

appears to be very common in the medium rings studied.

Since this method efficiently finds additional conformations from any starting geometry, it should be a valuable adjunct to any molecular mechanics program.

Acknowledgment. This work was supported by a grant from the National Science Foundation. I should like to dedicate this paper to Professor V. Prelog on the occasion of his 80th birthday.

Supplementary Material Available: A table of MM2 energies and dihedral angles for the best 7-15-membered cyclic, saturated hydrocarbons (3 pages). Ordering information is given on any current masthead page.

Convenient Routes to Vicinal Diamines. Coupling of Nitriles or *N*-(Trimethylsilyl)imines Promoted by $\text{NbCl}_4(\text{THF})_2$

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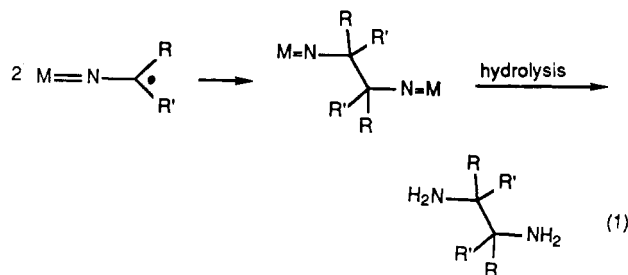
Received November 10, 1986

The reductive coupling of aldehydes or ketones leading to vicinal diols or olefins is promoted by a variety of reductants including low-valent early transition metals.¹ Among these, the most widely used are a series of titanium reagents derived from the reduction of titanium(III or IV) chloride.² Similar reactions involving carbon-nitrogen functions (e.g., imines) are less common. For example, unlike their carbonyl analogues, *N*-alkyl (or aryl) imines show little or no reactivity with low-valent titanium reagents.³ This is an unfortunate result in view of the fact that very few general routes to vicinal diamines are known in the literature and the majority of these rely on olefin addition reactions that require several steps to arrive at the desired diamine products.⁴ Carbon-carbon bond-forming routes to diamines are especially rare and are typically limited to the synthesis of *N,N*-disubstituted amines.⁵ Herein we report a convenient one-pot synthesis of unsubstituted vicinal diamines from either *N*-(trimethylsilyl)imines or nitriles employing the d^1 niobium reagent, $\text{NbCl}_4(\text{THF})_2$.

The approach toward vicinal diamine synthesis presented in this paper originated from considering the resonance structure one can write for a simple d^1 *N*-metal imine derivative (A and B). When M is an early transition metal, resonance structure



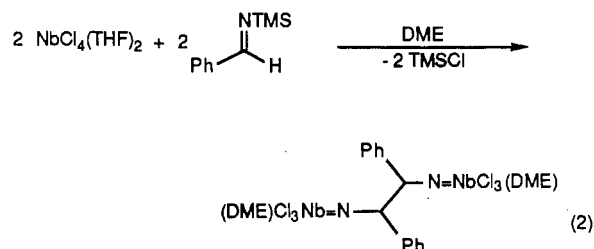
B represents a metal-imido function.⁶ Dimerization of this metal-protected α -amino radical would lead to the diimido compound shown in eq 1. Hydrolysis would then give the unsubstituted vicinal diamine. Related to this reaction are examples from low-valent metal alkoxide chemistry where homolytic car-



bon-oxygen bond cleavage leads to metal-oxo formation and the generation of free radicals.⁷

To examine this hypothesis we chose the d^1 niobium complex $\text{NbCl}_4(\text{THF})_2$ for two reasons, the first of which is related to its availability on large scales (>100 g) from commercially inexpensive niobium pentachloride.⁸ The second reason pertains to the well-documented existence of niobium-imido complexes (the proposed product in this reaction).⁶

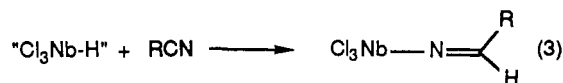
Reaction of $\text{NbCl}_4(\text{THF})_2$ with the trimethylsilyl imine of benzaldehyde in dimethoxyethane (DME) (eq 2) gives a yellow



crystalline product (60% isolated yield) that has been characterized⁹ as the diimido complex shown in eq 2. Hydrolysis of this material with 10% potassium hydroxide provided a quantitative yield of *d,l*-1,2-diphenylethylene-1,2-diamine, confirmed by comparison with an authentic sample.¹⁰ Hydrolysis of the entire reaction mixture (i.e., prior to crystal isolation) afforded a 69% yield of the same diamine as a 19:1 (*d,l*/meso) mixture of diastereomers. Five other examples of *N*-(trimethylsilyl)imines that have been coupled are shown in Table I.

