B) This compound (mp 141-142°) was similarly obtained from V in 100% yield.

<u>2,4,6-Tris(methylthio)-3,5-dichloropyridine (IV).</u> This compound, with mp 119-121° (from aqueous ethanol), was obtained in 95% yield from the potassium salt of IV and dimethyl sulfate as in the preparation of II. Found: Cl 24.7; S 33.4%. C₈H₉Cl₂NS₃. Calculated: Cl 24.8; S 33.6%.

 $\frac{2,4,6-\text{Tris}(\text{methylsulfonyl})-3,5-\text{dichloropyridine (I)}}{2,4,6-\text{Tris}(\text{methylsulfonyl})-3,5-\text{dichloropyridine (I)}}$ A total of 10 ml (0.09 mole) of 30% H₂O₂ was added to a cooled solution 2.8 g (0.01 mole) of V in 25 ml of trifluoroacetic acid, after which the mixture was allowed to stand at 20° for 12 h. It was then refluxed for 15 min and poured into ice water. The resulting precipitate was removed by filtration to give 3.2 g (85%) of a product with mp 285-287° (dec., from aqueous acetone). Found: Cl 18.6; S 25.1%. C₈H₉Cl₂NO₆S₃. Calculated: Cl 18.6; S 25.1%.

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REACTIONS OF PYRIDINIUM AND ISOQUINOLINIUM

PHENACYLIDES WITH NUCLEOPHILES

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The hydrolysis, alcoholysis, and hydrazinolysis of N-phenacylpyridinium bromide lead to the corresponding benzoic acid derivatives. In addition, 3,6-diphenylpyridazine is formed during hydrazinolysis. The hydrolysis and alcoholysis of N-phenacylisoquinolinium bromide lead to its dimerization, whereas hydrazinolysis gives a triazinoisoquinoline derivative.

The following three types of reactions, in addition to the formation of the corresponding ylids II (or through the intermediate formation of the latter), can be proposed for N-phenacylpyridinium and N-phenacylisoquinolinium cations (I) on reaction with nucleophiles:



We have investigated the hydrolysis, alcoholysis, and hydrazinolysis of N-phenacylpyridinium and Nphenacylisoquinolinium bromides under comparable conditions and have found that the behavior of these salts in these reactions differs markedly. A phenacylation reaction (type C) was not recorded in a single case. N-Phenacylpyridinium bromide reacts completely via a scheme of the B type on standing with aqueous alkali to

Donetsk Branch, L. V. Pisarzhevskii Institute of Physical Chemistry, Academy of Sciences of the Ukrainian SSR. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 372-374, March, 1976. Original article submitted January 3, 1975.

This material is protected by copyright registered in the name of Plenum Publishing Corporation, 227 West 17th Street, New York, N.Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$7.50. benzoic acid, in agreement with the data in [1]. Alcoholysis in the presence of triethylamine gives the corresponding ester IV ($Nu = OCH_3$) in quantitative yield. The hydrazination of N-phenacylpyridinium bromide also proceeds primarily via the same type B scheme; however, in addition to benzhydrazide IV ($Nu = NHNH_2$), still another substance with the composition $C_{16}H_{12}N_2$ is formed in 2-5% yield in this case. On the basis of analysis, physicochemical properties, and comparison with a sample obtained by alternative synthesis from dibenzoylethane (X) [2], this compound was identified as 3,6-diphenylpyridazine (IX). Although the formation of the latter is also associated with cleavage of the CH_2-N bond, it cannot be ascribed to a phenacylation variant of the C type. We propose the following reaction scheme, including carbenoid cleavage of the intermediate azine bisylid VIII:



The fact of splitting out of pyridine and formation of pyridazine IX [of course, also in low yield (5-7%)] from azine VII by the action of alkali serves as a confirmation of this scheme. Azine VII itself is formed readily in high yield by heating N-phenacylpyridinium bromide with a half molar amount of hydrazine hydrate in acetic acid.

In contrast to the pyridinium salt, N-phenacylisoquinolinium bromide gives only ylid XII, stabilized in the form of dimer XIII, on hydrolysis by alkalis or on alcoholysis in the presence of triethylamine:



The structure of XIII is confirmed by the experimentally found molecular weight and the spectral data. Its IR spectrum does not contain the characteristic absorption of a betaine grouping [3] but does contain the usual $\nu_{C=O}$ absorption band at 1680 cm⁻¹.

In contrast to the pyridinium analog, the hydrazination of N-phenacylisoquinolinium bromide proceeds initially in the ring via a scheme of the A type with subsequent cyclization to triazinolsoquinoline derivative XIV. The structure of the latter (in particular, the difference from alternative N-aminoimidazole structure XV) was proved by elementary and functional analyses and was confirmed by its IR spectrum. Slightly soluble dimer XIII apparently exists in solution in equilibrium with monomer XII, and the equilibrium is shifted markedly to favor the dimer; prolonged refluxing of XIII in alcohol with hydrazine gives the same triazine (XIV).

