Diaziridines. 2. Isomerization of *N*-Carbamoyldiaziridines

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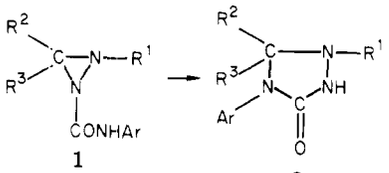
Elucidation of the thermal isomerization products **2** of *N*-carbamoyldiaziridines **1** by X-ray crystallography and ^{13}C NMR spectroscopy has shown that they have triazolidinone ring structures. In accordance with the triazolidinone structure, **2** gives the same semicarbazide as the corresponding **1** on hydrolysis.

In a previous paper,[2] it was reported that 1-cyclohexyl-2-(phenylcarbamoyl)-3-methyl-3-phenyldiaziridine (**1a**) isomerized to a higher melting compound on heating at 100 °C for a short period. We tentatively assigned the triazolidinone structure **2a** on the basis of spectroscopic analyses. We have now confirmed the structure of **2**

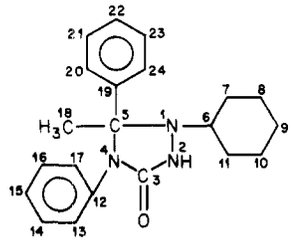


1 **2**

a, $R^1 = C_6H_{11}$; Ar = Ph; R^2 = Ph; R^3 = Me; **b**, R^1 = *n*-Bu; Ar = Ph; R^2 = Ph; R^3 = Me; **c**, $R^1 = C_6H_{11}$; Ar = *m*-chlorophenyl; R^2 = Ph; R^3 = Me; **d**, $R^1 = C_6H_{11}$; Ar = *p*-chlorophenyl; R^2 = Ph; R^3 = Me; **e**, $R^1 = C_6H_{11}$; Ar = *p*-methoxyphenyl; R^2 = Ph; R^3 = Me

unambiguously. This paper describes the ^{13}C NMR spectroscopy and the X-ray crystallography of **2**. Mention is also made of the hydrolysis of **2** and some of the related compounds.

The proton decoupled ^{13}C NMR spectrum of **2a** (Me_2SO-d_6) gave seven peaks corresponding to eight sp^3 carbons in the region between 19.2 and 83.9 ppm, seven peaks of 12 aromatic carbons between 124.4 and 144.7 ppm, and one peak of one carbonyl carbon at 158.7 ppm (Table I). The single frequency off-resonance decoupling experiments (sford) were used to determine the number of the protons attached to each carbon, and the results are also shown in Table I. The peak at 83.9 ppm (singlet) is reasonably assigned to the sp^3 carbon with two nitrogen substituents [C(5)], and the peak at 158.7 ppm (singlet) is assigned to the urea carbonyl carbon [C(3)], being compatible with the triazolidinone structure.



Replacement of the cyclohexyl group at N(1) with *n*-butyl in **1** did not affect the isomerization. Thus, **1b** isomerized very smoothly to **2b** on heating at 100 °C for 1.5 h. The ^{13}C NMR spectrum of **2b** compares very favorably with that of **2a** in corroboration of the assigned

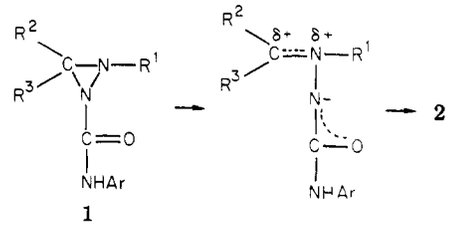
Table I. ^{13}C NMR Spectrum of **2a** in Me_2SO-d_6

absns obsd	sford	assignt
19.2	q	C(18)
24.5, 25.3, 27.8, 31.1	m	C(7)-C(11)
59.1	d	C(6)
83.9	s	C(5)
124.4, 124.8, 126.1, 127.8, 128.3	m	C(13)-C(17), C(20)-C(24)
136.5	s	C(19)
144.7	s	C(12)
158.7	s	C(3)

structure. There has been observed a peak at 83.9 (singlet) and at 158.5 ppm (singlet) assignable to C(5) and C(3), respectively (for the numbering see Figure 1).

