NEW METHOD FOR THE PREPARATION OF N-ARYL-AND N-ALKYLPYRROLIDONES AND SOME OF THEIR PROPERTIES

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UDC 547.745:541.69

A simple method for the preparation of N-aryl- and N-alkylpyrrolidones has been worked out on the basis of the reaction of γ -butyrolactone with the hydrochlorides of primary amines. Active fungicides were found among the synthesized compounds.

One of the major methods for the preparation of N-substituted pyrrolidones is the reaction of γ -butyrolactone with primary amines at temperatures above 250°C under considerable pressure [1,2].

In our search for new, nontoxic pesticides among N-aryl- and N-alkylpyrrolidones we have studied the possibility of obtaining them by the reaction of γ -butyrolactone with the hydrochlorides of primary aromatic and aliphatic amines. γ -Butyrolactone reacts with these salts comparatively readily without applied pressure and solvents at 60-210° to form good yields of the corresponding N-aryl- and N-alkylpyrrolidones.

$$RNH_2$$
 HCI + O + HCI + H₂O

The reaction of γ -butyrolactone with the hydrochlorides of primary aromatic amines proceeds by heating equimolecular amounts of the starting compounds (or a slight excess of γ -butyrolactone) at 60-210° for 4-20 h [3]. The corresponding arylpyrrolidones were obtained in 85-98% yields. γ -Butyrolactone reacts with greater difficulty with the salts of methyl- and ethylamine, and the yields of the corresponding N-alkylpyrrolidones are 20-33%.

In a study of the properties of the pyrrolidones, we brominated N-phenylpyrrolidone and N-(o-methoxyphenyl)pyrrolidone. It was observed that the hydrobromide of the p-bromo-substituted phenyl-pyrrolidone is initially formed, from which the corresponding base is obtained in good yield by heating with NaHCO₃ solution.

The yields, constants, and analyses of the new compounds are presented in Table 1.

Comp.	Aryl	Мр	Empirical formula	Found %				Calc. %				Vield
				с	н	N	halo- gen	с	н	N	halo- gen	%
I III IV V VI	2,3-Dimethylphenyl 2-Chlorophenyl 4-Chlorophenyl 3,4-Dichlorophenyl 4-Bromophenyl 2-Methoxy-4-bromo- phenyl	50-5162-6393-9482-8396-97150-152	$\begin{array}{c} C_{12}H_{15}NO\\ C_{10}H_{10}CINO\\ C_{10}H_{10}CINO\\ C_{10}H_{9}CI_{2}NO\\ C_{10}H_{9}CI_{2}NO\\ C_{10}H_{10}BTNO\\ C_{11}H_{12}BTNO_{2} \end{array}$	76,0 61,3 61,0 52,1 50,1 48,7	7,7 5,1 5,3 4,1 4,2 4,5	7,3 7,3 7,0 6,2 6,0 5,1	18,4 18,3 31,3 33,0 29,5	76,2 61,4 61,4 52,2 50,0 48,9	7,9 5,1 5,1 3,9 4,2 4,4	7,5 7,2 7,2 6,1 5,8 5,2	18,1 18,1 30,9 33,3 29,6	91 92 90 93 90 92

TABLE 1. N-Arylpyrrolidones

Ya. V. Samoilov Scientific-Research Institute of Fertilizers and Combination Insecticide-Fungicides, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 773-774, June, 1971. Original article submitted December 9, 1969.

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The pesticidal properties of the synthesized pyrrolidones were studied by the All-Union Scientific-Research Institute of Chemical Agents for the Protection of Plants. All proved to be active fungicides.

We thank N. M. Golyshin and É. A. Dvoichenkova for studying the physiological activity of these substances.

EXPERIMENTAL

<u>N-Methylpyrrolidone</u>. Methylamine hydrochloride [33.7 g (0.5 mole)] was added gradually with stirring at 170° to 86 g (1.0 mole) of γ -butyrolactone, and the mixture was heated at 195-203° for 15 h. After cooling, the unchanged hydrochloride was removed by filtration to give 73 g of mother solution which, according to gas-liquid chromatography,* contained 20.5% N-methylpyrrolidone and 79.5% γ -butyrolactone.

<u>N-Phenylpyrrolidone</u>. Aniline hydrochloride [122.4 g (0.95 mole)] was added gradually at 80-120° to 120 g (1.4 mole) of γ -butyrolactone, and the mixture was heated with stirring at 160-200° for 12 h until hydrogen chloride evolution had ceased. The cold reaction mass was diluted with water and filtered, and the crystalline reaction product was dried to give 149 g (98%) of product with mp 65-66° (from petroleum ether) (mp 67-68° [2]).

The following were similarly obtained (yields in parentheses): N,N'-m-phenylenebis(pyrrolidone) (85%), N- α -naphthylpyrrolidone (95%), N- β -naphthylpyrrolidone (96%), N,N'-p,p'-diphenylbis(pyrrolidone) (96%) (the properties of these compounds were in agreement with the data in [2]), and new pyrrolidones I-IV (see Table 1).

<u>N'-p-Bromophenylpyrrolidone</u>. A solution of 10 g of bromine in 50 ml of dry carbon tetrachloride was added gradually at 18-20° to a solution of 10 g of N-phenylpyrrolidone in 50 ml of carbon tetrachloride, and the mixture was stirred for 2 h and cooled to 15°. The crystalline reaction product was filtered and vacuum dried to give 18 g (94%) of the hydrobromide with mp 118-120° (from petroleum ether). Found %: C 37.8; H 3.2; Br 49.8; N 4.1. $C_{10}H_{10}BrNO \cdot HBr$. Calculated %: C 37.5; H 3.4; Br 49.8; N 4.4. The hydrobromide (10 g) was dissolved in 75 ml of water, and the solution was heated and made alkaline with sodium bicarbonate. The resulting precipitate was filtered, washed with water, and dried to give 7 g of p-bromophenylpyrrolidone (V). 2-Methoxy-p-bromophenylpyrrolidone was similarly obtained.

LITERATURE CITED

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- 3. S. S. Kukalenko and N. A. Gracheva, USSR Author's Certificate No. 226,615 (1968); Byull. Izobr., No. 29 (1968).

^{*} This was accomplished with a Griffin chromatograph with a column 2.7 m long and 5 mm in diameter packed with Cellite-545 (60/80 mesh) impregnated with SKTFT-50 silicone rubber amounting to 20% of the weight of the support. The gas carrier (helium) flow rate was 1.8 liter/h, and the column temperature was 148°.