Preparation of Stable Primary Enamines: 1-Aminobutadienes by Allyl Grignard Addition to Aryl Cyanides Followed by Controlled Hydrolysis

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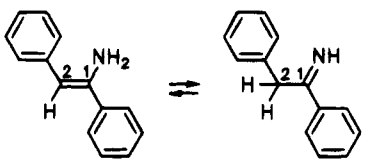
From thermochemical data it is suggested that 1-aminobutadienes are more stable than their nonconjugated imine tautomers by about 2 kcal mol^{-1}. High level ab initio calculations have established the thermodynamic preference of the conjugated primary enamines over their β,γ-unsaturated ketimine isomers in the gas phase. This general prediction of an increased stability of primary enamines by butadiene conjugation has been confirmed experimentally with a variety of representative examples. Allyl Grignard addition to a number of aryl or hetaryl cyanides followed by controlled hydrolysis yields the respective β,γ-unsaturated ketimine systems that subsequently rearrange completely to their 1-aminobutadiene isomers. Rearrangement to the thermodynamically more favored α,β-unsaturated imine tautomers is kinetically inhibited and, hence, not observed in these systems. In some cases conjugated enamine formation is already observed at the stage of the organometallic intermediates.

Introduction

The primary enamine ⇌ imine tautomeric equilibrium is strongly dependent on substituents attached at carbon atoms in the α- and β-positions to the functional group. Carbonyl substituents at C1 destabilize the ketimine isomer **2** and thus lead to a high enamine concentration under equilibrium conditions. Carbonyl groups at C2, on the other hand, stabilize the carbanion character and thus strongly favor the enamine tautomer (**2**).[1] Experimental studies by H. Ahlbrecht[2] and others[3] have shown that alkyl and aryl groups at C1 have only a negligible influence on the enamine ⇌ imine equilibrium whereas alkyl groups at C2 markedly disfavour the alkenamine. Aryl substituents at C2 increase the primary enamine stability; e.g. the tautomeric equilibrium **1** ⇌ **2** in chloroform is close to 1:1.



1 **2**

We have recently prepared 1,6-diamino-1,3,5-hexatrienes **5**[4] by means of an organometallic template reaction.[5] These tail-to-tail-connected conjugated primary enamines are very stable. A theoretical investigation has revealed that such systems are thermodynamically stabilized primary enamines.[6] It may be that the butadiene conjugation is sufficient to tip the enamine ⇌ imine balance so far to the conjugated alkenamine side that the 1-aminobutadiene tautomers become the only observed isomers under the conditions of thermodynamic control without the aid of further stabilizing functional groups.[7,8] This idea is supported by our recent observa-

† Quantum chemical calculations.

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(1) Recent examples: Blake, A. J.; McNab, H.; Monahan, L. C. *J. Chem. Soc., Perkin Trans 2* **1991**, 2003. Barluenga, J.; del Pozo Losada, C.; Olano, B. *Tetrahedron Lett.* **1992**, *33*, 7579. Barluenga, J.; Tomás, M.; Ballesteros, A.; Santamaria, J.; López-Ortiz, F. *J. Chem. Soc., Chem. Commun.* **1994**, 321. Erian, A. W.; Aziz, S. I.; Negun, A. M.; Sherif, S. M.; *J. Chem. Res. (S)* **1993**, 352. Koyama, H.; Kawato, T.; Kanatomi, H.; Matsushita, H.; Yonetani, K. *J. Chem. Soc., Chem. Commun.* **1994**, 579. Reviews: Reinhoudt, D. N. *Adv. Heterocycl. Chem.* **1977**, *21*, 253. Hickmott, P. W. *Tetrahedron* **1982**, *38*, 2050. Cook, A. G. *Enamine Synthesis, Structure and Reactions*; Marcel Dekker: New York, 1988. Chiang, Y.; Kresge, A. G. *Science* **1991**, *253*, 395. Erian, A. W. *Chem. Rev.* **1993**, *93*, 1991. Patai, S.; Rappoport, Z. (Series Eds.). *The Chemistry of Functional Groups: The Chemistry of Enamines,* Z. Rappoport, Ed.; Wiley: New York, 1994.

(2) Ahlbrecht, H.; Kröhnke, F. *Liebigs Ann. Chem.* **1967**, *701*, 126. Ahlbrecht, H. *Tetrahedron Lett.* **1968**, 4421. Ahlbrecht, H.; Rauchschwalbe, G. *Tetrahedron Lett.* **1971**, 4897. Ahlbrecht, H.; Papke, G. *Tetrahedron Lett.* **1972**, 4443. *Tetrahedron* **1974**, 2571. Ahlbrecht, H.; Hanisch, H.; Funk, W.; Kalas, R. D. *Tetrahedron* **1972**, *28*, 5481. Ahlbrecht, H.; Fischer, S. *Tetrahedron* **1973**, *29*, 659. Ahlbrecht, H.; Blecher, J.; Hanisch, H.; Papke, G.; Reiner, M. T. *Tetrahedron* **1973**, *29*, 3079. Ahlbrecht, H.; Funk, W.; Reiner, M. T. *Tetrahedron* **1976**, *32*, 479. Ahlbrecht, H.; Kalas, R. D. *Liebigs Ann. Chem.* **1979**, 102. See also: Duhamel, L.; Duhamel, P.; Legal, J.-C. *Bull Soc. Chim. Fr.* **1972**, 3230. Picard, J. P.; Aizpurua, J. M.; Elynsufi, A.; Kowalski, P. *J. Organomet. Chem.* **1990**, *391*, 13.

(3) Pickard, P. L.; Vaughan, D. J. *J. Am. Chem. Soc.* **1950**, *72*, 876. Pickard, P. L.; Polly, G. W. *J. Am. Chem. Soc.* **1954**, *76*, 5169. Clark, R. A.; Parker, D. C. *J. Am. Chem. Soc.* **1970**, *92*, 7257. Shin, C.; Masaki, M.; Onta, M. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1657. Ollinger, P.; Remp, W.; Junek, H. *Monatsh. Chem.* **1974**, *105*, 346. Pfau, M.; Ribiere, C. *Bull Soc. Chim. Fr.* **1971**, 2584. Brocas, J. M.; de Jeso, B.; Pommier, J.-C. *J. Organomet. Chem.* **1976**, *120*, 217. de Jeso, B.; Pommier, J.-C. *J. Chem. Soc., Chem. Commun.* **1977**, 565. Ohtsuka, Y. *J. Org. Chem.* **1978**, *43*, 3231. Compagnon, P. L.; Gasquez, F.; Kimny, T. *Synthesis* **1986**, 948. Sevin, A.; Masure, D.; Giessner-Prettre, C.; Pfau, M. *Helv. Chim. Acta* **1990**, *73*, 552. Walsh, P. J.; Baranger, A. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 1708. Smith, B. J.; Radom, L. *J. Am. Chem. Soc.* **1992**, *114*, 36. Review: Shainyan, B. A.; Mirskova, A. N. *Russ. Chem. Rev.* **1979**, *48*, 107.

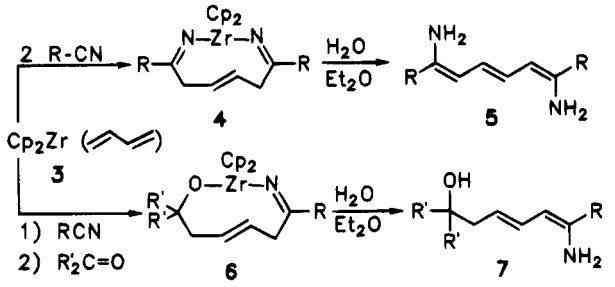
(4) Erker, G.; Pfaff, R.; Krüger, C.; Nolte, M.; Goddard, R. *Chem. Ber.* **1992**, *125*, 1669. Erker, G.; Pfaff, R. *Organometallics* **1993**, *12*, 1921. Wingbermühle, D.; Sarter, C.; Erker, G. *Inorg. Chim. Acta* **1994**, *222*, 193. Erker, G.; Wingbermühle, D.; Grehl, M.; Fröhlich, R. *Chem. Ber.* **1994**, *127*, 1331.

