Anal. Calcd for $C_{14}H_{18}Cl_2O_2Si$: C, 53.0; H, 5.72. Found: C, 53.61; H, 5.77.

2,2-Dichloro-3-hydroxy-4-methyl-4-phenylcyclobutanone (9c). The hydrolysis of 2.0 g (0.0063 mol) of **9b** afforded 1.34 g (87%) of **9c** as a yellow oil at 95–99 °C (0.1 mm): IR 3600–3350, 1797, 1610, 1498, 1450, 1265, 840 cm^{-1}; NMR δ 7.25 (m, 5 H), 6.2 (s, 1 H), 4.90 (m, 1 H), 1.64 (m, 3 H); mass spectrum, m/e (no M) 247 (0.02), 245 (0.03), 232 (0.02), 230 (0.03), 165 (2.2), 163 (3.3), 147 (9.8), 132 (100), 105 (34.8), 104 (43.5), 79 (18.5), 77 (19.6).

2,2-Dichloro-3-(trimethylsiloxy)cyclobutanone (10b). From 0.025 mol of trichloroacetyl chloride, 0.035 mol of silyl enol ether **10a**, and 4.8 g of activated zinc was attained 4.8 g (84%) of **10b** as a yellow oil at 45–50 °C (0.2 mm): IR 1808, 1260, 845 cm^{-1}; NMR δ 4.61 (m, 1 H), 3.31 (m, 2 H), 0.37 (s, 9 H); mass spectrum, m/e (no M) 213 (4.5), 211 (6.5), 186 (64.9), 184 (100), 171 (32.5), 169 (46.8), 101 (92.0), 75 (77.9), 74 (76.6), 59 (62.3).

2,2-Dichloro-3-hydroxycyclobutanone (10c). Hydrolysis of 2.0 g (0.0088 mol) of **10b** afforded 1.1 g (81%) of **10c** as a clear colorless oil at 35–40 °C (0.02 mm): IR 3600–3300, 1802, 1370, 1190, 855 cm^{-1}; NMR δ 4.79 (m, 1 H), 4.6 (s, 1 H), 3.44 (m, 2 H); mass spectrum, m/e (M + 2) 156 (4.9), (M) 154 (7.4), 128 (5.5), 126 (9.1), 114 (5.9), 112 (100), 110 (29.6), 71 (85.0), 43 (72.0).

3-Cyclohexenespiro[3′,3′]dichloro-4′-(trimethylsiloxy)cyclobutan-2′-one (11b). From 0.025 mol of trichloroacetyl chloride, 0.035 mol of silyl enol ether **11a**, and 5.1 g of zinc was obtained 6.13 g (84%) of **11b** as an oil at 80–85 °C (0.025 mm): IR 1801, 1440, 1375, 1260, 1190, 875, 845 cm^{-1}; NMR δ 5.61 (m, 2 H), 4.29 (s, 1 H), 2.31–1.95 (m, 6 H), 0.25 (s, 9 H); mass spectrum, m/e (no M) 259 (2.4), 257 (3.6), 186 (8.4), 184 (13.1), 182 (7.1), 169 (3.6), 167 (5.5), 147 (64.3), 108 (52.4), 80 (25.8), 79 (23.8), 73 (100).

3-Cyclohexenespiro[3′,3′]dichloro-4′-hydroxycyclobutan-2′-one (11c). From 2.05 g (0.007 mol) of **11b** was isolated 1.32 g (85%) of **11c** as an oil at 79–85 °C (0.05 mm): IR 3600–3350, 1795, 1650, 1435, 1152, 845 cm^{-1}; NMR δ 5.62 (m, 2 H), 4.39 (s, 1 H), 4.02 (s, 1 H), 2.29–1.95 (m, 6 H); mass spectrum, m/e (no M) 202 (2.6), 152 (3.9), 111 (100), 84 (15.3), 83 (23.1), 82 (46.2).

