(±)-Valeranone (1). As in the preparation of **13**, a solution of 11.8 mg (0.0535 mmol) of **25** in 1 mL of freshly distilled acetic acid was hydrogenated in a Parr apparatus at 3–3.5 atm for 19 h in the presence of 30 mg of PtO_2 catalyst. The reaction mixture was filtered and evaporation of the solvent gave 18.5 mg of colorless liquid. Flash chromatography (1:9 ether–hexane) gave 12.5 mg of a 9:1 mixture of diastereomeric alcohols **26**. Data for the separated major isomer included the following: IR 3480, 1735 (acetic acid, trace), 1465, 1380, 1370, 1255, 1200, 1180, 1055, 1030, 975, 960; ^{1}H NMR δ 0.83 (6 H, d), 1.01 (3 H, s), 1.02 (3 H, s), 0.80–1.90 (14 H, m), 3.30 (1 H, s), 4.05 (1 H, t); TLC R_f 0.26 (1:4 ether–hexane). To a solution of 30 mg (0.14 mmol) of PCC in 100 μL of dry CH_2Cl_2 was added a solution of 8.2 mg (0.036 mmol) of the major isomer that was separated from the mixture **26** in 200 μL of dry CH_2Cl_2. The reaction mixture was stirred for 1 h, decanted, triturated with ether (4 × 1 mL), and filtered through silica gel to give 8.1 mg of crude **1**. Flash chromatography (1:19 ether–hexane) afforded 7.0 mg (86%) of **1** as a colorless liquid that was homogeneous by TLC: IR 1710, 1460, 1435, 1390, 1380, 1325, 1275, 1250, 1160, 1050, 940, 835 (IR of natural (−)-**1**:[6] 1695, 1451, 1420, 1374, 1362, 1305, 1258, 1238, 1148, 1040, 934, 827 cm^{-1}); ^{1}H NMR δ 0.81 (3 H, s), 0.86 (6 H, d), 1.06 (3 H, s), 1.15–2.45 (13 H, m) [^{1}H NMR of authentic (−)-**1**:[6] δ 0.81 (s), 0.86 (d), 1.06 (s), 1.15–2.45 (m)]; ^{13}C NMR δ 16.8, 19.8, 20.0, 21.8, 24.7, 24.9, 32.1, 32.9, 36.2, 37.0, 37.5, 38.5, 38.6, 53.1, 217.2; TLC R_f 0.45 (1:4 ether–hexane).

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Registry No. (±)-**1**, 50302-14-2; (±)-*cis*-**2**, 113998-31-5; (±)-*trans*-**2**, 113998-50-8; (±)-**6**, 113998-33-7; **7**, 113998-51-9; **7** (chloride), 113998-32-6; **8**, 1122-20-9; **9**, 37457-15-1; **10**, 113998-34-8; **11**, 113998-35-9; (±)-*cis*-**12**, 113998-36-0; (±)-*trans*-**12**, 113998-49-5; (±)-**13**, 50302-15-3; (±)-**14**, 113998-37-1; (±)-**15**, 113998-38-2; (±)-**16**, 113998-39-3; (±)-**17**, 113998-40-6; (±)-**20**, 113998-41-7; (±)-4β,7β-**21**, 113998-42-8; (±)-4α,7β-**21**, 113998-46-2; (±)-4β,7α-**21**, 113998-47-3; (±)-4α,7α-**21**, 113998-48-4; (±)-**22**, 113998-43-9; (±)-**23**, 113998-44-0; (±)-**25**, 113998-45-1; (±)-4α-**26**, 114127-47-8; (±)-4β-**26**, 114127-46-7; $Br(CH_2)_2Br$, 106-93-4.

Synthesis, Characterization, and Thermolysis of 7-Amino-7-azabenzonorbornadienes

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Synthetic routes are given for the facile preparation of mono- and dibenzo-7-amino-7-azanorbornadienes **4** and **5**. For **5** the key intermediate *N*-benzylisoindole (**9**) was treated with benzyne, generated via reaction of *o*-bromofluorobenzene with magnesium in THF to give tertiary amine **10**. *N*-Bromosuccinimide-mediated debenzylation of **10** gave secondary amine **13**, which was then aminated by *O*-(mesitylsulfonyl)hydroxylamine (MSH). Similarly amination of monobenzo amine **25** gave **4**, which, however, proved to be unstable and therefore best isolated as the [(9-fluorenylmethyl)oxy]carbonyl (FMOC) derivative **27**. Deblocking of **27** by means of diethylamine gave amine **4** as needed. Upon standing overnight in ether, free **4** underwent self-reduction to give dihydro derivative **29**, whereas, in the presence of ethyl phenylpropiolate, cinnamate and dihydrocinnamate esters were formed. The simplest explanation for these results is that a reducing species is ejected upon thermolysis of **4**. Nonstereospecific reduction occurred in contrast to the stereospecific reduction that occurred in the presence of authentic diimide precursor **23**. Compounds **4** and **5** upon thermolysis in the presence of both acetic acid and propiolate ester led to stereospecific cis reduction. These results suggest that under acidic conditions protonated diimide is generated from both **4** and **5** whereas under neutral conditions **4** may yield azamine or a mixture of azamine and diimide. Direct involvement of **4** and **20** in reduction processes was, however, not eliminated. Thermolysis of **5** under neutral conditions is dependent on the solvent used. In DMF, clean conversion to 9,10-dihydroanthracene occurs whereas complex reaction mixtures are observed in benzene, chloroform, or THF.

Introduction

Although unstable under ordinary conditions, diimide **1** has been generated by a variety of techniques[1] and is now a well-characterized species, most important as a transiently produced reducing agent. The situation is otherwise in the case of the isomeric azamine **2** (aminonitrene, 1,1-diazene).[1-3] On the other hand, there is a long history of studies related to the 1,1-disubstituted derivatives[4] of **2**, and recently some of these species have even been obtained as stable entities in solution.[5]

1 **2**

Some time ago,[6] we initiated a study of the possible thermal elimination of the azamine fragment **2** from a series of 7-amino-7-azanorbornadienes **3–5**. In the

(1) For brief reviews of theoretical questions and early experimental efforts on diimide and azamine, see: (a) Pasto, D. J.; Chipman, D. M. *J. Am. Chem. Soc.* **1979**, *101*, 2290. (b) Casewit, C. J.; Goddard, W. A., III *J. Am. Chem. Soc.* **1980**, *102*, 4057.

(2) In this paper we use the nomenclature adopted by Smith in his definitive work: Smith, P. A. S. *Derivatives of Hydrazine and Other Hydronitrogens Having N–N Bonds*; Benjamin/Cummings: Reading, MA, 1983; p 212.

(3) For a recent study of the possible matrix isolation of azamine and references to earlier work, see: Sylwester, A. P.; Dervan, P. B. *J. Am. Chem. Soc.* **1984**, *106*, 4648.

(4) For reviews on the chemistry of substituted azamines, see: (a) Lemal, D. M. In *Nitrenes*; Lwowski, W., Ed.; Interscience: New York, 1970; p 345. (b) Ioffe, B. V.; Kuznetsov, M. A. *Russ. Chem. Rev. (Engl. Transl.)* **1972**, *41*, 131. (c) Anselme, J.-P. *Nippon Kagaku Zasshi* **1971**, *92*, 1065. (d) Hünig, S. *Helv. Chim. Acta* **1971**, *54*, 1721.

(5) (a) Hinsberg, W. D., III; Schultz, P. G.; Dervan, P. B. *J. Am. Chem. Soc.* **1982**, *104*, 766. (b) McIntyre, D. K.; Dervan, P. B. *J. Am. Chem. Soc.* **1982**, *104*, 6466. (c) Miller, R. D.; Gölitz, P.; Janssen, J.; Lemmens, J. *J. Am. Chem. Soc.* **1984**, *106*, 1508.

(6) Barr, D. Ph.D. Thesis, University of Massachusetts, Amherst, MA, 1965.

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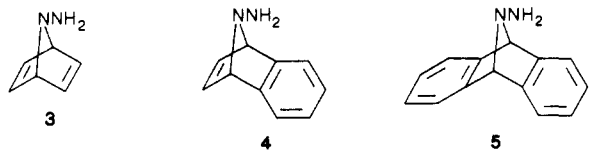
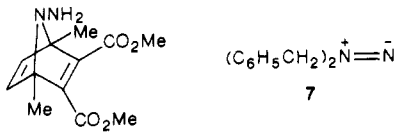


3 4 5

meantime, other workers[7-9] have synthesized or generated derivatives of **3** and noted their facile decomposition with ejection of the elements of N_2H_2. As an example, heating 2,5-dimethyl-1-aminopyrrole with dimethyl acetylenedicarboxylate in chloroform resulted in the formation of a mixture of dimethyl maleate and dimethyl 3,6-dimethylphthalate.[7] This reaction was rationalized as occurring via the transiently formed Diels–Alder adduct **6** followed by



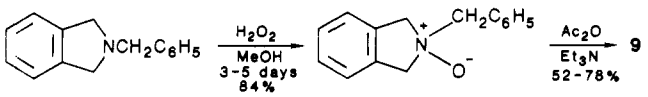
6 7

expulsion of **2**. The data were considered not to distinguish between direct reduction of acetylene to olefin by **2** or reduction subsequent to isomerization of **2** to **1**. Similar experiments[8] leading to the *N,N*-dibenzyl derivatives of **6** gave comparable results, the products isolated being those expected[4] to arise from initial extrusion of **7**.

