Thermal Reactions of α-Diazo Ketones with Molecular Oxygen. A. Reaction of Azibenzil (I) with Molecular Oxygen.—Molecular oxygen gas (280 l.) was introduced to a benzene solution (85 ml of benzene) of azibenzil (8.5 g, 0.038 mol) for 4.5 hr at refluxing temperature. Into the reaction mixture, water (40 ml) and ether (40 ml) were added. From the organic layer, benzene and ether were removed under reduced pressure. Methanol (100 ml) was added to the residue. After the methanol solution was cooled, white powders precipitated. The benzene (20 ml) solution of the white powders was subjected to chromatography on silica gel. Elution with benzene gave tetraphenylglycolide (II), which was recrystallized from ethyl acetate. From the filtered solution, methanol was distilled and ether (10 ml) was added. The ether solution was cooled to give a yellow solid (VII). The filtered ether solution gave V. The yields are shown in Table I.

The water layer offered no product. Tetraphenylglycolide (II) had mp 190–193°; ir 1750 cm^{-1} ($\nu_{C=O}$ of ester group); ^{1}H nmr ($CDCl_3$) τ 2.5–3.4 (Ph).

^{13}C nmr ($CHCl_3$) exhibited peaks at 166 corresponding to the ester group along with the peak at 129 ppm (Ph), from TMS over the range of 126–235 ppm.

The uv spectra of II have no absorption corresponding to *cis*-stilbene [292 mμ (ϵ 1.01 × 10^{4}) in THF] type over the range of 280–310 mμ, indicating no double bond in the structure of II.

Anal. Calcd for $C_{28}H_{20}O_4$: C, 79.98; H, 4.79; mol wt, 420. Found: C, 79.85; H, 4.85; mol wt, 432.

Moreover, II was identified by mixture melting point with the authentic sample,[13] mmp 189–192°. Bisbenzilketazine (VII) and diphenylacetic acid (V) were identified respectively by infrared spectral comparison and the mixture melting point with authentic samples: VII, mmp 200–201° (lit.[14] mp 202°), and VII, mmp 148° (lit.[7a] mp 148°).

B. Reaction of Diazoacetophenone (VIII) with Molecular Oxygen.—Into a xylene solution (80 ml of xylene) of diazoacetophenone (7.3 g, 0.05 mol), molecular oxygen gas (280 l.) was passed for 4.5 hr at 130–140°. The products were separated by chromatography using silica gel as the adsorbent. The products, corresponding butenolide (IX), mp 107–108°, and the dimer X, mp 288–289°, were obtained in the yields shown in Table I. These products were identified by infrared spectral comparison and the mixture melting point, 107–108 and 288–289°, respectively, with the samples (lit.[8a] mp of IX 107–108°; mp of X 288–289°).

C. Reaction of Methylbenzoyldiazomethane (XI) with Molecular Oxygen.—Molecular oxygen gas (280 l.) was passed into a toluene solution (toluene 100 ml) of methylbenzoyldiazomethane (6.4 g, 0.04 mol) for 4.5 hr at 110–115°. Absorption of a cyclic ester group (1750 cm^{-1}) was absent in the ir spectrum of the reaction mixture. The products, vinyl phenyl ketone (XII) and phenyl methylacetic acid (VI), were obtained by using silica gel chromatography. The yields are shown in Table I. Vinyl phenyl ketone was identified by infrared spectral and boiling point comparison with the authentic sample, bp 115° (18 mm) [lit.[7c] bp 115° (18 mm)]. Phenylmethylacetic acid, obtained after hydrolysis, was identified by the sample (lit.[15] mp 265–268°).

D. Reaction of Phenylacetyldiazomethane (III) with Molecular Oxygen.—To a benzene solution (benzene 70 ml) of phenylacetyldiazomethane (3.2 g, 0.02 mol), molecular oxygen gas (280 l.) was added for 4.5 hr at 60–70°. Water (20 ml) and ether (20 ml) were added into the reaction mixture. The organic layer was separated, from which benzene and ether were evaporated under reduced pressure. To the residue, methanol (100 ml) was added. The methanol solution was cooled to give the white powders. The benzene (20 ml) solution of the white powders was subjected to chromatography on silica gel. Elution with benzene gave 3,6-dimethyl-3,6-diphenylglycolide (IV), which was recrystallized from ethyl acetate. From the filtered solution, methanol was evaporated to offer phenylmethylacetic acid (VI), which was identified by infrared spectral comparison and mixture melting point with authentic sample, mmp 286–288° (lit.[15] mp 288–289°). The yields are shown in Table I.