(5) Erker, G.; Berlekamp, M.; López, L.; Grehl, M.; Schönecker, B.; Krieg, R. *Synthesis*, **1994**, 212. For related template reactions see: Yasuda, H.; Tatsumi, K.; Nakamura, A. *Acc. Chem. Res.* **1985**, *18*, 120. Yasuda, H.; Nakamura, A. *Angew. Chem.* **1987**, *99*, 745. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 723. Yasuda, H.; Okamoto, T.; Matsuoka, Y.; Nakamura, A.; Kai, J.; Kanehisa, N.; Kasai, N. *Organometallics* **1989**, *8*, 1139. Erker, G.; Sosna, F.; Betz, P.; Werner, S.; Krüger, C. *J. Am. Chem. Soc.* **1991**, *113*, 564. Erker, G.; Sosna, F.; Zwettler, R.; Krüger, C. *Organometallics* **1989**, *8*, 450. Erker, G.; Sosna, F.; Noe, R. *Chem. Ber.* **1990**, *123*, 821. Erker, G.; Sosna, F.; Zwettler, R.; Krüger, C. *Z. Anorg. Allg. Chem.* **1990**, *581*, 16. Erker, G.; Sosna, F. *Organometallics* **1990**, *9*, 1949. Erker, G.; Sosna, F.; Pfaff, R.; Noe, R.; Sarter, C.; Kraft, A.; Krüger, C.; Zwettler, R. *J. Organomet. Chem.* **1990**, *394*, 99. Erker, G.; Pfaff, R.; Krüger, C.; Werner, S. *Organometallics* **1991**, *10*, 3559.

(6) Erker, G.; Pfaff, R.; Kowalski, D.; Würthwein, E.-U.; Krüger, C.; Goddard, R. *J. Org. Chem.* **1993**, *58*, 6771.

0022-3263/95/1960-5284$09.00/0

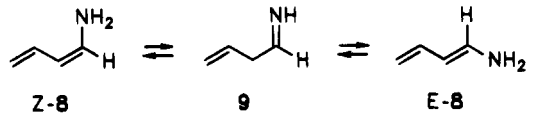
tion that compounds containing a stable 1-aminobutadiene subunit (**7**) have become available by a variation of our template synthesis.[9] This interpretation has been further supported by a theoretical investigation and by the development of a synthetic route to simple 1-aminobutadiene systems, both of which are described in this paper.



R = Aryl, Alkyl; R' = Aryl, Alkyl

Results and Discussion

Theoretical Studies. The heat of hydrogenation of 1-butene is 30.2 kcal mol^{-1}. The butadiene hydrogenation to butane is exothermic by 56.5 kcal mol^{-1} under standard conditions, which is 3.9 kcal mol^{-1} less than expected from the 1-butene reference value. This difference is attributed to the thermochemical conjugation energy of butadiene, i.e. the combined σ- and π-energy that is gained by bringing two vinyl groups into conjugation.[10] This effect is additive. The 1,3,5-hexatriene heat of hydrogenation is 79.4 kcal mol^{-1} which is 8.4 kcal mol^{-1} less than the sum of the 1-butene (2×) and *trans*-2-butene heats of hydrogenation. Thus the thermochemical conjugation energy of each CH_2=CHCH=CH unit in 1,3,5-hexatriene is 4.2 kcal mol^{-1}. In contrast, the heat of hydrogenation of styrene (to ethylbenzene) is only 28.1 kcal mol^{-1}; that means that the thermochemical conjugation energy of the arylalkene (2.1 kcal mol^{-1}) is ca. 2 kcal mol^{-1} less than that of butadiene.[10]



If these values are applied to the 1-aminobutadiene (**8**) ⇌ allylaldimine (**9**) equilibrium problem with the thermodynamic **1** ⇌ **2** 1:1 situation serving as the reference (see above), it is expected that the **8** ⇌ **9** equilibrium is shifted toward the enamine side by ca. 2 kcal mol^{-1}. In other words, a conjugated enamine should be ca. 2 kcal mol^{-1} more stable than its imine tautomer simply because of the 1,3-diene thermochemical conjugation energy, if the thermodynamic data of the corresponding hydrocarbon systems are valid when nitrogen-containing substituents are attached at these frameworks. The validity of this assumption cannot be taken for granted, but it would be of a great general interest to know whether such thermochemical data, which have been measured with very high accuracy and are available for a great variety of hydrocarbon systems,[10] can be reliably applied for such reactive substituted systems (as primary enamines or imines) from which such data are not easily available with sufficient accuracy experimentally because of their elusive nature or their high chemical reactivity. We have, therefore, studied the equilibrium between 1-aminobutadienes and their aldimine tautomers by quantum chemical calculations.

Table 1. Calculated Energy Differences of Pairs of Enamine/Imine Isomers (kcal/mol)

enamine/imine	ΔE^a 6-31+G*	ΔE^a MP2/6-31+G*
10/11	6.14	5.77
(*E*)-**8**/(*E*)-**12**	6.24	5.15
(*E*)-**8**/**9**	0.42	−0.95
(*Z*)-**8**/(*E*)-**12**	7.02	5.72
(*Z*)-**8**/**9**	1.19	−0.38
13/14	6.63	5.92
(*E*)-**15/16**	2.89	1.35
17/18	6.78	4.87

[a] Energy of the enamine relative to its best imine isomer, positive ΔE-values indicate that the enamine isomer is less favored under equilibrium conditions than the corresponding imine.

Ab Initio Computational Studies. As in our previous study[6] we again combine our experimental results with high level quantum mechanical ab initio calculations. The main question of this study concerns the relative energies of the various imine/enamine tautomers in view of the thermodynamics and kinetics of possible mutual interconversions. The 6-31+G* basis set[11] of the GAUSSIAN 92 program package[12] was used throughout for complete geometry optimizations. All structures obtained correspond to minima on the potential energy surface as indicated by frequency calculations (NIMAG = 0). As previously, the differences in zero point energies of the enamines and the corresponding imines were found to be very small (Table 1); they are therefore not taken into explicit consideration in the determinations of the relative energies. Effects of electron correlations were estimated by use of second-order Møller–Plesset theory.[13]

By calibration with a recent, very thorough theoretical study of the vinylamine-acetaldimine tautomerism by Lammertsma and Prasad,[14] we have recognized that our basis set employed produces a reasonable estimate for the equilibria in question. Both, the diffuse functions (+) and the inclusion of electron correlation (MP2) are essential for an adequate description of these systems. Thus, MP2/6-31+G*//6-31+G* total energies are the basis of the following discussion (total energies, zero point

(7) For related examples of conjugated tertiary enamines see: Potthoff, B.; Breitmeier, E. *Chem. Ber.* **1987**, *120*, 255. Snowden, R. L. S.; Brauchli, R.; Wüst, M. *Helv. Chim. Acta* **1990**, *73*, 640. Braisted, A. C.; Schultz, P. G. *J. Am. Chem. Soc.* **1990**, *112*, 7430. Katrizky, A. R.; Long, Q.-H.; Lue, P. *Tetrahedron Lett.* **1991**, *32*, 3597. Sustmann, R.; Rogge, M.; Nüchter, U.; Bandmann, H. *Chem. Ber.* **1992**, *125*, 1647, 1657. Review: Hickmott, P. W. *Tetrahedron* **1984**, *40*, 2989.

