2,3-DIPHENYL-1,2,3-TRIAZOLO[1,5-a]PYRIMIDINIUM SALTS

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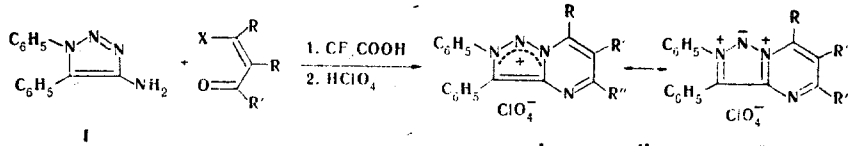
2,3-Diphenyl-1,2,3-triazolo[1,5-a]pyrimidinium salts, the structure of which was confirmed by the PMR spectra, were obtained by condensation of 4-amino-1,5-diphenyl-1,2,3-triazole with β-diketones and their analogs in trifluoroacetic acid. The corresponding 4-acylvinylaminotriazoles are formed by the action of alkali on these salts. It was established that the salts with a methyl group in the 7 position do not form polymethine dyes, whereas the 5,7-dimethyl derivative does gives dyes owing to the activity of the methyl group in the 5 position. The ability of the 5,7-dimethyl derivative to undergo cyanine condensations is explained by the betaine cationic structures of the salts obtained.

The annelation of the pyrimidinium ring by condensation of protonated β-amino nitrogen heterocycles with β-diketones and their analogs has been investigated rather extensively. As a rule, α-amino derivatives, which are capable of lactim–lactam tautomerism, are used in this reaction, and pyrimidinium salts with active methyl groups in the α and γ positions with respect to the quaternary bridge nitrogen atom are formed. The only examples of amines of another type, which are incapable of the indicated tautomerism, is 4-amino-2,5-diphenylthiazole, which undergoes the condensation under consideration to give thiazolo[3,4-a]pyrimidinium salts that are incapable of undergoing cyanine condensations [1].

In the present research we investigated the condensation of 1-substituted 4-amino-1,2,3-triazole with β-diketones and their analogs in acidic media in order to obtain derivatives of the previously unknown 1,2,3-triazolo[1,5-a]pyrimidinium cation, which can be classified as a betaine cation [2]. 4-Amino-1,5-diphenyl-1,2,3-triazole (I), which is a nontautomeric amine, was used as the starting amine. It reacts in trifluoroacetic acid with β-diketones, β-chlorovinyl ketones or aldehydes, and formylacetone acetal to give 1,2,3-triazolo[1,5-a]pyrimidinium derivatives (IIa-i).

The structure of IIc-i and the direction of the reaction of amine I with unsymmetrical carbonyl components were established by means of the PMR spectra. Benzoylacetone undergoes this condensation to give a mixture of isomers IIc and IId in a ratio of 3:1 when the reaction is carried out in concentrated solution and when the components are heated on a water bath, as indicated in the experimental section.



I A II Б

II a R=R″=CH₃, R′=H; b R=R″=C₆H₅, R′=H; c R=CH₃, R′=H, R″=C₆H₅; d R=C₆H₅, R′=H, R″=CH₃; e R=CH₃, R′=R″=H; f R=R′=H, R″=CH₃; g R=C₆H₅, R′=R″=H; h R=R′=CH₃, R″=H; i R=H, R′=R″=CH₃; j R=CH₃, R′=H, R=*p*-dimethylaminostyryl; k R=CH₃, R′=H, R=3-(3methylbenzoxazolinylidene)-1,3-propanedienyl; X=OH, Cl

Only one isomer (IIc) is formed in a doubly diluted (with trifluoroacetic acid) solution without heating. The ratio of the isomers in the reaction mixture was determined from the ratio of the signals of the methyl groups at 2.72 and 2.57 ppm, which belong to the 7-CH_3 and 5-CH_3 groups, respectively (for IIa, δ7-CH_3 = 2.70 ppm, and δ5-CH_3 = 2.52 ppm). The assignment of these signals was made in analogy with other pyrimidinium salts [3]. In addition, the position of the substituents in salt IIc is confirmed by the character of the signal of the phenyl substituent bonded to the pyrimidine ring, which give two groups of

