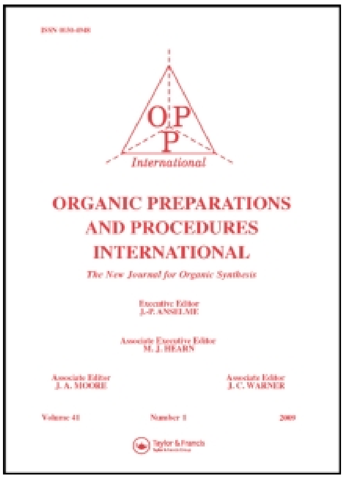

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A NEW PORPHINOGEN TYPE COMPOUND

O. Tsuge[a]; M. Tashiro[a]; Y. Kiryu[a]
[a] Research Institute of Industrial Science, Kyushu University, Fukuoka, Japan

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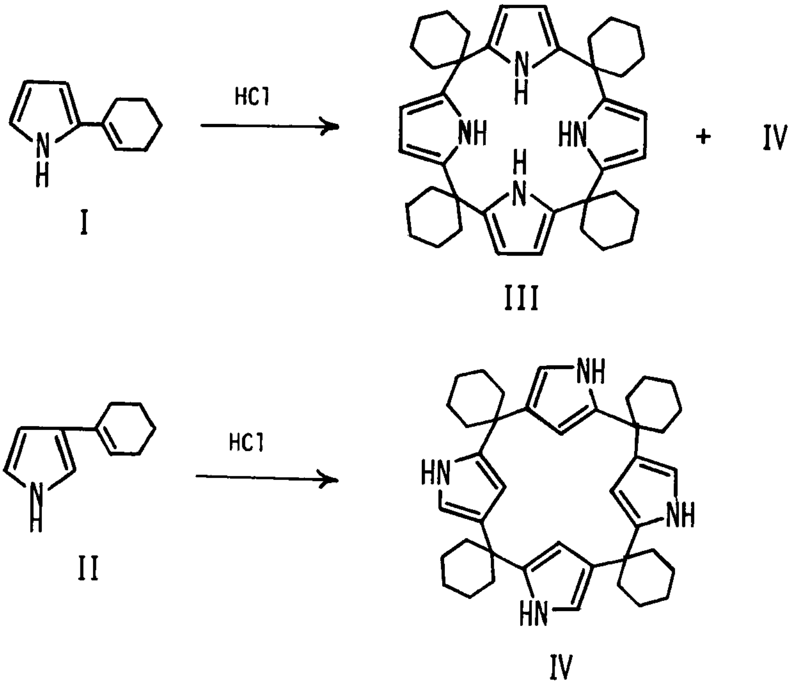
A NEW PORPHINOGEN TYPE COMPOUND

O. Tsuge*, M. Tashiro and Y. Kiryu

Research Institute of Industrial Science, Kyushu University,
Hakozaki, Higashi-ku, Fukuoka 812, Japan

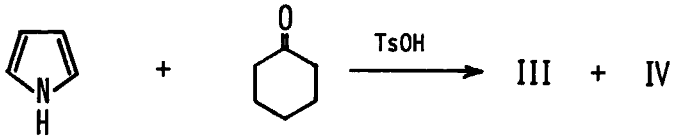
In porphinogen compounds formed from the acid-catalyzed condensation of pyrrole with carbonyl compounds such as acetone[1] and cyclohexanone,[2] all four bridge carbons are linked to the α-positions of the pyrrole nuclei. Recently, it has been found that the reaction of pyrrole with 1-(1-pyrrolidinyl)cyclohexene afforded 2-(1-cyclohexenyl)- (I) and 3-(1-cyclohexenyl)-pyrrole (II) together with other products.[3] New porphinogen type compounds were expected to be formed in the acid-catalyzed reaction of I and II. The



present paper deals with the formation of a new porphinogen type compound in which all four bridge carbons are alternately linked to the α- and β-positions of the pyrrole nuclei.

When a solution of I in diethyl ether was treated with dry hydrogen chloride, two tetramers, III and IV, were obtained in 21.5 and 5.5% yields respectively. Under similar conditions, II afforded a 63.4% yield of IV as a sole isolated product. The ir and nmr spectra of III were identical with those of an authentic sample of 21,22,23,24-tetrazaquaterene-2,7,12,17-tetraspirocyclohexane prepared by the reported method.[2] As no suitable solvents could be found, the nmr spectrum of IV could not be determined. However, the structure of IV was deduced to be a new porphinogen type compound in which all four bridge carbons are alternately linked to the α- and β-positions of the pyrrole nuclei because IV was formed from both I and II.

