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Synthesis and Structure of Stable Metal-Coordinated 1-Azirines[1a]

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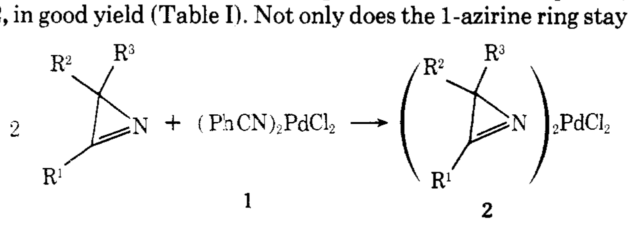
1-Azirines were found to form stable complexes with $PdCl_2$ or $PtCl_2$. These represent the first isolable transition-metal complexes of azirines. Compared to the free azirines, the palladium complexes **2** exhibit an unusually high stability toward air, moisture, and UV light. Thermolysis leads to formation of nitriles. An x-ray structural analysis of **2a** reveals coordination of the nitrogen with palladium, resulting in a 2:1 azirine/$PdCl_2$ complex with a trans configuration. The C–C–N bond angle is only 50.2° and the exocyclic C–C bond attaching the three-membered ring to a substituent is somewhat shortened (1.44 Å), suggesting a high degree of s character in the exocyclic bonds. Infrared and ^{13}C correlations for these complexes are discussed.

The strained 1-azirine ring system has been the subject of recent intensive studies.[2] Theoretical as well as practical considerations make the still unavailable 2-azirine ring system an interesting synthetic target.[3] In our efforts to prepare the elusive 2-azirine system stabilized by coordination to transition metals,[4] we felt that one possible route might involve transition-metal complexes of 1-azirines as precursors. Although 1-azirines are capable of acting as typical Schiff bases, coordinating via the nitrogen nonbonded electron pair, the few reported reactions of 1-azirines with metals have given only ring-opened products.[5–7] In the reaction of 2-phenyl-1-azirine with $CuBr_2$[5] or $M(CO)_6$ (M = Cr, W, MO),[6] no metal complexes containing azirine fragments were identified. Several complexes containing ring-opened fragments were isolated from the reaction of $Fe_2(CO)_9$ with 2-phenyl-1-azirine.[7]

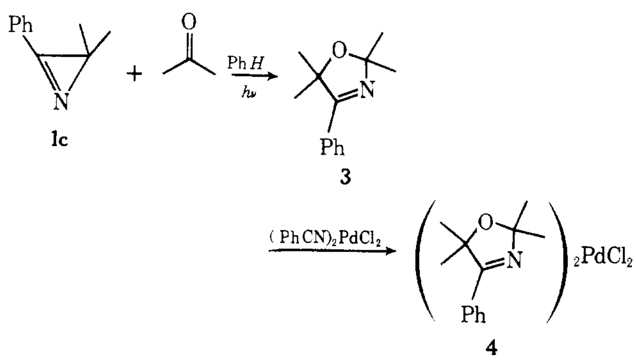
Results

We have now been successful in preparing the first isolable transition metal–azirine complexes. Thus, we found that 2 equiv of a variety of 1-azirines, **1**, react with dichlorobis(benzonitrile)palladium(II) to give stable trans complexes, **2**, in good yield (Table I). Not only does the 1-azirine ring stay



intact, but the azirine moiety seems to be protected from the usual decomposition 1-azirines undergo, without the necessity of exclusion of moisture and oxygen. For instance, complex **2d** stored at room temperature with no special precautions for over a year was unchanged. The azirine **1d** decomposes within days.

Coordination of the azirine also changes its susceptibility to photolysis. Thus, the complex **2c** was recovered (87%) unchanged after 14 h of irradiation. Under these conditions, the uncomplexed azirine **1c** converted into oxazole, **3** (89%), after 3.5 h.[8] We found that the oxazole itself reacts with $(PhCN)_2PdCl_2$ to give the bisoxazole complex **4**, but this



product was not detected in the photolysis of **2c** in the presence of acetone. Since the azirines **1** can be regenerated from **2** by treatment with triphenylphosphine, the complex formation serves as a protection of the azirine moiety.

