of 70 eV, and inlet temperatures of 70°C (V-XVI) and 80°C (I-IV). Compounds I-XVI were synthesized according to previously described methods [1-4]. Their purities were assessed by TLC, GLC, IR, PMR, and mass spectroscopy. Mass spectra of the deuteroanalogs VIII, X, and XIII were obtained under conditions of spontaneous deuterium exchange between compounds VII, IX, and XII in the vapor phase with CD₃OH vapor in the ionizing chamber of the mass spectrometer.

LITERATURE CITED


QUATERNIZATION OF PYRIDINES WITH HALOADAMANTANES

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The quaternization of pyridine and its 3- and 4-derivatives with 1-haloadamantanes has been carried out in the presence of a small quantity of water in the pyridines.

The quaternization reaction of pyridines with alkyl halides is well known [1]. However, its use for quaternization of compounds with a halogen atom at the bridgehead has received virtually no study. It is known that under severe conditions 1-bromoadamantane reacts with pyridine [2], 4-methylpyridine and isoquinoline [3].

We have previously obtained adamantylpyridinium salts by a conjugated haloamination reaction of 1,3-dehydroadamantane and 3,7-dimethylenebicyclo[3.3.1]nonane [4, 5] and also by interaction of 3,7-dimethylenebicyclo[3.3.1]nonane with pyridine hydrochloride [6].

In this work, we have investigated the quaternization reaction of pyridine derivatives with haloadamantanes in order to develop a preparative method of obtaining the corresponding salts and also to determine the effect of the substituents in the pyridine ring on the reaction. It transpired that the quaternization reaction of pyridine and its 3- and 4-derivatives occurs only with 1-bromo adamantane (Ia) and 1-iodo adamantane (Ib), while 1-chloroadamantane does not react with pyridine up to a temperature of 300°C.

In this reaction an important part is played by water. If pyridine is completely dehydrated, the yields of products are small and the temperature needed for carrying out the reaction is high. When water is added (0.2% of the quantity of pyridine) the reaction temperature is reduced to 50-70°C and the yields of pyridinium salts are substantially increased (compare [2, 3]). We determined the content of water in the pyridines by means of PMR and supplemented it to a level of 0.2%. The property of water to accelerate the ionization of 1-halo adamantanes was used by Stetter [8] when alkylating toluene with 1-bromo adamantane.

It should be noted that the quaternization reaction of pyridine derivatives with 1-halo adamantanes is sensitive to steric factors. Thus, with pyridine derivatives having a substituent at the 2-position reaction does not take place, while increasing the water content in such pyridines only leads to hydrolysis of the halo adamantanes. Adamantyl salts are not obtained from 2-picoline, 2,3-lutidine, 2,4,6-collidine, or quinoline, although the corresponding salts have been obtained [5] by a conjugated haloamination reaction of 3,7-dimethylenecyclo[3.3.1]nonane with quinoline and 2-picoline. A quaternary salt is not formed when the reaction is attempted with triethylamine, evidently also because of steric factors.

*For previous communication, see [7].