We have confirmed these assignments by a single-crystal X-ray analysis of **2b**. An ORTEP perspective drawing of **2b** is shown in Figure 1. Interatomic distances and angles are given in Table II (available as supplementary material). Maximum distortion of bond angles occurs at C(5) in the triazolidinone ring [N(1)–C(5)–N(4) = 98.2 (3)°]. Deviations from the best plane through various atom groups are shown in Table III (supplementary material). The triazolidinone ring has a distorted half-chair conformation: the atoms N(2), C(3), N(4), and O are coplanar, and the atoms N(1) and C(5) are displaced from the plane by –0.39 and 0.18 Å, respectively.

The isomerization of *N*-carbamoyldiaziridines (**1**) to triazolidinones (**2**) did not occur when the substituents at the ring carbon in **1** were changed: 1-cyclohexyl-2-(phenylcarbamoyl)-3-phenyldiaziridine (**1f**),[2] 1-cyclohexyl-2-(phenylcarbamoyl)-3-ethyl-3-phenyldiaziridine (**1g**), and 1-cyclohexyl-2-(phenylcarbamoyl)-3,3-dimethyldiaziridine (**1h**)[3] failed to give **2** under similar conditions. We have assumed the intermediacy of a 1,3-dipole for the isomerization of **1** to **2**.[2] The failure of **1f** to isomerize to **2** may



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(1) (a) Mitsui Toatsu Chemicals Inc. (b) Shionogi Research Laboratory, Shionogi and Co., Ltd.

(2) A. Nabeya, Y. Tamura, T. Kodama, and Y. Iwakura, *J. Org. Chem.*, **38**, 3758 (1973).

(3) (a) E. Schmitz and D. Habisch, *Rev. Chim., Acad. Repub. Pop. Roum.*, **7**, 1281 (1962); (b) *Chem. Abstr.*, **61**, 4331 (1964); (c) E. Schmitz, D. Habisch, and C. Gründemann, *Chem. Ber.*, **100**, 142 (1967). This compound was once reported as having a triazolidinone structure (ref 3a and 3b) and later proved to have the diaziridine ring intact by the same authors (ref 3c).

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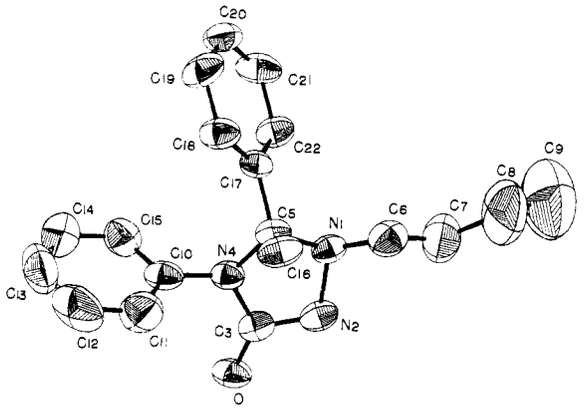
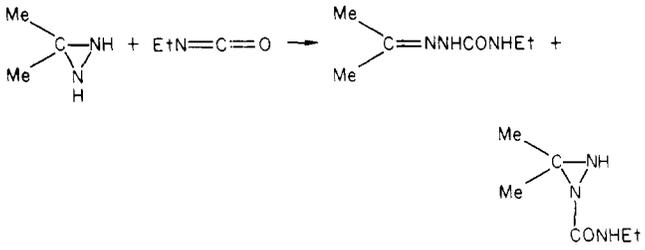


Figure 1. ORTEP drawing of the 1-*n*-butyl-4,5-diphenyl-5-methyl-1,2,4-triazolidin-3-one molecule.

be attributed to the insufficient stability of such an intermediate. Recently, the isomerization of 1-aroyl-2,-3,3-trialkyldiaziridines to 2-aryl-4,5,5-trialkyl-Δ^2-1,3,4-oxadiazolines was reported by Heine et al.[4] They gave us information[5] that the 1-aroyldiaziridines having only one group on C(3) did not isomerize to the oxadiazolines. Why **1g** and **1h** do not isomerize to **2** is not clear so far and is left for future study.

