CHEMISTRY OF OXALYL DERIVATIVES OF METHYL KETONES.

V.* REACTION OF AROYLPYRUVIC ACIDS AND THEIR DERIVATIVES WITH o-AMINOTHIOPHENOL

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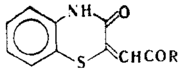
It was established by IR, UV, and PMR spectroscopy that 2-phenacylidenebenzo-1,4-thiazin-3-ones are formed in the reaction of o-aminothiophenol with aroylpyruvic acids or 5-arylfuran-2,3-diones. 2-Carbomethoxy-2-phenacyl-1,3-benzothiazolines were isolated in the reaction of o-aminothiophenol with aroylpyruvic acid esters.

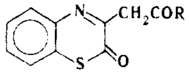
Aroylpyruvic acids react with o-phenylenediamine [2] to give 3-phenacylidine-2-quinoxalones and with o-aminophenol to give 3-phenacylidenebenz-2H-1,4-oxazin-2-ones. It has been established by means of PMR spectroscopic methods that the double bond in the latter is not located in the ring, as previously assumed, but is shifted to the exo position [3].

In connection with research on the peculiarities of the structures of heterocycles containing phenacyl substituents, it seemed of interest to us to study the reaction of aroylpyruvic acids (I) and their esters (II), as well as 5-arylfuran-2,3-diones (III), which can be considered to be α-lactones of enol form I, with o-aminothiophenol (IV).

Cyclic products were isolated when the reaction between I and IV was carried out in refluxing toluene or dioxane for 1 h. The IR spectroscopic data and the results of functional analysis provide evidence for the absence of a free carboxyl group in the reaction products, and this repudiates the alternative benzothiazepinone structure. In the case of cyclization to give benzothiazinones the products may have one of the following structures:



A



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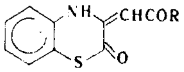

C

TABLE 1. Physical Constants of Va-g

Compound	mp, °C	Found, %					Empirical formula	Calc., %					Synthetic method	Yield, %
		C	H	Hal	N	S		C	H	Hal	N	S		
Va	190—191	67,9	3,7	—	4,7	10,7	$C_{16}H_{11}NO_2S$	68,3	3,9	—	4,9	10,7	A B	72 93
Vb	183—184	69,2	4,3	—	4,7	10,4	$C_{17}H_{13}NO_2S$	69.1	4,4	—	4,7	10,9	A B	75 76
Vc	177—178	65,3	3,9	—	4,8	10,0	$C_{17}H_{13}NO_3S$	65,5	4,1	—	4,5	10,2	A B	73 98
Vd	167—168	69,6	5,0	—	4,7	10,1	$C_{18}H_{15}NO_2S$	69,9	4,8	—	4,5	10,3	A	77
Ve	180—181	64,1	2,8	11,5	4,3	10,6	$C_{16}H_{10}ClNO_2S$	64,6	3,1	11,3	4,5	10,5	A	89
Vf	184—185	56,3	2,9	23,1	4.0	9,4	$C_{16}H_{10}BrNO_2S$	56,6	2,7	23,0	4,0	9,1	A B	74 78
Vg	191—192	67,9	3,7	6,0	5,2	10,8	$C_{16}H_{10}FNO_2S$	68,2	3,3	6,3	5,4	10,8	A	82

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*See [1] for communication IV.

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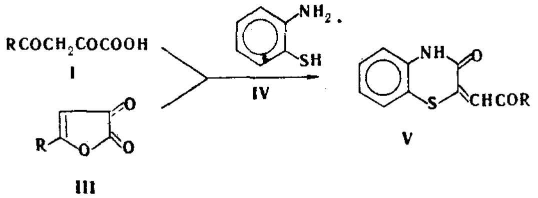
TABLE 2. Physical Constants of VIa-d

Compound	mp, °C	Found, %		Empirical formula	Calc., %		Yield, %
		N	S		N	S	
VIa	159—160	5,0	10,2	$C_{17}H_{15}O_3NS$	4,6	10,2	98
VIb	146—147	4,4	10,1	$C_{18}H_{17}O_3NS$	4,2	9,9	86
VIc	151—152	4,1	9,2	$C_{18}H_{17}O_4NS$	4,0	9,3	85
VId	148—149	4,0	9,3	$C_{17}H_{13}ClNO_3S$	4,0	9,2	91

Bands at 3330-3340 cm^{-1} (NH stretching vibrations) and 1655-1670 cm^{-1} (C=O stretching vibrations) are present in the IR spectra of the cyclization products. The position of the latter band is very close to that of the carbonyl absorption in the spectrum of 2-quinolone [4] and is not in agreement with the literature data for 1-thia-2-coumarones (1620-1640 cm^{-1}), and this makes it possible to exclude structure B.