(8) For representative examples of syntheses of primary enamines under kinetic control see: Ripoll, J. L.; Lebrun, H.; Thuillier, A. *Tetrahedron* **1980**, *36*, 2497. Vallee, Y.; Ripoll, J.-L.; Maume, D. *J. Anal. Appl. Pyrolysis* **1988**, *14*, 171.

(9) López, L.; Berlekamp, M.; Kowalski, D.; Erker, G. *Angew. Chem.* **1994**, *106*, 1168, *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1114.

(10) Roth, W. R.; Adamczak, O.; Breuckmann, R.; Lennartz, H.-W.; Boese, R. *Chem. Ber.* **1991**, *124*, 2499, and references cited therein.

(11) 6-31+G* basis set: Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294.

(12) GAUSSIAN 92, Revision B, Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzales, C.; Martin, R. L.; Fox, D. J.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A., Gaussian, Inc., Pittsburgh PA, 1992.

(13) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. Frisch, M. J.; Krishnan, R., Pople, J. A. *Chem. Phys. Lett.* **1980**, *75*, 66.

(14) Lammertsma, K.; Prasad, B. V. *J. Am. Chem. Soc.* **1994**, *116*, 642. See also: Pappalardo, R. R.; Marcos, E. S.; Ruiz-Lopez, M. F.; Rinaldi, D.; Rivail, J.-L. *J. Am. Chem. Soc.* **1993**, *115*, 3722. Bouchoux, G.; Penand-Berruyer, F.; Nguyen, M. T. *J. Am. Chem. Soc.* **1993**, *115*, 9728.

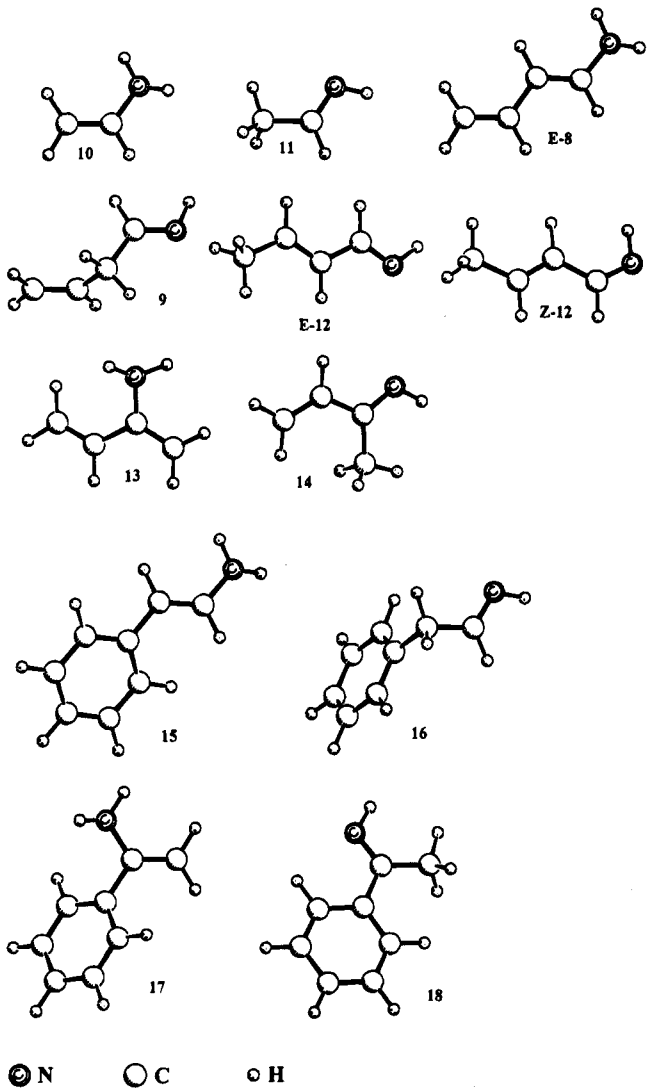


Figure 1. Calculated minimum structures of isomeric enamine/imine pairs.

energies, and dipole moments: Table 1; relative energies of the enamines, compared to their best imino tautomers: Table 2).

Vinylamine 10 (H_2C=CHNH_2). Starting point for our discussion is the equilibrium of the parent vinylamine **10**/acetaldimine **11** system. Our computational method produces a thermodynamic difference of ca. 5.8 kcal/mol in favor for the imine tautomer **11**; the best literature value available (G2 theory) is 3.9 kcal/mol.[14] Thus, we may expect, that our basis sets artificially overestimate slightly the stability of the imine tautomer. Inspite of the thermodynamics, which favor strongly the imine tautomer, according to literature data, vinylamines have a surprisingly long lifetime and are only slowly converted into the corresponding imine forms.[1-3] Thus, high activation barriers are responsible for the relative kinetic stability of such primary enamines.

Effects of additional π-conjugation by vinyl and phenyl substituents in α or β position of the parent vinylamine system were elaborated by computations of all of the possible conformers and configurational isomers of 1- and 2-aminobutadiene **8, 13** (for earlier MINDO3 calculations see ref 15) and 1- and 2-aminostyrene **15, 17** and of their respective imine isomers **9, 12, 14, 16,** and **18**. For the sake of clarity, only the energetically best structure of each system (global minimum) is discussed (see Figure 1 and Table 2).[16]

1-Aminobutadiene 8 (CH_2=CHCH=CHNH_2). Our calculations predict the all-trans form (*E*)-**8** ((*E*)-s-trans-conformation) to be lowest in energy of all possible conformational and configurational isomers (E_{rel} = 0.00 kcal/mol); for instance, the (*Z*)-s-trans-form (*Z*)-**8** is by ca. 0.6 kcal/mol higher in energy. Among the possible imine forms, two tautomers have to be considered, the nonconjugated imine (1-azapenta-1,4-diene) **9** and the conjugated 1-azapenta-1,3-diene **12**. As anticipated, the conjugated all-trans isomer (*E*)-**12** corresponds to the global minimum of this part of the potential energy hyperface. This structure (*E*)-**12** is favored by ca. 5.2 kcal/mol over the best 1-aminobutadiene form (*E*)-**8**; the corresponding isomer (*Z*)-**12** with a ZC=N double bond is slightly (ca. 1.2 kcal/mol) less favorable. The effects of butadiene-like π-π conjugation in such systems amount to ca. 6 kcal/mol, as indicated by the relative energy of the nonconjugated 1-azapenta-1,4-diene **9** (E_{rel} = 6.09 kcal/mol, compared to (*E*)-**12**). It is remarkable, that theory predicts a higher relative energy (ca. 1 kcal/mol) for this isomer (**9**) than for the primary 1-aminobutadiene (*E*)-**8**. With regard to our experiments (vide supra) we conclude that the equilibrium of tautomers of 1-aminobutadienes/1-azapenta-1,4-dienes by a formal 1,3 hydrogen shift lies on the side of the observed 1-aminobutadienes for thermodynamic reasons. In contrast, our data indicate further that tautomerism of the 1-aminobutadienes toward the thermodynamically more stable 1-azapenta-1,3-dienes (like **12**) by a formal 1,5 hydrogen shift must be precluded for kinetic reasons, since obviously high activation barriers prevent the spontaneous isomerization. Experimental studies have often revealed slow tautomerization not only for enamine/imine equilibria, but also for enolizations.[17]

Thus, the unexpected stability of primary 1-aminobutadienes is explained from our theoretical data from thermodynamic as well as kinetic argumentations.

