J. Am. Chem. Soc. **1993,** *115,* 1177-1178 1177

down to 77 K. The appearance of the g_3 tensor in the ESR spectrum is a result of the distribution of ruthenium isotopes of different nuclear spins in the complex and deserves further comments. The observed hyperfine coupling which makes up 29.8% of the signal (sextet, $A = 3.37 \times 10^{-3}$ cm^{-1}) is due to coupling to the ^{99}Ru ($I = {}^5/_2$, 12.7%) and ^{101}Ru ($I = {}^5/_2$, 17.1%) isotopes, and the remaining, more intense singlet results from that fraction of the complex that contains the other ruthenium isotopes (I = 0, 70.2%).

Obviously, there remain many unanswered questions regarding the electronic structure of $Ru_2(dpf)_4(C{\equiv}CC_6H_5)_2$. A thorough investigation of the chemical, electrochemical, and spectroscopic properties of this complex as well as the synthesis of other Ru_2^{6+} complexes[27] is under way.

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(27) $Ru_2(ap)_4(C{\equiv}CC_6H_5)_2$ has been synthesized by a modification of the procedure described in ref 21. The crystal structure and other properties are currently under investigation.

New Route to Substituted Piperidines via the Stevens [1,2]-Shift of Ammonium Ylides

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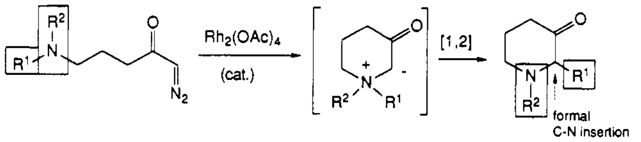
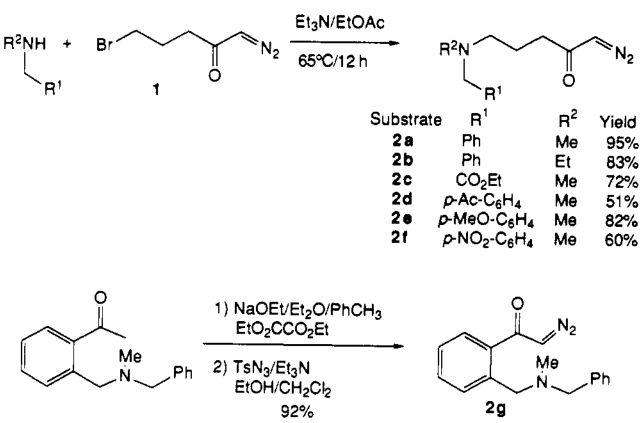
Piperidine rings are frequently encountered structural components in alkaloid natural products. Recently, we have investigated an approach to functionalized cyclic amines via ammonium ylides. The Stevens rearrangement of ammonium ylides has often been the subject of mechanistic studies since its initial observation,[1] yet it has been only sporadically applied to organic synthesis.[2] Potential problems include competing Hofmann eliminations[3] or Sommelet-Hauser rearrangements,[4] as well as controllable generation of the ylide intermediate. However, we felt that the benefits of the reaction (successive formation of strategic carbon-nitrogen and carbon-carbon bonds) demanded a closer examination of its applicability to synthesis.

An attractive method for direct generation of the requisite cyclic ylides involves rhodium(II)-catalyzed decomposition of diazo carbonyl compounds[5] bearing dialkylamino substituents six centers away from the carbenoid center (eq 1).[6-8] Stevens [1,2]-shift of one of the exocyclic groups would result in a new nitrogen heterocycle in which the carbenoid carbon had formally undergone insertion between N and R^1. Although competing C-H insertion might be a concern in those cases where a five-centered transition state was accessible,[9] we felt that the electron deficient carbenoid would preferentially react at the site of greatest electron density, the amino lone pair. We report here the successful implementation of this strategy and its utility in the synthesis of 2-substituted piperidin-3-ones.



(1)

Scheme I



Substrate	R^1	R^2	Yield
2a	Ph	Me	95%
2b	Ph	Et	83%
2c	CO_2Et	Me	72%
2d	*p*-Ac-C_6H_4	Me	51%
2e	*p*-MeO-C_6H_4	Me	82%
2f	*p*-NO_2-C_6H_4	Me	60%

The most convenient route to the desired substrates proved to be direct alkylation of secondary amines with 5-bromo-1-diazo-2-pentanone (**1**)[10] (Scheme I). In this way, diazo ketone substrates **2a-f** were prepared in 51-95% yield. Compound **2g** was efficiently obtained from 2′-acetyl-*N*-benzyl-*N*-methylbenzylamine via deacylative diazo transfer on the oxalacetyl derivative.[11]

Table I lists the results obtained from addition of compounds **2a-g** to a catalytic amount of $Rh_2(OAc)_4$ in dichloromethane. A major concern was the known high affinity of amines for the empty coordination sites on the dimeric catalyst.[12] The only prior successful example of ammonium ylide generation from Rh-carbenoids overcame this problem by use of extremely long addition times.[5a] In the event, substrates **2a-f** gave good to excellent yields of the desired 3-piperidone [1,2]-shift products **3a-f** *without resort to high-dilution conditions or slow addition.* Benzo-fused