2,2-Dimethyl-3-(trimethylsiloxy)cyclobutanone (1d). A 2.8-g (0.011 mol) portion of **1b** in 10 mL of cyclohexane saturated with azobis(isobutyronitrile) was added dropwise over 30 min to 12.2 g (0.041 mol) of tri-*n*-butyltin hydride in 20 mL of cyclohexane under a nitrogen atmosphere. The solution was heated at reflux for an additional 12 h. Removal of the solvent under reduced pressure and vacuum distillation afforded 1.24 g (61%) of **1d** at

40–45 °C (0.5 mm): IR 1782, 1451, 1258, 906 cm^{-1}; NMR δ 4.11 (m, 1 H), 3.05 (m, 2 H), 1.01 (s, 3 H), 0.99 (s, 3 H); mass spectrum, m/e (M) 186 (4.5), 171 (64.3), 158 (41.6), 130 (93.5), 128 (100), 116 (89.6), 76 (92.2), 71 (79.2), 58 (97.4).

Anal. Calcd for $C_9H_{18}O_2Si$: C, 58.00; H, 9.73. Found: C, 58.1; H, 9.62.

2,2-Dimethyl-3-isopropyl-3-(trimethylsiloxy)cyclobutanone (5d). From 4.65 g (0.016 mol) of dichlorocyclobutanone **5b**, 14.5 g (0.05 mol) of tri-*n*-butyltin hydride, and a catalytic amount of azobis(isobutyronitrile) was isolated 2.38 g (67%) of **5d** at 70–75 °C (0.5 mm): IR 1782, 1468, 1260, 1083, 845 cm^{-1}; NMR δ 2.78 (m, 2 H), 1.81 (m, 1 H), 1.1–0.75 (m, 12 H), –0.04 (s, 9 H); mass spectrum, m/e (M) 228 (7.8), 213 (9.1), 186 (48.1), 171 (20.8), 158 (44.2), 143 (54.5), 91 (18.2), 77 (84.4), 73 (100), 43 (61.0).

3-Cyclohexenespiro-4′-(trimethylsiloxy)cyclobutan-2′-one (11d). From 4.97 g of **11b**, 19.8 g (0.068 mol) of tri-*n*-butyltin hydride, and a catalytic amount of azobis(butyronitrile) was isolated 2.35 g (62%) of **11d** at 50–55 °C (0.15 mm): IR 1784, 1468, 1252, 1184, 1154, 887 cm^{-1}; NMR δ 5.4 (m, 2 H), 4.0 (d of d, 1 H), 2.84 (m, 2 H), 1.92 (m, 4 H), 1.53 (m, 2 H), –0.06 (s, 9 H); mass spectrum, m/e (M) 224 (8.8), 182 (100), 167 (10.3), 142 (14.7), 108 (70.6), 92 (44.1), 75 (47.1), 73 (76.5).

Anal. Calcd for $C_{12}H_{20}O_2Si$: C, 64.24; H, 8.99. Found: C, 64.36; H, 9.43.

Notes

A Novel Ring Enlargement Involving Electrophilic Attack on the Dienolate Anion Derived from 7,8-Bis(trimethylsilyloxy)-cis-bicyclo[4.2.0]octa-3,7-diene
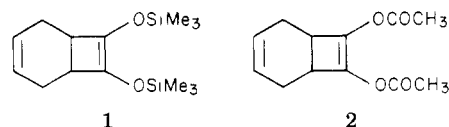
Louis A. Carpino* and Jung-Hsien Tsao

Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003

As a protecting group for the hydroxyl function the trimethylsilyl group is often too sensitive to be carried through a series of reactions without suffering premature deblocking.[1] We encountered an instance of this difficulty during attempts to dehydrogenate the readily available bis(trimethylsilyl) enol ether 1 to the corresponding cy-

clohexadiene.[2] For that reason we investigated the replacement of the trimethylsilyl groups of 1 by a more stable protective group, for example, acetyl, as in diacetate 2. Although 2 was not obtained, the results led to the uncovering of a novel rearrangement which we wish to describe in the present note.

In view of the common technique of cleaving enol trimethylsilyl ethers with alkyl lithium reagents,[3] we sought

(1) Compare E. J. Corey and A. Venkateswarlu, *J. Am. Chem. Soc.*, **94**, 6190 (1972).

(2) L. A. Carpino and J.-H. Tsao, *J. Org. Chem.*, accompanying paper.

