in the form of a neutral alcohol and corresponding to the retention of the charge on the bridgehead enol ether, peaks associated with the elimination of a neutral bridgehead olefin and charged alcohols are virtually absent; such a situation also exists for 2-alkoxytetrahydropyrans.[8] (iii) The loss of alkoxy radical from the molecular ion to provide the oxonium ion i requires the 9-oxyl radical cation.

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Synthesis of 1-Azatricyclo[5.2.1.0^{4,10}]decane[1]

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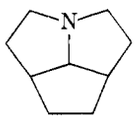
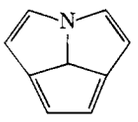
The title compound (**1**) has been synthesized by the reductive cyclization of 2,5-bis(cyanomethyl)cyclopentanone (**5**) with a Raney Ni and, in better yield, with a Raney Co catalyst. The pK_a of **1** is 8.50. Attempts to introduce unsaturation into the system were unsuccessful. Treatment of the *N*-benzyl quaternary salt with butyllithium gave Hofmann elimination and Stevens rearrangement products, but fragmentation occurred with the *N*-methyl quaternary salt. Other cyclopentanone condensation experiments are described.

Our interest in the behavior of quarternary salts of cyclic amines with base[3] and in new heterocyclic, nonalternant, conjugate-unsaturated systems[4] led to consideration of the 1-azatricyclo[5.2.1.0^{4,10}]decane structure (**1**), a possible precursor to 7a*H*-cyclopent[*gh*]-1-azapentalene (**2**) which would



1



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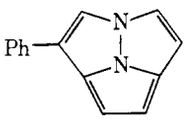
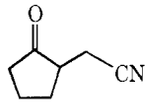


3

be an azaannulene with a 10 π-electron periphery distorted from planarity by the tetrahedral bridge atom. The closest analogy found was 1-phenyl-8-azacycl[2.2.2]azine (**3**) which was noted to exhibit ^{1}H NMR absorption only in the aromatic region,[5] but which has an unshared electron pair on the central nitrogen.

Leonard and Middleton[6] attempted to prepare **1** and the corresponding 1-azatricyclo[6.2.1.0^{4,11}]hendecane by the high-pressure hydrogenation of the oximes of diethyl cyclopentanone-2,5-diacetate and cyclohexanone-2,6-diacetate, respectively. They attributed the failure of the method to the assigned trans stereochemistry of the carbethoxymethyl groups (introduced by alkylation of the ketone enolate anion), and the formation of the trans product to steric factors. Later, however, Bohlmann et al.[7] showed the cyclohexanone diester to be the cis isomer. Thus, the failure to achieve the tricyclic system was apparently due to the reaction conditions. Subsequently, Mandell et al.[8] prepared *cis*-2,6-bis(cyanomethyl)cyclohexanone using Stork's enamine synthesis[9] and reductively cyclized it to the tricyclic amine in low yield.

Application of Mandell's procedure to the monoalkylation of cyclopentanone with chloroacetonitrile gave a 10% yield of the 2-cyanomethyl derivative (**4**) as compared to 35–45% reported[8] and verified by us for cyclohexanone. A comparable yield disparity has been observed with ethyl bromoacetate as the alkylating agent.[10] The use of dioxane as the solvent and morpholine as the base raised the yield of **4** to ca. 30%, which was still not satisfactory. The procedure of Gutsche et al.[11] of a one-pot reaction of cyclopentanone, pyrrolidine, and one equivalent of chloroacetonitrile was then tried and gave 31% of **4** plus a small amount of **5**. The use of two equivalents of



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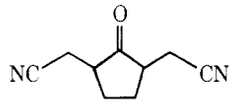
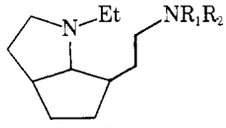


5

chloroacetonitrile and one additional equivalent of triethylamine afforded yields of 42 and 31%, respectively. A two-step procedure with the isolation of **4** gave appreciably lower yields of **5**. Hydrolysis of **5** formed the known corresponding dicarboxylic acid. An attempt to prepare **4** by the alkylation of the anion of *N*-cyclohexyliminocyclopentane[12] gave only tarry products.

