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Organic Photochemical Reactions. XXX. Photoreactions of *N,N*-Dimethylpyruvamide in Methanol and Ethanol[1,2]

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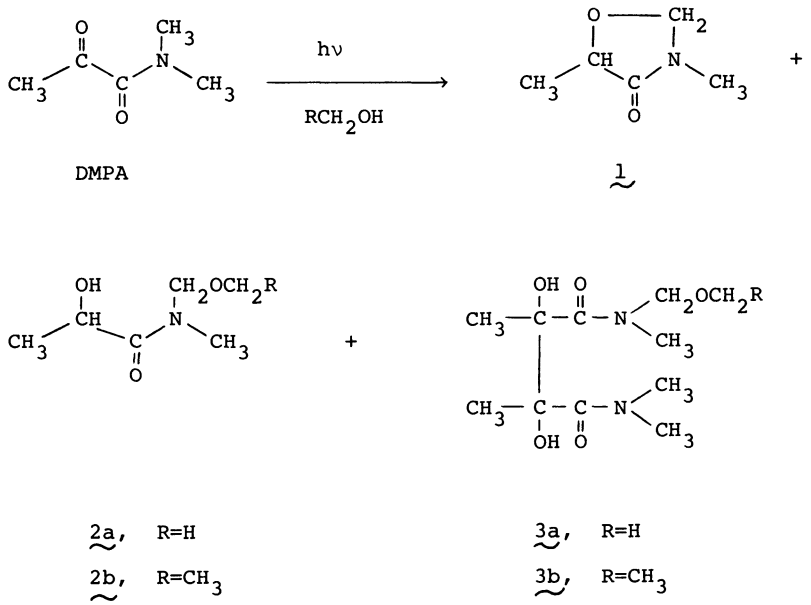
The photoreactions of *N,N*-dimethylpyruvamide (DMPA) in methanol and ethanol were investigated. Irradiation of DMPA in methanol gave three products (3,5-dimethyl-4-oxazolidinone, 2-hydroxy-*N*-methyl-*N*-(methoxymethyl)propanamide, and 2,3-dihydroxy-2,3-dimethyl-*N,N,N'*-trimethyl-*N'*-(methoxymethyl)-butanediamide) in good yields. The product distribution was dependent on the concentration of DMPA and methanol. Similarly, irradiation of DMPA in ethanol gave three products (3,5-dimethyl-4-oxazolidinone, 2-hydroxy-*N*-methyl-*N*-(ethoxymethyl)propanamide, and 2,3-dihydroxy-2,3-dimethyl-*N,N,N'*-trimethyl-*N'*-(ethoxymethyl)butanediamide). The mechanism for the formation of these products is discussed.

Extensive photochemical studies of α-oxo amides have recently been performed by Aoyama's group;[3-6] they considered both synthetic and mechanistic points. They reported that irradiation of *N,N*-dialkylpyruvamides in methanol gave 4-oxazolidinones as a sole product in quantitative yields.[3] In our recent study of the photoadditions of pyruvamides to alkenes,[7] we found that irradiation of *N,N*-dimethylpyruvamide (DMPA) in methanol gave not only 3,5-dimethyl-4-oxazolidinone (**1**), but also the adducts of DMPA with methanol (**2a** and **3a**) in good yields. In this paper we wish to report on the photochemical reactions of DMPA with methanol and ethanol, and to discuss the mechanism for the formation of the photoproducts.

Results and Discussion

Irradiation of DMPA in methanol resulted in the formation of three products (**1**, **2a**, and **3a**) in good yields. These products were separated by preparative GC or column chromatography on silica gel. Their structures were determined by IR, ^{1}H- and ^{13}C-NMR, mass spectra, and elemental analyses, as detailed in the experimental section. Product **1** was assigned as a derivative of 4-oxazolidinones.[3] Product **2a** was the 1:1 adduct of DMPA and methanol, whereas product **3a** was found to be 2:1 adduct of DMPA and methanol on the basis of the elemental analyses and mass spectra. **2a** was characterized as 2-hydroxy-*N*-methyl-*N*-(methoxymethyl)propanamide by IR, ^{1}H- and ^{13}C-NMR spectra.[2] **3a** was found to be the stereoisomeric mixtures of 2,3-dihydroxy-2,3-dimethyl-*N,N,N'*-trimethyl-*N'*-(methoxymethyl)butanediamide from the ^{1}H- and ^{13}C-NMR spectra. Similarly, irradiation of DMPA in ethanol gave three products (**1**, **2b**, and **3b**).

