A solution of crude **8** (0.2 g) and tetracyanoethylene (0.14 g) in benzene (6 mL) was stirred at 60 °C for 10 min. The solvent was evaporated under reduced pressure, and the residue was recrystallized from ethanol–benzene (10:1) to give the 1:1 adduct **10**: 0.25 g (74%); mp 216–217 °C; IR (Nujol) 2260 (CN) cm^{-1}; NMR δ ($CDCl_3$) 1.10 (m, 1 H, H-1), 1.59 (m, 1 H, H-2), 1.68 (m, 1 H, H-1′), 3.86 (m, 2 H, H-3, H-6), 5.20 (dd, 2 H, J = 9.0, 4.3 Hz, H-2′, H-7′), 6.16 (dd, 2 H, J = 9.0, 3.0 Hz, H-3′, H-6′), 6.38 (d, 2 H, J = 4.4 Hz, H-4, H-5), 6.60 (t, 2 H, J = 3.0 Hz, H-4′, H-5′). Anal. Calcd for $C_{20}H_{14}N_4$: C, 77.42; H, 4.51; N, 18.06. Found: C, 77.28; H, 4.68; N, 18.01.

Quantum Yield Determination. A solution of **la–h** (0.0087 mmol) and **2** (10 mmol) in benzene (100 mL) was prepared. The solution in a Pyrex tube was degassed with nitrogen and irradiated at 3650 Å by use of a filter. The light output was monitored by potassium ferrioxalate actinometry according to the method of Hatchard and Parker.[5]

The consumption of **la–h** was monitored by UV spectroscopy by use of the 0–0 absorption band (λ_{max}; see Table IV). Several measurements were taken at different conversions (<10% conversion), and the average value was used. The results were shown in Table IV.

Fluorescence Quenching. Samples (3 mL) containing 2.4 × 10^{-5} M anthracene derivatives **1g** and **1f** and varying concentrations of cyclohepta-1,3,5-triene (**2**) in benzene were placed in optical path length quartz cells (1 × 1 cm). The intensities were measured three times for each cell, and an average value for each sample was used. The results are shown in Figure 3 and Table V.

Acknowledgment. The authors thank Professor T. Sasaki of the Faculty of Engineering, Nagoya University, for many helpful discussions. We are also grateful to Master Masato Sugiura for helpful discussions and experimental assistance.

Registry No. 1a, 779-02-2; **1b**, 602-55-1; **1c**, 781-43-1; **1d**, 1499-10-1; **1e**, 120-12-7; **1f**, 1210-12-4; **1g**, 1217-45-4; **1h**, 523-27-3; **2**, 544-25-2; **3a**, 36773-81-6; **3e**, 1627-06-1; **4a**, 75378-73-3; **4b**, 75378-74-4; **4e**, 75378-75-5; **5e**, 42916-01-8; **5f**, 59410-57-0; **6f**, 59410-56-9; **6g**, 75378-76-6; **6h**, 75378-77-7; **7a**, 75378-78-8; **7b**, 75378-79-9; **7c**, 75378-80-2; **7d**, 75378-81-3; **7f**, 75378-82-4; **8h**, 831-18-5; **10**, 75400-72-5; tetracyanoethylene, 670-54-2.

Mechanism of the Photochemical Wolff Rearrangement. The Role of Conformation in the Photolysis of α-Diazo Carbonyl Compounds

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Investigation of photochemical processes of several α-diazo carbonyl compounds reveals that the Wolff rearrangement to form ketene takes place directly from the singlet excited state of the *s-Z* conformer whereas the excited state of the *s-E* conformer dissociates nitrogen to generate singlet carbonyl carbene, which either undergoes characteristic carbenic reactions, e.g., insertion and 1,2-hydrogen shift, or gives rise to ketene. The migratory aptitude as well as the relative efficiency of other competing reactions from singlet carbene is shown to be an important factor in determining which reaction pathway is favored. Substantial amounts of singlet carbene can be formed even under sensitized conditions, presumably via intersystem crossing from initially formed triplet carbene.

The photochemistry of α-diazo carbonyl compounds has received much attention recently both from chemists interested in the nature and mechanisms of the reactions undergone by these species[1] and from others interested in using them as labeling reagents for active sites of enzymes.[2] Thus, carbenes produced upon irradiation of α-diazo carbonyl compounds have been known to undergo insertion and/or addition reactions and hence to be useful reactive intermediates for introduction of the carbonylmethylene group. The photolysis is, however, often accompanied by the Wolff rearrangement (WR) which has diminished the utility of these compounds as a ketocarbene source. The WR, on the other hand, has found wide use as the crucial step in the Arndt–Eistert synthesis.[3] It has also attracted much interest industrially[4] as a photoresist process. It is very important to elucidate, then, the exact nature which controls the two competitive pathways in the photolysis of α-diazo carbonyl compounds. Although the WR has been the subject of numerous mechanistic investigations,[1] a satisfactory rationalization of this reaction has not yet been achieved. Involvement of free ketocarbene in the WR was first reported by Wolff[5] and is still favored by many authors, although there are few direct proofs for the intermediacy of ketocarbene. More recently, Kaplan and Meloy[6] proposed a one-step, concerted rearrangement by studies of hindered internal rotation about the C–C bond in diazo ketones. They have suggested that diazo ketones exist as an equilibrium mixture of *s-Z* and *s-E* forms and that only the *s-Z* form is responsible for the WR with migration accompanying loss of nitrogen due to stereoelectronic reasons. There is evidence,[7] on the other hand, that under certain conditions some diazo compounds are protonated and that therefore the WR takes place in the diazonium ion. Despite the wealth of data which has been

