NEW EXAMPLE OF KETO–ENOL TAUTOMERISM

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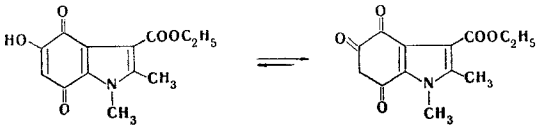
We have found that acid hydrolysis of 1,2-dimethyl-3-carbethoxy-4,5-dioxo-7-dimethylaminoindole gives a mixture of 1,2-dimethyl-3-carbethoxy-5-hydroxy-4,7-dioxoindole (I) and 1,2-dimethyl-3-carbethoyx-4,5,6,7-tetrahydro-4,5,7-trioxoindole (II), which were isolated from the mixture by recrystallization from alcohol. Enol I dissolves in alcohol and precipitates from solution in the form of reddish-orange crystals, whereas ketone II is colorless and practically insoluble in organic solvents. They also differ with respect to their melting points [for enol I, mp 175.5-176.5° (from alcohol); for ketone II, mp 203-205° (dec.)] and IR spectra [for I: 3250 (OH), 1635-1700 cm^{-1} (C=O); for II: 1645-1745 cm^{-1} (C=O)]. At the same time, I and II have identical molecular weights (263), determined by mass spectrometry; the mass spectra of the two compounds are identical, and fragmentation proceeds from the trioxo form in both cases. The compounds also do not differ with respect to the results of elementary analysis. (Found for I: C 59.5; H 5.2; N 5.5%. Found for II: C 59.2; H 5.0; N 5.4%. $C_{13}H_{13}NO_5$. Calculated: C 59.3; H 5.0; N 5.3%.)



I II

Both enol I and ketone II dissolve in alkali to give violet-colored solutions. A mixture of enol I and ketone II is formed when the alkaline solutions are acidified. Enol I is converted to ketone II when it is heated with acids (for example, in alcohol with dilute hydrochloric acid). Consequently, there is some basis to assume that we have observed a new example of keto–enol tautomerism and have isolated both tautomers.

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