be weighed in tared flasks without incident. Triazole **75** exhibits intense IR absorption at 2200 cm^{-1} (=N_2). *Dry* **75** was typically used as soon as it was prepared, but could be stored in the dark at room temperature for several weeks without incident or apparent decomposition. In solution, **75** decomposes in a matter of hours at room temperature.

Reaction of 3-Diazo-5-phenyl-3*H*-1,2,4-triazole (75) with 1-Morpholinylcyclohexene (61). A solution of **75** (0.80 g, 4.7 mmol) in dichloromethane (10 mL) was added to **61** (1.0 g, 5.9 mmol) in dichloromethane (5 mL) at -60 °C. On warming the clear red solution (1 h) to room temperature, a precipitate formed. Evaporating the reaction mixture yielded a residue, which crystallized from hot 1,2-dichloroethane to give 6,7,8,9-tetrahydro-2-phenyl[1,2,4]triazolo[5,1-*c*][1,2,4]benzotriazine (**76**; 0.73 g, 62%) as a pale tan solid: mp (1,2-dichloroethane) 242 °C; IR (KBr) 2945 and 2920 (aliphatic CH), 1618 (aromatic), 1564, 1538, 1445, 1364, 1282, 798, and 690 cm^{-1}; ^1H NMR (DMSO-d_6) δ 8.50-8.20 (m, 2 H, Ph 2,6-H), 7.90-7.60 (m, 3 H, Ph 3,4,5-H) 3.00-250 (m, 4 H, 6,6,9,9-H of benzo group), and 2.35-2.00 (m, 4 H, 7,7,8,8-H of benzo group). Anal. Calcd for $C_{14}H_{13}N_5$: C, 66.92; H, 5.21; N, 27.87. Found: C, 67.03; H, 5.60; N, 27.70.

Reaction of 75 with 1-Piperidinylcyclohexene (25). To a solution of **25** (0.95 g, 5.7 mmol) in dichloromethane (5 mL) at -60 °C was added **75** (0.80 g, 4.7 mmol) in dichloromethane (10 mL). A solid precipitated from the red solution as the mixture warmed to room temperature (1 h). After evaporation of the solvent and recrystallization of the residue, **76** (0.75 g, 64%) was obtained identical with that from **75** and **61**. Additional products were isolated from the mother liquors, but the yield of **76** did not change by altering the time between addition and workup.

Synthesis of 6,7,8,9-Tetrahydro-2-phenyl[1,2,4]triazolo-[5,1-*c*][1,2,4]benzotriazine (75) from (5-Phenyl-1,2,4-triazol-3-yl)hydrazinium Tetrafluoroborate (79) and 1,2-Cyclohexanedione (80). 5-Phenyl-1,2,4-triazole-3-diazonium tetrafluoroborate (2.6 g, 10 mmol) was added in small portions to a stirred solution of stannous chloride (9.0 g, 20 mmol) in concentrated hydrochloric acid (5 mL) and 48% tetrafluoroboric acid (5 mL) at 0 °C. After the mixture had been stirred for 5 min, solid (5-phenyl-1,2,4-triazol-3-yl)hydrazinium tetrafluoroborate was collected. The wet solid was immediately added to **80** (1.20 g, 10 mmol) in acetonitrile (10 mL). The mixture was stirred for 1 h, diluted with 2 volumes of water, and neutralized with excess sodium bicarbonate. The solid was recrystallized from 1,2-dichloroethane, yielding **76** (0.60 g, 23%). This product is identical with that from reactions of **75** with enamines **61** and **25**.

Acknowledgment. We gratefully acknowledge the National Cancer Institute and the National Science Foundation for generous support of this research.