Results and Discussion

Synthesis of 7-Amino-7-azadibenzonorbornadiene. Since all of our attempts to date to synthesize easily an appropriate stable precursor to hydrazine **3** have proved unsuccessful, we turned our attention to **5**, expected[10] to be the more stable of the two benzoannelated derivatives. The simplest route to **5** involved amination of the corresponding secondary amine **13** (Scheme I).

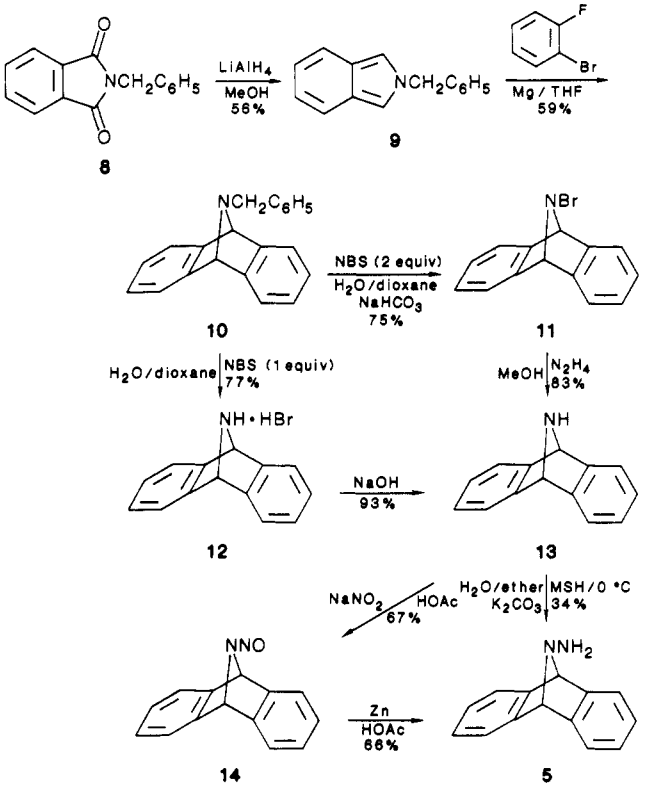
A key intermediate in the synthesis of secondary amine **13**, *N*-benzylisoindole (**9**), was obtained in 56% yield by a modification of the method of Garmaise and Ryan[11] involving pretreatment of $LiAlH_4$ with 2 equiv of methanol prior to direct reduction of *N*-benzylphthalimide. Garmaise and Ryan had used sodium bis(2-methoxyethoxy)-aluminum hydride (29% yield). Unmodified lithium aluminum hydride leads to complete reduction to the isoindoline **15**, which we found could also be converted to **9** via prior oxidation (84%) and dehydration (52–78%) of *N*-oxide **16**.[12]



15 16 (1)

Benzyne addition to **9** was carried out according to the general method of Wittig.[13] Difficulties were initially

Scheme I



encountered in debenzylation of tertiary amine **10**, neither catalytic (Pd–C/H_2)[14] nor nitrosative[15] methods proving successful. Excellent results were, however, obtained with the Henbest technique,[16] which involves treatment with *N*-bromosuccinimide in aqueous dioxane. The resulting hydrobromide salt **12** is stable toward ring opening in contrast to the situation observed for the analogous monobenzo derivative, which suffers opening of the strained ring to give α-naphthylamine hydrobromide.[6]

In some cases of applying the Henbest debenzylation procedure, the yield of hydrobromide **12** was very low and it was noted that significant quantitites of **10** remained unreacted. From the reaction mixture *N*-bromoamine **11** was isolated, and indeed it was found to be more convenient to use excess NBS and convert all of the substrate to the *N*-bromo compound. Reduction of **11** then gave amine **13** in 83% yield.

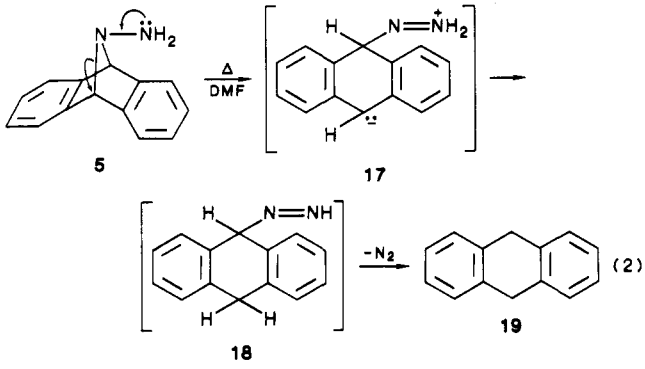
Initially, amine **13** was converted to nitrosamine **14**, which was reduced to the desired hydrazine **5** by means of zinc in the presence of acetic acid.[17] Other reducing agents often prescribed for the reduction of nitrosamines ($LiAlH_4$,[17] Pd–C,[17] Al(Hg)[18]) were unsatisfactory, leading to denitrosation or fragmentation to anthracene. A less tedious, more reliable route to **5** was subsequently developed involving direct amination of **13** by means of

(7) Schultz, A. G.; Shen, M. *Tetrahedron Lett.* **1979**, 2969.
(8) Schultz, A. G.; Shen, M.; Ravichandran, R. *Tetrahedron Lett.* **1981**, *22*, 1767.
(9) Shen, M.; Schultz, A. G. *Tetrahedron Lett.* **1981**, *22*, 3347.
(10) An instructive example of the expected stability sequence is provided by the norbornadienone series. See: (a) Birney, D. M.; Berson, J. A. *Tetrahedron*, **1986**, *42*, 1561. (b) Meinwald, J.; Miller, E. G. *Tetrahedron Lett.* **1961**, 253. (c) Bartlett, P. D.; Giddings, W. P. *J. Am. Chem. Soc.* **1960**, *82*, 1240. For an extensive review on the extrustion reactions of 7-heteronorbornadienes, see: Wong, H. N. C.; Ng, T.-K.; Wong, T.-Y. *Heterocycles* **1983**, *20*, 1815.
(11) Garmaise, D. I.; Ryan, A. *J. Heterocycl. Chem.* **1970**, 413.
(12) Compare: Kreher, R.; Seubert, J. *Angew. Chem.* **1964**, *76*, 682.
(13) (a) Wittig, G.; Behnisch, W. *Chem. Ber.* **1958**, *91*, 2358. (b) Wittig, G.; Reichel, B. *Chem. Ber.* **1963**, *96*, 2851. Recently the benzyne–isoindole reaction has seen significant practical synthetic application. See: (a) Gribble, G. W.; Allen, R. W.; Anderson, P. S.; Christy, M. E.; Colton, C. D. *Tetrahedron Lett.* **1976**, 3673. (b) Anderson, P. S.; Christy, M. E.; Colton, C. D.; Halczenko, W.; Ponticello, G. S.; Shepard, K. L. *J. Org. Chem.* **1979**, *44*, 1519.
(14) Baltzly, R.; Buck, J. S. *J. Am. Chem. Soc.* **1943**, *65*, 1984.
(15) Smith, P. A. S.; Pars, H. G. *J. Org. Chem.* **1959**, *24*, 1325.
(16) Dunstan, S.; Henbest, H. B. *J. Chem. Soc.* **1957**, 4905.
(17) For a listing of some of the classical methods of reducing nitrosamines to 1,1-disubstituted hydrazines, see: Lunn, G.; Sansone, E. B.; Keefer, L. K. *J. Org. Chem.* **1984**, *49*, 3470.
(18) (a) Carpino, L. A.; Santilli, A. A.; Murray, R. W. *J. Am. Chem. Soc.* **1960**, *82*, 2728. (b) Carpino, L. A. *J. Org. Chem.* **1969**, *34*, 461.

