Intramolecular Hydrogen Bonds in 2,2'-Dipyrrylmethanes and 2,2'-Dipyrrylmethenes

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2,2'-Dipyrrylmethanes containing the carbethoxy group in the 3- and 3'- positions show only a bonded N—H band. Each N—H is intramolecularly bonded to the carbethoxy group of the other ring. When a carbethoxy group is present in the 3- but not in the 3'-position, the compounds have one free and one bonded N—H. When neither the 3- nor the 3'-position contains a group capable of acting as a hydrogen acceptor, one observes only a free N—H band, indicating no hydrogen bond. In the dipyrrylmethenes, regardless of the nature of the substituents, one observes a very strong hydrogen bond, indicating the presence of an N—H---N bond. The effect of the nature and position of substituents upon the frequency of the bonded N—H band is discussed.

A number of investigators have reported infrared absorption spectral data for pyrroles, porphyrins, and related polypyrrole pigments.[1a–h] Although pyrrole itself has been studied in some detail, few of these substances have been examined under experimental conditions designed to provide the maximum information about hydrogen bonding effects. The dipyrrylmethenes and dipyrrylmethanes constitute two classes of compounds which are of importance as intermediates for the synthesis of porphyrins. Being interested in hydrogen bonding, we have studied the N—H stretching bands of a number of substituted pyrroles, dipyrrylmethanes, and dipyrrylmethenes in carbon tetrachloride solution. The results, which constitute the substance of this communication, show how steric and electronic factors influence hydrogen bonding in these compounds.

Pyrroles and Dipyrrylmethanes.—The frequencies and related spectral data for several substituted pyrroles are given in Table I. The free N—H band of 3,4,5-trisubstituted pyrroles which do not contain a carbethoxy group in the 5-position, is at 3484–3488 cm.$^{-1}$, the half-band width is about 15 cm.$^{-1}$, and the band intensity is about 5 × 10^3. When there is a carbethoxy group in the 5-position, the N—H band is slightly lowered to 3456 cm.$^{-1}$ and has a shoulder at 3485, indicating the possibility of a weak hydrogen bond in which the carbethoxy group in the 5-position acts as the hydrogen acceptor.

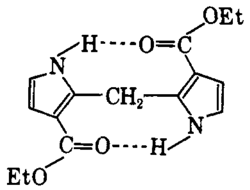
TABLE I

N—H BANDS OF SUBSTITUTED PYRROLES

No.	ν(cm.$^{-1}$)	$\nu_{1/2}$	A[a]	Substituents at position			
				5	4	3	2
I	3488	15	5200	CH_3	CH_3	Cbe[b]	H
II	3484	14	4300	CH_3	Cbe	CH_3	H
III	3456			Cbe	CH_3	Cbe	H
	3486 (shoulder)						
IV	3458			Cbe	CH_3	H	CH_3
	3486 (shoulder)						

[a] A is the integrated intensity. It is calculated from the formula A = $(\pi/2)$(peak intensity) $(\nu_{1/2})$/(concn.) (l); where concn. is in moles per l., and l is the cell length in cm. [b] Cbe = carbethoxy.

Twelve dipyrrylmethanes were studied and their spectral data are given in Table II. These compounds can be divided into three groups, according to the pattern of their N—H bands. The compounds of Group I have only one N—H band which, on the basis of its frequency, 3390–3400 cm.$^{-1}$, its half-band width of around 70 cm.$^{-1}$, and intensity of about 13 × 10^3, must be due to intramolecularly hydrogen-bonded N—H groups. The frequency and intensity of these bands do not change with dilution of the solutions. Each of the compounds of group I has a carbethoxy group in the 3- and 3'-positions and so we conclude that these compounds exist in the conformation shown below in which the hydrogen in position 1 is bonded to the carbethoxy in position 3', and the hydrogen in position 1' is bonded to the carbethoxy group in position 3.



Compounds of group II have two N—H bands, one due to an intramolecularly bonded N—H group and the other due to a free or very weakly bonded N—H group. The former bands are at lower frequencies and have larger intensities and half-band widths. These compounds have a carbethoxy group in the 3-position but not in the 3'-position, and so we conclude that these compounds exist in the conformation shown below which contains one free and one bonded N—H group.