High-pressure reduction of **5** in the presence of W-5 Raney nickel catalyst formed **1** (ca. 10%) along with three other compounds which were assigned structures as 1-ethyl-6-(2-aminoethyl)- (**6**), 1-ethyl-6-(2-ethylaminoethyl)- (**7**), and 1-ethyl-6-(2-diethylaminoethyl)cyclopentano[2,3]pyrrolidine (**8**) on the basis of their spectral characteristics. The ethyl groups in **6**–**8** came from the ethanol solvent.[13] Reduction in acetic acid gave essentially no **1**, but the use of glyme as the



6, $R_1 = R_2 = H$
7, $R_1 = H$; $R_2 = Et$
8, $R_1 = R_2 = Et$

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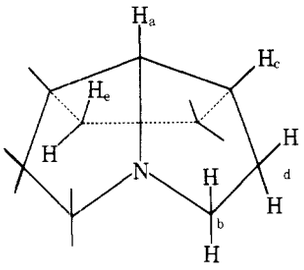
solvent increased the yield of **1** to ca. 25% and eliminated the ethylamine by-product formation. Predistillation of **5** from the Raney Ni to remove possible traces of halides toxic to the catalyst[14] did not improve the yield. Raney Co has also been used for the reduction of nitriles[15] and was found to give the highest yield (27%) of **1**, but also by-products which were not separable by distillation.

The structure of **1** was indicated by its elemental composition, the molecular ion in the mass spectrum, and the ^{1}H NMR spectrum which consisted of a distinct triplet for the central CH (a), a multiplet for the CH_2's (b) adjacent to the N and the other CH groups (c), and a multiplet for the other CH_2 groups (d and e) (**9**). When successive scans were taken

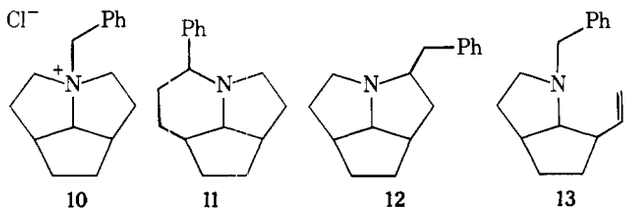


9

with increasing amounts of tris(dipivalomethanato)europium[16] present, the a signal showed the largest shift downfield and coalesced into a broad singlet and the b plus c signal was split into three 2H multiplets. For the latter, the multiplet which shifted the most was assigned to the exo b hydrogens which are nearer to the nitrogen electron pair and the europium, the next multiplet to the endo b hydrogens, and the last to the more remote c hydrogens. After the b and c multiplet had become resolved, the d plus e multiplet became a 4H quartet (d) and a triple-peaked 4H multiplet (e). Finally, at the point where resolution was lost, the d signal merged with the c signal.

The basicity of **1** and a series of tertiary amines was compared. The low solubility of **1** in water necessitated pK_a measurements in aqueous ethanol. The values obtained show that **1** is a stronger base than the others but not dramatically so. (See Table I.)

Treatment of benzyl quaternary salt **10** with strong base would be expected to give (i) benzylic hydrogen abstraction followed by a Stevens rearrangement to form **11**, (ii) α-methylene hydrogen abstraction followed by a Stevens rearrangement to form **12**, or a Sommelet rearrangement to form the 2-(*o*-tolyl) derivative of **1**, or (iii) Hofmann β-elimination with ring opening to form **13**. The benzyl group would hinder attack at the central CH and the rigid ring structure would make reaction of the benzylic carbon at this site less likely. With butyllithium as the base, two major products were isolated in a ratio of 2:3. Structure **11** is favored for one product



10 **11** **12** **13**

on the basis that this would arise from process i involving the more acidic benzylic α-hydrogens and that integration of the NMR spectrum showed only four hydrogens (α to N) in the region where the benzylic hydrogens in **12** would also be expected to be found.[17] The Sommelet product was excluded as the spectrum showed five phenyl hydrogens rather than four and no signal for a benzylic methyl group. The NMR spectrum

Table I. pK_a Values of 1 and Some Tertiary Amines[a]

Compound	Registry no.	pK_a
N-Ethylmorpholine	100-74-3	5.36
Triethylamine	121-44-8	7.45
N-Butylpyrrolidine	767-10-2	7.76
N-Ethylpiperidine	766-09-6	7.81
N-Ethylpyrrolidine	7335-06-0	8.01
1		8.50

[a] Aqueous ethanol solvent.