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Table I. (Azirine)$_2$·$PdCl_2$ Complexes (2)

Compd	R_1	R_2	R_3	Yield, %	mp,[a] °C
2a	*p*-Tolyl	H	H	91	*b*
2b	*p*-Anisyl	H	H	87	*c*
2c	Ph	Me	Me	89	143–147
2d	Ph	Me	H	89	126–128
2e	Ph	CO_2Me	H	95	165–170
2f	Ph	$CH(OMe)_2$	H	68	147–150
2g	Ph	CH_2OH	H	54	110–118
2h	Me	Me	H	64	*d*
2i	Me_2N	Me	Me	44	143–146

[a] Decomposition accompanied melting. [b] Darkened at 140–145 °C with decomposition at 195–205 °C without melting. [c] Darkened at 140–145 °C with decomposition at 175–180 °C without melting. [d] Darkened at 125–130 °C with decomposition at 185–190 °C without melting.

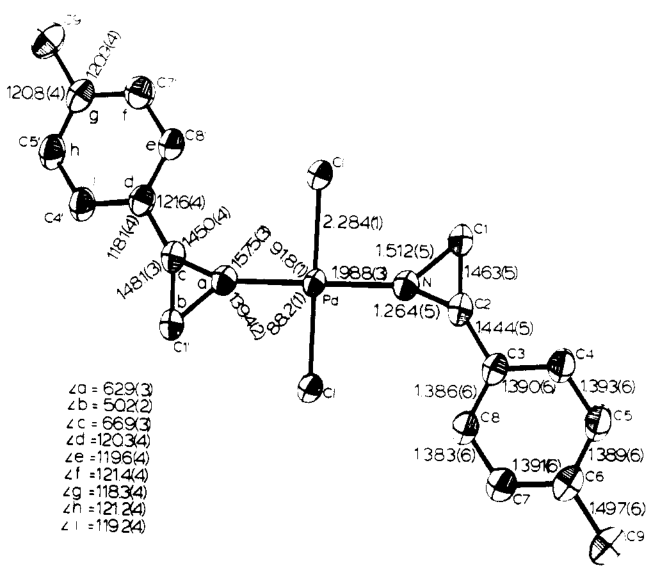
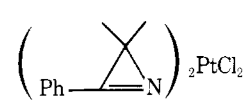


Figure 1. Bond lengths and angles for dichlorobis(2-*p*-tolyl-1-azirine)palladium(II), **2a**.

Thermal decomposition of the complexes **2** was somewhat dependent on conditions and was not a clean reaction. Pyrolysis of **2a** in refluxing chloroform or benzene gave a polymeric material. In the solid state at ca. 140 °C/0.1 mm, the major volatile product was *p*-tolunitrile, identified by IR and NMR. A number of minor products have not been identified.

The stability of the azirine–Pd complexes contrasts the behavior of substituted cyclopropenes which opens to π-allyl complexes with paladium chloride.[9] The Pt analogues of **2** are more difficult to prepare.[10a] Compound **5** was obtained in 52% yield by refluxing $(PhCN)_2PtCl_2$ with excess azirine, **1c**, in methylene chloride overnight. Complex **5** was the only Pt



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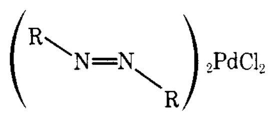
complex we were able to isolate in good purity, although the complexation of azirines **1a** and **1e** was also attempted. In general, the Pt compounds appeared to be less stable than the Pd ones.

