

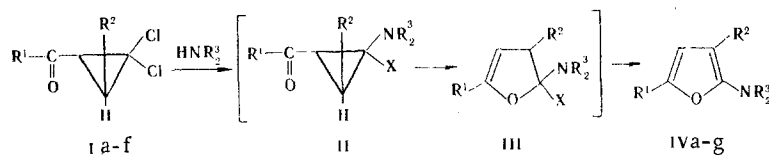
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The corresponding 5-aryl-2-alkylaminofurans were obtained in good yields by the reaction of 1-aryl-2,2-dichlorocyclopropanes with diethylamine, morpholine, and piperidine.

In view of their low stabilities, the synthesis of aminofurans that do not contain electron-acceptor substituents in the heterocyclic ring presents definite difficulties [1]. We have previously reported the formation of 5-phenyl-2-diethylaminofuran (IVa) by the reaction of 1-benzoyl-2,2-dichlorocyclopropane (Ia) with diethylamine [2]. Inasmuch as convenient methods for the synthesis of various 1-acyl-2,2-dichlorocyclopropanes have been developed [3, 4], it seems of interest to ascertain the possibility of the utilization of the indicated transformation as a general method for the preparation of substituted 2-dialkylaminofurans.

5-Aryl-2-dialkylaminofurans IVa-g are formed in good yields when solutions of 1-aryl-2,2-dichlorocyclopropanes Ia-g are heated with secondary amines at 50-60°C. The products are unstable in air; however, because of their high chromatographic mobilities, they can be readily isolated in the individual state from the reaction mixtures by means of column chromatography.



I-IV a $\text{R}^1 = \text{C}_6\text{H}_5$, $\text{R}^2 = \text{H}$, $\text{R}^3 = \text{C}_2\text{H}_5$; b $\text{R}^1 = p\text{-CH}_3\text{C}_6\text{H}_4$, $\text{R}^2 = \text{H}$, $\text{R}^3 = \text{C}_2\text{H}_5$; c $\text{R}^1 = 2,4,6\text{-(CH}_3)_3\text{C}_6\text{H}_2$, $\text{R}^2 = \text{H}$, $\text{R}^3 = \text{C}_2\text{H}_5$; d $\text{R}^1 = m\text{-NO}_2\text{C}_6\text{H}_4$, $\text{R}^2 = \text{H}$, $\text{R}^3 = \text{C}_2\text{H}_5$; e $\text{R}^1 = \text{C}_6\text{H}_5$, $\text{R}^2 = \text{CH}_3$, $\text{R}^3 = \text{C}_2\text{H}_5$; f $\text{R}^1 = \text{C}_6\text{H}_5$, $\text{R}^2 = \text{H}$, $2\text{R}^3 = (\text{CH}_2)_5$; g $\text{R}^1 = \text{C}_6\text{H}_5$, $\text{R}^2 = \text{H}$, $2\text{R}^3 = (\text{CH}_2)_2\text{O}(\text{CH}_2)_2$

In addition to aminofurans IVf,g, β -benzoylpropionic acid piperidide and morpholide were isolated in 45 and 50% yields, respectively, in the reaction of ketone Ia with piperidine and morpholine under similar conditions [1]. An increase in the reaction time and carrying out the reaction at higher temperatures had virtually no effect on the ratios of the resulting aminofurans and amides. Let us note that we have previously observed the ability of 1-acyl-2,2-dichlorocyclopropanes to undergo conversion to dialkylamides of γ -keto carboxylic acids in high yields as a result of their reaction with secondary amines in an aqueous ethanol medium and established that gem-dichlorocyclopropyl ketones that have a labile hydrogen atom in the cyclopropane ring in the α position relative to the carbonyl group undergo the reaction [4].

The conversion of ketones I to furans IV probably proceeds via nucleophilic substitution of the chlorine atoms through a step involving dehydrohalogenation [5] with the intermediate formation of cyclopropyl ketones II ($\text{X} = \text{Cl}$ or NR_2^3). Opening of the activated (by acyl and dialkylamino groups) three-membered ring in ketones II and subsequent intramolecular cyclization lead to dihydrofurans III ($\text{X} = \text{Cl}$ or NR_2^3), which are direct precursors of furans IV. The formation of β -benzoylpropionic acid amides in the reaction of ketone Ia with morpholine and piperidine is possibly the result of hydrolysis of dihydrofurans IIIf,g ($\text{X} = \text{NR}_2^3$) during workup of the reaction mixtures.