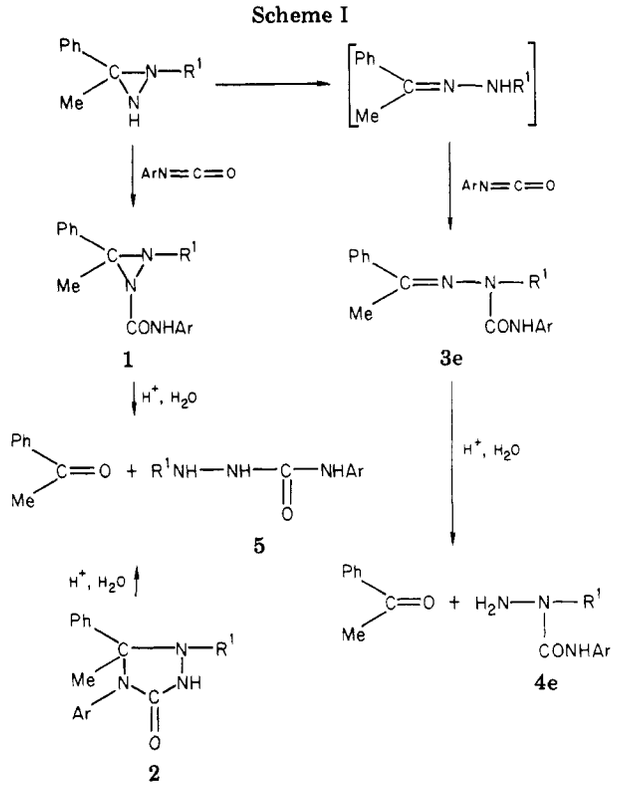
Abendroth[6] reported that the reaction of 3,3-dimethyldiaziridine with ethyl isocyanate gave 1-isopropylidene-4-ethylsemicarbazide along with the *N*-carbamoyldiaziridine.



Such a ring-open isomer has not been found in the thermal rearrangement of **1**. However, it was found that the reaction of 1-cyclohexyl-3-methyl-3-phenyldiaziridine with *p*-methoxyphenyl isocyanate gave a mixture of 1-(α-methylbenzylidene)-2-cyclohexyl-4-(*p*-methoxyphenyl)-semicarbazide (**3e**) and **1e**. Compound **3e** was formed even at a low temperature (5 °C), and the ratio of **3e**/**1e** increased when the reaction temperature was raised. A rearranged adduct like **3e** was not found with any of the other isocyanates tried under similar conditions. Thus, it is probable that the reactant diaziridine, which has still a free NH group, has first rearranged possibly by the catalytic action of the isocyanate[7] to a ring-open isomer, 1-cyclohexyl-2-(α-methylbenzylidene)hydrazine, and then the latter compound reacted with the isocyanate to give **3e**.

Acidic hydrolysis of **3e** readily gave acetophenone and 2-cyclohexyl-4-(*p*-methoxyphenyl)semicarbazide (**4e**) as expected from the structure (see Scheme I). An isomeric semicarbazide, 1-cyclohexyl-4-(*p*-methoxyphenyl)semicarbazide (**5e**), was obtained by the hydrolysis of **1e** under similar conditions. Such 4-aryl-1-cyclohexylsemicarbazides (**5**) were also obtained from **2**. Recrystallization of **2c** from 95% ethanol resulted in the decomposition of the material

Scheme I



R¹ = cyclohexyl; a, Ar = Ph; c, Ar = *m*-chlorophenyl; d, Ar = *p*-chlorophenyl; e, Ar = *p*-methoxyphenyl

and finally gave 1-cyclohexyl-4-(*m*-chlorophenyl)semicarbazide (**5c**). Compound **2d** gradually decomposed in ethanolic solution, and after several recrystallizations from the same solvent gave the semicarbazide **5d**, which was identical with the hydrolysis product from **1d**. The other triazolidinones were recrystallized from 95% ethanol without appreciable decomposition. Compound **2a** was completely hydrolyzed to give 1-cyclohexyl-4-phenylsemicarbazide (**5a**) on heating in 6 N HCl for 2 h.

