

ANIONIC σ -ADDUCTS OF 1-METHYL-3,5-DINITRO-2-PYRIDONE¹⁾

Yasuo TOHDA*, Masahiro ARIGA, Toshihide KAWASHIMA, and Eizo MATSUMURA
Department of Chemistry, Osaka Kyoiku University,
Minamikawahori-cho 4-88, Tennoji-ku, Osaka 543

Alkylammonium salts of anionic σ -adducts of 1-methyl-3,5-dinitro-2-pyridone with amine- and carbon-nucleophiles were isolated and characterized. All the nucleophiles are attached to C-6 of the pyridone nucleus. The carbon-adducts are more stable than the amine-adducts, which dissociate in dilute methanol solutions. The acetone-adduct was converted into 4-nitro-1-pyrrolidinylbenzene quantitatively by heating with pyrrolidine.

Anionic σ -adducts have been well known to be important intermediates of various reactions involving electron-deficient aromatic substrates.²⁾ Although such class of compounds has been widely studied in many aromatic systems, those in pyridone systems are scarcely known.³⁾ We recently found the interesting ring transformations of 1-substituted 3,5-dinitro-2-pyridones with ketonic nucleophiles to p-nitrophenols⁴⁾ and p-nitroanilines.⁵⁾ We report here isolation and characterization of anionic σ -adducts of 1-methyl-3,5-dinitro-2-pyridone (1), which have been expected as one of the intermediates of these reactions.^{2a,5)}

On treatment of 1 (1 mmol) with diethylamine (3 mmol) in THF (10 ml) at room temperature, orange red crystals (2) were precipitated quantitatively, which consisted of 1 and diethylamine in molar ratio of 1:2. Pyrrolidine also gave the similar 1:2 adduct (3) but less basic secondary amine such as N-methylaniline or tertiary amine such as triethylamine gave no isolable adduct.

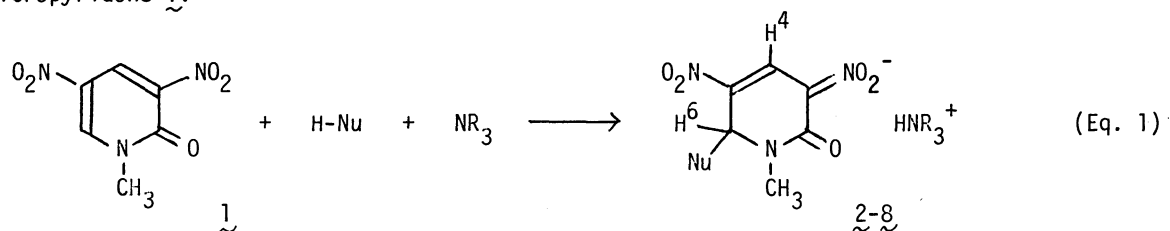
When 1 (1 mmol) was treated with diethyl malonate (2 mmol) in the presence of diethylamine (3 mmol) in THF (10 ml) at room temperature, yellow orange crystals (4) were afforded, which were composed of 1, diethyl malonate, and diethylamine in molar ratio of 1:1:1. Although 1 did not react with ketones such as cyclohexanone or acetophenone under the similar conditions, 1:1:1 adducts of 1, the ketones, and diethylamine (5 and 6) were obtained in 76% and 80% yields, respectively, by heating the mixtures at 70 °C for 2 h. A similar reaction of 1 with acetone and diethylamine gave no corresponding adduct but yielded N,N-diethyl-4-nitrobenzene as reported previously.⁵⁾ An acetone-adduct was obtained indirectly as following. Treatment of 1 (1 mmol) with equimolar guanidine (1 M methanol solution) in THF (10 ml) gave orange red crystals which consisted of 1, guanidine, and methanol in molar ratio of 1:1:1. By refluxing the crystals in acetone for 3 h, deep red precipitates (7) were obtained, which were composed of 1, acetone, and guanidine in molar ratio of 1:1:1. By a similar treatment with nitromethane instead of acetone, an adduct of 1 with nitromethane and guanidine (8) was also obtained.

