

value of H_0 at which $d\epsilon/dH_0$ reaches a maximum gives pK_a (Fig. 3). All values of H_0 were obtained from tables.⁴ The value of pK_a for pyrrole obtained from plots of the type shown in Figs. 2 and 3 is -0.27 .

DISCUSSION

The ultraviolet absorption spectrum of pyrrole in hexane consists of a strong band at $210\text{ m}\mu$ ($\epsilon = 15,000$) and a very weak band at $240\text{ m}\mu$ ($\epsilon = 300$).⁵ The high intensity absorption is probably due to $\pi \rightarrow \pi^*$ transitions but the low intensity band cannot be attributed to the presence of $n \rightarrow \pi^*$ transitions in pyrrole. It has been reported that this low intensity band was not observed in the spectra of a number of α and β -alkyl pyrroles in ethanol.⁶ On the other hand *N*-methylpyrrole has an absorption band in the $240\text{ m}\mu$ region⁷; this is probably due to the reduction in electronegativity of the nitrogen atom caused by the electron-releasing properties of the methyl group. This facilitates the participation of the nitrogen $2p$ electrons in conjugation with the π -electrons in the pyrrole ring. Fig. 1 shows the ultraviolet spectra

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of pyrrole in aqueous solutions containing perchloric acid. In no case was a low intensity band in the $240\text{ m}\mu$ region obtained. Therefore, on the basis of the ultraviolet spectra alone, it is apparently not possible to decide whether carbon protonation or nitrogen protonation occurs in pyrrole in the presence of acids.

The chemical reactions of pyrrole indicate that it is aromatic in character, the electrons on the nitrogen atom being delocalized on the four carbon atoms, thereby making the nitrogen atom a very poor proton acceptor. This, of course, implies that pyrrole should be a very weak base. This work has shown that pyrrole whose pK_a is -0.27 is a weaker base than has been expected. Unfortunately no pK_a values exist for related compounds for purposes of comparison. It would be of interest to determine the pK_a values of substances such as indole or carbazole, which should also be very weakly basic, and also the acid dissociation constants of substituted pyrroles, notably *N*-methylpyrrole.

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Studies in the Synthesis of 2,5-Diphenylpyrrole

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The synthesis of 2,5-diphenylpyrrole (III) from *trans*-1,4-diphenyl-2-butene-1,4-dione (I) via 1,4-diphenyl-1,4-butanedione (II) has been elaborated. Optimum conditions for the conversion of I to II have been found to be the palladium catalyzed pressure hydrogenation of I in isopropyl alcohol at room temperature. The pyrrole ring most effectively may be formed from II with ammonia under pressure at 140 – 145° .

The relative stability of 2,5-diphenylpyrrole (III) prompted us to include this compound in our investigations on new polymerizable heterocyclic compounds. Principally, there are two small-scale procedures for the synthesis of III, namely, by the ring-closing action of ammonia or ammonium acetate on either 1,4-diphenyl-1,4-butanedione^{1,2} (II) or ethyl phenacylbenzoylacetate.² For the planned investigations it was necessary to elaborate a route by which a pure grade of III could economically be synthesized in larger quantities. Such a path lay in the reaction sequence starting with *trans*-1,4-diphenyl-2-butene-1,4-dione (I), converting this into II and finally ring-closing this to III.

Chief difficulties in this reaction sequence were encountered particularly with the conversion of I

into II. Although a variety of methods for reducing I to II is known, the procedures either require costly reagents or give low yields or furnish II along with other by-products. The latter are frequently the result of a pronounced tendency of I to take a bimolecular course under certain reducing conditions. Thus, even in such reductions of I that superficially appear to proceed smoothly, for instance those effected by zinc,^{3,4} we found as by-product a colorless compound melting at 159° . It has twice the molecular weight of I but does not respond to any carbon-carbon double bond agents and is most probably 4,5-dibenzoyl-1,2-diphenyl-1,2-cyclohexanediol (IV).⁵