O-(mesitylsulfonyl)hydroxylamine (MSH).[19]

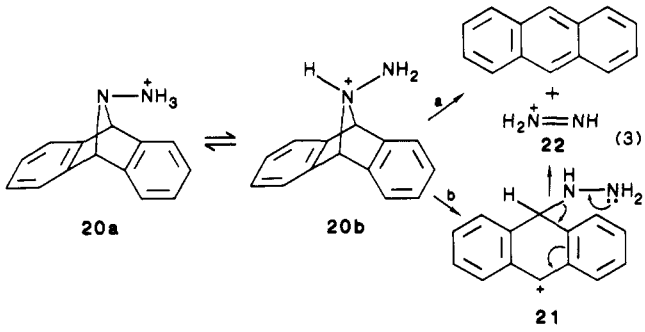
Thermolysis of 7-Amino-7-azadibenzonorbornadiene. Although nitrosamine **14** was easily handled under ordinary conditions, in contrast to the corresponding monobenzo analogue, it nevertheless was converted cleanly to anthracene and presumably nitrous oxide on refluxing in chloroform over a period of 18 h. By analogy, thermolysis of hydrazine **5** might be expected to yield anthracene and the azamine fragment. These expectations were not, however, realized in spite of the instability of **5**, which exhibited a half-life of approximately 4 h in deuteriated chloroform at 37 °C (NMR probe). In chloroform, benzene, or THF, a complex mixture of products resulted, among which was detected only a trace of anthracene. In contrast, in DMF, reaction proceeded cleanly to give, not anthracene, but 9,10-dihydroanthracene (**19**) in 87% yield.

Small amounts of **19** were also detected in benzene and THF, more in the latter solvent. This correlation with solvent polarity suggests a possible rationale for the formation of **19** as involving a dipolar intermediate (eq 2). By



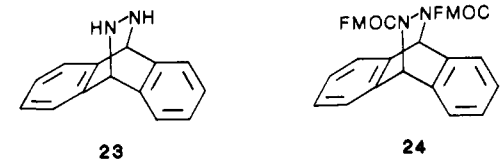
carrying out the reaction in DMF in the presence of 3 equiv of anthracene-d_{10}, we showed that **19** could not have arisen by prior fragmentation to anthracene followed by reduction by means of a free N_2H_2 species.

In striking contrast to the results in DMF or in benzene alone, thermolysis of **5** in benzene in the presence of acetic acid[20] led to the isolation of anthracene in 83% yield. In this case, protonated hydrazine **20** may yield **22** (protonated azamine or diimide) by direct cheletropic elimination or by a two-step process involving a cationic intermediate such as **21** (eq 3). Evidence for the intermediacy of **22**



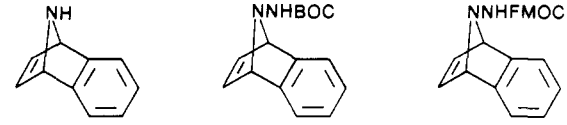
comes from a study of the thermolysis of **5** in the presence of acetic acid and diethyl fumarate: diethyl succinate is formed in 63% yield. In the absence of acetic acid only a small amount (<2%) of the succinate ester is produced.

Cation **22** may undergo deprotonation to diimide or possibly act itself as a reducing agent. A stereochemical study further confirmed the ejection of **22**. Thermolysis of **5** in ether at 40 °C in the presence of acetic acid and 5 equiv of ethyl phenylpropiolate gave anthracene (55%), ethyl dihydrocinnamate (2.9%), and *cis*-ethyl cinnamate (30.0%). No *trans*-ethyl cinnamate was detected (<0.3% by the gas chromatographic method used). Stereospecific cis hydrogenation is expected for diimide reductions.[21] This was confirmed for reduction under identical conditions of ethyl phenylpropiolate by the Corey–Mock[22] authentic diimide precursor **23**. Again there was no evidence



for any trans ester. Hydrazo compound **23** was prepared as described by Corey and Mock or alternatively via the bis[(9-fluorenylmethyl)oxy]carbonyl (FMOC)[23] derivative **24**. The FMOC derivative could be readily deblocked under mild conditions using a ternary mixture of diethylamine, acetonitrile, and methylene dichloride (1:1:1).

Synthesis and Thermolysis of 7-Amino-7-azabenzonorbornadiene. In view of the low yields of anthracene obtained by thermolysis of **5** under the nonacidic conditions required if direct fragmentation to **2** is to be considered a viable possibility, interest shifted to the monobenzo analogue **4**, which is expected to fragment more easily than **5**.[10] Direct amination of secondary amine **25**[24]



gave a solution that rapidly evolved gas at room temperature. Initial experiments having demonstrated the presence of **4** in solution (formation of the *p*-nitrobenzal derivative), we sought to obtain a stable derivative from which we could obtain the free hydrazine at will.

tert-Butyloxycarbonyl (*t*-BOC) derivative **26** was first synthesized (19%) by treatment of the reaction mixture following amination with di-*tert*-butyl pyrocarbonate. Two invertomers of structure **26** were obtained in a 3:2 ratio as determined by ^{1}H NMR spectroscopy. Similar invertomers have been observed in the case of the analogous *N*-chloro compound.[25] Although somewhat unstable in solution ($t_{1/2}$ ca. 0.9 h in $CDCl_3$ at 37 °C), *t*-BOC derivative **26** could be obtained analytically pure and stored in convenient solid form. Attempts were made to convert **26** to the free hydrazine **4** by first deblocking with hydrogen chloride in ether. Unfortunately, the acidic treatment caused ring opening and only derivatives of 1-naphthylhydrazine could be isolated.

Faced with these discouraging results, we turned to the analogous FMOC derivative **27** since the mild basic conditions required for FMOC cleavage were not expected to

(19) (a) Carpino, L. A. *J. Am. Chem. Soc.* **1960**, *82*, 3133. (b) Krause, J. G. *Synthesis* **1972**, 140. (c) Tamura, Y.; Minamikawa, J.; Ikeda, M. *Synthesis* **1977**, 1.

(20) Fragmentation of *N*-aminoaziridines is also facilitated by acidic reagents. See: Felix, D.; Müller, R. K.; Horn, U.; Joos, R.; Schreiber, J.; Eschenmoser, A. *Helv. Chim. Acta* **1972**, *55*, 1276.

(21) Anderson, D. J.; Gilchrist, T. L.; Horwell, D. C.; Rees, C. W. *J. Chem. Soc. C* **1970**, 576.

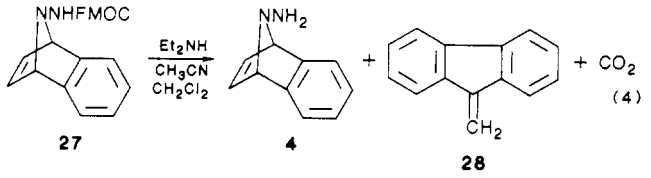
(22) (a) Corey, E. J.; Mock, W. L. *J. Am. Chem. Soc.* **1962**, *84*, 685. (b) Mock, W. L. Ph.D. Thesis, Harvard University, Cambridge, MA, 1965.

(23) Compare: Carpino, L. A.; Han, G. Y. *J. Org. Chem.* **1972**, *37*, 3404.

(24) Carpino, L. A.; Barr, D. E. *J. Org. Chem.* **1966**, *31*, 764.

(25) (a) Rautenstrauch, V. *J. Chem. Soc. D* **1969**, 1122. (b) Malpass, J. R.; Walker, M. P. *J. Chem. Soc., Chem. Commun.* **1979**, 585.

cause opening of the strained ring system. These expectations were fully realized. Treatment of the reaction mixture with 9-fluorenylmethyl chloroformate gave **27**, an easily purified solid of about the same stability as the *t*-BOC analogue. Deblocking of **27** by means of diethylamine in acetonitrile/methylene dichloride at 0 °C gave **4** along with dibenzofulvene (**28**) (eq 4). Diethylamine was



27 4 28 (4)

chosen as deblocking agent in order to ensure both volatility of the excess reagent and lack of reaction of the deblocking amine with byproduct **28**, thus allowing for facile chromatographic separation of **4** and **28** over silica gel at 0 °C. In this way, following removal of solvent, **4** could be obtained as a colorless oil in 86% yield whenever needed for further studies. The ^{1}H NMR spectrum showed that **4** existed as a pair of invertomers (bridgehead protons at δ 4.55 and 4.80). At 37 °C in $CDCl_3$, **4** exhibited a half-life of about 15 min with loss of the hydrazine being balanced by the buildup of peaks for naphthalene and a new compound, which exhibited a peak at δ 4.20, which was assigned to the bridgehead protons of the dihydro derivative **29**. The saturated hydrazine **29** could be isolated in 43% yield after a solution of **4** had been allowed to stand overnight in ether at room temperature. Self-reduction of **4** explains why several early attempts to reduce unsaturated nitrosamine **30** (Zn/HOAc; $LiAlH_4$) gave only dihydro derivative **29**, albeit in only trace amounts. In contrast to **4**, compound **29** was, as expected, thermally stable (bp 90 °C at 0.5 mm). In order to suppress formation of **29** during the synthesis of **4**, we added 4–5 equiv of norbornadiene prior to the amination step. The norbornadiene and subsequently formed norbornene and norbornane were removed along with dibenzofulvene during the final chromatographic purification step.

