δ 70.9, 41.5, 25.2, 20.1, 13.6, 11.6; configurational composition (cf. Figure 2), (2*S*,3*S*)-**10** 90.75%, (2*R*,3*R*)-**10** <0.5%, (2*R*,3*S*)-**11** 9.25%, (2*S*,3*R*)-**11** <0.5%; α^{20}_{D} −0.837° (*l* = 0.1 dm, neat), $[\alpha]^{20}_{D}$ −10.85° (*c* 1.18, anhydrous methanol), de = 81.5%, ee > 99.0%.

Acknowledgment. We thank Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie for support of this work. Thanks to Dr. B. Koppenhoefer, Tübingen, for useful discussions and to Dr. H. U. Siehl, Tübingen, for recording the ^{2}H NMR spectra are gratefully acknowledged.

Crystal Structures of Monensin B Lithium and Silver Salts

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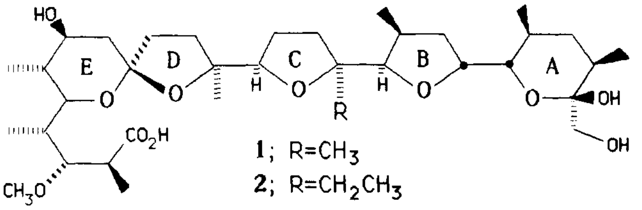
Received July 9, 1985

Monensin B (MonB, **1**) is one of the large group of internally charge-compensating ionophores known to possess interesting biological and physicochemical properties.[2]



1; R=CH$_3$
2; R=CH$_2$CH$_3$

MonB and the closely related Monensin A (**2**) show selectivity for sodium in complexation experiments in methanol[3]—a relatively rare selectivity profile for the naturally occurring monocarboxylic acid ionophores.

One approach to understanding the complexation properties of hosts such as the monensins involves analysis of single-crystal X-ray structures of various complexes. In a very interesting and provocative study, Duax has compared conformations in the crystal of various complexes of monensin A with the free acid.[4] It was found that the major conformational adjustments made by Monensin A when forced to accomodate cations in different environments involved changes in the torsion angles of bonds near the C-ring of the ionophore. Unfortunately, no three of the monensin A complexes studied to date shows the same pattern of hydration in the crystal, though it seems reasonable that the best comparison between crystal conformations would involve complexes with similar hydration.

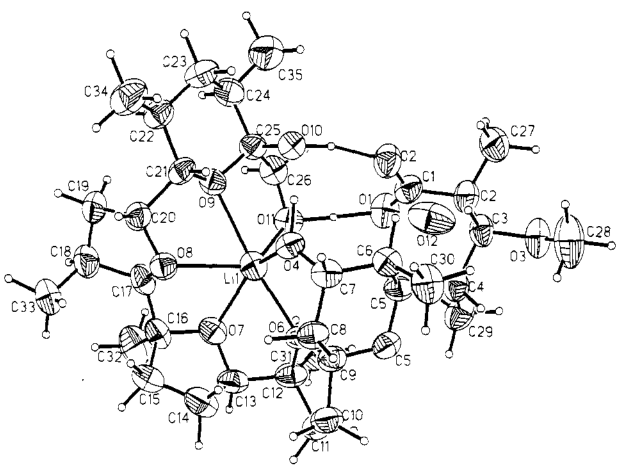


Figure 1. Crystal structure of monensin B lithium salt monohydrate showing the atomic numbering scheme utilized in the crystallography.