Identification. Evidence for the structure of complexes **2** was provided by IR, ^1H NMR, and ^{13}C NMR spectroscopy (Tables II–V). In addition, trans stereochemistry about the palladium atom in **2a** has been established by x-ray crystallography. It is assumed that the other Pd complexes also have trans stereochemistry. The stereochemistry for the Pt compound **5** is not certain, since the starting material, $(PhCN)_2PtCl_2$, has a cis configuration compared to *trans*-$(PhCN)_2PdCl$.[10b] However, the similarity between the ^1H NMR spectra of **5** and the Pd analogue **2c** suggest that **5** also has a trans configuration.

The infrared spectra of the complexes **2** show a strong band for the C=N bond. The position of the band (1762–1813 cm^{-1}) is shifted (27–42 cm^{-1}) to a higher frequency than found in the spectra of the uncomplexed azirines (Table II). This increase is consistent with several reports that Schiff bases show an increase in $\nu_{C=N}$ upon complexation.[11] The $\nu_{N=N}$ for coordinated azo compounds in the *trans*-Pd complexes **6** also increases relative to $\nu_{N=N}$ for the free ligand.[12] Complexes such as **7** are reported to have a lower $\nu_{C=N}$ than the nonmetalated, free Schiff base;[13] however, the metallo-



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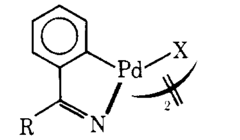

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cyclic structure of **7** mitigates a comparison with **2** in this regard.

The ^1H NMR spectra of the 1-azirine complexes **2** are very similar in appearance to the spectra of the free respective azirines **1**. There is, however, a consistent deshielding of the ortho protons in the 2-aryl-1-azirine complexes (Table III) of 0.3–0.5 ppm. Protons at the 3 position of the azirine ring are also deshielded considerably. For instance, the methylene protons of **2a** and **2b** show downfield shifts of 0.59 and 0.51 ppm, respectively, relative to the uncomplexed 1-azirine. The methine protons of **2d**, **2e**, **2f**, and **2g** show comparable deshielding (0.27–0.51 ppm).

In an effort to understand what may be responsible for the deshielding in the above complexes, we obtained ^{13}C NMR spectra for two of the 1-azirines, **1a** and **1c**, and their respective Pd complexes (Table IV). The results are somewhat surprising in that the chemical shift of C-2 of the azirine ring is affected very little by complexation.

Table II. IR Spectra[a] of 1-Azirines 1 and Complexed 1-Azirines 2

1-Azirine	Registry no.	$\nu_{C=N}$	Complexes	Registry no.	$\nu_{C=N}$	Other bands for 2
1a	**32687-33-5**	**1732**	**2a**	63989-17-3	1777	1608, 1322, 1187, 1034, 825
1b	32687-32-4	1730[b]	**2b**	63989-18-4	1772	1603, 1511, 1330, 1315, 1269, 1180, 1035, 844
1c	14492-02-2	1725	**2c**	63989-19-5	1762	1498, 1453, 1381, 1181
1d	16205-14-4	1738	**2d**	63989-20-8	1775	1600, 1455, 1385, 1328, 1168, 945
1e	18709-45-0	1768	**2e**	63989-21-9	1796	1740, 1598, 1455, 1440
1f	56900-68-6	1745	**2f**	63989-22-0	1780	1598, 1455
1g	52124-00-2	1730[c]	**2g**	63989-23-1	1769	3430 (br), 1600, 1450, 1325, 1315, 1158, 1085, 1035
1h	63989-39-9	1768[c]	**2h**	63989-24-2	1801	1385, 1365, 1091, 1052
1i	54856-83-6	1771	**2i**	63989-25-3	1813	1455, 1438, 1378, 1325, 1127, 1068, 1004

[a] $CHCl_3$ solution unless otherwise stated. [b] CCl_4 from ref 25. [c] CCl_4.