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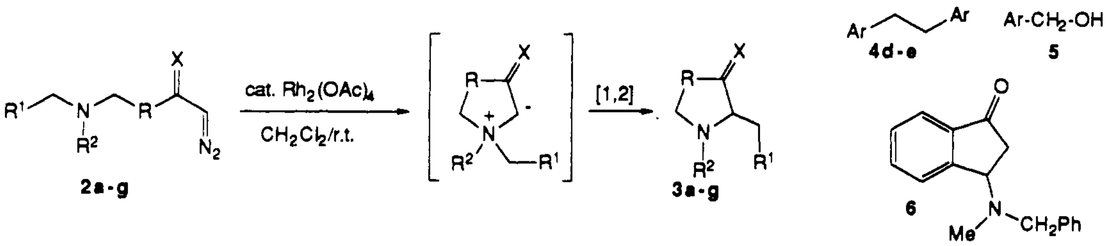
0002-7863/93/1515-1177$04.00/0

Table I. Treatment of ω-dialkylaminodiazoketones with $Rh_2(OAc)_4$[a]



substrate	R	X	R^1	R^2	[1,2] product (yield, %)[b]	other products[b]
2a	$(CH_2)_2$	O	Ph	Me	**3a** (99)	
2b	$(CH_2)_2$	O	Ph	Et	**3b** (91)	
2c	$(CH_2)_2$	O	CO_2Et	Me	**3c** (94)	
2d	$(CH_2)_2$	O	p-AcC_6H_4	Me	**3d** (71)	**4d** (25)
2e	$(CH_2)_2$	O	p-$MeOC_6H_4$	Me	**3e** (71)	**4e** (19)
2f	$(CH_2)_2$	O	p-$NO_2C_6H_4$	Me	**3f** (56)	**5** (5)
2g	o-C_6H_4	O	Ph	Me	**3g** (40)	**6** (23)

[a] Standard procedure: Substrates were dissolved in CH_2Cl_2 (0.05 M) and added dropwise by cannula to 3 mol % $Rh_2(OAc)_4$ in CH_2Cl_2 at room temperature over 0.5 h. After an additional 0.25 h, the reaction mixture was worked up and immediately chromatographed. [b] Isolated yields after chromatography. Satisfactory IR, ^1H and ^{13}C NMR spectra, and combustion analysis or HRMS data were obtained for substrates **2a–g** and their rearrangement products.

substrate **2g** gave a mixture of dihydroisoquinolone [1,2]-shift product **3g** and C–H insertion product **6**.

Importantly, complete migrating group selectivity was seen in all cases, consistent with the expectation that the carbon with the best radical stabilizing substituent will migrate.[13] As can be seen from the reaction of glycine derivative **2c**, migration was not limited to benzylic groups. Substrate **2b**, which proceeded through an N-ethylammonium ylide, showed no evidence of α',β-fragmentation to generate ethylene and 1-benzyl-3-piperidone.[14] Those cases involving substituted benzyl migrating groups actually showed a diminished yield of [1,2]-shift product, apparently due to a greater tendency for the presumed benzylic radical intermediate[7c,13] to suffer escape from the solvent cage and undergo homocoupling to give **4d,e** or reaction with oxygen to give **5**. However, we were unable to isolate any of the corresponding bis(3-piperidone) dimers.[15]

Despite the availability of a five-membered C–H insertion transition state to carbenoids derived from substrates **2a–f**, 3-aminocyclopentanones from this pathway were not observed.[16] The one exception was **2g**, which gave 3-aminoindanone **6** as a substantial byproduct, perhaps due to enforced proximity resulting from ortho disposition of the benzylic methylene and the carbenoid. It should also be noted that none of the isomeric 2-aminoindanone which would derive from competing [1,2]-shift of the *endocyclic* benzyl carbon was seen. A comparable result observed by Ollis et al. when the same ylide was generated by quaternization/deprotonation[17a] was rationalized in terms of poor benzylic overlap with the incipient radical during endocyclic C–N homolysis.

In summary, we have demonstrated that the overall sequence of rhodium-catalyzed carbenoid generation/ammonium ylide formation/Stevens [1,2]-shift utilizing acyclic γ-dialkylamino diazo carbonyl substrates can be applied to the synthesis of six-membered nitrogen heterocycles in good to excellent yields. Starting materials are easily prepared in one step from secondary amines. The key step is exceedingly simple and does not require high-dilution conditions. The use of this transformation in the synthesis of alkaloid targets is currently being investigated and will be reported in due course.

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Supplementary Material Available: Representative procedures for the synthesis of diazo ketones **2a** and **2g** and piperidone **3a** along with physical data for all substrates and their [1,2]-shift products (5 pages). Ordering information is given on any current masthead page.

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Molecular Sieving by a Perforated Langmuir–Blodgett Film[1]

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Molecular separations, via the use of synthetic membranes, are beginning to yield new and more energy-efficient methods for chemical processing.[2] Further advances in this area will require the creation of novel materials that exhibit high permeation selectivity (permselectivity) and high permeation rates.[3] We have previously outlined a strategy for the synthesis of perforated monolayers, based on the use of porous surfactants.[4,5] We have also proposed that such assemblies could be used to construct composite membranes that distinguish permeants on the basis of their molecular size. Here, we provide experimental verification of this concept. Specifically, we describe the synthesis and permeation characteristics of Langmuir–Blodgett (LB) multilayers

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[1] Supported by the Division of Basic Energy Sciences and the Department of Energy (DE-FG02-85ER-13403) and by Air Products and Chemicals, Inc., Allentown, PA.

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