EXPERIMENTAL

4'-Chloroanilide of 5-chloroanthranilic acid (III). To the ethylmagnesium iodide obtained from 37.5 g (0.24 mole) of ethyl iodide and 5.76 g (0.24 g-at) of magnesium in 90 ml of ether was added 15.3 g (0.12 mole) of 4-chloroaniline, and the mixture was heated for 30 min. A solution of 11.1 g (0.06 mole) of methyl 5-chloroanthranilate in 20 ml of water was added and the mixture was boiled again for 30 min, after which it was decomposed with a solution of ammonium chloride and the ethereal layer was separated off and treated with steam. The residue was crystallized from ethanol. Needles with mp 172–173° C. Yield 10.2 g (60%). Found, %: N 9.68. Calculated for $C_{13}H_{10}Cl_2N_2O$, %: N 9.96.

4'-Phenetidide of 3,5-dichloroanthranilic acid (IV). This was obtained similarly. Yield 85.3%. Needles (from ethanol) with mp 196–197° C. Found, %: N 8.39. Calculated for $C_{15}H_{14}Cl_2N_2O_2$, %: N 8.61.

6-Chloro-2-chloromethyl-3-(4'-chlorophenyl)quinazol-4-one (Ia). This was obtained from III and chloroacetyl chloride in glacial acetic acid solution. Yield 71%. Needles (from ethanol) with mp 182–183° C. IR spectrum: 1690 (CO), 1610, 1590, 1470 cm^{-1} (quinazolone bands). Found, %: C 52.90; H 2.58; N 8.40. Calculated for $C_{15}H_9Cl_3N_2O$, %: C 53.04; H 2.64; N 8.25.

6,8-Dichloro-2-chloromethyl-3-(4'-ethoxyphenyl)quinazol-4-one (Ib). This was obtained similarly from IV. Yield 50%. Needles (from ethanol) with mp 165–166° C. IR spectrum: 1688 (CO), 1632, 1595, 1508 cm^{-1} (quinazolone bands). Found, %: C 53.05; H 3.34; N 7.46. Calculated for $C_{17}H_{13}Cl_3N_2O_2$, %: C 53.24; H 3.44; N 7.30.

3-(4'-Chlorophenyl)-2-piperidinomethylquinazol-4-one (V). A mixture of 3.05 g (0.01 mole) of 2-chloromethyl-3-(4'-chlorophenyl)-quinazol-4-one and 1.7 g (0.02 mole) of piperidine in 20 ml of benzene was boiled for 2 hr, made alkaline with 10% sodium carbonate solution, and treated with steam. The precipitate was crystallized from ethanol. Yield 1.5 g. UV spectrum (in ethanol): λ_{max} (log ε) 229 nm (4.66) and 265 nm (4.07). IR spectrum: 1688 (CO), 1606, 1566, 1494 cm^{-1} (quinazolone bands). Compounds VI–XVIII were obtained similarly (table).

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Khar'kov Pharmaceutical Institute

Perm Pharmaceutical Institute

SYNTHESIS OF 1-ACRYLYL- AND 1-METHACRYLYL-SUBSTITUTED PYRAZOLINES AND PYRAZOLES

S. G. Matsoyan, E. G. Darbinyan, and Yu. B. Mitardzhyan

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1-Acrylyl- and 1-methacrylyl-substituted 3-methylpyrazolines, 3,5,5-trimethylpyrazolines, 3-methyl-5-phenylpyrazolines, 3-methyl-5-phenylpyrazoles, and 3,5-dimethylpyrazoles have been synthesized.

Until now, only a few N-acrylyl-substituted nitrogen-containing heterocycles were known. In this paper we report the synthesis of several 1-acrylyl-and 1-methacrylylpyrazolines and -pyrazoles by the reaction of acryloyl and methacryloyl chlorides with the corresponding 2-pyrazolines or pyrazoles in the presence of triethylamine. The substances formed are colorless liquids or crystals which readily polymerize.

EXPERIMENTAL

The initial 3,5,5-trimethylpyrazoline, 3-methyl-5-phenylpyrazoline, 3-methyl-5-phenylpyrazole, and 3,5-dimethylpyrazole were obtained by published methods [1-4]. The 3-methylpyrazoline was prepared as described by Matsoyan et al. [5].

Acylation of the pyrazolines and pyrazoles. With vigorous stirring and ice-water cooling, 0.15 mole of acryloyl or methacryloyl chloride was added dropwise to a mixture of 0.1 mole of the appropriate pyrazoline or pyrazole, 75 ml of dry ether, and 0.15 mole of triethylamine in such a way that the temperature of the reaction mixture remained at 5–10° C. Stirring at room temperature was continued for another 3 hr, and the precipitate that had formed (triethylamine hy-

