REACTIONS OF AROMATIC AND HETEROAROMATIC COMPOUNDS HAVING ELECTRON-ACCEPTOR SUBSTITUENTS

XX.* POSSIBLE PATHWAYS FOR THE FORMATION OF CHLORO DERIVATIVES IN THE BROMINATION OF COMPLEXES OF SOME CARBONYL COMPOUNDS OF THE FURAN SERIES WITH ALUMINUM HALIDES

L. I. Belen'kii, G. T. Gromova, and Ya. L. Gol'dfarb

UDC 547.724.1:542.944.1:543.422.25'544

The composition of the products formed in the bromination of complexes of furfural with $AlCl_3$ and methyl furan-2-carboxylate with $AlBr_3$ in chloroform and dichloroethane was studied by PMR spectroscopy and gas–liquid chromatography. Some literature data pertaining to these reactions are refined and corrected. The pathways for the formation of chloro derivatives under the examined conditions are discussed.

The bromination of furfural and methyl furan-2-carboxylate in the presence of aluminum chloride has been described in a communication by Chadwick and co-workers [2]. They are apparently unfamiliar with one of our recent papers devoted to the bromination of furfural complex with aluminum chloride [3]. In this connection, it seems expedient to us to report some new facts pertaining to the problems examined in [2, 3].

According to the data in [2], a mixture of 4-bromo, 5-chloro, 4,5-dibromo, and 5-chloro-4-bromo derivatives in a ratio of 20 : 2 : 40 : 4 is obtained by the action of 2 moles of bromine in the presence of 2.5 moles of $AlCl_3$ on furfural in dichloroethane at 50°, and 34% of the starting furfural is recovered. The absence in this mixture of even a small amount of 5-bromo-furfural seemed incomprehensible and contradicted our results [3], which we obtained under similar conditions (by the action of 1 mole of bromine on furfural in the presence of 2.5 moles of $AlCl_3$ in chloroform at 0°). As we have already noted [3], separation of the 4- and 5-bromofurfurals by gas chromatography is an extremely complex task, and this, in particular, explains the fact that 5-bromofurfural was not detected in the products of bromination of furfural by Roques and co-workers [4], whose study is cited in [2]. As one may suppose, the 5-bromo derivative also was not detected in [2] because only gas–liquid chromatography (GLC) was used to analyze the mixtures.

We therefore reproduced some of the experiments described by Chadwick and co-workers [2] using, as in [3], a combination of GLC and PMR methods for the analysis of the composition of the mixture. We ascertained that 20-25% of the starting furfural is recovered under the conditions presented in [2], and 4-bromo-, 5-bromo-, 5-chloro-, 4,5-dibromo-, and 5-chloro-4-bromofurfurals are formed in the ratio close

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*See [1] for communication XIX.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1464-1467, November, 1975. Original article submitted October 15, 1974.

TABLE 1. PMR Spectra of Halo Derivatives of Furfural and Methyl Furan-2-carboxylate

Compound	Chemical shift, δ, ppm					Spin–spin coupling constants, Hz	
	3-H	4-H	5-H	CHO	CH_3	J_{34}	J_{35}
4-Bromofurfural	7,14	—	7,61	9,60	—	—	~1
4-Chlorofurfural	7,16	—	7,65	9,62	—	—	0,6
5-Bromofurfural	7,08	6,49	—	9,45	—	3,6	—
5-Chlorofurfural	7,17	6,38	—	9,50	—	3,6	—
4,5-Dibromofurfural	7,19	—	—	9,50	—	—	—
5-Chloro-4-bromofurfural (according to the data in [2])	7,20	—	—		—	—	—
Methyl 4-bromofuran-2-carboxylate	7,14	—	7,55	—	3,85	—	1,0
Methyl 5-bromofuran-2-carboxylate	7,03	6,34	—	—	3,83	3,5	—
Methyl 5-chlorofuran-2-carboxylate	7,06	6,25	—	—	3,83	3,5	—
Methyl 4,5-dibromofuran-2-carboxylate	7,10	—	—	—	3,84	—	—
Methyl 5-chloro-4-bromofuran-2-carboxylate	7,14	—	—	—	3,84	—	—

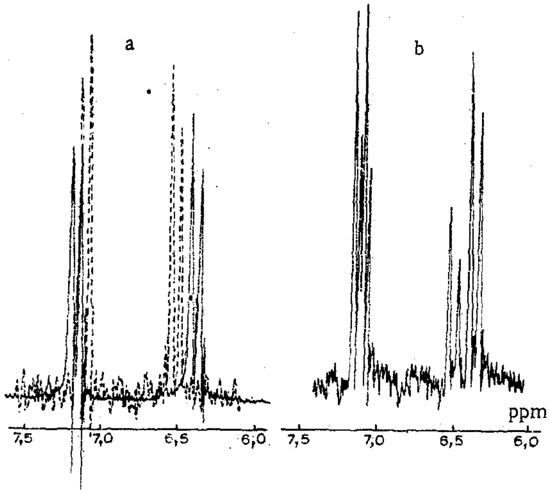
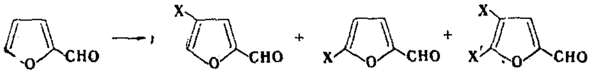


Fig. 1 Fragments of the PMR spectra (4-H and 3-H signals) of: a) 5-chlorofurfural (——) and 5-bromofurfural (----); b) a mixture of the same aldehydes.

to 30:10:5:40:10, respectively. In addition, ~0.5% 4-chlorofurfural and two unidentified compounds (~5%), possible 4-chloro-5-bromo- and 4,5-dichlorofurfurals, are detected.