29 30

To address the question of the nature of the labile coproduct accompanying naphthalene upon fragmentation of **4**, we warmed a sample in ether at 40 °C with 5 equiv of ethyl phenylpropiolate for 4 h. GC analysis showed naphthalene (59%), *cis*-ethyl cinnamate (4.2%), and *trans*-ethyl cinnamate (6.0%). The cis:trans ratio was thus 42:58, and since isomerization of the cis to trans isomer was minor under the conditions of the experiment (<1.6%), it is clear that some direct reduction of the acetylene to the trans ester must occur.

To verify that diimide would give only *cis*-cinnamate, we decomposed the Corey–Mock compound **23** under the same conditions used in the case of **4**. Reaction conditions could not be made exactly comparable, however, since **23** is relatively insoluble in ether and its complete decomposition required a far longer period. In this case GC analysis showed anthracene (73%), ethyl 3-phenylpropionate (1.3%), *cis*-ethyl cinnamate (20%), and *trans*-ethyl cinnamate (0.8%). Control reactions showed that a small degree of isomerization of the cis to the trans ester occurred, but due to the heterogeneous nature of the process and its lack of reproducibility, an exact numerical comparison of the extent of isomerization could not be obtained. Nevertheless, the overwhelming formation of the cis isomer is as expected for a typical diimide reduction. The efficiency of reduction with **23** is far greater than with **4** at least in part because of the self-reduction process, with loss of active agent, which occurs in the case of the latter.

When the thermolysis of **4** was carried out in the presence of both acetylenic ester and acetic acid, only naphthalene (50%) and *cis*-ethyl cinnamate (6.7%) were detected, a finding that agrees with results previously discussed for the dibenzo system. It seems likely that fragmentation of both mono- and dibenzo-7-amino-7-azanorbornadienes in the presence of acetic acid leads to protonated diimide formation. It is tempting to assume that free azamine is liberated in the direct thermolysis of **4**, thereby effecting nonstereospecific reduction of the acetylenic ester or possibly suffering partial isomerization to diimide, which may be responsible for the cis reduction product. A radical chain mechanism involving azamine was put forward by Lahti[26] as a possible explanation for the formation of trans olefins during the reduction of acetylenes by the related thermolysis of several *N*-aminoaziridines. Alternatively, as pointed out by a referee, direct reduction of the propiolate ester by **4** in either a concerted or stepwise process is also possible. Evidence of a discrete intermediate in this reaction as well as the related reduction processes involving **4** and **5** in the presence of acetic acid will be sought by application of Rebek's three-phase test.[27]

Experimental Section

Instrumentation and General Procedures. Melting points and boiling points were uncorrected. Infrared spectra were determined on Perkin-elmer Model 237B or 1310 spectrometers and ^{1}H NMR spectra on Perkin-Elmer R-12 (60 MHz) or R-32 (90 MHz) or Varian XL-200 (200 MHz) or XL-300 (300 MHz) instruments with Me_4Si as internal standard. All ^{13}C NMR spectra were recorded on a Varian Model XL-200 spectrometer at 50.3 MHz. Elemental analyses were carried out by the University of Massachusetts Microanalytical Laboratory under the direction of Greg Dabkowski. GC data were obtained on a Perkin-Elmer Model Sigma-2000 instrument using a flame ionization detector and a Perkin-Elmer LC-100 integrator. The column used was a 25-m fused silica capillary (i.d. = 0.1 mm) which contained bonded methyl silicone (0.25-μm film thickness) as stationary phase. All injections were performed by using helium as carrier gas at 45 psi. Each zone was maintained at the following temperatures: injector (215 °C), column (165 °C), detector (215 °C). Yields were based on *trans*-stilbene as internal standard.

***N*-Benzylisoindole (9).** To a stirred solution of 150 mL of dry THF in a 500-mL two-neck flask under N_2 at 0 °C was added 7.21 g of $LiAlH_4$ followed by a solution of 12.15 g of distilled MeOH in 150 mL of dry THF added dropwise at 0 °C over a period of 25 min. After the mixture was stirred for 5 min, the flask was immersed in a bath at −40 °C and treated with 15.00 g of *N*-benzylphthalimide[28] added over a few minutes. After being stirred for 30 min at −40 °C, the solution was warmed to 0 °C for an additional 30 min. Excess reducing agent was decomposed by dropwise addition of a solution containing 1.0 g of Na_2SO_4 in 9.0 mL of H_2O. After warming to room temperature, aluminum salts were filtered by suction and washed twice with 75-mL portions of acetone. The filtrate was dried and evaporated in vacuo at 40 °C to leave a yellow solid, which was stirred with 40 mL of 95% EtOH and the suspension then stored at −20 °C overnight. After filtration, the solid was washed with 40 mL of cold 95% EtOH and dried to give 7.3 g (56%) of the isoindole as a pale

(26) Lahti, P. M. *Tetrahedron Lett.* **1983**, *24*, 2343.
(27) (a) Rebek, J.; Gaviña, F. *J. Am. Chem. Soc.* **1974**, *96*, 7112. (b) Rebek, J.; Gaviña, F.; Navarro, C. *J. Am. Chem. Soc.* **1978**, *100*, 8113.
(28) (a) Gabriel, S. *Ber. Dtsch. Chem. Ges.* **1887**, *20*, 2227. (b) Ing. H. R.; Manske, R. H. F. *J. Chem. Soc.* **1926**, 2348.

yellow solid, mp 111–118 °C dec (lit.[12] mp 115–116 °C).

In a similar reaction carried out separately, evidence for the formation of the indoline **15** was obtained by ^{1}H NMR examination of the crude reaction mixture (singlet at δ 3.85). Although impurity peaks were present at positions close to this value, a rough estimate of the ratio of **9** to **15** was determined to be 3:1 by integration of the peaks at δ 5.28 and 3.85, respectively.

7-Benzyl-2,3:5,6-dibenzo-7-azabicyclo[2.2.1]hepta-2,5-diene (10). A 1000-mL three-neck flask that had been fitted with a pressure-equalizing dropping funnel and a condenser was flushed with N_2. After the addition of 1.95 g of Mg turnings and 25 mL of dry THF, 0.50 mL of 1,2-dibromoethane was added with stirring to activate the Mg. After initiation, as evidenced by warming, a solution of 9.70 g of *N*-benzylisoindole in 90 mL of dry THF was added and the mixture heated to reflux. Through the addition funnel, ca. one-fourth of a solution containing 8.93 g of *o*-fluorobromobenzene in 25 mL of THF was introduced. After the reaction had been initiated as evidenced by darkening and rapid spontaneous refluxing, the heating mantle was removed and refluxing was maintained by dropwise addition of the benzyne precursor. After complete addition, the dark solution was refluxed for 1.5 h and cooled to room temperature. A solution of 35 g of NH_4Cl in 120 mL of H_2O was added, and stirring was maintained until all excess Mg had been decomposed. The organic layer was separated and the aqueous layer extracted with two 50-mL portions of Et_2O. The organic extracts were combined, dried, and evaporated at 45 °C in vacuo to a dark brown oil, which was dissolved in 30 mL of acetone/Skellysolve B (1:1) and the solution cooled to −20 °C. Filtration gave 8.74 g (66%) of the bicyclic amine as a light olive-green powder, mp 138–142 °C. Recrystallization from 95% EtOH gave 8.30 g (63%) of the amine as a nearly white powder: mp 140–142 °C; ^{1}H NMR ($CDCl_3$) δ 3.50 (s, 2, CH_2), 4.95 (s, 2, bridgehead), 6.90–7.40 (m, 13, aromatic).

Anal. Calcd for $C_{21}H_{17}N$: C, 89.01; H, 6.05; N, 4.94. Found: C, 89.09; H, 5.98; N, 4.84.

2,3:5,6-Dibenzo-7-azabicyclo[2.2.1]hepta-2,5-diene Hydrobromide (12). A solution of 11.42 g of tertiary amine **10** in 130 mL of dioxane/H_2O (9:1) was treated with a solution of 7.12 g of NBS dissolved in 35 mL of the same solvent and the solution stirred at room temperature for 1–2 days. Removal of solvent by rotary evaporation gave a yellow solid, which was washed with acetone to remove succinimide. The residue (9.8 g) was recrystallized from warm EtOH to give 8.4 g (77%) of the pure hydrobromide, mp 160–200 °C dec. The analytical sample was obtained by three additional recrystallizations from ethanol, mp 130–200 °C dec.