A 1:1 adduct of 1 with sodium methoxide (9) was obtained by a reaction of 1 with equimolar sodium methoxide in methanol at room temperature. Among the adducts 2-9, only 9 could not be purified by recrystallization from methanol.⁶⁾

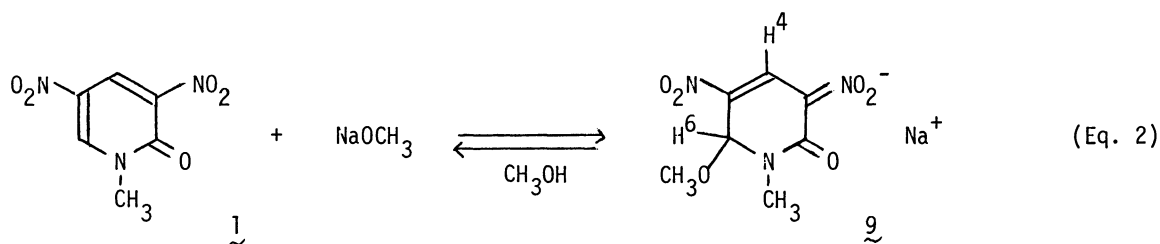
Spectroscopic data of 2-9 are listed in Table 1. ¹H-NMR spectra of the adducts show characteristics of anionic σ -adducts. Two ring protons of the adducts are found at different

regions; one at δ 8.5-8.8 and the other at δ 5.0-6.0. The shift for the higher field ring resonance depends on the electronegativity of the atom attached to the ring. For the methoxide-adduct (9), the resonance occurs at δ 6.0, those for the amine-adducts (2, 3) at δ 5.4-5.7, and those for the carbon-adducts (4-8) at δ 5.0-5.5. These shifts can be attributed to the protons bonding to sp^3 carbon atom of the ring (C-4 or C-6). The two ring protons are coupling each other ($J \sim 1.5$ Hz). In the adducts with the carbon-nucleophiles (4-8), the protons at higher field are also coupling with the α -protons of the nucleophiles. The coupling constants with the α -secondary protons are 4-5 Hz (6-8) and those with the α -tertiary protons are 1.3-3 Hz (4, 5). The same trends of the shifts and the coupling constants were reported in the case of anionic σ -adducts of 1,3,5-trinitrobenzene.^{2b,7)} The N-methyl protons of the adducts are found in higher fields by 0.5 ppm than that of 1. In IR spectra, the carbonyl band of 1 at 1698 cm^{-1} shifts to $1610\text{-}1640\text{ cm}^{-1}$ in the adducts. These facts can be attributed to delocalization of a negative charge in the pyridone nucleus of the adducts. Weak ammonium N-H stretching bands are observed at $2300\text{-}2800\text{ cm}^{-1}$. These spectroscopic data strongly indicate that they are anionic σ -adducts of 1.

In order to determine the structures of the adducts, 6-deuterio-1-methyl-2-pyridone was prepared by the method of Beak⁸⁾ and nitrated. The afforded 6-deuterio-1-methyl-3,5-dinitro-2-pyridone (1-d) was treated with some of the nucleophiles mentioned above. NMR spectra of the adducts of 1-d (2-d, 5-d, 7-d, and 9-d) show that the signals at δ 8.5-8.8 are singlet and the signals at δ 5.0-6.0 disappear. These results indicate that both carbon-, nitrogen-, and oxygen-nucleophiles are attached to C-6 of the dinitropyridone. (Eq. 1) The fact is rationalized by that the position is thought to be the terminal of the conjugation of 1,3-dinitro-1,3-butadiene system in the dinitropyridone 1.⁵⁾



The absorption maximum of 9 in methanol was found at 449 nm ($\epsilon = 3.11 \times 10^4$). Since its apparent molecular absorptivity depends on concentrations of 9 (10^{-5} - 2×10^{-1} M⁹⁾) and added sodium methoxide (0 - 10^{-2} M), it is evident that the formation of 9 is reversible in methanol as shown in Eq. 2. The equilibrium constant was determined to be $1 \times 10^4\text{ M}^{-1}$ at 10 - 15°C .



Electronic spectra of the ketone-adducts (5-7) in methanol show strong absorptions at 476-480 nm ($\epsilon \sim 3 \times 10^4$). Because their molecular absorptivities are independent on their concentrations, these species are not in equilibrium with 1. Stability of the ketone-adducts was also demonstrated by following reactions. On treating 5 or 6 with equimolar hydrochloric acid in cold water, protonated anionic σ -adducts were obtained as yellow precipitates, which slowly decomposed to 1 and the ketones in methanol at room temperature. By the same treatment, the amine-adducts (2, 3) and the malonate-

Table 1. $^1\text{H-NMR}$, IR, and Electronic Spectra of Anionic α -Adducts of 1-Methyl-3,5-dinitro-2-pyridone

