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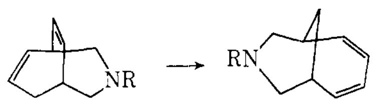
A Remarkably Facile 1,3-Sigmatropic Suprafacial Shift with Retention of Stereochemistry. Catalysis of Carbon–Carbon Bond Migration by an Amide Ion Substituent

Sir:

Since Woodward and Hoffmann[1] in 1965 first announced the principle of the conservation of orbital symmetry in concerted reactions, there have been refinements of the theory and the presentation of alternative schemes for discussion of pericyclic reactions.[2,3] One modification or clarification of the Woodward-Hoffmann rules[1] involves the allowed stereochemistry of 1,3 shifts, where it appears two concerted pathways can be available.[2a,3] A fine balance of opposing electronic and steric effects suggests that when migration by an electronically favored suprafacial inversion (si) pathway is sterically prohibited, the suprafacial retention (sr) pathway can proceed in a concerted manner. Herein we report a novel example of the sr 1,3 shift[5,6] in which a dramatic effect on reaction energetics results from hydrogen atom removal on a nitrogen substituent adjacent to the migrating center.[5]

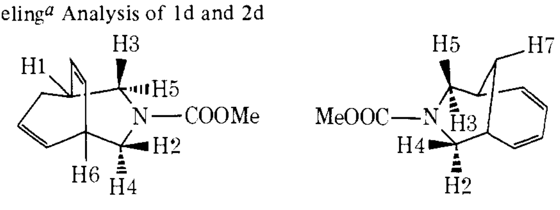
The *N*-benzyl[7] (**1b**) and *N*-carbomethoxy[8] (**1d**) derivatives of 3-azabicyclo[3.3.2]deca-6,9-diene (**1a**) have been purified by GLPC. Therefore, it was surprising when introduction of amine **1a** into a GLPC injector port heated to 250° (column temperature[10] 120°) was followed by isolation of only amine **2a**[11] (90% recovery), the product of 1,3-sigmatropic rearrangement. Even more surprising, if amine **1a** in either diethyl ether or *n*-pentane was treated with methyllithium at 30° after 1 min a complete conversion to amine **2**[12] (90% recovery) resulted.



1a, R = H
b, R = CH_2Ph
c, R = COOPh
d. R = COOMe

2a, R = H
b, R = CH_2Ph
c. R = COOPh
d. R = COOMe
e. R = COPh

Table I. Partial ^{1}H NMR (100 MHz) and Deuterium (D) Labeling[a] Analysis of 1d and 2d



1d **2d**

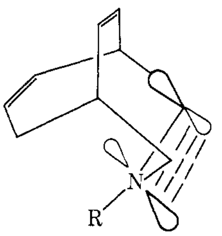
	1d		2d		Reaction path,[f] calcd %-one D for 2d		
Proton	Shift (δ)[b]	D (%)[c,d]	Shift[e] (δ)	D (%)	sr	rac (sr + si)	si
H2	2.73[g]	35 ± 3	4.09[k]	92[m] (90)[n]	93	77	62
H3	2.79[g]	58	(4.09)				
H4	3.02[h,i]	3.5	2.85[l]	8[m] (10)[n]	7	23	38
H5	3.36[h,j]	3.5	(2.85)				

[a] Standard deviations were used to determine the most probable error $\delta y/y = [(\delta a/a)^2 + (\delta b/b)^2 + \ldots]^{1/2}$. ^{1}H NMR of the phenyl carbamate derivatives 1c and 2c confirmed these results. [b] Benzene-d_6, 76°. [c] H2 + H3 = 93 ± 3%, the ratio (H2 + H3)/(H4 + H5) was determined via relative ^{1}H NMR peak areas. [d] The H2/H3 ratio was determined from relative ^{1}H NMR peak heights; J. A. Dale and H. S. Mosher, *J. Am. Chem. Soc.*, 90, 3732 (1968). [e] $CDCl_3$, 76°. [f] sr, si = suprafacial retention and inversion, respectively, rac = racemization. [g] d, *J* = 14 Hz. [h] Broad. [i] Irradiation of H6 (δ 2.51) collapses H4 to a d, *J* = 14 Hz. [j] Irradiation of H1 (δ 2.00) collapses H5 to a d, *J* = 14 Hz. [k] d, *J* = 13 Hz. [l] dd, *J* = 4 Hz, 13 Hz. [m] H2 + H3 = 92 ± 1% from 1a and methyllithium in ether or pentane. [n] H2 + H3 = 90 ± 2%, GLPC of 1a at 250° injection temperature.