Experimental Section

Melting points were determined on a Mel-Temp capillary melting point apparatus and are not corrected. ^{13}C NMR spectra were measured on a JEOL FX-60 spectrometer operating at 15.03 MHz and are recorded in ppm values from Me_4Si as internal standard. ^1H NMR spectra ($CDCl_3$) were measured on a JNM-PMX 60 NMR spectrometer and are recorded as δ values from Me_4Si as internal standard. IR spectra were taken on a Shimadzu IR-400 spectrometer.

1-*n*-Butyl-2-(phenylcarbamoyl)-3-methyl-3-phenyldiaziridine (1b). 1-*n*-Butyl-3-methyl-3-phenyldiaziridine was prepared in a similar way as mentioned previously[2] in the preparation of the 1-cyclohexyl derivative. From 3.5 g (0.02 mol) of α-methylbenzylidene-*n*-butylamine [bp 93 °C (5 mm)], 3.7 g of *n*-butylamine, and 2.5 g of hydroxylamine-*O*-sulfonic acid (HAOSA, 90% purity), 2.5 g (66%) of the diaziridine was obtained: bp 74 °C (0.15 mm); IR (film) 3200 cm^{-1} (NH); ^1H NMR δ 0.6–2.9 (m, 12), 1.67 (CH_3), ~7.2 (m, 5).

Anal. Calcd for $C_{12}H_{18}N_2$: C, 75.74; H, 9.54; N, 14.72. Found: C, 75.82, 75.94; H, 9.29, 9.51; N, 14.56, 14.44.

Similarly, 1-cyclohexyl-3-ethyl-3-phenyldiaziridine was obtained in 54% yield by starting from α-ethylbenzylidenecyclohexylamine [bp 95 °C (0.4 mm)], cyclohexylamine, and HAOSA: bp 101–104 °C (0.3 mm); IR (film) 3200 cm^{-1} (NH); ^1H NMR δ 0.5–3.2 (m, 16), ~7.3 (m, 5).

Reactions of the 2-unsubstituted diaziridines with isocyanates were carried out in ether. Except for the reaction with *p*-methoxyphenyl isocyanate, the reaction mixture was either heated at reflux or allowed to stand at room temperature until the TLC showed no starting diaziridine remained. The yields, physical

(4) H. W. Heine, L. M. Baclawski, S. M. Bonser, and G. D. Wachob, *J. Org. Chem.*, **41**, 3229 (1976).
(5) We thank Dr. Heine for the information.
(6) H. J. Abendroth, *Angew. Chem.*, **73**, 67 (1961).
(7) Whether the catalytic action was done by the isocyanate or some impurity therein is not clear so far.

Table VI. Yields, Physical Properties, and IR Data of 1[a]

compd	yield, %	mp, °C	IR (Nujol), cm^{-1} NH	IR (Nujol), cm^{-1} C=O
1b	50	82–84	3290	1690
1c	87	123–126	3300	1690
1d	97	128–130	3200	1675
1g	69	123–125	3310	1692

[a] Satisfactory analytical data (±0.3% for C, H, and N) were reported for all new compounds listed in the table. NMR data were consistent with the proposed structures.

Table VII. Yields, Physical Properties, and IR Data of 2[a]

compd	yield, %	mp, °C	IR (Nujol), cm^{-1} NH	IR (Nujol), cm^{-1} C=O
2b	83	146–148	3150	1705
2c	50	138–141	3190	1659
2d	45	165–166	3170	1703
2e	70	177–180	3200	1702

[a] Satisfactory analytical data (±0.3% for C, H, and N) were reported for all new compounds listed in the table. NMR data were consistent with the proposed structures.

properties, and the IR spectral data of 1 are listed in Table VI.

