**Table II. Atomic Coordinates for Monensin B Lithium Salt**

| atom | x/a | y/b | z/c |
|---|---|---|---|
| O(1) | 0.4810 (3) | 0.0076 (2) | 0.1207 (2) |
| O(2) | 0.4202 (3) | 0.1283 (2) | 0.0957 (2) |
| O(3) | 0.7326 (3) | 0.1354 (2) | -0.0055 (2) |
| O(4) | 0.4804 (2) | 0.2235 (2) | 0.2576 (1) |
| O(5) | 0.7491 (2) | 0.1461 (2) | 0.2224 (1) |
| O(6) | 0.6293 (2) | 0.0989 (2) | 0.3039 (1) |
| O(7) | 0.5022 (2) | 0.0169 (2) | 0.3908 (1) |
| O(8) | 0.3594 (2) | 0.1639 (2) | 0.3976 (1) |
| O(9) | 0.2557 (2) | 0.1336 (2) | 0.2920 (1) |
| O(10) | 0.2939 (2) | 0.1818 (2) | 0.1883 (1) |
| O(11) | 0.3891 (2) | 0.0184 (2) | 0.2337 (1) |
| O(12) | 0.5241 (4) | -0.1694 (3) | 0.0586 (2) |
| Li(1) | 0.4498 (6) | 0.1063 (5) | 0.3042 (4) |
| C(1) | 0.4824 (4) | 0.0618 (4) | 0.0865 (2) |
| C(2) | 0.5661 (4) | 0.0704 (3) | 0.0316 (2) |
| C(3) | 0.6562 (4) | 0.1402 (3) | 0.0476 (2) |
| C(4) | 0.7230 (4) | 0.1266 (3) | 0.1102 (2) |
| C(5) | 0.6652 (3) | 0.1564 (3) | 0.1730 (2) |
| C(6) | 0.6226 (4) | 0.2530 (3) | 0.1738 (2) |
| C(7) | 0.5779 (4) | 0.2744 (3) | 0.2414 (2) |
| C(8) | 0.6629 (4) | 0.2553 (3) | 0.2930 (2) |
| C(9) | 0.7121 (4) | 0.1626 (3) | 0.2866 (2) |
| C(10) | 0.8103 (4) | 0.1440 (4) | 0.3305 (3) |
| C(11) | 0.8020 (4) | 0.0429 (3) | 0.3432 (3) |
| C(12) | 0.6771 (4) | 0.0222 (3) | 0.3373 (2) |
| C(13) | 0.6194 (4) | 0.0194 (3) | 0.4031 (2) |
| C(14) | 0.6317 (5) | 0.0985 (4) | 0.4485 (2) |
| C(15) | 0.5267 (4) | 0.0968 (4) | 0.4882 (2) |
| C(16) | 0.4445 (4) | 0.0371 (3) | 0.4507 (2) |
| C(17) | 0.3373 (4) | 0.0791 (3) | 0.4289 (2) |
| C(18) | 0.2437 (4) | 0.1010 (4) | 0.4762 (2) |
| C(19) | 0.1706 (4) | 0.1564 (4) | 0.4315 (2) |
| C(20) | 0.2532 (4) | 0.2098 (3) | 0.3915 (2) |
| C(21) | 0.2258 (4) | 0.2187 (3) | 0.3185 (2) |
| C(22) | 0.1038 (4) | 0.2418 (3) | 0.3059 (2) |
| C(23) | 0.0771 (4) | 0.2254 (3) | 0.2349 (3) |
| C(24) | 0.1084 (4) | 0.1317 (4) | 0.2138 (2) |
| C(25) | 0.2328 (4) | 0.1195 (3) | 0.2255 (2) |
| C(26) | 0.2755 (4) | 0.0245 (3) | 0.2151 (2) |
| C(27) | 0.5073 (5) | 0.0945 (4) | -0.0318 (3) |
| C(28) | 0.7825 (7) | 0.2168 (4) | -0.0230 (3) |
| C(29) | 0.7652 (4) | 0.0286 (3) | 0.1168 (3) |
| C(30) | 0.7108 (5) | 0.3214 (3) | 0.1544 (3) |
| C(31) | 0.6535 (5) | -0.0606 (3) | 0.2980 (3) |
| C(32) | 0.4203 (6) | -0.0504 (4) | 0.4865 (3) |
| C(33) | 0.2781 (5) | 0.1534 (4) | 0.5367 (2) |
| C(34) | 0.0769 (5) | 0.3375 (4) | 0.3262 (3) |
| C(35) | 0.0742 (6) | 0.1145 (6) | 0.1467 (3) |

