the basis of these data we can estimate the chemical shift difference between the α protons of *N*-methylpyrrolidine in the absence of nitrogen inversion. In this case two of the α protons should be fully shielded both by the trans lone pair (0.50 ppm) and by the *cis-N*-methyl group (0.66 ppm); therefore the shift should amount to 1.16 ppm, which is in good agreement with the observed value of 1.08 ppm.[5]

The present conclusions are borne out by the results from the protonation experiments (Table I, column 2). In the presence of excess trifluoroacetic acid (TFA) the α protons of **2b** appear as one signal indicating a single protonated species. The α protons of **1b** and **3b** are split into two signals of equal areas with a chemical shift difference of 0.76–0.83 ppm, which presumably results from full-scale shielding of half of the α protons in **1b** and **3b** by a *cis-N*-methyl group. It is worthy of note that the high field signal of **3b** corresponds well with the chemical shift of the α protons of **2b**, both of which are fully shielded by a *cis-N*-methyl group.

From the data presented the following conclusions can be drawn. (1) The α protons of a pyrrolidine are shielded when situated trans to an electron pair and cis to an *N*-methyl group. (2) The chemical shift difference of 1.08 ppm observed at −100° between the α protons of *N*-methylpyrrolidine[5] is caused predominantly (0.66–0.83 ppm) by the *cis-N*-methyl group and to a lesser degree by the trans lone pair. (3) The stereochemistry of a symmetrically N,α,α'-trisubstituted pyrrolidine (and presumably any symmetrical nitrogen heterocycle) can be established by examination of the nmr spectrum of the protonated form. In the cis isomer the α protons should appear together, while in the trans isomer they should appear separately. (4) The treatment presented can easily be applied to assess the contribution of a trans lone pair and that of a *cis-N*-alkyl group to the shielding of α protons in any saturated symmetrical nitrogen heterocycle.

The shielding of α protons in azacycloalkanes by a trans lone pair[12] and by a *cis-N*-alkyl group seems to be a general phenomenon. A consequence of this is that in pairs of cis,trans isomers of *N*-alkyl-α,α' symmetrically disubstituted azacycloalkanes the α protons of the cis isomer should always appear in the nmr at higher field than those of the trans isomer. No exception to this was found in an extensive literature survey of nmr data of appropriate three-, five-, and six-membered azacycloalkanes.[13]

Further study of this problem in other ring systems is in progress.

Registry No.—**1a,** 123-75-1; **1b,** 120-94-5; **2a,** 22147-83-7; **2b,** 35657-63-7; **3a,** 22147-84-8; **3b,** 35657-66-0.

Acknowledgment.—We wish to thank Professor S. Sarel for his comments concerning this work.

The Reactivity of Diazo Ketones. IV.[1] Reaction of α-Diazo Ketones with Molecular Oxygen

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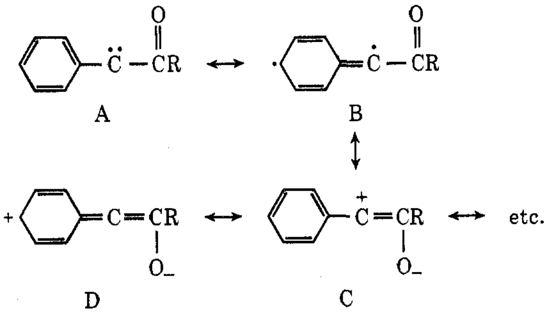
It was reported[1a] that PhC̈COR (R = Ph, Me) type ketocarbenes react with sulfur dioxide to give the ketosulfenes in competition with the Wolff rearrangement, while RC̈COPh (R = Me, H) type ketocarbenes do not react, but yield the products resulting from 1,2-hydrogen shift and a 1,3-dipolar addition reaction. In this case, it was suggested[1a] that the resonance form A or B of the PhC̈COR type ketocarbene as shown in Scheme I reacts with sulfur dioxide, for sulfur dioxide is known to react electrophilically and radically, but no nucleophilically.

Scheme I



In order to obtain further information on the reactivity of the ketocarbene, thermal or photochemical reactions of several α-diazo ketones with molecular oxygen were investigated.