EXPERIMENTAL

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

<u>Hydrolysis of N-Phenacylpyridinium Bromide.</u> Sodium benzoate, which was isolated in the form of benzoic acid, was obtained in quantitative yield when the pyridinium salt was heated or allowed to stand with a stoichiometric or excess quantity of aqueous sodium hydroxide solution.

Alcoholysis of N-Phenacylpyridinium Bromide. A solution of the salt in dry methanol was refluxed for 3 h in the presence of a stoichiometric (or excess) amount of dry triethylamine, after which the mixture was evaporated on a water bath, and the residue was treated with water and extracted three times with ether. The ether extracts were washed with water and dried with anhydrous $CaCl_2$. The ether was removed by distillation, and the residue was vacuum distilled to give methyl benzoate in 80% yield.

<u>Hydrazinolysis of N-Phenacylpyridinium Bromide</u>. A) A fivefold quantity of 99% hydrazine hydrate was added to the dry salt, and the mixture was allowed to stand for several hours. The resulting large crystals of the benzhydrazide were removed by filtration, washed with a small amount of cold water, and crystallized from water to give a product with mp 111-112°.

B) A solution of 2.78 g (10 mmole) of the salt in 10 ml of methanol was refluxed for 1 h with 1 ml (20 mmole) of 99% hydrazine hydrate, after which the mixture was evaporated to dryness, and the residue was extracted with dry benzene in a Soxhlet apparatus. The benzene extract was evaporated to dryness, and the residue was crystallized from benzene to give 1 g (75%) of the benzhydrazide.

C) A solution of 13.9 g (50 mmole) of the salt and 5 ml (100 mmole) of hydrazine hydrate in 50 ml of alcohol was refluxed for 2 h, after which the mixture was diluted to 500 ml with water and allowed to stand. After several hours, the resulting precipitate was separated, washed with water, and vacuum dried to give 0.1-0.3 g (2-5%) of product. Recrystallization from isopropyl alcohol with activated charcoal gave shiny almost colorless leaflets with mp 220-222° (mp 221-222° [2]). No melting-point depression was observed for a mixture of this product with a genuine sample of 3,6-diphenylpyridazine.

<u>Alcoholysis of N-Phenacylisoquinolinium Bromide</u>. A dilute solution of the salt in methanol was treated with a stoichiometric amount of dry triethylamine, after which the mixture was warmed up, and a voluminous precipitate formed immediately. The precipitate was removed by filtration, washed with methanol, and vacuum dried to give a yellow-orange product in quantitative yield. The product was only slightly soluble in ordinary solvents and had mp 197-200°. Found: C 82.4; H 5.5; N 6.0%; M 460 (Rast method). $C_{34}H_{26}N_2O_2$. Calculated: C 82.6; H 5.3; N 5.7%; M 494. IR spectrum, ν , cm⁻¹: 1630 (C = C) and 1680 (C = O). On the basis of these data the 7,15-dibenzoyl-6b,7,8,14b,15,16-hexahydropyrazino[1,2-a:4,5-a]diisoquinoline (XIII) structure was assigned to the product. The same compound was also obtained by treatment of the isoquinolinium salt with alkalis.

Hydrazinolysis of N-Phenacylisoquinolinium Bromide. A 0.2-mole sample of 99% hydrazine hydrate was added to a saturated solution of 0.1 mole of the salt in alcohol, and the mixture was refluxed for 2 h. It was then cooled and diluted with a fourfold amount of water. The resulting precipitate was separated, washed, and vacuum dried. The yellow-brown product was purified by reprecipitation from propanol by the addition of hexane to give yellow crystals of 3-phenyl-1,4,5,11b-tetrahydro-1,2,4-triazino[3,4-a]isoquinoline, with mp 155-157°, in 60% yield. Found: C 78.3; H 5.7; N 16.2%. $C_{17}H_{15}N_3$. Calculated: C 78.2; H 5.7; N 16.1%. IR spectrum, ν , cm⁻¹: 3255 (NH).

The same compound was obtained by refluxing stoichiometric amounts of hydrazine and dimer XIII in alcohol for 8-10 h and workup as described above.

<u>1,6-Di (N-pyridinium)-2,5-diphenyl-3,4-diaza-2,4-hexadiene Dibromide (VII)</u>. This compound was obtained by refluxing 27.8 g (100 mmole) of N-phenacylpyridinium bromide with 2.5 ml (50 mmole) of hydrazine hydrate in 50 ml of glacial CH₃COOH for 2 h. The mixture was cooled and diluted with four volumes of ether and allowed to stand overnight. The resulting precipitate was separated, washed with ether, and crystallized from isopropyl alcohol to give colorless crystals with mp 193-195° in 80% yield. Found: C 56.3; H 4.0; Br 28.9; N 10.2%. $C_{26}H_{24}Br_2N_4$. Calculated: C 56.5; H 4.3; Br 29.0; N 10.1%.

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