Reactions of 1-Cyclohexyl-3-methyl-3-phenyldiaziridine with *p*-Methoxyphenyl Isocyanate. An ethereal solution of 540 mg (2.5 mmol) of 1-cyclohexyl-3-methyl-3-phenyldiaziridine and 400 mg (2.7 mmol) of *p*-methoxyphenyl isocyanate [bp 110 °C (24 mm)] was allowed to stand at room temperature for 1 week. Concentration of the solution gave 400 mg of off-white crystalline solid which was found to be a mixture of **1e** and **3e**. Further concentration of the filtrate gave 80 mg of almost pure (by TLC) **1e**. Attempts to isolate either **1e** or **3e** from the mixture failed.

The result was much the same when the reaction mixture was allowed to stand at 5 °C for 2 weeks except that some reactant diaziridine was still found in the mixture.

Reaction in refluxing THF also gave a mixture of **1e** and **3e**. In this case, however, pure **3e** was obtained after a recrystallization of the reaction product from benzene–petroleum ether.

Compound **1e**: mp 129–132 °C; IR (Nujol) 3370 (NH), 1702 cm^{-1} (C=O); ^{1}H NMR δ 0.3–2.4 (br, 14), 1.72 (CCH_3), 3.73 (s, 3, OCH_3), 6.7–7.8 (m, 9), 7.93 (s, 1, NH).

Anal. Calcd for $C_{22}H_{27}N_3O_2$: C, 72.30; H, 7.45; N, 11.50. Found: C, 72.30; H, 7.45; N, 11.48.

Compound **3e**: mp 125–127 °C; IR (Nujol) 3250 (NH), 1640 cm^{-1} (C=N); ^{1}H NMR δ 0.7–2.1 (br, 10), 2.40 (s, 3, CCH_3), 3.70 (s, 3, OCH_3), 4.1 (br, 1, cyclohexyl α-H), 6.5 (s, 1, NH), 6.8–8.4 (m, 9).

Anal. Calcd for $C_{22}H_{27}N_3O_2$: C, 72.30; H, 7.45; N, 11.50. Found: C, 72.21, 72.19; H, 7.43, 7.42; N, 11.45, 11.50.

Isomerization of 1b to 2b. A 300-mg sample of **1b** was heated at 100 °C for 1.5 h under nitrogen. When the sample was cooled, crude **2b** solidified to a white mass, which was treated with ether–petroleum ether (bp 35–80 °C) to give 250 mg (83%) of crystals.

Isomerizations of other diaziridines (**1c**, **1d**, and **1e**) were carried out in much the same way as above except that these diaziridines were heated until they melted before the temperature was kept at 100 °C. The yields, physical properties and the IR spectral data of **2** were listed in Table VII.

Heating of **1g** either at 100 °C for 3 h, at 120 °C for 2.5 h, or in refluxing dioxane for 3 h all resulted in the recovery of the starting material contaminated with a hydrolysis product, **5a**.

Compound **1h** was found to dissociate to the starting diaziridine and the isocyanate on heating at above the melting point [mp 72–74 °C (lit.[3a] mp 73–75 °C)]. Thus, it did not seem to give any isomerized product but gave a hydrolysis product, 1-cyclohexyl-1,2-bis(phenylcarbamoyl)hydrazine,[8] after a prolonged heating at 80 °C.

