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SYNTHESIS AND PROPERTIES OF AZOMETHINES OF THE PYRAN SERIES

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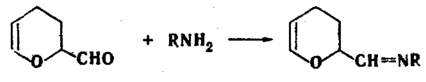
UDC 547.811'791.07

2-Formyl-Δ^5-dihydropyran reacts with amines to give azomethines. Δ^2-Triazolines are formed in the reaction of azomethines containing aromatic substituents with diazomethane. The structures of the compounds obtained were proved by means of UV and PMR spectroscopy.

Continuing our research on pyran compounds [1, 2], we studied the reactions of 2-formyl-Δ^5-dihydropyran I with amines. Azomethines II-IV (Table 1) are formed as a result of the reaction of I with allylamine, aniline, and p-bromoaniline. When azomethines III and IV are allowed to stand, they are converted to dimers V and VI. Azomethine II is stable during storage. Compound I reacts immediately with p-nitroaniline and anthranilic acid to give dimers VII and VIII.



I II-IV

II R=CH_2=CH—CH_2; III R=C_6H_5; IV R=p-BrC_6H_4

The data from the PMR and UV spectra (Table 2) are in agreement with the proposed structures of the compounds obtained. The UV spectra of I and II provide evidence for the transparency of the groupings entering into them in the near-UV region. The weak absorption at 346 nm in the spectrum of azomethine II, which in all likelihood is associated with the n → π* transition of the C=N bond, cannot be used for identification purposes in view of the very low intensity of the band. On the basis of this, the absorption observed in the spectra of the azomethine derivatives should be associated with the aryl fragment of the molecule, while the absorption bands of III at λ_{max} 242 and 285 nm can be regarded as the K and B bands of benzene (π → π*). The sensitivity of the bands to para substitution in the benzene ring (IV, VI, and VII) constitutes evidence in favor of this interpretation. The considerable bathochromic shift of the K and B bands of III as compared with benzene ($\Delta\lambda$ = 38 and 31 nm, respectively) and the smoothing out of the fine vibrational structure of the B band of benzene provide evidence for significant conjugation of the phenyl ring with the free electron pair of the nitrogen atom.

As expected, the intensities of the bands in the UV spectra of dimers V and VI are approximately doubled, while λ_{max} changes only slightly (2-6 nm).

It is well known that azomethines add diazomethane upon prolonged standing in the presence of water or methanol [4-6]. We carried out the addition of diazomethane to III and IV

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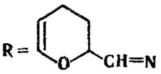
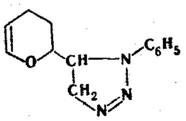
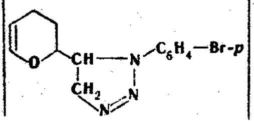
TABLE 1. Azomethines of the Pyran Series and Their Derivatives



№	Compound	bp, °C (mm) or mp, °C	Found, %				Empirical formula	Calc., %				Yield, %
			C	H	Br	N		C	H	Br	N	
II*	R—CH₂—CH=CH₂	100—102 (20)	71,3	8,4	—	9,2	$C_9H_{13}NO$	71,5	8,7	—	9,2	56
III	R—C₆H₅	163—164 (17)	76,6	7,0	—	7,2	$C_{12}H_{13}NO$	77,0	7,0	—	7,5	52,6
IV	R—C₆H₄—Br-*p*	129—131 (1)	53,8	4,3	—	5,5	$C_{12}H_{12}BrNO$	54,1	4,5	—	5,3	60,6
V	(R—C₆H₅)₂	156—157	76,6	6,9	—	7,5	$C_{12}H_{13}NO$	77,0	6,9	—	7,5	52
VI	(R—C₆H₄—Br-*p*)₂	157—159	54,4	4,5	29,1	5,3	$C_{12}H_{12}BrNO$	54,1	4,5	30,1	5,3	50
VII	(R—C₆H₄—NO₂)₂	208—210	61,8	5,0	—	11,8	$C_{12}H_{12}N_2O_3$	62,1	5,2	—	12,1	75
VIII	(R—C₆H₄—COOH-*o*)₂	97—98	67,4	5,4	—	5,8	$C_{13}H_{13}NO_3$	67,5	5,7	—	6,0	80,2
IX		118—119	68,0	6,7	—	18,3	$C_{13}H_{15}N_3O$	68,1	6,6	—	18,3	66
X		146—146,5	50,9	4,5	26,3	13,7	$C_{13}H_{14}BrN_3O$	50,6	4,5	26,0	13,6	45,4

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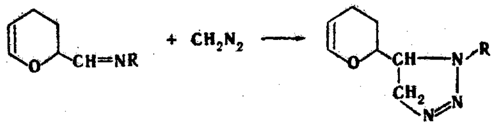
*This compound had n_D^{20} 1.4830, d_4^{20} 0.9656, MR_DH 44.70, and MR_DB 45.03.