non-hydrogen[7] atoms treated anisotropically converged with $R$ = 0.038 and $R_w$ 0.048.[8] The largest peak in the final difference Fourier synthesis (1 e/Å$^3$) was 1.34 Å from C(24). Examination of this region suggests there may be some epimerization occurring at C(24).

**Crystallographic data for MonB$^-$Li$^+$**: $C_{35}H_{59}O_{11}Li\cdot H_2O$, mol wt 680.8, orthorhombic, space group $P2_12_12_1$, $a$ = 12.014 (2) Å, $b$ = 14.978 (2) Å, $c$ = 20.724 (4) Å, $V$ = 3729 (1) Å$^3$, $F(000)$ = 1480, $Z$ = 4, $D_c$ = 1.21 g/cm$^3$, (Mo K$\alpha$) = 0.85 cm$^{-1}$. The data, collected on a Syntex P1 diffractometer ($\lambda$ = 0.710 69 Å) gave 3288 unique reflections with $F > 6\sigma(F)$. The light-atom coordinates from MonB$^-$Ag$^+$ were used as a starting point for refinement of MonB$^-$Li$^+$. The first difference map clearly showed the positions of the Li$^+$ and the $H_2O$ molecule. Blocked full-matrix least-squares refinement with all non-hydrogen[7] atoms treated with anisotropic thermal parameters converged with $R$ = 0.047 and $R_w$ = 0.059.[8] Again, the largest peak in the final difference Fourier synthesis (height 0.5 e/Å$^3$) was 1.36 Å from C(24).

For both molecules the only significant intermolecular contact involves the water oxygen, O(12), which appears to be strongly hydrogen bound to O(1) (MonB$^-$Li$^+$, 2.791 (6) Å; MonB$^-$Ag$^+$, 2.76 (1) Å) and relatively weakly bound to O(8) in a symmetry-related molecule[8] (MonB$^-$Li$^+$, 3.004 (5) Å; MonB$^-$Ag$^+$, 3.09 (1) Å).

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**Registry No.** 1, 30485-16-6; 1·Li, 99531-71-2; 1·Ag, 99531-72-3; 1·Na, 99571-13-8; 1·Li·$H_2O$, 99531-73-4; 1·Ag·$H_2O$, 99571-12-7; 1·Na·$H_2O$, 81642-38-8.

**Supplementary Material Available:** Tables of crystal data for both complexes and details of the structure determination, positional and thermal parameters and their esd values, bond distances, bond angles, and torsion angles (16 pages). (Listings of observed and calculated structure factors for monensin B silver and lithium salts are available from the author.) Ordering information is given on any current masthead page.

(6) Beurskens, P. T.; Bosman, W. P.; Doesburg, H. M.; Gould, R. O.; van den Hark, Th. E. M.; Prick, P. A.; Noordik, J. H.; Buerskens, G.; Parthasarthi, V.; BruinsSlot, H. J.; Haltiwanger, R. C. DIRDIF, Technical Report, 1983/1, Crystallography Laboratory, Toernooiveld, 6525 ED Nijmegen, The Netherlands.