A limiting feature of this reaction is the lack of general methods available for synthesizing *N*-(trimethylsilyl)imines. Those in Table I were prepared by the addition of $\text{LiN}(\text{SiMe}_3)_2$ to the appropriate aldehyde followed by quenching with trimethylsilyl chloride and distillation.¹¹ This method is limited to nonenolizable aldehydes or ketones.

The generation of niobium imines directly from nitrile insertion into a niobium(IV) hydride would provide a practical route to diamines (eq 3). Such insertion reactions have been reported



for a few well-characterized early-transition-metal hydrides.¹² The absence of any simple d^1 niobium halo hydrides¹³ in the literature

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(9) ¹H NMR (CD_2Cl_2) δ 3.57 (s, 3 H), 3.95 (s, 3 H), 4.08 (s, 4 H), 6.49 (s, 1 H), 7.20 (m, 5 H). Anal. Calcd for $\text{Nb}_2\text{C}_{22}\text{H}_{32}\text{Cl}_6\text{N}_2\text{O}_4$: C, 33.57; H, 4.39; N, 3.56. Found: C, 33.33; H, 4.14; N, 3.52.

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Table I^a

Method A						Method B					
NbCl ₄ (THF) ₂						RCN					
R-CH=NTMS						R-CH=NTMS					
KOH						KF; KOH					
R-CH(NH ₂)-CH(NH ₂)-R						R-CH(NH ₂)-CH(NH ₂)-R					
Entry	R	Method	Yield % ^b	d.s. (d:l:meso) ^c	Diamine	Entry	R	Method	Yield % ^b	d.s. (d:l:meso) ^c	Diamine
1		A	69	19:1		8		B	81	2:1	
		B	70	8:1		9		B	45	1.4:1	
2		A	70	24:1		10		B	50	1:1	
		B	49	4:1		11		B	56	1.3:1	
3		A	60	19:1		12		B	63	3:1	
		B	40	6:1		13		B	40	8:1	
4		A	43	18:1							
5		A	62	2:1							
		B	52	2:1							
6		B	60	2:1							
7		A	73	16:1							
		B	47	13:1							

^a All compounds were characterized by ¹H, ¹³C, IR, mass spectrometry and C, H, N analysis. ^b All yields are of isolated products. ^c Determined by ¹H NMR or GC. See supplementary material.

prompted us to search for an in situ route to such species. If a hydride could be generated in the presence of a nitrile, insertion might occur faster than decomposition of the hydride intermediate. This required choosing a hydride source that would react exclusively with the niobium reagent in the presence of a nitrile. As indicated in Table I, tributyltin hydride effectively meets this requirement.

Especially noteworthy is the fact that all of the diamines prepared by this method are suitable for further use directly after workup. This is a function of the diamine being retained on the niobium dimer, in the form of the diimido ligand, until basic hydrolysis is applied (hydrolysis of the diimido species is slow at neutral pH). First, the majority of the tributyltin chloride is removed by transforming it into an insoluble fluoride polymer (potassium fluoride quench¹⁴) with concomitant formation of a water-soluble niobium-imido complex. This is followed by an organic wash which removes any remaining nitrile along with any other organic products that are not attached to niobium via an imido linkage (including the tetrahydrothiophene¹⁶ solvent). Potassium hydroxide is then added to release the diamine. Representative procedures for the trimethylsilyl imine (method A, Table I) and nitrile (method B) coupling reactions are given below. All reactions were performed under a nitrogen atmosphere.

