

reactions of Butler, Bayer, and Gordon (3) but found that their directions yield 1,4-dibromoisoquinoline.

All of the hydrazones (II-X) formed water-insoluble, colored metal chelates which dissolved readily on addition of sufficient ethanol to the aqueous solutions. It is interesting that 1-hydrazinoisoquinoline (I) also formed colored chelates. In general, the pH range over which the metal chelates formed was from 3 to 11, except for the iron(II) chelates which formed between pH 5 and 9. Colors of the chelates in many cases were similar to those of their free ligands, especially those of I and VII. Listed in Table II are the colors of the iron(II), cobalt(II), nickel(II), and copper(II) chelates as well as their wavelengths of maximum absorbance and molar absorptivities.

The most promising hydrazone for use as a chromogenic reagent appears to be IV. Its chelates exhibit molar absorptivities in excess of  $2 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$  which is sufficient to enable trace metal determinations at the micromolar or 0.2-2.0- $\mu\text{g}$  level. Unfortunately the absorption bands of the various transition-metal chelates of IV overlap considerably so that accurate determination of one metal in the presence of the others is impractical without prior separation. Simultaneous determinations are also impractical except perhaps for iron and copper. Compound II, although less sensitive than IV, appears to be suitable for simultaneous determinations of iron, cobalt,

and nickel since the respective absorption bands are better resolved.

The hydrazones in their uncomplexed form undergo a pronounced color change from intense yellow to red on acidification. They may prove useful as indicators for pH and pK measurements of strong acids.

**Registry No.** I, 15793-94-9; II, 103837-15-6; III, 103837-16-7; IV, 103837-17-8; V, 103851-10-1; VI, 103837-18-9; VII, 103837-19-0; VIII, 103837-20-3; IX, 103837-21-4; X, 103837-22-5; isocarbostyryl, 491-30-5; hydrazine, 302-01-2; 2-formylpyridine, 1121-60-4; 2-formylquinoline, 5470-96-2; 2-formylquinoxaline, 1593-08-4; 1-formylisoquinoline, 4494-18-2; 3-formylisoquinoline, 5470-80-4; 2-formylpyrrole, 1003-29-8; 2-benzoylpyridine, 91-02-1; di-2-pyridyl ketone, 19437-26-4; 2-acetylpyridine, 1122-62-9.

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## Synthesis of 1,1'-Dibenzyl-5,5':7,7'-bis(hexano)bis[6(1H)-cycloheptatriazolone], a Novel Heterocyclic Ring System

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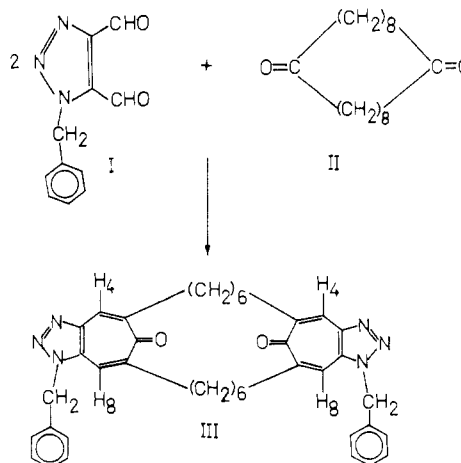
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The synthesis of 1,1'-dibenzyl-5,5':7,7'-bis(hexano)bis[6(1H)-cycloheptatriazolone] (III), an interesting example of a compound containing two triazolotropone systems within the same molecule, has been accomplished by the condensation reaction of 2 mol of 1-benzyl-1H-triazole-4,5-dicarboxaldehyde (I) with 1 mol of 1,10-cyclooctadecanedione (II).

Our continuing interest in the syntheses and reactions of triazole derivatives (1) has led us to prepare the novel ring system, 1,1'-dibenzyl-5,5':7,7'-bis(hexano)bis[6(1H)-cycloheptatriazolone] in order to study the effect of the polymethylene bridge on the aromaticity and planarity of a system which contains two triazolotropone systems within the same molecule (2, 3). The observed NMR chemical shift of 7.70 ppm from  $\text{Me}_4\text{Si}$  of the protons  $\text{H}_4$  and  $\text{H}_8$  can be attributed to an increase in the planarity of the triazolotropone system and also to the existence of a ring current which leads to the conclusion that this compound is aromatic in the tropone ring portion.

#### Experimental Section

1-Benzyl-1H-triazole-4,5-dicarboxaldehyde (I) was prepared according to the method of Henkel and Weygand (4). 1,10-



Cyclooctadecanedione (II) was prepared according to the procedure reported by Blomquist (5). Melting points were determined with a Thomas-Hoover Unimelt instrument and are uncorrected. NMR spectra were recorded on a Varian A-60 spectrometer using tetramethylsilane as an internal reference and shifts ( $\delta$ ) are reported in ppm.