In this context, we reinvestigated the acid-catalyzed condensation of pyrrole with cyclohexanone. Although the reaction under the influence of hydrochloric acid afforded only III as reported,[2] both III and IV were formed in the p-toluenesulfonic acid-catalyzed condensation.[4] When a solution of pyrrole and cyclohexanone in benzene was heated to reflux in the presence of catalytic amounts of p-toluenesulfonic acid for 30 min, III and IV were obtained in 74.0 and 8.2% yields respectively. However, both I and II were unchanged under similar conditions.



EXPERIMENTAL

All the melting points are uncorrected. The ir spectra were measured as KBr pellets, and the mass spectra were obtained on a Hitachi RMS-4 mass spectrometer with a direct inlet and an ionization energy of 70 eV. The nmr spectrum was determined at 60 MHz with a Hitachi R-20 nmr spectrometer with TMS as an internal reference.

Materials.- 2-(1-Cyclohexenyl)- (I) and 3-(1-cyclohexenyl)pyrrole (II) were prepared by the method reported previously.[3] I: mp. 45-46° (colorless plates), bp. 142-148°/19 mm. II: bp. 158-161°/17 mm (colorless oil).

The Acid-catalyzed Reaction of I.- When dry hydrogen chloride was slowly introduced into a solution of 0.4 g. of I in 30 ml of diethyl ether at 0°, 0.24 g. of yellow solid was deposited. The solid was dissolved in 25 ml of methanol and the solution was then refluxed for 30 min to give 0.11 g. of insoluble crystals. The crystals were washed with 30 ml of benzene to leave colorless crystals, which on recrystallization from nitrobenzene afforded 22 mg. (5.5%) of the new porphinogen compound IV, mp. 302-303° (dec.), as colorless needles.

Anal. Calcd. for $C_{40}H_{52}N_4$: C, 81.58; H, 8.90; N, 9.52.

Found: C, 81.43; H, 8.98; N, 9.49.

Ir cm^{-1}: 3405, 3450, 3480 (NH), 2980, 2860, 1570, 1450, 1425, 1180, 1120, 1055, 970, 900, 880, 810, 765, 700. Mass:m/e 588 (M^+).

Evaporation of the benzene washings *in vacuo* afforded a residue which on recrystallization from benzene gave 86 mg. (21.5%) of porphinogen compound III, mp. 270-271° (dec.), lit.[2] mp. 272-272.5°, as colorless needles.

Anal. Calcd. for $C_{40}H_{52}N_4$: C, 81.58; H, 8.90; N, 9.52.

Found: C, 81.45; H, 9.03; N, 9.49.

Ir cm^{-1}: 3440 (NH). Nmr ($CDCl_3$) δ: 1.48 (24H, broad, $C\underline{H}_2$), 1.95 (16H, broad, $C\underline{H}_2$), 5.97 (8H, d, J=2.9 Hz, β-protons of pyrrole rings), 7.10 (4H, broad, $N\underline{H}$). The ir and nmr spectra were identical with those of an authentic sample prepared by the reported method.[2]

The Acid-catalyzed Reaction of II.- Into a solution of 0.3 g. of II in 40 ml of diethyl ether was slowly introduced dry hydrogen chloride, giving 0.38 g. of yellow solid. The solid was dissolved in 10 ml of methanol, and the solution was then refluxed for 10 min to give insoluble colorless crystals. Recrystallization from nitrobenzene afforded 0.19 g. (63.4%) of colorless needles, whose ir spectrum was identical with that of IV.

The p-Toluenesulfonic Acid-catalyzed Condensation of Pyrrole with Cyclohexanone.- A solution of 10.0 g. (0.15 mol) of pyrrole and 14.6 g. (0.15 mol) of cyclohexanone in 50 ml of benzene was refluxed with 0.5 g. of *p*-toluenesulfonic acid for 30 min; during which time 1.8 ml of water was separated and crystals were formed. Filtration gave colorless crystals, which were extracted with hot benzene to leave 1.8 g. (8.2%) of IV. From the benzene extract 16.2 g. (74.0%) of III was obtained.

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*To whom inquiries should be addressed.

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3. M. Tashiro, Y. Kiryu, and O. Tsuge, Heterocycles, 2, 575 (1974).
4. The condensation of pyrrole with acetone under similar conditions gave the $\alpha,\beta,\gamma,\delta$-octamethylporphinogen[1] as a sole product.

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