# SYNTHESIS OF DIBENZOTETRAAZA[14]ANNULENES FROM 3-TRIMETHYLSILOXYACROLEINS

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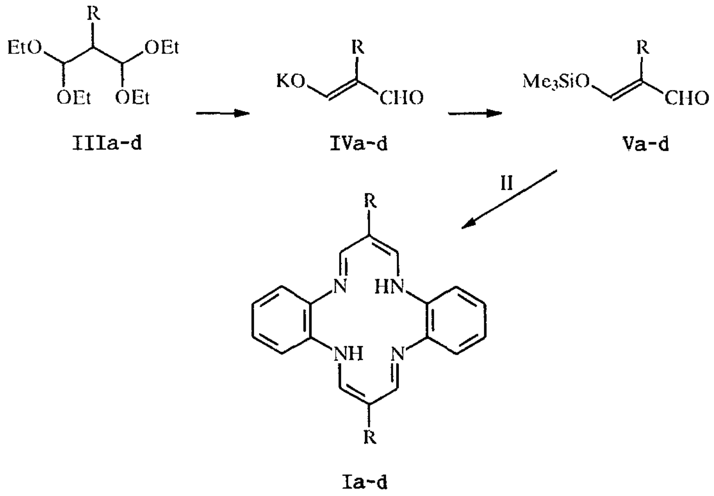
*7,16-Dialkyl-5,14-dihydrodibenzo[b,i][1,4,8,11]tetraza[14]annulenes have been synthesized from o-phenylenediamine and 2-alkyl-3-trimethyl-siloxyacroleins. The probable mechanism is discussed. It is shown that metallo complexes of 7,16-dialkyldibenzotetraaza[14]annulenes have been prepared in high yield under template conditions.*

5,14-Dihydrodibenzo[b,i][1,4,8,11]tetraaza[14]annulenes and their metallo complexes can find practical use as catalysts in oxidative–reductive processes, in analytical chemistry, and in semiconductor technology [1-3].

Although metallo complexes of 7,16-dibenzotetraaza[14]annulenes are readily obtained by template condensation of o-phenylenediamine (II) with bisdiethylacetals of substituted malonic aldehydes (III) [4], demetallation of these chelates by conventional methods [5] cannot be achieved. Among nontemplate synthetic methods for I the most successful is condensation of 3-alkoxyacroleins VI with o-phenylenediamine as fully studied in [6]. In a search for convenient novel methods of synthesizing the macrocycles I from available starting materials we have studied the reaction of o-phenylenediamine with alkyl 3-trimethylsiloxyacroleins Va-d.

We have synthesized 3-trimethylsiloxyacroleins V in 70-90% yield by silylation of enolates IV with trimethylchlorosilane in the presence of triethylamine in absolute ether with cooling [7, 8]. Enolates IV can be obtained from acetals III in almost quantitative yields.



I, III, IV, V a R = H, b R = $CH_3$, c R = $C_2H_5$, d R = $(CH_3)_2CH$

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TABLE 1. Choice of Optimum Cyclization Conditions

| Time, h | 1 | 3 | 5 | 10 |
|---|---|---|---|---|
| Solvent | Yields of Ic, % | | | |
| DMF | 16 | 19 | 19 | 17 |
| Quinaldine | 10 | 12 | 10 | |
| Butanol | 10 | 12 | 12 | 12 |
| Ethanol | 9 | 12 | 7 | |

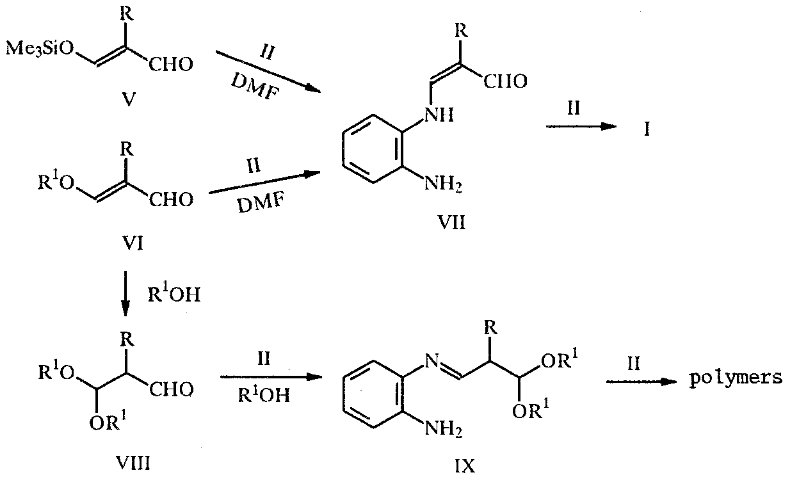
We have previously shown that refluxing 3-trimethylsiloxyacroleins V with o-phenylenediamine in organic solvent gives 7,16-disubstituted ligands I [9]. Excess of one or the other reagent has no effect on the yield of macrocycle I. To optimize the reaction time, choice of solvent, and selection of solvent and reagent concentration we have carried out a series of experiments. The results for reaction of Vc are given in Table 1. The best yield of Ic is achieved by refluxing equimolar amounts of II and Vc for 3 h in DMF. Using these conditions we have synthesized other ligands I. The yields and physical constants are given in Table 2.