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(1) For reviews see: (a) Kirmse, W. "Carbene Chemistry", 2nd ed; Academic Press: New York, 1971; p 475; (b) Moss, R. A., Jones, M., Eds. "Carbenes"; Wiley: New York, 1973; Vol. I, p 117; (c) Meier, H.; Zeller, K. P. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 32; (d) Ando, W. In "The Chemistry of Diazonium and Diazo Groups"; Patai, S., Ed.; Wiley: New York, 1978; Vol. I.

(2) Chowdhry, V.; Westheimer, F. H. *J. Am. Chem. Soc.* **1978**, *100*, 309 and references cited therein.

(3) (a) Bachman, W. E.; Struve, W. S. *Org. React.* **1942**, *1*, 38. (b) Weygand, F.; Bestman, H. S. "Syntheses using Diazoketones, Newer Methods of Preparative Organic Chemistry"; Academic Press: New York, 1964; Vol. III, p 451.

(4) (a) Dinaburg, M. S. "Photosensitive Diazo Compounds"; Focal Press: New York, 1964. (b) Deforest, W. S. "Photoresist Materials and Processes"; McGraw-Hill: New York, 1975.

(5) (a) Wolff, L. *Justus Liebigs Ann. Chem.* **1902**, *325*, 1902. (b) Wolff, L. *Ibid.* **1912**, *394*, 23.

(6) Kaplan, F.; Meloy, G. K. *J. Am. Chem. Soc.* **1966**, *88*, 950.

(7) Bartz, W.; Regitz, M. *Chem. Ber.* **1970**, *103*, 1463.

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Table I. Effect of Sensitizer and Quencher on Product Distributions in the Photolysis[a] of 1 in 2-Propanol

	% yield[b]				
additives	2	3	4	5	6
none	8.7	35.0	32.5	10.5	6.1
Q[c]	8.7	30.4	35.5	11.9	0
Ph_2CO[d]	4.0	5.5	trace	trace	61.9

[a] Irradiations were performed on a 25 mM solution of 1. [b] Yields were determined by GC and based on 1 used. [c] A tenfold excess of piperylenes was added. [d] Irradiated with monochromatic light of 335 nm in the presence of a fivefold excess of $Ph_2C{=}O$. More than 98% of the incident light was absorbed under these conditions.

gathered, no comprehensive answers to explain the various photochemical pathways of α-diazo carbonyl compounds seem to be available as yet. We have thus investigated the photochemical behavior of several α-diazo carbonyl compounds under various conditions in order to assign each reacting intermediate leading to various products and to elucidate the effects of ground-state conformational populations on the photochemical processes.

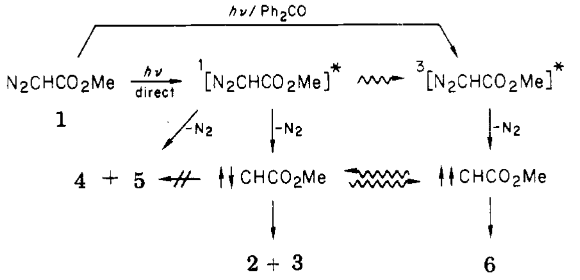
Results and Discussion

Photolysis in Alcohols. Ten years ago, DoMinh, Strausz, and Gunning found[8] in the photolysis of diazoacetate (1) a novel reaction product, i.e., exchange product 5, in addition to the normal reaction products (2–4) from (carboalkoxy)methylene (eq 1). They proposed that the

$$\underset{1}{N_2CHCO_2Me} \xrightarrow[i\text{-PrOH}]{h\nu} \underset{2}{i\text{-PrOCH}_2CO_2Me} + \underset{3}{Me_2C(OH)CH_2CO_2Me} + \underset{4}{MeOCH_2CO_2\text{-}i\text{-Pr}} + \underset{5}{i\text{-PrOCH}_2CO_2\text{-}i\text{-Pr}} + \underset{6}{CH_3CO_2Me} \quad (1)$$