The long-wave maximum in the UV spectra of the cyclic products is found at 240-260 nm. A comparison with the UV spectra of 3-phenacylidene-2-quinoxalone (440 nm) and 3-phenacylidenebenz-1,4-oxazin-2-one (420 nm) shows that replacement of the nitrogen or oxygen atoms in these heterocycles by a sulfur atom leads to a sharp hypsochromic shift of the long-wave maximum. As a consequence of the fact that transmission of the electronic effects in structure C, on the one hand, and in phenacylidenequinoxalones and phenacylidenebenzoxazinones, on the other, should be realized via analogous bonds, the position of the long-wave maximum should not differ substantially. In structure A, because of the less complete transmission of electronic interactions through the sulfur atom, one should expect a considerable hypsochromic shift of the chief absorption maximum, and this is observed for the investigated products.

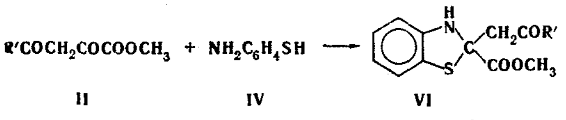
When one equivalent of sodium ethoxide is added to an alcohol solution of the cyclization product, an additional maximum at 342-355 nm due to interaction of the phenacylidene substituent with the condensed benzene ring because of enolization of the amide carbonyl group (structure A) appears. Thus, the IR and UV spectroscopic data provide evidence that the products of cyclization of I are 2-phenacylidenebenzo-1,4-thiazin-3-ones (V, Table 1, method A).



Va R=C_6H_5; b R=p-$CH_3C_6H_4$; c R=p-$CH_3OC_6H_4$; d R=p-$C_2H_5C_6H_4$; e R=p-ClC_6H_4; f R=p-BrC_6H_4; g R=p-FC_6H_4

Thiazinones V were also obtained in higher yields by reaction of III and IV in dioxane at room temperature (Table 1, method B). Structure V is indirectly confirmed by the fact that amines readily cleave the ring of III to give amides I, whereas thiophenols are not capable of bringing about this sort of cleavage.

2-Carbomethoxy-2-phenacyl-1,3-benzothiazolines (VIa-d, Table 2) were obtained by reaction between esters II and IV.



VI a R'=C_6H_5; b R'=p-$CH_3C_6H_4$; c R'=p-$CH_3OC_6H_4$; d R'=p-ClC_6H_4

The IR spectra of the reaction products contains bands at 1740-1745 cm^{-1} (stretching vibrations of an ester carbonyl group) and 3340-3350 cm^{-1} (stretching vibrations of an NH group). The long-wave absorption maximum in the UV spectrum is found at 256-283 nm. The PMR spectra contains the signals of three protons of the methyl group in the $COOCH_3$ residue (δ 2.35 ppm) and of two equivalent protons of the methylene group of the phenacyl group (3.85 ppm) and a multiplet at 7.66 ppm corresponding to the nine protons of the benzene rings.

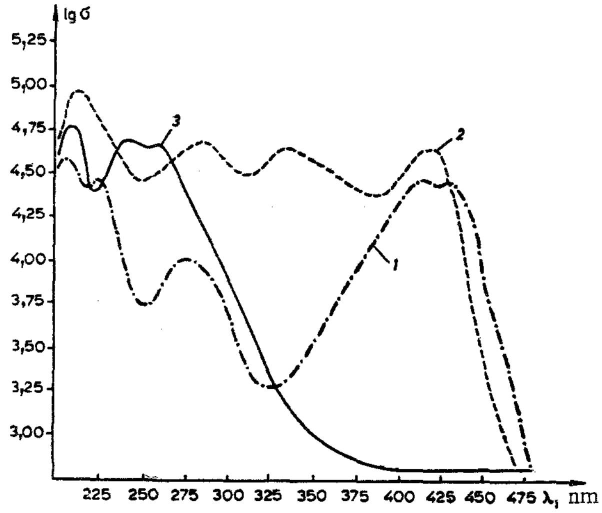


Fig. 1. UV spectra in ethanol: 1) 3-phenacylidenequinoxalzone; 2) 3-phenacyclidene-1,4-benzoxazin-2-one; 3) 2-phenacylidene-1,4-benzothiazin-3-one.

EXPERIMENTAL

The PMR spectra of the 2-carbomethoxy-2-phenacyl-1,3-benzothiazolines were recorded with an RS-60 spectrometer with hexamethyldisiloxane as the internal standard. The UV spectra of alcohol solutions of the compounds (10^{-4} M) were recorded with a Specord UV-vis spectrophotometer. The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer.

2-Phenacylidenebenzo-1,4-thiazin-3-ones (Va-g). A) A mixture of equivalent amounts of I and IV was refluxed in toluene or dioxane for 1 h, after which the solvent was evaporated, and the residue was recrystallized from isopropyl alcohol.

B) Furandiones III were subjected to the action of IV in dioxane at room temperature. After removal of the solvent, the product was recrystallized from isopropyl alcohol.

2-Carbomethoxy-2-phenacyl-1,3-benzothiazolines (VIa-d). A mixture of equivalent amounts of aroylpyruvic acid ester II and IV was fused at 120° for 1.5 min, and the product (VI) was recrystallized from acetonitrile.

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