LETTERS TO THE EDITOR

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PECULIARITIES IN THE HYDROGENATION OF ALKENYLFURANS WITH A DOUBLE BOND SITUATED IN THE 2, 3 POSITION TO THE RING

Yu. I. Tarnopol'skii and V. N. Belov

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Up to the present there has been no doubt about the possibility of selective hydrogenation of the side chain double bond in alkenylfurans [1]. In particular, catalysts consisting of palladium on carriers ($SrCO_3$ [2], $BaSO_4$ [3, 4]) have been used. They have been used to hydrogenate compounds with the double bond at various positions in the side chain [2-4], but not alkenylfurans with the double bond at the 2, 3 position. Having synthesized compounds of this latter type [5], the present authors attempted to hydrogenate selectively 2-(3-methylbuten-2-yl) furan and 2-(2, 3-dimethylbuten-2-yl) furan, but it was unexpectedly found that with $Pd/BaSO_4$ and at atmospheric pressure hydrogenation was non-selective, and gave the corresponding alkyltetrahydrofurans. Hydrogen uptake rate fell uniformly, and slowed down greatly when hydrogenation was complete.

Using the same catalyst, results for the selective hydrogenation of 2-vinylfuran [4] have been reproduced.

3.5 g 2-(3-methylbuten-2-yl) furan was hydrogenated at atmospheric pressure and room temperature, using 2 g 5% $Pd/BaSO_4$ in 25 ml dry ether, and after 9 hr 1560 ml (92%; at NTP) hydrogen, 890 ml being taken up in the first hour. When hydrogenation ceased, the catalyst was filtered off, the ether distilled off, 2–3 drops of bromine added to the residue (until a yellow color was obtained), which was then distilled under reduced pressure, to give 1.35 g (37%) 2-isoamyltetrahydrofuran, bp 79° (27 mm); d_4^{20} 0.8589; n_D^{20} 1.4340. Found: MR_D 43.1. Calculated for MR_D 43.6. The literature gives [3]: bp 172–173° (764 mm); d_4^{20} 0.8550; n_D^{20} 1.4330.

3 g 2-(2, 3-dimethylbuten-2-yl) furan was hydrogenated similarly. After 8 hr 1340 ml H_2 (98%) was absorbed, 660 ml being taken up in the first hour. Yield 2.3 g (74%) 2-(2, 3-dimethylbutyl) tetrahydrofuran, bp 92–93° (25 mm); d_4^{20} 0.8720; n_D^{20} 1.4415. Found: C 76.98; H13.06%; MR_D 47.5. Calculated for $C_9H_{20}O$: C 76.93; H 12.91%; MR_D 48.2.

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Mendeleev Institute of Chemical Technology, Moscow

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REACTION OF ANTHRAPYRIDONES WITH NUCLEOPHILIC REAGENTS

M. V. Kazankov and V. N. Ufimtsev

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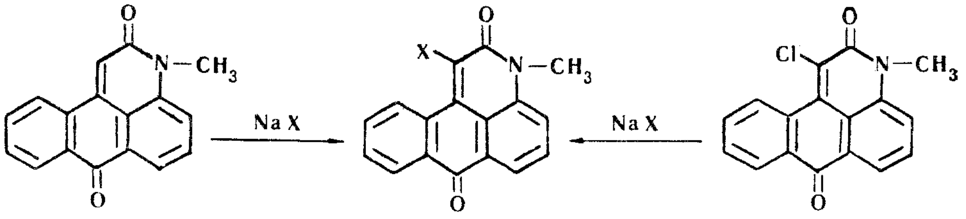
The present authors previously showed that anthrapyridone (7H-dibenz [f, ij] isoquinoline-2, 7 [3H] dione) (I) and N-methylanthrapyridone (II) react with aliphatic amines to give the corresponding 1-alkylaminoanthrapyridones [1]. Continuing the research, the reaction of anthrapyridones with other nucleophilic reagents has been studied. Boiling N-methylanthrapyridone with an aqueous dioxane solution of sodium hydroxide, gave a 50% yield of a compound which, after recrystallization from acetic acid had mp 299–300° C (decomp). Found: C 73.57, 73.71; H 3.80, 3.85; N 5.00, 5.22%. Calculated for $C_{17}H_{11}NO_3$: C 73.62; H 4.00; N 5.05%. The compound was identical in chemical properties, melting point, and IR spectrum with 1-hydroxy-N-methylanthrapyridone (III), prepared by the action of ethanolic alkali on 1-chloro-N-methylanthrapyridone (IV) by the method of [2].

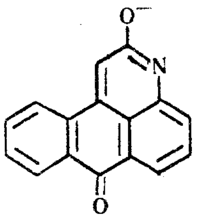


II

III X = OH;
VI X = CN

IV

The unsubstituted anthrapyridone I does not react with alkalies, which, actually, is bound up with formation of the enolate V.



V

The patent literature [3] states that heating of N-methylanthrapyridone with potassium cyanide in ethylene glycol leads to formation of a nitrile group, but the structure of the reaction product was not established. 1-Cyano-N-methylanthrapyridone (VI), obtained by reacting 1-chloro-N-methylanthrapyridone with sodium cyanide, was identical in properties and IR spectrum with the compounds synthesized as described in [3]. Thus the results given show that anthrapyridones can react with nucleophilic reagents to give the corresponding 1-derivatives.

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Scientific Research Institute for Intermediates and Dyes,
Moscow

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REACTION OF THYMINE AND 5-FLUOROURACIL WITH ACRYLONITRILE

R. A. Paegle, M. Yu. Lidak, and Yu. P. Shvachkin

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It is known [1] that acrylonitrile reacts smoothly with uracil in liquid ammonia at −50° C, giving only β-(uracil-N_3) propionitrile.* Reaction with thiouracil proceeds in exactly the same way [2].

Continuing research on methods of obtaining N-substituted hydropyrimidine systems, of interest as potential nuclein exchange antimetabolites, and as potential antiblastic compounds, a study has been made of the reaction of thymine and 5-fluorouracil with acrylonitrile. This gave respectively the hitherto unknown β-(thyminyl-N_3) propionitrile (I) and β-(5-fluorouracil-N_3) propionitrile (II).

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*Uracil is regarded as 2, 6-dioxotetrahydropyrimidine.