  0.51. IR spectrum: 1665 (C=O) and 845 cm<sup>-1</sup> (1,4-disubstituted ring) (according to the data in [9], the ketone has mp 152°).

3,6-Dibenzoyldibenzofuran. The ketone was purified by recrystallization from acetic acid or alcohol to give a product with mp 165°, M 376 (by mass spectrometry), and  $R_f$  0.80. IR spectrum: 1664 (C=O) and 705 cm<sup>-1</sup> (monosubstituted benzene ring) (according to the data in [1, 2], the ketone has mp 167-168°).

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#### DI- AND TRI(2-PYRON-6-YL)ARENES

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UDC 547.812.5.814.1:543.422.4.6

Condensation of di- and triacetylarenes with 1,1,1,3-tetrachloro-3-alkoxypropanes or  $\beta$ , $\beta$ dichloroacrolein in acidic media gave a number of (dichloropentadienyl)- and tris(dichloropentadienyl)-substituted aryl ketones, which, in the case of acetic acid in the presence of phosphoric acid, are converted to the corresponding di- and tri(2-pyron-6-yl)arenes. It was observed that nitric acid has an oxidation effect on 2-pyrones.

In a continuation of our earlier research [1] in the pyrone series we synthesized systems with two and three  $\alpha$ -pyrone rings separated by benzene rings and studied some of their reactions. We accomplished the synthesis of 1,4-di(2-pyron-6-yl)benzene (X), 1,4-(2-pyron-6-yl)diphenyl (XI), and sym-tri(2pyron-6-yl)benzene (XIII) from p-diacetylbenzene (I), 1,4-diacetyldiphenyl (II), and sym-triacetylbenzene (III), respectively, by the method in [2], which has been previously used for the synthesis of monopyrones.

$$H_{3}COC - \left( \bigcirc \right)_{n}^{L} COCH_{3} + 2 CCI_{3}CH_{2}CHOR \\ (2 CCI_{2} \Rightarrow CHCHO)$$

Moscow Technological Institute of the Meat and Dairy Industry, Moscow 109029. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 897-901, July, 1977. Original article submitted December 30, 1975; revision submitted October 29, 1976.

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