Table I. Atomic Coordinates for Monensin B Silver Salt

atom	*x*/*a*	*y*/*b*	*z*/*c*
Ag(1)	0.44221 (4)	0.10066 (4)	0.28690 (3)
O(1)	0.4658 (5)	−0.0046 (4)	0.1093 (3)
O(2)	0.4366 (5)	0.1439 (4)	0.1009 (3)
O(3)	0.7312 (4)	0.1321 (3)	−0.0125 (2)
O(4)	0.4910 (4)	0.2501 (4)	0.2429 (3)
O(5)	0.7538 (3)	0.1532 (3)	0.2190 (3)
O(6)	0.6356 (3)	0.1100 (4)	0.3011 (2)
O(7)	0.5093 (4)	0.0156 (3)	0.3897 (2)
O(8)	0.3535 (4)	0.1602 (3)	0.3953 (2)
O(9)	0.2342 (3)	0.1254 (3)	0.2872 (3)
O(10)	0.2836 (4)	0.1824 (3)	0.1861 (2)
O(11)	0.3503 (4)	0.0049 (3)	0.2147 (3)
O(12)	0.5410 (8)	−0.1633 (5)	0.0580 (5)
C(1)	0.4832 (6)	0.0713 (8)	0.0860 (4)
C(2)	0.5674 (7)	0.0764 (5)	0.0282 (3)
C(3)	0.6583 (6)	0.1434 (5)	0.0428 (3)
C(4)	0.7275 (6)	0.1316 (5)	0.1046 (4)
C(5)	0.6749 (6)	0.1660 (5)	0.1664 (4)
C(6)	0.6419 (6)	0.2653 (5)	0.1659 (4)
C(7)	0.5940 (6)	0.2922 (5)	0.2313 (4)
C(8)	0.6684 (6)	0.2698 (5)	0.2865 (4)
C(9)	0.7156 (6)	0.1738 (5)	0.2840 (5)
C(10)	0.8092 (6)	0.1565 (6)	0.3301 (4)
C(11)	0.8023 (6)	0.0565 (6)	0.3421 (4)
C(12)	0.6816 (6)	0.0354 (5)	0.3351 (4)
C(13)	0.6223 (6)	0.0288 (6)	0.4015 (4)
C(14)	0.6253 (6)	0.1132 (7)	0.4443 (4)
C(15)	0.5217 (6)	0.1053 (6)	0.4860 (4)
C(16)	0.4481 (7)	0.0369 (5)	0.4484 (3)
C(17)	0.3413 (6)	0.0750 (5)	0.4261 (4)
C(18)	0.2476 (6)	0.0884 (6)	0.4728 (4)
C(19)	0.1713 (7)	0.1410 (6)	0.4279 (4)
C(20)	0.2485 (5)	0.1996 (5)	0.3894 (4)
C(21)	0.2190 (6)	0.2138 (5)	0.3170 (4)
C(22)	0.1035 (6)	0.2456 (6)	0.3065 (4)
C(23)	0.0763 (6)	0.2438 (6)	0.2346 (4)
C(24)	0.0960 (6)	0.1460 (6)	0.2066 (4)
C(25)	0.2149 (5)	0.1208 (5)	0.2174 (4)
C(26)	0.2392 (6)	0.0271 (5)	0.2005 (4)
C(27)	0.5079 (7)	0.0970 (7)	−0.0349 (4)
C(28)	0.7891 (8)	0.2120 (6)	−0.0284 (5)
C(29)	0.7581 (7)	0.0286 (5)	0.1134 (4)
C(30)	0.7368 (7)	0.3263 (6)	0.1490 (5)
C(31)	0.6615 (7)	−0.0483 (5)	0.2978 (5)
C(32)	0.4328 (8)	−0.0500 (6)	0.4654 (4)
C(33)	0.2732 (8)	0.1396 (7)	0.5350 (4)
C(34)	0.0864 (8)	0.3407 (6)	0.3304 (6)
C(35)	0.058 (1)	0.144 (1)	0.1413 (6)

We have succeeded in obtaining X-ray crystal data for Monensin B Li$^+$ (MonB$^-$Li$^+$) and Ag$^+$ salts. The crystal

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[1] (a) Dreyfus Teacher-Scholar, 1983–1985. (b) Permanent address: Crystallography Laboratory, Toernooiveld, 6525 ED Nijmegen, The Netherlands.

[2] For recent reviews of ionophores, including monensin, see: (a) Dobler, M. "Ionophores and Their Structures"; Wiley-Interscience: New York, 1981. (b) "Polyether Antibiotics, Naturally Occurring Acid Ionophores, Vol. 1: Biology"; Westley, J. W., Ed.; Marcel Dekker: New York, 1982. (c) "Polyether Antibiotics, Naturally Occurring Acid Ionophores, Vol. 2: Chemistry"; Westley, J. W., Ed.; Marcel Dekker: New York, 1983.