3,6-Dimethyl-3,6-diphenylglycolide (IV) had mp 164–165°; ir 1750 cm^{-1} ($\nu_{C=O}$ of ester group); ^{1}H nmr ($CDCl_3$) τ 2.5–3.5 (10 H, phenyl), 8.0–8.6 (6 H, *S*-methyl).

^{13}C nmr ($CHCl_3$) showed peaks at 169 corresponding to the ester group along with the peak at 129 ppm (Ph) from TMS over the range of 126–235 ppm.

Anal. Calcd for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44; mol wt, 296. Found: C, 52.63; H, 5.37; mol wt, 285.

Photochemical Reactions of α-Diazo Ketones with Molecular Oxygen in Benzene.—Four α-diazo ketones as described in thermal reactions were used. Molecular oxygen (280 l.) was introduced into the benzene (300 ml) solution of α-diazo ketone (0.01 mol), which was irradiated by a high-pressure mercury lamp at 15–20°. The irradiation was stopped with disappearance of the absorption in ir caused by the diazo group. The products were separated in the manner as done in thermal reactions, respectively. The products and the yields are shown in Table II. These products were identified by infrared spectral comparison and mixture melting point with samples previously prepared.

Apparatus.—Ir spectra were taken on a Hitachi EPI-S2 type infrared spectrometer. Nmr spectra were obtained with a JNM3H-60 spectrometer. Mass spectra and uv spectra were run on a Hitachi VD-10001-A spectrometer and Hitachi EPS-3 spectrophotometer. Molecular weight was determined by a Hitachi Perkin-Elmer 115 apparatus.

Registry No.—I, 3469-17-8; II, 467-32-3; III, 3893-35-4; IV, 38436-21-4; VIII, 3282-32-4.

Acknowledgment.—The authors wish to thank Dr. H. Sugiyama (Research Institute for nonaqueous solution, Tohoku University) for his ^{13}C nmr measurement.

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[13] H. Staudinger, *Ber.*, **44**, 543 (1911).

[14] J. J. Ritter and G. M. Wiedemen, *J. Amer. Chem. Soc.*, **51**, 3583 (1929).

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Stereochemistry in Trivalent Nitrogen Compounds. XVIII. Slow Rotation about the Nitrogen-to-Carbonyl Bonds in *N,N'*-Biscarboethoxy-3,3,4,4-tetramethoxy-1,2-diazetidene[1a]

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The conformational processes associated with nmr line shape changes in *N,N'*-biscarboalkoxy cyclic hydrazines have been the subject of considerable experimental work and speculation.[2] Three different types of conformational changes have been discussed as possible sources for the coalescence phenomena observed in such systems: (a) nitrogen inversion,[3] (b) rotation about amide bonds,[4] and (c) ring flexion in six-membered rings or even in bicyclic ring systems. We have examined the nmr spectral behavior of *N,N'*-biscarboethoxy-3,3,4,4-tetramethoxy-1,2-diazetidene (1) in order to examine a system in which two of these factors could be controlled.

[1] (a) Part XVII: D. Kost and M. Raban, *J. Amer. Chem. Soc.*, **94**, 2533 (1972). (b) Alfred P. Sloan Foundation Fellow, 1972–1974.

[2] (a) J. E. Anderson and J. M. Lehn, *Tetrahedron*, **24**, 123 (1968); **24**, 137 (1968); and papers cited therein; (b) W. D. Phillips, unpublished results cited in W. D. Phillips, in "Determination of Organic Structures by Physical Methods," Vol. 2, Academic Press, New York, N.Y., 1962, Chapter 6; (c) B. Price, I. O. Sutherland and F. G. Williamson, *Tetrahedron*, **22**, 3477 (1966).

[3] Reviews: (a) J. M. Lehn, *Fortschr. Chem. Forsch.*, **15**, 311 (1970); (b) A. Rauk, L. C. Allen, and K. Mislow, *Angew. Chem., Int. Ed. Engl.*, **9**, 400 (1970); (c) J. Lambert in "Topics in Stereochemistry," Vol. VI, E. L. Eliel and N. L. Allinger, Ed., Wiley, New York, N. Y., 1971, p 19.

