precipitate was removed by filtration and dried in a vacuum. The solid was chromatographed over 80% Magnesol–20% cellulose, using 10:20:3 ethylene dichloride–hexane–methanol. The eluate was filtered on Whatman No. 50 paper and evaporated to dryness. It was then crystallized from hot pyridine, isoöctane and dried in a vacuum at room temperature for 12 hr.

Spectrum in pyridine—λ_{max} (mμ) α: I, 585; II, 557; III, 425; IV, 413. ϵ: I, 8.76 × 10^3; II, 1.91 × 10^4; III, 3.02 × 10^5; IV, 3.00 × 10^5.

Anal. Calcd. for $C_{36}H_{40}O_4N_4Mg \cdot 2(C_5H_5N)$: C, 71.27; H, 6.50. Found: C, 71.34; H, 6.55.

Acid treatment regenerated a compound having the spectrum of Mesoporphyrin IX.

Magnesium Octamethyl Porphyrin Dipyridine Complex.—For the preparation of this chelate the magnesium viologen reagent was used. After adding the octamethyl porphyrin, the solution was refluxed for 1 hr., then cooled, filtered, and poured into 200 ml. of water. The precipitate was allowed to settle for 1 hr. and then filtered off and dried in a vacuum. The magnesium complex was chromatographed over 80% Magnesol–20% cellulose using a 2:1 mixture of chloroform–pyridine. The eluate was evaporated to dryness in a vacuum and washed first with boiling hexane, then with a 1:2 mixture of acetone and water. Finally, it was crystallized from boiling pyridine and dried in a vacuum.

Spectrum in pyridine—λ_{max} (mμ): I, 584; II, 557; III, 425; IV, 412. ϵ: I, 6.44 × 10^3; II, 1.63 × 10^4; III, 2.85 × 10^5; IV, 1.93 × 10^5.

Anal. Calcd. for $C_{28}H_{28}N_4Mg \cdot 2(C_5H_5N)$: C, 75.68; H, 6.35. Found: C, 75.75; H, 6.09.

Magnesium Phthalocyanine Monopyridine Monoaquo Complex.—The preparation was performed with the magnesium viologen reagent. After adding the insoluble phthalocyanine, the suspension was refluxed for 0.5 hr., filtered, precipitated with water, filtered, and dried. The magnesium chelate was then dissolved in pyridine and precipitated by adding an excess of benzene. This precipitate was chromatographed over alumina using pyridine as the solvent. The pyridine was removed under vacuum and the product washed first with hot hexane and then with a mixture of 1:2 acetone–water. It was then crystallized from hot pyridine.

Spectrum in pyridine—λ_{max}(mμ): I, 680; II, 651; III, 614; IV, 588 (minor peak); V, 519 (minor peak). ϵ: I, 2.71 × 10^5; II, 3.71 × 10^4; III, 4.32 × 10^4.

Anal. Calcd. for $C_{32}H_{16}N_8Mg \cdot C_5H_5N.H_2O$: C, 70.11; H, 3.66. Found: C, 69.93, 70.38; H, 3.70, 3.69.

Syntheses and Reactions of Methyl Triphenylpyrrolecarboxylates[1]

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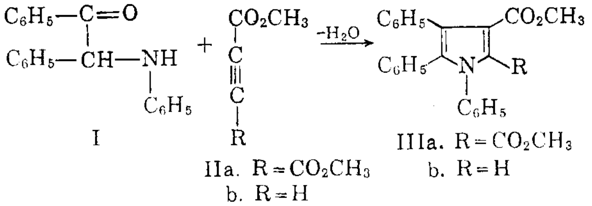
Received March 26, 1962

As part of a study of the reactions of sodium β-formyl-β-keto-α-nitropropionate,[4,5] it became necessary to synthesize several heretofore unknown, vicinally substituted triphenylpyrroles as intermediates for further investigations. On examination of Fisher-Hirschfelder molecular models of these compounds, it was apparent that none of the phenyl groups could lie coplanar with the pyrrole nucleus without interfering with a neighboring phenyl substituent. Therefore, it was of interest to investigate the possible existence of this type of molecular arrangement of substituted pyrroles.