WR of diazoacetate involves, instead of free carbene, ion pairs produced by a light-induced heterolysis, which either undergo internal return to give ketene or undergo anion exchange with solvent alcohol to form the exchange product (5). It is quite important to elucidate the excited-state multiplicities of each intermediate leading to carbene and rearrangement products in this interesting reaction since such studies would be expected to tell us the exact relationship between the carbenic routes and the WR process. Thus, we have examined the effect of sensitizer and quencher on the product distributions and results are listed in Table I. The addition of piperylene, an efficient quencher for triplet carbene[9] and presumably for the triplet excited state,[10] did not alter the product distributions of 2–5 though it completely suppressed the formation of 6, apparently arising[1] via the double hydrogen abstraction of the triplet carbene. This implies that not only the WR products (4 and 5) but also the carbenic products (2 and 3) are derived from the excited singlet state of 1. In marked contrast, when the photolysis of 1 was carried out in the presence of benzophenone with monochromatic light of 335 nm where >98% of the incident light was absorbed by the sensitizer, the rearrangement products (4 and 5) were almost completely suppressed concomitant with a significant increase in the formation of 6, whereas the insertion products were still formed in moderate yield. From the data, it is evident that 4 and 5 arise from a common intermediate (A) and 2 and 3 arise from a different intermediate (B). Since the photosensitized decomposition of 1 circumvents[11] the formation of the excited singlet state of 1, the results suggest the singlet-excited 1 as the most likely common intermediate A for 4 and 5. One might propose that the intermediate B may be the triplet carbene since the sensitization generates exclusively the triplet carbene via energy transfer and loss of nitrogen from the resulting triplet precursor diazo compound,[11] as is evident from the marked increase in the formation of 6. If this were the case, however, the addition of piperylene should have caused considerable suppression of the formation of 2 and 3 in the direct run. Furthermore it is generally accepted[1,12,13] that a key intermediate leading to the OH-insertion product is a singlet carbene. Thus, the structure for the intermediate B that best fits these data is that of a singlet carbene.

Scheme I



On the basis of the above assignments, a reasonable mechanism which explains the presently available data is given in Scheme I. Thus, 1 is excited to its excited singlet state, which can either give rise to the WR and exchange products directly or dissociate to give nitrogen and the singlet carbene. The singlet carbene subsequently undergoes OH and/or C–H[14] insertion into alcohol to give 2 and 3. Appreciable formation of 2 and 3 from the singlet carbene even in the sensitized decomposition can be interpreted as indicating that intersystem crossing of the triplet carbene to the singlet is possible, as has frequently been observed in other analogous carbene systems, e.g., $\ddot{C}HCOCH_3$,[16] $\ddot{C}HCONEt_2$,[13] and $\ddot{C}HCN$.[16]

The present mechanism for the photochemical process of 1 suggesting that the dissociation to the carbene and the intramolecular pathway take place in the excited singlet state at the same time is, however, not in accord with that suggested[16a] for the photochemical process of diazoacetone in which the singlet excited state exclusively undergoes the WR process and hence is not a precursor for the singlet ketocarbene. The reason for this discrepancy must lie in Kaplan and Meloy's suggestion[6] that the WR of an α-diazo ketone takes place through the conformational isomer, i.e., *s-Z*, in which the diazo group is lying trans to the migrating group, whereas the *s-E* isomer

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[8] DoMinh, T.; Strausz, O. P.; Gunning, H. E. *J. Am. Chem. Soc.* **1969**, *91*, 1261.

[9] See, for example: Moss, R. A. In ref 1b, p 153 ff.

[10] Exact triplet energy of 1 is not known at present. However, triplet-sensitized decomposition of 1 occurred with benzophenone (E_T = 69 kcal/mol) but not with anthraquinone (E_T = 62 kcal/mol), suggesting that piperylene (E_T = 59 kcal/mol) will quench the triplet excited state of 1.

[11] Roth, H. D.; Manion, M. L. *J. Am. Chem. Soc.* **1975**, *97*, 779.

[12] Tomioka, H.; Izawa, Y. *J. Am. Chem. Soc.* **1977**, *99*, 6128.

[13] Tomioka, H.; Kitagawa, H.; Izawa, Y. *J. Org. Chem.* **1979**, *44*, 3072.

[14] The singlet carbene insertion into C–H bonds of alcohol has been relatively limited at ambient temperature. It has been shown[15] in the reaction of vinylidene with alcohol that hydrogen bonding between the alcohol and the free electron pair orients the singlet carbene center into close proximity to the CH bond α to the hydroxy and thereby facilitates insertion. A similar hydrogen-bonding complex has been expected[15] in the case of (carboalkoxy)methylene.

[15] Beard, C. D.; Craig, J. C. *J. Am. Chem. Soc.* **1974**, *96*, 7950.

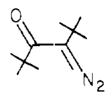
[16] (a) Roth, H. D.; Manion, M. L. *J. Am. Chem. Soc.* **1976**, *98*, 3392. (b) Roth, H. D. *Acc. Chem. Res.* **1977**, *10*, 85.

