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Photolysis of α-Diazo Ketones in the Gas Phase Monitored by Fourier Transform Infrared Spectrometry

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3-Diazo-2-butanone (1), 2,2,5,5-tetramethyl-4-diazo-3-hexanone (2), and 2-diazocyclohexanone (3) were photolyzed in the gas phase at low pressure. The course of the reactions was followed by FT IR spectroscopy. The Wolff rearrangement occurred to an extent of 70% for 1 and of about 40% for 2; the resulting ketenes were respectively somewhat photolabile and photostable. The ketene from 3 was quite unstable to photolysis, although it could be identified in the early part of the reaction. For irradiations at the laser line λ = 457.9 nm, the ratio of photolysis rates k_1/k_2 was at least 300, which suggests a concerted mechanism for the rearrangement of 1. Photolysis of 1 in the presence of argon to increase intermolecular collisions raised the production of dimethylketene to over 95%. In contrast, the Wolff rearrangement of 2 occurred in the gas phase but not in solution. The gas-phase reaction path may have its origin in the excited vibrational states of an electronic isomer of 2 or in those of the corresponding carbene.

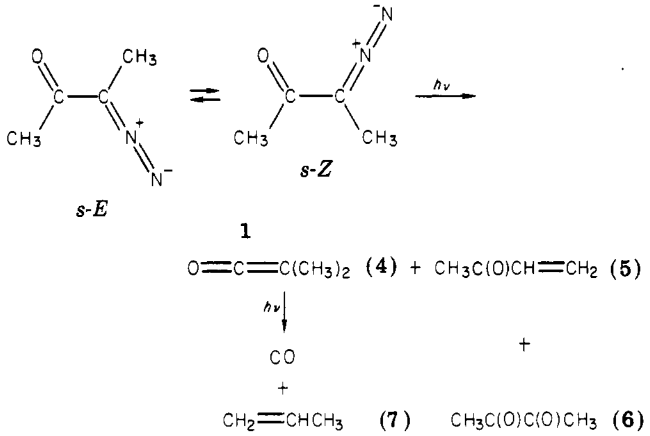
α-Diazo ketones, $R_1COC(N_2)R_2$, are known to undergo the Wolff rearrangement to ketenes, $R_1R_2C{=}C{=}O$, under photolytic or thermolytic conditions. The ketenes are often not isolated but rather identified through their addition products such as esters. Studies of the rearrangement of α-diazo ketones locked into specific conformations have suggested that these rearrangements are subject to conformational control.[1] Thus, photolysis of 3,3,6,6-tetramethyl-2-diazocyclohexanone, which is locked into an *s-Z* conformation, in CCl_4 or dioxane solution produced the Wolff rearrangement product 2,2,5,5-tetramethylcyclopentanone in 96% yield, whereas photolysis of 2,2,5,5-tetramethyl-4-diazo-3-hexanone, which is locked into an *s-E* conformation, in CCl_4, dioxane, or $Cl_2C{=}CCl_2$ gave 2,2,4,5-tetramethyl-4-hexen-3-one in 78% yield and none of the Wolff rearrangement product di-*tert*-butylketene.[1]

The photolysis of α-diazo ketones most likely proceeds from the excited vibrational states of their singlet electronic isomers.[2] From these states, competition can occur between photolysis and the collisional deexcitation of the molecules in the gas phase. The activation of these vibrational cascades by an increase in the frequency of intermolecular collisions may change the relative proportions of the reaction paths. Because of the importance of the hypothesis of conformational control, we felt that the gas-phase photochemistry of α-diazo ketones should be studied.

We have investigated the photolyses of 3-diazo-2-butanone (1), 2,2,5,5-tetramethyl-4-diazo-3-hexanone (2), and 2-diazocyclohexanone (3) in the gas phase at low pressures. The reactions were monitored by FT IR spectroscopy, enabling us to identify the principal reaction products and to follow their rates of formation. The products formed in the photolysis of 1 have been studied previously by mass spectroscopy.[3]

Photolysis of 3-Diazo-2-butanone (1). Irradiation of 1 at a pressure of 7 torr was carried out with polychromatic (λ ≥ 290 nm) and with monochromatic (λ = 457.9 nm) light. The products identified by IR are shown in Scheme I,[4] and their mole fractions as a function of irradiation time are shown in Table I.

