LETTERS TO THE EDITOR

SYNTHESIS OF 3-AMINO AND 3-ALKYLAMINO DERIVATIVES OF ISOFERVENULINE. FIRST INSTANCE OF DIRECT AMINATION OF THE 1,2,4-TRIAZINE RING AT POSITION 3

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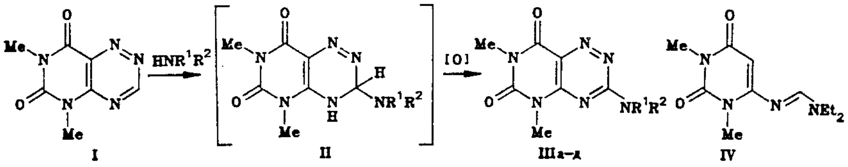
We have established that 5,7-dimethylpyrimido[4,5-e]-1,2,4-triazin-6,8-dione (isofervenuline) (I) is aminated and alkylaminated by Chichibabin's procedure under mild conditions, to form 3-amino- and 3-alkylamino derivatives (III) in good yield. Compound (I) was dissolved in liquid ammonia at −75°C; after 30 min oxidant, $KMnO_4$, was added to the mixture, and after another 15 min the ammonia was allowed to evaporate freely. The reaction was carried out similarly with alkylamines, with variation of reaction temperature between −70 and −40°C (depending on the alkylamine freezing point). Because $KMnO_4$ is not soluble in diethylamine, we used as oxidant the complex salt $[Ag(C_5H_5N)_2]MnO_4$. Apparently the reaction proceeds via formation of the covalent adduct (II), which then undergoes oxidative aromatization. It is of interest that when we tried to oxidize adduct IIe with 30% hydrogen peroxide it decomposed to eliminate nitrogen and form amidine (IV).

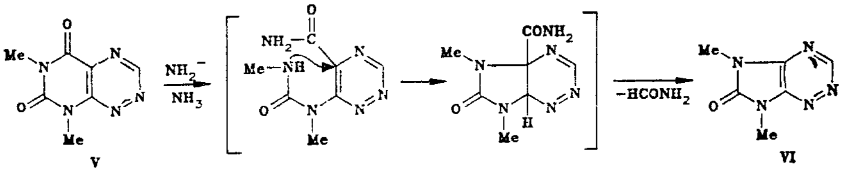


a $R^1=R^2=H$; b $R^1=H$, $R^2=Me$; c $R^1=H$, $R^2=Et$, d $R^1=R^2=Me$, e $R^1=R^2=Et$

Compounds. mp (°C), yield (%): IIIa, >330 (from water), 75; IIIb, 278-280 (from alcohol), 90; IIIc, 262-264 (from alcohol), 81; IIId, 208-209 (from alcohol), 89; IIIe, 157-158 (from alcohol), 76; IV, 127-129 (from octane), 88. Elemental analysis and IR and PMR spectra agree with the proposed structures.

The significance of this reaction is as follows: 1) it is the first instance of Chichaibabin amination of a 1,2,4-triazine ring at position 3. Hitherto direct amination of 1,2,4-triazines had yielded only their 5-amino derivatives [1]. 2) This is the first example of a reaction of isofervenuline with a nucleophile that is not accompanied by disruption of one of the rings [2, 3]. 3) The proposed method to obtain 3-aminoisofervenulines is more convenient than nucleophilic replacement of the 3-alkylthio- [4] and 3-alkylsulfonyl groups [5] in pyrimido[4,5-e]-triazine-6,8-diones.