The produced amounts of **1**, **2a**, and **3a** in the irradiation of DMPA in methanol increased linearly with the irradiation time (see Fig. 1). Therefore, these products can be considered to be the primary products from DMPA. Furthermore, it was confirmed that each product remains unchanged under the irradiation in methanol. The product distribution in the photoreaction of DMPA in methanol was found to depend on the concentration of DMPA; as the concentration of DMPA increases, **3a** increases and **1** decreases (see Table 1). The effects of methanol concentration on product yields are shown in Fig. 2. In the irradiation of benzene solutions containing 0.1 mol dm^{-3} DMPA and 0—22 mol dm^{-3} methanol, the yield of **1** remains almost constant, and the yield of **2a** gradually increases



Scheme 1.

as the concentration of methanol increases. The yield of **3a** is highest at *ca.* 1.5 mol dm^{-3} of methanol and decreases at higher methanol concentration. Thus, at very high concentration of methanol, **2a** becomes the major product. The quantum yields for the formation of **1**, **2a**, and **3a** in methanol solution of 0.2 mol dm^{-3} DMPA were as follows: ϕ_1=0.098; ϕ_{2a}=0.34; ϕ_{3a}=0.065.

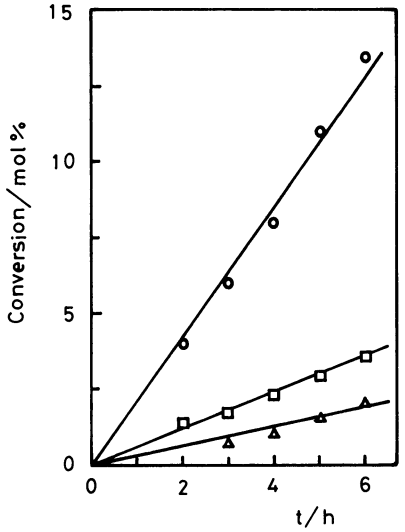


Fig. 1. Effects of irradiation time on product yields. □: **1**, ○: **2a**, △: **3a**. [DMPA]=0.2 mol dm^{-3} in methanol.

The formation of these products is most reasonably explained by a mechanism which involves a zwitterionic intermediate (**5**).[6] The formation of the oxazolidinone (**1**) and the methanol adducts (**2a** and **3a**) from the zwitterion (**5**) can be explained as shown in Scheme 2. Aoyama *et al.*[6] have proposed the mechanism in which the oxazolidinone and the methanol adduct are formed from the imminium ion (**6**), produced by the addition of proton to the zwitterion (**5**). However, it seems to be difficult to explain the formation of **3a** by the mechanism suggested by them.