The frequency of the bonded N—H band in the group II compounds is lower than the frequency of the same band in the group I compounds, indicating a somewhat

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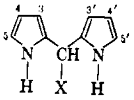
[1] (a) N. Fuson, M. L. Josien, R. L. Powell, and E. Utterback, *J. Chem. Phys.*, **20**, 145 (1952). (b) N. Fuson and M. L. Josien, *ibid.*, **20**, 1043 (1952). (c) U. Eisner and R. L. Erskine, *J. Chem. Soc.*, 971 (1958). (d) C. H. Gray, A. Neuberger, and P. H. A. Sneath, *Biochem. J.*, **47**, 87 (1950). (e) J. B. Falk and J. B. Willis, *Australian J. Sci. Research*, **4**, No. 4, 579 (1951). (f) D. W. Thomas and A. E. Martell, *J. Am. Chem. Soc.*, **78**, 1338 (1956). (g.) S. F. Mason, *J. Chem. Soc.*, 976 (1958). (h) C. S. Vestling and J. R. Downing, *J. Am. Chem. Soc.*, **61**, 3511 (1939).

NOTE ADDED IN PROOF: Since the presentation of an account of our work at the 142nd National Meeting of the American Chemical Society (Atlantic City, N. J., September, 1962; Abstracts, p. 84-Q), a related study of hydrogen bonding in porphyrins, dipyrrylmethenes, and dipyrrylmethanes by G. M. Badger and coworkers has appeared in the literature (*J. Chem. Soc.*, **1962**, 4329).

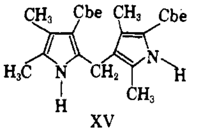
Our data for the dipyrrylmethenes are in general agreement with theirs, but we are in disagreement on the dipyrrylmethanes both with respect to the data and the interpretation. They found that two compounds containing the carbethoxy group in only the 5- and 5'-positions have bonded N—H bands at 3345 and 3364 cm.$^{-1}$, respectively. They attribute these bands to an intramolecularly bonded N—H in which the adjacent carbethoxy group is the hydrogen acceptor. We contend that these bands are due to *intermolecular* hydrogen bonding. These compounds have a strong tendency to associate and must be examined at very high dilution. Thus our compound, XI, at concentration of about 0.005 molar showed a strong band at 3355 cm.$^{-1}$ and a weaker band at 3454 cm.$^{-1}$. As the solution was diluted, the lower frequency became weaker and the higher frequency band became stronger showing that the 3355 cm.$^{-1}$ is due to an intermolecular hydrogen bond. Furthermore, our pyrroles III and IV, and our dipyrrylmethanes XI, XV, and XVI, all of which contain a 5-carbethoxy group, show no bonded N—H band below 3400 cm.$^{-1}$.

TABLE II

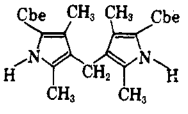
N—H BANDS OF SUBSTITUTED DIPYRRYLMETHANES



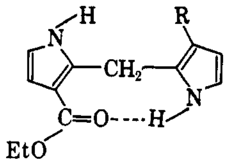
No.	Free N—H			Bonded N—H			Substituent at position							Group
	ν (cm.$^{-1}$)	$\nu^1/_2$	A	ν	$\nu^1/_2$	A	5	4	3	Bridge	3′	4′	5′	
V				3397	64	12500	CH_3	CH_3	Cbe	H	Cbe	CH_3	CH_3	I
VI				3401	80	13400	Cbe	CH_3	Cbe	H	Cbe	CH_3	CH_3	I
VII				3390	68	11700	Cbe	CH_3	Cbe	H	Cbe	CH_3	Cbe	I
VIII	3466	18	4500	3361	88	11600	CH_3	CH_3	Cbe	H	CH_3	Cbe	CH_3	II
IX	3448	30	5500	3378	78	17700	Cbe	CH_3	Cbe	H	CH_3	Cbe	CH_3	II
X	3458	20					CH_3	Cbe	CH_3	H	CH_3	Cbe	CH_3	III
XI	3454	20					Cbe	CH_3	C_2H_5	H	C_2H_5	CH_3	Cbe	III
XII	3446	30	4100				CH_3	Cbe	CH_3	CH_3	CH_3	Cbe	CH_3	III
XIII	3449	18	3400				CH_3	Cbe	CH_3	C_6H_5	CH_3	Cbe	CH_3	III
XIV	3454	25	7500	3328	90	17000	CH_3	Cbe	CH_3	CH_2Cbe	CH_3	Cbe	CH_3	
XV	3454	21												
XVI	3464	22	4200											