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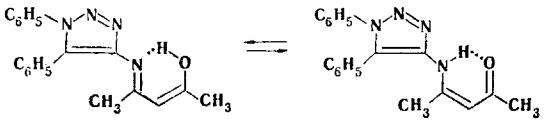
bands with a distance of no less than 0.5 ppm between them: this is characteristic for 5-C_6H_5 [4] (the phenyl substituents bonded to the triazole ring give signals at 7.2-7.3 ppm in all salts II). Formylacetone diethylacetal also undergoes condensation with amine I to give a mixture of isomers IIe and IIf in a ratio of 3:2 (from the ratio of the intensities of the signals of the methyl groups at 2.79 and 2.58 ppm). The correctness of the assignment of the signals of the methyl groups in these isomers is confirmed by constants of spin–spin coupling of 5-H with 6-H and of 7-H with 6-H: the first is 4.5 Hz, and the second is 6.5 Hz, as observed in [3]. The less soluble IIc and IIe isomers were isolated in pure form from both mixtures of isomers by means of fractional recrystallization. Phenyl β-chlorovinyl ketone undergoes the reaction under consideration to give the 7-phenyl isomer, as established from the PMR spectrum, in which the spin–spin coupling constant (SSCC) of the pyrimidine protons is ∿4 Hz, which, as demonstrated above, corresponds to the SSCC of the protons attached to C_5 and C_6. The reaction of amine I with a β-chlorovinyl aldehyde (3-chloro-2-methylbuten-2-al) gave a mixture of isomers IIh and IIi in a ratio of ∿1:1, which we were unable to separate into the components by recrystallization ($\delta 7\text{-}CH_3$ = 2.78, $\delta 5\text{-}CH_3$ = 2.57, and $\delta 6\text{-}CH_3$ = 2.40 and 2.33 ppm).

An aqueous alcohol solution of ammonia has no effect on salt IIa, whereas alkali converts it to an acylvinylaminotriazole, which exists in the tautomeric enol form III, as previously observed for other condensed pyrimidinium salts, such as pyrido[1,2-a]pyrimidinium salts [5].

In contrast to salts IIc and IIe, salt IIa is converted by the usual method to polymethine dyes, from which it can be concluded that cyanine condensations occur at 5-CH_3 and that the 7-CH_3 group is inactive.



III

As an example, styryl dye IIj and carbocyanine dye IIk were obtained from salt IIa. A 7-CH_3 signal is observed in the PMR spectrum of the styryl dye, whereas the 5-CH_3 signal vanishes; this confirms the above statement regarding the activity of the methyl groups. The deuteration of salt IIa when it is heated in a mixture of trifluoroacetic acid and heavy water (1:1 by volume) also shows that the methyl group in the 5 position is more active (by a factor of approximately three) than the methyl group in the 7 position (from the intensity of the 5- and 7-CH_3 signals in the PMR spectrum).

In conformity with chromaticity theory, salt IIa with structure A should not give dyes at all. As noted in [2], the ability to undergo cyanine condensations is explained here, as for other salts of this type, by betaine cation structure B.

EXPERIMENTAL

The PMR spectra of 10-15% solutions of the compounds in trifluoroacetic acid were recorded with a ZKR-60 spectrometer; the chemical shifts are presented on the δ scale with respect to hexamethyldisiloxane. The electronic spectra of 10^{-5} mole/liter solutions of the dyes in ethanol were recorded with an SF-10 spectrophotometer.

4-Amino-1,5-diphenyl-1,2,3-triazole was obtained by the method in [6] from acetophenone and phenyl azide with subsequent reduction of the intermediate with zinc dust.