Table

1-Acrylyl- and 1-Methacrylyl-substituted Pyrazolines and Pyrazoles

Compound	Bp, °C (pressure, mm)	n_D^{20}	d_4^{20}	Empirical formula	Found		Calculated		Yield, %
					N, %	MR_D	N, %	MR_D	
1-Acrylyl-3-methylpyrazoline	89 (1.5)	1.5315	1.0796	$C_7H_{10}N_2O$	20.15	39.60	20.26	37.32	60.8
1-Methacrylyl-3-methylpyrazoline	80 (1.5)	1.5148	1.0537	$C_8H_{12}N_2O$	18.60	43.52	18.39	42.97	86.6
1-Acrylyl-3,5,5-trimethylpyrazoline	80 (1.5)	1.5052	1.0106	$C_9H_{14}N_2O$	17.07	48.77	16.84	47.62	70.7
1-Methacrylyl-3,5,5-trimethylpyrazoline	74 (2)	1.4910	0.9907	$C_{10}H_{16}N_2O$	15.79	52.68	15.53	52.26	68.5
1-Acrylyl-3-methyl-5-phenylpyrazoline	160—161 (1.5)*	—	—	$C_{13}H_{16}N_2O$	13.16	—	13.05	—	60.7
1-Methacrylyl-3-methyl-5-phenylpyrazoline	142 (2)**	—	—	$C_{14}H_{16}N_2O$	12.12	—	12.26	—	79.4
1-Acrylyl-3-methyl-5-phenylpyrazole	134 (1.5)	1.6045	1.1336	$C_{13}H_{12}N_2O$	13.30	64.43	13.19	62.24	70.5
1-Methacrylyl-3-methyl-5-phenylpyrazole	137 (1.5)	1.5855	1.1100	$C_{14}H_{14}N_2O$	12.32	68.34	12.37	66.89	75.0
1-Acrylyl-3,5-dimethylpyrazole	68—69 (2.5)***	—	—	$C_8H_{10}N_2O$	18.28	—	18.64	—	78.0
1-Methacrylyl-3,5-dimethylpyrazole	64—65 (2)	1.5011	1.0294	$C_9H_{12}N_2O$	16.80	46.99	17.05	47.14	86.5

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*Mp 68-69° C (from nonane). **Mp 60-61° C (from nonane). ***Mp 37-38° C (from 50% ethanol).

drochloride) was filtered off. The filtrate was washed with water and dried with $MgSO_4$, and after the ether had been driven off the residue was distilled in vacuum in the presence of pyrogallol (polymerization inhibitor). Information on the substances obtained is given in the table.

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Institute of Organic Chemistry AS ArmSSR, Erevan

REACTIONS OF 1,5-DIKETONES

II. Reaction of Methylenedicyclohexanone and Tricyclohexanolone with Ammonium Acetate in Acetic Acid*

V. I. Vysotskii and M. N. Tilichenko

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The Chichibabin pyridine synthesis with methylenedicyclohexanone and tricyclohexanolone has been studied. It has been shown that under the conditions of the synthesis tricyclohexanolone is previously isomerized into methylenedicyclohexanone. The reaction products are sym-octahydroacridine, 12-hydroxy-Δ^{10}-dodecahydroacridine, and 5-azabicyclo[8,4,0]tetradecane-6,11-dione. The latter two substances are the products of the conversion of the Δ^{10}-dodecahydroacridine that arises as an intermediate.

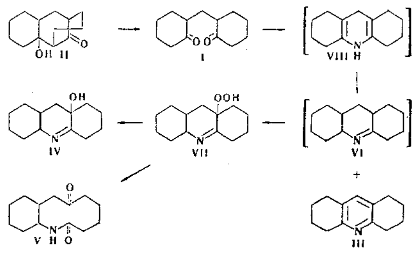
The initial products of the reaction of ammonium acetate with carbonyl compounds in acetic acid (the improved Chichibabin (Tschitschibabin) pyridine synthesis [2]) are, obviously, dihydropyridines. During the reaction they either disproportionate to form a mixture of pyridine and piperidine bases [3] or are oxidized to pyridines [2]. In the 1,5-diketone series the Chichibabin pyridine synthesis has so far been studied inadequately. It is known only [4] that some methylenedicyclanones give 2,3:5,6-dicyclanopyridines under these conditions.

We have carried out this reaction with 2,2'-methylenedicyclohexanone (I) and the product of its intramolecular ketolization—tricyclohexanolone (II). In both cases, sym-octahydroacridine (III)—the main reaction product—, 12-hydroxy-Δ^{10}-dodecahydroacridine (IV), and 5-azabicyclo[8,4,0]tetradecane-6, 11-dione (V) were isolated.

The identity of the results in the two cases indicates that tricyclohexanolone first isomerizes under the reaction conditions and then reacts as the diketone I. A similar decyclization process has been observed previously for 4-phenyl- and 4-furyltricyclohexanolones [5].

The formation of compounds IV and V becomes clear if it is assumed that in the process Δ^{10}-dodecahydroacridine (VI) is formed as an intermediate. It has been shown previously [6] that VI is oxidized in the air to 12-hydroperoxy-Δ^{10}-dodecahydroacridine (VII), which is subsequently reduced to 12-hydroxy-Δ^{10}-dodecahydroacridine or rearranges to form the macrocyclic ketolactam V. We have confirmed this hypothesis with the diketone I or the ketol II in an atmosphere of argon. When the reaction product obtained was oxidized with oxygen in heptane we obtained the hydroperoxide VII, identical with that obtained from authentic Δ^{10}-dodecahydroacridine (VI).

Compounds III and VI are apparently formed by the disproportionation of the decahydroacridine VIII produced initially:



EXPERIMENTAL

A mixture of 16.0 g (~0.08 mole) of the methylenedicyclohexanone I or the ketol II, 16.0 g (~0.2 mole) of ammonium acetate, and

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*For part I, see [1].