[3] Thermodynamics of complexation of Na$^+$ and K$^+$ by MonB in methanol has been determined in these laboratories by titration calorimetry: Walba, D. M.; Hermsmeier, M. *J. Chem. Soc., Chem. Commun.* **1985**, 383–384.

[4] Duax, W. L.; Smith, G. D.; Strong, P. D. *J. Am. Chem. Soc.* **1980**, *102*, 6725.

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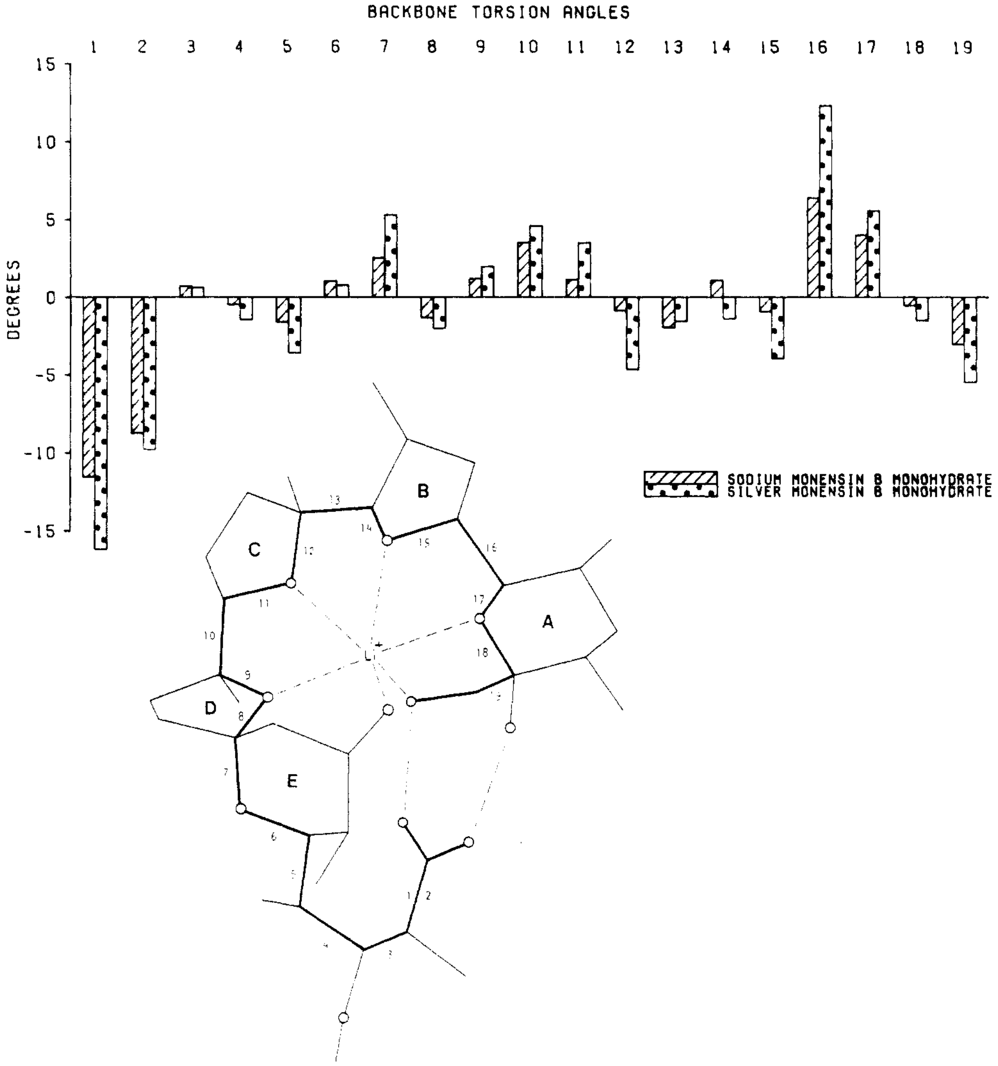

Figure 2. Differences between backbone torsion angles found for monensin B lithium complex (horizontal axis), and the corresponding torsion angles found for monensin B sodium and silver complexes. The numbering scheme used for the backbone bonds are shown in this depiction of the monensin B lithium complex.

structure of the Na^+ salt of MonB has been previously reported.[5] Interestingly, all three complexes show similar hydration in the crystal lattice, allowing for the first time for a direct comparison of MonB conformations in a highly "collapsed" state ($MonB^-Li^+$), an intermediate state ($MonB^-Na^+$), and an "expanded" state ($MonB^-Ag^+$).