TABLE 2. Spectral Characteristics of Azomethines and Their Derivatives

Compound	UV spectrum, λ_{max}, nm (log ε)	PMR spectrum, δ, ppm							
		pyran ring				$\mathrm{C}\genfrac{}{}{0pt}{}{\diagup O}{\diagdown H}$	CH=N	4-CH₂ and 5-H of triazoline ring	Ar
		3CH₂, 4CH₂	2-H	5-H	6-H				
I	>200	1,98 d	4,08 t	4,7 d	6,28 d	9,22			
II	>200, 346 (0,72)	1,98 d	4,2 t	4,6 t	6,2 d		7,45 two t		
III	>200, 242 (4,01), 285 (3,44)	2 d	4,45—4,8 m		6,24 d		7,95 d		7,2
IV	>200, 252 (4,22), 297 (3,46)	2 d	4,4—4,8 m		6,4 d		7,9 d		6,8—7,2
V	>200, 248 (4,28), 289 (3,85)								
VI	>200, 256 (4,39), 299 (3,82)								
IX	>200, 286 (4,14), 302 (4,08), sh 217 (4,22), sh 234 (4,01)	1,8 d			6,18 d			3,8—4,6 m	6,8—7,2
X	>200, 292 (4,17), 313 (4,02), sh 293 (3,94)	1,8 d			6,2 d			3,85—4,8 m	7,2

and isolated 1,2,3-Δ^2-triazolines of the pyran series (IX and X). The reactions take place in less than 15 h without a catalyst.



IX $R=C_6H_5$; X $R=p\text{-}BrC_6H_4$ IX, X

On the basis of the PMR spectra, Kadaba [5] demonstrated that diazomethane adds to azomethines with heterocyclic groupings to give 1,2,3-Δ^2-triazolines. Nucleophilic attack by the carbon atom of diazomethane on the carbon atom of the azomethine occurs during the reaction. The PMR spectra of the triazolines contain an ABC system of the three protons in the 4 and 5 positions of the triazoline ring at 4.6-5.0 ppm [5]. A study of the chemical shifts of the triazolines of the pyran series shows a similar picture, viz., an ABC system at 3.8-4.8 ppm (Table 2). The PMR spectrum of 3,4-phenyl-1,2,3-Δ^2-triazoline (XI) also contains an ABC system at 4.0-4.8 ppm.

The absorption bands in the UV spectra of the triazolines are shifted to even higher λ values; this may also be associated with an increase in the length of the conjugation chain. Replacement of the pyran ring in IX by a phenyl ring does not give rise to a substantial change in the spectral picture.

EXPERIMENTAL

The PMR spectra of the compounds were recorded with a Varian T-60 spectrometer (60 MHz) with tetramethylsilane as the internal standard. The UV spectra of absolute ethanol solutions of the compounds [$(3-7)\cdot 10^{-3}$ mole/liter] were recorded with a Specord UV-vis spectrophotometer.

2-Formyl-Δ^5-dihydropyran (I). It was formed by condensation of acrolein in benzene and had bp 54°C (22 mm) and n_D^{20} 1.4651 [bp 50-52°C (20 mm) and n_D^{20} 1.4655 [7]].

N-(2-Δ^5-Dihydropyranyl)methylene-N-allylamine (II). A 10-g (0.08 mole) sample of 2-formyl-Δ^5-dihydropyran I was added dropwise to a cooled (with cold water) solution of 5.08 g (0.08 mole) of allylamine in benzene at such a rate that the temperature did not rise above 30°C, after which the mixture was refluxed for 1 h and distilled.

N-(2-Δ^5-Dihydropyranyl)methyleneaniline III and N-(2-Δ^5-dihydropyranyl)methylene(p-bromoaniline) IV were similarly obtained.

N-(2-Δ^5-Dihydropyranyl)methyleneaniline Dimer (V). When II was allowed to stand, it was converted to the dimer. The latter, which was obtained as a white powder, was washed thoroughly with ether and analyzed.