Table II. Effect of Sensitizer on Product Distributions in the Photolysis[a] of 9 and 13 in Methanol

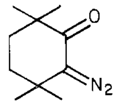
		% yield[b]	
α-diazo ketones	[Ph$_2$C=O], mM	10 or 14	OH insertion (12 or 15)
9	0	96.5	0
	125[c,d]	24.4	2.8
	250[e,d]	9.2	6.1
13	0	75.0	0
	125[c,d]	20.5	7.6
	250[e,d]	14.9	17.7

[a] Irradiations were performed on a 25 mM solution of diazo ketone. [b] Yields were determined by GC and based on diazo ketone used. [c] Irradiated through Pyrex filters. [d] GC analysis of the reaction mixture showed that several minor products were formed, including a double hydrogen abstraction product, e.g., 11. These byproduct were not further characterized but might account for the balance of the products. [e] Irradiated with monochromatic light of 350 nm. More than 98% of the incident light was absorbed under these conditions.

eliminates nitrogen to form a ketocarbene. The suggestions are mainly based on the studies of hindered internal rotation about the carbon–carbon bond in diazo ketones by NMR spectroscopy, in which two distinct peaks have been noted for the diazo methine group at lower temperature. A variable-temperature study of the NMR spectra of diazoacetone has demonstrated[6] that most (>92%) of the molecules exist as the *s-Z* form which leads to the WR product. Photolysis of diazoacetate, in which populations of the *s-Z* and *s-E* forms are shown to be approximately the same, would be expected, then, to result in the formation of the rearrangement and carbene products in a roughly equal ratio, as has been observed. Recently Kaplan et al. have reported[17] further evidence which shows the importance of the role of conformation in the decomposition of α-diazo ketones. Thus, di-*tert*-butyl substituted diazo ketone (7), an *s-E* dominated α-diazo ketone, gives



7



8

mainly the carbene product under thermal, photolytic, and catalytic conditions, whereas photolysis of diazocyclohexanone (8), an *s-Z* locked analogue of 7, results in almost exclusive formation of the ring-contracted ketene. The reluctance of 7 to undergo the WR is a strong argument, but it might just be that di-*tert*-butylketene resists formation in any event. Moreover, the fate of the carbene from 8 was uncertain. Thus, in order to obtain more comprehensive features, we examined the photochemical processes of other α-diazo ketones using quencher and sensitizer. Direct photolysis of diazo ketones (9 and 13) in methanol afforded the esters (10 and 14) resulting from the WR almost exclusively and no intermolecular reaction products, e.g., OH-insertion products, from singlet carbene were detected in each run (eq 2 and 3).

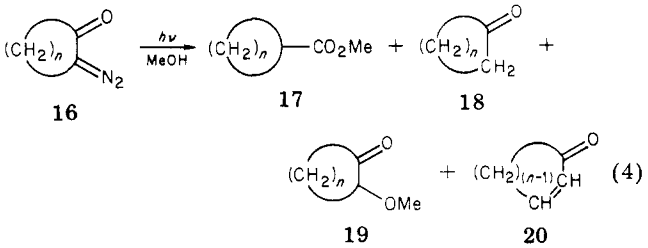
$$\underset{\mathbf{9}}{PhCH_2COCH{=}N_2} \xrightarrow[\text{MeOH}]{h\nu} \underset{\mathbf{10}}{PhCH_2CH_2CO_2Me} + \underset{\mathbf{11}}{PhCH_2COCH_3} + \underset{\mathbf{12}}{PhCH_2COCH_2OMe} \quad (2)$$

$$\underset{\mathbf{13}}{t\text{-}BuCOCH{=}N_2} \xrightarrow[\text{MeOH}]{h\nu} \underset{\mathbf{14}}{t\text{-}BuCH_2CO_2Me} + t\text{-}BuCOCH_3 + \underset{\mathbf{15}}{t\text{-}BuCOCH_2OMe} \quad (3)$$

Since the diazo ketones 9 and 13 have been shown[6] to exist predominantly as *s-Z* conformers, this can be reasonably explained in terms of the concept that the excited singlet state of *s-Z* conformers preferentially undergoes the WR to give ketene. When the irradiation was carried out in the presence of benzophenone as a triplet sensitizer, the WR products were greatly suppressed concomitant with appearance of OH-insertion products (12 and 15) and the double hydrogen abstraction product (11) (Table II). Formation of singlet-derived products (12 and 15) in the sensitized decomposition again implies that free singlet ketocarbene is generated from the initially formed triplet carbene by the intersystem crossing.

Surprisingly, the WR products could not be eliminated in the sensitized photolysis of 9 and 13 even under the conditions where >98% of the incident light is absorbed by the sensitizer. Since the photosensitized decomposition under such conditions circumvents the formation of the excited singlet state, the results strongly suggest[18] that the singlet carbene from 9 and 13 can either rearrange to ketone or undergo insertion into the OH bond of alcohols. Apparently, however, singlet ketocarbene is not involved in the photochemical WR of diazoacetate and diazoacetone. It is reasonable to assume that whether or not the singlet ketocarbene undergoes the WR is dependent upon the migratory aptitude of migrating group as well as the relative efficiency of the other competing reactions available for the singlet carbene. Thus, (carboalkoxy)carbene generated from diazoacetate (1) has a poor migrating group, i.e., RO,[1c] and hence undergoes carbenic reaction almost exclusively, whereas the migrating groups of carbenes from α-diazo ketones (9 and 13) have a much greater tendency[1c] to migrate than the alkoxy group and hence the WR process can effectively compete with the intermolecular carbenic reactions.