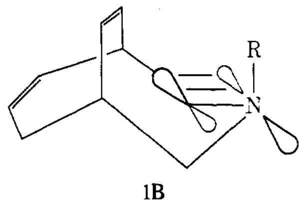
To study rearrangement stereochemistry amine **1a** was synthesized[13] with one deuterium atom selectively distributed among the positions α to nitrogen. Selectively labeled **1a** was then rearranged to labeled **2a** and the fate of the label during rearrangement was determined by ^{1}H NMR integration (Table I). Because of conformational mobility of **1**, dihedral angle relationships do not reveal whether H2/H3 or H4/H5 is the exo pair. However, the deuterated methylurethanes[8] **1d** and **2d** could be used to assign H3 of **1d**, and thence from coupling data all protons α to nitrogen. First, the endo proton H3 in **2d** was assigned by its W-plan[15] coupling with the bridge proton H7. Second, the exo proton H3 of **1d** has not undergone stereomutation during rearrangement so it has been transformed into endo proton H3 of **2d.** It then follows since **2d** has 92% of the label at the endo H2/H3 positions that the most deuterated shift position of **1d** at δ 2.79 (58% D) must correspond to exo proton H3.

Comparison of the situs of deuterium label of **1d** determined by ^{1}H NMR integration with the predicted deuterium label for various stereochemical possibilities (Table I) indicates net retention of stereochemistry (sr) during thermal or methyl lithium catalyzed sigmatropic rearrangement. The yield and stereochemical data, while consistent with a concerted mechanism, does not exclude stepwise ionic or radical pathways.[16] Error limits of the data do allow for contribution from random processes of 46% (77% sr, 23% si) during thermal rearrangement and 29% (85% sr, 15% si) during base catalyzed rearrangement of **1a.**

The most favorable overlap of the lone pair on nitrogen with the migrating σ bond results when R is exo in the N-anti conformation **1A** and R is endo in the N-syn conformation **1B.**[18] In both these conformations a substituent group, R = CH_2Ph or COOMe, is in the sterically more crowded position and should as observed raise the transition state energy relative to R = H. Removal of the nitrogen substituent



1A



1B

assures electron density overlap. Further theoretical interpretation and clarification of the role of counterions in the rearrangement of **1a** and related systems[19] are needed.

Acknowledgment. We thank Dr. Paul Schleyer for helpful comments.

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(10) Various XF-1150 and SF-96 on Chrom G columns were used with complete rearrangement irrespective of column. Some catalysis occurs during GLPC, since when **1a** was passed through an acid-washed glass-bead-filled quartz tube at 420° (0.25 mm) only 20% rearrangement of **1a** to **2a** resulted. Above 500° the amines decomposed. Unsuccessful thermal rearrangement of *N*-benzylamine **1b** by GLPC at increasing temperatures ultimately resulted only in decomposition.

(11) The structure of amine **2a** was confirmed by lithium aluminum hydride reduction of its benzoylamide **2e** to *N*-benzylamine **2b**.[7]

(12) Attempts to measure the rate of rearrangement by ^{1}H NMR were unsuccessful. When an NMR tube containing **1a** and methyllithium in ether was brought from −76° to 20° the spectrum remained unchanged. Above 30° the sample exploded.

(13) Deuterated *N*-benzylamine **1b** was synthesized as previously,[7] but substituting sodium borodeuteride for sodium borohydride. The benzyl group was cleaved[14] from **1b** using phenyl chloroformate (12 hr, $CHCl_3$, 80% yield) to afford **1c**. The carbamate was cleaved with excess methyllithium (8 hr, 4°, 20%) to give amine **1a**. Despite the rapidity of the room temperature reaction of **1a** with methyllithium no rearrangement to **2a** occurred under the cleavage conditions.

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(16) Reversible allylic Grignard addition to ketones is known.[17] We observed no trapping by methyl- or phenyllithium (35°) of the imine formally formed by ring opening of **1a** anion. After 4 hr polymerization occurred by some pathway.