Scheme I



A PQR absorption band with a Q branch at 2134 cm^{-1} (Figure 1A) was assigned to the $\nu_a(C{=}C{=}O)$ vibration of ketene 4, the IR spectrum of which has been described previously.[5] A set of vibrational-rotational lines superimposed on this absorption band was assigned to carbon monoxide. When the irradiation was conducted at 457.9 nm, only traces of CO were observed. In the reaction mixtures from irradiations at λ ≥ 290 nm, propene (7) was identified by its strong Q branch at 912 cm^{-1}, belonging to the vibrational-rotational band corresponding to the $\nu_{19}A''$ (γ-CH_2) mode.[6]

The photolysis of ketene 4 was investigated independently by irradiating a mixture of 4 (80%), 5 (18%), and 7 (2%) at λ ≥ 220 nm (see Experimental Section). The intensities of absorptions of 7 and CO increased in parallel as 4 disappeared. Reaction mixtures from the irradiation of 1 at 457.9 nm had IR spectra with two intense vibrational-rotational bands at 1703 and 951 cm^{-1}, each with a double Q branch, ascribed to the unsaturated ketone 5. When the irradiation was conducted at λ ≥ 290 nm, the spectra presented a more complex profile in the range

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(2) (a) Pacansky, J. *Polym. Eng. Sci.* **1980**, *20*, 1049. (b) Bargon, J.; Tanaka, K.; Yoshimine, M. In "Computational Methods in Chemistry"; Bargon, J., Ed.; Plenum: New York, 1980; p 239.

(3) Fenwick, J.; Frater, G.; Ogi, K.; Strausz, O. P. *J. Am. Chem. Soc.* **1973**, *95*, 124.

(4) The choice of $>C{=}N^+{=}N^-$ as the formula of the diazo group may be justified by the recent calculation of a structural weight of 0.40 of this mesomeric formula for diazoalkanes; among the seven other formulas, the next ones are $>\dot{C}{-}N{=}N\cdot$ and $>C^-{-}N^+{\equiv}N$ with structural weights of 0.29 and 0.16, respectively: Hiberty, P. C.; Ohanessian, G. *J. Am. Chem. Soc.* **1982**, *104*, 66.

(5) Fletcher, W. H.; Barish, W. B. *Spectrochim. Acta* **1965**, *21*, 1647.

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0022-3263/83/1948-0533$01.50/0

Table I. Gas-Phase Photolysis of 3-Diazo-2-butanone

	time^a for $\lambda \geqslant 290$ nm						time^a for $\lambda = 457.9$ nm			
parameter	0	1	2	3	6	10	0	30	60	80
% of 1^b	100^d	76	55	39	17	3	100	47	9	
mole fraction of 4^c		0.51	0.51	0.51	0.48	0.51		0.77	0.78	0.75
mole fraction of 5^c		0.17	0.17	0.18	0.21	0.19		0.20	0.18	0.19
mole fraction of 6^c		0.11	0.11	0.11	0.12	0.12				
mole fraction of 7^c		0.21	0.21	0.20	0.19	0.18		0.03	0.04	0.04

^{a} Irradiation time in minutes. ^{b} Percentage of the remaining α-diazo ketone. ^{c} Mole fractions of the reaction products. ^{d} The initial pressure was 7 torr.

