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Abstract

Full Text

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DIRECT SYNTHESIS OF 4-SUBSTITUTED SALTS OF 1-AZADEHYDROQUINOLIZINIUM

Recently we published a method for the synthesis of salts of 4-alkyl-1-azadehydroquinolizinium ([1]), based on the condensation of α-aminopyridine with acetals of acylacetaldehydes ([2]), followed by cyclization of the resulting condensation products by means of concentrated acids (HBr, $HClO_4$)

2-aminopyridine+$(R'O)_2CHCH_2COR \longrightarrow$ Schiff base $(N{=}CHCH_2COR) \xrightarrow{HX}$ 4-R-1-azadehydroquinoliziniu

where R = Alk; $R' = OCH_3^-$, $OC_2H_5^-$; $X = Br^-$, ClO_4^-.

In the present work we have considerably simplified the method, showing that these same compounds are formed upon direct condensation of β-chlorovinyl ketones with α-aminopyridine under the action of 70% hydrochloric acid

2-aminopyridine+ClCH=CHCOR $\xrightarrow{HClO_4}$ 4-R-1-azadehydroquinolizinium perchlorate

where $R = CH_3^-$, $C_3H_7^-$, $C_6H_5^-$.

The acetals of acylacetaldehydes ([2]), readily obtained from β-chlorovinyl ketones, enter into this type of ring-closure reaction to a heterocycle with the same result:

2-aminopyridine+$RCOCH_2CH(OCH_3)_2$ $\xrightarrow{HClO_4}$ 4-R-1-azadehydroquinolizinium perchlorate

where $R = CH_3^-$, $C_3H_7^-$, $C_6H_5^-$.

This variant of the method may have independent significance because the first homolog of the series of acetals of acylacetaldehydes—the acetal of acetoacetaldehyde—has recently become a technical product and is readily obtained from diacetylene, and syntheses based on it have acquired practical value ([3],[4]).

The developed method of synthesis also made it possible to obtain 4-phenyl-1-azadehydroquinolizinium perchlorate.

The structure of the salts obtained was proved in the preceding communication ([1]). The possible 2-substituted isomers, whose formation might have been assumed, were not found in either case.

Experimental Part

1. Perchlorate of 4-methyl-1-azadehydroquinolizinium (1).
a) To a mixture of 2 g of α-aminopyridine and 2 g of methyl-β-chlorovinyl ketone in 5 ml of absolute methyl alcohol, 4 ml of 70% perchloric acid was added. Strong heating of the reaction mass was observed. After 24 hours the precipitated solid was filtered off, and an additional small amount of salt was precipitated from the mother liquor with ether. Yield of 4-methyl-1-azadehydroquinolizinium perchlorate: 3.9 g (75% of theory), decomp. temp. 224–226° (from methanol).

b) Obtained analogously from 3 g of the dimethyl acetal of acetoacetaldehyde, 2 g of α-aminopyridine, and 3.5 ml of 70% perchloric acid in 5 ml of absolute methyl alcohol. Yield 3.65 g (72% of theory), decomp. temp. 223–226°. A mixed sample with an authentic specimen and with the specimen obtained according to variant a) gives no depression of the melting point.

2. Perchlorate of 4-propyl-1-azadehydroquinolizinium (1).
a) Obtained analogously from 1.5 g of propyl-β-chlorovinyl ketone, 1 g of α-aminopyridine, and 2 ml of 70% perchloric acid in 2.5 ml of absolute methyl alcohol. If the salt does not precipitate for a long time, it should be precipitated from the solution with absolute ether. Yield 2.5 g (82% of theory), m.p. 143–145° with decomposition (recrystallized from absolute methyl alcohol).

b) Obtained analogously from 1.8 g of the dimethyl acetal of propioacetaldehyde, 1 g of α-aminopyridine, and 1.7 ml of 70% perchloric acid in 2.5 ml of methyl alcohol. Yield 1.75 g (60.3% of theory), m.p. 144–145° with decomposition. A mixed sample with an authentic specimen and with the specimen obtained according to variant a) gives no depression of the melting point.

3. Perchlorate of 4-phenyl-1-azadehydroquinolizinium.
a) Obtained from 1.77 g of phenyl-β-chlorovinyl ketone, 1 g of α-aminopyridine, and 2 ml of 70% perchloric acid in 3 ml of absolute methyl alcohol. If the precipitate does not separate for a long time, it should be precipitated with ether. The precipitate is a mixture of 4-phenyl-1-azadehydroquinolizinium perchlorate and tribenzoylbenzene. 4-Phenyl-1-azadehydroquinolizinium perchlorate was separated from tribenzoylbenzene by fractional crystallization from methyl alcohol. Yield of 4-phenyl-1-azadehydroquinolizinium perchlorate: 0.35 g (10.8% of theory). Decomp. temp. 188–189°. Colorless flaky crystals, poorly soluble in water.

Found, %:	C 54.82;	55.02;	H 3.67;	3.64;	Cl 11.58; 12.00
$C_{14}H_{11}O_4N_2Cl$. Calculated, %:	C 54.81;		H 3.58;		Cl 11.58

b) Obtained from 2 g of the dimethyl acetal of benzoylacetaldehyde, 1 g of α-aminopyridine, and 1.7 ml of 70% perchloric acid in 2.5 ml of absolute methyl alcohol. Yield 0.45 g (12.7% of theory). Decomp. temp. 187-188°. A mixed sample with the specimen obtained according to variant a) gives no depression of the melting point.

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Note: Figure translations are in progress. See original paper for figures.