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Received February 27, 1975

Luminescent Osmium(II) and Iridium(III) Complexes as Photosensitizers

Sir:

The luminescent transition metal complexes $Ru(bipy)_3^{2+}$, $Ru(bipy)_2(CN)_2$, $Ru(phen)_3^{2+}$, and $Ru(phen)_2(CN)_2$ (bipy = 2,2′-bipyridine; phen = 1,10-phenanthroline) have been widely used as a versatile new class of photosensitizers.[1-12] Although possessing nearly ideal sensitizer properties, including intense fluid solution emissions, applications have been seriously restricted by their narrow range of donor energies (~18–19 kK) and excited-state reduction potentials. We report here the first successful use of highly luminescent Ir(III) and Os(II) complexes as photosensitizers. These complexes enormously increase the range of donor energies available (~15–23 kK) and roughly double the available number of luminescent transition-metal complex photosensitizers. A correspondingly wide range in the reducing power of the excited states is also expected.

Table I. Optical Properties of Os(II) and Ir(III) Photosensitizers in Methanol at ~21°

Complex[a]	E_0, kK	τ_0, μsec[b]
$Os(bipy)_3^{2+}$	14.9	0.049
$Os(phen)_3^{2+}$	15.3	0.183
$Os(phen)_2(Ph_2phen)^{2+}$	15.0	0.212
$Os(phen)_2[(SO_3Ph)_2phen]$	14.8	0.093
$Ir(bipy)_3^{3+}$	22.7	2.4
$Ir(phen)_3^{3+}$	22.5	2.9

[a] bipy = 2,2′-bipyridine; phen = 1,10-phenanthroline; Ph_2phen = 4,7-diphenyl-1,10-phenanthroline; $(SO_3Ph)_2phen^{2-}$ = disulfonated 4,7-diphenyl-1,10-phenanthroline. [b] Estimated accuracy ±5%. Precision ±1%.

Table I lists two iridium and four osmium complexes which sensitize photooxygenations of organic singlet-oxygen scavengers. Also listed are the zero-point donor energies, E_0's, and the mean lifetimes in deoxygenated methanol, τ_0's, at ~21°. Using either lasers or water-filtered tungsten lamp radiation, all complexes in O_2-saturated methanol yield rapid photooxidation of tetramethylethylene and trimethylethylene. The Os(II) complexes sensitize oxidation of thiourea, but the Ir(III) complexes are strongly quenched by thiourea and yield negligible O_2 uptakes. All successful photooxidations were catalytic in complex (10–100 mol of O_2 consumed/mol of sensitizer).

With the osmium complexes, $^1O_2$ was confirmed as the reactive species by comparing the mole ratio of the two hydroperoxides formed with that obtained using $^1O_2$ (obtained by Rose Bengal sensitized photooxidation). Within experimental error (~10%), the mole ratios of the products were the same. Similar experiments with $Ir(bipy)_3^{3+}$ (351, 356 nm) were hampered by the photosensitivity of the complex and apparent interference of the decomposition products with our analytical procedure.[13] By analogy with the Os(II) and Ru(II) complexes, we infer, however, that energy rather than electron transfer was the dominant quenching mode in all cases.

Energy-transfer efficiencies to O_2 are high (>0.5). For example, the Os(II) complexes are more efficient $^1O_2$ generators than Methylene Blue, absorb strongly across the entire visible and near uv, and are being studied for use in chemical actinometers for high power Kr, Ar, and He-Ne lasers. There does, however, appear to be a small component of nonenergy transfer quenching by O_2 with all complexes, except perhaps the iridium ones.[13]

Unlike the Os(II) complexes which exhibit no noticeable degradation under our experimental conditions, the iridium(III) complexes are somewhat photosensitive in methanol, which somewhat restricts their usage, although in other solvents such as dimethylformamide the sensitivity may be much less.[14,15] The photosensitivity is not a serious problem, however, for many mechanistic studies where only small conversions of acceptor are needed or where quenching of the luminescence only is required to establish the presence of electron transfer or a low lying quencher state and to measure rate constants. For example, see ref 3, 4, and 10 where good data were obtained even when the donor disappeared with yields >0.1–0.5.

$Os(bipy)_3^{2+}$, at least in methanol, has a very short life-