

17. E. Haselbach, A. Mannschreck, and W. Seitz, *Helv. Chim. Acta*, **56**, 1614 (1973).
18. M. Mintas, A. Mannschreck, and L. Klasinc, *Tetrahedron*, **37**, 867 (1981).
19. S. J. Brois, *Trans. Ann. N.Y. Acad. Sci.*, **31**, 931 (1969).
20. R. G. Kostyanovskii, G. K. Kadrokina, and K. S. Zakharov, *Dokl. Akad. Nauk SSSR*, **221**, 126 (1975).

THERMAL CONDENSATION OF PHTHALIMIDE WITH MALONIC ACID

V. N. Kopranenkov, E. A. Makarova,
and E. A. Luk'yanets

UDC 547.749.147'584'054.211'461.3.07:
542.953:541.11:548.737:543.51

When phthalimide is reacted with malonic acid in the presence of zinc acetate, 1-hydroxy-1-methyl-1H-3-(1-oxoisindolin-3-ylidenemethyl)isoindole, the zinc complex of 1-hydroxy-8,13:22,27-diimino-1,6:15,20-dinitrilotetrabenzob[d,l,q]eicosin, and zinc tetrabenzoporphin are formed depending on the temperature. The compounds have been characterized by their electronic absorption spectra, IR and mass spectra, and also by their x-ray photoelectron spectra. A possible scheme for the synthesis of zinc tetrabenzoporphin has been proposed.

In contrast to the anhydride condensation of phthalic anhydride [1, 2] the condensation of phthalimide with various active methylene components such as malonic acid or sodium acetate has not been fully studied. Meanwhile, this reaction is of interest from the point of view of research into convenient methods for synthesizing tetrabenzoporphins (TBP), which are being used in various branches of industry to an increasing extent.

There are reports in the literature about attempts to achieve this pathway for the synthesis of TBP. Thus, Helberger and coworkers [3] by reacting phthalimide with zinc acetate at 300°C obtained a 5:1 mixture of zinc TBP and zinc tetrabenzomonoazaporphin in negligible yield, while with ferrous acetate, ferrous TBP was formed with a yield of 0.2%. Reagents such as malonic acid or sodium acetate used by us in this reaction made it possible to reach a yield of 12% for TBP; and in the case of its tert-butyl-substituted analog, the yield reached 25% [4, 5]. As phthalimide sublimes when the temperature is increased, which has an effect on the yield of the final compound, it is more convenient to use potassium phthalimide. The optimum reaction conditions are: molar ratio of potassium phthalimide to malonic acid to zinc acetate 1:1.4:0.75; reaction temperature 340-360°C; reaction time 30 min to 1 h. The method developed has also successfully been used to obtain previously inaccessible polycyclic and unfamiliar meso-substituted analogs of TBP. Thus, starting from the imides of naphthalene-1,2- and naphthalene-2,3-dicarboxylic acids and also 1-phenylnaphthalene-2,3-dicarboxylic acids, tetra-1,2- and tetra-2,3-naphthoporphins [6] were obtained. When instead of malonic acid arylacetic acids are used in the reaction with phthalimide, meso-tetraaryl TBP products are formed [7, 8].

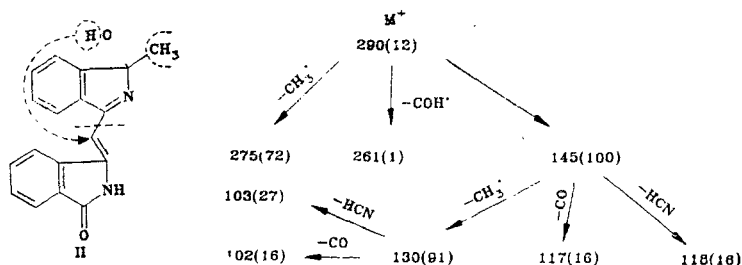
The subject of the present work is a study of the possible reaction scheme of phthalimide with malonic acid in the presence of zinc acetate and also the isolation and identification of some intermediate products. As it was impossible to determine the intermediates under the reaction conditions, it seemed to us desirable to investigate its stepwise pathway at lower temperatures, which in our opinion was also suitable for representing the process taking place under optimum conditions. Thus, when the reaction was carried out at 260°C, apart from unreacted phthalimide and a small quantity of 3-methylenephthalimidine (I) 1-hydroxy-1-methyl-1H-3-(1-oxoisindolin-3-ylidenemethyl)isoindole (II) was isolated as the main product, and its structure was confirmed from the data of elemental analysis and its IR and mass spectra. In the mass spectrum of compound II* a low-intensity peak from the

*Mass spectra of compounds II and III were recorded by V. K. Shevtsov (P. Lumumba Peoples' University).

