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PROTOTROPIC REARRANGEMENT IN THE DIPYRRYLMETHENE SERIES

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Dipyrrylmethenes with a substituent in the meso position are capable of isomeric transformations, which are manifested in the existence of differently colored forms. To explain this fact, Treibs has recently proposed the assumption that two forms exist in dipyrrylmethenes: methene and ethylene forms (^{1}).

To clarify the nature of isomeric transformations of this type, we investigated a series of dipyrrylmethenes substituted in the meso position by a carbethoxymethyl group

(I) $R_4 = R_5 = R'_3 = R'_5 = \mathrm{CH_3}$; $R_3 = R'_4 = \mathrm{COOC_2H_5}$.
(II) $R_3 = R_5 = R'_4 = R'_5 = \mathrm{CH_3}$; $R_4 = R'_3 = \mathrm{COOC_2H_5}$.
(III) $R_3 = R_5 = R'_3 = R'_5 = \mathrm{CH_3}$; $R_4 = R'_4 = \mathrm{COOC_2H_5}$.
(IV) $R_4 = R_5 = R'_4 = R'_5 = \mathrm{CH_3}$; $R_3 = R'_3 = \mathrm{COOC_2H_5}$.

The basis of the study was the electronic spectra of these compounds, as being most closely connected with the color of the substances.

Compound I, isolated in the condensation of the ethyl ester of 2,3-dimethylcarbethoxypyrrolyl-5-β-ketopropionic acid with 2,4-dimethyl-3-carbethoxypyrrole as the base (m.p. 147–148°), has a violet color and shows in the electronic spectrum several long-wavelength maxima (>400 mμ): 505, 584, and 685 mμ (Fig. 1, 1). Compound II, obtained by condensation of the ethyl ester of 2,4-dimethyl-3-carbethoxypyrrolyl-5-β-ketopropionic acid with 2,3-dimethyl-4-carbethoxypyrrole, is isolated as the base also in an intensely colored violet form with a red shade (m.p. 118–120°), and its spectrum has a long-wavelength maximum at 592 mμ (Fig. 1, 2). Further alkalization of alcoholic solutions of I and II leads to the disappearance of the long-wavelength maxima, and as a result almost coincident curves 3 and 4 (Fig. 1) are obtained, while the color of the solution becomes yellow. The bases isolated from the alkaline medium retain a light-yellow color and have melting points: "I yellow form" 184–185.5°, "II yellow form" 192–193.5°, and give no depression (m.p. of mixed sample 190–193°). The IR absorption spectra of these substances, given in Table 1, are identical. This makes it possible to conclude that "yellow form

I" and "yellow form II" are one and the same compound, and that the small difference in melting points is possibly due to rotational isomerism.

Table 1

Compound	Absorption maxima in the IR spectrum, cm^{-1}
I (violet)	3200 2990 2935 2875 1710 1510 1435 1420 1370 1250
I (violet)	1175 1150 1090 1035 1015 980 915 787
II (violet)	3305 2922 2940 2885 1710 1625 1510 1435 1420 1365
II (violet)	1255 1155 1090 1035 992 950 787
I (yellow)	3275 2990 2935 2880 1712 1680 1590 1515 1425 1380
I (yellow)	1330 1275 1180 1145 1100 1050 1038 990 965 948 915
II (yellow)	855 798 758

Upon acidification, solutions of the yellow forms I and II again become intensely colored (Fig. 1, 5, 6), but complete return to the original substances present before alkalization does not occur. This may be judged from the fact that, upon alkalization of yellow form II, a maximum at 505 mμ appears, which was absent in the violet form II isolated directly from the reaction mixture. This maximum is present in the violet form I, i.e., upon acidification of the yellow form II a mixture of the violet forms I and II is formed.

Fig. 1. Absorption spectra (in C_2H_5OH): 1 –I, 2 –II, 3 –I (NaOH), 4 –II (NaOH), 5 –I (HCl), 6 –II (HCl), 7 –V, 8 –V (HCl)

The mutual transformations of I and II can be explained by prototropic rearrangements under the influence of the pH of the medium, which lead to one or the other of the two intensely colored methene forms or to the ethylene yellow form.

$$\text{pyrrole keto ester fragment} + \text{pyrrole ester fragment} \longrightarrow \text{dipyrrolylmethene form (I)}$$

$$\text{dipyrrolylmethane form} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} \text{methene forms}$$

$$\text{pyrrole ester fragment} + \text{keto pyrrole ester fragment} \longrightarrow \text{dipyrrolylmethene form (II)}$$

