less steel column 3000 × 3 mm; stationary phase polyethylene glycol adipate, 20 wt. % on Celite-545 (100-120 mesh); carrier gas helium at 40-45 ml/min, analysis temperature 60°, evaporator temperature 275°.

LITERATURE CITED

1. S. Olsen and C. Rutland, Chem. Ber., 86, 361 (1953).
2. A. A. Gevorkyan, S. M. Kosyan, and D. I. Gezalyan, Arm. Khim. Zh., 26, 430 (1978).
3. T. I. Temnikova and S. N. Semenova, Molecular Rearrangements in Organic Chemistry [in Russian], Khimiya, Leningrad (1983), p. 91.
4. N. D. Cheronis and T. S. Ma, Micro and Semimicro Methods of Organic Functional Group Analysis [Russian translation], Khimiya, Moscow (1973).

SYNTHESIS OF 5-ARYL-2-ALKOXYFURANES FROM 1-AROYL-2,2-DICHLOROCYCLOPROPANES

O. G. Kulinkovich, I. G. Tishchenko,
and N. V. Masalov

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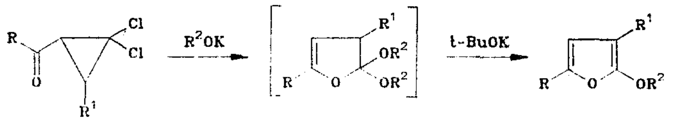
The reaction of 1-aroyl-2,2-dichlorocyclopropanes with a mixture of potassium tert-butylate and potassium methylate (or ethylate) in tert-butyl alcohol gives 5-aryl-2-methoxy(or ethoxy)furanes in good yield.

In studying the chemical properties of gem-dichlorocyclopropyl ketones which have a labile hydrogen in the cyclopropane ring in α-position to the carbonyl, we have found convenient ways to convert them to alicylic derivatives [1-3], 5-aryl-2-dialkylaminofuranes [4], and substituted 2,2-dialkoxy-2,3-dihydrofuranes [1, 2, 5]. In [6] we reported the synthesis of 5-aryl-2-ethoxyfuranes by the reaction of aluminum tert-butylate with the corresponding 2,2-diethoxy-2,3-dihydrofuranes. The present work is devoted to an investigation of a synthesis of alkoxyfuranes from gem-dichlorocyclopropyl ketones in which the separation of the unstable 2,2-dialkoxy-2,3-dihydrofuranes is avoided.

The alkoxyfuranes IIIa-e were obtained in good yield by the reaction of the 1-aroyl-2,2-dichlorocyclopropanes Ia-d with excess potassium tert-butylate and potassium methylate or ethylate in tert-butyl alcohol. According to TLC data, the dihydrofuranes IIa-e [5] form first; their conversion to IIIa-e at a rate sufficient for preparatory application requires an excess of strong base and an increase in temperature. The reaction of the ketones Ia-d with only potassium tert-butylate in tert-butyl alcohol forms a complex mixture of products, whereas in its absence the reaction with the potassium primary alcoholates stops at the stage of the dihydrofuranes IIa-e.



Ia-d IIa-e IIIa-e

I–III a R=C_6H_5, R^1=H, R^2=CH_3; b R=4-$CH_3C_6H_4$, R^1=H, R^2=CH_3; c R=4-$CH_3OC_6H_4$, R^1=H, R^2=CH_3; d R=C_6H_5, R^1=CH_3, R^2=CH_3; e R=C_6H_5, R^1=H, R^2=C_2H_5

We have already [1] considered the scheme by which 2,2-dialkoxy-2,3-dihydrofuranes are probably formed for dichlorocyclopropyl ketones. The splitting out of an alcohol molecule from dihydrofuranes IIa-e which contain aryl substituents is apparently due to the increased acidity of the methylene protons of the dihydrofurane ring, because we were unable to synthesize 5-methyl-2-methoxyfurane from 1-acetyl-2,2-dichlorocyclopropane by this method. In the latter case the reaction stopped at the previously described [2] 2-methyl-2,2-dimethoxy-2,3-dihydrofurane.

V. I. Lenin Belorussian State University, Minsk 220080. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1603-1605, December, 1984. Original article submitted February 12, 1984.