[4] Reviews: (a) W. E. Stewart and T. H. Siddall, III, *Chem. Rev.*, **70**, 517 (1970); (b) H. Kessler, *Angew. Chem., Int. Ed. Engl.*, **9**, 219 (1970).

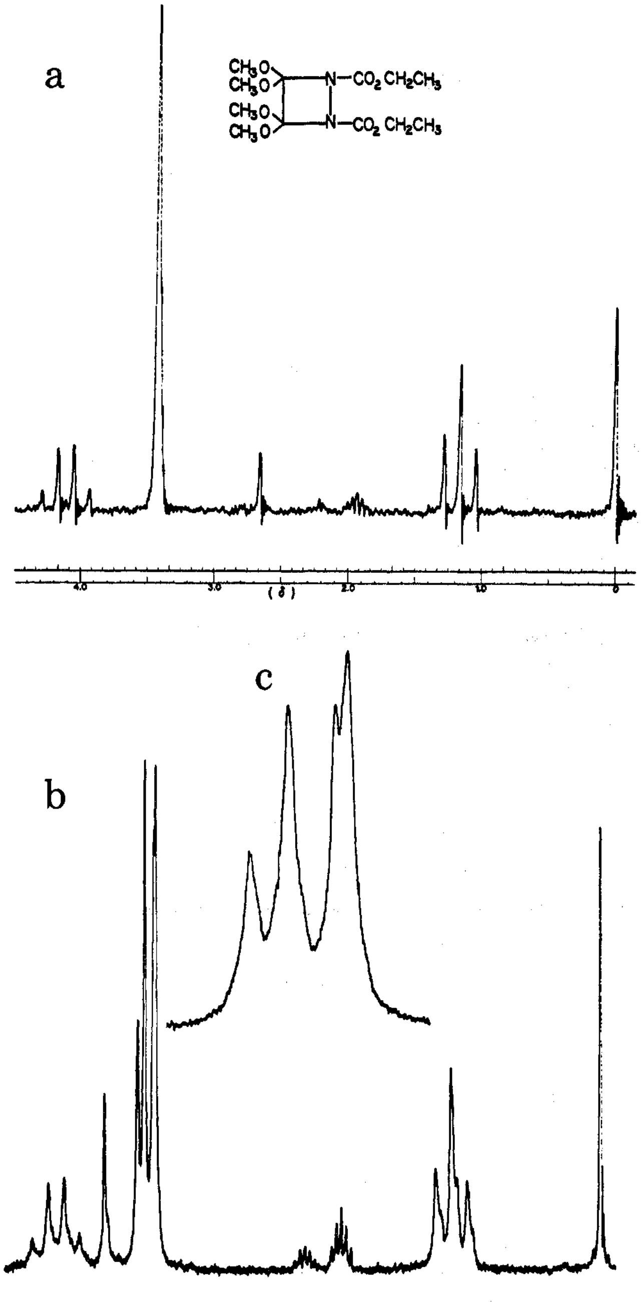
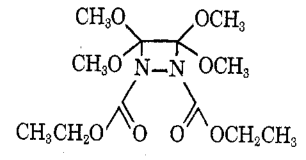


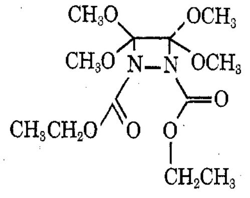
Figure 1.—Nmr spectra of **1** in acetone-d_6–toluene-d_8. (a) Spectrum recorded at room temperature; the peaks at δ 1.9, 2.2, and 2.7 are due to impurities toluene-d_7, acetone-d_5, and water, respectively. (b) Spectrum recorded at −65°. The peaks for acetone-d_5 and toluene-d_7 are unchanged, but the peak for the water impurity is shifted to δ 3.7. (c) Expanded scale spectrum of the methoxy region recorded at −65°.

The presence of the small ring system in **1** might be expected to affect both barriers to a and c. The ring strain present in four-membered rings is known to lower barriers to ring reversal and to increase barriers to nitrogen inversion. As a result, while the barrier to rotation about the nitrogen–carbonyl bond should be approximately the same in **1** as in six-membered ring analogs, the nitrogen inversion barrier should be higher, and the barrier to ring reversal should be much lower or absent. The only previous study on a similar compound is an investigation of *N,N'*-biscarboethoxy-3,3,4,4-tetrafluorodiazetidene.[2b] The chemical shift nonequivalence of geminal fluorine atoms observed in that study is consistent with barrier to nitrogen inversion[2b] or ring flexion.[2c] No evidence for slow rotation about amide bonds could be detected.