Scientific Research Institute of Organic Intermediates and Dyes, Moscow 103797. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 4, pp. 480-484, April, 1988. Original article submitted October 8, 1986.

molecular ion (M^+) was recorded at 290 (12).^{*} The high-intensity peak from the ion at 275 (72) is caused by elimination of a methyl group from M^+ and it indicates indirectly that it is situated at a saturated carbon atom [9]. A feature of the fragmentation is the presence of the peak with maximum intensity from the ion at 145, which is formed by cleavage of the bond between the exocyclic carbon atom and the 1H-isoindole fragment of the molecule with migration of a hydrogen atom probably from the hydroxyl group to the exocyclic carbon atom. The subsequent decomposition of this ion confirms its structure.

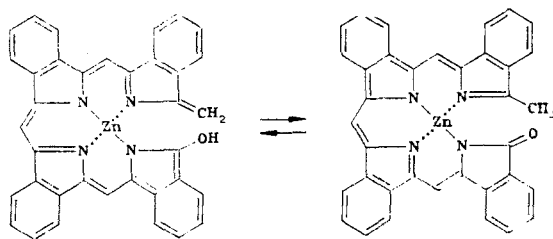
Scheme for decomposition of compound II by electron impact



In the IR spectrum of compound II there are absorption bands at 1730 ($C=O$), 2875-2985 ($C-H$), 3260 ($N-H$), and 3450 cm^{-1} (bonded $O-H$).

When the reaction is carried out at 300°C the formation of zinc TBP is detected in small quantities, and the main product is the zinc complex of 1-hydroxy-8,13:22,27-diimino-1,6:15,20-dinitrilotetrazabenzob[b,g,l,q]eicosin (III), the composition and structure of which are substantiated from the data of elemental analysis and the x-ray photoelectron, IR, and mass spectra.

In the x-ray photoelectron spectra[†] of compound III there are two peaks on the N1s curve (Fig. 1) with energy 398.4 and 400.2 eV, having a ratio of integral intensities equal to 2. The binding energy of 398.4 eV is consistent with the results for metalloporphyrins [10]. The higher value of the binding energy on the second curve for nitrogen may be due to the presence of the $C=O$ group in the molecule, which reduces the electron density on the neighboring nitrogen atom. Since the ratio of integral intensities is equal to 2, it is logical to assume that partial "transfer" of electron density along the π -system occurs from the nitrogen atom of the neighboring isoindole fragment. The O1s oxygen curve (Fig. 1) has a binding energy at 531.9 eV with half-width 2.7 eV, which corresponds to an energetically nonuniform state of the oxygen atoms in this compound. When the O1s line was resolved graphically into two components the binding energy for the oxygen atoms was 532.6 eV, which corresponds to the oxygen atom of a hydroxyl group, and 531.2 eV, which corresponds to the oxygen atom of a carbonyl group. The energy state of zinc ($Zn2p_{3/2} = 1021.5\text{ eV}$) corresponds to Zn^{2+} , which is in agreement with the results of [10]. From analysis of the x-ray photoelectron spectral data it is concluded that compound III exists in the crystalline state as a mixture of two tautomers:



This is also supported by the data of the IR and mass spectra. Thus, in the IR spectrum of compound III as a KBr pellet there is an absorption band at 1695 cm^{-1} , corresponding to stretching vibrations of the $C=O$ group, and there is also a broad band at $3100-3400\text{ cm}^{-1}$

^{*}The numbers for an ion in the text and scheme define the m/z value (peak intensity as a percentage of the maximum).

[†]Recorded and interpreted by T. M. Ivanova (Scientific Research Institute of Organic Intermediates and Dyes, Moscow).