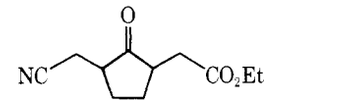
for **13** showed three hydrogens in the vinylic region and a pair of doublets for the nonequivalent benzylic hydrogens as has been noted by Reinecke for closely related compounds.[18] A third, very minor product was not characterized.

Heating **1** with sulfur (neat or in DMF) resulted in the evolution of hydrogen sulfide, but no volatile dehydrogenation product was obtained and heating with selenium caused only darkening. When **1** was heated at 350 °C with methyl oleate as hydrogen acceptor in the presence of Pd-C, no unsaturated product could be detected. Similarly, exposure of **1** to the Pd-C catalyst used for the dehydrogenative preparation of cyclopenta[*c*]thiapyran[19] in the vapor phase yielded no isolable unsaturated product. Unchanged **1** was recovered in good yield from both reactions with Pd-C.

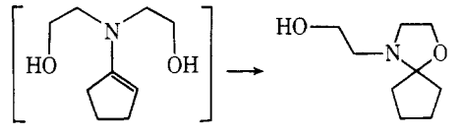
Mercuric acetate has been used to introduce a double bond into the 1-azatricyclo[8.4.1.0^{6,15}]hexadecane[7a,20] and indolizine[13b,21] structures. However, this reagent did not oxidize **1** and, subsequently, it was learned that the analogous bicyclic pyrrolizidine is also unreactive.[22] The use of lead tetraacetate gave lead diacetate (ca. 50%) and acetic acid, but again no unsaturated product could be isolated.

Application of the trityl cation method for the introduction of conjugate unsaturation into tertiary alkylamines[23] to **1** in acetonitrile led, after workup, to the BF_3 adduct of **1** and triphenylcarbinol, but no triphenylmethane. With dichloromethane solvent a small amount of triphenylmethane was formed, but no new isolable product.

Several other approaches to **1** having a functional group on carbon were qualitatively explored. Catalytic reduction of **4** gave the known *cis*-cyclopentano[2,3]pyrrolidine but the desired reductive bis-cyclization of cyanoester **14** did not occur. Condensation of cyclopentanone with iminodiethanol required acid catalysis and gave a high yield of a product which was not the desired enamine (**15**). The spectral prop-



14



15 **16**

erties suggested **16** which could form from subsequent acid-catalyzed cyclization.[24]

Experimental Section

Melting points and boiling points are uncorrected. NMR spectra were taken on a Varian A-60 or T-60 spectrometer with Me_4Si as internal standard unless otherwise specified. Infrared spectra were recorded with a Perkin-Elmer Model 21 or 137 spectrophotometer with sodium chloride prisms on thin films unless stated otherwise. Ultraviolet spectra were obtained on a Cary Model 14 recording spectrophotometer with 1-cm cells. Mass spectra were taken on an Associated Electrical Industries MS-9 spectrometer with matching to perfluo-

rotributylamine. Elemental analyses were performed by Dr. Alfred Bernhardt, 5251 Elbach über Engelskirchen, West Germany. Vapor phase chromatography was carried out on a Varian Aerograph Model 90P-3 with 5% SE-30 on Chromosorb G columns.

2-Cyanomethylcyclopentanone (4) and 2,5-Bis(cyanomethyl)cyclopentanone (5). A solution of 420 g (5 mol) of cyclopentanone and 380 g of pyrrolidine in 1 L of dry benzene was refluxed under N_2 until H_2O evolution (Dean-Stark trap) ceased. Triethylamine (522 g, 5.15 mol) was added to the cooled solution which was then heated to reflux and stirred. Chloroacetonitrile (760 g, 10 mol) was added slowly. After 3 h, the solvent was removed (reduced pressure), 500 mL of H_2O was added, and the mixture was stirred under reflux for 1 h. The separated aqueous phase was extracted with 2:1 benzene–ether. The combined extracts and original nonaqueous layer were washed successively with 10% HCl, 5% $NaHCO_3$, H_2O, and saturated NaCl. The aqueous extracts were extracted (liquid–liquid extractor) for 1 day with benzene. Distillation of the residue after solvent removal (vacuum) from the combined, dried (Na_2SO_4) organic phases gave 257 g (41.8%) of **4**, bp 105–120 °C (3–4 mm),[11] and 249 g (30.8%) of **5**, bp 180–190 °C (1 mm): IR 1740 (C=O) and 2250 cm^{-1} (C≡N). Anal. Calcd for $C_9H_{10}N_2O$: C, 66.65; H, 6.21; N, 17.21. Found: C, 66.50; H, 6.37; N, 17.34.