2-Aminobutadiene 13 (CH_2=CHCH(NH_2)=CH_2). Here, the thermodynamic situation of the enamine/imine tautomerism is quite similar. In fact, we again obtain the s-trans form **13** as the best structure for the enamine tautomer. However, as before, the energy lowest (conjugated) imine tautomer (*E*)-**14**, featuring a 2-methyl-1-azabutadiene structure, is favored by ca. 5.9 kcal/mol, a value that is close to the 1-aminobutadiene data. This similarity is mainly due to the fact that the imine tautomer **14** and the 2-aminobutadiene **13** are both

Table 2. Ab Initio Total Energies (au), Zero Point Energies (ZPE, kcal/mol), and Calculated Dipole Moments (DM, Debye) of the Enamine/Imine Isomers

enamine	6-31+G*	ZPE	DM	MP2/6-31+G*	imine	6-31+G*	ZPE	DM	MP2/6-31+G*
10	−133.06884(0)	46.45	1.554	−133.48990	**11**	−132.07862(0)	46.26	2.403	−133.49910
(*E*)-**8**	−209.95827(0)	69.11	2.089	−210.63201	(*E*)-**9**	−209.95894(0)	69.19	2.167	−210.63050
					(*E*)-**12**	−209.96822(0)	69.06	2.820	−210.64021
(*Z*)-**8**	−209.95704(0)	69.28	1.874	−210.63110	(*Z*)-**12**	−209.96651(0)	69.07	3.632	−210.63833
13	−209.95741(0)	69.26	1.232	−210.63169	**13**	−209.96797(0)	69.14	2.727	−210.64113
(*E*)-**15**	−362.62692(0)	101.43	1.883	−363.81075	(*E*)-**16**	−362.63152(0)	101.52	2.179	−363.81290
17	−362.62798(0)	101.48	1.257	−363.81358	**18**	−362.63878(0)	101.53	2.318	−363.82134

stabilized by significant π-conjugative interactions between C2 and C3 of the butadiene subunits. Since in this case no nonconjugated imine tautomer is possible, the observation of stable primary 2-aminobutadienes is predicted to be possible only for systems with high kinetic barriers between the two tautomers, but not for thermodynamic reasons. 2-Aminobutadienes have recently found interesting applications in acyclic and heterocyclic chemistry.[18]

2-Aminostyrene 15 (PhCH=CHNH$_2$). For steric reasons, the (*E*)-isomer of **15** corresponds to the energy lowest enamine form. The phenyl ring is found to lie well in plane with the vinyl moiety. The best corresponding imine tautomer **16** is predicted to be lower in energy by ca. 1.4 kcal/mol. Thus, we conclude, that in contrast to a vinyl group in the systems **8**, **9**, **12** a phenyl substituent in 2-position is not suited to overcome the thermodynamic preference for the imine form of the vinylamine/acetaldimine system **10**, **11**. These theoretical results agree well with experimental observations by Ahlbrecht et al.;[2] they found varying mixtures of both compounds depending on temperature and solvent polarity.

1-Aminostyrene 17 (CH$_2$=C(NH$_2$)(Ph)). Here, the thermodynamic situation of the enamine/imine equilibrium resembles much that of 2-aminobutadiene **13.** The imine form **18** is strongly favored over the cross-conjugated 1-aminostyrene **17** (E_{rel} of the enamine: 4.9 kcal/mol), certainly due to the π-conjugation realized in the acetophenonimine tautomer **18**; thermodynamic reasons disfavor the experimental observation of **17** in equilibrium with **18**, but here as above, high activation barriers may well preclude the rapid equilibration.

Experimental Investigations. Our theoretical studies have suggested that 1-amino-1,3-butadienes should be thermodynamically preferred over their nonconjugated imine tautomers. If they are kinetically protected from rearrangement to their conjugated imine tautomers,[17] such conjugated primary enamines should be stable and easy to prepare by a variety of straightforward preparative routes, provided that hydrolysis to the related nitrogen free carbonyl systems is prevented. We have therefore reacted allylmagnesium chloride with a number of organic nitriles. The resulting magnesium containing addition products were then subjected to a controlled hydrolysis.[19] Several representative examples are described below.

Allylmagnesium chloride, dissolved in diethyl ether, was slowly added to a solution of 2-cyanopyridine at room temperature. The organometallic addition product (see below) was isolated as a solid that was subjected to hydrolysis under various reaction conditions. Treatment with a small amount of water in a two-phase aqueous/ethereal suspension resulted in mixtures of the enamine **22a** and the corresponding ketone 1-oxo-1-(2-pyridyl)but-3-ene. Treatment of the magnesium compound with methanol led to a high amount of 1-amino-1-(2-pyridyl)-1,3-butadiene **22a**, but the product still contained a small quantity of carbonyl contaminations that could not be removed. Similarly, the reaction of the magnesium salt with HCl in ether gave the enamine only contaminated. Attempted protonolysis with *tert*-butyl alcohol was unsuccessful in our hands to produce the enamine at all. The best method for subsequent controlled hydrolysis of the allyl Grignard/nitrile addition product was treatment of an ethereal suspension with a few drops of concentrated aqueous ammonia. Conventional workup of the ethereal phase after several minutes of stirring consistently and reproducibly gave the conjugated enamine product in reasonable yield and purity.

From the reaction of 2-cyanopyridine with the allylmagnesium chloride reagent and subsequent controlled hydrolysis with aqueous ammonia in a two-phase system, as described above, we have isolated a single isomer of the enamine product, namely (1*Z*)-1-amino-1-(2-pyridyl)-1,3-butadiene [(*Z*)-**22a**] in 78% yield. The enamine shows IR (NH_2) bands at ν 3467 and 3355 cm^{-1}. It has a characteristic UV absorption at λ_{max} = 285 nm (ϵ 8900). The stereochemical assignment comes from a comparison with the ^{1}H NMR data of the related 1,6-diamino-1,6-diaryl-1,3,5-hexatriene systems **5**, the stereochemistry of which was secured by two X-ray crystal structure analyses.[4] Product (*Z*)-**22a** shows ^{1}H NMR signals (in benzene-d_6) of the olefinic part of the molecule at δ 5.84 (2-H), ~6.5 (3-H), 5.23 (4-H$_{trans}$), 5.00 (4-H$_{cis}$) with coupling constants ^2J = 2.0 Hz (4-H$_{cis}$, 4-H'$_{trans}$), ^3J = 11.1 Hz (2-H, 3-H), 16.6 Hz (3-H, 4-H$_{trans}$), 10.2 Hz (3-H, 4-H$_{cis}$), ^4J = 0.8 Hz (2-H, 4-H$_{cis}$) and 0.8 Hz (2-H, 4-H$_{trans}$). Our assignment is further supported by an irradiation experiment of the dienamine (*Z*)-**22a** using 350 nm light that resulted in the formation of the (*E*)-**22a** isomer. Prolonged irradiation at 350 nm in benzene-d_6 led to a photostationary equilibrium of (*Z*)-**22a**/(*E*)-**22a** of 52:48.

The formation of (1*Z*)-1-amino-1-(2-pyridyl)-1,3-butadiene (*Z*)-**22a** is thermodynamically controlled. We have hydrolyzed the organometallic allyl Grignard to (2-cyano)pyridine addition product at −30 °C (aqueous NH_3) and immediately analyzed the obtained product mixture by ^{1}H NMR spectroscopy (in toluene-d_8). At 240 K the solution contains a 4:1 imine to enamine mixture. We have detected two isomers of the nonconjugated imine **21** with a *syn*-**21a**:*anti*-**21a** ratio of 4:1.[20] The major product (*syn*-**21a**) is characterized by a ^{1}H NMR =N*H* resonance at δ 9.98 whereas the minor imine isomer exhibits its =N*H* signal at δ 11.90. The sample was slowly warmed to ambient temperature inside the NMR spectrometer and ^{1}H NMR spectra were monitored at several intermediate temperatures. During 7 h ca. 90%

(15) Koikov, L. N.; Terent'ev, P. B.; Gloriozov, I. P.; Bundel', Yu. G. *J. Org. Chem. USSR (Engl. Transl.)* **1984**, *20*, 832–838.