X and X' — Cl or Br

The chemical shifts of the protons of 5-chloro- and 5-bromofurfurals are quite close (see Table 1). The percentage of 5-bromofurfural in the mixture can be roughly determined by subtraction of the amount of the 5-chloro derivative (GLC data) from the total amount of these aldehydes (from PMR data). In addition, a more thorough analysis of the spectra of authentic samples and their mixtures (see Fig. 1) shows that at least the 4-H signals of these compounds and of unchanged furfural (δ 4-H 6.59 ppm) differ quite distinctly from one another. This creates an additional possibility for the determination of the composition of the products formed in the bromation of the furfural complex with $AlCl_3$. In particular, the ratio of 5-bromo- and 5-chlorofurfurals in the products of bromination at 0° [3] is ~3:1 (from PMR data); the remaining components are reliably determined by GLC. Thus under the conditions described by us [3], 4-bromo-, 4-chloro-, 5-bromo-, 5-chloro-, 4,5-dibromo-, and 5-chloro-4-bromofurfurals are formed in a ratio of 60:5:15:5:10:5. We note that the indicated mixture contains an appreciable amount (~5%) of the previously unidentified 4-chlorofurfural.

The interpretation of the pathways for the formation of chloro derivatives under the examined conditions is fraught with several difficulties. It has previously been assumed [4] that 5-chloro-4-bromofurfural arises as a result of nucleophilic substitution of one of the bromine atoms in 4,5-dibromofurfural by chlorine (from $AlCl_3$). 5-Chlorofurfural might have been similarly formed from 5-bromofurfural. 5-Bromofurfural was not detected in [2], and an extremely questionable pathway involving intramolecular migration of chlorine from $AlCl_3$, bonded at the CHO group in the complex, to the 5 position of the ring was proposed for the formation of the 5-chloro derivative. It should be stated that neither the first nor the second assumption is adequate to explain the observed formation of the 4-chloro derivative. In this connection, one can consider a third possibility – direct chlorination of the complex of furfural (or its monohalo derivatives) with aluminum halide. The source of chlorine in this case might be a reaction between bromine and aluminum chloride. Despite the apparent impossibility of displacement of chlorine from its salts by the less electronegative bromine, such processes are known [5] and are favored by higher temperatures; this is in agreement with the relatively higher yields of chloro derivatives at 50° [2] than at 0° [3].

The formation of chloro derivatives may occur even when the bromination is carried out with aluminum bromide rather than with aluminum chloride if a chlorine-containing solvent is used. It is known that chloro hydrocarbons give the corresponding bromo derivatives in high yields on reaction with aluminum bromide, and the $AlBr_3$ is converted to the chloride. These reactions take place even at room temperature and are sharply accelerated on heating [6, 7]. In particular, processes of this sort have been described for chloroform and dichloroethane [7]. However, the formation of aluminum chloride under the conditions of bromination of carbonyl compounds of the furan series can, of course, as in the cases considered above, lead to the development of chloro derivatives. In this connection, one might suppose that the formation of chloro and chlorobromo derivatives remained undetected in [2] in the bromination of methyl furan-2-carboxylate in dichloroethane in the presence of $AlBr_3$.* In fact, reproducing the experiment under the conditions in [2], we found that a mixture consisting of 5-chloro, 5-chloro-4-bromo, and 4,5-dibromo derivatives in a ratio of 3 : 79 : 18 (from GLC data) is obtained by the action of 2 moles of bromine.

Thus appreciable amounts of chloro derivatives that decrease sharply as the reaction is carried out at low temperatures are formed in a number of cases during bromination in the presence of $AlCl_3$ or $AlBr_3$ in a chlorine-containing solvent. The reactions of furfural and pyromucic acid ester that we examined in this research are undoubtedly not the only examples of such "anomalous" transformations.

EXPERIMENTAL

The chromatographic analyses were made with an LKhM-8m chromatograph with a flame-ionization detector; the carrier gas was nitrogen, the flow rate was 30 ml/min, and the stainless steel column (2 by 1500 mm) was filled with polyethylene glycol adipate (10%) on the Chromosorb R. The temperature during the analysis of the halofurfurals was 150° and the temperature during the analysis of the halo derivatives of furan-2-carboxylic acid was 165°.