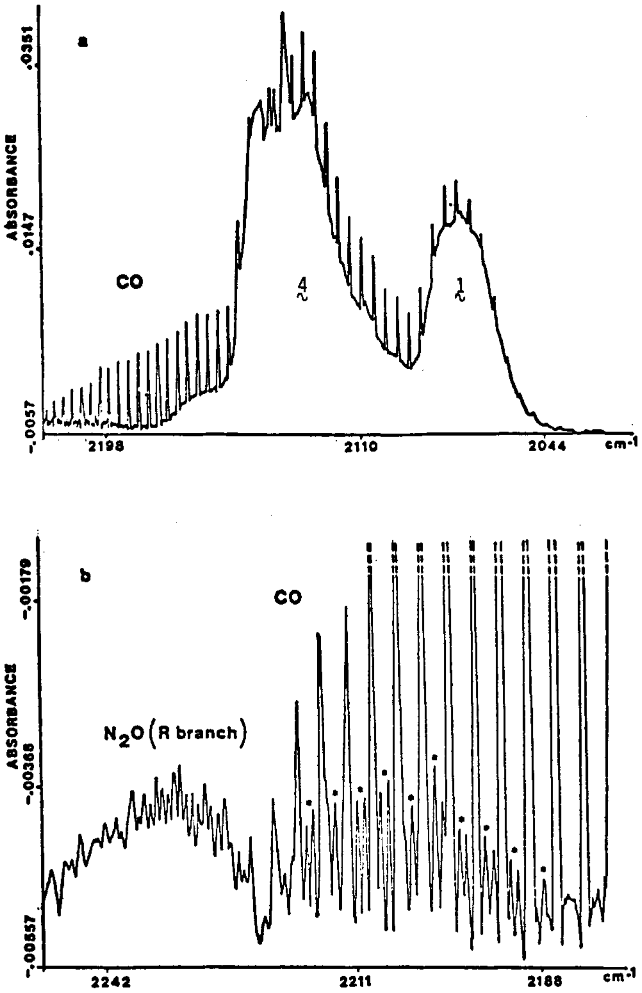

Figure 1. IR spectrum of the gas-phase reaction mixture from the photolysis of 3-diazo-2-butanone (1) after irradiation for 5 min at λ ≥ 290 nm: (a) the absorption bands of 1 and 4 and the set of vibrational–rotational lines of carbon monoxide; (b) vibrational–rotational lines of nitrous oxide (asterisked peaks for P branch) which appear at the base of the spectrum.

1800–1600 cm^{-1}, arising from the superposition of the ν(C=O) vibrational–rotational envelopes of 5 and 6, which had been recombined to fit exactly the spectra of the reaction mixtures. The proportions of these two compounds were readily determined through this procedure. Traces of N_2O were also detected in these reaction mixtures. Identification was made through the fine structure of the PR band,[7] centered at 2223 cm^{-1} and corresponding to the ν_3A vibration of N_2O; the P branch lines of N_2O were inserted between the stronger R branch lines of CO (Figure 1B).

In an earlier study of the gas-phase photolysis of 1 by Strausz et al.,[3] ethanal and propanal were found in the reaction products. Our reaction mixture spectra showed no absorption in the range 1800–1750 cm^{-1}, indicating the absence of these aldehydes, which show R branches at 1761 cm^{-1} for ethanal[8] and at 1763 cm^{-1} for propanal.[9] We believe that these aldehydes arose from the propanol that was present in equimolar amount with the 1 irradiated by Strausz et al. and was absent from our sample of 1. Moreover, Strausz et al. did not observe ketene 4, but only its products 7 and CO. They did not find any 6 but did find 2-butyne as a minor product. These differences probably reflect the fact that Strausz et al. condensed their reaction products and analyzed them by ionization in a mass spectrometer, conditions that are not favorable for the detection of unstable compounds such as 4. On the other hand, our IR spectroscopic method would not detect small quantities of 2-butyne.

The results in Table I show that either excitation of several singlet electronic isomers (λ ≥ 290 nm) or the selective excitation of the S_1 isomer (λ = 457.9 nm) produced a 4:1 ratio of the two reaction paths, one being the Wolff rearrangement with formation of 4 and 7 and the other leading to 5. This result is in agreement with the very short lifetimes (10^{-12}–10^{-14} s)[10] of the S_n ($n > 1$) electronic isomers; the corresponding processes are $S_n \rightarrow S_1$. It appears that the photolysis of 1 proceeds from the S_1 electronic isomer regardless of the irradiation conditions.

We were able to increase the proportion of Wolff rearrangement to more than 95% by irradiating a gaseous mixture of 1 (7 torr) and argon (1 bar) at 457.9 nm. These conditions increase the intermolecular collisions, shorten the lifetimes of the vibrational excited states of S_1, and are unfavorable to processes that have their origin in these states. Therefore, the Wolff rearrangement of 1 seems to be the only reaction path that has its origin in the lowest vibrational state of the S_1 electronic isomer.

Photolysis of a gaseous 1:20 mixture of 1 and methanol at λ ≥ 290 nm yielded ketene 4 in the same quantity and time as in photolysis of pure 1. We could not identify other reaction products from their IR spectra. Although the common hypothesis about the mechanism of the Wolff rearrangement involves formation of a carbene in the first step,[11] such an intermediate would have been trapped, at least in part, by the excess methanol. However, because the amount of ketene formed did not change, we suggest that the rearrangement occurs by a concerted mechanism, with methyl migration concomitant with the breaking of the carbon–nitrogen bond.

