LETTERS TO THE EDITOR

THE CONVERSION OF 3-PHENYLOXAZOLIDINE INTO p, p'-DI(3-OXAZOLIDYL)DIPHENYLMETHANE

S. R. Tulyaganov and F. Yu. Shakirova

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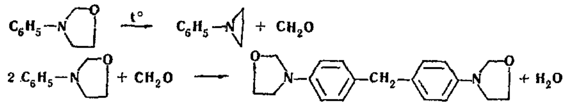
The opening of the oxazolidine ring under the action of organic acid derivatives has been reported in the literature [1].

In a study of the reaction of acetic anhydride with 3-phenyloxazolidine we isolated a colorless crystalline substance which proved, against expectation, to be p, p'-di(3-oxazolidyl)diphenylmethane (I). The I formed was identical with the p, p'-di(3-oxazolidinyl)diphenylmethane obtained from monoethanolaniline and formaldehyde in the presence of hydrochloric acid. When 3-phenyloxazolidine was heated in the absence of acetic anhydride, compound I was again formed. The formation of I can apparently be represented by the following scheme.



It was impossible to isolate the N-phenylethyleneimine formed as a by-product from the reaction mixture because of its resinification, apparently owing to its sensitivity to the action of heat, air, and various reagents [3].

It is known [4, 5] that p, p'-di(3-oxazolidinyl)diphenylmethane is the basis of phenol-oxazolidine moulding materials. The transformation of 3-phenyloxazolidine into p, p'-di(3-oxazolidinyl)diphenylmethane that we have observed makes it possible when necessary to obtain these materials directly from 3-phenyloxazolidine. Moreover, the formaldehyde liberated during the reaction may accelerate the process.

p, p'-Di(3-oxazolidinyl)diphenylmethane. A mixture of 10 g (0.07 mole) of 3-phenyloxazolidine and 10 ml (0.1 mole) of acetic anhydride was heated at 120°–130° C for 2 hr. After cooling, the mixture set to a light brown viscous mass. The crystals that deposited were separated off and recrystallized from ethanol. Yield 6.9 g (33%), mp 142° C. Found, %: N 9.10, 9.04. Calculated for $C_{19}H_{22}N_2O_2$, %: N 9.03.

A mixture with an authentic sample obtained by Petrov and Gosteva's method [3] melted without depression. The IR spectra of the two samples were identical.

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Institute of the Chemistry of Plant Substances,
AS Uzbek SSR, Tashkent

A NEW METHOD OF OBTAINING 4-QUINAZOLONES

L. I. Samarai, V. A. Bondar, and G. I. Derkach

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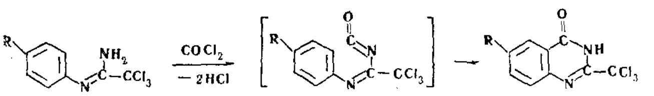
The action of phosgene on N-arylamidines in toluene gives 4-quinazolones in quantitative yields. The reaction probably takes place with the formation of isocyanates of carbimidic acids which are immediately converted into 4-quinazolones (cf. [1, 2])



a R = H; b R = OCH_3; c R = Cl

Ia–c

For example, a solution or a suspension of 0.2 mole of the amine in toluene is added slowly with stirring to a solution 0.04 mole of phosgene in 20 ml of anhydrous toluene cooled to −15° C. With the continuous passage of phosgene, the reaction mixture is gradually heated to 130°–140° C (bath temperature) and is kept there for 1 hr. The solvent is distilled off in vacuum to half the original volume and the 4-quinazolone that has precipitated is separated off, washed with ether, and dried. Yield 90–93%.

2-Trichloromethyl-4-quinazolone (Ia), mp 211°–212° C; the compound gave no depression of the melting point in admixture with a sample that we had obtained previously [1].

6-Methoxy-2-trichloromethyl-4-quinazolone (Ib), mp 206°–207° C (from a mixture of methanol and water). Found, %: C 41.29; H 2.43. Calculated for $C_{10}H_7Cl_3N_2O_2$, %: C 40.91; H 2.40.

6-Chloro-2-trichloromethyl-4-quinazolone (Ic), mp 252°–253° C (from a mixture of acetone and water). Found, %: C 36.48; H 1.34. Calculated for $C_9H_4Cl_4N_2O$, %: C 36.27; H 1.35%.

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Institute of Organic Chemistry,
AS Ukranian SSR, Kiev

PERIMIDINE IN THE CHICHIBABIN REACTION

A. F. Posharskii, I. S. Kashparov, and A. M. Simonov

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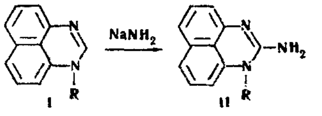
We have established that N-substituted perimidines (I) readily react with sodium amide in xylene or, which is somewhat better, methylaniline, forming the previously unknown 2-aminoperimidines (II) in high yield.



A solution of 0.01 mole of I in 10 ml of dry dimethylaniline was added with stirring to a suspension of 0.015 mole of $NaNH_2$ in 5 ml of dimethylaniline heated to 70°–80° C. After this, the temperature was slowly raised to 110°–115° C. The reaction took place vigorously and was practically complete after 10–15 min. Cooling and the treatment with water (10 ml) of the sodium derivative of the amine were carried out in an atmosphere of nitrogen. The amine formed was filtered off, washed with water, benzene, and petroleum ether, and recrystallized from water.

The 2-aminoperimidines (see table) form colorless crystalline substances of extremely high basicity ($pK_a^{25} \sim 8.0$ in 10% aqueous solution). They are readily acylated with the formation of 2-acylamino derivatives, but give azomethines on being boiled with p-nitrobenzaldehyde only with extreme difficulty.

We shall describe the synthesis and properties of I later.

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Rostov-on-Don State University

2-Aminoperimidines (II)

R	Mp, °C	Empirical formula	Found, %			Calculated, %			Yield, %	Mp, °C of the acetyl derivative (from water)
			C	H	N	C	H	N		
CH_3	236–237	$C_{12}H_{11}N_3$	72.85	5.58	21.29	73.07	5.62	21.30	95	218–219
C_2H_5	227–228	$C_{13}H_{13}N_3$	73.77	5.89	19.74	73.90	6.20	19.90	91	206–207
n-C_3H_7	167–168	$C_{14}H_{15}N_3$	74.67	6.81	18.87	74.63	6.71	18.65	70	151–152