(16) Details of the calculations corresponding to local minima are available from E.-U. W. upon request.

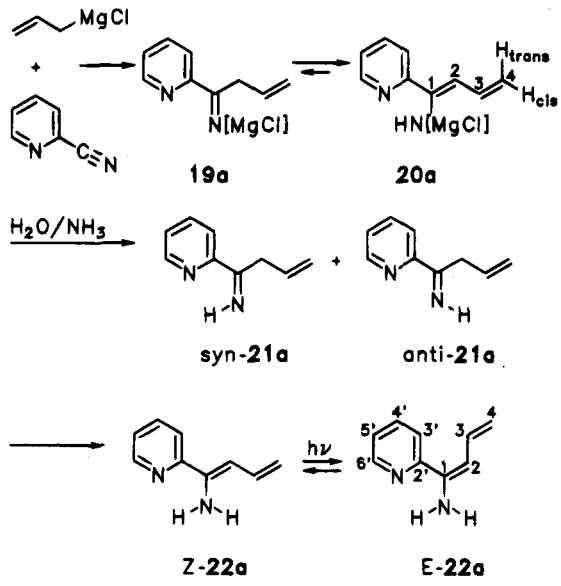
(17) For enols: Cederstav, A. K.; Novak, B. M. *J. Am. Chem. Soc.* **1994**, *116*, 4073. Bergens, S. H.; Bosnich, B. *J. Am. Chem. Soc.* **1991**, *113*, 958. Capon, B.; Guo, B.-Z.; Kwok, F. C.; Siddhanta, A. K.; Zucco, C. *Acc. Chem. Res.* **1988**, *21*, 135. Keeffe, J. R. Kresge, A. J. in Patai, S.; Rappoport, Z. (Series Eds.). *The Chemistry of Functional Groups: The Chemistry of Enols*, Rappoport, Z., Ed.; Wiley, New York, 1990; Chapter 7, pp 399–480. For enamines: Capon, B.; Wu, Z.-P. *J. Org. Chem.* **1990**, *55*, 2317. See also references 1–3.

(18) Barluenga, J.; Aznar, F.; Cabal, M.-P.; Valdés, C. *J. Chem. Soc. Perkin Trans. 1* **1990**, 633. López-Ortiz, F.; Peláez-Arango, E.; Palacios, F.; Barluenga, J.; Garciá-Granda, S.; Tejerina, B.; Garciá-Fernández, A. *J. Org. Chem.* **1994**, *59*, 1984 and references therein.

(19) Normal hydrolysis using aqueous acid, of course, leads to the formation of the corresponding ketones: Kharasch, M. S.; Reinmuth, O. *Grignard Reactions of Nonmetallic Substances*, Prentice-Hall: New York, 1954; pp 769–772. Canonne, P.; Foscolos, G. B.; Lemay, G. *Tetrahedron Lett.* **1980**, *21*, 155. For related reactions see: Orita, A.; Fukudome, M.; Ohe, K.; Murai, S. *J. Org. Chem.* **1994**, *59*, 477. Dutt, M.; Fravel, B.; Ford, G. P.; Biehl, E. R. *J. Org. Chem.* **1994**, *59*, 497.

(20) Ahlbrecht, H.; Fischer, S. *Tetrahedron* **1970**, *26*, 2837. Staab, H. A.; Vögtle, F.; Mannschreck, A. *Tetrahedron Lett.* **1965**, 697. Wurmb-Gerlich, D.; Vögtle, F.; Mannschreck, A.; Staab, H. A. *Liebigs Ann. Chem.* **1967**, *708*, 36. Karabatsos, G. J.; Lande, S. S. *Tetrahedron* **1968**, *24*, 3907. Hine, J.; Yeh, C. Y.; *J. Am. Chem. Soc.* **1967**, *89*, 2669. Perry, K. A.; Robinson, P. J.; Sainsbury, P. J.; Waller, M. J. *J. Chem. Soc. B.* **1970**, 700. Fraser, R. R.; Banville, *J. Chem. Soc., Chem. Commun.* **1979**, 47.

Scheme 1

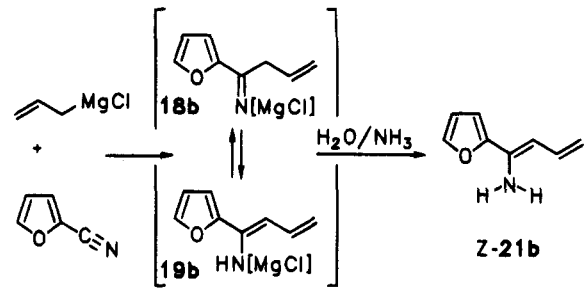


of the imines had tautomerized to the conjugated enamine (*Z*)-**22a** under these conditions. After 32 h at ambient temperature only the primary enamine (*Z*)-**22a** was present in the toluene-d_8 solution.

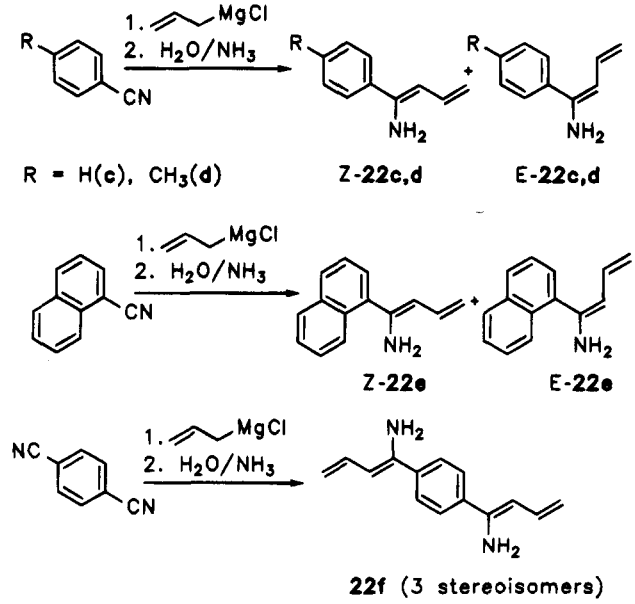
The question remains whether this imine ⇌ conjugated enamine tautomerism can only be observed at the stage of the final metal free products or if the magnesium-containing addition products exhibit the same behavior. To answer this question we have dissolved the allylmagnesium chloride/2-cyanopyridine addition product in tetrahydrofuran-d_8 and detected the N-metalated ketimine system **19a** by ^{1}H NMR spectroscopy. The nonconjugated 1-iminobut-3-ene moiety shows very characteristic signals at δ 6.22 (m, 1H, 3-H), 5.27 (m, 1H, 4-H_{trans}), 4.99 (m, 1H, 4-H_{cis}) and 3.94 (br d, 2H, CH_2). During 12 h at room temperature the Mg–imine system **19a** tautomerized completely. After that time under these conditions we have only detected the N-metalated conjugated enamine system **20a** by ^{1}H NMR spectroscopy in tetrahydrofuran-d_8 solution [^{1}H NMR signals at δ 6.82 (m, 1H, 3-H), 5.52 (d, 1H, ^3J = 11 Hz, 2-H), 4.73 (m, 1H, 4-H_{trans}), 4.40 (m, 1H, 4-H_{cis}), 3.94 (br s, 1H, NH)].

The reaction of 2-cyanofuran with allylmagnesium chloride proceeds similarly. ^{1}H NMR spectroscopy of the isolated organometallic adduct revealed that the primary product has a metalated ketimine structure (^{1}H NMR in benzene-d_6/tetrahydrofuran-d_8 (10:1): δ 5.25 (m, 1H, 4-H_{trans}), 4.99 (m, 1H, 4-H_{cis}), 3.51 (d, 2H, ^3J = 7.1 Hz, CH_2)). With time, tautomerization to the enamine isomer is observed. During 12 h the initial 80:20 imine to enamine mixture has changed to a ca. 50:50 mixture of isomers. Hydrolysis of the organomagnesium addition product with aqueous ammonia furnished a single conjugated primary enamine product to which we have assigned the structure of (*Z*)-**22b**.