XV

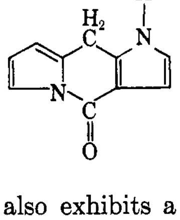


XVI

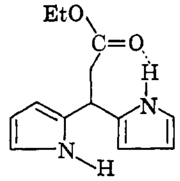


stronger hydrogen bond in the former group. This is probably due to the fact that when there is only one hydrogen bond in the molecule, one pyrrole ring can be rotated with respect to the other. This brings the hydrogen closer to the carbethoxy and thus makes for a stronger hydrogen bond. The presence of two hydrogen bonds prevents this rotation from occurring.

Further evidence for the close proximity of the carbethoxy group in position 3′ with the 1 N—H group can be gleaned from the ease with which certain dipyrrylmethanes included in groups I and II undergo an intramolecular condensation reaction to produce cyclic amides having the dipyrrolopyridone structure.[2a,b]



Compound XIV also exhibits a free and a bonded N—H band. This compound has a carbethoxy-bearing substituent group in the bridge position rather than in the 3- or 3′-position, and so it must have the conformation shown below.



Compounds in group III have only one N—H band which corresponds to a free or very weakly bonded N—H group. These compounds have no carbethoxy group either in the 3- or 3′-positions. Thus we can conclude that when a group which can act as a hydrogen acceptor is located in the 3- or 3′-position of the dipyrrylmethane molecule an intramolecular hydrogen bond will exist. When two such groups are present, both N—H groups will be hydrogen bonded.

Further evidence for the above interpretation is found in the carbonyl bands. It is well known that when an OH group is bonded to a carbethoxy the frequency of the carbonyl band is reduced by about 30 to 40 cm.$^{-1}$. The carbonyl band of compound XIII which is in group III (no hydrogen bond), is at 1705 cm.$^{-1}$. Compound IX, which is in group II, has two carbonyl bands, one at 1704 and the other at 1684 cm.$^{-1}$. Compound V, which is in Group I (no free N—H), has its carbonyl band at 1676 cm.$^{-1}$. The presence of the intramolecular hydrogen bond influences the solubility of these compounds. Thus saturated carbon tetrachloride solutions of compounds in Group I are about 0.02 *M;* those of Groups II and III average about 0.005 *M*. Two of the compounds of Group III give saturated solutions of 0.001 *M*.

When a pyrrole ring of a dipyrrylmethane is bridged at the 3-position as in the 2,3′-dipyrrylmethane (compound XV) and the 3,3′-dipyrrylmethane (compound XVI), the hydrogen is too far from the second ring for hydrogen-bonding to occur, hence these compounds have no intramolecular hydrogen bond.

Dipyrrylmethenes.—Vestling and Downing[1h] appear to have been the first investigators to determine the N—H stretching frequency of a dipyrrylmethene. Our data for the N—H bands of dipyrrylmethenes are shown in Table III. In contrast to the dipyrrylmethanes which have an intramolecular hydrogen bond only when a hydrogen acceptor group is

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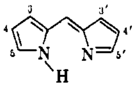
[2] (a) A. H. Corwin and R. C. Ellingson, *J. Am. Chem. Soc.*, **66**, 1146 (1944). (b) A. H. Corwin and S. R. Buc, *ibid.*, **66**, 1151 (1944).