Registry No. **7**, 922-69-0; **12**, 51285-29-1; **20**, 62072-11-1; **23**, 62072-19-9; **24**, 62072-18-8; **25**, 2981-10-4; **27**, 111005-20-0; **28**, 50846-98-5; **29**, 111005-21-1; **32**, 111005-22-2; **33**, 111005-23-3; **37**, 105851-05-6; **44**, 111005-24-4; **45**, 1122-84-5; **47**, 111005-25-5; **48**, 105851-04-5; **51**, 111005-26-6; **55**, 111005-27-7; **56**, 111005-28-8; **59**, 111025-76-4; **60**, 89108-47-4; **61**, 670-80-4; **63**, 111005-29-9; **65**, 111005-30-2; **66**, 111005-31-3; **67**, 64781-77-7; **68**, 18169-20-5; **70**, 111005-32-4; **71**, 16968-06-2; **72**, 111005-33-5; **73**, 64781-78-8; **74**, 111005-34-6; **75**, 80670-36-6; **76**, 111005-35-7; **79**, 111005-36-8; **80**, 765-87-7; $NCCH_2COC(CH_3)_3$, 59997-51-2; $H_2C{=}CHOC_2H_5$, 109-92-2; C_6H_5NCO, 103-71-9; $(C_2H_5)_2NCH{=}C(CH_3)_2$, 16826-16-7; 1-$C_{10}H_7NCO$, 86-84-0; $C_6H_5C{\equiv}CH$, 536-74-3; $H_2C{=}C(OCH_3)CH_3$, 116-11-0; 3-amino-5-*tert*-butylpyrazole, 82560-12-1; 3-benzamido-5-*tert*-butylpyrazole, 111005-15-3; 3-amino-5-phenylpyrazole, 1572-10-7; 5-phenyl-3-pyrazolediazonium chloride, 60270-00-0; 2-aminoimidazole sulfate, 42383-61-9; 1-(dimethylamino)cyclohexene, 13815-46-8; norbornene, 498-66-8; norbornadiene, 121-46-0; *tert*-butyl 4-imidazolecarbamate, 34665-48-0; 4-aminoimidazole dihydrochloride, 111005-19-7; 4-amino-5-phenyl-1,2,3-triazole, 32416-41-4; 4-amino-5-cyano-1,2,3-triazole, 16968-08-4; 3-amino-1,2,4-triazole, 61-82-5; 3-amino-5-phenyl-1,2,4-triazole, 4922-98-9; 5-*tert*-butyl-3-pyrazolediazonium tetrafluoroborate, 111005-17-5; 5-phenyl-3-pyrazolediazonium tetrafluoroborate, 111005-18-6; 5-phenyl-1,2,4-triazole-3-diazonium tetrafluoroborate, 28151-85-1; 1,2,4-triazole-3-diazonium nitrate, 59104-93-7.

Intramolecular Diels-Alder Reactions of 3*H*-Pyrroles Resulting from the Thermal Rearrangements of 2*H*-Pyrroles

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The syntheses of methyl- and phenyl-substituted 2*H*-pyrroles 8 bearing a but-3-enyl or pent-4-enyl side chain are reported. The thermolyses of 8 yielded tricyclic derivatives with the 2-azabicyclo[2.2.1]hept-2-ene moiety resulting from the intramolecular Diels-Alder additions of 3*H*-pyrrole intermediates. No product resulting from the intramolecular cycloaddition of 2*H*-pyrroles or of 1*H*-pyrroles was observed. Thermochemical analysis and ab initio STO-3G calculations on model compounds suggested that the 2-azabicyclo[2.2.1]hept-2-enes derivatives are the only possible products under the conditions of our thermolyses. The rates of the isomerizations of 8 into the corresponding 3*H*-pyrroles intermediates, as well as those of their cyclizations could be enhanced in the presence of the cation-radical $(4\text{-}BrC_6H_4)_3NSbCl_6$ or of a Lewis acid.