The various reaction mixtures from photolysis of 1 were kept at room temperature for several hours without any

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[7] Herzberg, G. "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules"; Van Nostrand: New York, 1954; p 384.

[8] Evans, J. C.; Bernstein, H. J. *Can. J. Chem.* **1956**, *34*, 1083.

[9] Worden, E. F. *Spectrochim. Acta* **1962**, *18*, 1121.

[10] Arnold, D. R.; Baird, N. C.; Bolton, J. R.; Brand, J. C. D.; Jacobs, P. W. M.; de Mayo, P.; Ware, W. R. "Photochemistry, An Introduction"; Academic Press: New York, 1974; p 99.

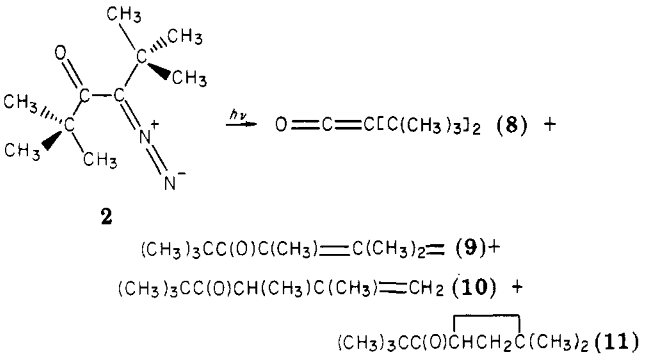
[11] The interconversion of carbenes R_1–CO–$\ddot{C}$–R_2 and R_1–$\ddot{C}$–CO–R_2 has been proven through isotope scrambling,[3] but the hypothesis of an oxirene intermediate has recently been challenged: Ogawa, Y.; Sawaki, Y.; Ohno, T. *J. Am. Chem. Soc.* **1982**, *104*, 216.

Table II. Gas-Phase Photolysis of 2,2,5,5-Tetramethyl-4-diazo-3-hexanone (λ ⩾ 290 nm)

time[a]	0	5	15	25	35	45	55	65	75	95
% of 2[b]	100	91	61	39	22	13	8	5	3	1
mole fraction of 8[c]		0.41	0.39	0.38	0.38	0.38	0.38	0.37	0.37	0.38

[a] See Table I, footnote *a*. [b] See Table I, footnote *b*. [c] Mole fractions of 8 with respect to α-diazo ketone consumed. These were estimated by assuming that the molar extinction coefficient of the ketene absorption band of 8 is the same as that of 4.

Scheme II



significant change in composition except for the experiment with methanol. In this case, 4 disappeared after 12 h; the simultaneous increase in an IR absorption band at 1761 cm^{-1} is attributed to the ester i-$C_3H_7CO_2CH_3$, formed by addition of methanol to ketene 4.

Photolysis of 2,2,5,5-Tetramethyl-4-diazo-3-hexanone (2). The experiments were conducted under the conditions used for the photolysis of 1. Irradiation of 2 at 457.9 nm for 6 h did not induce any reaction. Because the sensitivity limit of our IR technique was about 3% for a change in concentration, we estimate a ratio of photolysis rates as $k_1/k_2 \geq 300$. This difference in rates cannot be explained on the basis of molar extinction coefficients (ϵ), which are 20 and 26 L mol^{-1} cm^{-1}, respectively, for 1 and 2 at 415 nm. Again we suggest that a concerted mechanism governs the photolysis of 1.

The difference between the reactivities of 1 and 2 decreased notably when the irradiations were performed at $\lambda \geq 290$ nm. Here the ratio of photolysis rates was $k_1/k_2 = 10$, which must be offset by the difference in molar extinction coefficients: $\epsilon(1) = 8400$ and $\epsilon(2) = 2900$ L mol^{-1} cm^{-1} at $\lambda = 285$ nm.