The dimer of N-(2-Δ^5-dihydropyranyl)methylene(p-bromoaniline) (IV) was similarly obtained.

N-(2-Δ^5-Dihydropyranyl)methylene(p-nitroaniline) Dimer (VII). An 11.9-g (0.1 mole) sample of I was added to a solution of 14.6 g (0.1 mole) of p-nitroaniline in ether. Crystals precipitated when the mixture was stirred. Dimer VIII was similarly obtained.

3-Phenyl[4-(2-Δ^5-dihydropyranyl)]-1,2,3-Δ^2-triazoline (IX). A solution of 8 g (0.04 mole) of N-(2-Δ^5-dihydropyranyl)methyleneaniline II in 30 ml of diethyl ether was added at −5°C to 100 ml of an ether solution of diazomethane obtained from 20.6 g (10.2 mole) of nitrosomethylurea. The next day, the ether was removed by distillation. Triazoline X was similarly obtained.

3,4-Diphenyl-1,2,3-Δ^2-triazoline (XI). It was formed by the method in [4] and had mp 131-132°C (mp 130-131°C [4]).

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FUNCTIONAL DERIVATIVES OF THIOPHENE.

17.* SYNTHESIS OF THIENYLHYDRAZINE DERIVATIVES

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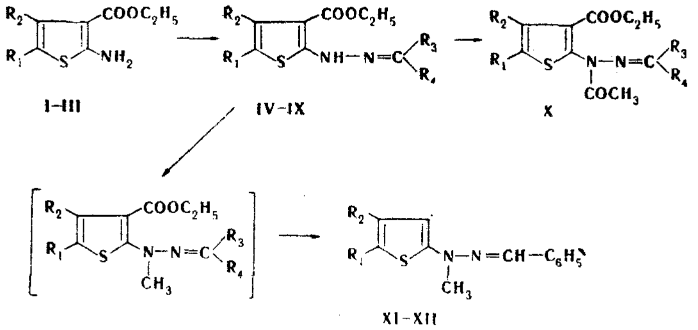
Substituted thienylhydrazones of aromatic aldehydes and cyclohexanone were obtained. It is shown that the sodium salts of the latter are readily acylated and alkylated. The hydrolysis of carbethoxythienylmethylhydrazones of benzaldehyde in alkaline media is accompanied by decarboxylation.

The diazotization of aminothiophene derivatives I-III was carried out by a previously proposed method [2]. The resulting diazonium salts were reduced without isolation with sodium hydrosulfite, after which aqueous suspensions of the products were treated with benzene solutions of aldehydes or ketones. As a result of this reaction, thienylhydrazones (IV-IX) of aldehydes and ketones were obtained. During a study of the properties of benzaldehyde thienylhydrazones it was shown that the latter readily form sodium salts under the influence of sodium methoxide. The sodium salt of benzaldehyde thienylhydrazone V is converted to benzaldehyde N-acetylthienylhydrazone (X) on reaction with acetyl chloride. Hydrolysis of the acetyl group rather than the carbethoxy group, as described in the hydrolysis of ethyl 2-acylaminothiophene-3-carboxylates [3], is observed when X is heated in an alkaline medium, and V is formed. The action of methyl iodide on the sodium salts of IV and V gave N-methyl derivatives, which were subjected to alkaline hydrolysis and decarboxylation without isolation. As a result, benzaldehyde N-methylthienylhydrazones (XI, XII) with a free 4 position were obtained.



I, IV, XI $R_1=R_2=CH_3$; II, V, VI, VII, X, XII $R_1=CH_3$, $R_2=C_6H_5$; III, VIII, IX $R_1+R_2=(CH_2)_4$; IV, V, VIII, X $R_3=H$, $R_4=C_6H_5$; VI, IX $R_3=H$, $R_4=p\text{-}C_6H_4NO_2$; VII $R_3+R_4=(CH_2)_5$

EXPERIMENTAL

Thienylhydrazones of Benzaldehyde (IV, V, and VIII), p-Nitrobenzaldehyde (VI and IX), and Cyclohexanone (VII). A solution of 2.7 g (40.5 mole) of sodium nitrite in 10 ml of water was added dropwise with stirring and cooling to –5°C to a solution of 40 mmole of I-III in a mixture of 90 ml of acetic acid and 30 ml of concentrated HCl, and the mixture was allowed to stand in an ice bath for 30 min. It was then poured into a well-stirred suspension

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*See [1] for Communication 16.

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