The PMR spectra of CCl_4 solutions of the compounds were recorded with a Varian DA-60-IL spectrometer with hexamethyldisiloxane as the internal standard.

Furfural and methyl furan-2-carboxylate were brominated under the conditions described in [2, 3].

Samples for GLC and PMR spectroscopy were obtained as described below.

4-Chlorofurfural. This compound was isolated by crystallization of a mixture obtained by chlorination of furfural in the presence of 2.5 moles of $AlCl_3$ in chloroform under conditions similar to those used for bromination [3, 8]; the product had mp 27-29° (from hexane). Found: C 46.1; H 2.4; Cl 27.1%. $C_5H_3ClO_2$. Calculated: C 46.0; H 2.3; Cl 27.2%.

5-Chlorofurfural. This compound was obtained by chlorination of furfural in CS_2 in the presence of benzoyl peroxide [9].

5-Chloro-4-bromofurfural [4, 10]. This compound was obtained by bromination of 5-chlorofurfural without a solvent in excess (2.5 moles) $AlCl_3$. The products contained ~25% unchanged starting compound.

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*One cannot exclude the possibility that there was a misprint in the description of this experiment (i in [2]), inasmuch as, in contrast to the remaining experiments in which the sum of the products is 100%, in this case the sum is 40%.

Methyl 4,5-Dibromofuran-2-carboxylate. This ester was obtained by bromination of methyl furan-2-carboxylate in excess of $AlCl_3$ without a solvent by the method in [2].

Samples of methyl 5-chloro- [2], 5-bromo- [11], 4-bromo-, and 5-chloro-4-bromofuran-2-carboxylate [2] were obtained from the corresponding aldehydes by oxidation with silver oxide and subsequent esterfication with methanol in the presence of sulfuric acid.

LITERATURE CITED

1. Ya. L. Gol'dfarb, G. P. Gromova, and L. I. Belen'kii, Izv. Akad. Nauk SSSR, Ser. Khim., 2275 (1974).
2. D. J. Chadwick, J. Chambers, G. D. Meekins, and R. L. Snowden, J. Chem. Soc., Perkin I, 1766 (1973).
3. L. I. Belen'kii, G. P. Gromova, and Ya. L. Gol'dfarb, Khim Geterotsikl. Soedin., 597 (1972).
4. B. Roques, M.-C. Zaluski, and M. Dutheil, Bull. Soc. Chim. France, 238 (1971).
5. Gmelins Handbuch der anorganischen Chemie, Eighth Edition, Vol. 7 (1931), p. 123.
6. G. Gustavson, Zh. Russk. Fiz. -Khim. Obshchestva, 13, 286 (1881).
7. C. Pouret, Bull. Soc. Chim. France, [3], 25, 191 (1901).
8. L. I. Belen'kii, G. P. Pokhil, and Ya. L. Gol'dfarb, USSR Author's Certificate No. 206568 (1968); Byull. Izobr., No. 1 (1968).
9. W. J. Chute and G. F. Wright, J. Org. Chem., 10, 541 (1945).
10. B. Roques, M.-C. Zaluski, M. Bonhomme, and M. Robba, Bull. Soc. Chim. France, 242 (1971).
11. A. Dunlop and F. Peters, The Furans, New York (1953).

5-ARYLFURAN-2,3-DIONES*

Yu. S. Andreichikov, Yu. A. Nalimova,
G. D. Plakhina, R. F. Saraeva,
and S. P. Tendryakova

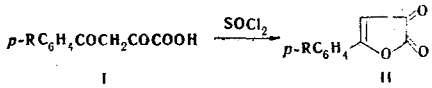
UDC 547.722.3'724'727'863'867.2

5-Arylfuran-2,3-diones were obtained by cyclization of aroylpyruvic acids in the presence of thionyl chloride. It is shown that the five-membered ring of 5-arylfuran-2,3-diones is unstable and is cleaved under mild conditions under the influence of nucleophilic reagents.

In contrast to their isomers, extremely little study has been devoted to arylfuran-2,3-diones. Only one study devoted to the synthesis of 4-benzoyl-5-phenylfuran-2,3-dione from oxalyl chloride and dibenzoylmethane is known [1].

We have found that cyclization, the products of which are 5-arylfuran-2,3-diones (II), occurs in the reaction of aroylpyruvic acids (I) with thionyl chloride (see Table 1).

A band corresponding to the vibrations of the ethylene bond appears in the IR spectra of the cyclization products. The characteristic band of the carbonyl group is shifted from 1625 (in the spectra of the starting compounds) to 1713 cm^{-1}. The absorption band of the lactone grouping, in conformity with the literature data [2], is found at 1840 cm^{-1}.



I II

I, II R = H, CH_3, CH_3O, Br, Cl

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*Communication I from the series "Chemistry of Oxalyl Derivatives of Methyl Ketones."

Perm Pharmaceutical Institute. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1468-1470, November, 1975. Original article submitted January 27, 1975.