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The Reaction of 2,4,6-Heptanetrione with *o*-Phenylenediamine[†]

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Synopsis. 2,4,6-Heptanetrione forms 2-acetyl-4-methyl-1,5-benzodiazepine with *o*-phenylenediamine in alkaline ethanol. In acidic ethanol, it would be expected that the 2-acetyl-4-methyl-1,5-benzodiazepinium cation would be formed. Contrary to expectations, however, the cation seems to be unstable. 2,4-Dimethyl-1,5-benzodiazepinium salt was obtained instead.

2,4,6-Heptanetrione(diacetylacetone: daa) forms metal complexes through its oxygen atoms[1–2] and forms Schiff bases with ethylenediamine[3] in analogy with 2,4-pentanedione(acetylacetone), whereas it does not form dithio- or trithiodiacetylacetonato metal complexes.[4] The reaction of daa with *o*-phenylenediamine(opd) was studied.

By adding a potassium hydroxide ethanol solution to a mixture of daa and opd in ethanol, red crystals of 2-acetyl-4-methyl-1,5-benzodiazepine were obtained. On the other hand, in an ethanol solution containing hydrochloric acid, its azepinium cation seems to be destroyed and to become 2,4-dimethyl-1,5-benzodiazepinium.

Experimental

Instruments. The infrared spectra were obtained by the KBr disk or Nujol mull procedure, using a IRA-1-type infrared spectrophotometer of the Japan Spectroscopic Co., Ltd. The electronic spectra were obtained with a Shimadzu Double-beam Spectrophotometer UV-200 in 64% w/w aqueous methanol, with the ionic strength of 0.3. The NMR spectra of the $CDCl_3$ solution were obtained with a Hitachi Perkin-Elmer Model-R-20 NMR Spectrometer. Tetramethylsilane(TMS) was used as the standard. The mass spectra were obtained with a Hitachi Model-RMU-6M-GC Mass Spectrometer.

The Syntheses of the Compounds. Diacetylacetone[1] was synthesized from dehydroacetic acid by the method of Bethell and Maitland.[5] 2-Acetyl-4-methyl-1,5-benzodiazepine was synthesized from daa and opd according to the method of Thile and Steimmig[6] as follows. Daa (0.71 g, 5×10^{-3} mol) in 20 ml of an ethanol solution was added to opd(0.54 g, 5×10^{-3} mol) in 2 ml of hot ethanol containing 1 ml of acetic acid, and then potassium hydroxide in ethanol was added to the mixture. The red crystals thus formed were filtered off and recrystallized from ethanol. (Found: C, 72.88; H, 6.60; N, 13.04%. Calcd for $C_{13}H_{14}N_2O$: C, 72.90; H, 6.54; N, 13.80%). Molecular weight, 214 (from the mass spectra). The compound forms orange crystals with cadmium chloride in ethanol.

On the other hand, when gaseous hydrochloric acid was added to the mixture (daa+opd+CH_3COOH) mentioned above, the solution turned violet. By adding petroleum ether, violet-colored crystals were obtained. The results of the elemental analyses agree with those of 2,4-dimethylbenzodiazepinium chloride.[7] (Found: C, 53.56; H, 6.98; N, 11.21%. Calcd for $C_{11}H_{13}N_2\cdot 2H_2O$: C, 53.99; H, 7.00; N, 11.45%).

Results and Discussion

The proton NMR spectra of the red compound are shown in Table 1. The spectra fit the structure shown in Fig. 1, 2-acetyl-4-methyl-1,5-benzodiazepine.

Table 1. NMR Spectral data

δ/ppm	Integrated for	Assignment
11.75	1H	hydrogen bond
6.75	4H	phenyl
4.90	1H	methine
3.39	2H	methylene
1.98	3H	methyl
1.81	3H	methyl

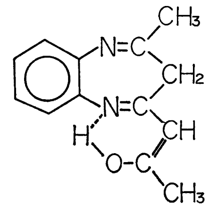

Fig. 1. 2-Acetyl-4-methyl-1,5-benzodiazepine.

The IR spectra also support the above assignment. The free C=O band which is usually expected about 1700 cm^{-1} was not observed, while three bands were observed in the 1515—1660 cm^{-1} region. These bands are likely to consist of (C=N), (C=C), and hydrogenbonded (C–O), or a mixture of them.[8]

On the other hand, the spectra of the violet compound obtained from the acidic solution are completely identical with those of the 2,4-dimethylbenzodiazepinium chloride, which does not show a peak at 1660 cm^{-1}.

The electronic spectra of the red azepine solution do not show any peak in the 350—600 nm range, whereas the addition of hydrogen chloride produced the band at 510 nm. This wavelength agrees well with that reported for the diazepinium cation.[9] (Fig. 2). The peak increased with the acid concentration, with an isosbestic point at 410 nm. It is, therefore, likely that the 2-acetyl-4-methyl-1,5-benzodiazepinium cations present in the solution. The 2,4-dimethyl-1,5-benzodiazepinium salt, however, was obtained

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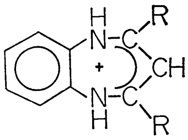

Fig. 2. Diazepinium cation.

by condensation or by adding petroleum ether. The acetyl group must interact with H^+ and be severed in an acidic solution, although the acetyl group was not determined to do so. The acetyl group seems to be relatively easily hydrolyzed because of the stabilization of the seven-membered azepinium ring, which has a resonance system.

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