From an analogous reaction of 21 g (0.25 mol) of cyclopentanone, 18 g (0.25 mol) of pyrrolidine and 19 g (0.25 mol) of chloroacetonitrile in 150 mL of benzene wherein triethylamine was absent,[11] the hydrolysis of the intermediate iminium salt was effected by refluxing for 1.5 h with 100 mL of 1:1 methanol–H_2O, and 100 mL of saturated NaCl was added prior to extraction with benzene–ether, giving 9.6 g (31%) of **4**, bp 105–120 °C (3–4 mm) and ca. 0.5 g of higher boiling material containing **5**.

2,5-Bis(carboxymethyl)cyclopentanone. A 1-g sample of **5** was refluxed for 1 h with 10 mL of concentrated HCl. Water (50 mL) was added and the solution was extracted with ether. Evaporation of the solvent from the combined, dried extracts gave 2,5-bis(carboxymethyl)cyclopentanone, mp 176–177.5 °C (lit.[25] 177 °C), after recrystallization from methanol: molecular ion at *m/e* 200.076 (Calcd for $C_9H_{12}O_5$: 200.068).

1-Azatricyclo[5.2.1.0^{4,10}]decane (1). A. With W-5 Ni in Ethanol. Reductive cyclization of a solution of 10 g (0.062 mol) of **5** in 130 mL of absolute ethanol in the presence of 4–5 g of W-5 Raney Ni catalyst was carried out in a stirring autoclave at 1650 psi of H_2 at 135 °C for 8 h. The catalyst was separated from the cooled (internal coil in autoclave) mixture by centrifugation, and the ethanol was removed under vacuum. Distillation of the residue gave 2.43 g of clear liquid, bp 75–130 °C (1 mm), which was separated into four fractions by preparative VPC on an SE-30 column at 190 °C.

The first fraction, ca. 1.5 g (11%), was identified as **1**: molecular ion at *m/e* 137.119 (calcd 137.120); NMR (CCl_4) δ 3.6 (t, 1 H), 2.7 (m, 6 H), 1.6 (m, 8 H). Anal. Calcd for $C_9H_{15}N$: C, 78.78; H, 11.02; N, 10.21. Found: C, 78.81; H, 11.07; N, 10.29.

The *picrate* crystallized from ethanol: mp 295 °C (dec) with block preheated to 280 °C. Anal. Calcd for $C_{15}H_{18}N_4O_7$: C, 49.18; H, 4.95; N, 15.29. Found: C, 49.53; H, 5.08; N, 15.24.

The properties of the second fraction (ca. 0.4 g) were in agreement with those expected for **6**: molecular ion at *m/e* 182.185 (Calcd for $C_{11}H_{22}N_2$: 182.178); NMR (CCl_4) δ 1.2 (t, 3 H, CH_2CH_3); IR poorly resolved doublet at 3350 cm^{-1} (NH_2); positive Hinsberg tests for primary and tertiary amino groups.

The third fraction (ca. 0.2 g) was not characterized beyond measurement of the molecular ion at *m/e* 199.166 and the observation of no signal for a methyl or ethyl group in the NMR spectrum.

B. With W-5 Ni in Ethanol (Dilute). The procedure in **A** was followed except that 500 mL of absolute ethanol was used. Fractionation of the crude product (4.7 g, bp 50–140 °C at 1.5 mm) by preparative VPC at 200 °C (exit tube packed with glass wool and effluent gas bubbled through ethanol) yielded ca. 0.5 g (3.75%) of **1** as the first fraction.

The second fraction gave ca. 2.2 g (17%) of **7**: molecular ion at *m/e* 210.209 (Calcd: 210.209); NMR (CCl_4) δ 1.1 (2 t, 6 H, CH_2CH_3). Anal. Calcd for $C_{13}H_{26}N_2$: C, 74.21; H, 12.46; N, 13.32. Found: C, 74.03; H, 12.43; N, 13.50.