It is very important, then, to compare the relative efficiency of intramolecular carbenic reaction with that of the WR from singlet carbene. Photochemical behavior of α-diazocycloalkanones (16) is of special interest in this connection, since these compounds have a methylene group adjacent to the diazo function and hence the singlet carbene from 16 is expected to undergo rapid 1,2 H shift.[19] Direct irradiation of 16, *s-Z* locked molecules, in methanol gave the WR product (17) almost exclusively. Sensitized



a, *n* = 4; b, *n* = 5

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[17] Kaplan, F.; Mitchell, M. L. *Tetrahedron Lett.* **1979**, 759.

[18] There has been evidence to support that singlet ketocarbene undergoes the WR. For example, the intermediate generated from dimethylsulfonium phenacylide behaved very much like that produced by photodecomposition of diazoacetophenone: Trost, B. M. *J. Am. Chem. Soc.* **1966**, *88*, 1587; **1967**, *89*, 138. Moreover, the WR is one of the dominant features in the oxidation of acetylene derivatives, where intervention of a ketocarbene is generally postulated: McDonald, R. N.; Schwab, P. A. *J. Am. Chem. Soc.* **1964**, *86*, 4866; Stille, J. K.; Whitehurst, D. D. *Ibid.* **1964**, *86*, 4871; Ciabattoni, J.; Campbell, R. A.; Renner, C. A., Concannon, P. W. *Ibid.* **1970**, *92*, 3826.

[19] (a) Yamamoto, Y.; Murahashi, S.-I.; Moritani, I. *Tetrahedron* **1975**, *31*, 2663. (b) Chang, K.-T.; Shechter, H. *J. Am. Chem. Soc.* **1979**, *101*, 5082.

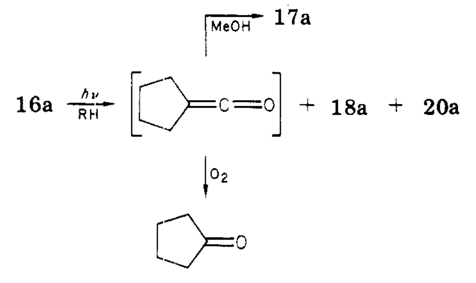
Table III. Photolysis[a] of α-Diazocycloalkanones

α-diazo ketone	solvent	additive	% yield[b] 17	18	19	20	21
16a	MeOH	none	>99	*c*	*c*	*c*	
	MeOH	Ph_2CO[d]	38.3	<1	1.7	1.9	
	PhH[e]	MeOH[f]	2.5	<1		3.3	59.3
	PhH[g]	MeOH[f]	15.9	8.7		1.0	*c*
	PhH[e]	Ph_2CO,[d] MeOH[f]	~1	1.2		3.4	25.5
	CX[e]	MeOH[f]	3.0	4.7		4.7	50.9
	CX[e]	Ph_2CO,[d] MeOH[f]	<1	35.7		2.1	5.7
16b	MeOH	none	>99	*c*	*c*	*c*	
	MeOH	Ph_2CO[d]	37.4	~1	*c*	9.2	

[a] Irradiations were performed on a 25 mM solution of **16**. [b] Yields were determined by GC and based on **16** used. [c] Trace. [d] Irradiated (>355 nm) in the presence of a fivefold excess of $Ph_2C{=}O$. See also footnote *d* in Table II. [e] Nondegassed solvents were used. CX = cyclohexane. [f] Methanol was added in the dark after irradiation. [g] Degassed at $<10^{-4}$ mmHg.

irradiation of **16** afforded cycloalkenone **20** arising from 1,2 H shift in addition to OH-insertion product **19**, but **17** was still formed as the main product even under these conditions (Table III). Accepting that a rapid triplet to singlet interconversion is possible also in this carbene system, these results indicate that the WR from singlet ketocarbene is much more efficient[20] than 1,2 H shift at least in this cyclic system.

Photolysis in Aprotic Media. There is evidence that under certain conditions some diazo compounds are protonated and that therefore the WR takes place in the diazonium ion. For example, nitrogen evolution in diazocyclohexanone (**16a**) was shown[7] to be sensitive to the presence of alcohols and amines. Moreover, Padwa et al. have proposed[21] that diazoacetophenone in alcohol solvent was hydrogen bonded and photodecomposed to a hydrogen-bonded singlet carbene, which then rearranged. In order to examine the involvement of diazonium ion as a possible intermediate in the photochemical WR, we investigated the photolysis of **16a** in aprotic media, i.e., benzene and cyclohexane. Direct photolysis of **16a** in nondegassed benzene followed by addition of methanol in the dark resulted in the formation of cyclopentanone (**21**) as main product along with other minor products including **18a** and **20a** (Table III). Although the expected WR



21

(5)

product (**17a**) was found to be only a minor product under these conditions, control experiments showed that **21** was derived from ketene via rapid photo- and/or autoxidation[22] by dissolved molecular oxygen. When irradiation was carried out in degassed benzene, followed by addition of methanol in the dark, the ester **17** was obtained as the main product. Sensitized irradiation of **16a** in nondegassed benzene also gave cyclopentanone, albeit in lower yield. Similar results were obtained in the photolysis with cyclohexane. The increased yield of **18a** in the sensitized run in this solvent implies intervention of the triplet ketocarbene. These results suggest that free singlet ketocarbene, presumably generated from the initially formed triplet carbene by intersystem crossing, can undergo the WR and that the protonated precursor diazo ketone and/or protonated singlet carbene is not a necessary intermediate in the photochemical WR. The fact that the ester **17** was formed as almost the exclusive product even in the irradiation of **16a** in frozen methanol at −196 °C (vide infra), where the proton-donor activities of alcohols are greatly depressed, also supports the above assumption.

