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A New Coloring Matter of the Color Reaction of Acetone with 1,3,5-Trinitrobenzene

The color reaction of acetone with 1,3,5-trinitrobenzene to give a purple red coloration has been explained to form the Meisenheimer type complex of acetone in the presence of a base.[1]

Spectrophotometric studies of the improved spot test[2] showed that the developed color gave the Meisenheimer type spectrum only when a large excess of acetone was used, and gave a new type spectrum in the usual spot test in which a small amount of sample was used in the presence of excessive 1,3,5-trinitrobenzene.

To clarify the reaction mechanism, we separated two coloring matters (I and II) in crystalline forms from the reaction mixture carried out under the conditions of the spot test by using thin-layer chromatographic techniques (adsorbent: Wakogel B-5, solvent: *n*-BuOH saturated 3% ammonium hydroxide).

I was identified as the Meisenheimer type complex of acetone.[1] On the other hand, the aqueous solution of II gave the new type absorption spectrum. The present communication discusses the structure of II, the main coloring matter of the color reaction.

II [purple red plates (from acetone and benzene), UV and Visible $\lambda_{max}^{H_2O}$ mμ: 262, 480, IR ν_{max}^{KBr} cm^{-1}: 1725 (CO), 1550, 1345 (NO_2)] showed no melting point and exploded when ignited or heated rapidly. The elementary analyses were C, 36.77; H, 2.76; N, 14.37; Na, 8.00. The molecular weight was about 300 by the Barger–Rast method.[3] From the above results, the constitution of II was assumed as $C_9H_8O_7N_3Na$ (293.18) (*Anal.* Calcd. for C, 36.89; H, 2.73; N, 14.34; Na, 7.84). Fig. 1 shows the nuclear magnetic resonance (NMR) spectrum of acetone-d_6 solution of II. The signal at 8.51 ppm was assigned to a ring proton in an original 1,3,5-trinitrobenzene ring system. By the irradiation at 4.52 ppm (2H, a poorly-resolved quartet), a triplet at 5.72 ppm (1H, J=3.0 cps) became a singlet, and two quartets (two double doublets) at 3.10 ppm (2H, J=4.0 and 13.1 cps) and 2.56 ppm (2H, J=1.6 and 13.1 cps) turned to sharp two doublets (both 2H, J=13.1 cps) respectively. These doublets have been explained as two groups of geminal protons on carbon atoms adjacent to a carbonyl group in a rigid cyclohexanone system.

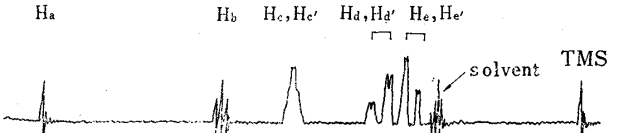

Fig. 1. NMR Spectrum of Acetone-d_6 Solution of II

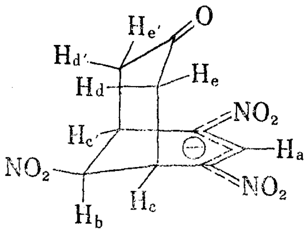

Chart 1

On the basis of the above results, the structure of the anion group ($C_9H_8O_7N_3^+$) of II was assumed as shown in Chart 1.

The constitution and the structure of the anion group of II were confirmed by the chemical and physical investigations of the crystalline color products separated from the reaction mix-

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[1] J. Meisenheimer, *Ann.*, 323, 205 (1902); M. Kimura, *Yakugaku Zasshi*, 73, 1219 (1953); for recent reviews, see T. Nambara, *Bunsekikagaku*, 13, 184 (1964); R. Foster and C.A. Fyfe, *Rev. Pure and Appl. Chem.*, 16, 61 (1966).

[2] T. Momose, Y. Ohkura and K. Kohashi, *Chem. Pharm. Bull.* (Tokyo), 11, 301 (1963).

[3] G. Barger, *Chem. Ber.*, 37, 1745 (1910); K. Rast, *ibid.*, 54, 1979 (1921); S. Akiya, *Yakugaku Zasshi*, 57, 967 (1937).

ture of aliphatic carbonyl compounds such as methyl ethyl ketone and diethyl ketone with 1,3,5-trinitrobenzene in diethylamine and piperidine respectively.

Diethylamine and piperidine salts of the anion group of II had already been obtained in the form of precipitates, but their structures have not been resolved.[4] Our data of them are as follows. Diethylamine salt: deep red needles, mp 152—154° (uncorr.) (from acetone and ether). *Anal.* Calcd. for $C_9H_8O_7N_3 \cdot C_4H_{12}N$: C, 45.34; H, 5.85; N, 16.27. Found: C, 45.40; H, 5.90; N, 16.15. Piperidine salt: deep purple red plates, mp 174—176° (uncorr.) (from methanol). *Anal.* Calcd. for $C_9H_8O_7N_3 \cdot C_5H_{12}N$: C, 47.18; H, 5.65; N, 15.72. Found: C, 47.31; H, 5.68; N, 15.64.

Further details of the studies will be published in the near future.

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[4] R. Foster and C.A. Fyfe, *Tetrahedron*, **22**, 1831 (1966).