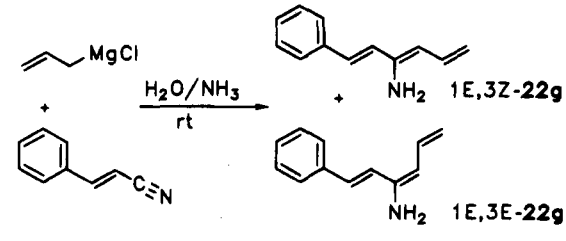
In these systems the formation of the conjugated primary enamine from the β,γ-unsaturated ketimine is thermodynamically controlled. Therefore, it is surprising that in each of the above described systems only a single isomer of the 2-furyl- and 2-pyridyl-substituted enamine systems was obtained in the thermally controlled reactions. This may be due to some influence of the hetarene substituent because this clear preference of the *Z*-alkenamine formation is lost when the heteroatom-free aryl substituents are employed.



Benzonitrile was treated with 1 mol equiv of the allyl Grignard reagent and subsequently hydrolyzed under controlled conditions to give the conjugated primary enamine 1-amino-1-phenyl-1,3-butadiene **22c** in 64% yield. The product consists of a 70:30 mixture of the (*Z*)-**22c** and (*E*)-**22c** isomers (for details of their characterization see the Experimental Section). Similarly, a 80:20 mixture of (*Z*)- and (*E*)-**22d** was obtained from allylmagnesium chloride and *p*-methylbenzonitrile while the reaction starting from 1-cyanonaphthalene gave (*Z*)-**22e** and (*E*)-**22e** in a 85:15 ratio. Both cyano groups of terephthalic dinitrile were employed in the allyl Grignard addition/controlled hydrolysis sequence. We have isolated the corresponding *p*-phenylene bisenamine **22f** in 65% yield as a mixture of three stereoisomers (80% major isomer).



As expected, our two-step reaction sequence can be used to prepare stable extended conjugated primary enamine systems as well. We have reacted *trans*-cinnamic nitrile with allylmagnesium chloride. Subsequent hydrolysis (H_2O/NH_3) gave 3-amino-1-phenyl-1,3,5-hexatriene in an overall yield of 72%. Again a mixture of two stereoisomers (1*E*,3*Z*)-**22g** and (1*E*,3*E*)-**22g** was obtained (70:30 ratio).



Conclusions

Both the theoretical and the experimental work carried out in this study show that simple nonfunctionalized primary enamines are not as elusive as common feeling of organic chemists may suggest. Conjugation of the alkenamine moiety with a single carbon–carbon double bond is sufficient to make the enamine tautomer thermodynamically more favorable than its nonconjugated β,γ-unsaturated ketimines tautomer. On the other hand, the α,β-unsaturated ketimines are by 5–6 kcal mol^{-1} more stable than the corresponding 1-aminobutadiene systems but there is convincing experimental evidence that the butadieneamine ⇌ 1-azabutadiene equilibration has a high activation barrier under the conditions of our experimental investigation. Therefore, a great variety of substituted 1-aminobutadienes can very easily be prepared and studied. They are theoretically interesting molecules which are protected from rearrangement to their nonconjugated alkenimine tautomers thermodynamically and are prevented from isomerization to the more stable conjugated alkenimines on kinetic grounds. The metastable conjugated primary enamine systems are easily prepared and isolated by the routes outlined above; they represent potentially useful reagents in organic synthesis, which deserve intensive further investigation.

Experimental Section

Reactions with organometallic compounds were carried out in an inert atmosphere (argon) using Schlenk type glassware or in a glovebox. Solvents were dried and distilled under argon prior to use. Allylmagnesium chloride was prepared according to a general literature procedure.[21] The organic nitriles employed in this study were commercially available.

General Procedure for the Preparation of the 1-Amino-1-aryl(or hetaryl)-1,3-butadienes. To a solution of 5 mmol of the aryl cyanide in 50 mL of ether was added dropwise a 0.48 M ethereal solution of the allylmagnesium chloride reagent (5 mmol) at room temperature. The reaction mixture was stirred for 24 h at ambient temperature and then concentrated in vacuo to a volume of ca. 10 mL. Pentane (25 mL) was added and the precipitated organometallic product collected by filtration. It was suspended in ether and hydrolyzed by dropwise addition of 0.1 mL of concentrated aqueous ammonia solution. After 10 min of stirring the ethereal phase was separated and dried over magnesium sulfate. Solvent was removed in vacuo to yield the 1-amino-1-aryl-1,3-butadiene product.

1-Amino-1-(2-pyridyl)-1,3-butadiene (22a). 2-Cyanopyridine (0.50 g, 4.80 mmol) dissolved in 50 mL of ether was treated with 10.0 mL of a 0.48 M ethereal allyl Grignard solution (4.80 mmol) and worked up as described above to give 0.55 g (78%) of (*Z*)-**22a** as an oil. ^{1}H NMR (benzene-d_6): δ 8.31 (m, 1H), 7.27 (dt, 1H, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.0 Hz), 6.94 (m, 1H), 6.65–6.45 (m, 2H), 5.84 (dt, 1H, $^3J_{HH}$ = 11.1 Hz, $^4J_{HH}$ = 0.8 Hz), 5.23 (ddd, 1H, $^3J_{HH}$ = 16.6 Hz, $^2J_{HH}$ = 2.0 Hz, $^4J_{HH}$ = 0.8 Hz), 5.00 (ddd, $^3J_{HH}$ = 10.2 Hz, $^2J_{HH}$ = 2.0 Hz, $^4J_{HH}$ = 0.8 Hz), 4.67 (s, 2H). ^{13}C NMR (benzene-d_6, DEPT): δ = 154.1 (C), 148.0 (CH), 131.9 (C), 135.5, 121.9, 118.9 (CH), 111.9 (CH_2), 101.4 (CH). IR (NaCl): ν = 3467 (m), 3355 (m), 3090 (w), 2925 (w), 1630 (s), 1584 (vs), 1466 (vs), 1374 (s), 1150 (s), 1000 (s), 887 (m), 793 (s) cm^{-1}. HRMS: Calcd 146.08439. Found: 146.08394. UV (CH_2Cl_2, 117 μmol/l): λ_{max} = 285 nm, ϵ_{max} = 8900.

(*Z*)-**22a** was irradiated in a Pyrex vessel with 350 nm light inside a Rayonett-reactor. The (*Z*)-**22a**/(*E*)-**22a** ratio was 80:20 after 10 min, 73:27 after 20 min, 66:34 after 30 min, 56:44 after 40 min, and remained almost constant at 52:48 after 55 min of irradiation (as judged by ^{1}H NMR spectroscopy in benzene-d_6). From the photostationary mixture the ^{1}H NMR data of E-**22a** were obtained. ^{1}H NMR (benzene-d_6): δ 8.40 (m, 1H), 5.58 (d, 1H, $^3J_{HH}$ = 11.3 Hz), 5.09 (ddd, 1H, $^3J_{HH}$ = 16.6 Hz, $^2J_{HH}$ = 2.2 Hz, $^4J_{HH}$ = 1.3 Hz), 4.85 (ddd, 1H, $^3J_{HH}$ = 10.1 Hz, $^2J_{HH}$ = 2.2 Hz, $^4J_{HH}$ = 0.9 Hz), 3.80 (s, 2H), four resonances of the pyridyl substituent under signals of (*Z*)-**22a**. ^{13}C NMR (benzene-d_6, DEPT): δ 155.0 (C), 149.4 (CH), 134.5 (C), 135.6, 124.6, 122.7 (CH), 110.3 (CH), 105.6 (CH_2).