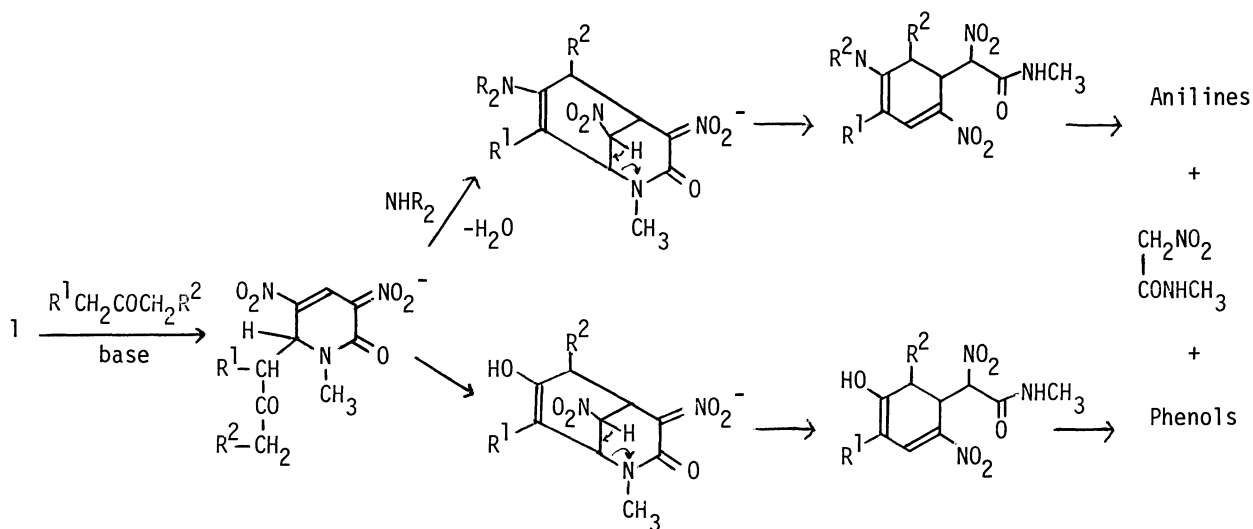
Adduct ^{a)}	Decomposition point (°C)	$^1\text{H-NMR}$ Spectra (DMSO- d_6)		IR Spectra (Nujol) (cm ⁻¹)	Electronic Spectra (MeOH) λ_{max} (nm)
		H ⁴	H ⁶		
2	b)	8.69 (broad s)	5.43 (broad s)	1632	449 ^{c)} (4.10)
2-d	b)	8.69 (s)	-	1627	448 ^{c)} (4.12)
3	b)	8.67 (d, 1.5Hz)	5.69 (d, 1.5Hz)	1633	448 ^{c)} (4.03)
4	95-98	8.57 (d, 1.4Hz)	5.43 (dd, 1.4 and 3.1Hz)	1644	449 ^{c)} (3.25)
4-d	117-119	8.60 (s)	-	1642	450 ^{c)} (3.30)
5	172-175	8.64 (d, 1.3Hz)	5.48 (t, 1.3Hz)	1627	479 (4.40)
6	153-155	8.49 (d, 1.3Hz)	5.19 (broad t, 5Hz)	1624	478 (4.42)
6-d	151-155	8.49 (s)	-	1623	480 (4.45)
7	178-182	8.55 (d, 1.3Hz)	5.05 (td, 5 and 1.3Hz)	1620	476 (4.48)
8	176-180	8.61 (d, 1.3Hz)	5.34 (broad t, 4Hz)	1646	472 (4.53)
9	d)	8.78 (d, 1.7Hz)	5.99 (d, 1.7Hz)		449 (4.49)
9-d	d)	8.76 (s)	-		

a) Notations of the adducts are shown in Eq. 1. b) The adducts slowly decomposed to 2 by heating gently.

c) The peaks are attributed to 9 by methanolysis of the adducts. d) Not isolated.

adduct (4) decomposed to 1 immediately. The strong absorption peak of the nitromethane-adduct (8) at 472 nm slowly changed to a weak peak at 450 nm. Its half life was 100 minutes at 10 °C. The latter peak seems to be attributed to 9 by methanolysis of 8. Electronic spectra of the amine-adducts (2, 3) and the malonate-adduct (4) in methanol show weak peaks at 450 nm. These may also be due to dissociation of the adducts to 1 and 9 in the dilute solutions. The secondary amine-adducts (2, 3) are so labile that they easily decompose to 1 by heating on a hot plate at 60-70 °C (Table 1).

When the acetone-adduct (7) was treated with pyrrolidine at 80 °C for 5 h in pyridine, 4-nitro-1-pyrrolidinylbenzene was obtained quantitatively. This fact shows that the anionic σ -adducts like 7 are one of the intermediates of the ring transformations of 1-substituted 3,5-dinitro-2-pyridones with ketonic nucleophiles to p-nitrophenoles⁴⁾ or p-nitroanilines⁵⁾. A plausible mechanism of the transformation is shown as below.



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