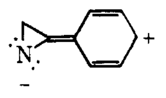
Table III. ^{1}H NMR Spectra of Dichlorobis(1-azirine)-palladium(II) Complexes (δ, $CDCl_3$)

Compd	Ortho H	Meta and para H	Other
2a	8.30	7.45	2.50 (3 H, s), 2.19 (2 H, s)
2b	8.32	7.08	3.95 (3 H, s), 2.15 (2 H, s)
2c	8.35	7.70	1.60 (6 H, s)
2d	8.27	7.60	2.75 (1 H, q, J = 4.9 Hz), 1.50 (6 H, d, J = 4.9 Hz)
2e	8.47	7.70	3.83 (3 H, s), 3.12 (1 H, s)
2f	8.38	7.63	4.80 (1 H, d, J = 1.5 Hz), 3.60 (3 H, s), 3.50 (3 H, s), 2.78 (1 H, d, J = 1.5 Hz)
2g	8.33	7.73	4.17 (1 H, ddd, J = 14, 7, 1 Hz), 3.63 (1 H, ddd, J = 14, 7, 3.5 Hz), 3.15 (1 H, d, J = 7 Hz), 2.90 (1 H, dd, J = 3, 1 Hz)
2h			2.70 (3 H, s), 2.30 (1 H, q, J = 4.5 Hz), 1.27 (3 H, d, J = 4.5 Hz)
2i			3.30 (3 H, s), 3.00 (3 H, s), 1.40 (6 H, s)

Table IV. ^{13}C NMR Spectra of 1a, 2a and 1c, 2c ($CDCl_3$, ppm Rel to Me_4Si)

Carbon	1a	2a	Δ	1c	2c	Δ
C-2	165.12	166.14	1.02	177.70	177.84	0.14
C-3	21.74	22.23	0.49	33.88	39.70	5.82
Subst C	123.09	119.21	−3.88	126.04	122.17	−3.87
o,m-C	129.54, 129.97	130.13 132.55		128.87, 129.11	129.25, 131.83	
p-C	143.57	147.07	3.50	132.41	134.84	2.43
CH_3	19.37	20.77	1.40	24.66	23.64	−1.02

By contrast, some atoms farther removed from the coordination site are affected much more. The para carbon (*p*-C) in the phenyl ring, for instance, is shifted downfield in both complexes **2a** and **2c**. This implies that the complexed azirine moiety acts as a greater electron sink than the free 1-azirine group. Electron-withdrawing groups are reported to lower (wrt benzene at 128.7 ppm) the ^{13}C NMR chemical shifts of para carbons in monosubstituted benzenes.[14] In a comprehensive study of ^{13}C NMR of 1-azirines,[15] the resonance contributor **8** was proposed to explain why the azirine moiety acts as an electron-withdrawing group.[16] A similar resonance contributor, **9**, enhanced by coordination to the Pd atom, could explain the downfield shift at *p*-C in **2a** and **2c**. On the other hand, contributions from structure **9** should decrease the $\nu_{C=N}$ in the IR spectra, which is opposite to our observation.



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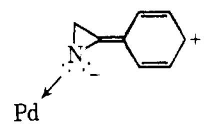

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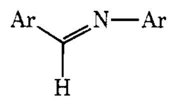
These results suggest that there is more than one effect controlling the ^{13}C chemical shifts in **2a** and **2c** and that for C-2 the effects fortuitously almost cancel each other.

X-ray structure. The crystal structure[17] of **2a** is shown in Figure 1. The ligands have a trans configuration about the planar Pd atom. The azirine and phenyl rings are essentially coplanar with a dihedral angle of 1.0° between them. The azirine ring is tilted about the Pd–N bond 11.6° from the coordination plane of the Pd.

The structure of the azirine portion of **2a** is of special importance, since there is no record of the bond lengths and angles in 1-azirines. The C(2)=N bond, 1.264 (5) Å, is somewhat shorter than the C=N bond found in salicylimine–Pd complexes, 1.286–1.294 Å,[18] or dichlorobis(cyclohexanone oxime)palladium(II), 1.29 Å.[19] However, the Schiff bases **10**



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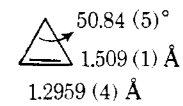

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are reported to have C=N bond lengths of 1.237–1.281 Å[20] so that the C(2)=N bond in **2a** is not unusually short.