A convenient synthesis of substituted pyrroles is the recently reported[6] Michael condensation of the hydrochloride of an α-(primary)amino ketone and dimethyl acetylenedicarboxylate (IIa) in the presence of sodium acetate. As a test of the applicability of the reaction to the synthesis of N-substituted pyrroles, the hydrochloride of desylaniline (I) was condensed with IIa in the presence of sodium acetate to give a 39% yield of dimethyl 1,4,5-triphenylpyrrole-2,3-dicarboxylate (IIIa). However, by a slight modification of the described procedure, IIIa was obtained in 79% yield from the condensation of desylaniline and IIa alone. Similarly, by the condensation of I and methyl propiolate (IIb), methyl 1,4,5-triphenylpyrrole-3-carboxylate (IIIb) was obtained in 70% yield. The mechanism proposed[6] is consistent with our observations that in the condensation of I and IIb the product formed is the 3-carbomethoxypyrrole IIIb, and not the isomeric 2-carbomethoxypyrrole.

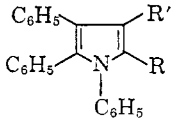


I

IIa. $R = CO_2CH_3$
b. $R = H$

IIIa. $R = CO_2CH_3$
b. $R = H$

In no instance, however, were the corresponding intermediate hydroxypyrrolines[6] isolated in the formation of IIIa and IIIb. Hydrolysis of IIIa and IIIb in alcoholic potassium hydroxide followed by acidification gave the corresponding acids, 1,4,5-triphenylpyrrole-2,3-dicarboxylic acid (VI) and 1,4,5-triphenylpyrrole-3-carboxylic acid (VII), respectively. Decarboxylation of VII proceeds smoothly in quinoline with copper chromite catalyst to give 1,2,3-triphenylpyrrole (VIII).



VI. R, R′ = CO_2H
VII. R = H; R′ = CO_2H
VIII. R, R = H

The orientation of the condensation reaction of I and IIb to give IIIb was established as shown by

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[1] Supported in part by Research Grant No. CY-2240 of the National Institutes of Health, U.S. Public Health Service.

[2] United States Steel Foundation Fellow 1960–1962.

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[4] P. E. Fanta, R. A. Stein, and R. M. W. Rickett, *J. Am. Chem. Soc.*, **80**, 4577 (1958).

[5] P. E. Fanta, R. M. W. Rickett, and D. S. James, *J. Org. Chem.*, **26**, 938 (1961).

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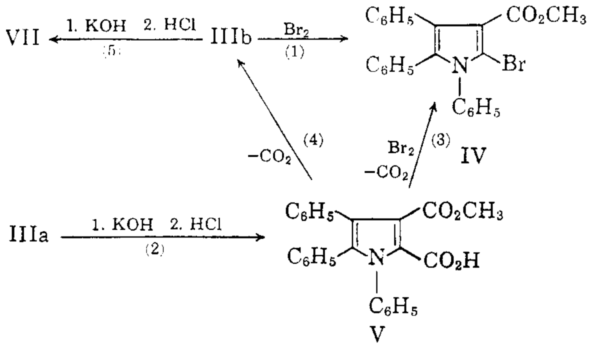
the accompanying reaction scheme. First, methyl 2-bromo-1,4,5-triphenylpyrrole-3-carboxylate (IV) was obtained on bromination of IIIb. Then the selective hydrolysis[7-9] of IIIa with an equimolar amount of potassium hydroxide in ethanol followed by acidification gave methyl 2-carboxy-1,4,5-triphenylpyrrole-3-carboxylate (V). Bromination of V was accompanied by decarboxylation[7b,10,11] to give the same bromopyrrole as was obtained from IIIb in reaction 1. Impurities in the bromopyrrole obtained by reaction 3 were difficult to remove, and the melting point of this material could not be raised completely to that of the product obtained by reaction 1. However, a mixed melting point of the two products was not depressed below the lower melting material, and their infrared spectra proved to be identical.



Further proof of the structure of IIIb was obtained by decarboxylation of V in quinoline–copper chromite mixture by reaction 4 to give a product identical to IIIb. Hydrolysis of this product gave the same acid, VII, as was obtained by the hydrolysis of IIIb in reaction 5. Although, as was experienced before, traces of impurities were difficult to remove from the products obtained from reaction 4 and subsequent hydrolysis to VII, their mixed melting points with respective authentic samples of IIIb and VII were not depressed, and their infrared spectra were also identical with those of the corresponding samples.