The third fraction gave ca. 1.5 g (10%) of **8**: molecular ion at *m/e* 238.240 (Calcd: 238.241); NMR (CCl_4) δ 1.0 (t, 6 H, CH_2CH_3), 1.1 (t, 3 H, CH_2CH_3). Anal. Calcd. for $C_{15}H_{30}N_2$: C, 75.55; H, 12.69; N, 11.75. Found: C, 75.53; H, 12.68; N, 11.60.

Compounds **7** and **8** were unstable to air, and CCl_4 solutions became brown in a few hours.

C. With W-5 Co in DME. A solution of 15 g (0.093 mol) of **5** in 450 mL of 1,2-dimethoxyethane was treated with H_2 at 2000 psi and 170 °C in the presence of 7–8 g of W-5 Raney Co for 6 h. The contents were removed from the autoclave and the solution was decanted from the catalyst. Removal of the solvent under vacuum and distillation of the residue gave 3.8 g (30%) of **1**, bp 85–95 °C (15 mm), containing ca. 10% (VPC) of by-products.

***cis*-Cyclopentano[2,3]pyrrolidine.** A mixture of 15 g (0.122 mol) of **4**, 405 g of W-5 Raney Ni, and 450 mL of dry 1,2-dimethoxyethane was stirred and heated at 170 °C under 2500 psi of H_2 in an autoclave for 12 h. The contents of the reaction vessel were removed and centrifuged. The solvent was removed (vacuum) from decanted supernatant liquid. Distillation of the residue gave 5.03 g (37%) of *cis*-cyclopentano[2,3]pyrrolidine, bp 75–100 °C (30–40 mm): *picrate*, mp 111–113 °C (lit.[26] 111 °C); 3,5-dinitrobenzoate, mp 201–202 °C (lit.[26] 201–203 °C).

pK_a Measurements. A solution of 0.02 mol of the amine in 25 mL of 80% ethanol was titrated potentiometrically with 0.0996 N HCl on a Radiometer Type TTTlc automatic titrator recording pH change as a function of volume. At the midpoint (pH = pK_a)[27] the solution was 57% ethanol.

Reaction of Benzyl Quaternary Chloride 10 with *n*-Butyllithium. To 2 g of **1** dissolved in ethanol was added 2 g of benzyl chloride. The solvent was evaporated and the residual salt was extracted with hexane and then covered with 300 mL of hexane. To the stirred mixture was added 30 mL of 1.6 M butyllithium. After 5 days, 30 mL of H_2O was added and the separated aqueous layer was extracted with hexane. The solvent was removed from the combined, dried organic layer and extracts and the residue was chromatographed (neutral Al_2O_3, benzene). VPC showed three compounds (6:9:1) and the first two were collected on a preparative VPC (SE-30, 275 °C). The first fraction (1 g, 30%) was assigned the structure of 2-phenyl-1-azatricyclo[6.2.1.0^{5,11}]undecane (**11**): molecular ion at *m/e* 227.169 (Calcd: 227.167); NMR (CCl_4) δ 7.2 (s, 5 H), 3.2 (m, 1 H), 2.6 (m, 3 H), and 1.6 (m, 12 H). Anal. Calcd for $C_{16}H_{21}N$: C, 84.53; H, 9.31; N, 6.16. Found: C, 84.39; H, 9.13; N, 6.05.

The second fraction (1.5 g, 47%) was assigned the structure 1-benzyl-6-vinylcyclopentano[2,3]pyrrolidine (**13**): molecular ion at *m/e* 227.19 (Calcd: 227.167); NMR (CCl_4) δ 7.2 (s, 5 H), 6.1 (p, 1 H, vinyl), 5.0 (t, 2 H, vinyl), 4.1 (d, 1 H, PhCH_2, J = 13 Hz), 2.98 (d, 1 H, PhCH_2, J = 13 Hz), 2.7 (m, 3 H, N–CH), and 1.6 (m, 8 H, ring CH_2). Anal. Calcd for $C_{16}H_{21}N$: C, 84.53; H, 9.31; N, 6.16. Found: C, 84.47; H, 9.26; N, 6.13.