Crystallography. Crystals of $C_{19}H_{23}N_3O$ (**2b**) are monoclinic: a = 12.560 (2), b = 5.693 (1), c = 26.849 (3) Å; d_m = 1.180, d_c = 1.179 g cm^{-3} for Z = 4; space group $P2_1/c$. Three-dimensional intensity data were collected on a Hilger and Watts automatic four-circle Y 290 diffractometer controlled by a PDP 8 computer. Least-squares refinement of 25 strong reflections produced an orientation matrix for data collection as well as the cell dimensions. Integrated intensities were measured for $\theta < 27.5°$ by the θ–2θ scan technique with Mo Kα radiation. A standard reflection was monitored every 10 reflections to check crystal stability. Of 4014 independent reflections (recorded at room temperature), 2316 had intensities $I > 3\sigma(I)$ and were used in the analysis. The intensities were corrected for Lorentz and polarization factors, but no absorption corrections were applied.

The structure was solved by the multiple-solution methods from the 267 reflections having $E > 1.50$ by using the program DIRECTER[9] for automatic structure analysis. The program automatically selects three kinds of origin sets as input to the tangent refinement. This procedure yielded 96 starting sets as input to the tangent refinement. Selection of the best phase set in tangent refinement is based on the low values of R and Q and the high values of α and t. On this bases, an E map was calculated, and the atomic coordinates of 21 light atoms were found, and a subsequent difference Fourier map revealed the remainder of the molecule. The atomic coordinates of the 23 atoms were refined isotropically by the full-matrix least-squares calculations to R = 0.155. A difference Fourier synthesis computed at this stage revealed the positions of the 20 hydrogen atoms, and these were then included in later refinement (the disordered methyl hydrogens at C(9) were omitted). The final five cycles of full-matrix least-squares refinement decreased R to 0.087 for the 2316 observed reflections. The carbon, nitrogen, and oxygen atoms were refined anisotropically and the hydrogen atoms isotropically (B values were fixed at 2.00 Å^2).

Hydrolysis of 3e. Compound **3e** (80 mg) was dissolved in 3 mL of ethanol, and to the solution was added 1 mL of 6 N HCl. The yellow color of **3e** disappeared immediately. The solution was concentrated, and the residue was dissolved in water. The aqueous solution was washed with ether to remove acetophenone and basified with NaOH to give white solid. Extraction of the aqueous layer with benzene and the subsequent evaporation of the solvent gave 40 mg (70%) of 2-cyclohexyl-4-(*p*-methoxyphenyl)semicarbazide: mp 168–170 °C; IR (Nujol) 3350, 3200 (NH), 1630 cm^{-1} (C=O); ^{1}H NMR δ 0.7–2.3 (br, 10), 3.46 (s, 2 NH_2) 3.72 (s, 3, Me), 4.3 (br, 1, cyclohexyl α-H), 6.5–7.5 (q, 4), 8.40 (s, 1 NH).

Anal. Calcd for $C_{14}H_{21}N_3O_2$: C, 63.85; H, 8.04; N, 15.96. Found: C, 63.95, 63.84; H, 8.02, 8.02; N, 15.96, 15.97.

Hydrolysis of 1e. Treatment of **1e** with 6 N HCl in ethanol in the same way as above gave acetophenone and 72% of **5e**: mp 152–154 °C; IR (Nujol) 3310, 3250, 3200 (NH), 1660 cm^{-1} (C=O); ^{1}H NMR δ 0.7–2.3 (br, 10), 2.6 (br, 1, cyclohexyl α-H), 3.50 (s, 1, 1-NH), 3.73 (s, 3, Me), 6.30 (s, 1, 2-NH), 6.7–7.6 (q, 4), 7.96 (s, 1, 4-NH).

Anal. Calcd for $C_{14}H_{21}N_3O_2$: C, 63.85; H, 8.04; N, 15.96. Found: C, 63.79, 63.64; H, 7.98, 7.98; N, 15.91, 15.89.

Hydrolysis of 2. Recrystallization of **2c** from 95% ethanol gave crystals of **5c**: mp 125–129 °C; IR (Nujol) 3290, 3250, 3200 (NH), 1665 cm^{-1} (C=O); ^{1}H NMR δ 0.5–2.3 (br, 10), 2.7 (s, 1, cyclohexyl α-H), 3.60 (s, 1, 1-NH), 6.6–7.9 (m, 5, aromatic H and 2-NH), 7.00 (2-NH), 8.26 (s, 1, 4-NH).