(7) Methyl hydrogen atoms were refined as part of an idealized methyl group. Other hydrogen atoms attached to carbon atoms were included in idealized sp$^3$ conformations riding on the carbon to which they were attached. Hydrogen atoms attached to oxygen were included in observed positions again riding on the atoms to which they were attached. Hydrogen atoms in the $H_2O$ molecule were not located. Sheldrick, G. M. "SHELX76, A Program for Crystal Structure Determination"; University of Cambridge, England, 1976. In addition, the data reduction program was written in this laboratory. Other programs were contained in or derived from the Northwestern Crystallographic Computing Library of Dr. J. A. Ibers.

(8) Symmetry relation; 1.0 - $x$, $y - {}^1/_2$, ${}^1/_2 - z$.

## Photochemical Reactions of *N,N'*-Dialkylpiperazinetetrones

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Piperazinetetrone may be viewed as a composite of two imides, i.e., a *cyclic diimide*.[1] It is well-known that $\alpha$-dicarbonyl compounds exhibit considerably different photochemical behavior from that of monocarbonyl compounds.[2] Therefore, the photochemical reactions of piperazinetetrones are of interest in connection with that of the extensively investigated cyclic imides.[3] It has been recently reported that *N,N'*-dimethyl-piperazinetetrone (**1a**) undergoes decarbonylation on irradiation to give *N,N'*-dimethylimidazolidinetrione.[4] In relation to our previous studies on photochemical reactions of nitrogen-containing $\alpha$-dicarbonyl compounds,[5] we now report photochemical hydrogen abstraction of *N,N'*-dialkylpiperazinetetrones.

The piperazinetetrone (**1d**) shows a strong $\pi,\pi^*$ band at 242 nm and an $n,\pi^*$ band in the region of 330–345 nm as

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(2) Wagner, P. J.; Zepp, R. G.; Liu, K.; Thomas, M.; Lee, T.; Turro, N. J. *J. Am. Chem. Soc.* **1976**, *98*, 8125 and references cited therein.

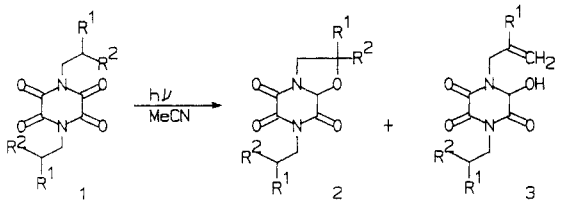
(3) (a) Kanaoka, Y. *Acc. Chem. Res.* **1978**, *11*, 407. (b) Maruyama, K.; Ishitoku, T.; Kubo, Y. *J. Org. Chem.* **1981**, *46*, 27. (c) Mazzocchi, P. H. *Org. Photochem.* **1981**, *5*, 421–471.

(4) Wamhoff, H.; Kleimann, W. *J. Chem. Soc., Chem. Commun.* **1981**, 743.

(5) (a) Aoyama, H.; Sakamoto, M.; Kuwabara, K.; Yoshida, K.; Omote, Y. *J. Am. Chem. Soc.* **1983**, *105*, 1958. (b) Aoyama, H.; Sakamoto, M.; Omote, Y. *J. Chem. Soc., Chem. Commun.* **1982**, 119. (c) Aoyama, H.; Ohnota, M.; Sakamoto, M.; Omote, Y. *Tetrahedron Lett.* **1984**, *25*, 3327.

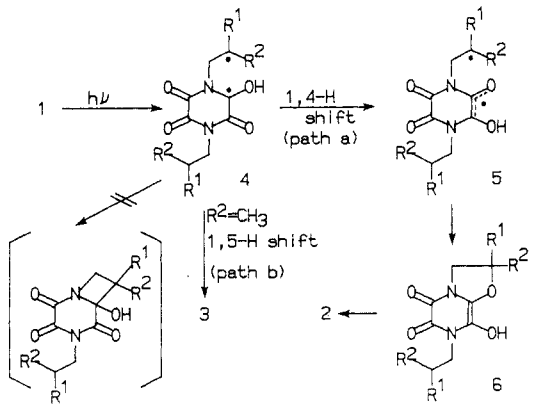
0022-3263/86/1951-0247$01.50/0 

**Scheme I**



| | | |
|---|---|---|
| b, $R^1 = R^2 = H$ | 55% | |
| c, $R^1 = H$; $R^2 = Me$ | 24% | 27% |
| d, $R^1 = R^2 = Me$ | 58% | 24% |