It is also interesting to compare the structure of the azirine ring in **2a** with cyclopropene, **11**.[21] The small angle in the two rings is not significantly different, 50.84 (5)° for **11** and 50.2 (2)° for **2a**, but it does appear to be slightly smaller in the azirine ring. In order to accommodate the C=N bond in the three-membered ring, the C(1)–N bond has stretched to 1.512 (5) Å, an unusually long C–N bond distance.[21b] The C(1)–C(2) bond in the azirine is only 1.463 (5) Å, making the three-membered ring a somewhat lopsided triangle.[22] The corresponding C–C bond in cyclopropene is 1.509 (1) Å.

Finally, both the C(2)–C(3), 1.444 (5) Å, and Pd–N, 1.988 (3) Å, distances are slightly shorter than expected, 1.461–1.496 Å and and 2.00–2.09 Å,[23] respectively. This may be due to the high degree of s character found in the C(2) atom of 1-azirines[24] and assumed to be present in the nitrogen atom of the C=N bond as well. The short Pd–N bond may be due to metal backbonding. Otherwise, the bonds and angles are ordinary.

Table V. Formation of 2 from 1

Complex	$(PhCN)_2PdCl_2$, mmol	1, mmol	Solvent,[a] mL	Solvent,[b] mL	Yield of 2,[d] mmol	Comments
2a	3.94	7.94	50 B	100 P	3.58	Yellow powder–orange crystals from $CHCl_3$
2b	0.85	1.70	10 B	10 H	0.74	Yellow powder
2c	5.2	10.7	60 M	100 E	4.6	Orange crystals after 2 days at −25 °C
2d	1.31	2.75	10 M	20 P	1.16	Yellow crystals
2e	2.61	5.71	25 B	25 E	2.47	Yellow powder
2f	2.09	4.19	25 B	25 C	1.43	Yellow powder after 4 days at −4 °C
2g	0.78	2.38	30 B	40 E	0.43	E added after concentrating B to 10 mL—yellow powder
2h	2.74	*c*	50 B	75 P	1.75	Orange crystals after 12 h at −25 °C
2i	1.3	2.7	15 M	30 E	0.57	Orange needles after 2 days at −25 °C

[a] Reaction solvent: B, benzene; M, methylene chloride; CH, chloroform. [b] Precipitating solvent: P, pentane; H, hexane; E, ether; C, cyclohexane. [c] An excess of **1h** was generated in situ by photolysis of 2-azido-1-butene. [d] Consistent C, H, N analyses were obtained for the complex.

Experimental Section

General. All melting points were determined on a Fisher-Johns melting point block and are uncorrected. IR spectra were obtained on a Perkin-Elmer 267 spectrometer. ^{1}H NMR spectra were taken with either a Varian A60-A or EM-360 spectrometer. ^{13}C NMR spectra were recorded with a Varian HA-100 spectrometer. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

The 1-azirines, **1a**,[25] **1b**,[25] **1c**,[26] **1d**,[27] **1f**,[28] **1g**,[29] **1h**,[27] **1i**,[30] used for complex preparation were prepared by known methods.

Dichlorobis(1-azirine)palladium(II) (2). General Procedure. Method A. Two equivalents of 1-azirine was added to a suspension of $(PhCN)_2PdCl_2$ in benzene (10 mL/1.0 mmol), the mixture was stirred for 15 min, and twice the volume of pentane or ether was added. The product was collected by filtration, washed with ether, and was pure enough for most purposes.

Method B. Substituting CH_2Cl_2 (10 mL/1.0 mmol) as solvent, the solution was cooled to −25 °C overnight after adding 2 equiv of pentane or ether.