A number of reports[2] on the photochemical reactions of diaryldiazomethane and the thermal reactions of tetraarylethylenes with molecular oxygen have been published. These reactions are explained by the addition of diarylcarbenes to molecular oxygen[2−4] (Scheme II).

A "carbonyl oxide" (E) has been suggested[4] as the primary product[4b] in the formation of cyclic peroxide[4a] from the photooxidation of diphenyldiazomethane. Also, the formation of benzophenone from the "carbonyl oxide" (E) on irradiation of diphenyldiazomethane in solid air matrix at 20°K has been reported.[4c]

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[12] *Although this phenomenon is usually viewed as shielding of α protons trans to a lone pair,*[1−4] *it may also be viewed as deshielding by a skew or cis related lone pair:* C. C. Price, *Tetrahedron Lett.*, 4527 (1971). We thank Dr. C. C. Price for directing our attention to his results.

[13] No data were found for appropriate azetidines and hexahydroazepines.

[1] (a) M. Tanaka, T. Nagai, and N. Tokura, *J. Org. Chem.*, **37**, 4106 (1972); (b) T. Nagai, M. Tanaka, and N. Tokura, *Tetrahedron Lett.*, 6293 (1968); (c) M. Tanaka, T. Nagai, and N. Tokura, *ibid.*, 4979 (1972).

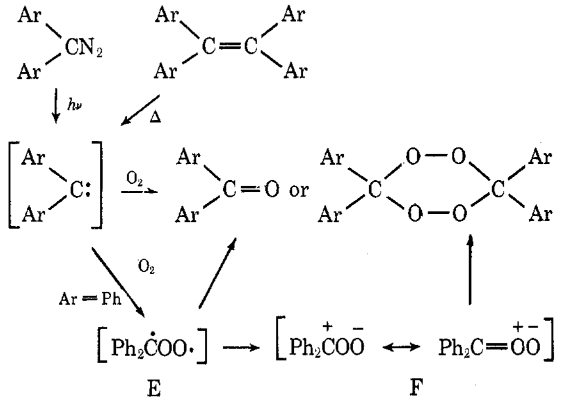
[2] (a) H. Staudinger, E. Anthes, and F. Pfenninger, *Ber. Deut. Chem. Ges.*, **49**, 1928 (1916); (b) W. Kirmse, L. Horner, and H. Hoffman, *Justus Liebigs Ann. Chem.*, **619**, 19 (1958); (c) P. D. Bartlett and T. G. Traylor, *J. Amer. Chem. Soc.*, **84**, 3408 (1962); (d) R. W. Murray and A. M. Trozzolo, *J. Org. Chem.*, **26**, 3109 (1961).

[3] V. Franzen and H. I. Joschek, *Justus Liebigs Ann. Chem.*, **633**, 7 (1960).

[4] (a) P. D. Bartlett and T. G. Traylor, *J. Amer. Chem. Soc.*, **84**, 3408 (1962). (b) Peroxidic zwitterion F is suggested to be formed from the radical structure E as shown in Scheme II: R. W. Murray and A. Suzui, *ibid.*, **93**, 4963 (1971). (c) Benzophenone is suggested to be obtained from the related carbonyl oxide, but the mechanism of the deoxygenation from the carbonyl oxide is not determined.[2c]

Scheme II

Reaction of Diaryldiazomethane or Tetraarylethylene with Molecular Oxygen

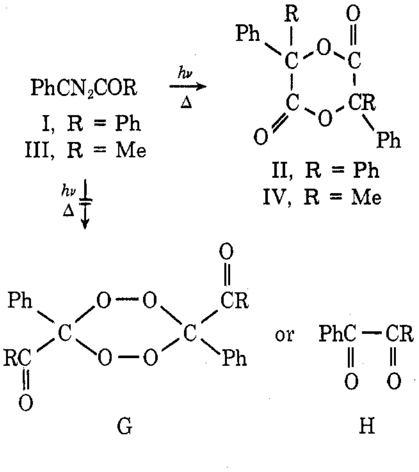


On the other hand, only indirect information[5,6] on the reaction of ketocarbene with molecular oxygen has been obtained from the photolysis of azibenzil in organic glass around 77°K. The photolysis gave a very small amount of benzil[6] besides ketene and a high yield of solvent-substituted deoxybenzoin.