When the isomer of compound (I), the natural antibiotic fervenuline (V), is reacted with $KNH_2/NH_3/KMnO_4$ under analogous conditions it is converted to the known compound [6] 5,7-dimethylimidazo-[4,5-e]-1,2,4-triazin-6-one (VI), (67% yield, mp 144-145°C). Probably the reaction goes by the following scheme (cf. [2]):



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LITERATURE CITED

1. Kh. van der Pas, Khim. Geterotsikl. Soedin., No. 8, 1011 (1987).
2. S. V. Shorshnev, S. E. Esipov, A. I. Chernyshev, A. F. Pozharskii, I. M. Nanavyan, and V. V. Kuz'menko, Khim. Geterotsikl. Soedin., No. 11, 1555 (1987).
3. S. V. Shorshnev, A. I. Chernyshev, S. E. Esipov, A. F. Pozharskii, V. V. Kuz'menko, and A. V. Gulevskaya, Khim. Geterotsikl. Soedin., No. 12, 1697 (1987).
4. L. von Heinisch, J. Prakt. Chem., 311, 438 (1969).
5. Yu. A. Azev, N. N. Vereshchagina, I. Ya. Postovskii, E. L. Pidemskii, and A. F. Goleneva, Khim.-farm. Zh., No. 11, 50 (1981).
6. S. V. Porshnev, S. E. Esipov, N. I. Yakushkina, N. A. Klyuev, V. G. Zhil'nikov, and A. I. Chernyshev, Khim. Geterotsikl. Soedin., No. 9, 1252 (1987).

TEMPLATE CONDENSATION OF o-PHENYLENE DIAMINE WITH VINYLOGS OF A FORMYLATING COMPLEX

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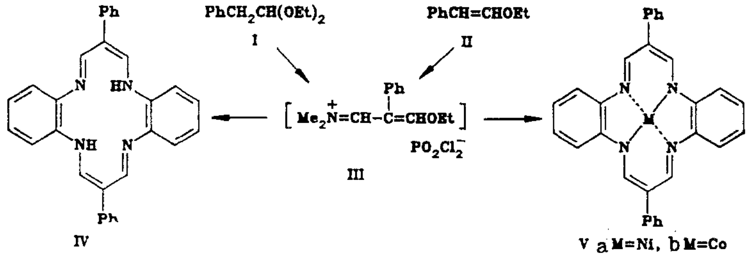
In studying the reaction of vinylogs of a formylating complex with primary amines, we have discovered that o-phenylene diamine takes part in template condensation with intermediate (III) to form the metal complex 7,16-diphenyldibenzo[b, i][1,4,8,11]-tetraaza[14]annulene (Va, b). Methods have previously been described for synthesizing aryl-substituted dibenzotetraazaannulenes and their metal complexes from o-phenylene diamine and various three-carbon synthones, such as 3-dimethylamino-2-phenylacrolein [1, 2] or 2-phenyl-3-ethoxyacrolein [2].

Intermediate (III), synthesized from DMFA, phosphorus oxychloride, and acetal (I) or ether (II) by the procedure of [3], was treated with concentrated soda solution, extracted, and boiled in alcohol with equimolar amounts of o-phenylene diamine and cobalt or nickel acetate.



After the reaction mixture was cooled to room temperature, compounds (Va, b) precipitated as fine dark brown crystals, with mp >300°C.

Nickel complex Va: 28% yield based on starting acetal (I). IR spectrum (in KBr tablets): 1332 (Ar—N—C), 1460, 1480 (C=C, C=N, macrocyclic skeleton), 1590 (C=N), 1610 cm^{-1} (C=C of aromatic ring). UV spectrum (DMFA): λ_{max} 490 nm, log ε 4.72. Cobalt complex Vb: 33% yield based on starting ether II. IR spectrum (in KBr tablets): 1330 (Ar—N—C), 1462, 1480 (C=C, C=N, macrocyclic skeleton), 1596 (C=N), 1602 cm^{-1} (C=C of aromatic ring). UV spectrum (DMFA): λ_{max} 425 nm, log ε 4.30.

The elemental composition and the molecular weight determined by mass spectrometry agree with the calculated values.

This is a template reaction; it proceeds with satisfactory yield (although lower than in [2]) only in the presence of salts of bivalent metals. Ring closure also occurs in the absence of template ions; under these reaction conditions the yield of ligand (IV) was no more than 2%.

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