Anal. Calcd for $C_{14}H_{12}BrN$: C, 61.33; H, 4.41; Br, 29.15; N, 5.11. Found: C, 61.40; H, 4.45; Br, 29.00; N, 5.17.

7-Bromo-2,3:5,6-dibenzo-7-azabicyclo[2.2.1]hepta-2,5-diene (11). A mixture of 3.96 g of tertiary amine **10**, 1.40 g of $NaHCO_3$, and 50 mL of dioxane/H_2O (9:1) was stirred at room temperature. To the mixture was added 5.32 g of NBS, and stirring was continued for 24 h, during which time a heavy white precipitate separated. Most of the solvent was removed at 45 °C in vacuo. The residue was partitioned between 100 mL of 5% NaOH and 100 mL of CH_2Cl_2 and the organic layer separated. The aqueous layer was extracted with 25 mL of CH_2Cl_2, and the combined organic extracts were dried and evaporated to give a yellow oily solid. Dissolving in 110 mL of hot EtOAc/EtOH (1:1) and cooling to −20 °C gave 2.84 g (75%) of the bromide as pale yellow flakes, which showed no distinct melting point but blackened above about 130 °C: ^{1}H NMR ($CDCl_3$) δ 5.40 (s, 2, bridgehead), 6.95–7.50 (m, 8, aromatic). Under similar conditions, secondary amine **13** and 1 equiv of NBS gave the *N*-bromo compound in 64% yield. One recrystallization from 95% EtOH gave the analytical sample.

Anal. Calcd for $C_{14}H_{10}BrN$: C, 61.78; H, 3.71; N, 5.15. Found: C, 61.79; H, 3.62; N, 5.12.

2,3:5,6-Dibenzo-7-azabicyclo[2.2.1]hepta-2,5-diene (13). Method A. A suspension of 0.442 g of bromoamine **11** in 5.0 mL of MeOH was cooled to 0 °C with stirring. Over a 3-min period, a solution of 0.20 g of hydrazine hydrate in 4.0 mL of MeOH was added dropwise. During this period the solid completely dissolved. After being stirred for an additional 5 min at 0 °C, the solution was warmed to room temperature, and most of the MeOH evaporated in vacuo at 25 °C. The residue was cooled to 0 °C with stirring, 10 mL of 3% HCl solution was added, and the mixture was filtered to remove a trace of solid. After rinsing with 5.0 mL of cold H_2O, the filtrate was cooled in an ice bath and made strongly basic by the slow addition of 1.0 g of KOH pellets. The precipitated solid was suction-filtered, washed thoroughly with cold H_2O, and air-dried to give 0.259 g (83%) of the amine as a nearly white powdery solid, mp 109.5–111.0 °C.

Method B. A solution of 3.9 g of hydrobromide **12** in water was treated with excess NaOH, which gave 2.5 g (93%) of the crude amine upon filtration and drying. As obtained, the amine was pure enough for further use. Two sublimations at 60 °C (0.05 mm) gave an analytical sample: mp 109.5–110.5 °C; ^{1}H NMR ($CDCl_3$) δ 3.15 (br s, 1, NH), 5.30 (s, 2, bridgehead), 6.8–7.40 (m, 8, aryl).

Anal. Calcd for $C_{14}H_{11}N$: C, 87.01; H, 5.74; N, 7.25. Found: 86.95; H, 5.65; N, 7.45.

7-Nitroso-2,3:5,6-dibenzo-7-azabicyclo[2.2.1]hepta-2,5-diene (14). A solution of 1.93 g of amine **13** in 25 mL of glacial acetic acid and 10 mL of water was cooled in an ice/salt bath and an aqueous solution of 1.38 g of $NaNO_2$ added with stirring while the temperature was maintained at 0 °C. A yellow solid separated at once. After the mixture was stirred in the bath for an additional hour, the yellow solid was filtered, washed with water, dried, and recrystallized from benzene/Skellysolve F to give 1.48 g (67%) of the nitrosamine as yellow needles: mp 160–200 °C dec; ^{1}H NMR[29] ($CDCl_3$) δ 6.75 (br s, 2, bridgehead), 7–7.5 (m, 8, aryl).

Anal. Calcd for $C_{14}H_{10}N_2O$: C, 75.65; H, 4.54; N, 12.61. Found: C, 75.89; H, 4.69; N, 12.70.

7-Amino-2,3:5,6-dibenzo-7-azabicyclo[2.2.1]hepta-2,5-diene (5). Method A. To a mixture of 222 mg of nitrosamine **14** in 25 mL of ice-cold 95% ethanol was added 3 mL of glacial acetic acid. The mixture was stirred in the ice bath for 15 min following the addition of 3.25 g of zinc powder and filtered by suction into an aqueous sodium hydroxide solution. The white zinc salts were filtered, and the ethanol was removed from the filtrate by a rotary evaporator. Recrystallization from Skellysolve F by cooling in a dry ice/acetone bath gave 0.14 g (66%) of the hydrazine derivative as a white solid; mp 100 °C dec; ^{1}H NMR ($CDCl_3$) δ 3.30 (br s, 2, NH), 5.00 (s, 2, bridgehead), 6.9–7.50 (m, 8, aryl).

Anal. Calcd for $C_{14}H_{12}N_2$: C, 80.74; H, 5.81; N, 13.45. Found: C, 81.00; H, 5.85; N, 13.59.

Method B. A two-phase system consisting of 2.67 g of amine **13** in 75 mL of Et_2O and 5.0 g of K_2CO_3 in 50 mL of H_2O was cooled with stirring to 0 °C. During a 15-min period, 2.97 g of MSH was added in small portions with vigorous stirring. After 15 min at 0 °C, 25 mL of H_2O and 25 mL of CH_2Cl_2 were added, and the mixture was warmed to room temperature to dissolve a white precipitate. The aqueous phase was washed with 25 mL of CH_2Cl_2, and the combined organic layers were washed with three 25-mL portions of 3% HCl solution. The acidic extracts were cooled to 0 °C, and a sufficient amount of KOH pellets was added with swirling to cause the solution to become strongly basic. The mixture was extracted with two 25-mL portions of CH_2Cl_2, and the extracts were dried and evaporated at 20 °C in vacuo to give a light yellow solid. ^{1}H NMR analysis showed this solid to be an almost equal mixture of the hydrazine and the starting amine. The solid was dissolved in a minimum amount (ca. 5 mL) of CH_2Cl_2, 50 mL of hexane was added, and the solution was cooled to −20 °C. Filtration of the precipitated solid gave 1.12 g (39%) of the crude hydrazine as a tan-colored solid, mp 94 °C dec. The solid was redissolved and precipitated by using the same volumes of solvent as before to give 0.99 g (34%) of the hydrazine as off-white needles, mp 96 °C dec, identical with the sample described from method A.

From the organic layer after acid extraction there was obtained 0.50 g (20%) of anthracene. Recovery of unused starting amine was achieved by evaporating the combined filtrates, refluxing the solid residue in 30 mL of toluene for 30 min, cooling to room

(29) Only broad singlets are observed at room temperature in $CDCl_3$ for the bridgehead protons of **14** and **30**. Ring strain might be expected to lower the coalescence temperature (T_c) of the peaks due to the α-protons, but even in the case of the more highly strained *N*-nitrosoazetidine system, T_c (ca. 180 °C for Me_2NNO) is only lowered to about 130 °C. See: Bumgardner, C. L.; McCallum, K. S.; Freeman, J. P. *J. Am. Chem. Soc.* **1961**, *83*, 4417. A temperature-dependence study of the NMR spectra of these curious compounds is planned.

temperature, and extracting with two 20-mL portions of 3% HCl solution. The aqueous layer was washed with 5 mL of toluene, filtered, and cooled in an ice bath, and a sufficient amount of KOH pellets was added to cause the solution to become strongly basic. The precipitate was filtered by suction, washed with H_2O, and air-dried to give 0.65 g (24%) of the amine, mp 107–109.5 °C. The amine was purified by use of decolorizing carbon in ether followed by recrystallization from a minimum amount of Skellysolve C with cooling to −20 °C to give 0.56 g (21%) of **13** as nearly white flakes, mp 109.5–111.0 °C.