Spectroscopic Characterization of the Organometallic Products (19a, 20a) Obtained from the Allyl Magnesium Chloride Addition to 2-Cyanopyridine. The organometallic addition product was collected by filtration as described above. A sample was dissolved in tetrahydrofuran-d_8 and an ^{1}H NMR spectrum of the metalated ketimine **19a**, which was the major product (>80%) present in the solution, was monitored. ^{1}H NMR of **19a** in tetrahydrofuran-d_8: δ 9.18 (d, 1H, $^3J_{HH}$ = 4.5 Hz), 8.10–7.75, 7.36 (each m, 3H), 6.22 (m, 1H), 5.27 (m, 1H), 4.99 (m, 1H), 3.94 (d, 2H, $^3J_{HH}$ = 6.6 Hz).

After 12 h at room temperature tautomerization to the metalated enamine **20a** was almost complete. ^{1}H NMR (tetrahydrofuran-d_8): δ 8.87 (m, 1H), 7.82, 7.62, 7.11 (each m, 3H), 6.82 (m, 1H), 5.52 (d, 1H, $^3J_{HH}$ = 11 Hz), 4.73 (br d, 1H), 4.40 (br d, 1H), 3.94 (br s, 1H).

1-Amino-1-(2-furyl)-1,3-butadiene (22b). Reaction of 0.50 g (6.48 mmol) of 2-cyanofuran in 50 mL of ether with 13.5 mL of a 0.48 M ethereal allylmagnesium chloride solution gave 0.61 g (70%) of (*Z*)-**22b** as a slightly yellow colored oil. ^{1}H NMR (benzene-d_6): δ 6.95 (m, 1H), 6.36 (m, 1H), 6.10, 6.02 (each m, each 1H), 5.85 (d, 1H, $^3J_{HH}$ = 11.4 Hz), 5.11 (ddd, 1H, $^3J_{HH}$ = 16.6 Hz, $^2J_{HH}$ = 2.1 Hz, J_{HH} = 0.8 Hz), 4.92 (ddd, 1H, $^3J_{HH}$ = 10.2 Hz, $^2J_{HH}$ = 2.1 Hz, $^4J_{HH}$ = 0.8 Hz), 3.10 (br s. 2H). ^{13}C NMR (benzene-d_6, DEPT): δ 131.2 (6), 128.6 (CH), 117.3 (C), 110,7 (CH_2), 109.9, 103.8, 99.5 (-CH). IR (NaCl): ν 3360 (br), 2959 (s), 2925 (s), 1717 (m), 1675 (s), 1629 (ss), 1569 (m), 1481 (s), 1261 (ss), 1159 (s), 1092 (ss), 1016 (ss), 915 (m), 884 (m), 801 (s), 745 (s) cm^{-1}. HRMS: Calcd 135.0684. Found 135.0681. UV (CH_2Cl_2, 80 μmol): λ_{max} = 302 nm, ϵ_{max} = 14393. Anal. Calcd for C_8H_9NO (135.1): C, 71.09; H, 6.71; N, 10.36. Found: C, 71.48; H, 6.89; N, 9.76. A sample of the magnesium containing intermediate product was dissolved in a benzene-d_6/tetrahydrofuran-d_8 10:1 solvent mixture. ^{1}H NMR spectroscopy revealed an initial [Mg]-ketimine (**19b**): [Mg]-enamine (**20b**) ratio of 80:20 that changed during 12 h to a ca. 50:50 ratio. ^{1}H NMR (benzene-d_6/tetrahydrofuran-d_8: 10:1) (imine:enamine: ca. 50:50): [Mg]-ketimine: δ 7.70 (m, 1H), 6.50–5.80 (m, 3H), 5.25 (m, 1H), 4.99 (m, 1H), 3.51 (d, 2H, $^3J_{HH}$ = 7.1 Hz). [Mg]-enamine: δ 7.70 (m, 1H), 6.50–5.80, 5.55 (br d, 1H), 5.10–4.70 (each m, overlapping with imine signals).

1-Amino-1-phenyl-1,3-butadiene (22c). Reaction of 0.50 g (4.85 mmol) of benzonitrile in 50 mL of ether with 10.5 mL of a 0.48 M ethereal allylmagnesium chloride solution yielded 0.45 g (64%) of a 70:30 mixture of (*Z*)-**22c** and (*E*)-**22c** as a yellow oil. ^{1}H NMR (D_6)-benzene) (*Z*)-**22c**: δ 7.50–7.00 (m, 5H), 6.39 (m, 1H), 5.49 (dt, 1H, $^3J_{HH}$ = 11.2 Hz, $^4J_{HH}$ = 0.8 Hz), 5.13 (ddd, 1H, $^3J_{HH}$ = 17.3 Hz, $^2J_{HH}$ = 2.2 Hz, J_{HH} = 0.8 Hz), 4.93 (ddd, 1H, $^3J_{HH}$ = 10.3 Hz, $^2J_{HH}$ = 2.3 Hz, $^4J_{HH}$ = 0.8 Hz), 3.25 (s, 2H). (*E*)-**22c**: δ 7.50–7.00 (m, 5H), 6.53 (m, 1H), 5.37 (d, 1H, $^3J_{HH}$ = 11.2 Hz), 5.02 (ddd, 1H, $^3J_{HH}$ = 16.6 Hz, $^2J_{HH}$ = 2.3 Hz, J_{HH} = 0.8 Hz), 4.72 (ddd, 1H, $^3J_{HH}$ = 10.2 Hz, $^2J_{HH}$ = 2.2 Hz, $^4J_{HH}$ = 0.8 Hz), 2.88 (s, 2H). ^{13}C NMR (chloroform-*d*, DEPT) (both isomers): δ 145.3, 142.4, 139.0, 137.3 (C), 134.6, 130.9, 128.6, 128.2, 128.0, 125.5 (CH), 111.6, 108.4 (CH_2), 103.6, 102.5 (CH). IR (NaCl): ν = 3454 (m), 3363 (m), 3079 (m), 3056 (m), 3025 (m), 2961 (s), 2924 (m), 1629 (vs), 1575 (m), 1492 (m), 1445 (s), 1373 (s), 1261 (m), 1092 (s), 1073 (s), 1027 (s), 919 (m), 870 (m), 803 (s), 761 (s), 697 (vs) cm^{-1}. HRMS: Calcd 145.08915. Found: 145.08881. UV (CH_2Cl_2, 275 μmol/L): λ_{max} = 302 nm, ϵ_{max} = 4500.

1-Amino-1-(1-tolyl)-1,3-butadiene (22d). Treatment of 4-methylbenzonitrile (0.50 g, 4.26 mmol) in 50 mL of ether with 8.90 mL of a 0.48 M ethereal allylmagnesium chloride solution as described above gave 0.42 g (62%) of a 80:20 mixture of (*Z*)-**22d** and (*E*)-**22d** as a yellowish oil. ^{1}H NMR (benzene-d_6) (*Z*)-**22d**: δ 7.32, 6.90 (each d, 4H, $^3J_{HH}$ = 7.8 Hz), 6.44 (m, 1H), 5.48 (d, 1H, $^3J_{HH}$ = 11.2 Hz), 5.10 (ddd, 1H, $^3J_{HH}$ = 16.6 Hz, $^2J_{HH}$ = 2.2 Hz, J_{HH} = 0.8 Hz), 4.93 (ddd, 1H, $^3J_{HH}$

(21) Benson, R. F.; Mc Kusick, B. C. *Organic Syntheses*, Robjohn, N., Ed.; Wiley: New York, 1963; Coll. Vol. IV, p 746.