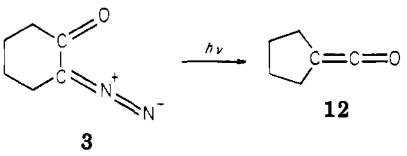
The reaction mixtures from gas-phase photolysis of 2 had IR spectra with an absorption band centered at 2100 cm^{-1}, which is attributed to 8 (Scheme II).[12] From the intensity of this band, we estimated the concentration of 8 by assuming equality of the molar extinction coefficients of the ν_a(C=C=O) band of 4 and 8. Table II gives the results at different reaction times and shows that the proportion of 8 among the reaction products is about 40% and that it does not change as the reaction proceeds. Three other reaction products that were identified from the photolysis of 2 in solution[1] are shown in Scheme II.[13]

Table III. Photolysis of 2 in Solution

irradiation λ, nm	solvent	products[a] 9	10	11
λ ⩾ 290[b]	THF	0.85	0.03	
454 ⩽ λ ⩽ 514[c]	CCl_4	0.81	0.03	0.16
λ ⩾ 290[d]	CCl_4 (+O_2)[e]	0.87	0.08	0.05
λ ⩾ 290[d]	CCl_4 (+N_2)[e]	0.70	0.25	0.05

[a] Mole fractions of the reaction products. [b] Reference 22. [c] Reference 1. [d] This work. [e] The gas was bubbled into the solution before irradiation.

Scheme III



The IR spectra of the reaction mixtures had a strong absorption band at 1700 cm^{-1}, but it was not possible to distinguish among the contributions of the reaction products 9–11 to this absorption. Two other possible reaction products, 2,2,5,5-tetramethyl-3,4-hexanedione and 2,2,4,4-tetramethyl-3-pentanone, are excluded because their strong absorption bands at 898 and 978 cm^{-1}, respectively, are missing from the IR spectra of the reaction products.

The gas-phase photolysis of 2 gave very small amounts of CO; as the reaction time was 7 times that of the photolysis of 1, ketene 8 appears to be more stable than 4. As we had observed for 1, the gas-phase photolysis of 2 at $\lambda \geq 290$ nm gave traces of N_2O. Its concentration increased when small amounts of air were admitted to the gas cell before irradiation.

Previous photolyses of 2 in CCl_4 solution at $454 \leq \lambda \leq 514$ nm[1] and in THF solution at $\lambda \geq 290$ nm[22] gave neither a ketene nor its products. As shown in Table III, we got similar results by photolysis of 2 in CCl_4 solution at $\lambda \geq 290$ nm in the presence of either nitrogen or oxygen. In contrast, we found that large amounts of ketene 8 are formed in the gas-phase photolysis of 2. Apparently, conformational control is not operating in the gas phase.

Photolysis of 2-Diazocyclohexanone (3). Owing to the low vapor pressure of 3, it was necessary to heat the reaction cell to 70 °C at 10^{-5} torr to attain a concentration of 7×10^{-6} mol L^{-1} in the gas phase. At this temperature the rate of thermal decomposition was low enough to permit study of the photolytic reaction without significant interference from the thermal reaction.

The principal reaction product was identified as ketene 12 (Scheme III), whose ν_a(C=C=O) envelope was centered at 2124 cm^{-1}. Its concentration in the reaction mixture first increased to 23% of the initial concentration of 3 and then decreased to zero. Ketene 12 appears to be the only reaction product formed directly from 3, and it is destroyed at a rate about 3 times that of the initial reaction. The data reported in the Experimental Section are consistent with this hypothesis. Moreover, the reaction mixtures did not show any IR absorption band at 1670 cm^{-1}, indicating absence of 2-cyclohexenone, the elimination product. The

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[12] Corresponding to the vibrational mode ν_a (C=C=O), this absorption is at a lower frequency ($\Delta\nu$ = 34 cm^{-1}) than that of 4 according to the ν(C=O) frequency shift ($\Delta\nu$ = 31 cm^{-1}) of the corresponding ketones ($((CH_3)_3C)_2C$=O and $(CH_3)_2C$=O in the gas phase.