Atomic coordinates for $MonB^-Ag^+$ and $MonB^-Li^+$ are given in Tables I and II, respectively. The crystal structure of $MonB^-Li^+$ is shown in Figure 1, along with the atomic numbering scheme used in the crystallography. The data for all three complexes are presented in graphical form in Figure 2. This figure gives torsion angle differences for the backbone bonds of $MonB^-Na^+$ and $MonB^-Ag^+$ complexes relative to the Li^+ complex (the horizontal axis in the figure). It is interesting to note that the deviations around the C-ring are relatively small compared to those at bonds 16, 1, and 2.

Several aspects of the data shown in the figure deserve comment. First, note that, in every backbone bond, the Ag^+ complex shows the same or greater deviations from the Li^+ complex "standard" than the Na^+ complex. Thus, the entire molecule seems to "breath out" upon complexation of Na^+ (relative to Li^+) and farther out upon complexation of Ag^+. Also, most of the molecule remains relatively fixed upon accommodation of cations with differing crystal radii. The major change appears focused on bond 16, between the A ring and the B ring of MonB. This bond seems to act as the swivel. In our interpretation, the carboxyl anion, which is bonded to the A-ring via two H bonds, simply follows the motion of the A-ring, resulting in the observed large torsion angle changes at bonds 1 and 2. Note also that the carboxyl grouping is not flat—the torsions at bonds 1 and 2 differ considerably.

It is hoped that these types of data will prove useful in understanding the relationship between the conformational energy surface and the cation selectivity patterns exhibited by hosts such as monensin, with the ultimate goal being directed design of more highly ion-selective hosts. Within this context, the data presented herein suggest that an increase in sodium selectivity could be achieved by changes in the steric environment at bond 16 of monensin.

Experimental Section

Crystallographic data for $MonB^-Ag^+$: $C_{35}H_{59}O_{11}Ag{\cdot}H_2O$, mol wt 781.731, orthorhombic, space group $P2_12_12_1$, $a = 12.278$ (6) Å, $b = 14.981$ (9) Å, $c = 20.431$ (9) Å, $V = 3758$ (3) Å^3, $F(000) = 1656$, $Z = 4$, $D_c = 1.38$ g cm^{-3}, (Mo Kα) = 0.82 cm^{-1}.

The data, collected on a Syntex P$\bar{1}$ diffractometer ($\lambda = 0.71069$ Å) gave 3052 unique observed ($F_o > 6\sigma(F_o)$) reflections. The structure was solved by using the program DIRDIF, with the position of the silver atom determined from a Patterson, used as a starting point.[6] Blocked full-matrix least-squares refinement with all

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(5) Barrans, P. Y.; Alleaume, M. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1982**, *B38*, 1144–1149.

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 Kα) = 0.85 cm^{-1}. The data, collected on a Syntex P1 diffractometer ($\lambda = 0.71069$ 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 $R_\omega = 0.059$.[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).

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We also thank the Colorado Heart Association and the Research Corp. for financial assistance and the Eli Lilly Co. for a generous gift of the monensin complex.

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.

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[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 α-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 α-dicarbonyl compounds,[5] we now report photochemical hydrogen abstraction of *N,N'*-dialkylpiperazinetetrones.

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

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[1] For composite molecule description of carbonyl compounds, see: (a) Larson, D. B.; Arnett, J. F.; McGlynn, S. P. *J. Am. Chem. Soc.* **1973**, *95*, 6928. (b) Wittel, K.; McGlynn, S. P. *Chem. Rev.* **1977**, *77*, 745.

[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.

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