7,8-Bis[[(9-fluorenylmethyl)oxy]carbonyl]-2,3:5,6-dibenzo-7,8-diazabicyclo[2.2.2]octa-2,5-diene (24). A solution of 4.02 g of anthracene and 10.72 g of 9-fluorenylmethyl azodiformate[23] in 55 mL of toluene was refluxed with stirring under N_2 for 8 h. Evaporation of the toluene gave an oily solid, which was dissolved in 30 mL of warm acetone and treated with 110 mL of Et_2O. The solution was stored at −20 °C for a few days and filtered to give 12 g (81%) of the bis-FMOC adduct as a fine white powder. The ^1H NMR spectrum of this material showed that solvent was still present. In order to effect its removal, we precipitated 1 g of the solid by dissolving in 10 mL of CH_2Cl_2, adding 20 mL of CH_3OH, and cooling to −20 °C. Filtration followed by drying overnight in vacuo gave 0.91 g of the adduct as a fine crystalline material; mp 125–132 °C; ^1H NMR ($CDCl_3$) δ 3.90–4.60 (m, 6, $CHCH_2$), 6.23 (br s, 2, bridgehead), 7.00–7.90 (m, 24, aromatic); IR (KBr) 1754, 1708 cm^{-1} (C=O). The ^1H NMR spectrum showed a small impurity peak at δ 1.6 which did not disappear upon further attempts at purification. TLC analysis with elution by means of 40% EtOAc in hexane showed only a single spot (R_f 0.54). The analytical sample was prepared by an additional precipitation from the same solvent system; mp 125–131 °C.

Anal. Calcd for $C_{44}H_{32}N_2O_4$: C, 80.95; H, 4.95; N, 4.29. Found: C, 80.71; H, 4.99; N, 4.19.

2,3:5,6-Dibenzo-7,8-diazabicyclo[2.2.2]octa-2,5-diene (23). To a solution of 0.991 g of adduct **24** in 70 mL of CH_2Cl_2 was added 7.0 mL of CH_3CN. The solution was cooled to 0 °C with stirring, and 7.0 mL of Et_2NH was added dropwise over a 5-min period. After the mixture was stirred at 0 °C for 25 min, the solvents were evaporated at this temperature with the aid of a vacuum pump; final pressure ca. 1 mm. The resulting yellow solid was suspended in 8.0 mL of Et_2O at 0 °C and reevaporated as before to remove residual Et_2NH. With stirring at 0 °C, 15 mL of 3% HCl, 8.0 mL of Et_2O, and 8.0 mL of hexane (all precooled to 0 °C) were added, and the mixture was transferred to a separatory funnel. The aqueous layer was separated, the organic layer (containing some suspended solid) was further extracted with 8.0 mL of H_2O at 0 °C, and the extracts were combined with the previous aqueous layer. The aqueous portion was quickly filtered and made basic by the dropwise addition of a solution of 1.3 g of KOH in 5.0 mL of H_2O at 0 °C. The heavy precipitate was stirred at 0 °C for 5 min, filtered, and washed with cold water. After being allowed to air-dry briefly, the precipitate was dried to constant weight with the aid of a vacuum pump at room temperature to give 0.181 g (57%) of the hydrazine as an off-white powder. When a capillary tube containing a sample of this material was placed in a heating block maintained at 125 °C, rapid evolution of gas was noted although no melting took place. Above 170 °C the solid began to shrink and turn brown. Complete melting did not occur until 215 °C: ^1H NMR ($CDCl_3$) δ 2.25 (br s, 2, NH), 5.20 (s, 2, bridgehead), 7.05–7.50 (m, 8, aryl). The compound was identified by comparison of its IR and ^1H NMR spectra with those of an authentic sample prepared by the method of Corey and Mock.[22]

7-(*tert*-Butyloxycarbonyl)-2,3-benzo-7-azabicyclo[2.2.1]-hepta-2,5-diene. By an improved method the yield of this key intermediate can be nearly doubled over that described previously[24] using 45.0 g of 1-(*tert*-butyloxycarbonyl)pyrrole, 47.2 g of *o*-fluorobromobenzene, and 6.90 g of Mg. After separation of the THF layer, 400 mL of H_2O was added to the aqueous layer and the mixture was extracted twice with two 150-mL portions of CH_2Cl_2. The combined organic extracts were dried and evaporated in vacuo to a dark oil. Most of the excess (*tert*-butyloxycarbonyl)pyrrole was removed by Kugelrohr distillation at 65 °C (0.50 mm). Raising the temperature to 125 °C at this pressure caused the distillation of a yellow oil, which solidified on cooling. The solid was dissolved in 250 mL of hot hexane and the mixture filtered to remove a trace of insoluble solid and cooled to −20 °C overnight. The precipitated solid was washed with cold hexane and air-dried to give 35.8 g (55%) of the adduct as small white crystals, mp 72.5–74.0 °C (lit.[24] mp 72–73 °C). By evaporation of the filtrate to a volume of 125 mL followed by seeding and cooling to −20 °C, an additional 2.0 g of adduct was obtained to give a total yield of 37.8 g (58%).

2,3-Benzo-7-azabicyclo[2.2.1]hepta-2,5-diene (25). This modification of an earlier method[24] avoids losses due to the unexpectedly high water solubility of the amine. A suspension of 29.6 of the hydrochloride salt of **25** in 400 mL of Et_2O was cooled to 0 °C with stirring. A solution of 20.0 g of KOH in 30 mL of H_2O was rapidly added dropwise. Stirring was continued at 0 °C until no more solid remained suspended in the Et_2O layer. The Et_2O layer was decanted and the residue washed twice with two 50-mL portions of Et_2O. The combined extracts were dried and evaporated in vacuo. Distillation gave 19.6 g (83%) of the amine as a viscous clear oil, bp 60–65 °C (0.50 mm) [lit.[24] bp 60 °C (0.4 mm)], which was stored under N_2 at −20 °C. The ^1H NMR spectrum, which did not show the presence of any 1-naphthylamine, matched the spectrum of an authentic sample.

7-[(*tert*-Butyloxycarbonyl)amino]-2,3-benzo-7-azabicyclo[2.2.1]hepta-2,5-diene (26). A two-phase system consisting of 3.513 g of amine **25** in 60 mL of Et_2O and 6.0 g of K_2CO_3 in 30 mL of H_2O was cooled with stirring to −5 °C in an ice/salt bath. Over a 12-min period was added 5.282 g of MSH in small portions with vigorous stirring. After 30 s, a cold solution of 4.818 g of di-*tert*-butyl pyrocarbonate in 15 mL of Et_2O was added dropwise over a 3-min period. Stirring was continued at this temperature for 30 min, and the entire mixture was quickly filtered by suction into a flask immersed in an ice bath. The white solid was washed with 20 mL of Et_2O and 20 mL of CH_2Cl_2, and the organic layer of the filtrate was quickly separated. After drying at 0 °C, the organic extract was evaporated at 5 °C with the aid of a water aspirator to give a light yellow oil. The oil was dissolved in 6.0 mL of Et_2O, 25 mL of cold hexane was added, and the resulting solution was stored at −20 °C overnight. The precipitated solid was collected by suction filtration, washed with cold hexane, and air-dried to give 1.19 g (19%, based on MSH) of the (*tert*-butyloxycarbonyl)hydrazine as a white powdery solid: mp 90.5–91.0 °C dec, gas evolution; ^1H NMR ($CDCl_3$) δ 1.40 [(s, major) and 1.45 (s, minor) totalling 9 H, $C(CH_3)_3$], 4.70 [(t, major) and 4.95 (br s, minor) totalling 2 H, bridgeheads of two invertomers], 5.60 [(br s, major) and 6.35 (br s, minor) totalling 1 H, NH's of two invertomers, both D_2O exchangeable], 6.78–7.50 (m, 6, olefinic + aromatic). The ratio of the two invertomers as determined by integration of the peaks at δ 4.70 and 4.95 was 3:2. IR (KBr): 3340, 3230 (NH), 1735, 1685 cm^{-1} (C=O). The analytical sample was prepared by two precipitations from cold CH_2Cl_2/hexane followed by cooling to −20 °C; mp 94.5 °C dec.

Anal. Calcd for $C_{15}H_{18}N_2O_2$: C, 69.73; H, 7.04; N, 10.85. Found: C, 69.62; H, 6.97; N, 10.96.