Method A: To a dry 1-L flask was added NbCl₄(THF)₂⁸ (10.0 g, 26.4 mmol) followed by dimethoxyethane¹⁵ (ca. 450 mL). The mixture was stirred until the NbCl₄(THF)₂ dissolved (5–10 min, producing an orange solution); then a solution of *N*-(trimethylsilyl)benzylideneimine (4.68 g, 26.4 mmol) in dimethoxyethane (10 mL) was added. The reaction was stirred for 4 h, becoming yellow-green in color and forming a yellow precipitate. The dimethoxyethane was removed in vacuo and the residue was

treated with potassium hydroxide (10% w/v, ca. 125 mL). After it was stirred for 20 min, the solution was extracted with diethyl ether (3 × 100 mL), and the organic layers were combined. After the mixture was dried with MgSO₄, the ether was removed in vacuo yielding an off white solid which was recrystallized from hexane/ether to afford white needles (1.93 g) of 1,2-diphenylethylene-1,2-diamine (entry 1 in Table I).

Method B: To a dry 500-mL flask was added NbCl₄(THF)₂ (10.0 g, 26.4 mmol) and tetrahydrothiophene¹⁶ (ca. 300 mL). To the stirring solution was added benzonitrile (2.72 g, 26.4 mmol) followed by tributyltin hydride (7.68 g, 26.4 mmol). After 6 h, potassium fluoride (10% w/v, ca. 100 mL) was added and the mixture vigorously stirred for 20 min. The solids which formed were removed by suction filtration. The filtrate was extracted with ethyl ether (2 × 100 mL) and the ether fractions were discarded. Potassium hydroxide (10% w/v, ca. 150 mL) was added and the mixture stirred for 20 min. The resulting solution was extracted with ethyl ether (3 × 100 mL). The organic layers were combined, dried (MgSO₄), and filtered and the ether was removed in vacuo to give white crystalline diamine (entry 1 in Table I).

No cyclization¹⁷ to five- or six-membered rings was observed when 5-hexenenitrile was used (entry 8 in Table I), suggesting that there is no long-lived carbon radical character associated with this system (see A ↔ B). Further work concerned with extending this chemistry to include intramolecular cyclization reactions as well as other applications of NbCl₄(THF)₂ and analogous d¹ metal reagents in organic synthesis will be reported in the future.

Acknowledgment. Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for the support of this research and to the

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National Science Foundation for a Presidential Young Investigator Award (Grant CHE-8552735).

Supplementary Material Available: Full NMR, IR, and mass spectral data and C, H, N analysis information for compounds 1-13 (6 pages). Ordering information is given on any current masthead page.

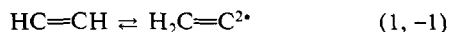
Pyrolysis of Acetylene: A Thermal Source of Vinylidene

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Received November 21, 1986

Nonempirical molecular orbital calculations reveal that vinylidene exists in shallow (~ 4 kcal/mol) minimum of the C_2H_2 potential energy surface at about 40 kcal/mol above ground-state acetylene; on the other hand, dynamical considerations, tunneling included, set an upper limit of about 10 ps for its lifetime toward rearrangement to acetylene.¹⁻⁴ Rational skepticism thus prevails about the possibility of detecting such species either by chemical or spectroscopic means. The recent finding that the CH_2 scissors and $C=C$ stretching vibrations of $H_2C=C^{2*} \ ^1A_1$ can be excited up to 12 kcal/mol by electron photodetachment of its anion does not really improve the prospects since an even shorter time scale is involved in such event.⁵ In this connection the thermal intramolecular scrambling observed in the system $HC=^{13}CDC=DC=^{13}CH$, which apparently requires a discrete symmetrical intermediate resembling vinylidene, looks more auspicious.⁶ We now report the results of kinetic and trapping experiments performed in acetylene/benzene and acetylene/toluene mixtures above 820 K by modulated beam dynamic mass spectrometry which provide direct evidence of vinylidene participation in chemical reactions. Under such conditions the fast equilibrium



precedes carbene addition to the aromatic ring thereby circumventing kinetic restrictions arising from the short lifetime of vinylidene.