Preparation of Salts IIa-i. A solution of 1-2 mmole of amine I in 0.3-0.6 ml of trifluoroacetic acid was mixed with a 10-50% excess of acetylacetone, dibenzoylmethane, benzoylacetone, 3,3-diethoxy-2-butanone, phenyl β-chlorovinyl ketone, or 3-chloro-2-methylbuten-2-al, and the solution was allowed to stand at room temperature for a few hours or heated on a water bath for 10-15 min. Ether (5-6 ml) and a twofold to threefold excess of 57% perchloric acid were then added, and the resulting precipitate was washed repeatedly with ether and recrystallized from ethanol (see Table 1).

4-(2-Acetyl-1-methylvinylamino)-1,5-diphenyl-1,2,3-triazole (III). A solution of 0.02-0.03 g of sodium hydroxide in 2-3 ml of water was added to a warm (40-50°C) solution of 0.2 g of salt IIa in 10 ml of aqueous (1:1) ethanol, and the mixture was cooled. The precipitated crystals were washed repeatedly with water and recrystallized from aqueous ethanol.

TABLE 1. Characteristics of the Compounds Obtained

Compound	mp, °C	Found, %		Empirical formula	Calc., %		Yield, %
		Cl	N		Cl	N	
IIa	257—258	9,0	14,1	$C_{19}H_{17}ClN_4O_4$	8,9	14,0	80
IIb	303—305	6,9	10,8	$C_{29}H_{21}ClN_4O_4$	6,8	10,7	73
IIc	290—292	7,7	—	$C_{24}H_{19}ClN_4O_4$	7,7	—	95*
IIe	224—225	9,3	—	$C_{18}H_{15}ClN_4O_4$	9,2	—	92†
IIg	255—256	7,9	12,4	$C_{23}H_{17}ClN_4O_4$	7,9	12,5	98
IIj	290—291	6,9	—	$C_{28}H_{26}ClN_5O_4$	6,7	—	89
IIk	180—182	6,1	—	$C_{29}H_{24}ClN_5O_5$	6,4	—	36
III	121—122	—	17,6	$C_{19}H_{18}N_4O$	—	17,6	96

*This is the yield of a mixture of isomers IIc and IId in a ratio of 3:1.
†This is the yield of a mixture of isomers IIe and IIf in a ratio of 3:2.

PMR spectrum (in deuterodimethyl sulfoxide): 2.03 and 2.16 (singlets of two methyl groups), 5.45 (s, vinyl proton), 7.25-7.75 (m, aromatic protons), and 12.63 ppm (s, chelate proton of the acylvinylamino group). The PMR spectrum of the reaction product in trifluoroacetic acid was identical to the spectrum of salt IIa because of conversion of III to IIa under these conditions. A $\nu_{C=O}$ band at 1640 cm^{-1} is observed in the IR spectrum (KBr pellet); a band for a chelate proton is absent.

Preparation of the Dyes. Styryl IIj. A mixture of 0.2 g (0.05 mmole) of salt IIa, 0.15 g (1 mmole) of p-dimethylaminobenzaldehyde, and 1 ml of acetic anhydride was refluxed for 20 min, after which it was cooled, and the dye that precipitated from the red solution was removed by filtration, washed with alcohol and ether, and recrystallized from acetic acid. UV spectrum: λ_{max} 506 nm (ε 67,000). PMR spectrum: 2.70 (3H, s, 7-CH_3) and 3.27 ppm (6-H, s, dimethylamino group).

Carbocyanine IIk. A mixture of 0.2 g (0.5 mmole) of salt IIa, 0.19 g (0.53 mmole) of 2-(2-anilinovinyl)-3-methylbenzoxazolium methosulfate, and 1.5 ml of acetic anhydride was heated to the boiling point, and 0.1 ml of triethylamine was added. The resulting intensely red solution was refluxed for another 2 min and allowed to stand for 15 min. The reaction product was liberated in the form of an oil by the addition of ether and began to crystallize when it was triturated repeatedly with ether. The product was recrystallized from ethanol. UV spectrum: λ_{max} 547 nm (ε 81,000).

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