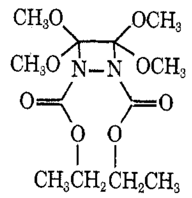
The variable-temperature nmr spectra of **1** exhibit only a single coalescence phenomenon in the neighborhood of −40 to −20°. Below this temperature range the methoxy groups appear as four singlets in acetone-d_6–toluene-d_8 (Figure 1), or as two singlets in acetone-d_6. The coalescence of the four methoxy singlets is consistent with the interconversion of the three isomers **1a**, **1b**, and **1c**.



1a



1b



1c

The most deshielded of the low-field singlets most likely arises from the methoxyl groups in the *out–out* isomer **1c**, which appear from models to be in the deshielding region of the carbamate carbonyl groups. The other low-field singlet would then arise from the methoxyls cis to the carbonyl in the *in–out* isomer, **1b**. The upfield methoxy singlets are associated with **1a** and the methoxy groups cis to the ethoxy group in **1b**. Based on the integrated intensities of the four peaks obtained by computer simulation, A:B:C:D = 18:29:24:29, we estimate the relative concentrations of **1a**:**1b**:**1c** to be 24:58:18. The differences in free energies of formation were thus obtained by complete line shape analysis: $\Delta G_{-65°}$ (**1b** → **1a**) = 0.3 kcal/mol, $\Delta G_{-65°}$(**1b**→**1c**) = 0.5 kcal/mol; as was the free energy of activation: $\Delta G_{-27°}^{\ddagger}$ (**1b** → **1a**) = 13.6 kcal/mol.

In acetone-d_6 the low-field pair of singlets ("out" methoxyls) apparently coincide, as do the two high-field singlets ("in" methoxyls), and only two singlets are observed. The torsional barrier was obtained at the coalescence point in acetone-d_6 using the approximate formula,[5] $k_c = (\pi/\sqrt{2})\Delta\nu$: $T_c = -25°$, $\Delta\nu = 3$ Hz, $\Delta G_c^{\ddagger} = 13.8$ kcal/mol. The values obtained in both solvent systems are fairly similar to those obtained by Anderson and Lehn for restricted rotation in bicyclic analogs of **1**.[2a]

No evidence for slow nitrogen inversion could be detected down to −125°. Apparently, even with the ring strain present in the four-membered diazetidine ring and the presence of a nitrogen–heteroatom bond, nitrogen inversion remains rapid. Our results are in accord with the conclusions[2a] that slow nitrogen inversion is not responsible for nmr line shape changes in biscarboalkoxy cyclic hydrazines and that barriers in

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[5] For evidence of the reliability of this approach, see D. Kost, E. Carlson, and M. Raban, *Chem. Commun.*, 656 (1971).

the neighborhood of 13–14 kcal/mol can be ascribed to amide torsional barriers. Our results, however, are in striking contrast with those reported for the analagous compound in which the methoxy groups are replaced by fluorine atoms.[2b] Unless accidental equivalence is responsible for the differences in the two systems, it would appear that replacement of fluorine by methoxy both raises the amide barrier and lowers the barrier to nitrogen inversion[2b] (or ring reversal[2c]).

Experimental Section

N,*N*′-Biscarboethoxy-3,3,4,4-tetramethoxy-1,2-diazetidene was prepared as previously reported.[6]

The nmr spectra were measured on a Varian A-60A spectrometer equipped with a Varian variable-temperature probe using *ca.* 10% solutions. Temperatures were determined using methanol spectra as described in the Varian Manual. Rate constants and equilibrium constants were determined by matching experimental spectra with theoretical spectra. The theoretical spectra were generated using Saunder's Many Site NMR Lineshape Program.[7] This program allows the calculation of nmr spectra involving exchange between n sites ($2 \leq n \leq 25$) which must be uncoupled, but need not have the same population. The two "out" methoxy groups of **1b** which are diastereotopic with respect to the "in" methoxy groups were treated as two separate isomers. Exchange was assumed to be possible between **1a** and both sites in **1b** and between **1c** and both sites in **1b**, but not directly between **1a** and **1c**, nor between the "in" and "out" sites of **1b**. The chemical shift differences and the relative populations were temperature dependent and were determined by iterating to obtain the best fit.