TABLE III

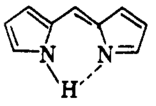
N—H BANDS OF 2,2′-DIPYRRYLMETHENES

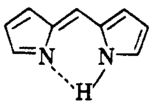


No.	ν(cm.$^{-1}$)	$\nu^1/_2$	A^a	Substituent at position 5	4	3	3′	4′	5′
XVII	3295	118	7870	Cl	CH_3	Cbe^b	CH_3	Cbe	CH_3
XVIII	3293	117	7100	Br	CH_3	Cbe	CH_3	Cbe	CH_3
XIX	3289	129	9500	Cbe	CH_3	C_2H_5	C_2H_5	CH_3	Cbe
XX	3278	166	8400	CH_3	C_2H_5	CH_3	CH_3	C_2H_5	CH_3
XXI	3265	106	6030	CH_3	Cl	CH_3	CH_3	Cl	CH_3
XXII	3263	140	9580	CH_3	H	CH_3	CH_3	H	CH_3
XXIII	3263	156	9800	Cl	CH_3	Cbe	Cbe	CH_3	Cl
XXIV	3252	196	10600	CH_3	Cbe	CH_3	Cbe	CH_3	CH_3
XXV	3247	154	10200	CH_3	Cbe	CH_3	CH_3	C_2H_5	CH_3
XXVI	3236	175	8300	CH_3	CH_3	Cbe	Cbe	CH_3	CH_3
XXVII	3226	232	13900	CH_3	Cbe	CH_3	Cbe	CH_3	Cbe
XXVIII	3221	220	16400	CH_3	Cbe	CH_3	CH_3	Cbe	CH_3

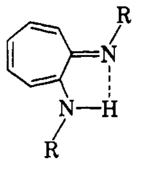
[a] Intensity, A = $\pi/2(\nu_{1/2})$ (peak height)/(concn.) (l) where concn. is in moles/l., and l is the cell length in cm. [b] Cbe is carbethoxy.

located at the 3- or 3′-position, the dipyrrylmethenes all show a hydrogen bond, even when there is no such hydrogen acceptor present. Consequently these compounds must exist in a more or less planar conformation containing an N—H---N hydrogen bond as shown below. Assuming that the C—C and C—N bonds are all of equal length, 1.4 Å., which is the approximate distance in the phthalocyanines, and assuming the normal N—H distance of 1.05 Å., the H---N distance turns out to be 2.1 Å. and the N—H---N angle is 117°.





The N—H frequency of these compounds is considerably lower than that of the dipyrrylmethanes or of pure liquid pyrrole (3404 cm.$^{-1}$) indicating a very strong hydrogen bond, despite the unfavorable N—H ---N angle of 117°. Other things being equal, the strongest hydrogen bond occurs when the bond angle at hydrogen is 180°. We believe that the strength of this hydrogen bond is due to the fact that the potential energy curve for the N—H stretch has a symmetrical double minimum, each minimum corresponding to one of the structures shown above. Documentation of the evidence for this effect has been given by Bellamy.[3] It is interesting to note that another type of compound which also has an intramolecular N—H---N bond possessing a symmetrical double minimum, exhibits its N—H band at 3247 cm.$^{-1}$ in the same range as the dipyrrylmethenes. This compound is the recently reported N,N′-dimethyl-1-amino-7-imino-1,3,5-cycloheptatriene having the structure shown.[4]



As shown in Table II, the frequency of the N—H band of the dipyrrylmethenes varies from 3295 cm.$^{-1}$ to 3221 cm.$^{-1}$. This variation in frequency is believed to be due to the difference in strength of the hydrogen bond and is to be explained on the basis of the effect of the substituents and their positions on the hydrogen bond. Accompanying the decrease in N—H frequency that is observed as one reads the second column of Table III, there is a general increase in half-band width (column 3) and intensity (column 4). This behavior is characteristic of hydrogen-bonded systems.

Let us consider first the symmetrically substituted compounds. The compound XX, in which all the substituents are alkyl groups, has its N—H band at 3278 cm.$^{-1}$. Replacing the alkyl groups in the 4- and 4′-positions with hydrogen (compound XXII), which is more electron-attracting than the alkyl group, results in a lowering of the N—H frequency to 3262 cm.$^{-1}$. Replacing the alkyl groups in the 3- and 3′-positions with the still more electron-attracting carbethoxy group (compound XXVI) reduces the N—H frequency to 3236 cm.$^{-1}$. When the carbethoxy groups are in the 4- and 4′-positions (compound XXVIII), the frequency is still lower at 3221 cm.$^{-1}$.