**Scheme II**

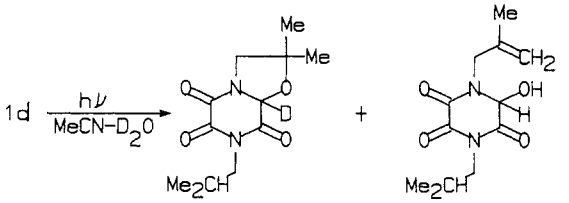


a shoulder. The assignment of the n,$\pi^*$ band is based on the solvent dependence and the extinction coefficient ($\epsilon$ 50–80). The n,$\pi^*$ band appears in the longer wavelength region than that of cyclic imides (~240 nm)[3c] as expected.[6]

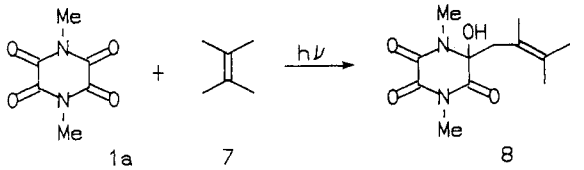
Irradiation of *N,N'*-diethylpiperazinetetrone (**1b**) in acetonitrile with a high pressure mercury lamp under argon through a Pyrex filter gave a cyclization product (**2b**). Photolysis of an *N,N'*-dipropyl derivative (**1c**) yielded an intramolecular oxidation–reduction product (**3c**) along with **2c** (Scheme I). Photoreaction of *N,N'*-diisobutylpiperazinetetrone (**1d**) afforded a similar result. The structures of the products were determined on the basis of elemental analyses and spectral data. The structure of **3d** was further confirmed by hydrogenation followed by oxidation of the resulting product with chromic trioxide in pyridine to **1d**. The structure of **2d** was supported by the finding that treatment of **3d** with *p*-toluenesulfonic acid in refluxing benzene afforded **2d**. In spite of the facile isomerization in the presence of acid, **2** was proved to be a primary product in the photoreaction of **1**, because (a) both **2** and **3** increased in parallel during irradiation and (b) photolysis of **3d** did not produce **2d**.

The formation of **2** and **3** is explained in terms of a diradical intermediate (**4**) formed by $\gamma$-hydrogen abstraction by the carbonyl group (Scheme II). 1,4-Hydrogen shift of the diradical (**4** → **5**) followed by C–O bond formation gives an enol (**6**), and ketonization of **6** affords **2** (path a). Similar hydrogen shift in 1,4-diradicals has been reported in the photoreactions of $\alpha$-diketones.[7] It may be conceivable that the diradical **5** is formed directly from **1** by $\delta$-hydrogen abstraction by the remote carbonyl group. However, molecular models clearly show that this mechanism is improbable because the $\delta$-hydrogens cannot approach the n orbital of the carbonyl oxygen atom.[8] The

**Scheme III**



**Scheme IV**



formation of **3** is reasonably explained by 1,5-hydrogen shift of the diradical (path b). Analogous reactions have been reported in the photochemistry of cyclic imides.[9] This mechanism was supported by the following experiment. When **1d** was irradiated in acetonitrile containing $D_2O$ (15%), almost complete incorporation of a deuterium atom at the methine group of **2d** was observed, whereas no deuterium atoms were incorporated in **3d** (Scheme III). This finding is compatible with intermediacy of the enol **6** in the formation of **2** and also supports path b in which the methine hydrogen of **3d** arises from the isobutyl group rather than from the solvents. It is worth noting that the 1,4-diradical **4** does not undergo the usual type II processes (elimination and cyclization), since it is known that 1,4-diradicals formed in photolysis of cyclic imides undergo type II cyclization as a main reaction.[3c] Similar phenomena were observed in the photoreactions of imidazolidinetriones.[5c]

