and then the precipitate of sodium chloride was filtered off and the ethanol was distilled off from the filtrate. The oily residue was treated with alkali and was then dissolved in chloroform and passed through a column of Al_2O_3. Compounds **Ib–Ie**, which were not passed through the column, were additionally recrystallized (see table). Because of the decomposition and oxidation of compounds I on vacuum distillation, we limited ourselves to the chromatographic purification of the oily compounds **Ia**, **If**, and **Ig**.

B) A mixture of 0.02 mole of benzimidazole and 0.01 mole of the corresponding alkyl chloromethyl sulfide in 30 ml of absolute benzene was boiled for 3 hr. The precipitate of benzimidazole hydrochloride that had deposited was filtered off, and the benzene was distilled off from the filtrate. The residual oil was purified as described above.

REFERENCES

1. A. F. Pozharskii, A. M. Simonov, E. A. Zvezdina, and N. K. Chub, KhGS [Chemistry of Heterocyclic Compounds], **3**, 889, 1967.

2. B. P. Fedorov and R. M. Mamedov, Izv. AN SSSR, OKhN, 1626, 1962.

3. E. C. Milner, S. Snyder, and M. M. Joullie, J. Chem. Soc., 4151, 1964.

4. A. F. Pozharskii, A. M. Simonov, E. A. Zvezdina, and V. A. Anisimova, KhGS [Chemistry of Heterocyclic Compounds], **5**, 869, 1969.

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SYNTHESIS OF 1,4-DIARYL-2,5-DIOXOPIPERAZINES

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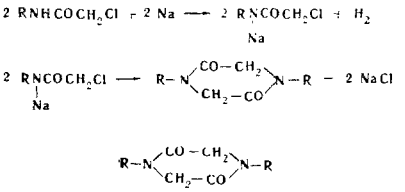
A new method for the synthesis of 1,4-diaryl-2,5-dioxopiperazines by the condensation of chloroacetanilides in the presence of sodium in anhydrous solvents, has been developed. The evolution of hydrogen shows the nucleophilic nature of the condensation.

Dioxopiperazines have been the subject of numerous investigations because of their relationship with the amino acids and peptides. The synthetic methods for obtaining dioxopiperazines consist in fusing amino acids and their derivatives in a current of inert gas or in solvents [1].

1,4-Diaryl-2,5-dioxopiperazines have been obtained [2] by the brief action of alcoholic alkalies on chloroacetyl derivatives. However, this synthesis is accompanied by side reactions which complicate the isolation of the end products. In recent years, it has been shown that the condensation of α-chloroacetamides also takes place under the action of sodium amide in liquid ammonia [3].

In attempting to develop the synthetic limits to the use of α-chloroacetamides, we have found a simpler



R	Mp, °C	Empirical formula	IR spectra, cm^{-1}					Found, %			Calculated, %			Yield, %
				C_{ar}—N	C—N—C_{ar}	>C=O	CH_2	C	H	N	C	H	N	
C_6H_5	262—263	$C_{16}H_{14}O_2N_2$	1600	1258	1440	1665—1675	1457	72.20	5.83	10.20	72.18	5.26	10.50	57
p-$CH_3C_6H_4$	252—253	$C_{18}H_{18}O_2N_2$	1520	1258	1437	1665—1675	1473	73.31	5.85	9.72	73.40	6.12	9.52	49
p-$CH_3OC_6H_4$	257—258	$C_{18}H_{18}O_4N_2$	1520	1252	1472	1665—1675	1472	66.57	5.78	8.55	66.27	5.52	8.58	62
p-$C_2H_5OC_6H_4$	266—267	$C_{20}H_{22}O_4N_2$	1590	1250	—	1665—1675	1480	68.00	6.56	8.25	67.80	6.21	7.91	41
β-$C_{10}H_7$	313—314	$C_{24}H_{18}O_2N_2$	1607	1278	1445	1665—1675	1470	78.65	5.31	8.00	78.68	4.92	7.65	57

and more reliable method for obtaining dioxopiperazines.