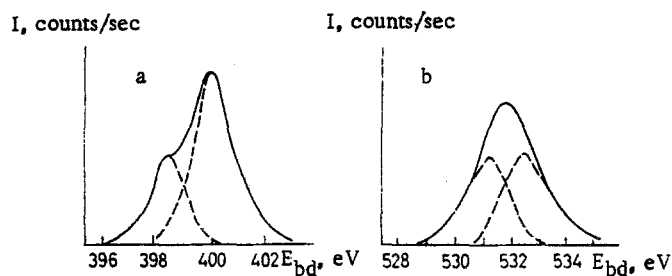


Fig. 1

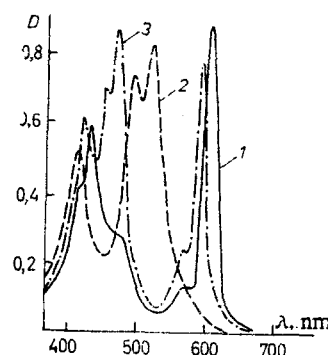


Fig. 2

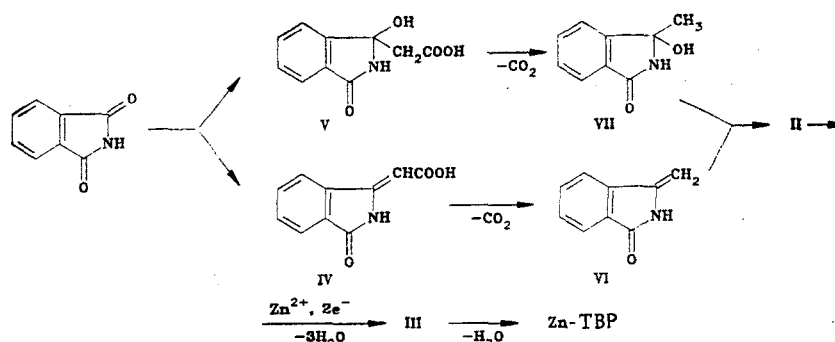
Fig. 1. X-Ray photoelectron spectra of compound III: a) N1s line; b) O1s line.

Fig. 2. Electronic absorption spectra of compound III: 1) in pyridine; 2) in acetic acid; 3) in acetone.

relating to stretching vibrations of the bonded hydroxyl group. The bands in the region $2870\text{--}2970\text{ cm}^{-1}$ are due to stretching vibrations of the C-H bonds. In the electron-impact mass spectrum there are low-intensity peaks from M^+ at 590/592/594 in the region of high m/z values. The medium-intensity peaks at 573/575/577 and 562/564/566 correspond to the separation from M^+ of hydroxyl and carbonyl groups respectively. The 548/550/552 ion is formed by elimination of an $\text{N}=\text{C}=\text{O}$ fragment, and the 460/462/464 ion is due to elimination of a 1-methylisoinidole fragment. The presence of ions at 579, 566, and 533 (based on the ^{64}Zn isotope) in the mass spectrum is probably due to thermal destruction of the initial substance. This conclusion is supported by the change in form of the mass spectrum when the admission temperature of the substance into the ion source is varied.

The presence of two tautomeric forms of compound III is also clearly shown by the change in its electronic absorption spectrum according to the type of solvent. Thus, in the spectrum of its bright green solution in pyridine (Fig. 2) there is an intense absorption band at 608 nm, while in acetic acid the color of solution changes to crimson and there is a doublet in the spectrum at 518 and 490 nm. In neutral organic solvents such as acetone bands from both forms are present but they undergo a hypsochromic shift. In acetic acid medium protonation of the macrocycle probably also takes place at the same time. When compound III is reprecipitated from sulfuric acid solution with water, a metal-free compound is obtained — the benzo analog of bilatriene, having absorptions at 522, 492, 422, 406, and 384 nm in ethyl acetate.

On the basis of the data obtained, the formation of zinc TBP from phthalimide, malonic acid, and zinc acetate can be represented by the following scheme:



Malonic acid reacts with phthalimide to give either the product of crotonic condensation — 3-carboxymethylenephthalimidine (IV) — or the product of aldol addition to the carbonyl group — 3-hydroxy-3-carboxymethylphthalimidine (V). Decarboxylation of these leads to the formation of 3-methylenephthalimidine (VI) and 3-hydroxy-3-methylphthalimidine (VII) respectively. It should be noted that the formation of phthalimidine VI is also detected in the reaction mixture using chromatographic methods. Subsequently, condensation of compounds VI and VII gives dimer II, which in the presence of zinc ion gives the zinc complex III — the precursor of zinc TBP. A comparative synthesis of zinc TBP should be carried out

with porphyrins using the polypyrrole condensation method [11]. In our case compounds II and III may be regarded as the benzo analogs of pyrromethenes and bilatrienes respectively.

On the basis of the scheme presented above it is to be expected that the synthesis of zinc TBP from compounds II-VII will occur with higher yields than from phthalimide. We have shown that when compounds II, IV, and VI are melted together with zinc acetate at 340-360°C for 1 h, zinc TBP is formed with yields of 36, 30, and 19% respectively. When compound III is heated to 360°C with a mixture of zinc acetate and sodium acetate, zinc TBP is formed in 38% yield.