(3) (a) G. Stork and P. F. Hudrlik, *J. Am. Chem. Soc.*, **90**, 4462 (1968); (b) H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, **34**, 2324 (1968).

to cleave 1 with methyllithium and subsequently acetylate the resulting dianion.[4] An ether solution of 1 was treated with 2 equiv of methyllithium, and the solution was refluxed for 4 h and then treated with acetyl chloride. The NMR spectrum of the product (A) showed two different methyl singlets at δ 1.47 and 2.08, clearly inconsistent with the desired diacetate 2. When A was subjected to allylic bromination by 1 equiv of N-bromosuccinimide in refluxing carbon tetrachloride in the presence of a free radical initiator, a vigorous reaction took place with the evolution of hydrogen bromide. Workup gave a compound B of composition $C_{12}H_{10}O_4$ which showed two methyl singlets at δ 1.53 and 2.11 and a multiplet for four protons in the aromatic region at 7.96. The ^{13}C NMR spectrum of A was revealing in that in addition to an ester carbonyl peak at δ 169.3 there appeared a peak at 210.4 due to a simple ketone function. These data suggested structures 3 and 4 for A and B, respectively. Compound 4 has already
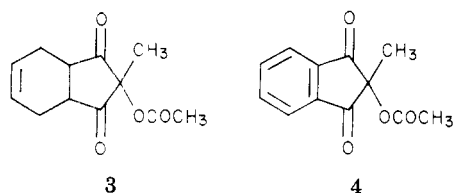
been described by Spencer and co-workers[5] and its identity with our compound B has been confirmed by comparison of its infrared and NMR spectra with those of an authentic sample. Spencer obtained 4 by treatment of 2-methyl-indan-1,3-dione with lead tetraacetate. Identification of 4 establishes structure 3 for compound A. Once the structure of 3 was established, the bromination reaction was re-examined. Two molar equivalents of N-bromo-succinimide in refluxing carbon tetrachloride gave the aromatic compound 4 in 36% yield. Addition of bromine to a methylene dichloride solution of 3 at −20 to −15 °C
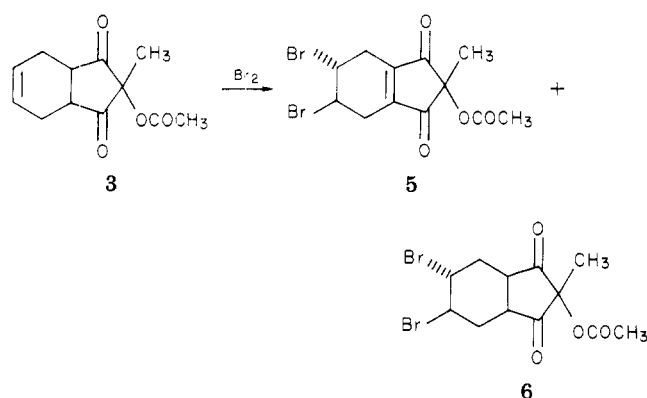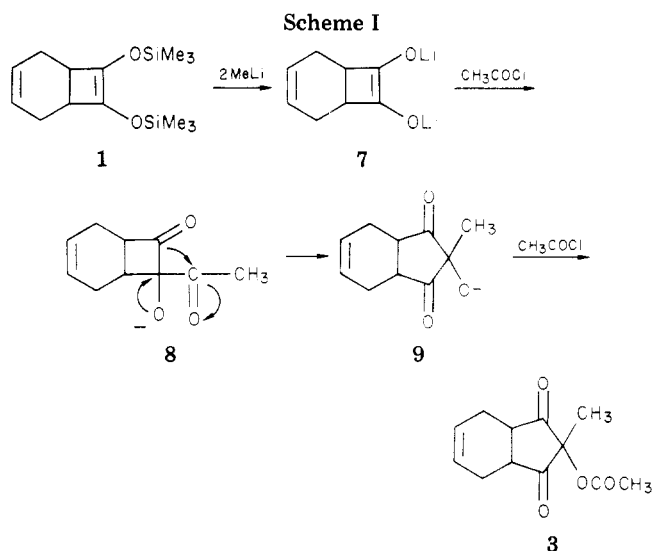

gave a mixture of the dibromides 5 and 6. At a lower temperature (−35 to −25 °C) and in a less polar medium $(CCl_4-CH_2Cl_2)$, 6 was formed exclusively (60%) by suppression of the substitution reaction leading to 5. Treatment of 5 with 2 equiv of DBN at room temperature gave 4 in quantitative yield.

