

LETTERS TO THE EDITOR

PREPARATION OF 1,4-DIPHENYLPIPERAZINE

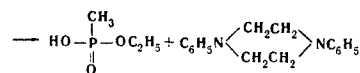
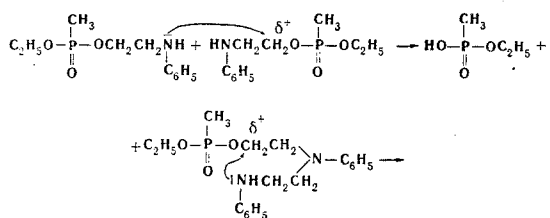
O. P. Kor'yakov, P. M. Zavlin, and V. V. Razumovskii

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 4, No. 6, p. 1131, 1968

UDC 547.861.3:543.422.4

When 17.3 g of ethyl β -phenylaminoethyl methylphosphonate (n_D^{20} 1.5491, structure established on the basis of the results of microanalysis and infrared spectroscopy) isolated from the product of the interaction of ethyl methylphosphonochloridate and β -phenylaminoethanol, was subjected to thermal decomposition, in the absence of a solvent, in a current of argon at 200° C for 1 hr, 8.1 g (92%) of 1,4-diphenylpiperazine was formed. After two recrystallizations from *o*-xylene, it had mp 164–164.5° C (according to the literature [1–3], mp 164–165° C).

Formation of 1,4-diphenylpiperazine in the case under consideration is apparently the result of successive processes of inter- and intramolecular alkylation of the amino group of the ethyl β -phenylaminoethyl methylphosphonate, taking place in the following way:



In addition to 1,4-diphenylpiperazine, a mixture of polyphosphonates, apparently products of the polycondensation of ethyl methylphosphonate, is formed.

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Bonch-Bruевич Leningrad Electro-technical Institute of Communication

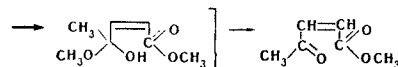
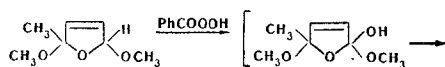
PREPARATION OF METHYL β -ACETYLACRYLATE

R. I. Kruglikova, L. N. Kralinina, and T. V. Boyarinova

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When 2,5-dimethoxy-2,5-dihydroxylane (I) was oxidized with perbenzoic acid, instead of the expected 3,4-epoxy-2,5-dimethoxy-tetrahydroxylane, methyl β -acetylacrylate (II) was formed. This compound has been obtained previously in other ways [1–4]. It is interesting that II possesses bacteriostatic activity against *Escherichia coli*, *Mycobacterium tuberculosis* and *Pneumococcus* [4]. The constants of the II that we obtained and of its dinitrophenylhydrazone agreed with those given in the literature. Furthermore, the structure of II was confirmed by its IR and NMR spectra. The IR spectrum had strong absorption bands at 1725 and 1680 cm^{-1} and a less intense band at 1645 cm^{-1} . The NMR spectra had two singlets with chemical shifts of 2.24 ppm ($\text{CH}_3\text{C}=\text{O}$) and 3.76 ppm ($\text{CH}_3-\text{O}-\text{C}=\text{O}$) and a doublet at 6.67 and 6.77 ppm ($-\text{CH}=\text{CH}-\text{C}=\text{O}$) with intensities of 3:3:2.



Obviously, in view of the fact that the multiple bond in the 2,5-dialkoxy-2,5-dihydrofurans is not oxidized under these conditions [5], the perbenzoic acid oxidizes the acetal group and the reaction takes place in the manner shown above. We consider this course of the reaction the most probable, since there is information on the oxidation with peracetic acid of α, β -saturated acetals to the corresponding esters [6].

A similar conversion was observed in the oxidation of 2,5-dimethoxy-2,5-dihydrofurfuryl alcohol with performic acid (β -benzoyloxydehydrolevulinic acid was obtained) [7].

Compound II has been obtained by the oxidation of I with a twofold excess of perbenzoic acid in chloroform solution, yield 58%, mp 61–62° C (from *n*-hexane); 2,4-dinitrophenylhydrazone, mp 200–202° C.

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Lomonosov Moscow Institute of
Precision Chemical Engineering

SYNTHESIS OF 2-VINYLOXYPYRIDINE

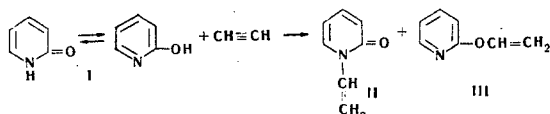
G. G. Skvortsova and S. M. Tyrina

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The idea of the existence of 2-hydroxypyridine (I) in two forms, of which 2-pyridone (Ia) is the most stable, is generally accepted, and the presence in the free crystalline state of the tautomeric hydroxypyridine form (Ib) has frequently been doubted [1, 2].

It has been shown previously [3, 4] that when I is vinyliated in the presence of caustic potash only N-vinyl-2-pyridone (II) is obtained. Assuming that the reaction of I with acetylene can take place at two reaction centers, we have attempted to effect the synthesis of III.



As a result of a study of the influence of the medium and various catalysts on the vinylation of I, we succeeded in obtaining, in addition to II, the new vinyl ether III. It has been established for the first time that, in the presence of heavy-metal chlorides and acetates, I reacts with acetylene under pressure forming mainly 2-vinyloxy-pyridine (III) and only small amounts of II. The structure of III has been confirmed by IR and NMR spectroscopy.

2-Vinyloxy-pyridine. Yield 42%, bp 59-60° C (15 mm), d_4^{20} 1.0244, n_D^{20} 1.5205. Found, %: C 69.40; H 5.94%; MR_D 35.97. Calculated for C_7H_7NO , %: C 69.40; H 5.82%; MR_D 35.24.

N-Vinyl-2-pyridone. Yield 15%, bp 107° C (6 mm), d_4^{20} 1.1220, n_D^{20} 1.5960.

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Irkutsk Institute of Organic Chemistry,
Siberian Division, AS USSR