Resonance structures containing charge separation for the dicarbethoxy-substituted dipyrrylmethenes are shown in Fig. 1. In the structures labeled "A" the nitrogen bearing the hydrogen has a positive charge. Such structures make the hydrogen more acidic and hence strengthen the hydrogen bond. In structures labeled "B" the nitrogen which acts as the hydrogen acceptor carries a positive charge. These structures make this nitrogen less basic and hence decrease the strength of the hydrogen bond. In the 3,3′-dicarbethoxy compound the B structure is less stable than the A structure because in each of the B structures the nitrogen bearing the positive charge has only six outer electrons. Therefore the A structures make a greater contribution to the actual resonance structure and the net result is that the intramolecular hydrogen bond is strengthened and the N—H frequency is lowered by the introduction of the carbethoxy groups in the 3- and 3′-positions. For the 4,4′-dicarbethoxy compound no B structures can be drawn; therefore this compound has a still stronger hydrogen bond and lower N—H

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(3) L. Bellamy and P. Rogasch, *Proc. Roy. Soc.* (London), **257**, 98 (1960).

(4) W. R. Brasen, E. E. Holmquist, and R. E. Benson, *J. Am. Chem. Soc.*, **83**, 3125 (1961).

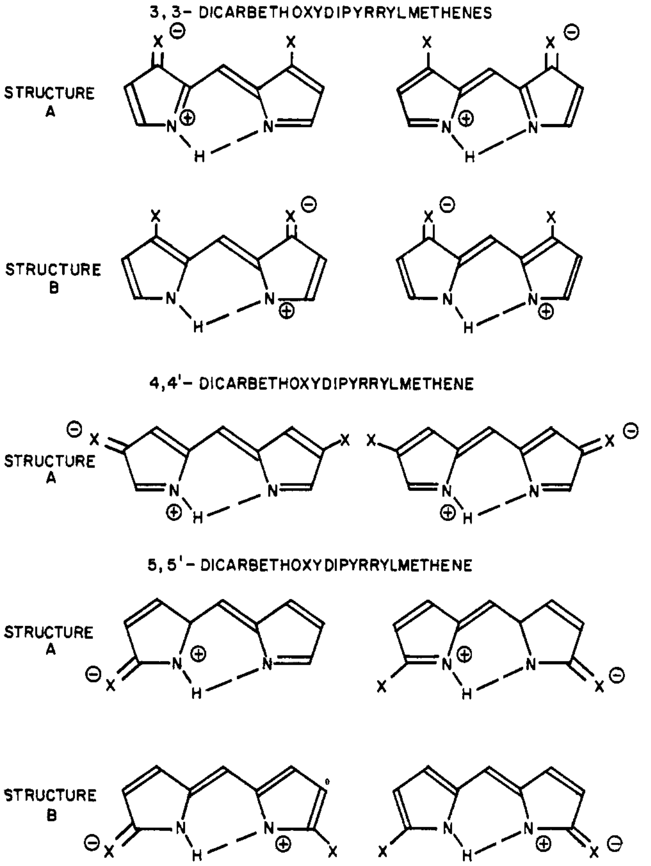
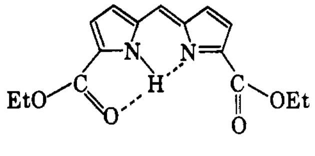


Fig. 1. Resonance structures of dicarbethoxydipyrrylmethenes.

frequency. On the basis of these arguments the 5,5'-dicarbethoxy compound whose structures are also given in Fig. 1 should have an N—H frequency similar to that of the 3,3' compound. In point of fact, introduction of the carbethoxy groups in the 5,5'-positions (compound XIX) produces a weakening of the hydrogen bond and an increase in frequency. We explain this apparent anomaly in the following manner: The hydrogen bond is bent; that is to say, the N—H---N angle is considerably less than 180°. The carbethoxy group in the 5-position can also act as a hydrogen acceptor, albeit a weak one. Its interaction with the hydrogen tends to pull the hydrogen away from the nitrogen acting as the hydrogen acceptor and this weakens the hydrogen bond, as illustrated below.