The formation of 3 is of interest from both a synthetic and mechanistic point of view and can be rationalized by

Scheme I

the sequence of reactions shown in Scheme I. Anion 8, formed by C-acylation of the presumed dianion 7, could undergo ring enlargement in a process analogous to the benzilic acid rearrangement to give anion 9 with subsequent attack by another mole of acetyl chloride to give 3. Benzilic acid rearrangements involving migration of a carbonyl group are not unprecedented,[6] but ring enlargements of this type appear to be unknown. In several cases benzilic acid rearrangements of cyclobutene-1,2-diones have been reported to give ring contraction products.[7] For example tricyclic compound 10 gives
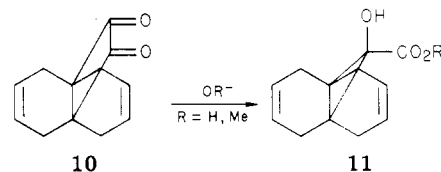
compound 11 in 90–100% yield under mildly basic conditions.[7a]

Experimental Section[8]

2-Acetoxy-2-methyl-Δ^5-tetrahydroindan-1,3-dione (3). By means of a syringe, 62 mL of ethereal methyllithium (1.65 M) was introduced quickly into a magnetically stirred solution of 14.13 g of 1[9] in 90 mL of anhydrous ether under an atmosphere of N_2. After being refluxed for 3.5–4 h, the solution was cooled in an ice bath, and a solution of 11 g of acetyl chloride in 55 mL of ether was added over a period of 15 min while keeping the temperature near 10 °C. After being stirred for an additional 20 min, the mixture was poured into 300 mL of ice water. The organic layer was separated and combined with two additional 100-mL portions of ether used to extract the aqueous layer. The combined extracts were washed rapidly with 30 mL of cold saturated $NaHCO_3$ solution, two 100-mL portions of H_2O, and 30 mL of saturated NaCl solution. The dried ($MgSO_4$) solution was concentrated on

(4) Since the present work was completed, several cases have been reported involving the generation of dienolates from bis(trimethylsilyl) enol ethers and methyllithium and their subsequent reaction with electrophilic reagents. See (a) T. Wakamatsu, K. Akasaka, and Y. Ban, *Tetrahedron Lett.*, 3879 (1974); (b) D. P. Bauer and R. S. Macomber, *J. Org. Chem.*, 41, 2640 (1976); (c) T. Wakamatsu, K. Akasaka, and Y. Ban, *Tetrahedron Lett.*, 2751 (1977).

(5) T. A. Spencer, A. L. Hall, and C. F. von Reyn, *J. Org. Chem.*, 33, 3369 (1968). We wish to thank Professor Spencer for kindly providing a sample of 4 for comparison purposes.

(6) (a) R. Nietzki and T. Benckiser, *Ber.*, 18, 499, 1833 (1885); 19, 293 (1886); (b) R. Nietzki, *ibid*, 20, 1617 (1887); 23, 3136 (1890); (c) J. F. Corbett, *J. Chem. Soc. C*, 2408 (1967).

(7) (a) J. J. Bloomfield, J. R. S. Irelan, and A. P. Marchand, *Tetrahedron Lett.*, 5647 (1968); (b) A. de Groot, D. Oudman, and H. Wynberg, *ibid.*, 1529 (1969); (c) H. D. Scharf, W. Droste, and R. Liebig, *Angew. Chem.*, 80, 194 (1968).

(8) Melting points and boiling points are uncorrected. Infrared spectra were obtained on Beckmann IR-10 and Perkin-Elmer 237B instruments, ^1H NMR spectra were obtained on Varian A-60 and Perkin-Elmer R-12 instruments with Me_4Si as internal standard. The ^{13}C NMR spectra were obtained through the courtesy of Professor K. L. Williamson and Dr. M. Hasan of Mt. Holyoke College on a Varian HA-100 instrument. Elemental analyses were carried out by the University of Massachusetts Micro-analytical Laboratory under the direction of Charles Meade and Gregory Dabkowski and associates.