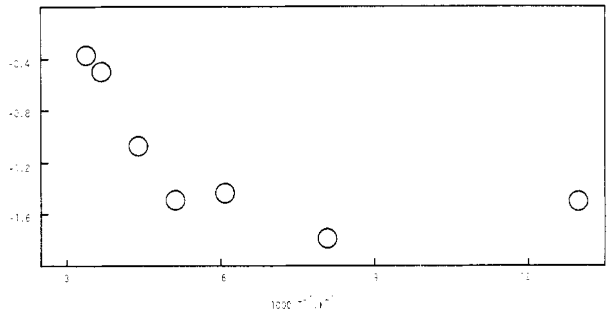


Figure 1. Product distributions as a function of temperature in the photolysis of **1** in 2-propanol.

Effect of Temperature. The primary importance of the ground-state conformation would be established conclusively by studying the influence of temperature upon the product distributions. It has been reported,[23] for example, that photolysis of diazo ketone $RCOC(CH_2R')N_2$ yields the α,β-unsaturated ketone as the major product at room temperature; however, at higher temperature, the ketene rearrangement product is obtained. The results are explained[6] by assuming that the higher energy conformations are more populated as the temperature is raised. Thus, the preference of the *s-E* form at room temperature as a result of steric interaction leads to the α,β-unsaturated ketone. On the other hand, when the temperature is raised, enough energy may be available to overcome steric interaction and give an appreciable amount of *s-Z* form which leads to the rearrangement product. We have also examined the product distributions as a function of temperature in the direct photolysis of diazoacetate in alcohol and the results are shown graphically in Figure 1. As the

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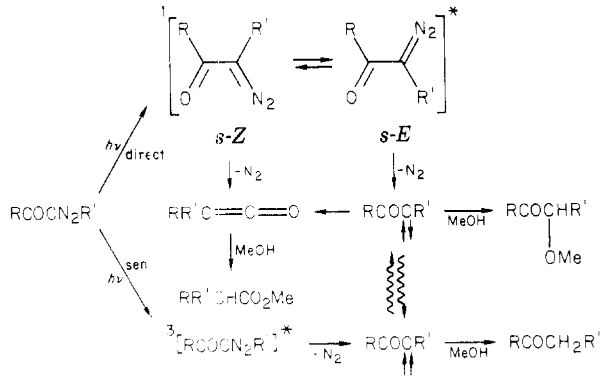
(20) This is in sharp contrast with that observed in the photolysis of the open chain analogue, i.e., methyl diazopropionate, which afforded only methyl acrylate upon direct irradiation: Sohn, M. B.; Jones, M., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 8280. The reluctance of singlet carbene from **16** to undergo H migration might be ascribable, at least in part, to some restriction to the perpendicular orientation of a migrating hydrogen with respect to the empty orbital.

(21) Padwa, A.; Layton, R. *Tetrahedron Lett.* **1965**, 2167.

(22) Turro, N. J.; Chow, M.-F.; Ito, Y. *J. Am. Chem. Soc.* **1978**, *100*, 5580.

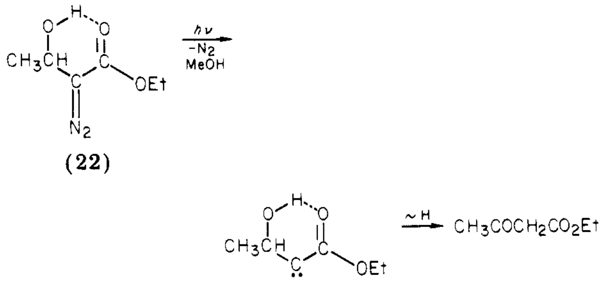
(23) Franzen, V. *Justus Liebigs Ann. Chem.* **1957**, *602*, 199.