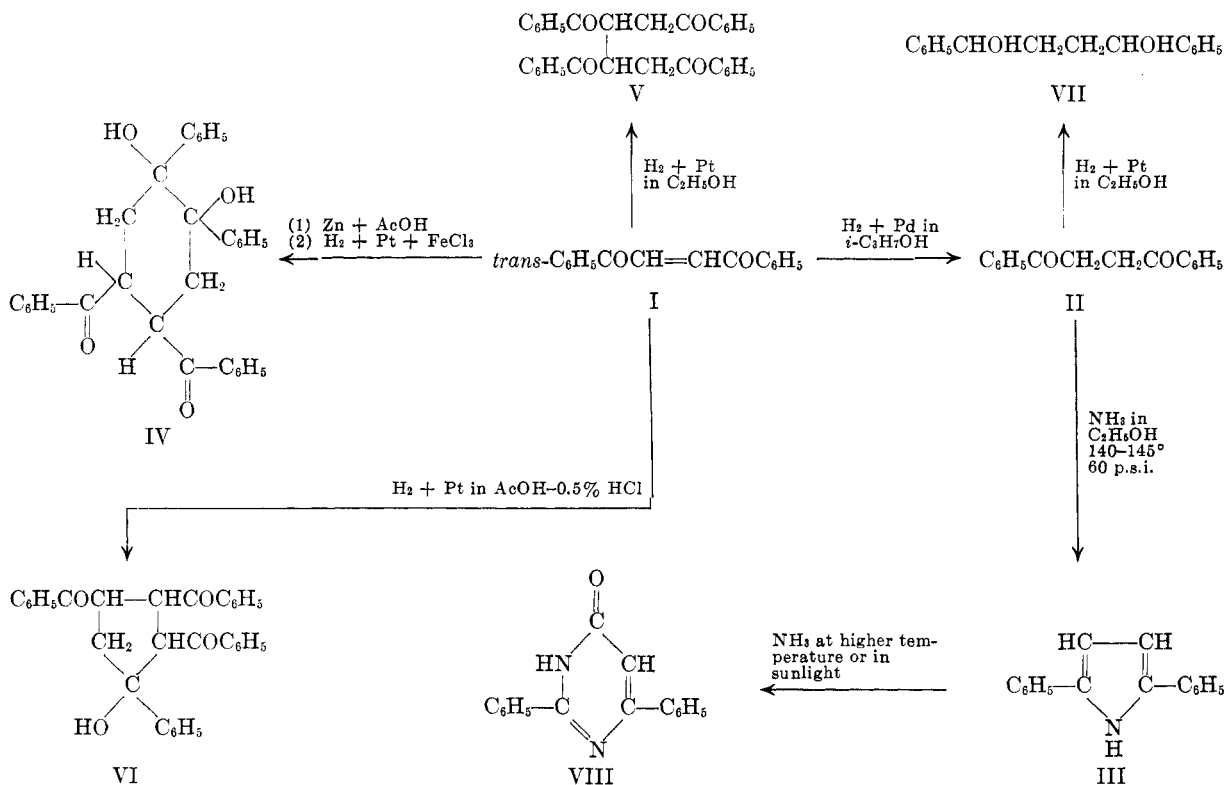
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Moreover, in one of the most simple and attractive reducing methods of I, the catalytic hydrogenation, II is accompanied most of the time by products of higher melting point ranges. Among the products resulting from the platinum catalyzed reduction of I, 1,2,3,4-tetrabenzoylbutane (V),^{5,6} 1-phenyl-2,3,4-tribenzoyl-1-cyclopentanol (VI)⁶ and IV⁷ have been identified. Based on the fact that small amounts of acid effect normal hydrogenation of the double bond in pseudocodeine,⁸ a method was worked out⁶ by which I was said to be catalytically reducible in ethylacetate at atmospheric pressure furnishing a 90–95% yield of II. However, even under these conditions II is formed along with considerable amounts of higher melting materials. In view of the fact that II in the presence of platinum will undergo further reduction to 1,4-diphenyl-1,4-butanediols (VII),⁶ we have investigated reductions of I with palladium catalysts. Our experiments have led to finding a set of conditions under which a 67% yield of pure II may be obtained. These conditions may be summarized as carrying out the palladium catalyzed reduction of I in isopropyl alcohol at room temperature and an initial hydrogen pressure of 60 p.s.i.

A very effective means of following the course and testing the completion of reduction was by infrared spectroscopy. The infrared spectrum of I has been

obtained previously⁹ but covered the range of 700–1600 cm^{-1} only. Furthermore, the sample had been milled in mineral oil so that the region between 1470–1570 cm^{-1} could not be evaluated since this was obliterated by strong bands of mineral oil itself. Because of this, it proved to be necessary for our purpose to measure the infrared spectra of I and II over the full range of 700–4000 cm^{-1} and to use the potassium bromide dispersion method. Upon comparing the two infrared spectra of I and II, it becomes apparent that, aside from several joint absorption bands, the two compounds exhibit several individual marked frequencies by which their authenticity and purity may be identified. To the absorption bands that both compounds have in common belong all those associated with the aromatic nucleus, namely, the $\text{C}-\text{H}$ stretching mode at 3010–3030 cm^{-1} , the $\text{C}=\text{C}$ skeletal in-plane vibrations at 1590–1600 cm^{-1} and 1440–1450 cm^{-1} , the 990–1020 cm^{-1} bands typical of substituted aromatic rings, and the CH out-of-plane deformations between 710–800 cm^{-1} . Another band common to both I and II is the carbonyl stretching absorption at 1180–1190 cm^{-1} exhibited by most aromatic ketones.¹⁰

