not very useful for differentiation purposes. From Lespieau's[23] and Derfer's[24] data on the Raman and infrared spectra of substituted cyclopropanes it is possible to pick out a series of medium bands in the range 878–840 cm.$^{-1}$. Cleveland[25] lists 842 cm.$^{-1}$ and 879 cm.$^{-1}$ as very strong bands of 1,1-dimethylcyclopropane and spiropropane, respectively. It becomes of interest, therefore, to search the region between 900 cm.$^{-1}$ and 830 cm.$^{-1}$ to see if any such characteristic band might be found in the *i*-steroids which does not have a counterpart in the normal steroids.

The medium weak band at *ca.* 894 cm.$^{-1}$ and the band of medium intensity at *ca.* 861 cm.$^{-1}$ have already been mentioned as being present in all the five *i*-steroids containing a methoxy group. The sixth *i*-steroid studied, *i*-cholestan-6-one, has bands of comparable intensity at slightly higher frequencies than each of these, namely, at 903 cm.$^{-1}$ and 873 cm.$^{-1}$. If these two bands are included with the other sets of bands, either of these two band sets might be considered as a candidate for the cyclopropane ring deformation vibration. More model compounds are being studied in order to see whether or not this tentative assignment will prove significant.[26]

Acknowledgments.—We would like to express our appreciation to Dr. Percy L. Julian, Director of Research and Manager of Fine Chemicals, The Glidden Company, Soya Products Division, Chicago, Illinois, for suggesting the interest of this problem. We are indebted to Dr. Julian and his associate, Dr. Edwin W. Meyer, for supplying us with all the compounds reported, and for several interesting discussions during the course of the research. We wish to thank Dr. Jean Lecomte who, in the initial stages of this problem, gave one of us guidance and hospitality in his laboratory at The Sorbonne, Paris. We want also to acknowledge the technical assistance of Mr. Brandt Kuperstock and Mr. Robert Powell. This investigation was supported by a research grant from the National Cancer Institute, U. S. Public Health Service.

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(24) J. M. Derfer, E. E. Pickett and C. E. Boord, THIS JOURNAL, **71**, 2482 (1949).

(25) F. F. Cleveland, M. J. Murray and W. S. Gallaway, *J. Chem. Phys.*, **15**, 742 (1947).

(26) In a private communication, dated 2/22/51, Dr. D. H. R. Barton of Birkbeck College Research Laboratory, the University of London, states that he has assigned the 1010 cm.$^{-1}$ band in the infrared spectrum of *i*-cholestane to a cyclopropane ring vibration. Our results (discussed above in the paragraph entitled "Bands present in all the compounds") do not contradict this assignment for the 1019 ± 5 cm.$^{-1}$ band especially since the one *i*-steroid exception, *i*-cholestanone, has a medium weak band nearby at 1007 cm.$^{-1}$. This *ca.* 1000 cm.$^{-1}$ band should therefore be taken into consideration also. It could not be used alone, however, to distinguish between normal and *i*-steroids because the former also have a band, sometimes equally intense, in this region.

NASHVILLE, TENNESSEE RECEIVED FEBRUARY 7, 1951

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORQUIMA S. A., SÃO PAULO, BRAZIL]

α,γ- and β,γ-Dipyridyl

BY P. KRUMHOLZ

The dipyridyl, previously reported as the β,γ-isomer, has been shown to be α,γ-dipyridyl. It seems probable, on the basis of spectroscopic and electrochemical evidence, that the first structure is to be assigned to a base previously isolated from the products of the thermal decomposition of pyridine.

Studying the properties of isomeric dipyridyls[1] we found that the behavior of β,γ-dipyridyl, first isolated by Smith,[2] does not correspond to the assumed constitution. The second basic dissociation constant of Smith's dipyridyl is near to that of the α,β-isomer but about a hundred times smaller than that of β,β'- or γ,γ'-dipyridyl.[1] Smith based the constitution of his dipyridyl on the isolation of nicotinic and isonicotinic acid from the products of the permanganate oxidation of the dipyridyl. We decided therefore to repeat this oxidation under carefully controlled conditions.