The effect of substituents upon the N—H frequency of the unsymmetrically substituted compounds is more difficult to explain because here we are concerned not only with the effects of the substituents which have been previously discussed, but also with the effect of the substituent upon the shape of the potential energy curve. If the unsymmetrical arrangement of substituents causes one of the tautomeric forms shown above to be more stable than the other, then the potential energy curve will not have a symmetrical double minimum, but the minimum corresponding to the more stable tautomer will be lower than the minimum corresponding to the less stable tautomer. This will reduce the effectiveness of the double minimum in strengthening the hydrogen bond. The data indicate that in some instances the unsymmetrically substituted compounds have a symmetrical potential energy curve and in other instances they do not. Referring again to Table III, replacing one of the alkyl groups with a carbethoxy in the 4-position (compound XXV) lowers the N—H frequency by 31 cm.$^{-1}$. Introducing a second carbethoxy into the 4'-position to produce the symmetrical compound (XXVIII) results in a further decrease of the N—H frequency by 26 cm.$^{-1}$. Since the introduction of one carbethoxy group produces a shift of about one-half of that produced by the introduction of two carbethoxy groups, we conclude that the two tautomeric forms of the unsymmetrical monocarbethoxy compound must be of about equal energy. A different conclusion must be drawn for the unsymmetrical 3,4'-dicarbethoxydipyrrylmethene (compound XXIV). On the basis of electronic effect, one would expect the N—H frequency of this compound to be intermediate between that of 3,3'- and that of the 4,4'-dicarbethoxy compounds. As shown in Table III, the unsymmetrical compound has its N—H band at 3252 cm.$^{-1}$, whereas the two corresponding symmetrical compounds have their N—H bands at 3236 cm.$^{-1}$ and 3221 cm.$^{-1}$, respectively. In this case it is believed that one tautomeric form is more stable than the other, resulting in an unsymmetrical potential energy curve and hence a weaker hydrogen bond than in the corresponding symmetrical compounds.

An even more striking example of the effect of the unsymmetrical arrangement of substituents upon the strength of the hydrogen bond may be found in the data for compounds XVII, XXIII, and XXVIII. The N—H band of the unsymmetrical compound XVII occurs at 3295 cm.$^{-1}$, while the corresponding symmetrical compounds, XXIII and XXVIII, have their N—H bands at 3263 and 3221 cm.$^{-1}$, respectively.

Since we do not understand the reason for the two different types of behavior exhibited by the unsymmetrical compounds discussed above, it is felt that a discussion of the N—H frequencies of the other unsymmetrical compounds given in Table III is not warranted at this time.

Experimental

Preparation of Materials. Pyrroles.—Pyrroles I,[5] II,[5] III[6a] and IV[6b] were prepared by procedures previously reported in the literature.

Dipyrrylmethanes.—Each of the dipyrrylmethanes employed in this study is listed below, together with the appropriate reference: V,[7] VI,[8] VII,[6a] VIII,[9] IX,[10] X,[11] XI,[12] XII,[13] XIII,[14] XIV,[5] XV,[12] and XVI.[15]

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[5] G. G. Kleinspehn and A. H. Corwin, *J. Am. Chem. Soc.*, **76**, 5641 (1954).

[6] (a) A. H. Corwin, W. A. Bailey, Jr., and P. Viohl, *ibid.*, **64**, 1267 (1942). (b) G. G. Kleinspehn, **77**, *ibid.*, 1546 (1955).

[7] H. Fischer and H. Beller, *Ann.*, **444**, 238 (1925).

[8] G. G. Kleinspehn, unpublished results.

[9] G. G. Kleinspehn, A. E. Briod, and W. S. Caughey, "Syntheses of Four Isomeric Tetramethyltetracarbethoxyporphyrins," paper presented at the 135th National Meeting of the American Chemical Society, Boston Mass., April, 1959. This paper is now in preparation for publication.

[10] B. Harrell and A. H. Corwin, *J. Am. Chem. Soc.*, **78**, 3135 (1956).

[11] O. Piloty, J. Stock, and E. Dormann, *Ber.*, **47**, 1124 (1914).

