SYNTHESIS OF 4,6-DIPHENACYLPYRIMIDINES

L. P. Prikazchikova, B. M. Khutova, and V. M. Cherkasov

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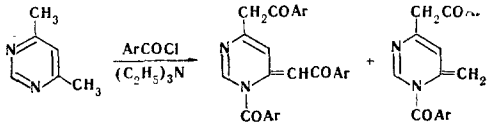
Reaction of 4,6-dimethylpyrimidine with the acyl chlorides of aromatic carboxylic acids gave N-acyl-4-phenacyl-6-acylmethylidynepyrimidines, which undergo alcoholysis to give the corresponding diketones – 4,6-diphenacylpyrimidines.

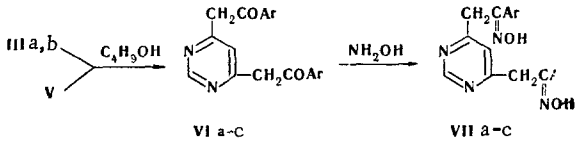
We have previously shown [1] that the reaction of 4,6-dimethylpyrimidine (I) with the acyl chlorides of aromatic carboxylic acids (II) gives N-acyl-4-phenacyl-6-methylenepyrimidines (IV), which are hydrolyzed to 4-phenacyl-6-methylpyrimidines. By changing the reagent ratio and the workup of the reaction mixture we obtained, in addition to IV, which were previously described as the only reaction products, N-acyl-4-phenacyl-6-acylmethylidyne pyrimidines (III), which are isolated when methanol is added to the residue remaining after removal of the excess triethylamine and acid chlorides from the reaction mixture.



I III a,b IV a,b

Compounds III and IV are obtained in yields of 10 and 40%, respectively. A trisubstituted base was isolated as the hydrochloride (V) in the reaction of pyrimidine I with anisoyl chloride. One of the two possible structures corresponding to tautomeric forms of dimethylpyrimidine [1] is presented for III.

The N-acyl group in trisubstituted bases III and hydrochloride V is unstable, and the corresponding 4,6-diphenacylpyrimidines (VI) are formed during the alcoholysis of these compounds. The formation of diketones is proved by the production of dioximes (VII).



VI a-c VII a-c

III, IV, VI, VII a Ar = C_6H_5; b Ar = p-ClC_6H_4; VI, VII Ar = p-$CH_3OC_6H_4$

The IR spectrum of pyrimidine I contains absorption bands at 2930 (methyl group), 3020 (=CH_2 group), and 3450 cm^{-1} (NH group). The presence of the characteristic absorption band for the NH group confirms the tautomerism of 4,6-dimethylpyrimidine.

Absorption bands at 1650 (carbonyl group) and 905 (=CH group) are observed in the IR spectrum of base III, while an absorption band at 1640 cm^{-1} (carbonyl group) is observed in the IR spectrum of 4,6-diphenacylpyrimidine.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer.

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TABLE 1. Characteristics of the Synthesized Compounds

Compound	mp, °C	Empirical formula	Found, %			Calculated, %			Yield, %
			C	H	N	C	H	N	
IIIa	145—148	$C_{27}H_{20}N_2O_3$	76,7	4,8	—	77,1	4,8	—	9
IIIb	212—214	$C_{27}H_{17}Cl_3N_2O_3$	61,9	3,1	—	61,9	3,3	—	10
V	163—165	$C_{30}H_{26}N_2O_6 \cdot HCl$	66,1	4,9	—	65,9	5,1	—	39
VIa	116—118	$C_{20}H_{16}N_2O_2$	75,8	5,1	9,0	75,8	5,1	8,9	47
VIb	170—173	$C_{20}H_{14}Cl_2N_2O_2$	62,3	3,9	—	62,4	3,7	—	91
VIc	155—156	$C_{22}H_{20}N_2O_4$	69,9	5,2	7,5	70,2	5,4	7,4	50
VIIa	164—166	$C_{20}H_{18}N_4O_2$	69,5	5,5	16,0	69,4	5,2	16,2	70
VIIb	203—205	$C_{20}H_{16}Cl_2N_4O_2$	57,7	3,8	13,4	57,4	3,9	13,5	77
VIIc	204—205	$C_{22}H_{22}N_4O_4$	65,2	5,5	—	65,0	5,5	—	94

N-Acyl-4-phenacyl-6-acylmethylidynepyrimidines (IIIa, b) and N-(p-Anisoyl)-4-(p-methoxyphenacyl)-6-(p-anisoylmethylidyne)pyrimidine Hydrochloride (V). A solution of 0.06 mole of II in 10 ml of absolute benzene was added with stirring to a solution of 0.02 mole of I and 0.06 mole of triethylamine in 10 ml of absolute benzene, and the mixture was refluxed for 2 h. It was then cooled, and the triethylamine hydrochloride (50% yield) was removed by filtration. The filtrate was vacuum evaporated, and methanol was added to the residue. A yellow precipitate of III, which was removed by filtration and purified by reprecipitation from benzene solution by the addition of methanol, separated from the solution after 5-10 min.

Hydrochloride V precipitated from the methanol solution 20-30 min after the addition of methanol (hydrogen chloride is obtained as a result of alcoholysis of the residual anisoyl chloride) (Table 1).

N-Acyl-4-phenacyl-6-methylenepyrimidines (IVa, b). These compounds were obtained after separation of III from the methanol solution, in analogy with the method in [1]. Compounds IV were identical to the compounds described in [1].

4,6-Diphenacylpyrimidines (VIa-c). A solution of 0.001 mole of III or V in 20 ml of butanol was refluxed for 3 h. The completeness of alcoholysis was monitored by means of thin-layer chromatography (TLC) on activity II Al_2O_3 with benzene–methanol (10 : 1) and development in UV light. After cooling, the precipitated VI was removed by filtration and crystallized from alcohol (Table 1).

4,6-Diphenacylpyrimidine Dioximes (VIIa-c). A bright-yellow suspension of 0.002 mole of VI and 0.004 mole of hydroxylamine hydrochloride in 15 ml of alcohol and 15 ml of pyridine was allowed to stand for 2-3 days, during which the solid dissolved, and the solution became colorless.

The solution was vacuum evaporated, water was added to the residue, and the resulting precipitate was removed by filtration. Crystallization from alcohol gave shiny white crystals of VII.

LITERATURE CITED

1. V. M. Cherkasov, L. P. Prikazchikova, B. M. Khutova, I. F. Vladimirtsev, and I. V. Boldyrev, Khim. Geterotsikl. Soedin., 1132 (1973).