Anal. Calcd for $C_{13}H_{18}ClN_3O$: C, 58.31; H, 6.78; N, 15.69. Found: C, 58.27, 58.33; H, 6.78, 6.80; N, 15.64, 15.72.

Similarly, **2d** gave **5d** on heating in 95% ethanol: mp 157–159 °C; IR (Nujol) 3300, 3260, 3180 (NH), 1658 cm^{-1} (C=O); ^{1}H NMR δ 0.5–2.3 (br, 10), 2.7 (br, 1, cyclohexyl α-H), 3.5 (s, 1, 1-NH), 6.27 (s, 1, 2-NH), 6.9–7.7 (m, 4), 8.17 (s, 1, 4-NH).

Anal. Calcd for $C_{13}H_{18}ClN_3O$: C, 58.31; H, 6.78; N, 15.69. Found: C, 58.32, 58.46; H, 6.77, 6.75; N, 15.68, 15.66.

Treatment of **1d** with 6 N HCl in ethanol gave a crystalline product (mp 157–159 °C) which was found to be identical with **5d** with all respects, mmp 157–159 °C.

Compound **2a** was recovered after being heated at 80 °C in a mixture of 6 N HCl (0.5 mL) and ethanol (1 mL) for 2 h. When heated in 6 N HCl to reflux for 2 h, it completely decomposed

(8) M. Busch and K. Linsenmeier, *J. Pract. Chem.*, [2] **115**, 232 (1927).

(9) H. Koyama and K. Okada, *Acta Crystallogr., Sect. A*, **31**, 18 (1975).

to give **5a**, mp 139–141 °C, in 80% yield.

Acknowledgment. Financial support for A.N. by a Grant Aid for Scientific Research is gratefully acknowledged. We thank Dr. J. A. Moore for many useful suggestions.

Registry No. **1b**, 71463-01-9; **1c**, 71463-02-0; **1d**, 71463-03-1; **1e**, 71463-04-2; **1g**, 71463-05-3; **1h**, 14491-89-5; **2a**, 41316-38-5; **2b**, 71463-06-4; **2c**, 71463-07-5; **2d**, 71463-08-6; **2e**, 71463-09-7; **3e**, 71463-10-0; **4e**, 71463-11-1; **5a**, 41316-45-4; **5c**, 71463-12-2; **5d**, 71463-13-3; **5e**, 71463-14-4; 1-*n*-butyl-3-methyl-3-phenyldiaziridine, 71463-15-5; 1-cyclohexyl-3-ethyl-3-phenyldiaziridine, 41316-28-3; α-methylbenzylidene-*n*-butylamine, 6907-75-1; α-ethylbenzylidenecyclohexylamine, 6125-76-4; HAOSA, 2950-43-8; *p*-methoxyphenyl isocyanate, 5416-93-3; 1-cyclohexyl-1,2-bis(phenylcarbamoyl)hydrazine, 41316-46-5; acetophenone, 98-86-2.

Supplementary Material Available: Table II, interatomic distances and angles; Table III, deviations from the best plane through various atom groups; Tables IV and V, final positional and thermal parameters (5 pages). Ordering information is given on any current masthead page.