[12] H. Fischer and P. Halbig, *Ann.*, **447**, 123 (1926).

[13] H. Fischer and E. Bartholomaus, *Z. Physiol. Chem.*, **87**, 264 (1913)

[14] F. Feist, *Ber.*, **35**, 1653 (1902).

[15] H. Fischer and C. Nenitzescu, *Ann.*, **443**, 113 (1925).

Dipyrrylmethenes.—Dipyrrylmethenes XVII,[16] XVIII,[17] XX,[18] XXIII,[9] XXII,[19] XXIV,[9] XXVI,[20] XXVII,[20] and XXVIII[21] are previously reported compounds. It appears that methenes XIX and XXI have not yet been recorded in the literature. Methene XXV has been prepared previously but was obtained by an alternative condensation reaction for use in the present study.

2-(5-Carboxy-3-ethyl-4-methyl-2-pyrrolyl)methylene-3-ethyl-4-methyl-2*H*-pyrrolenine-5-carboxylic Acid, Diethyl Ester (XIX).—This methene was prepared *via* the brominative oxidation of the corresponding methane (XI) in carbon tetrachloride solution, a method used successfully by Brunings and Corwin[20] for the preparation of a number of related methenes. The methane (750 mg.) was dissolved in carbon tetrachloride (50 ml.) and a solution of 0.105 ml. of bromine in the same solvent was then added. The resulting methene hydrobromide failed to separate as a solid even upon addition of hexane, so after subsequent addition of chloroform to dissolve a small amount of separated brownish viscous oil, the product was converted to its free base by treatment with 2-(dimethylamino)ethanol. The resulting solution was washed once rapidly with water and then evaporated to dryness *in vacuo* to give the orange free base. After repeated recrystallization from hexane, the product melted sharply at 112.5°.

Anal. Calcd. for $C_{21}H_{28}N_2O_4$: C, 67.72; H, 7.58; N, 7.52. Found: C, 67.73, 67.61; H, 7.57, 7.69; N, 7.71, 7.64.

2-(4-Chloro-3,5-dimethyl-2-pyrrolyl)methylene-4-chloro-3,5-dimethyl-2*H*-pyrrolenine (XXI).[22]—The corresponding 4,4′-free methene base (XXII) (200 mg.) was dissolved in glacial acetic acid (2.0 ml.). Sulfuryl chloride (0.20 ml.) was then added all at once with vigorous stirring. The red hydrochloride which separated almost immediately was collected by filtration, washed with ether, then converted to the crude free base in chloroform solution by shaking with calcium hydroxide. After filtration through a short alumina column to remove calcium salts and other impurities, the filtrate was evaporated to dryness. The residue was then chromatographed on alumina in benzene solution, followed by recrystallization from methanol: m.p. 160–162.5° (dec.).

Anal. Calcd. for $C_{13}H_{14}N_2Cl_2$: C, 58.00; H, 5.24; N, 10.41. Found: C, 57.97, 57.89; H, 4.89, 5.01; N, 10.14, 10.29.

2-(4-Ethyl-3,5-dimethyl-2-pyrrolyl)methylene-3,5-dimethyl-2*H*-pyrrolenine-4-carboxylic Acid, Ethyl Ester (XXV).—This compound has been previously prepared[15] *via* the acid-catalyzed condensation of 4-ethyl-3,5-dimethyl-2-pyrrolecarboxaldehyde with ethyl 2,4-dimethyl-3-pyrrolecarboxylate. We have obtained the same methene from a condensation of ethyl 5-formyl-2,4-dimethyl-3-pyrrolecarboxylate with 3-ethyl-2,4-dimethylpyrrole.

Anal. Calcd. for $C_{18}H_{24}N_2O_2$: C, 71.97; H, 8.05; N, 9.33. Found: C, 71.77, 71.98; H, 7.85, 7.77; N, 9.14, 9.28.