Pyrolyses were carried out in a 122-cm³ fused silica reactor coupled to a on-line modulated beam mass spectrometer (EMBA II, Extrel) via a molecular leak. An all-glass mixer was used to homogenize gas mixtures prior to expansion into the heated reactor. This setup was adequate for the continuous monitoring of reactants and products including labile or unvolatile species. Reproducible kinetic results could be routinely obtained by alternating "conditioning" pyrolyses at about 200 K above reaction temperatures. Acetylene was purified by passage through water and subsequently distilled at -90 °C. Reagent grade benzene and toluene were further purified by vacuum distillation. Ethylene (Matheson) was used as received. Second-order rate constants for the decomposition of neat acetylene up to 50% conversions as well as those derived from its pseudo-first-order decay in about 10-fold excess of benzene or toluene are shown in Figure 1. All are very similar in the range 820-970 K, leading to an average

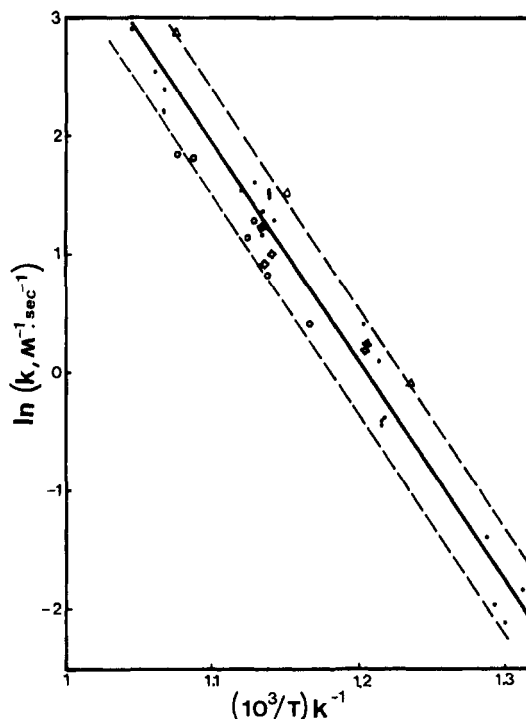


Figure 1. Rate constants for reaction between $2C_2H_2$ (\bullet), $2C_2H_2$ in excess of N_2 (\square), $C_2H_2 + C_6H_6$ (\circ), and $C_2H_2 + C_6H_5CH_3$ (Δ) as function of temperature. Broken lines correspond to $(k \pm 2\sigma)$.

activation energy of 37 ± 2 kcal/mol in accord with earlier measurements for acetylene pyrolysis.⁷ This clearly suggests a common mechanism, further confirmed by product analyses. Thus the self-reaction of C_2H_2 leads first to vinylacetylene but soon evolves into benzene whose fragment at m/z 52 overlaps the molecular ion of C_4H_4 .⁸ Proper analysis of the composite signal indicates that the concentration of C_4H_4 initially rises and then levels off, revealing decomposition or further reaction with C_2H_2 . On the other hand, the mass spectra of reacting $C_2H_2:C_6H_6$ mixtures display a series of major products at m/z $78 + 26n$, $n = 1, 2, 3$, and 4 (Figure 2a). Since benzene is verifiably stable under all conditions, these species obviously involve the sequential addition of C_2H_2 and are tentatively assigned to polyvinyl benzenes, both for kinetic and thermodynamic reasons and on the basis of the conspicuous pattern of M^+ , $(M-1)^+$, and $(M-2)^+$ signals also observed in the reported mass spectra of divinyl benzenes.⁹⁻¹² When toluene replaces benzene, large signals at m/z 117 and 118 (but not at m/z 104), corresponding to methyl styrene isomers, appear early in the course of reaction (Figure 2b).⁹ In this case the higher reactivity of toluene (see Figure 1) apparently prevents further addition of C_2H_2 units past the first step, strongly suggesting the electrophilic nature of the intermediate involved.¹³ The crucial issue of whether this is the vinyl radical or a reactive isomer of acetylene such as $H_2C=C^{2*}$ or a triplet state 3C_2H_2 is now addressed. Since ethylene is known to undergo thermal disproportionation into vinyl and ethyl radicals, it was thought that the identity of the products formed by decomposing ethylene in excess toluene should provide a clue to this question.¹⁴ Now in addition to methylstyrene, styrene itself m/z 104, divinyl benzenes m/z 130, and traces of methylethylbenzene m/z 120 were also detected (Figure 2c). The new species certainly derive from vinyl radical displacement of the methyl group in toluene and methyl styrenes, a process otherwise inaccessible to carbenes.

We have recently shown that a vinyl radical chain mechanism for acetylene thermal dimerization is untenable on kinetic and

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