Experimental[12]

Preparation of Desylaniline (I).—A mixture of 23.3 g. (0.1 mole) of desyl chloride and 18.6 g. (0.2 mole) of aniline in 200 ml. of ethanol was refluxed for 4 hr., cooled, and filtered to give 20.8 g. of yellow crystals. One recrystallization from ethanol gave desylaniline as long, yellow needles, m.p. 97.4–98.6° (lit.,[13] m.p. 97–98°).

Desylaniline hydrochloride was prepared by the method previously described.[13]

Preparation of Methyl Propiolate (IIb).—A mixture of 25 g. of propiolic acid and 30 g. of 10% methanolic sulfuric acid was refluxed gently for 46.5 hr. The solution was cooled and extracted three times with 20-ml. portions of very nearly saturated aqueous sodium chloride. The resulting organic layer was then extracted with 5% aqueous sodium bicarbonate until the aqueous discard was basic to litmus. After washing with water the organic layer was dried thoroughly with anhydrous sodium sulfate then with anhydrous magnesium sulfate. The resulting solution was distilled and the fraction boiling at 96–102.5° (lit.,[14] b.p. 102°) was collected. The yield of methyl propiolate was 14.7 g. and was used directly in subsequent reactions.

Dimethyl 1,4,5-Triphenylpyrrole-2,3-dicarboxylate (IIIa).—A mixture of 1.43 g. (5 mmoles) of desylaniline (I) and 1.42 g. (10 mmoles) of dimethyl acetylenedicarboxylate (IIa) in 15 ml. of methanol was refluxed for 2 hr. The reaction mixture was cooled in an ice chest and then filtered. This gave 1.60 g. (79%) of white powder, m.p. 167–169° (uncorr.) Two recrystallizations from ethanol gave fine, white microcrystals, m.p. 165.4–167.0°; infrared absorption: $\nu_{max}^{CH_2Cl_2}$ 1720 (s) (C=O), 1210 (s) (C—O).

Anal. Calcd. for $C_{26}H_{21}NO_4$ (411): C, 75.89; H, 5.15; N, 3.40. Found: mol. wt. (ebul. in benzene), 397; C, 75.79; H, 5.19; N, 3.33.

Methyl 1,4,5-Triphenylpyrrole-3-carboxylate (IIIb). A. Condensation of Desylaniline (I) and Methyl Propiolate (IIb).—A mixture of 1.43 g. (5 mmoles) of I and 0.84 g. (10 mmoles) of IIb in 15 ml. of methanol was heated to reflux for 16 hr. After the mixture was cooled in an ice chest and filtered, 1.22 g. (70%) of a light cream-colored solid was collected, m.p. 170–171° (uncorr.). Short, white needles were obtained after one recrystallization from ethanol, m.p. 167.8–168.6°; infrared absorption: $\nu_{max}^{CH_2Cl_2}$ 1719 (s) (C=O), 1220 (s) (C—O).

Anal. Calcd. for $C_{24}H_{19}NO_2$: C, 81.56; H, 5.42; N, 3.96. Found: C, 81.59; H, 5.43; N, 4.17.

B. Decarboxylation of V.—A mixture of 1.0 g. (2.5 mmoles) of V and 50 mg. of copper chromite in 3 ml. of freshly distilled quinoline was heated to 190° and maintained at that temperature for 15 to 20 min. The mixture was cooled to room temperature and 35 ml. of ether was added. After filtering the mixture the filtrate was transferred to a separatory funnel and extracted with dilute aqueous hydrochloric acid. The ethereal layer was washed with water then evaporated to dryness on a steam bath. A little ethanol was added, the mixture was cooled, and then filtered giving 0.70 g. of white powder. Repeated recrystallization from ethanol gave fine, white needles, m.p. 150–162° (uncorr.). This compound, in spite of its low melting point, was identical with the sample obtained in procedure A above upon its infrared examination in methylene chloride.