Spectroscopic Measurements.—The spectra were obtained with a Perkin-Elmer Model 21 Infrared spectrometer equipped with a calcium fluoride prism. The slit program was 955. The substances were dissolved in carbon tetrachloride to give solutions of 0.02*M* or less. The cell thickness varied from 1 to 5 cm., depending upon the concentration. Substances containing hydrogen-bonded N—H groups were run at different concentrations. The extinction coefficients of these compounds were found to be constant. The concentrations and cell thicknesses were adjusted so that the optical density at the absorption maximum was in the range of 0.3 to 0.7.

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(16) A. H. Corwin and K. W. Doak, *J. Am. Chem. Soc.*, **77**, 464 (1955).

(17) A. H. Corwin and P. Viohl, *ibid.*, **66**, 1137 (1944).

(18) H. Fischer, P. Halbig, and G. Walach, *Ann.*, **452**, 268 (1927).

(19) H. Fischer and W. Zerweck, *Ber.*, **56**, 526 (1923).

(20) K. J. Brunings and A. H. Corwin, *J. Am. Chem. Soc.*, **66**, 337 (1944).

(21) H. Fischer and W. Zerweck, *Ber.*, **55**, 1947 (1922).

(22) The authors wish to thank Jimmie G. Tolar for his assistance in the preparation of this compound.

Acylations of Dilithio β-Diketones with Aliphatic Esters to Form 1,3,5-Triketones. Cyclizations to 4-Pyrones and 4-Pyridones

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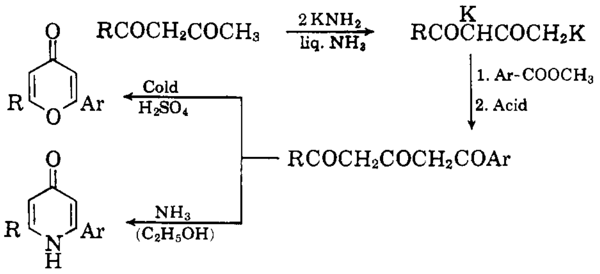
Although dipotassiobenzoylacetone appeared to ionize the α-hydrogen of ethyl acetate, dilithio β-diketones underwent acylations with this and other aliphatic esters to form the corresponding 1,3,5-triketones. Certain of the triketones were prepared from two different combinations of β-diketones and esters. These products were converted by cyclizations to corresponding 2,6-disubstituted 4-pyrones and 4-pyridones. These reactions, together with related ones described previously, furnish convenient, general methods for the synthesis of these three types of compounds.

Recently,[2,3] such β-diketones as acetyl- and benzoylacetones were aroylated at the terminal methyl group with aromatic esters through their dipotassio salts to form the corresponding 1,3,5-triketones, which were cyclized to give pyrones and pyridones (Scheme A).[4]



Scheme A

However, dipotassiobenzoylacetone failed to undergo acylation with phenyl propionate under similar conditions.[3] Since the starting β-diketone was recovered, ionization of the α-hydrogen of the ester was assumed to have occurred.[3]

We likewise recovered benzoylacetone after treatment of its dipotassio and disodio salts with ethyl acetate, no triketone being isolated. Since dilithiobenzoylacetone, but not dipotassiobenzoylacetone underwent an aldol type condensation with acetophenone,[5,6] it seemed possible that the dilithio salt might similarly undergo acylation with ethyl acetate and higher aliphatic esters. This has been realized. Thus, dilithio-

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(1) National Science Foundation Cooperative Graduate Fellow (1959–1962).

(2) C. R. Hauser and T. M. Harris, *J. Am. Chem. Soc.*, **80**, 6360 (1958).

(3) R. J. Light and C. R. Hauser, *J. Org. Chem.*, **25**, 538 (1960).

(4) The dianions of the intermediate dialkali salts are represented as dicarbanions, although other resonance forms may contribute more to the structure of the molecule.

(5) R. J. Light and C. R. Hauser, *J. Org. Chem.*, **26**, 1716 (1961).

(6) For other examples of such a metallic cation effect involving carbanions and acetophenone, see W. R. Dunnavant and C. R. Hauser, *ibid.*, **25**, 503 (1960); C. R. Hauser and W. R. Dunnavant, *ibid.*, **25**, 1296 (1960); W. I. O'Sullivan, F. W. Swamer, W. J. Humphlett, and C. R. Hauser, *ibid.* **26**, 2306 (1961).