The photoreaction of **1d** was sensitized by acetone, but quenching by 1,3-pentadiene was quite inefficient. This fact suggest that the photoreaction of **1** involves rapid hydrogen abstraction from the n,$\pi^*$ triplet states, although singlet reactions cannot be excluded from the available data.

When *N,N'*-dimethylpiperazinetetrone (**1a**) was irradiated in the presence of 2,3-dimethyl-2-butene (**7**), an adduct (**8**) formed via intermolecular hydrogen abstraction (Scheme IV) was obtained in a good yield.[10] No oxetans (Paterno–Buchi reaction products) were obtained in the reaction in contrast to the fact that both succinimides and glutarimides react with **6** on irradiation to give the corresponding oxetans in high yields.[11]

In conclusion, *N,N'*-dialkylpiperazinetetrones **1**, cyclic diimides, undergo hydrogen abstraction on irradiation as in the case of cyclic imides. However, the behavior of the 1,4-diradicals from **1** is considerably different from those from cyclic imides. Although $\gamma$-hydrogen abstraction is quite common in the photochemistry of carbonyl compounds, cyclization involving C–O bond formation like path a is without precedent to out best knowledge.[12,13]

(6) $\alpha$-Dicarbonyl compounds show the n,$\pi^*$ bands at longer wavelength regions than the corresponding monocarbonyl compounds: Arnett, J. F.; McGlynn, S. P. *J. Phys. Chem.* **1975**, *79*, 626 and references cited therein.

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(8) For stereoelectronic requirements for hydrogen abstraction by excited carbonyl groups, see: Turro, N. J.; Weiss, D. S. *J. Am. Chem. Soc.* **1968**, *90*, 2185.

(9) Kanaoka, Y.; Migita, Y.; Koyama, K.; Sato, Y.; Nakai, H.; Mizoguchi, T. *Tetrahedron Lett.* **1973**, *14*, 1193.

(10) A similar photoaddition of *N*-methylphthalimide to 2,3-dimethyl-2-butene has been reported: Mazzochi, P. H.; Klinger, L. *J. Am. Chem. Soc.* **1985**, *107*, 7567.

(11) Maruyama, K.; Ogawa, T.; Kubo, Y. *Chem. Lett.* **1978**, 1107.

(12) The C–O bond formation in photoaddition of ether to an $\alpha$-diketone has been reported: Rigaudy, J.; Paillous, N. *Bull. Chim. Soc. Fr.* **1971**, 576.

## Experimental Section

Melting points are uncorrected. Yields are isolated yields. A Halos high pressure mercury lamp (1000 W) was used as an irradiation source.

**General Procedure for Synthesis of *N,N'*-Dialkylpiperazinetetrones 1.** *N,N'*-Dialkyloxamide (1 g) and oxalyl chloride (5 g) was placed in a sealed tube and heated to 120 °C for 4 h. The excess oxalyl chloride was removed by evaporation under reduced pressure, and the residue was recrystallized from acetonitrile–benzene.

**1,4-Dimethylpiperazinetetrone (1a)** has been reported.[14]

**1,4-Diethylpiperazinetetrone (1b):** mp 210–211 °C; IR (KBr) 1680 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.12 (t, 6 H, $J$ = 7 Hz, $CH_3$), 3.77 (q, 4 H, $CH_2$); $^{13}C$ NMR ($CDCl_3$) $\delta$ 11.7 (q), 35.8 (t), 153.9 (s); mass spectrum (CI), $m/z$ 199 (M + 1). Anal. Calcd for $C_8H_{10}N_2O_4$: C, 48.48; H, 5.08; N, 14.13. Found: C, 48.60; H, 5.15; N, 14.20.