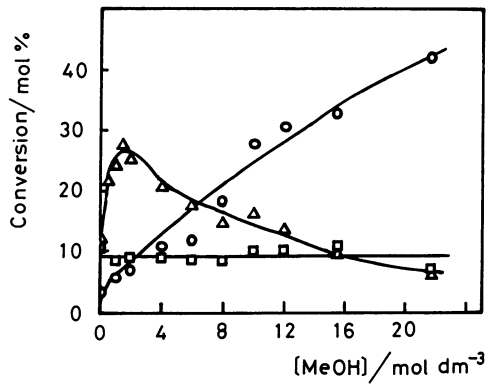
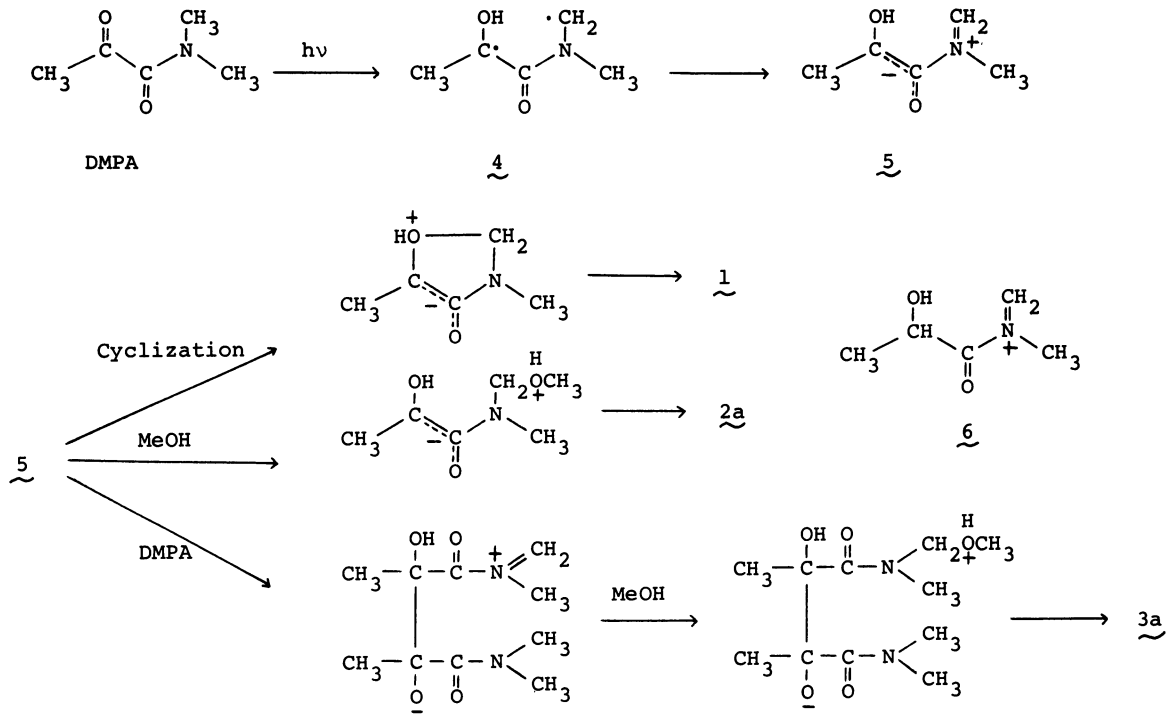


Fig. 2. Effects of methanol concentration on product yields. □: **1**, ○: **2a**, △: **3a**. [DMPA]=0.1 mol dm^{-3}.

Table 1. Concentration effects on products distribution in the photoreactions of DMPA in methanol

DMPA/g	MeOH/cm^3	Irradiation time/h	Products distribution/%		
			1	**2a**	**3a**
8.3	200	72	37	54	9
8.2	140	30	24	55	21
5.5	45	140	12	53	35



Scheme 2.

Experimental

General. ^{1}H-NMR spectra were recorded on a JEOL JNM-MH 100 machine, ^{13}C-NMR spectra on a JEOL FX 60 machine, IR spectra on a Hitachi IR 260-50 and a JASCO IRA-1 spectrometer, and mass spectra on a JEOL D-300 machine. GC were performed on a Shimadzu GC-6AM and a Hitachi 163 apparatus using a column of Si DC 550 or DEGS at 170 °C. *N,N*-Dimethylpyruvamide (bp 103—105 °C/25 mmHg[†]; lit, bp 53.8 °C/4.5 mmHg[8]) was prepared by the permanganate oxidation[9] of *N,N*-dimethyllactamide (bp 113—116 °C/14 mmHg), which in turn was prepared from the reaction of methyl lactate and anhydrous dimethylamine.[10]