The reaction of α-chloroacetamides with sodium has not hitherto been studied. The work carried out in this direction has shown that in anhydrous media in the presence of sodium the chloroacetanilides form 2,5-dioxopiperazines (see table).

At temperatures of about 20° C no appreciable reaction takes place in 2 hr, but at only 40° C the reaction is complete in 1 hr.

To elucidate the influence of the solvents on the field of dioxopiperazines we carried out a series of experiments using various solvents (benzene, toluene, anisole, chlorobenzene). The results showed that the solvents have no substantial influence on the yield of dioxopiperazines.

To confirm the structure of the compounds obtained we recorded their IR spectra (see table). The spectra were taken on a UR-10 spectrophotometer. The substances were studied in the form of tablets with KBr.

EXPERIMENTAL

Synthesis of 1,4-diaryl-2,5-dioxopiperazines. With heating, in a flask fitted with a stirrer, reflux condenser, and thermometer, 0.023 mole of chloroacetanilide was dissolved in 70 ml of anhydrous benzene or toluene. The contents of the flask were brought to 60° C and 0.023 g-at of comminuted metallic sodium was added, after which the evolution of hydrogen, identified chromatographically, was observed. During the whole of the experiment, the solution was stirred vigorously and was thermostatted at 60 ± 2° C. After 1 hr, the flask was rapidly cooled, the mixture was filtered, and the precipitate was washed with hot ethanol to eliminate α-chloroacetamide and sodium. Then the crystals were treated with water until the reaction was neutral and the test for chloride ion was negative, and they were crystallized from acetic acid.

The constants of the diphenyl- and di-p-tolyldioxopiperazines obtained correspond to those given in the literature [4].

REFERENCES

1. M. Augustin, Wiss. Z. Univ. Halle, **15**, 553, 1966.

2. F. Reverdin, Helv. Chim. Acta, **6**, 87, 1923.

3. S. Sarel and A. Greenberger, J. Org. Chem., **23**, 330, 1958.

4. C. Bischoff and A. Hausdörfer, Ber., **25**, 2771, 1892; Beilst., **24**, 265, 1936.

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INDOLE DERIVATIVES

XXXVIII. Synthesis of 2-O-(Indol-3'-ylalkyl)Glycerols*

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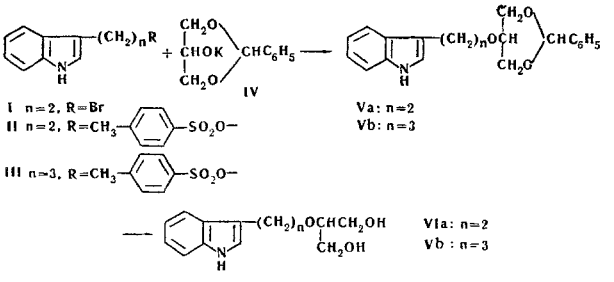
1,3-O-Benzylidene derivatives of 2-O-(indol-3'-ylalkyl)glycerols have been obtained by the reaction of ω-(indol-3-yl)alkyl tosylates with potassium 1,3-O-benzylideneglyceroxide. The removal of the benzylidene group by reduction with sodium in liquid ammonia has led to 2-O-(indol-3'-ylalkyl)glycerols. The tuberculostatic activity of the latter has been studied.

We have previously obtained 1-O-(indol-3'-ylalkyl) glycerols [1]. In the present work we have performed the synthesis of the 2-O-(indol-3'-ylalkyl)glycerols VI isomeric with them by the following route:



Potassium benzylideneglyceroxide (IV) was alkylated with tryptophyl tosylate (II) and with homotryptophyl tosylate (III), and also with indol-3-ylethyl bromide (I), with the formation of the 1,3-O-benzylidene-2-O-

*For part XXXVII, see [1].