**1,4-Dipropylpiperazinetetrone (1c):** mp 203–207 °C; IR (KBr) 1680 $cm^{-1}$; $^1H$ NMR ($Me_2SO$-$d_6$) $\delta$ 0.89 (t, 6 H, $J$ = 8 Hz, $CH_3$), 1.4–1.8 (m, 4 H, $CH_2$), 3.68 (t, 4 H, $J$ = 7 Hz, $NCH_2$); $^{13}C$ NMR ($Me_2SO$-$d_6$) $\delta$ 11.4 (q), 20.1 (t), 42.5 (t), 154.4 (s); mass spectrum (CI), $m/z$ 227 (M + 1). Anal. Calcd for $C_{10}H_{14}N_2O_4$: C, 53.09; H, 6.23; N, 12.38. Found: C, 53.09; H, 6.34; N, 12.39.

**1,4-Diisobutylpiperazinetetrone (1d):** mp 174–175 °C; IR (KBr) 1680 $cm^{-1}$; $^1H$ NMR ($Me_2SO$-$d_6$) $\delta$ 0.89 (d, 12 H, $J$ = 7 Hz, $CH_3$), 1.7–2.2 (m, 2 H, CH), 3.56 (d, 4 H, $J$ = 7 Hz, $CH_2$); $^{13}C$ NMR ($Me_2SO$-$d_6$) $\delta$ 20.3 (q), 26.7 (d), 48.0 (t), 154.6 (s); mass spectrum (CI), $m/z$ 255 (M + 1); UV $\lambda_{max}$ ($CH_3CN$) 242 nm ($\epsilon$ 14 000) and 330 nm (sh, 80), $\lambda_{max}$ ($C_6H_6$) 345 nm (sh, 50). Anal. Calcd for $C_{12}H_{18}N_2O_4$: C, 56.68; H, 7.13; N, 11.01. Found: C, 56.36; H, 7.10; N, 10.91.

**General Procedure for Photolysis.** A solution of 1 (400 mg) in acetonitrile (40 mL) was deaerated by bubbling through argon and irradiated with a high pressure mercury lamp through a Pyrex filter for 2–4 h. After evaporation of the solvent, products were isolated by chromatography on silica gel.

**4-Ethyl-1,4-diaza-7-oxabicyclo[4.3.0]nonane-2,3,5-trione (2b):** mp 204–205 °C; IR ($CHCl_3$) 1670 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.22 (t, 3 H, $J$ = 7 Hz, $CH_3$), 3.5–4.5 (m, 6 H, methylenes), 5.43 (s, 1 H, CH); $^{13}C$ NMR ($CDCl_3$) $\delta$ 12.8 (q), 36.6 (t), 43.7 (t), 65.3 (t), 83.2 (d), 150.6 (s), 156.9 (s), 163.9 (s); mass spectrum (CI), $m/z$ 199 (M + 1). Anal. Calcd for $C_8H_{10}N_2O_4$: C, 48.48; H, 5.08; N, 14.13. Found: C, 48.59; H, 5.11; N, 14.16.

**8-Methyl-4-propyl-1,4-diaza-7-oxabicyclo[4.3.0]nonane-2,3,5-trione (2c):** mp 105–109 °C; IR ($CHCl_3$) 1680 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.95 (t, 3 H, $J$ = 7 Hz, $CH_3$), 1.49 (d, 3 H, $J$ = 7 Hz, $CH_3$), 1.3–1.8 (m, 2 H, $CH_2$), 3.3–4.1 (m, 4 H, $NCH_2$), 4.3–4.6 (m, 1 H, $OCHCH_3$), 5.52 (s, 1 H, OCHN); $^{13}C$ NMR ($CDCl_3$) $\delta$ 11.2 (q), 18.6 (q), 20.8 (t), 42.9 (t), 50.3 (t), 74.1 (d), 83.4 (d), 150.6 (s), 157.2 (s), 164.0 (s). Anal. Calcd for $C_{10}H_{14}N_2O_4$: C, 53.09; H, 6.23; N, 12.38. Found: C, 52.95; H, 6.26; N, 12.36.