Methyl 2-Bromo-1,4,5-triphenylpyrrole-3-carboxylate (IV). A. Reaction of IIIb with Bromine.—To a solution of 1.36 g. (3.8 mmoles) of IIIb in 8 ml. of chloroform was added 0.62 g. (3.9 mmoles) of bromine. The mixture was shaken and disappearance of the reddish brown color began immediately. The resulting solution was allowed to stand with occasional shaking for 1.5 hr. A stream of nitrogen gas was bubbled through the solution to displace as much of the hydrogen bromide gas as possible after which the solution was evaporated under reduced pressure to a pale yellow oil. On adding a few drops of ethanol and scratching the walls of the flask a white solid separated. After cooling then filtering this gave 1.62 g. of white powder. Two

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[12] The infrared spectra of all compounds were taken with a Perkin-Elmer Infracord spectrophotometer, and absorption frequencies are measured in units of cm.$^{-1}$. The elemental analyses were done by Micro-Tech Laboratories, Skokie, Illinois. All melting points are corrected, unless otherwise indicated.

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[14] I. N. Nazarov, S. N. Ananchenko, and I. V. Torgov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, **95** (1959).

recrystallizations from ethanol gave blunt, white crystals, m.p. 167.4–168.8°; infrared absorption: $\nu_{max}^{CH_2Cl_2}$ 1717 (s) (C=O), 1225 (s-m) (C—O).

Anal. Calcd. for $C_{24}H_{18}NO_2Br$: C, 66.67; H, 4.20; N, 3.24; Br, 18.49. Found: C, 65.87, 65.63, 65.97; H, 4.16, 4.34, 4.38; N, 3.34, 2.95; Br, 18.95.

B. Reaction of V with Bromine.—To a solution of 0.20 g. (0.5 mmole) of V in 3 ml. of chloroform was added 0.08 g. (0.5 mmole) of bromine. The mixture was stirred for 2 hr. and the product worked up as outlined above for the reaction with IIIb. This gave 0.15 g. of a white powder which after repeated recrystallization from ethanol melted at 161–165° (uncorr.). A mixed melting point with the sample prepared by method A was not depressed. The infrared spectrum of this material in methylene chloride was also identical with the above sample.

Methyl 2-Carboxy-1,4,5-triphenylpyrrole-3-carboxylate (V).—To a hot mixture of 6.17 g. (15 mmoles) of IIIa in 150 ml. of ethanol was added 0.84 g. (15 mmoles) of potassium hydroxide. The mixture was stirred under reflux for 16 hr., cooled to room temperature, and then poured into 800 ml. of water. After adding 45 ml. of 5% sodium bicarbonate, the aqueous mixture was extracted twice with 200 ml. of ether. The combined ether extracts were washed with water and the aqueous washings added to the above basic aqueous layer. The ethereal solution was dried with anhydrous sodium sulfate, evaporated to dryness to give 1.24 g. of starting material IIIa. The combined basic aqueous mixture from above was acidified with 15 ml. of concentrated hydrochloric acid then extracted three times with 250-ml. portions of ether. The combined ether extracts were washed with water, dried with anhydrous sodium sulfate, and evaporated to dryness on a steam bath. After filtering this gave 4.06 g. of a white solid. Two recrystallizations from a water–ethanol mixture gave fine, white needles, m.p. 169.8–170.9°[15]; infrared absorption: $\nu_{max}^{CH_2Cl_2}$ near 2600 (m-w) (H-bonded O—H), 1724 (s) (ester C=O), 1631 (s) broad (acid C=O), 1336 (s), 1228 (s) (C—O).

Anal. Calcd. for $C_{25}H_{19}NO_4$: C, 75.55; H, 4.82; N, 3.53. Found: C, 75.43; H, 4.82; N, 3.52.

1,4,5-Triphenylpyrrole-2,3-dicarboxylic Acid (VI).—A mixture of 1.0 g. (2.4 mmoles) of IIIa and 4.0 g. of potassium hydroxide in 20 ml. of ethanol was refluxed for 35 min. The mixture was cooled then filtered, and the white solid was collected and dissolved in 160 ml. of water. The aqueous solution was extracted with ether then acidified with 5 ml. of concentrated hydrochloric acid. After extracting the acidic mixture three times with 50-ml. portions of ether, the combined ether extracts were concentrated to near dryness. On cooling this gave after filtering 0.90 g. of white powder. Two recrystallizations from ethanol gave fine, white needles, m.p. 260.4–263.4°,[15] infrared absorption: ν_{max}^{KBr} near 3450 (m) (O—H), near 2500 (w) (H-bonded O—H), 1675 (s) (broad) (C=O), 1287 (s) and 1225 (s) (C—O).