Since the time of the controversy whether the lower melting isomer of I were assigned the *cis* or *trans* configuration,^{11,12} considerable work has been

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done on this question. However, the infrared spectrum does not seem to have been consulted in this respect. Yet it contains strong bands at 970, 1290, and 1310 cm.^{-1} which arise from $-\text{CH}=\text{CH}-$ deformation vibrations. Of these, the first has been shown to be an out-of-plane deformation mode appearing with trans double bonds only,¹³ while the latter two are commonly associated with $-\text{CH}=\text{CH}-$ in-plane deformation vibrations of *trans* disubstituted ethylenes.¹⁴ The strong absorption at 1640 cm.^{-1} in the spectrum of I may be assigned to the stretching vibration of the carbonyl group, this being in conjugation with the ethylenic C=C link.

According to the common rule that the carbonyl group of saturated ketones absorbs at a frequency that is about 40 cm.^{-1} higher than that of a C=C conjugated C=O group, one would expect a shift to 1680 cm.^{-1} upon hydrogenating I to II. The infrared spectrum of II indeed confirms this expectation. In addition to this, two more bands typical of saturated ketones^{10,15} appear in the spectrum of II, namely, at 1220 and 1350 cm.^{-1} . Of course, in successful hydrogenation experiments the aforementioned bands arising from $-\text{CH}=\text{CH}-$ vibrations must not show up any more. Instead, the C—H stretching band due to the newly formed $-\text{CH}_2-\text{CH}_2-$ group appears at 2910 cm.^{-1} .

Our investigations of a suitable method for synthesizing III on a larger scale resulted in finding that the ring-closing reaction of II by means of ammonia, a method initiated by Holleman and later improved through introduction of a pressure technique by Allen *et al.*,⁴ is best suited. However, we also found that the temperature in this reaction step is critical, in that with increasing temperature a red discoloration of the reaction mixture accompanied by the formation of a higher melting compound becomes prevailing. This thermal effect is most prob-

ably identical with the light-induced action of ammonia on III resulting in a ring expansion with formation of 2,6-diphenyl-4(3)-pyrimidone (VII).¹⁶ Optimum temperature for the ammonia-pressure-conversion of II to III has now been found to be at 140–145°.

EXPERIMENTAL¹⁷

1,4-Diphenyl-1,4-butanedione (II). The *trans*-1,4-diphenyl-2-butene-1,4-dione (I) used was a commercial grade which, prior to hydrogenation, was recrystallized from ethanol and exhibited then a melting point of 111–112°.

A suspension of 75 g. (0.3 mole) of I, 1 g. of 10% palladium on powdered charcoal catalyst, and 20 ml. of conc. hydrochloric acid in 2000 ml. of isopropyl alcohol was agitated at room temperature in an autoclave¹⁸ under an initial hydrogen pressure of 60 p.s.i. until an amount of 0.95–1.0 mole of hydrogen had been taken up (approx. 15 min.). Then the mixture is heated to boiling and filtered hot. Upon cooling, 51 g. (67% yield) of long white needles of II was obtained, m.p. 147–148°. A specimen prepared for analysis and the infrared spectrum by recrystallization from absolute ethyl alcohol melted at 148–149°.

Anal. Calcd. for $\text{C}_{16}\text{H}_{14}\text{O}_2$: C, 80.65; H, 5.92. Found: C, 80.73; H, 5.80.

2,5-Diphenylpyrrole (III). To 1000 ml. of absolute ethyl alcohol saturated with dry ammonia gas under ice cooling was added 150 g. (0.6 mole) of powdered II and the mixture heated in a sealed pressure vessel¹⁸ for 6 hr. at 140–145°. After cooling, the reaction contents were poured into 2000 ml. of water when III was precipitated as a pale yellow solid. Vacuum-filtered and dried, it amounted to 134 g. (97% yield based on II) and melted at 142–144°. It could best be purified by recrystallization from a 4:1 ethyl alcohol-water mixture; silver gray scales, m.p. 143–144°.

Anal. Calcd. for $\text{C}_{16}\text{H}_{13}\text{N}$: C, 87.63; H, 5.98; N, 6.39. Found: C, 87.49; H, 6.01; N, 6.50.

The infrared measurements were made on a Perkin-Elmer double beam spectrophotometer, Model 137. The spectra refer to potassium bromide disks.

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