Scheme II



temperature is lowered, the rearrangement products (4 and 5) from the *s-Z* conformer decrease whereas the insertion products (2 and 3) of carbene from the *s-E* conformer increase. This could be explained similarly in terms of the effect of temperature upon the population of each conformer. It has been suggested,[24] however, that, for most of the molecules of general formula $RCOCH{=}N_2$, the *s-Z* conformer is preferred to the *s-E* one as a result of steric interaction as well as through space interaction between the carbonyl and the diazo group. That a certain stabilizing effect is present in the *s-Z* conformer is shown by the clear predominance of the *s-Z* species over the *s-E* one (*s-Z*/*s-E* = 7/3) in diazoacetaldehyde, $HCOCH{=}N_2$, where the *s-E* form would have been favored in the absence of a stabilizing effect, as shown by models constructed using van der Waals radii. It would be expected from the suggestion that the WR is favored at lower temperature. Apparent decrease in the WR product at lower temperature can be attributable, then, to a finite activation energy to migration of the alkoxy group which is known[1c,25] to be an inefficient migrating group. Thus, as the temperature is lowered, migration of the alkoxy group becomes less efficient and photochemical and/or thermal conversion of the *s-Z* form to *s-E* form leading to the carbenic products comes to compete effectively with the WR. Although similar temperature studies were also carried out with other α-diazo carbonyl compounds (**9**, **13**, and **16a**), the yield of WR product was not affected at all even in the irradiation in frozen alcohol at −196 °C, indicating that alkyl group migration is too efficient to be suppressed even at this low temperature.

Concluding Remarks. From the data, we propose a reasonable reaction scheme to explain the photochemical processes of α-diazo carbonyl compounds, suggesting that the ground-state conformation plays an important role in the photodecomposition of α-diazo carbonyl compounds and that the photochemical WR takes place directly from the singlet excited state and partly from the singlet ketocarbene (Scheme II). We point out here that the reaction mechanism outlined in Scheme II could be applied to account for the photochemical process of other more complicated polyfunctional diazo compounds. For example, photolysis of α-diazo-β-hydroxybutyrate (**22**) afforded acetoacetate, resulting from 1,2 H shift of the singlet carbene, and no other expected products, e.g., WR and insertion products, were detected under any conditions including sensitized and low-temperature photolytic runs (eq 6). The findings can be rationalized by assuming that **22** is *s-E* locked as a result of intramolecular hydrogen bonding between carbonyl group and hydroxy group. The fact that the infrared absorption band arising from the C=O stretching vibration of **22** is shifted to lower frequency compared to that of the other simple diazo carbonyl compounds implies the presence of such hydrogen bonding. More interestingly, a similar explanation can be used to account for the dependence of product distributions on the structure in the irradiation of diazo phosphoryl compound **23** in alcohol (eq 7). Thus, photolysis of **23** in methanol has been reported[26] to give, in addition to OH-insertion product (**24**) of the phosphoryl carbene, the product (**25**) resulting from the Wolff-type rearrangement followed by nucleophilic trap by methanol, whose ratio is dependent upon the structure of **23**. Irradiation of **23a**, for example, gives phenyl-migration product **25a** almost exclusively, whereas **23b** affords only OH-insertion product **24b** upon irradiation. Obviously, in **23a**, the *s-Z* conformer which is assumed to lead to Ph shift is sterically more stable than the other conformers where the interaction between phenyl and diazo function is more severe. In **23b**, on the other hand, the *s-E* conformer is highly preferred as a result of steric interaction, resulting in a negligible occurrence of the rearrangement process. Similarly, almost exclusive formation of OH-insertion product (**24c**) in the photolysis of **23c**, in spite of appreciable formation of **25d** in a similar irradiation of **23d**, can be attributable to the intramolecular hydrogen bonding in **23c**, which is thus locked in the *s-E* conformer.



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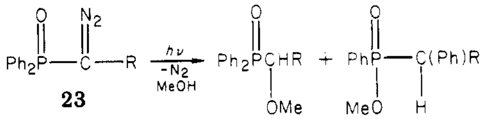
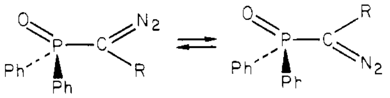


23 24 25 (7)

a, R = H; b, R = Ph; c, R = $CONH_2$; d, R = CO_2Et



s-Z *s-E*

Experimental Section

IR spectra were determined on a JASCO IR-G recording spectrometer. H^1 NMR spectra were determined on a JEOL JNM-MH-100 NMR spectrometer. GC analyses were performed on a Yanagimoto instrument, Model G-180, with a flame-ionization detector. The following columns were used: A, 5.0 mm × 2.0 m 10% OV-17 on 60–80-mesh Diasolid L; B, 5.0 mm × 2.0 m 5% PEG 20M on 60–80-mesh Diasolid L.

Starting Materials. All diazo compounds employed (**1**,[27] **9**,[28] **13**,[28] **16**,[29] **22**[30]) were prepared according to the literature procedure and purified just prior to use. All diazo compounds showed

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satisfactory spectroscopic data. Commercial alcohols, benzene, cyclohexane, and piperylenes were purified by distillation.

Authentic Samples for Identification of Reaction Products. The syntheses of the alkoxyacetates **2–4** and the β-hydroxybutyrate **5** have been published[31] elsewhere. α-Methoxy ketones (**12**, **15**, **19a**, and **19b**) were prepared[32] by treatment of the corresponding α-diazo ketone with boron trifluoride in methanol. Methyl *tert*-butylacetate (**14**) was prepared by esterification of the corresponding acid, obtained[33] by bromoform reaction of neopentyl methyl ketone.[34] Cycloalkylformates (**17**) were obtained from the corresponding cycloalkylformic acids.[35] Satisfactory spectroscopic data have been obtained for all authentic compounds. All other reagents were obtained from commercial sources.