Dialkylaminofurans IVa-c can be obtained in somewhat lower yields also by refluxing solutions of 1-aryl-2,2-dichlorocyclopropanes Ia-c and diethylamine in tetrahydrofuran (THF) (see Table 1). At the same time, we were unable to extend this reaction to 1-alkanoyl-2,2-

TABLE 1. Characteristics of the Synthesized 5-Aryl-2-dialkylaminofurans IVa-e

Compound	n_D^{20}	PMR spectrum, ppm	Found, %			Empirical formula	Calc., %			Yield, % ^a
			C	H	N		C	H	N	
IVa	1,5723 ^b	7,50-6,90 (5H, m, Ar); 6,43 (1H, d, $J=3$ Hz, 4-H); 4,90 (1H, d, $J=3$ Hz, 3-H); 3,20 (4H, q, $J=7$ Hz, 2CH ₂); 1,10 (6H, t, $J=7$ Hz, 2CH ₃)	78,3	8,1	6,3	C ₁₄ H ₁₇ NO	78,1	8,0	6,5	70
IVb	1,5598	7,30 (2H, d, $J=9$ Hz, Ar); 6,97 (2H, d, $J=9$ Hz, Ar); 6,66 (1H, d, $J=3$ Hz, 4-H); 4,90 (1H, d, $J=3$ Hz, 3-H); 3,25 (4H, q, $J=7$ Hz, 2CH ₂); 2,30 (3H, s, p -CH ₃); 1,13 (6H, t, $J=7$ Hz, 2CH ₃)	78,3	8,5	5,9	C ₁₅ H ₁₉ NO	78,6	8,4	6,1	75
IVc	1,5405	6,78 (2H, s, Ar); 6,65 (1H, d, $J=3$ Hz, 4-H); 4,96 (1H, d, $J=3$ Hz, 3-H); 3,15 (4H, q, $J=7,6$ Hz, 2CH ₂); 2,25 (6H, s, 2CH ₃); 2,18 (3H, s, CH ₃); 1,30 (6H, t, $J=7$ Hz, 2CH ₃)	79,1	9,3	5,7	C ₁₇ H ₂₃ NO	79,3	9,0	5,5	81
IVd	1,6123	8,15-8,06 (1H, m, Ar); 7,88-7,51 (2H, m, Ar); 7,32 (1H, t, $J=8$, Ar); 6,65 (1H, d, $J=3$ Hz, 4-H); 4,98 (1H, d, $J=3$ Hz, 3-H); 3,15 (4H, q, $J=7$ Hz, 2CH ₂); 1,22 (6H, t, $J=7$ Hz, 2CH ₃)	60,4	5,5	10,2	C ₁₄ H ₁₆ N ₂ O ₃	60,0	5,7	10,0	50 ^c
IVe	1,5462	7,55-7,03 (5H, m, Ar); 6,32 (1H, s, 4-H); 2,98 (4H, q, $J=7$ Hz, 2CH ₂); 1,73 (3H, s, 3-CH ₃); 0,98 (6H, t, $J=7$ Hz, 2CH ₃)	78,9	8,2	6,3	C ₁₅ H ₁₉ NO	78,6	8,4	6,1	70

^aThe yields of aminofurans IVa-c were, respectively, 52, 42, and 30% when solutions of 10 mmole of ketones Ia-c and 50 mmole of diethylamine in 10 ml of dry THF were refluxed for 8 h. ^bAt 17°C. ^cIn the case of refluxing for 1 h.

dichlorocyclopropanes. Under the investigated conditions the corresponding dialkylaminofurans were formed in only trace amounts; this is possibly associated with the lower lability of the allylic hydrogen atom of the dihydrofuran ring in intermediate III.

The structures of the compounds obtained were established on the basis of the results of elementary analysis and data from the PMR spectra.

EXPERIMENTAL

The PMR spectra of solutions of the compounds in CCl₄ were recorded with a Varian HA-100 or Tesla BS-467 (60 MHz) spectrometer with tetramethylsilane as the internal standard. The course of the reaction and the purity of the compounds obtained were monitored by means of thin-layer chromatography (TLC) on activity II Al₂O₃ (development with iodine vapors).