In the present study, α-diazo ketones as described in Scheme IV were used.

Reactions of α-diazo ketones with molecular oxygen did not proceed at ordinary temperature, but did readily by the thermal or photochemical decomposition of α-diazo ketones in aromatic solvents. The thermal or photochemical reactions of $PhCN_2COR$ (R = Ph, Me) type diazo ketones with molecular oxygen gave tetraphenylglycolide (II) and 3,6-dimethyl-3,6-diphenylglycolide (IV), respectively, instead of the peroxides (G) or ketones (H) (Scheme III).

Scheme III



Thermal reactions were carried out around the decomposition point of diazo ketones (Scheme IV and Table I). However, from only Table I, it is too difficult to discuss the substituent effect of these reactions, for the reaction conditions are different in temperature and solvent. Keeping in mind this point, under similar conditions, the photochemical reactions were achieved (Scheme IV and Table II).

Scheme IV

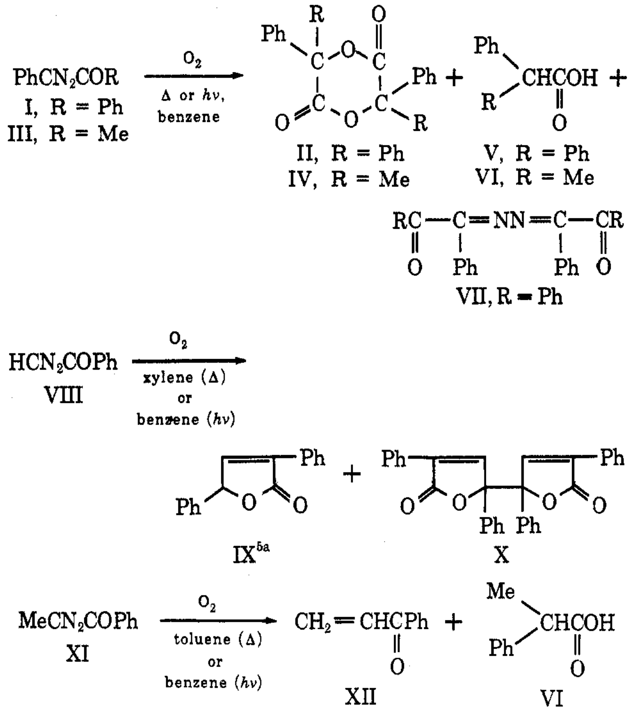


Table I

Thermal Reaction[a] of $R_1CN_2COR_2$ with O_2

R_1	R_2	Solvent	Temp, °C	Products (yield, mol %)[b]
Ph	Ph	Benzene	70–80	II (40), V (21), VII (15)
H	Ph	Xylene	130–140	IX (6), X (37)
Me	Ph	Toluene	110–115	XII (54), VI (2)
Ph	Me	Benzene	60–70	IV (43), VI (8)

[a] Reaction time 4.5 hr. [b] The yields are in mole per cent based on unrecovered starting material for V, VI, and XII, based on a 0.5 mol of unrecovered starting material for II, IV, VII, and IX, and based on a 0.25 mol of unrecovered starting material for X.

Table II

Photochemical Reaction[a] of $R_1CN_2COR_2$ with O_2 in Benzene at 15–20°

R_1	R_2	Time, hr	Products (yield, mol %)
Ph	Ph	6	II (41), V (17), VII (trace)
H	Ph	8	IX (26), X (18)
Me	Ph	9	XII (58), VI (trace)
Ph	Me	4	IV (49), VI (2)

[a] The irradiation was undertaken by using a 300-W high-pressure mercury lamp in a Pyrex tube at 15–20°.

The results of photochemical reactions resembled those of thermal reactions.

