## STUDIES ON 2,4,5-TRIARYLIMIDAZOLES.

1. SYNTHESIS OF SUBSTITUTED DERIVATIVES OF 1,4-BIS(4,5-DIPHENYLIMIDAZOL-2-YL)BENZENE AND "QUINOID" OXIDATION PRODUCTS

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Triarylimidazoles have recently attracted attention [1] for various reasons including their possible use in image recording [2]. In order to study the photochemical properties of substituted imidazoles, we synthesized a number of new derivatives of 1,4-bis(4,5-diphenylimidazol-2-yl)benzene (Ia). Products (Ib-e) were obtained in 80-90% yield and (If) in 55% yield by a general method.



The compounds synthesized are yellowish crystalline products which darken upon standing in the light and have only slight solubility in most solvents with the exception of DMF, DMSO, and pyridine. Solutions of (Ib-f) fluoresce.

The structure of (Ib-f) was confirmed by the similarity of their UV spectra with characteristic maxima in the vicinity of 300 and 350 nm,  $\varepsilon = 1.5 \cdot 10^4 - 4.5 \cdot 10^4$  to the spectrum of known (Ia), IR spectra (broad NH group bands are found with maxima at ~ 3450 nm, and OH and C-O group bands are also found for (Ie) and (If)), and the unequivocal method of synthesis involving condensation of the corresponding substituted benzils and terephthalic aldehyde in the presence of ammonium acetate [3] by analogy to (Ia). Derivatives of (IIa) were obtained in ~ 70% yield from (Ib-d) by a general oxidation method using alkaline potassium ferricyanide in aqueous dioxane. The generally accepted quinoid structure is used. The violet crystalline oxidation products (IIb-d) were isolated from benzene or benzene- hexane as greenish needles with a bronze hue. The structure of (IIb-d) is based on the general method of synthesis analogous to (IIa) [4] and the similarity of their electronic absorption spectra to the spectrum of (IIa) (maxima at 610-630 nm,  $\varepsilon \simeq 2.5 \cdot 10^4$ ) and mass spectral data showing the presence of singly and doubly charged molecular ions. The  $\nu N \sim H$  band at 3450 nm is not seen in their IR spectra. Products (IIb-d) are strong oxidizing agents and their dark violet solutions in benzene are decolored in the light. The photochemical transformations of (IIb-d) are currently under study.

A dark orange product which is extremely insoluble in the solvents studied was obtained by the analogous oxidation of 1,4-bis(phenanthro[9,10-d]imidazol-2-yl)benzene (III). Its structure is tentatively (IV)



The starting 4,4'-dihalobenzils used in the synthesis of (Ic) and (Id) were obtained by the catalytic method of Weiss and Appel [5] from the corresponding 4,4'-dihalobenzoins which, in turn, were synthesized by a modification of the method of Hakimelahi et al. [6]. Samples of 4,4'-dimethoxy- and hydroxybenzils were obtained by known procedures.

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## EXPERIMENTAL

The UV and visible spectra were taken on a Specord UV-VIS spectrometer in methanol for (Ib-f) and in benzene for (IIb-d). The IR spectra were taken on a UR-20 spectrometer on KBr pellets. The mass spectra were taken on a Varian MAT CH-6 spectrometer.

Synthesis of 4,4'-Difluorobenzoin. A sample of 4.2 g 4-fluorobenzaldehyde was dissolved in a mixture of 18 ml DMF and 6 ml DMSO with 0.38 g NaCN and the thick brown mass was let stand for 65 h at 20°C. The gel was then mixed with 200 g ice-water. The oily substance isolated gradually hardened. The crystalline slurry obtained was filtered and washed well with water with water pumping to yield 3.6 g (86%) crude 4,4'difluorobenzoin as light-pink crystals which were purified by recrystallization from ethanol, mp 85°C. A sample of 4,4'-dichlorobenzoin was similarly obtained.

Synthesis of 4,4'-Dichlorobenzil. A sample of 3 g 4,4'-dichlorobenzoin was dissolved in 10 ml hot acetic acid, and 1g ammonium nitrate and 0.25 g Cu(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O were added. The mixture was heated at reflux for 2 h. After cooling, the reaction mixture hardened into a light-colored crystalline mass which was separated on a filter and washed with a minimal amount of glacial acetic acid and a large quantity of water to yield 2 g (65%) 4,4'-dichlorobenzil, mp 194°C. A sample of 4,4'-difluorobenzil(83%, mp 115°C from benzene) was obtained analogously. Samples of 4-hydroxy- and 4,4'-dihydroxybenzils were obtained by known methods from 4-methoxyand 4,4'-dimethoxybenzils by refluxing with HBr in acetic acid.

<u>1,4-Bis(4,5-diarylimidazol-2-yl)benzenes</u> were synthesized by the general method of Drefahl [3] from the corresponding benzils and terephthalic aldehyde by refluxing in acetic acid for 2 h. Samples of (Ib-f) were obtained in 95, 91, 93, 82, and 55% yields, respectively. In the case of (Ie) and (If), the condensation products were isolated from the reaction mixture upon cooling without dilution with water.

Oxidation of (Ib-d) was carried out by the general method of Sakaino et al. [4] in the dark. The quinoid products were separated as dark violet precipitates which were filtered avoiding light and washed with water. Products (IIc) and (IId) were crystallized from benzene-hexane, while (IIb) forms golden needles from benzene. A nonmelting dark green substance which is not significantly soluble in ordinary solvents was obtained in the oxidation of (III).

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## CONCLUSIONS

1. 1,4-Bis(4,5-diarylimidazol-2-yl)benzenes were synthesized by the condensation of 4,4'-dimethoxy-, 4,4'-dichloro-, 4,4'-difluoro-, 4,4'-dihydroxy-, and 4-hydroxybenzils with terephthalic aldehyde and ammonium acetate.

2. Oxidation of bisimidazoles using potassium ferricyanide yielded 3,6-bis(4,5-diarylimidazol-2-ylidene)-cyclohexa-1,4-dienes, where the aryl groups were 4-methoxyphenyl, 4-chlorophenyl, and 4-fluorophenyl.

## LITERATURE CITED

- 1. B. S. Tanaseichuk, Khim. Geterotsikl. Soedin., 1299 (1972).
- 2. L. A. Cescon, West German Pat. No. 1,772,534 (1972); Chem. Abstr., 77, 27439 (1972).
- 3. G. Drefahl, J. Prakt. Chem., 23, 225 (1964).
- 4. Y. Sakaino, H. Kakisawa, T. Kusumi, and K. Maeda, J. Org. Chem., 44, 1241 (1979).
- 5. M. Weiss and M. Appel, J. Am. Chem. Soc., 70, 3666 (1948).
- 6. G. H. Hakimelahi, C. B. Boyce, and H. S. Kasmai, Helv. Chim. Acta, 60, 342 (1977).