Anal. Calcd. for $C_{24}H_{17}NO_4$: C, 75.18; H, 4.47; N, 3.66. Found: C, 75.05; H, 4.59; N, 3.65.

1,4,5-Triphenylpyrrole-3-carboxylic Acid (VII). A. Hydrolysis of IIIb Obtained from the Condensation of I and IIb.—To a hot mixture of 1.78 g. (5 mmoles) of IIIb in 75 ml. of ethanol was added 1.18 g. of potassium hydroxide. The mixture was refluxed for 19 hr., cooled, and filtered. The white solid was suspended in 1000 ml. of water, 15 ml. of 5% aqueous sodium bicarbonate was added, and the mixture was extracted with ether. The aqueous layer was acidified with 10 ml. of concentrated hydrochloric acid then extracted eight times with 100-ml. portions of ether. The combined ether layers were washed with water, dried with anhydrous sodium sulfate, then stripped of solvent until only a solid residue remained. The residue was collected in a filter funnel, washed with ether, and air-dried. This gave after recrystallization from glacial acetic acid fine, white needles, m.p. 272.5–273.5°,[15] infrared absorption: ν_{max}^{KBr} near 2550 (w) (H-bonded O—H), 1688 (s) (with shoulder near 1650) (C=O), doublet: 1226 and 1212 (s-m) (C—O).

Anal. Calcd. for $C_{23}H_{17}NO_2$: C, 81.39; H, 5.05; N, 4.13. Found: C, 81.43; H, 5.05; N, 4.22.

B. Hydrolysis of the Product Obtained by Decarboxylation of V.—A mixture of 0.45 g. of the material and 0.38 g. of potassium hydroxide in 25 ml. of ethanol was refluxed for 16.5 hr. The product was worked up in an analogous manner as above. This gave 0.36 g. of white powder, and after repeated recrystallizations from glacial acetic gave fine, white needles, m.p. 266.8–268.4°.[15] The mixed melting point of this material with the above sample was not depressed below 269°, and the two samples were proven to be identical by their infrared examination in potassium bromide.

1,2,3-Triphenylpyrrole (VIII). Decarboxylation of VII.—A mixture of 0.2 g. of VII and 0.02 g. of copper chromite catalyst in 2 ml. of freshly distilled quinoline was heated gradually to 205–210° and maintained at this temperature for 1.5 hr. The mixture was cooled to room temperature, 25 ml. of ether was added, and the mixture filtered. The filtrate was extracted with dilute aqueous hydrochloric acid, and the organic layer separated and washed with water. Evaporation of the ethereal solution to near dryness, cooling, then filtering gave 0.14 g. of light tan needles. One recrystallization from ethanol gave fine, white needles, m.p. 179.8–180.0°, infrared absorption: $\nu_{max}^{CH_2Cl_2}$ near 3030 (m-w) (C—H), 1596 (s-m) and 1497 (s) (C=C).

Anal. Calcd. for $C_{22}H_{17}N$: C, 89.46; H, 5.80; N, 4.74. Found: C, 89.20; H, 5.80; N, 4.75.

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[15] Compound melted with moderate to vigorous evolution of gas.

Conjugate Addition of Aryl Grignard Reagents to Unsaturated Azlactones in the Presence of Cuprous and Cobaltous Chlorides[1]

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Received March 26, 1962

It is well established that aryl Grignard reagents react with unsaturated azlactones to give products of 1,2-addition. Thus, for example, 2-phenyl-4-benzylidene-5(4H)-oxazolone (I) reacts with excess phenylmagnesium bromide to give 1,1-diphenyl-2-benzamidocinnamyl alcohol (II) and 2,5,5-triphenyl-4-benzylidene-2-oxazoline (III).[3–6] No products of 1,4-addition to the α,β-unsaturated moiety have been isolated under these conditions. It has also been shown that alkyl Grignard reagents give exclusive 1,4-addition with these compounds.[7] More recently, we have reported that the labile geometric isomer of I reacts with aryl

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(2) On leave of absence from N.B.S. College, Hyderabad (India).

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