Recrystallization was carried out by dissolving the complex in a minimum amount of either $CHCl_3$ or CH_2Cl_2 and allowing ether to diffuse into the solution at −5 °C. Exact procedures and amounts for individual compounds are given in Table V.

Dichlorobis(2,2,5,5-tetramethyl-4-phenyl-3-oxazoline)palladium (II) (4). A solution of $(PhCN)_2PdCl_2$ (215 mg, 0.56 mmol) and **3** (230 mg, 1.13 mmol) in 50 mL of benzene was stirred several hours. Removal of the solvent gave a yellow solid which was washed with ether. Recrystallization from $CHCl_3$/ether by diffusion at −20 °C gave orange-yellow crystals (245 mg, 0.42 mmol, 75%): IR ($CHCl_3$) 1655 (m, br), 1465 (m), 1447 (m), 1389 (m), 1376 (s), 1368 (m), 1144 (m), 1018 (s), 910 (s), 841 (m) cm^{-1}; NMR ($CDCl_3$) δ 7.77 (2 H, m), 7.47 (3 H, m), 1.40 (6 H, s), and 1.30 (6 H, s).

Dichlorobis(3,3-dimethyl-2-phenyl-1-azirine)platinum(II) (5). $(PhCN)_2PtCl_2$[31] (500 mg, 1.06 mmol) and **1e** (600 mg, 4.14 mmol) were refluxed in 25 mL of CH_2Cl_2 (purified through Al_2O_3) for 24 h. An equal amount of ether was added and the solution was cooled to −25 °C. Yellow crystals (225 mg) were collected by filtration. A second crop (80 mg) was obtained giving 0.549 mmol (52%) of **5**: IR ($CHCl_3$) 1760, 1600 (m), 1455 (s), 1380 (s), 1180 (s) cm^{-1}; NMR ($CDCl_3$) δ 8.27 (2 H, m), 7.79 (3 H, m), and 1.67 (6 H, s).

Regeneration Azirine 1a from the Complex. To **2a** (100 mg, 0.23 mmol) in 5 mL of $CHCl_3$ and 20 mL of benzene was added triphenylphosphine (210 mg, 0.80 mmol) in 10 mL of benzene. After stirring overnight at 25 °C solvent was removed and the residue triturated with ether. Dichlorobis(triphenylphosphine)palladium (115 mg, 0.16 mmol, 72%) was collected as a yellow powder and recrystallized from $CHCl_3$/pentane at −20 °C, mp 268–272 °C. The filtrate was concentrated and ^{1}H NMR analysis indicated approximately equal amounts of **1a** and triphenylphosphine. Kugelrohr distillation gave **1a** (30 mg, 0.20 mmol, 49%), pure by NMR.

Crystallography. The yellow parallel-piped crystals of **2a** are monoclinic, space group $P2_1/n$,[32] with a = 8.963 (3), b = 11.268 (3), c = 8.991 (1) Å, and β = 99.98 (2)°. The observed density of 1.646 (5) g/mL is in agreement with the calculated density, 1.632 g/mL, for Z = 2.

Intensity measurements were made on a crystal ground to a spherical shape (d = 0.35 mm) using a Syntex Pl autodiffractometer equipped with a graphite monochromated Mo Kα source (θ–2θ scans). Some 1800 independent reciprocal lattice points were surveyed within a single quadrant to 2θ = 50° and 1358 were used in the refinement.

Since the Pd atom was in a special position, the determination of only one Cl atom from a Patterson map was sufficient. Three cycles of least-squares refinement on the Cl atom positional parameters, the scale factor, and the isotropic temperature factors for Pd and Cl gave R = 0.28 and wR = 0.36. From a difference Fourier map, the positions of all the nonhydrogen atoms were obtained. Inclusion of all these atoms as carbons in further isotropic refinement resulted in R = 0.10 and wR = 0.13. After determining the position of the N atom in the azirine ring,[33] anisotropic refinement converged at R = 0.047 and wR = 0.064. A difference map revealed the position of all nine H atoms. Idealized positions were used in the final refinement to give R = 0.039 and wR = 0.047. The standard deviation of an observation of unit weight was 1.88.[34]

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Registry No.—**3**, 17582-72-8; **4**, 63989-26-4; **5**, 63989-27-5; $(PhCN)_2PdCl_2$, 15617-18-2.