[13] Only one conformer of 2 is shown on Scheme II. This may be justified by an approximate value of 4 kcal mol^{-1} for the free energy difference between the *s-Z* and *s-E* conformers. This value corresponds to the difference between the steric interaction of the cis *tert*-butyl groups in the *s-Z* conformer and the two 1,3-syn interactions experienced by the carbonyl and the diazo groups with methyl groups. For the first of these interactions, we may refer to the example of di-*tert*-butylethylene isomers with $G°_Z - G°_E$ = 9.5 kcal mol^{-1}: Turner, R. B.; Nettleton, D. E.; Perelman, M. *J. Am. Chem. Soc.* **1958**, *80*, 1430. Each of the last two interactions may be estimated to 2.5 kcal mol^{-1}, the value of a 1,3-syn interaction between a cyano and a methyl group: Tichý, M.; Orahovats, A.; Sicher J. *Collect. Czech. Chem. Commun.* **1970**, *35*, 459.

independent photolysis of **12** gave products that were not identified except for traces of CO. Two IR absorption bands appeared at 1713 and 1600 cm^{-1}, but their intensities were too low for bands of principal reaction products. Some products may have been removed from the gas phase by condensation.

Our results are in agreement with previous observations that the Wolff rearrangement is almost the only reaction path for photolysis of 2-diazocyclohexanones. Irradiation of **3** in methanol solution at $\lambda \geq 290$ nm gave 99% of methyl cyclopentanecarboxylate, the addition product of methanol to **12**.[14] It was reported that irradiation of 3,3,6,6-tetramethyl-2-diazocyclohexanone in CCl_4 solution at $454 \leq \lambda \leq 514$ nm gives the corresponding ketene in 96% yield.[1]

For irradiations of **1** and **3** in the gas phase at $\lambda \geq 290$ nm, the ratio of the photolysis rates k_3/k_1 is 1.3. As the molar extinction coefficients of these compounds are very alike, their reactivities are similar, but they are both more reactive than **2**. If a concerted mechanism governs the photolyses of **1** and **3**, it may be that the propensity of **3** to be in a pure *s-Z* conformation[15] counterbalances the difficulty of ring contraction.

Discussion

Our results support the hypothesis that the Wolff rearrangement in the photolysis of **1** proceeds by a concerted mechanism, at least when the irradiation is performed at 457.9 nm. Because each of the conformers of an α-diazo ketone has its own electronic isomer, the concerted mechanism must be associated with a specific conformer. We believe this to be the *s-Z* conformer, which can allow methyl migration to be concomitant with loss of nitrogen.

A second important result is the occurrence of a Wolff rearrangement in the gas-phase photolysis of **2**. This result is inconsistent with the conformational control suggested[1] by the absence of ketene **8** from the products of photolysis conducted in solution. Accordingly, the reaction path that leads to ketene **8** may have its origin in the excited vibrational states of the S_1 electronic isomer of **2** and/or in those of the corresponding carbene.

In the gas-phase photolysis of **1**, the increase in collisional deexcitation of the excited vibrational states has an opposite effect on the selectivity of the Wolff rearrangement, which increases with increasing pressure. We suggest that this behavior is typical of a concerted mechanism.

Two minor reaction products, **6** in the photolysis of **1** and N_2O in photolyses of **1** and **2** at $\lambda \geq 290$ nm, must have arisen from adventitious traces of oxygen in the photolysis cell. The reaction that leads to **6** must resemble that in the photolysis of $C_6H_5COC(N_2)C_6H_5$ at 77 K, which gives from 0% to 12% $C_6H_5COCOC_6H_5$ in the presence of increasing concentrations of oxygen; the intermediate trapped by oxygen should be the carbene in its triplet state.[16]

The transformation of a diazoalkane, $R_1R_2C{=}N^+{=}N^-$, into the corresponding ketone, $R_1R_2C{=}O$, has been explained as involving cycloaddition of O_2 in the first step, leading to a 1,2-dioxa-3,4-diazole derivative.[17] Although the cleavage of such an unstable intermediate might give the ketone and N_2O, the latter has not been detected. For reactions of α-diazo ketones, such a hypothesis would establish a link between the two oxidation products. However, photolysis of **1** gave a much larger amount of **6** than of N_2O, and we never observed 2,2,5,5-tetramethyl-3,4-hexanedione from the photolysis of **2**, which gave more N_2O than was formed from **1**.