The dipyridyl in question was prepared from a pure picrate (m.p. 215/216°) obtained by fractional crystallization of the picrates from the product of thermal decomposition of pyridine.[3] The picrate was decomposed by potassium hydroxide, the free base extracted with ether and after evaporation of the solvent recrystallized twice from hexane. The m.p. of the dipyridyl was 60.8–61.3°; two more crystallizations from hexane raised the m.p. to 61.1–61.5°. It was free of α,α'-dipyridyl as shown by the absence of the very sensitive color reaction with ferrous salts and could contain only traces of the liquid α,β-isomer, as on addition of 10% of the latter melting begins at 51°, being completed at 57.5°.

Five hundred mg. of the dipyridyl m.p. 60.8–61.3° was boiled under reflux with a solution of 4 g. of potassium permanganate in 100 ml. of water until the color of the permanganate disappeared completely (3 to 6 hours). The filtered liquid was concentrated to about 10 ml., carefully neutralized with hydrochloric acid, using congo red paper as indicator, and evaporated on the steam-bath to dryness. The residue was triturated with 5 ml. of cold absolute ethanol, filtered, and washed with a few ml. ethanol. After evaporation an oily residue remained, which was dissolved in 5 ml. of water and precipitated at 40° by dropwise addition of a saturated aqueous solution of copper acetate, until further additions yielded no more precipitate. Any excess of copper acetate must be avoided, as it dissolves the copper salt of picolinic acid. After collection, washing with a little water and drying, 130 mg. of a violet, crystalline copper salt was obtained, easily identified as the copper salt of *picolinic acid* by its typical crystal form, its solubility in hot water and the formation of α,α'-dipyridyl by dry heating.[4] The identification was further confirmed by recovery of the free acid from the copper salt. The latter was decomposed in hot aqueous solution by hydrogen sulfide, the filtered solution evaporated to dryness and the residue recrystallized from benzene. The m.p. of the acid was 135–136°. A mixture with an authentic sample of picolinic acid (m.p. 136–137°)

(1) P. Krumholz, THIS JOURNAL, **73**, 3487 (1951).

(2) C. R. Smith, *ibid.*, **46**, 414 (1924).

(3) P. Krumholz, *Selecta Chimica*, **8**, 1 (1949).

(4) F. Blau, *Monatsh.*, **10**, 375 (1889).

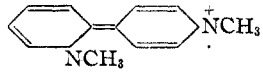
melted at 135.5–137°. The presence of picolinic acid may, moreover, be shown directly in the neutralized solution of the oxidation products by its reaction with ferrous sulfate.

The residue remaining after the extraction of picolinic acid, was extracted three times with 20 ml. of boiling ethanol. The filtered solution was evaporated to dryness, the solid residue washed with a very small quantity of cold water, in order to remove any potassium chloride, and recrystallized twice from a few ml. of ethanol, using for the second time active carbon for decoloration. We obtained 30 mg. of a colorless amorphous acid with a m.p. of 315° (closed tube, totally immersed in the bath). A pure sample of isonicotinic acid was found to melt at the same temperature as well as a mixture of both samples. For further identification we prepared the copper salts of both acids, by precipitation of the aqueous solutions with copper acetate. On dissolving the salts in boiling 10% acetic acid and crystallizing the solution slowly, typical crystals were obtained, which were in every respect identical in both cases, showing no resemblance whatsoever to the copper salt of nicotinic acid, crystallized under similar conditions.

Thus the dipyridyl of m.p. 61.5°, m.p. of the monopicrate 215–216°, is obviously α,γ-dipyridyl and not the β,γ-isomer.

From the solution of the salt residue, remaining after the alcohol extraction, copper acetate precipitates a green, very sparingly soluble amorphous salt. Decomposing its aqueous suspension with hydrogen sulfide and evaporating the filtrate on the water-bath, we obtained 150 mg. of oxalic acid as prismatic needles melting at 102° which, on drying in vacuum, lose water of crystallization and melt at 183°. It was easily identified as oxalic acid which obviously represents the rest of the totally oxidized dipyridyl skeleton.