Irradiation of DMPA in Methanol. A solution of DMPA (8.2 g) in 140 cm^3 of methanol was irradiated in a Pyrex doughnut-type vessel under nitrogen with a 300 W high pressure mercury lamp for 30 h. After removal of the solvent, the residue was distilled under reduced pressure to give a liquid (bp 63—130 °C/3 mmHg, 8.3 g) and a viscous oily residue (2.2 g). GC analysis of the distillate showed that it was composed of three products (**1**, **2a**, and **3a**) with the area ratio of 24:55:21. Products **1** and **2a** were isolated by preparative GC on Si DC 550 or DEGS column at 150 °C, and **3a** was isolated by column chromatography on silica gel.

3,5-Dimethyl-4-oxazolidinone (1): IR ($CHCl_3$) 1705, 1100, 1025 cm^{-1}; ^{1}H-NMR (CCl_4) δ=1.31 (3H, d, J=7 Hz, CH_3CH), 2.83 (3H, s, NCH_3), 4.18 (1H, q, J=7 Hz, CH_3CH), 4.92 (2H, s, OCH_2N); ^{13}C-NMR (C_6D_6) δ=17.4 (q, CH_3CH), 26.5 (q, NCH_3), 74.5 (d, CH_3CH), 81.5 (t, OCH_2N), 172.7 (s, C=O); MS m/z 115 (M^+). Found: C, 51.90; H, 7.97; N, 11.95%. Calcd for $C_5H_9NO_2$: C, 52.16; H, 7.88; N, 12.17%.

*2-Hydroxy-*N*-methyl-*N*-(methoxymethyl)propanamide (2a)*: IR ($CHCl_3$) 3420, 1650, 1100 cm^{-1}; ^{1}H-NMR (CCl_4) δ=1.28 (3H, d, J=7 Hz, CH_3CH), 2.91 and 2.96 (3H, s, NCH_3), 3.17 and 3.26 (3H, s, OCH_3), 3.94 (1H, br. s, OH), 4.28—4.60 (1H, m, CH_3CH), 4.64 —4.90 (2H, m, NCH_2O); ^{13}C-NMR (C_6D_6) δ=20.9 and 21.8 (q, CH_3CH), 33.4 and 33.7 (q, NCH_3), 55.6 (q, OCH_3), 65.2 (d, CH_3CH), 78.6 and 80.8 (t, NCH_2O), 174.7 (s, C=O); MS m/z 147 (M^+). Found: C, 48.74; H, 9.16; N, 9.47%. Calcd for $C_6H_{13}NO_3$: C, 48.97; H, 8.90; N, 9.52%.

*2,3-Dihydroxy-2,3-dimethyl-*N,N,N′*-trimethyl-*N′*-(methoxymethyl)butanediamide (3a)*: Bp 121—123 °C/2 mmHg; IR ($CHCl_3$) 3340, 1600, 1100 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=1.46 (6H, br. s, CH_3C), 2.91, 2.94, 3.30, 3.38, and 3.41 (s, 12H, NCH_3 and OCH_3), 4.69, 4.87, 5.14, and 5.30 (2H, d, J=10 Hz, NCH_2O), 5.89, 6.08, and 6.23 (2H, br. s, OH); ^{13}C-NMR (CCl_4) δ=18.2 and 19.1 (q, CH_3C), 32.7, 34.0, 36.9, and 37.8 (q, NCH_3), 54.3 and 55.1 (q, OCH_3), 78.3 and 79.5 (t, NCH_2O), 79.5 (s, CH_3COH), 177.8 and 186.6 (s, C=O); MS m/z 263 (M^++1, by CI). Found: C, 50.48; H, 8.50; N, 10.65%. Calcd for $C_{11}H_{22}N_2O_5$: C, 50.37; H, 8.45; N, 10.68%.