Nitrous oxide could originate from the cleavage of a 1,2,3-oxadiazole derivative, which is the valence isomer of an α-diazo ketone.[18] Such a reaction should also produce an alkyne, $R_1C{\equiv}CR_2$. The reverse reaction, a cycloaddition, is surely involved as a first step in the reaction of N_2O with alkynes at high pressure (100–500 bars) and high temperature (200–300 °C);[19] the subsequent steps would be valence isomerization to an α-diazo ketone, Wolff rearrangement to a ketene, and addition of an alcohol. The products were esters $R_3OCOCHR_1R_2$, obtained in 80% yields. Owing to the related features of these reverse reactions, it would be useful to establish, by isotopic labeling, the origin of the oxygen atom of the N_2O produced in this side reaction of the gas-phase photolysis of α-diazo ketones.

Experimental Section

3-Diazo-2-butanone (1). This compound was prepared according to Muchowski method[20] by passing a methylene chloride (freshly purified)[21] solution of the mono-*p*-toluenesulfonylhydrazone of 2,3-butanedione through a cooled column filled with basic alumina (pH 9.5). The solvent was removed to afford the crude α-diazo ketone in 84% yield. Purification was performed by distillation: bp 22 °C (1 torr); ^1H NMR (CCl_4) δ 2.00 (3 H,s), 2.20 (3 H,s); IR (gas) 2078 (R), 2073 (Q), 2069 (P), 1682 (R), 1675 (Q), 1670 (P), 1328 (R), 1323 (Q), 1308 (R), 1302 (P) cm^{-1}; UV–vis[22] (gas) 280, 420 nm.

2,2,5,5-Tetramethyl-4-diazo-3-hexanone (2). The oxidation of the monohydrazone of pivaloin was carried out by the method of Newman and Arkell.[23] The yield of crude product was 80%, and several distillations were performed at room temperature (0.3 torr) to get purified material: ^1H NMR (CCl_4) δ 1.17 (9 H, s), 1.23 (9 H, s); IR (gas) 2062, 1648, 1303 cm^{-1}; UV–vis[1] (gas) 294, 425 nm.

2-Diazocyclohexanone (3). The Muchowski method[20] was used. The mono-*p*-toluenesulfonylhydrazone of 1,2-cyclohexanedione (10 g) dissolved in 100 mL of a 50:50 solvent mixture of CH_2Cl_2 and CH_3OH was passed two times through a column filled with 100 g of basic alumina. After removal of the solvents, 3.7 g of **3** was collected (88% yield). Purification was performed by distillation: bp 68 °C (1.5 torr);[22] IR (gas) 2090, 1643, 1341, 1302 cm^{-1}; UV–vis, see ref 22.

Photolysis Experiments. Before the admission of the α-diazo ketone, the IR gas cell (10-cm length) equiped with KBr windows was pumped to 10^{-5} torr. The gas-phase concentrations were 10^{-4}, 10^{-5}, and 7×10^{-6} mol L^{-1}, respectively, for **1**–**3** as estimated through the absorbance of the $\nu_a(C{=}N{=}N)$ IR band. The irradiations were conducted by using either a mercury lamp with a water-cooled Pyrex jacket ($\lambda \geq 290$ nm) or a spectral line of an ionized argon laser ($\lambda = 457.9$ nm). The data are reported in Tables I–III.

Photolysis of 4. The gas mixture obtained after irradiation of **1** at $\lambda = 457.9$ nm was further photolyzed with polychromatic light ($\lambda \geq 220$ nm) from a high-pressure mercury lamp with a quartz envelope. After 0, 5, 30, 90 and 150 min of irradiation, the molar fractions were as follows: **4** (0.80, 0.74, 0.65, 0.42, 0.25), **5** (0.18, 0.19, 0.21, 0.25, 0.24), **7** (0.02, 0.07, 0.14, 0.39, 0.51).

Photolysis of 3. Irradiation of **3** in the gas phase at $\lambda \geq 290$ nm gave after 0, 1, 2, 3, and 4 min, respectively, the following concentrations ($\times 10^6$ mol L^{-1}): **3** (7, 4, 2.4, 1.3, 0.8), **12** (0, 1.6, 0.2, 0.2, 0.1). Two consecutive first-order reactions were postulated[24] to account for these results.

