HETERODIENE SYNTHESIS

V.* TRANSAMINATION OF AZOMETHINES WITH AMIDINES OF CARBOXYLIC ACIDS – NEW METHOD FOR THE PREPARATION OF 1,2-DIHYDRO-sym-TRIAZINES

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Transamination occurs in the reaction of amidines of benzoic and trichloro- and trifluoroacetic acids with azomethines obtained from aniline and various aromatic aldehydes; two molecules of the resulting benzylideneamidines react to give 1,2-dihydro-sym-triazines via the Diels–Alder scheme with the liberation of imino aldehydes.

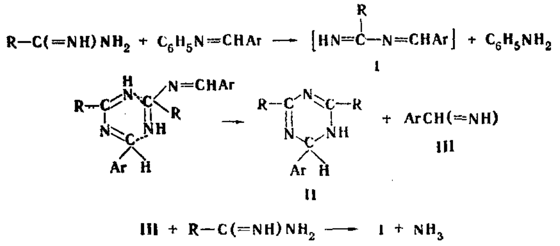
It is known [2-4] that in the reaction of azomethines with amines, an amine is displaced from the azomethine if the amine entering into the reaction is a stronger base. One should therefore have expected that amidines of benzoic and trichloro- and trifluoroacetic acids would displace aniline from azomethines.

It was found that the final products of the reactions of azomethines with amidines of carboxylic acids are 1,2-dihydro-sym-triazines, which, as we have previously reported, were obtained by the reaction of amidines of carboxylic acids with aldehydes [1, 5].

This reaction confirms the previously proposed scheme for the formation of 1,2-dihydro-sym-triazines (II) from substituted benzalamidines (benzylideneamidines) (I) as intermediates, since only benzylideneamidines can be the initial products in the transamination of azomethines with amidines.

Compound I could not be isolated from the reaction mixture; this was also the case in the reactions of amidines with aldehydes, probably owing to their high rate of conversion to II via the Diels–Alder scheme.

As seen from the reaction scheme, one molecule of II is formed from two molecules of I, and imino aldehyde III is liberated. The reaction yields reach 80% in those cases where 1 or 0.5 mole of azomethine is used per mole of amidine, since the III formed in the reaction reacts with the amidine to give I.



This sort of reaction is confirmed by the fact that the same amount of ammonia is liberated in both cases, while the unchanged azomethine is recovered in the case of equimolar amounts of azomethine and amidine. The latter fact indicates that the rate of the reaction of III with amidines is greater than the rate of the reaction of amidines with azomethines.

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*See [1] for communication IV.

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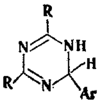
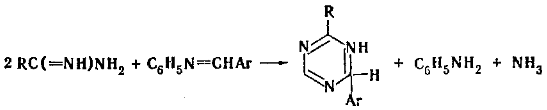
TABLE 1. 2-Aryl-4,6-Disubstituted 1,2-Dihydro-sym-triazines



Comp.	R	Ar	mp, °C	Yield, %
IIa	C_6H_5	C_6H_5	174—175	88
IIb	C_6H_5	p-$(CH_3)_2NC_6H_4$	170—172	84
IIc	CCl_3	C_6H_5	151—152	72
IId	CCl_3	p-$(CH_3)_2NC_6H_4$	163—165	70
IIe	CF_3	C_6H_5	108—110	70
IIf	CF_3	p-ClC_6H_4	126	60
IIg	C_6H_5	p-ClC_6H_4	154—155	70
IIh	CCl_3	p-ClC_6H_4	130—132	80
IIi	CF_3	p-$(CH_3)_2NC_6H_4$	127—128	80

The reaction of amidines of acids with azomethines proceeds more readily than with aldehydes, considerably fewer resinification products are formed, and dihydro-sym-triazines are isolated in purer form.

Thus the reaction to form II as a result of transamination of azomethines with amidines of carboxylic acids is expressed by the equation



The reaction of 2,2,2-trichloroethylideneaniline (IV) with the amidines of benzoic and trichloroacetic acids was carried out to obtain II with an electronegative substituent in the 2 position. Because of the great electronegative effect of the trichloromethyl group in the azomethine and the strong nucleophilicity of the amidines, very stable addition products (V) were obtained instead of transamination to form II.

$$\underset{IV}{Cl_3CCH{=}NC_6H_5} + R{-}C({=}NH)NH_2 \longrightarrow \underset{Va,b}{RC({=}NH)NHCHNHC_6H_5CCl_3}$$

Va $R{=}C_6H_5$; Vb $R{=}CCl_3$

EXPERIMENTAL

2-Aryl-4,6-Disubstituted 1,2-Dihydro-sym-triazines (IIa-i). 1) A solution of 0.03 mole of the acid amidine and 0.015 mole of the azomethine in 15-20 ml of dry chloroform or ethanol was refluxed for 3.5-4 h, during which ammonia was liberated. The solution was then cooled to precipitate II in 60-90% yield. The products were purified by crystallization from alcohol or benzene to give colorless crystalline substances that are quite soluble in acetone and chloroform (Table 1). The ammonia was trapped with 0.2 N HCl. The NH_3 found ranged from 0.0161 to 0.0173 equivalent.

2) A solution of 0.016 mole of the amidine and 0.016 mole of the azomethine in chloroform or ethanol was allowed to stand at room temperature for 3-5 days, after which the precipitated product was removed by filtration to 60-80% yields of IIa-i. Compounds IIa-f were described in [1, 5] and were identified from their melting points. IIg. Found,%: C 73.0; H 4.4; Cl 10.1. $C_{21}H_{16}ClN_3$. Calculated,%: C 72.9; H 4.7; Cl 10.3. IIh. Found,%: C 31.2; H 1.5; Cl 58.6. $C_{11}H_6Cl_7N_3$. Calculated,%: C 30.8; H 1.4; Cl 57.9. IIi. Found,%: F 32.9; N 16.8. $C_{13}H_{12}F_6N_4$. Calculated,%: F 33.6; N 16.5.

N-(1-Phenylamino-2,2,2-trichloroethyl)benzamidine (Va). A solution of 1.2 g (1 mmole) of benzamidine in chloroform was added to a solution of 2.2 g (1 mmole) of 2,2,2-trichloroethylideneaniline in 2 ml of dry chloroform. The reaction mixture began to warm up, and colorless crystals precipitated. The mixture was held at 70° for 2 h and worked up to give 2.3 g (70%) of a product with mp 148-149° (alcohol). Found,%: C 52.5; H 4.3; Cl 30.7; N 12.2. $C_{15}H_{14}Cl_3N$. Calculated,%: C 52.6; H 4.1; Cl 31.0; N 12.3.

N-(1-Phenylamino-2,2,2-trichloroethyl)trichloroacetamidine (Vb). An 11.4-g (0.05 mole) sample of 2,2,2-trichloroethylideneaniline was added to a solution of 8 g (0.05 mole) of trichloroacetamidine in 30 ml of absolute benzene, and the mixture was held at room temperature for 5 days. The precipitate was removed by filtration to give 7.2 g (40%) of a product with mp 81-83° (petroleum ether). Found,%: Cl 54.7. $C_{10}H_9Cl_6N_3$. Calculated,%: Cl 55.4.

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