Supplementary Material Available. Tables VI–VIII; structural parameters of **2a**, rms vibrational amplitudes, bond lengths, bond angles and least-square planes will appear following this article in the microfilm edition of this journal (5 pages). Ordering information is given on any current masthead page.

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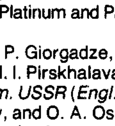

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(33) One of the atoms included as carbon had an isotropic temperature factor significantly less than the others (2.1 vs. 3.0–4.8) and was in a position consistent with a N atom in the azirine ring.

(34) In the calculations, the scattering factors for Pd^{2+} and Cl^- were those of

Cromer and Waber,[35] and these light atom scattering curves were taken from the tabulations of Hanson et al.[36] The effects of anomolous dispersion were included in the calculated structure factors with the values of $\Delta f'$ and $\Delta f''$ for Pd and Cl taken from the report of Cromer.[37] The data were reduced and the Patterson maps calculated on a Data General NOVA 1200 using programs written in this laboratory. All further calculations were done on the CDC 6400 at the University of Colorado using programs supplied by Dr. James Ibers.

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Attempted Synthesis of a Keto Diazene: Reactions of Propargylic Amines, Sulfamides, and Ureas

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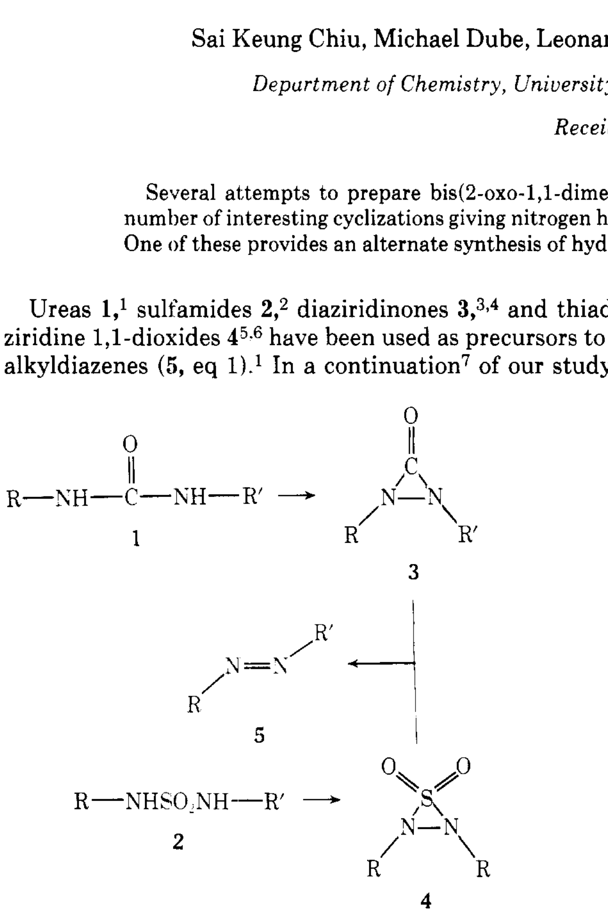
Several attempts to prepare bis(2-oxo-1,1-dimethylpropyl)diazene (**5e**) from propargylic derivatives led to a number of interesting cyclizations giving nitrogen heterocycles (isoxazole **11**, imidazolidinones **22**, and pyrazole **27**). One of these provides an alternate synthesis of hydantoins (imidazolidinediones **23**).