The diiodo methylate of α,γ-dipyridyl, prepared by heating the base with excess methyl iodide and some methanol in a sealed tube at 100°, produces with zinc dust in neutral or slightly acid solution a deep violet coloration, very sensitive to oxidation by oxygen, most probably due to the formation of a quinonoid radical as



similar to that obtained from γ,γ'-dipyridyl.[5]

The identification of Smith's dipyridyl as being the α,γ-isomer, is in contradiction to the claimed preparation of this dipyridyl by Meyer.[6]

This author isolated a liquid base from the products of the thermal decomposition of pyridine, producing a picrate m.p. 201° and yielding on oxidation with permanganate isonicotinic acid and minute quantities of picolinic acid. According to Meyer this dipyridyl is identical with the (crude) base, isolated previously by Roth[7] as the only product of the thermal decomposition of pyridine and producing a picrate m.p. 208°. It is most probable that those bases were mixtures of isomeric dipyridyls.

Similarly, the supposed α,γ-dipyridyl (m.p. picrate 208°) prepared by Morgan and Burstall[8] from the product of the reaction of pyridine with ferric chloride, cannot be this isomer, as the picrate m.p. 215° and from it Smith's dipyridyl, were obtained from the same mixture of isomeric dipyridyls.

So far, no evidence whatsoever exists showing that β,γ-dipyridyl has already been prepared. From the thermal decomposition products of pyridine[8] we isolated a small quantity of a picrate m.p. 199–201°, whose content of picric acid corresponds closely to that of a dipyridyl dipicrate (picric acid calcd. 74.6%; found 73.6, 74.4, 73.4%). A 50-mg. sample of the free (liquid) base, oxidized with potassium permanganate, gave a negative picolinic acid test with ferrous sulfate. Copper acetate precipitated a minute quantity of amorphous copper salts which could not be further identified. The dipyridyl in question is a biacid base, whose dissociation constants[1] are very close to the constants of β,β'- and γ,γ'-dipyridyl. As the ultraviolet absorption spectrum of α,β-dipyridyl is similar to the superposition of the spectra of α,α' and β,β'-dipyridyl,[1] we compared the spectrum of the dipyridyl in question with a "synthetic" spectrum, composed from the spectra of β,β' and γ,γ' dipyridyl. As shown in Fig. 1, the similarity is surprising. The same is the case for the original and "synthetic" spectra of the bi-hydrochlorides shown in Fig. 2. This supports very strongly the assumption that the dipyridyl in question is the lacking β,γ isomer. Definite proof, however, has still to be given by isolation of the carboxylic acids from the product of the permanganate oxidation.

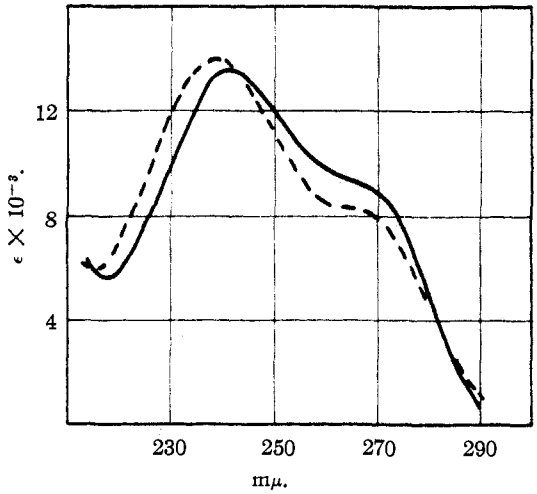


Fig. 1.— —, β,γ-Dipyridyl (?); – – –, β,β' + γ,γ'-dipyridyl.

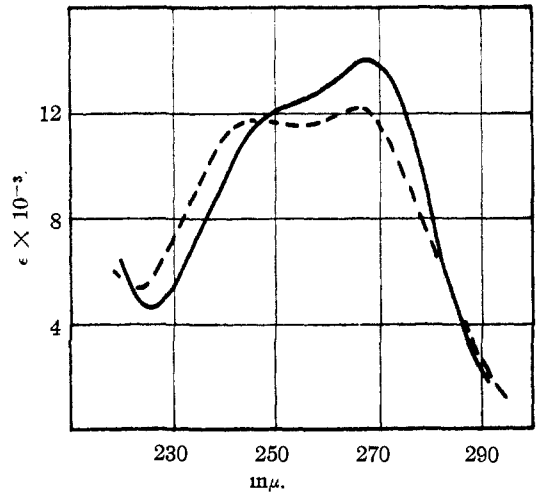


Fig. 2.— —, β,γ-Dipyridyl (?)·2HCl; – – –, β,β' + γ,γ'-dipyridyl·2HCl

SÃO PAULO, BRAZIL RECEIVED NOVEMBER 13, 1950

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