7-[[[(9-Fluorenylmethyl)oxy]carbonyl]amino]-2,3-benzo-7-azabicyclo[2.2.1]hepta-2,5-diene (27). A solution of 2.339 g of amine **25** in 40 mL of Et_2O was cooled with stirring to −10 °C in an ice/salt bath. During a 15-min period, 0.879 g of MSH was added in small portions. A few minutes after the start of the addition, a white precipitate formed. Stirring was continued at this temperature for an additional 9 min, and a cold solution of 2.222 g of mesitylenesulfonic acid dihydrate in 30 mL of Et_2O was added dropwise over a 9-min period. Preferential precipitation of the mesitylenesulfonic acid salt of **25** occurs. After 3 min, the suspension was filtered through an ice-jacketed frit into a stirred mixture at 0 °C of 0.740 g of FMOC-Cl,[23] 15 mL of Et_2O, and 15 mL of 10% Na_2CO_3 solution. The amine salt was washed with 20 mL of Et_2O at 0 °C, the filtrate being combined with the FMOC-Cl solution. The mixture was stirred for 15 min at this temperature, and 30 mL of CH_2Cl_2 and 10 mL of H_2O (both at 0 °C) were added to dissolve a small amount of white precipitate. The organic layer was quickly separated, dried, and evaporated at 0 °C with the aid of a water aspirator to give a partially solidified oil. The residue was stirred with 6.0 mL of cold Et_2O in an ice/salt bath until a heavy precipitate formed. After the addition of 25 mL of cold MeOH, the suspension was stirred at this temperature for 20 min and stored at −20 °C for several hours. After being suction-filtered, the solid was washed with cold MeOH, briefly

air-dried, and finally dried to constant weight at room temperature with the aid of a vacuum pump. This gave 0.517 g (33%, based on MSH) of the hydrazide as a white powder: mp 83 °C dec; ^{1}H NMR ($CDCl_3$) δ 4.00–4.55 (m, 3, $CHCH_2$), 4.70 [(t, major) and 4.90 (br s, minor) totalling 2 H, bridgeheads of two invertomers], 5.80 [(br s, major) and 6.50 (br s, minor) totalling 1 H, NH's of two invertomers, both D_2O exchangeable], 6.75–7.90 (m, 14, olefinic + aromatic). The ratio of the two invertomers as determined by integration of the peaks at δ 4.70 and 4.90 was 7:3. IR (KBr): 3200 (NH), 1745 (sh), 1730, 1710 cm^{-1} (C=O). The recovered amine salt was obtained after air-drying as a white powder (4.06 g). The analytical sample was prepared by several precipitations from cold CH_2Cl_2/hexane with cooling to −20 °C; mp 84 °C dec.

Anal. Calcd for $C_{25}H_{20}N_2O_2$: C, 78.92; H, 5.31; N, 7.36. Found: C, 78.69; H, 5.41; N, 7.25.

7-Amino-2,3-benzo-7-azabicyclo[2.2.1]hepta-2,5-diene (4). A solution of 0.145 g of FMOC compound **27** in 1.5 mL of CH_2Cl_2, 1.5 mL of MeCN, and 0.15 mL of norbornadiene was stirred in an ice bath. During a 2-min period, 1.5 mL of Et_2NH was added dropwise, and stirring was continued at this temperature for 1 h. The solvents were evaporated at 0 °C with the aid of a vacuum pump (final pressure = 1.5 mm) to give an oil. The oil was dissolved in 1.5 mL of CH_2Cl_2 (0 °C) and the solution placed on top of an ice-jacketed column (i.d. = 14 mm) which contained 2.0 g of silica gel (100–200 mesh). An additional 1.5 mL of CH_2Cl_2 (0 °C) was added to the flask as a wash solvent and transferred to the column. The column was eluted with 5.0 mL of CH_2Cl_2 (0 °C) to remove dibenzofulvene and any naphthalene that might have been present and the solution discarded. Further elution with 8.0 mL of MeOH (0 °C) gave, after evaporation at 0 °C with the aid of a vacuum pump (final pressure = 1.5 mm), a nearly colorless oil. To this oil was added 3.0 mL of Skellysolve F (0 °C), and the mixture was swirled at 0 °C for 5 min in an attempt to cause crystallization. Since no solidification occurred, the solvent was reevaporated at 0 °C with the aid of a vacuum pump (final pressure = 0.5 mm). Upon standing in the ice for 5–10 min, no solidification was observed. ^{1}H NMR analysis in $CDCl_3$ showed peaks at δ 3.05 (br s, NH_2), 4.55 [(t, major) and 4.80 (br s, minor), bridgeheads of two invertomers], 6.80–7.90 (m, olefinic + aromatic). The absence of dibenzofulvene (**28**) was confirmed by the lack of a peak at δ 6.0. In similar experiments the oil obtained after chromatography was weighed quickly at room temperature. The amount corresponded to a yield of 86–97%. No attempt was made to obtain an analytically pure sample.

The $CDCl_3$ solution (37 °C) was unstable, gas evolution being noted on standing. The formation of increasing amounts of both naphthalene and the dihydro derivative **29** was observed on the basis of ^{1}H NMR spectra that were taken continuously.

The ***p*-nitrobenzal derivative** had the following characteristics: mp 116–118 °C dec; ^{1}H NMR ($CDCl_3$) δ 5.50 (t, 2, bridgehead), 6.85–7.50 (m, 6, olefinic + aromatic), 7.5–7.85 (m, 3, CH=N, meta to NO_2), 8.00–8.35 (m, 2, ortho to NO_2).

Anal. Calcd for $C_{17}H_{13}N_3O_2$: C, 70.15; H, 4.50; N, 14.40. Found: C, 70.18; H, 4.54; N, 14.50.

7-Amino-2,3-benzo-7-azabicyclo[2.2.1]hept-2-ene (29). A stirred solution of 3.2 g of 7-nitroso-2,3-benzo-7-azabicyclo-[2.2.1]hept-2-ene and 6 g of zinc dust in 200 mL of 95% EtOH was cooled to 0 °C in an ice/salt bath. A solution of 6 mL of glacial HOAc, 6 mL of water, and 12 mL of 95% EtOH was added dropwise at such a rate as to keep the temperature below 6 °C. Stirring was continued for 1 h at 0 °C, and after filtration the solvent was removed with the aid of a water aspirator at room temperature. To the resulting oily solid was added a solution of 10 g of NaOH in 100 mL of water, and the aqueous solution was extracted three times with 50-mL portions of ether. Drying ($MgSO_4$) and removal of solvent under reduced pressure at room temperature gave a clear oil. Distillation at 0.5 mm over solid KOH from an oil bath maintained at 90 °C gave 1 g (34%) of the hydrazine as a white solid, mp 50–54 °C. Sublimation gave white crystals: mp 53–55 °C; ^{1}H NMR ($CDCl_3$) δ 1.0 (m, 2, 2,3-endo), 2.0 (m, 2, 2,3-exo), 2.8 (s, 2, NH_2), 4.0 (t, 2, bridgehead), 7.1 (m, 4, aryl).

Anal. Calcd for $C_{10}H_{12}N_2$: C, 74.96; H, 7.55; N, 17.49. Found: C, 75.10; H, 7.60; N, 17.34.

The ***p*-nitrobenzal derivative**, obtained in the normal manner, after sublimation at 150 °C (0.05 mm), had mp 181–182 °C. The same compound was obtained by hydrogenation (Pd–C/EtOAc) of the corresponding unsaturated derivative.

Anal. Calcd for $C_{17}H_{15}N_2O_2$: C, 69.61; H, 5.15; N, 14.33. Found: C, 69.56; H, 5.08; N, 14.24.

Thermolysis of 7-Amino-2,3-benzo-7-azabicyclo[2.2.1]-hepta-2,5-diene (4) in the Presence of Ethyl Phenylpropiolate. (1) In Et_2O. A solution of 0.147 g (0.386 mmol) of FMOC compound **27** in 1.5 mL of CH_2Cl_2, 1.5 mL of CH_3CN, and 0.15 mL (1.5 mmol) of norbornadiene was stirred in an ice bath. During a 2-min period, 1.5 mL of Et_2NH was added dropwise, and stirring was continued at this temperature for 1 h. The solvents were evaporated at 0 °C with the aid of a vacuum pump (final pressure = 1.5 mm) to an oil. The oil was dissolved in 1.5 mL of CH_2Cl_2 (0 °C) and the solution deposited on top of an ice-jacketed column (i.d. = 14 mm) which contained 2.0 g of silica gel (100–200 mesh). An additional 1.5 mL of CH_2Cl_2 (0 °C) was added to the flask as a wash solvent and transferred to the column. The column was eluted with 5.0 mL of CH_2Cl_2 (0 °C) and the solution discarded. Further elution with 8.0 mL of MeOH (0 °C) gave, after evaporation at 0 °C with the aid of a vacuum pump (final pressure = 0.7 mm), a nearly colorless oil. The flask containing the oil was flushed with N_2 and placed in a dry ice bath. With swirling, 2.0 mL of anhydrous Et_2O was introduced slowly and the solution was reevaporated at 0 °C as before (final pressure = 0.7 mm) to an oil. The oil was weighed quickly (<1 min) at room temperature and amounted to 0.058 g (0.37 mmol, 95%). The flask was flushed with N_2 and immersed in an ice bath, and a solution of 0.32 g (1.8 mmol, 5 equiv) of ethyl phenylpropiolate in 2.0 mL of anhydrous Et_2O was introduced via syringe. The flask was quickly immersed in an oil bath at 40 °C and stirred at this temperature for 4 h under N_2. By GC analysis, amounts (average of two injections) of the following were obtained: naphthalene (0.22 mmol, 59%), *cis*-ethyl cinnamate (0.016 mmol, 4.2%), and *trans*-ethyl cinnamate (0.022 mmol, 6.0%). The ratios of *cis*- to *trans*-cinnamates for two consecutive injections were 41:59 and 42:58. Addition of small quantitites of authentic *cis*- and *trans*-cinnamates enhanced the intensities of the peaks which had been attributed to these esters without producing any new peaks. In view of the low yields of reduction products, the reaction was repeated four times, twice qualitatively and twice quantitatively. The second quantitative run gave essentially the same results as described above (cis:trans ratio 42:58). From a similar experiment it was shown that *cis*-ethyl cinnamate was not isomerized to the trans isomer (<1.6%) under the conditions of the reaction.