**2-Hydroxy-1-(2-propenyl)-4-propylpiperazine-3,5,6-trione (3c):** mp 101–102 °C; IR ($CHCl_3$) 3350 and 1670 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.93 (t, 3 H, $J$ = 7 Hz, $CH_3$), 1.4–1.8 (m, 2 H, $CH_2$), 3.4–4.1 and 4.3–4.7 (m, 4 H, $NCH_2$), 5.1–5.5 (m, 3 H, NCHO and olefinic), 5.5–6.0 (m, 1 H, olefinic), 6.1 (br d, 1 H, OH); $^{13}C$ NMR ($CDCl_3$) $\delta$ 11.2 (q), 20.6 (t), 42.7 (t), 46.4 (t), 77.3 (d), 120.5 (t), 130.2 (d), 153.1 (s), 156.3 (s), 166.7 (s); mass spectrum (CI), $m/z$ 227 (M + 1). Anal. Calcd for $C_{10}H_{14}N_2O_4$: C, 53.09; H, 6.23; N, 12.38. Found: C, 52.70; H, 6.21; N, 12.26.

**8,8-Dimethyl-4-isobutyl-1,4-diaza-7-oxabicyclo[4.3.0]nonane-2,3,5-trione (2d):** mp 141–142 °C; IR ($CHCl_3$) 1685 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.91 (d, 6 H, $J$ = 6 Hz, $CHMe_2$), 1.45 (s, 3 H, $CH_3$), 1.51 (s, 3 H, $CH_3$), 1.8–2.2 (m, 1 H, CH), 3.1–4.0 (m, 4 H, $NCH_2$), 5.67 (s, 1 H, NCHO); $^{13}C$ NMR ($CDCl_3$) $\delta$ 20.0 (q), 25.3 (q), 26.8 (q), 26.9 (d), 48.0 (t), 54.9 (t), 81.1 (s), 82.1 (d), 150.5 (s), 157.5 (s), 165.3 (s); mass spectrum (CI), $m/z$ 255 (M + 1). Anal. Calcd for $C_{12}H_{18}N_2O_4$: C, 56.68; H, 7.13; N, 11.01. Found: C, 56.61; H, 7.12; N, 10.96.

**2-Hydroxy-1-(2-methyl-2-propenyl)-4-isobutylpiperazine-3,5,6-trione (3d):** mp 136–139 °C; IR ($CHCl_3$) 3320 and 1680 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 0.90 (d, 6 H, $J$ = 6 Hz, $CHMe_2$), 1.71 (s, 3 H, $CH_3$), 1.9–2.2 (m, 1 H, CH), 3.4–3.9 (m, 2 H, $NCH_2$), 3.84 and 4.54 (AB q, 2 H, $J$ = 15 Hz, $NCH_2$), 4.95 (br d, 2 H, olefinic), 5.34 (br d, s on addition of $D_2O$, 1 H, NCHO), 6.2 (br d, 1 H, OH exchangeable); $^{13}C$ NMR ($CDCl_3$) $\delta$ 20.0 (q), 20.1 (q), 26.8 (d), 47.3 (t), 48.9 (t), 77.1 (d), 114.7 (t), 137.9 (s), 153.5 (s), 156.5 (s), 166.9 (s); mass spectrum (CI), $m/z$ 255 (M + 1). Anal. Calcd for $C_{12}H_{18}N_2O_4$: C, 56.68; H, 7.13; N, 11.01. Found: C, 56.37; H, 7.14; N, 10.93.