Photochemical Reactions and Analyses. All irradiations were conducted by using a Halos 300-W high-pressure mercury lamp with a water-cooled quartz jacket. In the general procedure, ca. 0.05 mmol of diazo compound was added to 2 mL of solvent in a Pyrex tube of 5-mL capacity. The tube was suspended in a transparent Pyrex Dewar flask fitted with coolant and irradiated until all of the precursor molecule was destroyed. The coolants were water (24 °C), solid CO_2–EtOH (−78 °C), liquid nitrogen–isopentane (−110 and −155 °C), and liquid nitrogen (−196 °C). Control experiments ruled out the interconversion of the products during the irradiation and also showed that no reaction occurred in the absence of light. Product identification and absolute yields were determined by standard GC techniques.

Sensitized experiments were performed with a monochromatic light in the presence of 5–10 molar excess benzophenone so as to assure that >98% of the incident light was absorbed by the sensitizer.

Acknowledgment. Support of this work by the Asahi Glass Foundation is gratefully acknowledged.

Registry No. **1**, 6832-16-2; **2**, 17639-73-5; **3**, 6149-45-7; **4**, 17640-21-0; **5**, 17639-74-6; **6**, 79-20-9; **9**, 4250-02-6; **10**, 103-25-3; **11**, 103-79-7; **12**, 29417-89-8; **13**, 6832-15-1; **14**, 10250-48-3; **15**, 39195-77-2; **16a**, 3242-56-6; **16b**, 18202-04-5; **17a**, 4630-80-2; **17b**, 4630-82-4; **18a**, 108-94-1; **18b**, 502-42-1; **19a**, 7429-44-9; **19b**, 1121-18-2; **20a**, 930-68-7; **20b**, 1121-66-0; **21**, 120-92-3; 2-propanol, 67-63-0; methanol, 67-56-1.

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Nonconvergent Cycloaddition Pathways for Thermal vs. Photochemical Reaction of *N*-Isobutenylpyrrolidine with Dimethyl Fumarate

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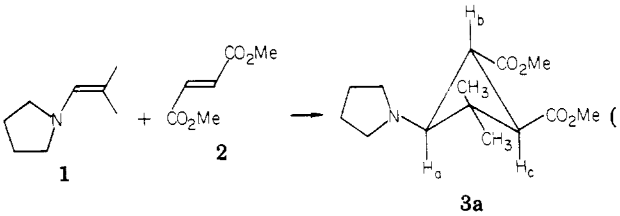
The thermal reaction of the title compounds proceeds via a reversibly formed 1,4-zwitterion intermediate to yield the thermodynamically most stable [2 + 2] cycloadduct. The rate of the thermal reaction is substantially faster in moderately polar vs. nonpolar solvent. In contrast, the photochemical reaction of the title compounds occurs only in nonpolar solvent and yields a stereoisomer of the thermal adduct. Photochemical cycloaddition is not observed for several other α,β-unsaturated esters and enamines. The mechanism of the photochemical reaction and the failure to observe photochemical ionic [2 + 2] cycloaddition are discussed.

Thermal [2 + 2] cycloaddition reactions are known to occur via concerted $[_\pi 2_s + {}_\pi 2_a]$, stepwise-biradical, and stepwise-zwitterionic mechanisms. Photochemical concerted $[_\pi 2_s + {}_\pi 2_s]$ and stepwise-biradical (singlet and triplet) cycloaddition reactions are also well-known; however, there is at present no bona fide example of a photochemical zwitterionic [2 + 2] cycloaddition reaction. Epiotis and Shaik[1] recently predicted the occurrence of photochemical ionic $[_\pi 2_s + {}_\pi 2_s]$ cycloadditions and noted the absence of examples. In an attempt to obtain experimental evidence for ionic photochemical cycloaddition, we have investigated the photochemical reactions of several enamines with α,β-unsaturated esters. Previous investigations have established the formation of a zwitterionic intermediate in the thermal cycloaddition reaction between these classes of alkenes.[2,3] We report that the cycloaddition of *N*-isobutenylpyrrolidine (**1**) and dimethyl fumarate (**2**) can be effected either thermally or photochemically and that a zwitterionic intermediate is formed in the thermal but not in the photochemical reaction.

Results

Mixing of **1** and **2** in dry acetonitrile results in formation of a yellow charge-transfer complex (Figure 1), which slowly fades to yield a colorless solution from which the adduct **3a** can be isolated (eq 1). The structure **3a** is assigned on the basis of spectral data. Mass spectral fragmentation of **3a** yields predominantly the two possible aminum radical retro [2 + 2] fragments (eq 2). The stereochemistry of **3a** is assigned on the basis of the large



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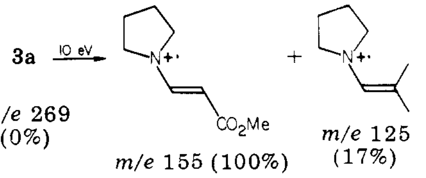

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