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IR Spectroscopy. The IR spectra of the α-diazo ketones, of the reaction mixtures, and of certain authentic reaction products were recorded in the gas phase and in solution (CCl_4) with a FT IR spectrometer (Nicolet 7199) equiped with an MCT detector in the range 4000–400 cm^{-1}. For certain IR absorption bands of **1** and **5–7** in the gas phase the molar extinction coefficients (L mol^{-1} cm^{-1}) were directly determined through the Beer–Lambert law; the concentrations were estimated from the pressure in the IR cell, easily measured for these compounds: **1**, 2073 cm^{-1} (ε 544); **5**, 948 cm^{-1} (ε 55); **6**, 1723 (ε 222), 1733 cm^{-1} (ε 257); **7**, 912 cm^{-1} (ε 323).

For **4**, the molar extinction coefficient was determined indirectly from the experimental spectrum recorded in the gas phase by Fletcher and Barish:[5] 2130 cm^{-1} (ε 593). The same value was used for **8** and for **12**. Owing to the low vapor pressure of **2** and of **3**, their gas-phase concentrations were estimated indirectly from the comparison of their IR spectra in the gas phase and in solution by using Hirota's formula.[25] The molar extinction coefficients were evaluated for the gas phase: **2**, 2062 cm^{-1} (ε 732); **3**, 2090 cm^{-1} (ε 449).

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Registry No. **1**, 14088-58-5; **2**, 51884-33-4; **3**, 3242-56-6; **4**, 598-26-5.

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Sulfonamidyls. 5. Electron Spin Resonance Spectroscopic Evidence for Four- and Five-Membered-Ring Sulfonamidyls and Sulfonyl Nitroxides

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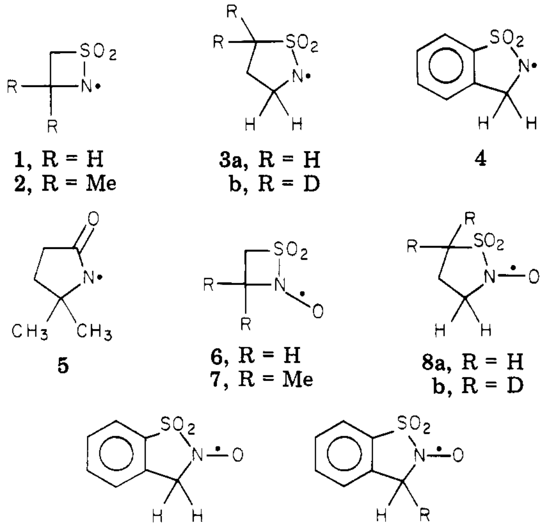
Cyclic sulfonamidyl radicals, generated by photolysis of the *N*-bromo (or *N*-chloro) β- and γ-sultams **1–3** and of *N*-bromo-2,3-dihydro-1,2-benzisothiazole 1,1-dioxide (**4**) have been characterized by solution ESR studies. The nitrogen and β hyperfine splitting constants of **1–4** are in agreement with a Π_N electronic ground state involving a planar geometry around the nitrogen free radical center. The corresponding nitroxides (**6–9**) were generated from **1–4** by reaction with nitrogen dioxide. In the same way, four additional sulfonyl nitroxides (**10–13**), derived from 3-alkyl-1,2-thiazoline 1,1-dioxide systems, were generated and studied by ESR. The possible geometry around the nitroxide nitrogen atom and further conformational implications are discussed.

The question of the electronic configuration of carboxamidyl ($R_1CO\dot{N}R_2$) and sulfonamidyl ($R_1SO_2\dot{N}R_2$) radicals has been the subject of several recent investigations both by electron spin resonance (ESR) spectroscopic methods[1-3] as well as by ab initio MO quantum chemical calculations.[4] There is now general agreement that both types of amidyls reside in rather similar electronic ground states. However, the quantum mechanical results[1b] revealed a significant difference. Whereas the ground state of sulfonamidyls is a Π_N state well-separated from the Σ_N configuration, there is evidence that the ground state of carboxamidyls is a composite of configurations which in a planar geometry would be called Π and Σ. In particular a bent Σ_N state may contribute significantly. Recent results obtained by Ingold and co-workers[2d] are also suggestive for a tendency of the carboxamidyls to adopt a twisted geometry, involving a contribution of the Σ_N state. Furthermore, the

Chart I



1, R = H
2, R = Me

3a, R = H
b, R = D

4

5

6, R = H
7, R = Me

8a, R = H
b, R = D

9

10, R = Me
11, R = *n*-Bu
12, R = *i*-Pr
13, R = cyclopentyl

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