(2) In Et_2O with HOAc. The hydrazine (0.059 g, 0.37 mmol, 97%) was first prepared exactly as described by using the same quantity of FMOC hydrazide **27**. The flask was flushed with N_2 and immersed in an ice bath, and a solution of 0.32 g (1.8 mmol, 5 equiv) of ethyl phenylpropiolate in 2.0 mL of anhydrous Et_2O containing 0.10 mL of HOAc was introduced via syringe. By GC analysis, amounts (average of two injections) of the following were obtained: naphthalene (0.19 mmol, 50%) and *cis*-ethyl cinnamate (0.025 mmol, 6.7%). From GC analysis of standard mixtures containing the *trans*-cinnamate, it was concluded that a maximum amount corresponding to 0.001 mmol (0.3% yield) of the *trans*-cinnamate would have been detected.

Thermolysis of 7-Amino-2,3:5,6-dibenzo-7-azabicyclo-[2.2.1]hepta-2,5-diene (5) in the Presence of Ethyl Phenylpropiolate and HOAc. A solution of 0.076 g (0.365 mmol) of hydrazine **5** in 2.0 mL of anhydrous Et_2O, 0.10 mL of HOAc, and 0.32 g (1.84 mmol, 5 equiv) of ethyl phenylpropiolate was heated under N_2 to 40 °C in an oil bath with stirring for 17 h. Most of the solvent was removed at 25 °C in vacuo to give an oily solid. By GC analysis, amounts (average of two injections) of the following were obtained: anthracene (0.20 mmol, 55%), ethyl 3-phenylpropionate (0.0053 mmol, 2.9%), and *cis*-ethyl cinnamate (0.11 mmol, 30%). From GC analysis of standard mixtures containing the *trans*-cinnamate, it was concluded that a maximum amount corresponding to 0.001 mmol (0.3% yield) of the *trans*-cinnamate would have been detected.

Thermolysis of 2,3:5,6-Dibenzo-7,8-diazabicyclo[2.2.2]-octa-2,5-diene (23) in the Presence of Ethyl Phenylpropiolate. (1) In Et_2O. A suspension of 0.076 g (0.365 mmol) of hydrazine **23** in 2.0 mL of anhydrous Et_2O which contained 0.32 g (1.84 mmol, 5 equiv) of ethyl phenylpropiolate was heated under N_2

with stirring to 40 °C in an oil bath for 24 h. Complete solution was never obtained. Most of the solvent was removed at 20 °C in vacuo to give an oily solid. ^{1}H NMR analysis of the residue showed that all starting hydrazine had been consumed. By GC analysis, amounts (average of two injections) of the following were obtained: anthracene (0.27 mmol, 73%), ethyl 3-phenylpropionate (0.0024 mmol, 1.3%), *cis*-ethyl cinnamate (0.074 mmol, 20%), and *trans*-ethyl cinnamate (0.0029 mmol, 0.80%). The ratio of *cis*- to *trans*-cinnamate for two consecutive injections was 97:3 and 96:4. A second independent run gave essentially the same results.

(2) In Et_2O with HOAc. A suspension of 0.076 g (0.365 mmol) of **23** in 2.0 mL of anhydrous Et_2O, 0.10 mL of HOAc, and 0.32 g (1.8 mmol, 5 equiv) of ethyl phenylpropiolate was heated under N_2 with stirring to 40 °C in an oil bath for 24 h. Complete solution was never obtained. Most of the solvent was evaporated at 20 °C in vacuo to give an oily solid. ^{1}H NMR analysis showed that a significant amount of starting hydrazine (as its HOAc salt) was present. By GC analysis, yields (average of two injections) of the following were obtained: anthracene (0.23 mmol, 63%), ethyl 3-phenylpropionate (0.0037 mmol, 2.0%), and *cis*-ethyl cinnamate (0.088 mmol, 24%). A second independent run gave essentially the same results.

GC data used to determine identities and yields in the various reduction studies were [compound, retention time (minutes), response factor (normalized to *trans*-stilbene)]: naphthalene, 5.77, 0.789; ethyl 3-phenylpropionate, 7.72, 0.702; *cis*-ethyl cinnamate, 8.20, 0.673; saturated hydrazine **29**, 9.35, –; ethyl phenyl propiolate, 10.33, 0.740; *trans*-ethyl cinnamate, 10.67, 0.712; *trans*-stilbene (internal standard), 24.87, 1.00; anthracene, 32.54, 0.943.

Thermolysis of 7-Amino-2,3:5,6-dibenzo-7-azabicyclo-[2.2.1]hepta-2,5-diene (5) in DMF. A solution of 0.110 g of hydrazine **5** in 5.0 mL of spectral grade DMF was immersed in an oil bath at 75–80 °C and stirred at this temperature under N_2 for 1 h. The solution was cooled to room temperature and poured into 10 mL of H_2O. The precipitate was collected by suction filtration, washed with H_2O, and air-dried to give 0.083 g (87%) of a slightly yellow powder, mp 99–105 °C (lit.[30] mp 104–105 °C), identified as 9,10-dihydroanthracene on the basis of melting point and IR and ^{1}H NMR spectral comparisons with an authentic sample. Recrystallization from 75% EtOH/H_2O did not raise the melting point. The ^{1}H NMR spectrum taken of the recrystallized material showed that a very small amount of anthracene was present.

Thermolysis of 7-Amino-2,3:5,6-dibenzo-7-azabicyclo-[2.2.1]hepta-2,5-diene (5) in Benzene with HOAc. A solution of 0.168 g of hydrazine **5** in 5.0 mL of dry benzene and 0.30 mL of glacial acetic acid was heated with stirring under N_2 in an oil bath maintained at 50–55 °C. The solvent was evaporated at 25 °C in vacuo, leaving an off-white solid. ^{1}H NMR analysis of the solid showed that no starting material was present. Silica gel chromatography with elution by Skellysolve F gave 0.120 g (83%) of a white, flaky solid, mp 206–214 °C, identified as anthracene by IR and ^{1}H NMR analysis. In a similar experiment performed without HOAc, it was shown that anthracene was a very minor component as judged by ^{1}H NMR analysis of the residue obtained after evaporation. The complex reaction mixture was not examined further.

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Registry No. **4** (isomer 1), 113972-73-9; **4** (isomer 2), 113974-01-9; **4** (*p*-nitrobenzal), 113859-63-5; **5**, 113859-52-2; **8**, 2142-01-0; **9**, 25473-60-3; **10**, 113859-53-3; **11**, 113859-54-4; **12**, 113859-55-5; **13**, 113859-56-6; **14**, 113859-57-7; **15**, 35180-14-4; **16**, 113859-58-8; **19**, 613-31-0; **23**, 6705-66-4; **24**, 113859-60-2; **25**, 5176-20-5; **25** (*N*-BOC deriv), 5176-28-3; **25**·HCl, 5176-29-4; **25**·mesitylenesulfonate, 113859-62-4; **26** (isomer 1), 113859-59-9; **26** (isomer 2), 113972-74-0; **27** (isomer 1), 113972-75-1; **27** (isomer 2), 113972-76-2; **28**, 4425-82-5; **29**, 113859-61-3; **29** (*p*-nitrobenzal), 113892-40-3; **30**, 5176-34-1; MSH, 36016-40-7; *o*-FC_6H_4Br, 1072-85-1; (*E*)-$EtO_2CCH{=}CHCO_2Et$, 623-91-6; $EtO_2C(CH_2)_2CO_2Et$, 123-25-1; $C_6H_5C{\equiv}CCO_2Et$, 2216-94-6; $C_6H_5(CH_2)_2CO_2Et$, 2021-28-5; (*Z*)-$C_6H_5CH{=}CHCO_2Et$, 4610-69-9; (*E*)-$C_6H_5CH{=}CHCO_2Et$, 4192-77-2; anthracene, 120-12-7; 9-fluorenylmethyl azodiformate, 35661-53-1; 1-(*tert*-butoxycarbonyl)pyrrole, 5176-27-2.

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