Generation of α-Keto Cations. Quantitative Aspects

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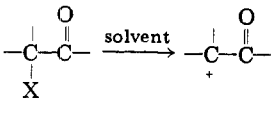
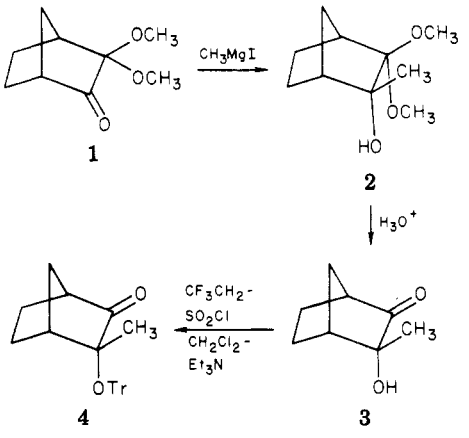
exo-3-Methylbicyclo[2.2.1]heptan-2-on-*endo*-3-yl tresylate (**4**) undergoes acetolysis to give two unrearranged products, ketone **5** and keto acetate **6**, along with rearranged keto acetate **7** and ketone **8**. These products are suggested to arise via the intermediacy of a discrete α-keto cation **9**. The α-methyl-d_3 isotope effect is 1.47 and suggests an extremely large demand for hyperconjugative stabilization. The rate-retarding effect of the α-keto group is estimated at $10^{7.3}$ in this system. *exo*-3-Arylbicyclo[2.2.1]heptan-2-on-*endo*-3-yl mesylates and trifluoroacetates **19–24** also give solvolysis products derived from α-keto cations. These benzylic α-keto cations are not prone to rearrange when the aryl group is phenyl, *p*-toluyl, *p*-thioanisyl, or *p*-anisyl, but rearrangement can occur with the *p*-trifluoromethyl substituent. The effect of aryl substituents on the rate of solvolysis suggests a ρ^+ value of about −7.1, again implying a large demand for aryl stabilization. Bicyclo[2.2.1]heptan-2-on-*exo*-3-yl triflate (**34**) also solvolyzes readily to give products consistent with neighboring σ participation and not via a discrete secondary α-keto cation. A similar k_Δ process also accounts for the rapid solvolysis of the triflate derivative of pivaloin, **39**. The triflate and mesylate derivatives of α-hydroxycyclohexanone are very labile and gave unrearranged acetolysis products. A deuterium-labeling study supports a mechanism involving enolization followed by solvolysis of an enol allylic triflate.

Recently we have been interested in the chemistry of α-keto triflates.[2] We have found that these substrates undergo a diversity of mechanistic processes when treated with bases and nucleophiles. During the course of these studies, it became obvious that certain of these triflates were surprisingly reactive even in the absence of strong nucleophiles. This suggested solvolytic processes despite the presence of the potent electron-withdrawing carbonyl group.



We therefore wanted to determine whether solvolytically generated α-keto cations were viable intermediates. While such intermediates have been suggested in the past,[3] not much is known about the effect of the carbonyl group on the rate of generation of a cationic species. Our additional objectives were therefore to determine, quantitatively, the destabilizing effect of the α-keto group on a carbocationic center and to evaluate rearrangement processes in such cations.

Scheme I



Results and Discussion

Tertiary α-Keto Systems. The norbornyl system, with its semipredictable rearrangement patterns, appeared to be ideal for an evaluation of α-keto cation systems. It was felt that, initially, tertiary α-keto cation systems would be the easiest to generate and evaluate quantitatively. Our initial synthetic target was, therefore, a derivative of keto alcohol **3**. This α-hydroxy ketone was prepared in a straightforward manner from the ketone **1** and methyl-

(1) Alfred P. Sloan Fellow, 1977–1979.
(2) (a) Creary, X.; Rollin, A. J. *J. Org. Chem.* **1977**, *42*, 4226–30. (b) Creary, X.; Rollin, A. J. *Ibid.* **1979**, *44*, 1017–20.
(3) (a) Karavan, V. S.; Temnikova, T. I. *J. Org. Chem. USSR. (Engl. Transl.)* **1966**, *2*, 1399–1404. (b) Temnikova, T. I.; Karavan, V. S. *J. Gen. Chem. USSR. (Engl. Transl.)* **1964**, *34*, 3204–10. (c) McDonald, R. N.; Tabor, T. E. *J. Am. Chem. Soc.* **1967**, *89*, 6573–8. (d) McDonald, R. N.; Tabor, T. E. *J. Org. Chem.* **1968**, *33*, 2934–41. (e) Begûe, J. P.; Malissard, M. *Tetrahedron* **1978**, *34*, 2095–103 and references therein.

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