2-(Ethylcarboxymethyl)-5-(cyanomethyl)cyclopentanone (14). A solution of 61.5 g (0.5 mol) of **4**, 35.5 g (0.5 mol) of pyrrolidine, and 200 mL of dry toluene was refluxed until the evolution of H_2O (Dean-Stark trap) had ceased. To the cooled solution was added 61.5 g (0.4 mol) of ethyl chloroacetate and the mixture was refluxed with stirring overnight. Most of the solvent was removed. The residue was stirred with 100 mL of H_2O for 2 h, refluxed for 5 min, cooled, and extracted with 2:1 benzene–ether. Distillation of the residue after removal of the solvent from the combined, washed (10% HCl, 5% $NaHCO_3$, H_2O, saturated NaCl), dried extracts gave 37 g (60%) of unchanged **4**, bp 85–95 °C (0.5 mm), and 22.5 g of liquid, bp 95–135 °C (0.5 mm), which contained 85% (VPC) of one substance. Two further distillations gave ca. 15 g (17%) of pure product: bp 135 °C (0.3 mm); molecular ion at *m/e* 209.107 (Calcd: 209.105); IR 1750 and 2250 cm^{-1}; NMR (CCl_4) δ 4.1 (q, 2 H), 2.6 (m, 10 H), 1.3 (t, 3 H). Anal. Calcd for $C_{11}H_{15}NO_3$: C, 63.14; H, 7.23; N, 6.69. Found: C, 63.17; H, 7.08; N, 6.79.

4-(2-Hydroxyethyl)-1-oxa-4-azaspiro[4.4]nonane (16). A solution of 8.4 g (0.1 mol) of cyclopentanone, 10.5 g (0.1 mol) of iminodiethanol, and 0.1 g of *p*-toluenesulfonic acid in 250 mL of benzene was refluxed under N_2 until 1.9 mL of H_2O (calcd: 1.8 mL) was evolved. The solvent was evaporated and distillation of the residue gave 15.3 g (90%) of **16**: bp 142–152 °C (15 mm); molecular ion at *m/e* 171.123 (Calcd for $C_9H_{17}NO_2$: 171.126); IR 3300, 1750, and 1050 cm^{-1}; NMR (CCl_4) δ 4.1 (s, 1 H), 3.8 (t, 2 H), 3.5 (t, 2 H), 2.9 (t, 2 H), 2.6 (t, 2 H) and 1.6 (s, 8 H).

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Registry no.—**1**, 38594-89-7; 1 picrate, 64010-75-9; **4**, 51004-14-9; **5**, 64010-74-8; **6**, 64010-73-7; **7**, 64010-72-6; **8**, 64010-71-5; **11**, 64010-70-4; **13**, 64010-69-1; **14**, 64010-68-0; **16**, 64034-89-5; chloroacetonitrile, 107-14-2; *cis*-cyclopentano[2,3]pyrrolidine, 2030-37-7; benzyl chloride, 100-44-7; ethyl chloroacetate, 105-39-5.

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

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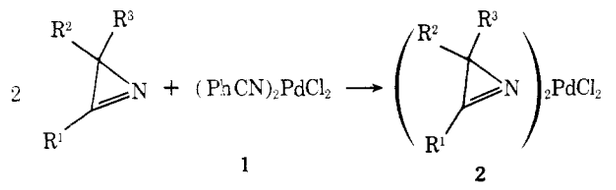
1-Azirines were found to form stable complexes with $PdCl_2$ or $PtCl_2$. These represent the first isolable transition-metal complexes of azirines. Compared to the free azirines, the palladium complexes **2** exhibit an unusually high stability toward air, moisture, and UV light. Thermolysis leads to 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]

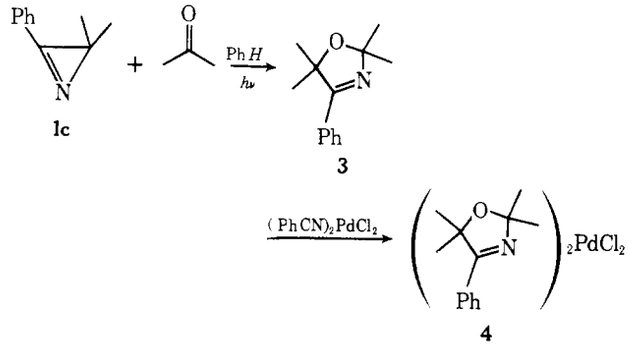
Results

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.



1 2

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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