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TABLE 1. Properties of Compounds Ic and IIIa-e

Compound	mp, °C	PNR spectrum, ppm (J, Hz)	Found, %		Empirical formula	Calc. %		Yield, %
			C	H		C	H	
Ic	32—33	7,98 (2H, arom.H, d, J=9), 6,84 (2H, d, J=9, arom.H), 3,75 (3H, s, CH_3O), 3,10 (1H, q, J=7, J=10, CH, cyc.), 2,23 (1H, t, J=7, CH_2, cyc.), 1,72 (1H, q, J=7, J=10, CH_2, cyc.)	54,2	3,9	$C_{11}H_{10}O_2Cl_2$	53,9	4,1	66
III a	52—53	7,52—6,62 (5H, m, H arom. H),37 (1H, d, J=3, 4-H), 5,05 (1H, d, J=3, 3-H), 3,76 (3H, s, CH_3O).	76,1	5,9	$C_{11}H_{10}O_2$	75,9	5,7	75
III b	35—36	7,31 (2H, d, J=9, arom. H), 6,96 (2H, d, J=9, arom. H), 6,24 (1H, d, J=3, 4-H), 5,00 (1H, d J=3, 3-H), 3,70 (3H, s, CH_3O), 2,25 (3H, s, CH_3)	76,9	7,8	$C_{12}H_{12}O_2$	76,6	7,7	72
IIIc	47—48	7,33 (2H, d, J=9, arom. H), 6,73 (2H, d, J=9, arom. H), 6,22 (1H, d, J=3, 4-H), 5,03 (1H, d, J=3, 3-H), 3,76 (3H, s, CH_3O arom.), 3,66 (3H, s, CH_3O)	70,4	7,0	$C_{12}H_{12}O_3$	70,6	7,1	68
IIId	—	7,53—6,92 (5H, m, arom. H), 6,23 (1H, s, 4-H), 3,85 (3H, s, CH_3O), 1,82 (3H, s, CH_3)	76,3	7,4	$C_{12}H_{12}O_2$	76,6	7,7	63
IIIe	30—31	7,42—6,90 (5H, m, arom. H), 6,35 (1H, d J=3, 4-H), 5,10 (1H, d., J=3, 3-H), 4,07 (2H, q, J=7, CH_2), 1,41 (3H, t, J=7, CH_3)	76,8	7,5	$C_{12}H_{12}O_2$	76,6	7,7	45

The structure of the alkoxyfuranes IIIa-e was established from their PMR spectra. In the case of the 2,5-disubstituted furanes IIIa-c, e the furane ring protons appear as a typical AX system with spin—spin constant of 3 Hz.

EXPERIMENTAL

PMR spectra were obtained in CCl_4 with Varian HA-100 (100 MHz) or Tesla BS-467 (60 MHz) spectrometers, with TMS as internal standard. The course of the reaction and the purity of the products was monitored by TLC on standard-activity Al_2O_3 II (development with iodine vapor). The properties of the synthesized compounds are shown in Table 1.

1-Aroyl-2,2-dichlorocyclopropanes Ia, b, d were obtained by a known procedure [7].

1-(4-Methoxybenzoyl)-2,2-dichlorocyclopropane Ic was obtained by the procedure of [3], by the reaction of the Grignard reagent from 3.12 g (0.13 mole) Mg and 22.44 g (0.12 mole) p-bromoanisole in 160 ml absolute THF, with a solution of 17.35 g (0.1 mole) of dichlorocyclopropanecarboxyl chloride in 40 ml absolute THF at −78°. After the usual workup and recrystallization from 2-propanol, 16.17 g of ketone Ic was separated.

5-Phenyl-2-methoxyfurane IIIa. A mixture of 2.15 g (0.01 mole) of 1-benzoyl-2,2-dichlorocyclopropane (Ia), 1.0 ml (0.025 mole) of methyl alcohol, and 20 ml of tert-butyl alcohol was added dropwise with stirring to a solution of potassium tert-butylate in tert-butyl alcohol (obtained by dissolving 3.9 g (0.1 mole) of K in 20 ml of tert-butyl alcohol at 15-20°). The mixture was then boiled with stirring for 5 h. tert-Butyl alcohol was distilled off in vacuum. The residue was treated with 50 ml of water and extracted with three 50-ml portions of ether. The ether extracts were dried with sodium sulfate. The ether was distilled off in vacuum and the residue was chromatographed on an Al_2O_3 column. Eluent, hexane. The yield of furane IIIa was 1.31 g.

5-(4-Methylphenyl)-2-methoxyfurane, IIIb, was obtained by the procedure given above from 2.29 g (0.01 mole) of ketone Ib. The yield of IIIb was 1.35 g.