(9) J. J. Bloomfield, *Tetrahedron Lett.*, 587 (1968).

a water bath (25 °C) to 25 mL with a rotary evaporator. After being cooled at -5 °C for 5 h, the precipitated solid was filtered and washed with an ether–pentane mixture (1:1; v/v) which had previously been cooled to dry ice–acetone temperatures. The crude material (3.35–3.75 g) was recrystallized from ether to give 2.9–3.5 g (26–30.7%) of the pure dione 3 as white needles: mp 114–115 °C; IR (CHCl$_3$) 1780 (sh), 1740 cm^{-1} (C=O); ^{1}H NMR (CDCl$_3$) δ 1.47 (s, 3, CH$_3$), 2.08 (s, 3, CH$_3$CO), 2.34 (m, 4, CH$_2$), 3.10 (m, 2, CHCH$_2$), 5.90 (m, 2, =CH); MS (80 eV), m/e 222 (parent); ^{13}C NMR (CHCl$_3$) 210.4 (ketonic C=O), 169.3 (ester C=O), 127.3 (vinylic carbons), 81.1 (COCOCH$_3$), 42.3 (CH$_2$CHCO), 22.2 (CH$_2$), 19.1 (CH$_3$COO), 18.4 (CH$_3$COCOCH$_3$).

An analytical sample was prepared by recrystallization from ether followed by sublimation at 85 °C (0.3 mm), mp 114.5–115 °C.

Anal. Calcd for C$_{12}$H$_{14}$O$_4$: C, 64.85; H, 6.35. Found: C, 64.86; H, 6.45.

2-Acetoxy-2-methylindan-1,3-dione (4). A mixture of 0.66 g of 3, 1.18 g of N-bromosuccinimide, and a few grains of benzoyl peroxide in 20 mL of CCl$_4$ (spectrum grade) was refluxed with magnetic stirring under N$_2$ for 40 min. Since the reaction had not been initiated by this time, a second portion of benzoyl peroxide was added and refluxing was continued. Within 40 min the reaction was initiated as evidenced by the appearance of a brown color and the evolution of HBr. When the brown color had disappeared, heating was continued for an additional hour. Succinimide was removed by filtration, and the filtrate was diluted with 25 mL of CH$_2$Cl$_2$ and washed with four 15-mL portions of saturated NaHCO$_3$ solution and four 20-mL portions of H$_2$O. The solution was dried (MgSO$_4$) and rotary evaporated at 25 °C. The residue was dissolved in a small amount of ether, and hexane was added to the cloud point. After the solution was cooled in a dry ice–acetone bath at -40 to -35 °C for several hours, 0.21 g of solid, mp 91–93 °C, was obtained. A second crop (0.05 g) was obtained from the mother liquor. Sublimation of the combined material gave 0.23 g (36%) of 4, mp 94–96 °C (lit.[5] mp 100.5–101 °C), identified by infrared and NMR spectral comparisons with an authentic sample: IR (CHCl$_3$) 1760 (sh), 1730 cm^{-1} (C=O); ^{1}H NMR (CDCl$_3$) δ 1.52 (s, 3, CH$_3$), 2.11 (s, 3, CH$_3$CO), 7.96 (m, 4, aryl); ^{13}C NMR (CHCl$_3$) δ 196.5 (ketonic C=O), 169.4 (ester C=O), 138.2 (CH–C–CO), 135.9 and 123.6 (remaining aryl carbons), 78.6 (COCOCH$_3$), 19.2 (CH$_3$COO), 18.4 (CH$_3$COCOCH$_3$); MS (80 eV), m/e 218 (parent).

Anal. Calcd for C$_{12}$H$_{10}$O$_4$: C, 66.05; H, 4.62. Found: C, 66.19; H, 4.71.

8-Acetoxy-3,4-*trans*-dibromo-8-methylbicyclo[4.3.0]-nona-7,9-dione (6). To a magnetically stirred solution of 0.67 g of 3 in 25 mL of CCl$_4$ (spectrum grade) and 5 mL of dry CH$_2$Cl$_2$ maintained between -35 and -25 °C with a dry ice–acetone bath was added 2–3 drops of Br$_2$ under an atmosphere of N$_2$. After a short induction period, the bromine color disappeared and the remaining Br$_2$ (total 0.48 g) was added over a period of 1 h. After the solution was warmed to room temperature, 35 mL of CH$_2$Cl$_2$ was added, and the solution was washed with 30 mL of saturated NaHCO$_3$ solution, 30 mL of H$_2$O, and 30 mL of saturated NaCl solution. Removal of solvent from the dried (CaSO$_4$) solution left 1.05 g of white solid, mp 118–120 °C dec. Recrystallization from ether gave 0.75 g (65%) of 6 as white crystals: mp 125.5–126.5 °C dec; IR (CHCl$_3$) 1780 (sh), 1740 cm^{-1} (C=O); NMR (CDCl$_3$) δ 1.48 (s, 3, CH$_3$), 2.1 (s, 3, CH$_3$CO), 2.25–2.96 (m, 4, CH$_2$), 3.3 (m, 2, CH$_2$CHCO), 4.5 (m, 2, CHBr). The analytical sample was obtained by two recrystallizations from CH$_2$Cl$_2$–ether (1:12; v/v), mp 127–127.5 °C.