In contrast to the reaction of 3-alkoxyacroleins VI, reaction of II and V using high boiling quinoline bases as solvent did not lead to an increased yield of macrocycle I. The yields of I from acroleins V and VI are in a limited range when using DMF solvent amounting to 17-25 and 19-20%. By contrast to 3-alkoxyacroleins VI [6] the 3-trimethylsiloxyacroleins V and diamine II in alcohol do not form polymeric Schiff bases.

The latter difference in behavior of V and VI can be explained in terms of the mechanism of reaction of acroleins with aromatic 1,2-diamines [6]. According to this mechanism, two pathways are possible only one of which leads to macrocyclization. The favorable case begins with nucleophilic substitution of the alkoxy group of acrolein VI by the amino group of diamine II and formation of intermediate VII with the terminal aldehyde group controlling subsequent formation of the macrocycle.

In alcoholic medium the alcohol can add to the conjugated double bond of VI to form acetal VIII, which with diamine II forms the intermediate IX. Acetalization of the $\beta$-carbonyl function tends to telomerization and not to macrocyclization.

Reaction of an alcohol with V is also possible but nucleophilic attack of the solvent in this case is directed not at the sp$^2$-hybridized carbon but at the silicon atom [7]. As a result of this attack, the O—Si bond is broken to generate a new carbonyl group. As a result of reaction with II, the intermediate will have the structure VII. Hence formation of dibenzotetraaza[14]annulenes from 3-trimethylsiloxyacroleins in commonly used solvents will not form polymers of Schiff bases and irreversibly contaminate the target macrocycle.



I, V, VI, VII, VIII, IX R = H, $CH_3$, $C_2H_5$, $(CH_3)_2CH$; R$^1$ = $CH_3$, $C_2H_5$

The ligands I can be metallated by usual methods [10] to give the metallo complexes of the 7,16-disubstituted dibenzotetraaza[14]annulenes. Template synthesis of these chelates is also possible from acroleins V as shown by the preparation of Xa,b from equimolar amounts of II, Vc, and nickel or cobalt acetate tetrahydrates. The yields of the chelates X were 60-70%.

TABLE 2. Yields and Data for Ligands Ia-d

| Compound | Empirical formula | mp (solvent) | $M^{+*}$ | Electronic spectrum, $\lambda_{max}$ (log ε) | Yield, % |
|---|---|---|---|---|---|
| Ia | $C_{18}H_{16}N_4$ | 296...298 (benzonitrile) | 288 | 386 (4,81) | 20 |
| Ib | $C_{20}H_{20}N_4$ | 288...290 (DMF) | 316 | 388 (4,72) | 25 |
| Ic | $C_{22}H_{24}N_4$ | 199...200 (DMF) | 344 | 388 (4,79) | 19 |
| Id | $C_{24}H_{28}N_4$ | 189...191 (DMF) | 372 | 380 (4,58) | 17 |

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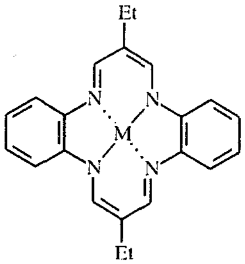
*Mass spectrometric determination.



Xa M = Ni, b M = Co

Hence this macrocyclic condensation of o-phenylenediamine with 3-trimethylsiloxyacroleins can be suitable for synthesis of both 7,16-dialkyl substituted dibenzotetraaza[14]annulenes and their metallo complexes.

## EXPERIMENTAL

Electronic spectra were obtained on a Specord UV-vis instrument using DMF solvent. Mass spectrometric determination of molecular weights was made using a JEOL GMS D-3 instrument.

Elemental analytical data for C, H, and N agreed with that calculated.

**5,14-Dihydrodibenzo[b,i][1,4,8,11]tetraaza[14]annulene (Ia).** A mixture of 3-trimethylsiloxyacrolein Va (0.72 g, 5 mmole) and o-phenylenediamine (0.54 g, 5 mmole) in DMF (1 ml) was refluxed for 3 h and cooled to room temperature. The precipitate was filtered, washed with ether, and dried in air. Yield 0.14 g.

**7,16-Dialkyl-5,14-dihydrodibenzo[b,i][1,4,8,11]tetraaza[14]annulenes Ib-d** were prepared similarly from acroleins Vb-d.

**7,16-Diethyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecinato Nickel(II) (Xa).** A mixture of 2-ethyl-3-trimethylsiloxyacrolein Vc (0.86 g, 5 mmole), o-phenylenediamine (0.54 g, 5 mmole), and nickel(II) acetate tetrahydrate (0.67 g, 2.5 mmole) in DMF (2 ml) was refluxed for 3 h, cooled to room temperature, and the precipitate filtered, washed with ethanol and ether, and dried in air. Yield 0.68 g (68%).

**7,16-Diethyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecinato cobalt(II) (Xb)** was obtained similarly from II, Vc, and cobalt(II) acetate tetrahydrate to give a 70% yield of product. The electronic spectra of Xa,b agreed with those reported [4].

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