In these substituted dipyrrolylmethenes, the influence of electronegative substituents and of their position in the rings on the structure is clearly manifested.

of the compounds obtained. The violet form I is more stable. Isolation of the violet form II is associated with considerable difficulties because of its strong tendency to pass into the yellow ethylene form when the pH is changed. In addition, compound II shows a tendency to split off alcohol with formation of a lactam, which may form already during the synthesis of II.

$$\text{II} \longrightarrow \text{(V)}$$

Structural formula V and absorption spectra

Figure 1: Structural formula V and absorption spectra

Bright-yellow lactam V (m.p. 135-137°), in whose spectrum the long-wavelength maxima are absent (Fig. 1, 7), evidently exists in the ethylene form, and upon acidification of the solution with conc. hydrochloric acid this compound passes into a violet form with a reddish shade, possessing a long-wavelength maximum at 595 mμ (Fig. 1, 8), while absorption in the region of 400 mμ drops sharply.

Fig. 2. Absorption spectra (in C_2H_5OH): 1 –III, 2 –III (NaOH), 3 –III (HCl), 4 –IV, 5 –IV (HCl)

It may be assumed that the lower stability of II is connected with the presence of a carbethoxy group in position 3′. This is confirmed by the following examples. Compound III, in which the carbethoxy substituents are in positions $4, 4'$, is isolated as the base in the form of an intensely colored compound (m.p. 167-169°). In its electronic absorption spectrum (Fig. 2, 1) there is a series of long-wavelength maxima at 495, 565, and 670 mμ. After alkalization, the violet color of the solution changes to light yellow, and in the absorption spectrum the long-wavelength maxima disappear completely while the ultraviolet region remains almost unchanged (Fig. 2, 2), i.e., a transition to the ethylene form occurs. However, an attempt to isolate the yellow ethylene form is unsuccessful because of the reverse conversion of the substance into the methene form, which is also formed upon acidification (Fig. 2, 3).

Compound IV, in which the carbethoxy substituents are in positions 3,3′, behaves in the opposite manner. In contrast to the preceding compound, this compound in the free state has a light-yellow color (m.p. 159-160°), and in its spectrum the long-wavelength maxima are completely absent (Fig. 2, 4). In the presence of a considerable concentration of hydrochloric acid (up to 5 N), this compound acquires a violet color, and a long-wavelength maximum at 545 mμ appears in its spectrum (Fig. 2, 5), indicating the formation of the methene form. It is not possible to isolate IV in the methene form, since upon neutralization of the solution a reverse transition to the yellow form occurs. Thus, one may draw the general conclusion that the presence of electronegative substituents in positions 3 and 3′ promotes the existence of the ethylene form and hinders the formation of the methene form, which in this case exists only in salts ($\hat{}2$). The arrangement of electronegative substituents in positions 4 and 4′, however, favors the occurrence of the methene form.

Compounds I and II, in which the carbethoxy substituents are present both in positions 3 and 4′ and in 4 and 3′, can be isolated both in the methene and in the ethylene form. The presence of an electronegative substituent in position 3′ has a greater influence on the tendency to exist in the ethylene form than in position 3.

The mutual transformations considered—from methene forms into ethylene

Fig. 3. Titration curves with 0.01 N NaOH. 1 –III, 2 –I, 3 –II

Figure 2: Fig. 3. Titration curves with 0.01 N NaOH. 1 –III, 2 –I, 3 –II

forms and back—proceed at definite concentrations of hydrogen ions. Figure 3 gives titration curves of the compounds considered with a centinormal aqueous solution of caustic soda. The intensity at the absorption maxima of the corresponding methene forms served as the indicator. The cessation of the change in lg ϵ with continuing change in pH (inflection points on the titration curves) indicates completion of the transformation into the ethylene form, which has no long-wavelength maxima. The reverse transition to the methene form occurs most readily in the case of compound III, which has no free ethylene form; IV, which for this purpose requires larger amounts of added concentrated hydrochloric acid, passes into the methene form with the greatest difficulty. Compounds I and II behave in an intermediate manner, in accordance with their property of being isolable both in the methene form and in the ethylene form.

Fig. 3. Titration curves with 0.01 N NaOH. 1 –III, 2 –I, 3 –II

The investigation carried out of the transformations of substituted dipyrrylmethenes occurring in solutions with different pH, and the study of the electronic and IR spectra and other properties of these substances, has shown that the compounds under investigation undergo rearrangements under these conditions. The different forms of the substances existing at different pH values of the medium are related to one another as structural isomers and differ in the positions of the double bonds. The transition of some forms into others occurs by the type of prototropic rearrangements.

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