Confirmation of the structure of II or IV was made, as will be described in the Experimental Section, from elemental analysis, molecular weight determination, ir, ^1H nmr, ^{13}C nmr spectra, and the reaction. Moreover, II was identified by the mixture melting point method with the authentic sample.[7a]

In these reactions of $R_1CN_2COR_2$ type diazo ketones (R_1 = Ph, Me, H; R_2 = Ph, Me) with molecular oxygen, a remarkable substituent effect was observed,

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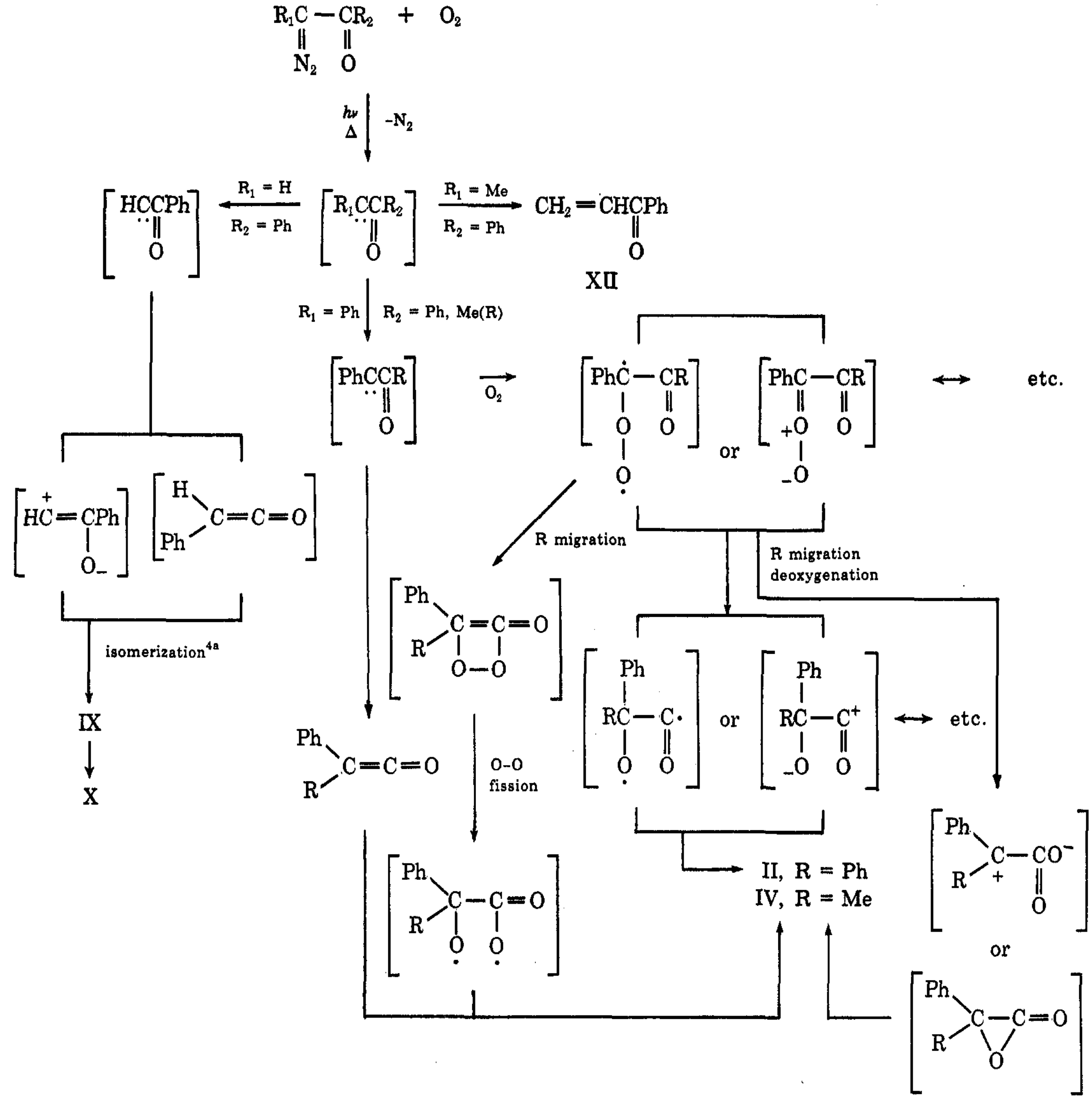
[5] A. M. Trozzolo, *Accounts Chem. Res.*, **1**, 329 (1968).