Registry No.—**1,** 10200-65-4.

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[6] R. W. Hoffmann and H. Hauser, *Angew. Chem.*, **76**, 346 (1964).

[7] M. Saunders, *Tetrahedron Lett.*, 1699 (1963). See also C. S. Johnson, Jr., in "Advances in Magnetic Resonance," Vol. 1, J. S. Waugh, Ed., Academic Press, New York, N. Y., 1965, Chapter 2.

The Stereochemistry of the Hydroboration Reaction

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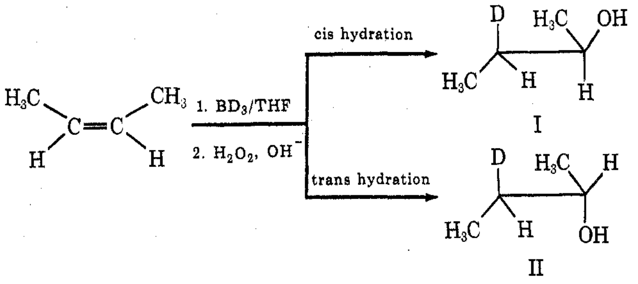
In the course of our efforts to elucidate the stereochemistry of various organoborane reactions, we had reason to deuterioborate *cis*- and *trans*-2-butene, respectively, and oxidize the resultant organoboranes. Nmr analysis of the resultant 2-butanol-*3-d* from the respective reaction mixtures demonstrates conclusively that the hydroboration–oxidation sequence is a stereospecific cis-hydration reaction.

The hydroboration–oxidation sequence is generally accepted as a method to achieve cis-hydration of alkenes. Evidence to that effect has been accumulating for a number of years.[1–5] However, essentially all of the studies have been carried out on cyclic systems. In general the products observed were the thermodynamically most stable ones. In one instance, it was demonstrated that isomeric acyclic alkenes could be hydroborated and then oxidized to produce different diastereomeric alcohols.[5] However, the configurations of the starting alkenes[6] and the product alcohols[7] were assigned by analogy to a related system.

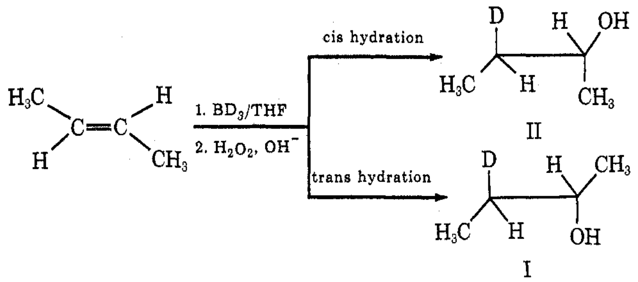
Results and Discussion

The 2-butene system would seem to be an ideal choice for the study of the stereochemistry of the hydroboration–oxidation sequence. The molecule contains a plane of symmetry with two stereoequivalent trigonal carbon atoms. Unlike cyclic or conjugated systems, free rotation of the tetrahedral addition or oxidation intermediates is possible, and if such rotation were to occur, there should be limited steric bias to affect the product distribution.

One could then visualize two possible products from the deuterioboration–oxidation sequence for *cis*-2-butene. The *erythro*-2-butanol-*3-d* (I) would arise from overall cis-hydration, whereas a trans-hydration would produce the *threo*-2-butanol-*3-d* (II).



The stereochemistry of the resultant products would, of course, be reversed in the case of *trans*-2-butene. The *threo*-2-butanol-*3-d* (II) would arise from overall cis-hydration, whereas a trans-hydration would produce the *erythro*-2-butanol-*3-d* (I).



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[3] H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, **83**, 2544 (1961).

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[5] E. L. Allred, J. Sonnenberg, and S. Winstein, *J. Org. Chem.*, **25**, 26 (1960).

[6] D. J. Cram, *J. Amer. Chem. Soc.*, **71**, 3883 (1949).

[7] S. Winstein and G. C. Robinson, *ibid.*, **80**, 170 (1958).

[8] L. M. Jackman and N. S. Bowman, *ibid.*, **88**, 5565 (1966).