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).

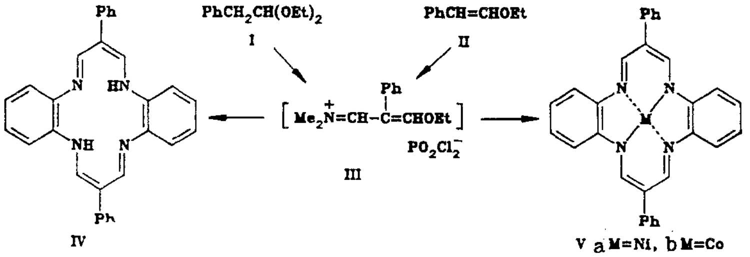
TEMPLATE CONDENSATION OF o-PHENYLENE DIAMINE WITH VINYLOGS OF A FORMYLATING COMPLEX

S. M. Makin, P. I. Broido,
and A. I. Pomogaev

UDC 547.898'553.1'381.54.386

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%.

Institute of Fine Chemical Technology, Moscow 119831. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1697-1698, December, 1988. Original article submitted December 12, 1987.

0009-3122/88/2412-1405$12.50 © 1989 Plenum Publishing Corporation

LITERATURE CITED

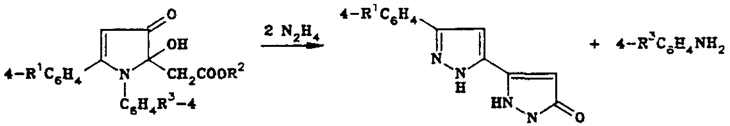
1. Yu. G. Yatluk and A. L. Suvorov, USSR Auth. Cert. 1,084,274; Byull. Isobret., No. 13, 67 (1984).
2. K. Asahi and S. Suga, U. S. Patent 4,460,036; Chem. Abstr., 100, 209,894 (1980).
3. S. M. Makin, O. A. Shavrygina, M. I. Berezhnaya, and T. P. Kolobova, Zh. Org. Khim., 8, 1394 (1972).

RECYCLIZATION OF 2-ALKOXYCARBONYLMETHYL-1,5-DIARYL-2-HYDROXY-2,3-DIHYDROPYRROL-3-ONES BY HYDRAZINE

V. O. Koz'minykh
and Yu. S. Andreichikov

UDC 547.775'727.723.07

4-Aroyl-3-hydroxy-1,5-diphenyl-2,5-dihydropyrrol-2-ones recyclize to pyrrolo-[3, 4-c]-pyrazoles [1] by the action of hydrazine. At the same time 3,5-dihydroxy-4-p-methoxybenzoyl-5-methoxycarbonyl-1-phenyl-2,5-dihydropyrrol-2-one is cleaved by hydrazine to form 5-p-methoxyphenyl-3-pyrazolecarboxylic anilide [2]. In our study of the reaction of 1,5-diaryl-2-alkoxycarbonyl-methyl-2-hydroxy-2,3-dihydropyrrol-3-ones (Ia-c) [3] with 70% aqueous hydrazine in ethanol we unexpectedly isolated 5-aryl-3-(5-oxo-1,2-dihydro-3-pyrazolyl)pyrazoles (IIa-c) in 67-79% yields.



I a-c

II a-c

Apparently the formation of compounds (IIa-c) is due to the reaction of hydrazine with the acyclic oxo form of the starting compounds (Ia-c), viz., the esters of 6-aryl-6-arylamino-3,4-dioxo-5-hexenoic acids.

To a solution of 0.01 mole of compounds (Ia-c) in 100 ml of 96% ethanol was added 0.02 mole of 70% aqueous hydrazine; the mixture was boiled for 3 h. The precipitate was filtered off and recrystallized from acetone or 1:1 DMSO—water to give compounds (IIa-c).

Compound IIa. 72% yield, mp 325-326°C (dec.). IR spectrum: (mineral oil); 3320-3310, 3230-3200 (NH), 1627 cm^{-1} (amide CO). PMR spectrum (in DMSO-D_6): 5.88 (1H, s, CH), 6.98 (1H, s, CH), 7.60 (5H, m, C_6H_5), 11.80 m.d. (1H, br. s, NH). Mass spectrum – m/z (relative intensity, %): 226 (100) $[M]^{+\cdot}$, 169 (67) $[M-CH_3NCO]^{+\cdot}$, 128 (3) $[C_6H_5C_4{\equiv}C{-}C{\equiv}NH]^+$, 104 (5) $[C_6H_5C{\equiv}NH]^+$, 103 (4) $[C_6H_5CN]^{+\cdot}$, 102 (4) $[C_6H_5C{\equiv}CH]^{+\cdot}$, 77 (11) $[C_6H_5]^+$.

Compound IIb. 67% yield, mp 316-317°C (dec.).

Compound IIc. 79% yield, mp 319-320°C (dec.).

LITERATURE CITED

1. Yu. S. Andreichikov, V. L. Gein, and I. N. Anikina, Zh. Org. Khim., 22, 1749 (1986).
2. Yu. S. Andreichikov, A. N. Maslivets, and L. I. Smirnova, Zh. Org. Khim., 23, 2254 (1987).
3. Yu. S. Andreichikov and V. O. Koz'minykh, Zh. Org. Khim. (1989) [sic].

Perm' Pharmaceutical Institute, Perm' 614600. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, p. 1698, December, 1988. Original article submitted April 27, 1988.

0009-31222/88/2412-1406$12.50 © 1989 Plenum Publishing Corporation