= 10.2 Hz, $^2J_{HH}$ = 2.2 Hz, $^4J_{HH}$ = 0.8 Hz), 3.43 (s, 2H), 2.37 (s, 3H). (*E*)-**22d**: δ 6.51 (m, 1H), 5.39 (d, 1H, $^3J_{HH}$ = 11.0 Hz), 5.05 (ddd, 1H, $^3J_{HH}$ = 16.6 Hz, $^2J_{HH}$ = 2.2 Hz, J_{HH} = 0.8 Hz), 4.69 (ddd, 1H, $^3J_{HH}$ = 10.2 Hz, $^2J_{HH}$ = 2.2 Hz, $^4J_{HH}$ = 0.8 Hz), 3.10 (s, 2H), 2.39 (s, 3H). ^{13}C NMR (chloroform-*d*, DEPT) (major isomer): δ = 145.3, 142.4, 137.8 (C), 134.7, 133.8, 128.6, 128.7, 128.4, 126.4, 126.1, 125.4, 125.3 (CH), 118.2 (C), 111.0, 108.0 (CH_2), 103.3, 101.7 (CH), 21.0, 20.9 (CH_3). IR (NaCl): ν = 3459 (w), 3375 (w), 3260 (w), 3030 (s), 2921 (s), 1678 (m), 1632 (vs), 1608 (vs), 1568 (s), 1511 (vs), 1453 (vs), 1369 (vs), 1261 (s), 1180 (s), 1018 (s), 811 (vs), 680 (vs) cm^{-1}. HRMS: Calcd 159.10478. Found: 159.10442. UV (CH_2Cl_2, 88 μmol): λ_{max} = 267 nm, ϵ_{max} = 14 347.

1-Amino-1-(1-naphthyl)-1,3-butadiene (22e). Reaction of 0.50 g (3.26 mmol) of 1-cyanonaphthalene in 30 mL of ether with 6.80 mL of a 0.48 M ethereal allylmagnesium chloride solution gave 0.45 g (70%) of a 85:15 mixture of (*Z*)-**22e** and (*E*)-**22e**. ^{1}H NMR (chloroform-*d*): (*Z*)-**22e**: δ 8.30, 8.15, 7.87, 7.50 (each m, 7H), 5.89 (m, 1H), 5.74 (d, 1H, $^3J_{HH}$ = 11.0 Hz), 4.92 (dd, 1H, $^3J_{HH}$ = 16.4 Hz, $^2J_{HH}$ = 2.2 Hz), 4.54 (dd, 1H, $^3J_{HH}$ = 10.0 Hz, $^2J_{HH}$ = 2.2 Hz), 3.66 (s, 2H). (*E*)-**22e**: δ 6.66 (m, 1H), 5.28 (dt, 1H, $^3J_{HH}$ = 11.2 Hz, $^4J_{HH}$ = 0.7 Hz), 5.13, 4.98 (each m, 2H), 3.90 (s, 2H). ^{13}C NMR (chloroform-*d*, DEPT) (major isomer): δ 144.0, 135.1, 133.5 (C), 134.8, 128.4, 128.0, 126.9, 126.3, 125.8, 125.1 (CH), 111.0 (C), 107.9 (CH_2), 105.0 (CH). IR (NaCl): ν 3468 (m), 3368 (m), 3206 (w), 3049 (m), 2968 (m), 2924 (m), 1631 (ss), 1592 (s), 1398 (s), 1361 (s), 1240 (s), 802 (ss), 779 (ss) cm^{-1}. HRMS: Calcd 195.10480. Found: 195.10437. UV (CH_2Cl_2, 205 μmol): λ_{max} = 280 nm, ϵ_{max} = 5753.

1,4-Bis(1-amino-1,3-butadien-1-yl)benzene (22f). Terephthalic dinitrile (0.40 g, 3.12 mmol) in 50 mL of ether was treated with 13.0 mL of a 0.48 M ethereal solution of allylmagnesium chloride. Workup as described above gave 0.43 g (65%) of **22f** (three isomers, major component ca. 80%). ^{1}H NMR (chloroform-*d*), (major isomer, ca 80%): δ 7.61−7.30 (2H), 6.54 (m, 1H), 5.47 (d, 1H, $^3J_{HH}$ = 11.2 Hz), 5.10 (ddd, 1H, $^3J_{HH}$ = 16.7 Hz, $^2J_{HH}$ = 1.9 Hz, $^4J_{HH}$ = 0.8 Hz), 4.94 (ddd, 1H, $^3J_{HH}$ = 10.3 Hz, $^2J_{HH}$ = 1.9 Hz, $^4J_{HH}$ = 0.8 Hz), 3.75 (s, 2H). ^{13}C NMR (chloroform-*d*, DEPT), (major isomer), one C not detected: δ 141.8, 138.8 (C), 132.1, 130.9, 126.0, 125.5 (CH), 112.1 (CH_2), 102.9 (CH). IR (NaCl): ν = 3420 (m), 3337 (m), 3080 (w), 2966 (w), 2911 (w), 1631 (vs), 1609 (vs), 1426 (s), 1366 (s), 1261 (m), 1097 (m), 1048 (m), 1014 (m), 986 (m), 871 (vs), 848 (vs), 814 (s), 663 (s) cm^{-1}. HRMS: Calcd 212.13135. Found: 212.13085. UV (CH_2Cl_2, 75 μmol/L): λ_{max} = 271 nm, ϵ_{max} = 12 502.

3-Amino-1-phenyl-1,3,5-hexatriene (22g). *trans*-Cinnamic nitrile (0.50 g, 3.87 mmol) in 50 mL of ether was treated with 8.06 mL of a 0.48 M ethereal allylmagnesium chloride solution and worked up as described above to yield 0.48 g (72%) of a 70:30 mixture of (1*E*,3*Z*)-**22g** and (1*E*,3*E*)-**22g**. ^{1}H NMR (benzene-d_6), (major isomer): δ 7.40−6.90 (m, 6H), 6.40 (d, 1H, $^3J_{HH}$ = 8.5 Hz), 6.40 (m, 1H), 5.30 (d, 1H, $^3J_{HH}$ = 11.3 Hz), 5.15 (ddd, 1H, $^3J_{HH}$ = 16.6 Hz, $^2J_{HH}$ = 2.0 Hz, $^4J_{HH}$ = 0.8 Hz), 4.96 (ddd, 1H, $^3J_{HH}$ = 10.3 Hz, $^2J_{HH}$ = 2.0 Hz, $^4J_{HH}$ = 0.9 Hz), 3.05 (s, 0.7H (major isomer (1*E*,3*Z*)-**22g**), 2.71 (s, 0.3H (minor isomer)). ^{13}C NMR (chloroform-*d*, DEPT), (major isomer): δ 139.8, 136.7 (C), 130.6, 128.5, 127.4, 127.2, 126.9, 126.3 (CH), 113.1 (CH_2), 109.8 (CH). IR (KBr): ν = 3436 (w), 3023 (m), 2919 (s), 1635 (vs), 1623 (vs), 1600(vs), 1493 (s), 1447(s), 1261 (vs), 1100 (s), 1071 (s), 801 (vs), 754 (s), 698 (vs) cm^{-1}. HRMS: 171.1047. Found: 171.1044. UV (CH_2Cl_2, 109 μmol/L): λ_{max} = 320 nm, ϵ_{max} = 10 342. Anal. Calcd for $C_{12}H_{13}N$ (171.2): C, 84.16; H, 7.66; N, 8.18. Found: C, 83.71; H, 7.33; N, 8.03.

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Supporting Information Available: Full details of the ab initio calculations (GAUSSIAN 92 archive entries) and copies of ^{1}H and ^{13}C NMR spectra (13 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfiche version of the journal, and can be ordered from the ACS; see current masthead page for ordering information.

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