**1,1-Dibenzyl-5,5':7,7'-bis(hexano)bis[6-(1H-cycloheptatriazolone)] (III)**. A mixture of 1-benzyl-1H-triazole-4,5-dicarboxaldehyde (0.43 g, 0.002 mol), 1,10-cyclooctadecanedione (0.28 g, 0.001 mol), and 0.4 g of KOH in 50 mL of methanol was heated under reflux for 3 h. The mixture was cooled and the precipitate was collected by suction filtration. Crystallization from chloroform-petroleum ether afforded 0.52 g (66%) of III, mp 240-242 °C; NMR ( $\text{CDCl}_3$ )  $\delta$  7.70 (s, 4 H,  $\text{H}_4$ , and  $\text{H}_8$ ), 7.10-7.40 (br, 10 H, ArH), 5.75 (s, 4 H, ArCH<sub>2</sub>), 2.30-3.0 (br, 8 H, C=C-CH<sub>2</sub>), and 0.90-1.70 (br, 16

H, CH<sub>2</sub>). Elemental analysis (C, H, N) were obtained and submitted for review and were within  $\pm 0.3\%$  of the theoretical values.

Registry No. I, 103532-75-8; II, 13747-10-9; III, 103532-76-9.

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## Application of Dipolar Cycloaddition Reaction toward the Synthesis of Polyfunctionality Heterocycles

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**Dipolar cycloaddition reactions of 2,4,6-trimethylbenzonitrile oxide with two disubstituted acetylenes and with a disubstituted ethylene were used for the synthesis of polyfunctionality isoxazole and 2-isoxazoline ring systems.**

The 1,3-dipolar cycloaddition reactions of nitrile oxides have been considered one of the best methods for the synthesis of isoxazole and 2-isoxazoline ring systems upon their reactions with substituted acetylenes (1-5) and ethylenes (6-12).

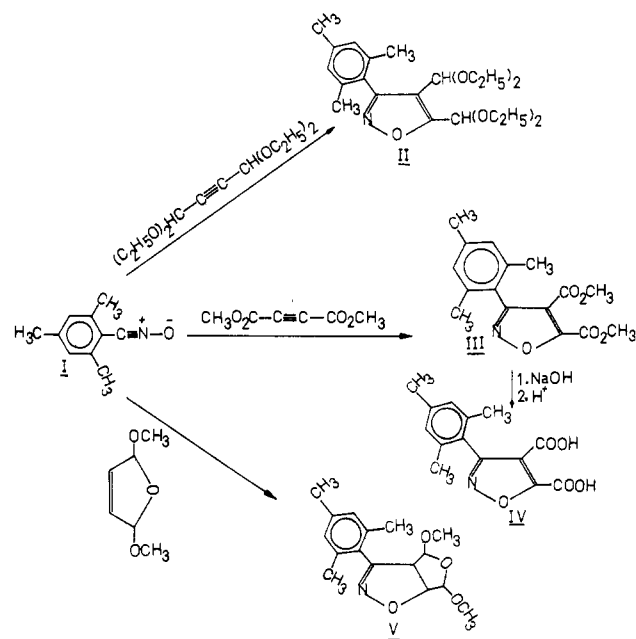
Most of the reported literature concern with the dialkylisoxazoles (3-5), dialkylisoxazolines (6-10) and with the monofunctional aldehydes (2, 11, 12) or esters (1, 8). Yet, not much work have been reported on the synthesis of polyfunctional groups on the isoxazole ring. However, the lack of polyfunctional groups of the isoxazole and isoxazoline ring systems prompted us to the synthesis of isoxazoledicarboxaldehyde and isoxazole diester. I report in the present paper details on the reaction of the stable aromatic nitrile oxide, 2,4,6-trimethylbenzonitrile oxide (I), with two disubstituted acetylenes and with a disubstituted ethylene as shown in Scheme I.

#### Experimental Section

2,4,6-Trimethylbenzonitrile oxide was prepared according to the method reported by Grundmann (13). Acetylenedicarboxaldehyde bis(diethyl acetal) was prepared from acetylene and triethyl orthoformate by the method described by Wohl (14). Melting points were determined by using a Thomas-Hoover Unimelt instrument and are reported uncorrected. The nuclear magnetic resonance spectra were taken on a Varian A-60 spectrometer using tetramethylsilane as an internal reference and shifts ( $\delta$ ) are reported in ppm.

**Preparation of 3-(2,4,6-Trimethylphenyl)-4,5-isoxazoledicarboxaldehyde Tetrakis(ethyl acetal) (II)**. To a solution of 4.83 g (0.03 mol) of 2,4,6-trimethylbenzonitrile oxide in 100 mL of tetrahydrofuran was added 6.90 g (0.03 mol) of acetyl-

Scheme I



enedicarboxaldehyde bis(diethyl acetal). The resulting mixture was heated under reflux for 6 h. The solvent was removed on a rotary evaporator at diminished pressure. Distillation of the remaining liquid yielded 9.03 g (77%) of the product, bp 173-177 °C/1 mmHg. The product was solidified near room temperature, mp 44-45 °C; NMR ( $\text{CDCl}_3$ )  $\delta$  6.85 (2 H, s), 5.87 (1 H, s), 5.13 (1 H, s), 3.15-3.90 (8 H, m), 2.32 (3 H, s), 2.10 (6 H, s), 0.93-1.38 (12 H, m).

**Dimethyl 3-(2,4,6-Trimethylphenyl)-4,5-isoxazoledicarboxylate (III)**. To a solution of 4.83 g (0.03 mol) of 2,4,6-trimethylbenzonitrile oxide in 80 mL of tetrahydrofuran was added 4.26 (0.03 mol) of dimethyl acetylenedicarboxylate. The mixture was heated under reflux for 1 h. After removal of the