EXPERIMENTAL

Electronic absorption spectra were recorded on a Hitachi-356 spectrophotometer using rectangular quartz cells of width 10 mm, with solution concentration $\sim 10^{-5}$ moles/liter. IR spectra were recorded on a UR-20 spectrometer in KBr pellets. Mass spectra of compounds II and III were obtained on a Varian MAT-44S mass spectrometer (admission temperatures of the substance into the ion source were 180 and 320°C, respectively, ionizing voltage 70 eV). The x-ray photoelectron spectra of compound III were recorded on a EC-100 spectrometer using AlK_{α} x-ray emission with $E = 1486.6$ eV. Spectra were recorded at room temperature in the same operating system for the spectrometer. Pressure in the chamber was $1.33 \cdot 10^{-5}$ Pa. The C1s line from the hydrocarbons of diffusion oil was used as the internal standard. The binding energy of the C1s electrons was taken to be 285 eV. Deconvolution of the unresolved spectra of $Al2p_{3/2}$ was carried out using a PDP-11/03 computer.

1-Hydroxy-1-methyl-1H-3-(1-oxoisindolin-3-ylidenemethyl)isoindole (II). A mixture of 2 g (10.8 mmole) of potassium phthalimide, 1.5 g (14.4 mmole) of malonic acid, and 2.2 g (10.1 mmole) of zinc acetate dihydrate was heated for 1 h in a current of helium at 260°C. The mixture was cooled, dissolved on heating in 50 ml of a 10% solution of caustic soda, filtered, and acidified with hydrochloric acid (1:1) to pH ~ 4 . The precipitate was separated, dissolved in 30 ml of chloroform, transferred to a chromatography column filled with silica gel (4×30 cm), and eluted with a chloroform-ethyl acetate-ethanol (10:10:1) mixture to give 0.45 g (29%) of compound II; R_f 0.46 (Silufol, chloroform-ethyl acetate-ethanol, 10:10:1); mp 233-234°C (ethyl acetate). IR spectrum: 1730 (C=O), 2875-2985 (C-H), 3260 (N-H), 3450 cm^{-1} (O-H). M^+ 290. Found: C 73.9; H 4.9; N 9.6%. $C_{18}H_{14}N_2O_2$. Calculated: C 74.5; H 4.9; N 9.7%.

Zinc Complex of 1-Hydroxy-8,13:22,27-diimino-1,6:15,20-dinitrilotetrabenzo[b,g,l,q]eicosin (III). A mixture of 2 g (10.8 mmole) of potassium phthalimide, 1.5 g (14.4 mmole) of malonic acid, and 2.2 g (10.1 mmole) of zinc acetate dihydrate was heated for 1 h in a current of helium at 300-320°C. The mixture was cooled, washed with 250 ml of aqueous ethanol (1:1) and then with 100 ml of hot DMF until the filtrate was colorless. The residue was dissolved in 50 ml of hot pyridine and the solution filtered through a layer of alumina (3×10 cm, Brockmann activity II). The solvent was removed and 0.56 g (35%) of compound III was obtained. IR spectrum: 1695 (C=O), 2870-2970 (C-H), $3100-3400\text{ cm}^{-1}$ (bonded O-H). M^+ 590 (^{64}Zn). Found: N 9.0%. $C_{36}H_{22}N_4OZn$. Calculated: N 9.5%.

Zinc Tetrabenzoporphin. A. A mixture of 0.3 g (1.6 mmole) of compound IV [12] and 0.26 g (1.19 mmole) of zinc acetate dihydrate was heated for 1 h in a current of nitrogen at 350-360°C; the mixture was cooled and washed successively with 100 ml of hot water and 100 ml of 80% ethanol. The residue was dissolved in 50 ml of DMF and diluted with 200 ml of water. The precipitate that formed was filtered, washed on the filter with 100 ml of 80% ethanol, dried at 60-80°C, dissolved in 25 ml of pyridine, transferred to a chromatography column filled with alumina (4×40 cm), and eluted with a pyridine-ether (1:4) mixture to give 0.085 g of BTP zinc complex, containing 0.064 g of pure product according to spectral analysis,* total yield 30%.

B. Under the same conditions 0.3 g (2.1 mmole) of compound VI and 0.33 g (1.5 mmole) of zinc acetate dihydrate gave zinc TBP in 18% yield.