Ureas **1**,[1] sulfamides **2**,[2] diaziridinones **3**,[3,4] and thiadiaziridine 1,1-dioxides **4**[5,6] have been used as precursors to dialkyldiazenes (**5**, eq 1).[1] In a continuation[7] of our study of



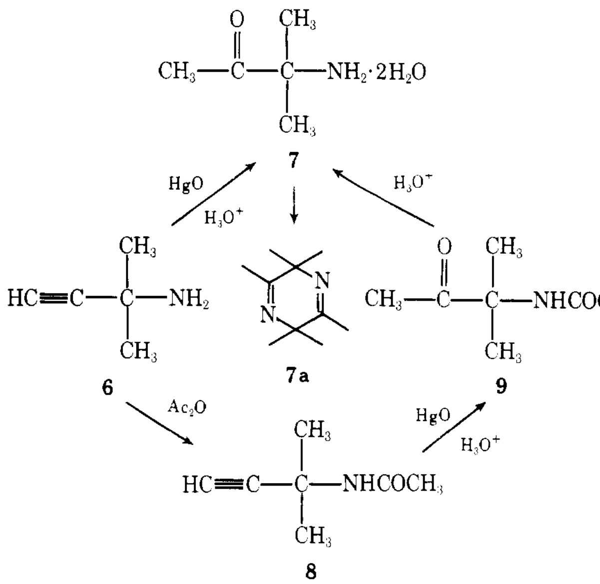
(1)

(a) R = $HC{\equiv}CC(CH_3)_2$—; R′ = $(CH_3)_3C$—
(b) R = R′ = $HC{\equiv}CC(CH_3)_2$—
(c) R = $CH_3COC(CH_3)_2$—, R′ = $(CH_3)_3C$—
(d) R = $HC{\equiv}CC(CH_3)_2$—, R′ = $CH_3COC(CH_3)_2$—
(e) R = R′ = $CH_3COC(CH_3)_2$—

diazenes as models of radical stabilities, we were interested in synthesizing a diazene with a β keto R group such as **5c** or **5e**. Since substituted acetylenes can be considered synthons of keto groups by hydration of the triple bond, we considered the four following methods as possible routes to ketodiazene **5c,e**: (a) hydration of 1,1-dimethylpropargylamine (**6**), (b) hydration of β-substituted propargylsulfamides **2a,b**, (c) hydration of propargyldiaziridinones **3a,b** or thiadiaziridine 1,1-dioxides **4a,b**, and (d) hydration of propargyldiazenes **5a,b**. These attempts have not been completely successful, but have led to some interesting chemistry described herein.

Results and Discussion

(a) Hydration of 1,1-Dimethylpropargylamine. 1,1-Dimethylpropargylamine (**6**) was considered as a precursor to 3-amino-3-methyl-2-butanone (**7**) so that the latter could be directly converted to diazene **5e** with IF_5[1,8] or first converted to urea **1e** or sulfamide **2e** and then to the diazene **5e**.[1] However, hydration of the propargylamine **6** proceeded in very low yield (<5%). Similarly, hydration of acetylated propargylamine **8** followed by acidic hydrolysis also gave unsatisfactory results (~13% overall from **6**, eq 2). While this amine



(2)

has been reported previously as the monomeric amine hydrochloride salt,[9] spectral data seem to indicate that in completely dehydrated form the "amine" appears to be dimeric (**7a**, see Experimental Section). An x-ray analysis is presently being attempted.

The Ritter reaction of 3-hydroxyl-3-methyl-2-butanone (**10**) was selected as an alternative route to **7** by hydrolysis of the expected amide. However, our initial attempts employing the normal aqueous workup recovered only "unreacted" starting material. More careful low-temperature workup gave two products, 4-hydroxy-2,4,5,5-tetramethyl-2-oxazoline (**11**, 17% yield) and 3-oxo-2-methyl-2-butyl acetate (**12**, 22% yield). A reaction sequence explaining the recovery of starting material is illustrated in eq 3. Isolated oxazoline **11** was converted to ester **12** under mild hydrolytic conditions and **12** was converted back to **10** by hydrolysis of the ester under more rigorous conditions.

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