**Conversion of 3d into 1d.** Compound **3d** (100 mg) in ethanol (50 mL) was hydrogenated over Pd–C (5%, 50 mg) for 2 h. The reaction mixture was filtered and evaporated. The crude product was dissolved in pyridine (20 mL) containing $CrO_3$ (100 mg). The mixture was set aside for 2 h and then treated as usual. The product (62 mg) isolated by chromatography was proved to be **1d** by IR, NMR, and TLC.

**Conversion of 3d into 2d.** A solution containing **3d** (100 mg), *p*-toluenesulfonic acid (50 mg), and benzene (15 mL) was refluxed for 2 h. The product (41 mg) isolated by chromatography was identified as **2d** by IR, NMR, and TLC.

**Photolysis of 1d in the Presence of $D_2O$.** Irradiation of **1d** in $CH_3CN$ containing $D_2O$ was done as described above. The $^1H$ NMR spectrum of compound **2d** obtained in this experiment did not show the signal at $\delta$ 5.67 (vide supra), whereas that of compound **3d** exhibited the signal at $\delta$ 5.34 (s, 1 H).

**1,4-Dimethyl-2-hydroxy-2-(2,3,3-trimethyl-2-propenyl)-piperazine-3,5,6-trione (8).** A solution containing 180 mg of **1a**, 1 mL of 2,3-dimethyl-2-butene, and 50 mL of $CH_3CN$ was irradiated in a Pyrex vessel under argon for 3 h. Solvent was removed in vacuo, and the product was separated by flash chromatography on silica gel. Compound **8** (172 mg, 64%) showed the following: mp 167–168 °C; IR (KBr) 3360 and 1660 $cm^{-1}$; $^1H$ NMR ($Me_2SO$-$d_6$) $\delta$ 1.47 (s, 3 H, $CH_3$), 1.57 (s, 6 H, $CH_3$), 2.64 and 2.87 (AB q, 2 H, $J$ = 14 Hz, $CH_2$), 3.06 (s, 3 H, $NCH_3$), 3.20 (s, 3 H, $NCH_3$), 3.46 (s, 1 H, OH); $^{13}C$ NMR ($Me_2SO$-$d_6$) $\delta$ 19.5 (q), 20.7 (q), 20.8 (q), 27.3 (q), 27.5 (q), 43.7 (t), 86.5 (s), 120.3 (s), 133.4 (s), 152.0 (s), 156.7 (s), 170.3 (s). Anal. Calcd for $C_{12}H_{18}N_2O_4$: C, 56.68; H, 7.13; N, 11.01. Found: C, 56.29; H, 7.01; N, 11.13.

**Registry No.** **1a**, 35141-14-1; **1b**, 99687-11-3; **1c**, 99687-12-4; **1d**, 99687-13-5; **2b**, 99687-14-6; **2c**, 99687-15-7; **2d**, 99687-17-9; **3c**, 99687-16-8; **3d**, 99687-18-0; **8**, 99687-19-1; *N,N'*-diethyloxamide, 615-84-9; *N,N'*-dipropyloxamide, 14040-77-8; *N,N'*-diisobutyloxamide, 14040-76-7; oxalyl chloride, 79-37-8; 2,3-dimethyl-2-butene, 563-79-1.

(13) Recently, we have reported photocyclization of $\alpha$-oxoamides which is formally similar to the present cyclization, but the mechanisms of the two reactions are completely different; see ref 5a.

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## Unambiguous Preparation of a $N_\alpha$,$N_\beta$ Chemodifferentiated $\alpha,\beta$-Diaminopropionic Ester through Michael Addition onto a Dehydroalanine Derivative

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2,3-Diaminopropionic acid (1), a simple but not a common amino acid, can be found as a constituent of several bioactive natural products such as tuberactinomycin,[1] bleomycins,[2] quisqualic acid,[3] edeine,[4] $\alpha$- and $\beta$-*N*-oxalyl-L-$\alpha,\beta$-diaminopropionic acids[5,6] or antibiotic A 19009.[7]

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