C. A mixture of 0.15 g (0.52 mmole) of dimer II and 0.24 g (1.1 mmole) of zinc acetate dihydrate was heated for 1 h in a current of nitrogen at 360°C and purified according to

*The intensity of the long-wavelength absorption band at 632 nm with $\log \epsilon$ 5.18 [13] was used to determine the yield of zinc TBP.

method A to give 0.65 g (44%) of zinc TBP, which contained 0.053 g of pure product according to spectral analysis, total yield 36%.

D. A mixture of 0.25 g (0.42 mmole) of compound III, 0.09 g (0.41 mmole) of zinc acetate dihydrate, and 0.85 g (10.4 mmole) of sodium acetate was heated for 0.5 h in a current of nitrogen at 360°C; and after purification according to method A, 0.10 g of reaction product was obtained, containing 0.09 g (38%) of pure zinc IBP according to spectral analysis.

LITERATURE CITED

1. V. P. Oskhaya, Anhydride Condensation [in Russian], Zinatne, Riga (1973).
2. S. V. Vinogradova, V. V. Korshak, S. I. Salazkin, and G. M. Chelidze, *Zh. Prikl. Khim.*, **44**, 1389 (1971).
3. J. H. Helberger and D. B. Hever, *Annalen*, **536**, 173 (1938).
4. E. A. Luk'yanets, V. N. Kopranenkov, E. A. Makarova, V. A. Vazhnina, and A. M. Vorotnikov, USSR Inventor's Certificate No. 881,101; *Byull. Izobret.*, No. 42, 133 (1981).
5. V. N. Kopranenkov, E. A. Makarova, and E. A. Luk'yanets, *Zh. Obshch. Khim.*, **51**, 2727 (1981).
6. V. N. Kopranenkov, S. N. Dashkevich, A. M. Vorotnikov, and E. A. Luk'yanets, *Zh. Obshch. Khim.*, **55**, 900 (1985).
7. V. N. Kopranenkov, S. N. Dashkevich, and E. A. Luk'yanets, USSR Inventor's Certificate No. 889,675; *Byull. Izobret.*, No. 46, 140 (1981).
8. V. N. Kopranenkov, S. N. Dashkevich, and E. A. Luk'yanets, *Zh. Obshch. Khim.*, **51**, 2513 (1981).
9. A. A. Polyakova and R. A. Khmel'nitskii, *Mass Spectrometry in Organic Chemistry* [in Russian], Khimiya, Leningrad (1972), p. 367.
10. D. H. Karweik and N. Winograd, *Inorg. Chem.*, **15**, 2336 (1976).
11. N. S. Enikolopyan (editor), *Porphyrins (Structure, Properties, and Synthesis)* [in Russian], Nauka, Moscow (1985).
12. R. P. Linstead and G. A. Rowe, *J. Chem. Soc.*, Part 2, 1070 (1940).
13. R. P. Linstead and F. T. Weiss, *J. Chem. Soc.*, No. 11, 2975 (1950).

MOLECULAR STRUCTURE OF N-MESITYL-6H-ANTHRA[9,1-bc]PYRROL-6-ONE

G. V. Gridunova, V. E. Shklover,
Yu. T. Struchkov, R. A. Alimova,
and M. V. Gorelik

UDC 548.739.547.673.759.3

The molecular and crystalline structure of 1-(2,4,6-trimethylphenyl)-6H-anthra[9,1-bc]pyrrol-6-one was determined by the x-ray structural method. There is a larger uniformity of the bonds in the benzene ring of the isoindole fragment than in the N-substituted isoindoles; this derives from the electronic influence of the keto group. The structure of the whole molecule does not have marked 1,10-anthraquinoid character.

Pyrrolanthrone (6H-anthra[9,1-bc]pyrrol-6-ones, I) is a little-studied heterocyclic polycondensed system, the first stable examples of which [1-3] were obtained recently, as were the related systems of thiophenanthrone (II) [3] and furananthrone (III) [4]. Compounds of the type (I)-(III) are the benzoylene derivatives of isoindole, benzo[c]thiophene, and benzo[c]furan, and have the formal structure of 1,10-anthraquinonemethides. For the understanding of their properties [3, 4], it is important to know the extent of the localization of the ortho-quinoid structure in the benzoheterocyclic fragment, and of the 1,10-anthroquinoid structure in the whole molecule. The question is considered in the present paper taking as an example the pyrrolanthrone system (I) and its comparison with the isoindole system.

Scientific Research Institute of Organic Intermediates and Dyes, Moscow 103787. A. N. Nesmeyanov Institute of Heteroorganic Compounds, Moscow 117813. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 4, pp. 485-490, April, 1988. Original article submitted September 9, 1986; revision submitted May 25, 1987.