Anal. Calcd for C$_{12}$H$_{14}$O$_4$Br$_2$: C, 37.73; H, 3.69; Br, 41.83. Found: C, 37.84; H, 3.71; Br, 41.79.

When this reaction was carried out in CH$_2$Cl$_2$, and the crude product was recrystallized from CH$_2$Cl$_2$–ether (1:5; v/v), there was obtained a mixture which consisted of white granules and green-white needles which could be separated manually. The white granules were shown to be 6, obtained in 11% yield. Repeated recrystallization of the green-white needles from CH$_2$Cl$_2$–ether (1:5; v/v) gave 10% of 5: mp 183–186 °C; IR (CHCl$_3$) 1740, 1715 cm^{-1} (C=O); NMR (CDCl$_3$) δ 1.45 (s, 3, CH$_3$), 2.05 (s, 3, CH$_3$CO), 3.35 (m, 4, CH$_2$), 4.7 (m, 2, CHBr), which was identified by treatment with 2 equiv of 1,5-diazabicyclo[4.3.0]-5-nonene (DBN) in CH$_2$Cl$_2$ at room temperature (16 h). There

was obtained compound 4, mp 100–102 °C, in 91% yield.

Proton Nuclear Magnetic Resonance Studies of Alkenylboranes. On the Presence of Diastereomers in Certain Alkenylboranes

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Previously we reported the relative importance of mesomeric B–C π-bonding forms in alkenyl- and alkynylboranes.[1] An unanswered question remained concerning the ^{13}C chemical shifts for (1-hexenyl)disiamylborane (1): two kinds of signals appeared in the C^2 region

1
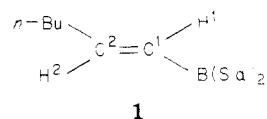
Sia = CHMeCHMe$_2$

(δ 155.2 and 154.4, in parts per million from Me$_4$Si; converted by using δ_C(C$_6$D$_6$) 128.7). Other alkenylboranes, such as butyl (1-hexenyl)boronate, methyl bis(1-hexenyl)borinate, and (1-hexenyl)(1,2-phenylenedioxy)borane, exhibited one signal in their C^2 regions as would be expected. We now decipher the origin of the two kinds of signals by investigating the ^{1}H NMR spectra of alkenyl-disiamylboranes and related boranes.

To solve this problem, we examined ^{1}H NMR spectra of various types of (5-decenyl)- and (1-hexenyl)boranes. (5-Decenyl)disiamylborane (2) exhibited a triplet–triplet signal in the olefinic H^2 region as shown in Figure 1. The corresponding H^2 signal of 1 became more complex due to long-range coupling (Figure 2). On the other hand, (5-decenyl)dicyclohexylborane (3) exhibited a simple triplet signal as shown in Figure 3. Irradiation of the methylene protons helped to analyze the olefinic proton. Chemical shifts of alkenylboranes which exhibit two kinds of olefinic signals are summarized in Table I, and those which exhibit one olefinic signal are summarized in Table II.

Two reasons may be considered for the two kinds of olefinic signals (Table I). First, there is the possibility that two stereoisomers are present on the NMR time scale at room temperature due to the restricted rotation around the boron–carbon bonds.[2] The ^{1}H NMR spectrum of 1 at various temperatures (-76 to +83 °C) remained essentially unchanged. Second, the present observation may be rationalized by the presence of diastereomers (racemic

(1) Y. Yamamoto and I. Moritani, *J. Org. Chem.*, **40**, 3434 (1975).
(2) J. F. Blount, P. Finocchiaro, D. Gust, and K. Mislow, *J. Am. Chem. Soc.*, **95**, 7019 (1973); J. P. Hummel, D. Dust, and K. Mislow, *ibid.*, **96**, 3679 (1974).