5-(4-Methoxyphenyl)-2-methoxyfurane, IIIc, was obtained by the procedure given above from 2.45 g (0.01 mole) of ketone Ic. The yield of IIIc was 1.39 g.

5-Phenyl-3-methyl-2-methoxyfurane, IIId, was obtained by the procedure given above from 2.29 g (0.01 mole) of ketone Id. The yield of IIId was 1.18 g, n_D^{18} 1.5767.

5-Phenyl-2-ethoxyfurane, IIIe, was obtained by the procedure given above from 2.15 g (0.01 mole) of ketone Ia, 1.46 ml (0.025 mole) of ethanol, 3.9 g (0.1 mole) of K, and 40 ml of tert-butyl alcohol. The yield of IIIe was 0.85 g.

LITERATURE CITED

1. I. G. Tishchenko, O. G. Kulinkovich, Yu. V. Glazkov, and M. K. Pirshtuk, Zh. Org. Khim., 11, 576 (1975).
2. I. G. Tishchenko, O. G. Kulinkovich, and N. V. Masalov, Zh. Org. Khim., 16, 1203 (1980).
3. I. G. Tishchenko, O. G. Kulinkovich, and N. V. Masalov, Synthesis, No. 4, 268 (1982).
4. O. G. Kulinkovich, I. G. Tishchenko, and N. V. Masalov, Khim. Geterotsikl. Soedin., No. 8, 1928 (1983).
5. I. G. Tishchenko, O. G. Kulinkovich, and Yu. V. Glazkov, Zh. Org. Khim., 11, 581 (1975).
6. R. Scarpati, M. L. Graziano, and R. A. Nicolaus, Gazz. Chim. Ital., No. 8, 1317 (1967); Chem. Abstr., 68, 10486 (1968).
7. I. G. Tishchenko, O. G. Kulinkovich, and N. V. Masalov, Zh. Org. Khim., 18, 991 (1982).

REACTION OF ARYLFURANES WITH HYDROGOEN SULFIDE AND HYDROGEN SELENIDE UNDER CONDITIONS OF ACID CATALYSIS

V. G. Kharchenko, S. P. Voronin, T. I. Gubina,
I. A. Markushina, and A. F. Oleinik

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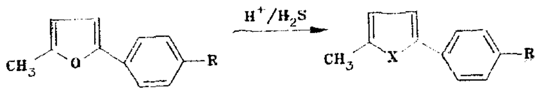
For the first time arylsubstituted furanes have been reacted with hydrogen sulfide and hydrogen selenide under the influence of proton acids. The respective arylthiophenes and arylselenophenes were obtained.

We have previously reported a new addition reaction of furanes with hydrogen sulfide and hydrogen selenide under conditions of acid catalysis, by which dialkylfuranes and furanes containing various functional-group substituents are converted to the respectively theophene and selenophene analogs [1-3].

The present work is a study of the application of this reaction to a new group of furanes, viz., arylfuranes of various structures. According to our data, arylfuranes I-V react with hydrogen sulfide and hydrogen selenide under conditions of acid catalysis to form the respective thiophenes and selenophenes:



I-V   VI-XIV

I, VI, XI R=H; II, VII, XII R=CH_3; III, VIII R=OCH_3; IV, IX, XIII R=Cl; V, X, XIV R=Br; VI—X X=S; XI—XIV X=Se

When the reaction is carried out in a medium of concentrated acid (HCl, $HClO_4$, CF_3COOH), in addition to the desired products, the products of the hydrolytic cleavage of the furanes are also separated from the reaction mixture, viz., the respective 1,4-dicarbonyl compounds [2, 3]. Therefore in this work we used as acid component a 2-3.2 M solution of dry hydrogen chloride in absolute ethyl alcohol.

With the reaction of 2-methyl-5-p-tolylfurane with hydrogen sulfide as an example, the optimum process conditions were developed. The results are shown in Table 1. The best yields of desired product were obtained at 50° and 3.2 M hydrogen chloride.

Conversion of arylfuranes I-V to the respective arylthiophenes VI-X and arylselenophenes XI-XIV was carried out under similar conditions. The yields of desired products were 50-75%. We established that conversion of I-V requires 10-50 h, as compared with 1-1.5 h for the 2,5-dialkylfuranes. This is probably related to the different electron densities in the heterocycle due to the substituents.

N. G. Chernyshevskii Saratov State University, Saratov 410601. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1606-1608, December, 1984. Original article submitted May 12, 1983; revision submitted August 17, 1983.