The 1-aryl-2,2-dichlorocyclopropanes were obtained by the method in [3].

1-(m-Nitrobenzoyl)-2,2-dichlorocyclopropane (Id). A mixture of 8 ml of fuming HNO₃ and 12 ml of concentrated H₂SO₄ was added dropwise with vigorous stirring to a solution of 21.5 g (0.1 mole) of ketone Ia in 30 ml of concentrated H₂SO₄ while maintaining the temperature at -15 to -20°C, after which the mixture was stirred at this temperature for 20 min. It was then heated up to -5°C and poured into a mixture of 150 g of ice with 300 ml of water, and the aqueous mixture was extracted with ether (three 100-ml portions). The ether extracts were washed with a saturated solution of sodium bicarbonate and dried with sodium sulfate. The solvent was removed by distillation, and the residue was recrystallized from ethanol to give 13.5 g (54%) of ketone Id with mp 75-76°C. PMR spectrum: 7.90-8.81 (4H, m, Ar), 3.34 (1H, q, 1-H, $J=7$ and 10 Hz), 2.39 (1H, t, 3-H, $J=7$ Hz), and 2.02 ppm (1H, q, 3-H, $J=7$ Hz). Found: C 41.5; H 2.9; N 5.3%. C₁₀H₇Cl₂NO₃. Calculated: C 41.2; H 2.7; N 5.4%.

General Method for the Preparation of 5-Aryl-2-dialkylaminofurans (IVa-g). A solution of 10 mmole of ketone I in 25 ml of the corresponding secondary amine was heated at 50-60°C

for 4 h, after which the excess amine was removed with a rotary evaporator, the residue was treated with 100 ml of ether, and the precipitated amine hydrochloride was removed by filtration. The solvent was removed *in vacuo*, and the residue was chromatographed with a column packed with Al_2O_3 in hexane. The characteristics of the compounds obtained are presented in Table 1.

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RING-CHAIN TAUTOMERISM AND THERMO- AND PHOTOCHROMISM OF

3-(1-HYDROXY-4-METHYL-2-NAPHTHYL)PROPENAL IMINES*

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A series of previously undescribed 3-(1-hydroxy-4-methyl-2-naphthyl)propenal imines was synthesized. In the crystalline state all of the imines, except the N-(p-nitrophenyl)imine, have an open o-quinoid structure, whereas in solutions in nonpolar solvents they exist in the cyclic 2H-chromene form. In polar solvents the imines display ring-chain tautomeric equilibrium of the 2H-chromene and o-quinoid forms, the relative percentages of which are determined by the character of the substituent in the amino component of the molecule and by the polarity of the solvent. The N-(p-nitrophenyl)imine has the 2H-chromene structure in the solid phase and in solvents.

We have previously shown that 3-(2-hydroxy-1-naphthyl)propenal N-arylimines have the cyclic 2H-chromene structure in the crystalline state, whereas the N-alkylimines have an open quinoid structure [2]. In solutions in nonpolar solvents all of the imines exist in the form of cyclic structures, whereas in polar solvents one observes the establishment of a ring-chain tautomeric equilibrium between the 2H-chromene and quinoid forms, the relative percentages of which are determined by the polarity of the solvent and the character of the substituent in the amino component of the molecule, is established in polar solvents [2, 3]. The photo- and thermochromic properties of these compounds have been studied [3].

In the present paper we present the results of a study of the structure of the previously undescribed 3-(1-hydroxy-4-methyl-2-naphthyl)propenal imines; we also studied their equilibrium thermal and phototransformations. We described the preparation of 3-(1-hydroxy-4-methyl-2-naphthyl)propenal in [4] and the 3-(1-hydroxy-4-methyl-2-naphthyl)propenal imines by the reaction of the aldehyde and the corresponding amines in ethanol. Their crystals had the deep dark-violet or bright-red color that is characteristic for conjugated quinoid structures of the B type. Only V, the crystals of which are light yellow, constitutes an exception.

*Communication 14 from the series "Photochromic and thermochromic spirans." See [1] for communication 13.