Irradiation of DMPA in Ethanol. A solution of DMPA (5.9 g) in 140 cm^3 of ethanol was irradiated in a Pyrex vessel for 40 h. After removal of the solvent, the residue was distilled under reduced pressure to give a liquid (bp 45—105 °C/0.5 mmHg, 6.1 g) and a viscous oily residue (1.3 g). GC analysis of the distillate showed that three products (**1**, **2b**, and **3b**) with the area ratio of 57:18:25 were present. Products **1** and **2b** were isolated by preparative GC, and **3b** was isolated by column chromatography on silica gel.

*2-Hydroxy-*N*-methyl-*N*-(ethoxymethyl)propanamide (2b)*: IR ($CHCl_3$) 3420, 1650, 1080 cm^{-1}; ^{1}H-NMR (CCl_4) δ=1.12—1.38 (3H, m, OCH_2CH_3), 1.27 (3H, d, J=7 Hz, CH_3CH), 2.97 (3H, s, NCH_3), 3.41 (2H, q, J=7 Hz, OCH_2CH_3), 3.60 (1H, br. s, OH), 4.24—4.56 (1H, m, CH_3CH), 4.62—4.93 (2H, m, NCH_2O); ^{13}C-NMR ($CDCl_3$) δ= 15.1 (q, OCH_2CH_3) 20.9 and 21.9 (q, CH_3CH), 32.7 and 33.9 (q, NCH_3), 63.8 (t, OCH_2CH_3), 64.6 (d, CH_3CH), 76.8 and 78.7 (t, NCH_2O), 176.5 (s, C=O); MS m/z 161 (M^+). Found: C, 52.33; H, 9.15; N, 8.72%. Calcd for $C_7H_{15}NO_3$: C, 52.15; H, 9.38; N, 8.69%.

*2,3-Dihydroxy-2,3-dimethyl-*N,N,N′*-trimethyl-*N′*-(ethoxymethyl)butanediamide (3b)*: Bp 101—102 °C/0.5 mmHg; IR ($CHCl_3$) 3320, 1600, 1100 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=1.10—1.42 (3H, m, OCH_2CH_3), 1.48 (6H, br. s, CH_3C), 2.91, 2.96, 3.38, and 3.42 (9H, s, NCH_3), 3.30—3.64 (2H, m, OCH_2CH_3), 4.68, 4.87, 5.14, and 5.30 (2H, d, J=10 Hz, NCH_2O), 5.90, 6.07, and 6.23 (2H, br. s, OH); ^{13}C-NMR (C_6D_6) δ=16.0 (q, OCH_2CH_3), 19.2 and 20.3 (q, CH_3C), 34.3, 35.3, 37.9, and 38.8 (q, NCH_3), 63.9 (t, OCH_2CH_3), 78.3 and 79.8 (t, NCH_2O), 81.2 (s, CH_3COH), 179.1 and 180.9 (s, C=O); MS m/z 277 (M^++1, by CI). Found: C, 51.91; H, 8.96; N, 10.05%. Calcd for $C_{12}H_{24}N_2O_5$: C, 52.16; H, 8.75; N, 10.14%.

The Ratio of 1: 2a: 3a under Various Conditions. In the experiments on the effects of irradiation time, solutions (4 cm^3) of DMPA (0.2 mol dm^{-3}) in methanol were placed in 10 mm Pyrex tubes. The samples were degassed by four freeze-pump-thaw cycles at $\approx 10^{-5}$ mmHg and sealed. The tubes were irradiated for 1—6 h with a merry-go-round apparatus using a Halos PIH 300 mercury lamp in a water bath. After the irradiation, an internal standard (vanilin) was added to each tube, and product yields were determined by GC analysis. The calibration factors were 0.69 for **1**, 3.22 for **2a**, and 2.06 for **3a**. In the experiments of the effects of methanol concentration, degassed benzene solutions (4 cm^3) containing 0.1 mol dm^{-3} of DMPA and 0—22 mol dm^{-3} of methanol were irradiated for 1 h. Light Intensities in quantum yield measurements were determined by tris(oxalato)ferrate(III) actinometry.[11]

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[†] 1 mmHg≈133.322 Pa.

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