[6] The deoxygenation process in the formation of benzil is not made clear, but the reaction of phenyl benzoyl carbene with molecular oxygen is suggested.[5]

[7] (a) C. S. Marrel, F. D. Hager, and E. C. Caudle, *Org. Syn.*, **3**, 45 (1923); (b) G. Baddeley, G. Holt, and J. Kenner, *Nature* (*London*), **163**, 776 (1949); (c) V. Franzen, *Justus Liebigs Ann. Chem.*, **602**, 199 (1957).

SCHEME V



namely, PhCN$_2$COR (R = Ph, Me) type diazo ketones gave cyclic diesters (II, IV). By contrast, RCN$_2$COPh (R = H, Me) type diazo ketones afforded the products resulting from 1,2-hydrogen shift[7b,c] and 1,3-dipolar[8] addition reaction of the ketocarbene intermediate.

Tetraphenylglycolide (II) was not obtained from the reaction of diphenylketene or bisbenzilketazine (VII) with molecular oxygen under the same conditions as the thermal reaction of azibenzil (I) with molecular oxygen.

Thus, the interaction of the Ph$\ddot{C}$COR type ketocarbene generated from the corresponding diazo ketones with molecular oxygen followed by R migration may be postulated for the formation of the cyclic diesters. The possible intermediates are described in Scheme V.

The reactivity of R$_1\ddot{C}$COR$_2$ type ketocarbenes with molecular oxygen resembles that[1a] with sulfur dioxide (Table III).

TABLE III

REACTIVITY OF R$_1\ddot{C}$COR$_2$ WITH O$_2$ OR SO$_2$

R$_1$	R$_2$	O$_2$	SO$_2$
Ph	Ph	+ (Carbonyl oxide)	+ (Ketosulfene)
H	Ph	− (1,3-Dipolar addition)	− (1,3-Dipolar addition)
Me	Ph	− (1,2-Hydrogen shift)	− (1,2-Hydrogen shift)
Ph	Me	+ (Carbonyl oxide)	+ (Ketosulfene)

Then, it is proposed that the radical reactivity of Ph$\ddot{C}$COR type ketocarbenes may be due to the resonance[9] form B as shown in Scheme I.

Experimental Section

Materials.—Azibenzil (I), mp 78° (lit.[10] mp 78°), and phenyl acetyl diazomethane (III), mp 59–60° (lit.[10] mp 59–60°), were prepared by diazo transfer reactions from the related ketones.

Diazoacetophenone (VIII), mp 48–50° (lit.[11] mp 49–50°), and methyl benzoyl diazomethane (XI),[11] which is the liquid diazo compound recrystallized[12] from ether at −70°, were obtained by the reaction of benzoyl chloride with related diazoalkanes.

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(8) (a) D. Yates and T. J. Clark, *Tetrahedron Lett.*, 435 (1961); (b) R. Huisgen, G. Binsch, H. Konig, and H. J. Sturm, *Angew. Chem.*, **73**, 368 (1961); (c) G. Binsch, *ibid.*, **75**, 634 (1963); (d) W. Kirmse and L. Horner, *Justus Liebigs Ann. Chem.*, **625**, 34 (1959).

(9) (a) The resonance of divalent carbon with the phenyl ring has been proposed; see W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, p 214; (b) R. W. Murray and A. M. Trozzolo, *J. Org. Chem.*, **26**, 3109 (1961).

(10) M. Regitz, *Chem. Ber.*, **98**, 1210 (1965).

(11) F. Arndt and B. Eistert, *ibid.*, **68**, 200 (1935).

(12) M. Regitz, *Angew. Chem.*, **79**, 733 (1967).

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 $\times$ 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).

[15] W. Johnson, *ibid.*, **24**, 686 (1902).

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.

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(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).