Introduction

The 2*H*- and 3*H*-pyrroles[1] are 1-aza and 2-aza dienes, respectively, that are potential synthetic precursors for the preparation of polycyclic heterocycles via Diels-Alder cycloadditions.[2-4] To our knowledge, only the 2,2,3,4,5-pentachloro-2*H*-pyrrole (1) has been explored thus far for

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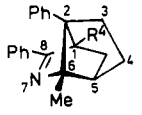
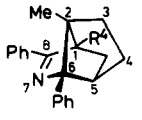
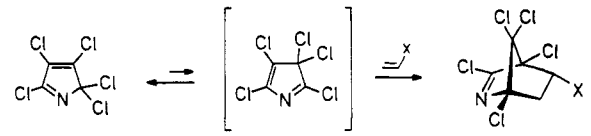
Table I. Product Distributions in the Thermolyses of 2-But-3-enyl-2*H*-pyrroles 8a,b,e,f,i and of the Resulting Azatricyclononene Derivatives 10–13 in C_6H_6 (Isolated Yields)

	products				
reactants	 **10a,b**	 **11a,b**	 **12a,b**	 **13a,b**	reactn conditions [±2 °C]
8a (R^4 = H)	55% **10a**	13% **11a**	*a*	*a*	1.0 M, 210 °C, 24 h
8b (R^4 = Me)	50% **10b**	28% **11b**	7% **12b**	*a*	1.5 M, 228 °C, 24 h
8e (R^4 = H)	*a*	*a*	32% **12a**	53% **13a**	0.6 M, 168 °C, 67 h
	a	*a*	29% **12a**[c]	36% **13a**[c]	0.3 M, 168 °C, 40 h[b]
8f (R^4 = Me)	*a*	*a*	61% **12b**	*a*	0.5 M, 168 °C, 69 h
8i (R^4 = H)	76% **10a**[c]	24% **11a**[c]	traces of **12a**	traces of **13a**	0.2 M, 169 °C, 69 h
10a/11a (3:1)	>95% **10a**	*a*	*a*	*a*	0.2 M, 211 °C, 49 h
10a	>95% **10a**[c]	*a*	*a*	*a*	0.3 M, 208 °C, 65 h[d]
12a/13a (3:7)	*a*	*a*	>95% **12a**[c]	*a*	0.2 M, 196 °C, 48 h
12a	*a*	*a*	>95% **12a**[c]	*a*	0.4 M, 227 °C, 24 h[d]
11b	63% **10b**[c]	30% **11b**[c]	7% **12b**[c]	*a*	0.2 M, 227 °C, 72 h[d]
10b/11b/12b (8:1:1)	63% **10b**[c]	24% **11b**[c]	13% **12b**[c]	*a*	0.3 M, 235 °C, 48 h[d]

[a] Less than 5% of these products could not be detected by ^{1}H NMR of the crude reaction mixture. [b] 35% of unreacted **8e** was recovered. [c] Relative proportions as determined from the ^{1}H NMR spectrum of the crude reaction mixture. [d] 40–70% of polymeric material is formed under these conditions.

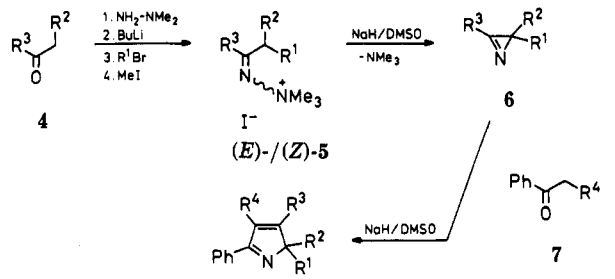
its intermolecular Diels–Alder reactivity.[5-7] On heating with styrene,[5] cyclopentene,[6] cyclohexadiene,[6] *trans*-piperylene,[6] and vinyl acetate,[7] **1** gave the corresponding 2-azanorbornenes **3** resulting presumably from the cycloadditions of the isomeric 3*H*-pyrrole **2**.



1 **2** **3**

To our knowledge, an intramolecular Diels–Alder reaction involving such cyclic 1-aza or 2-aza dienes has not been reported thus far. We now describe the preparation of new 2*H*-pyrroles derivatives substituted with methyl or phenyl groups and with a but-3′-enyl or pent-4′-enyl side chain.[8] The thermolyses of these compounds should either lead to direct intramolecular cycloadditions giving 1-azabicyclo[2.2.1]hept-2-ene derivatives or undergo first [1,5]-sigmatropic shifts[9,10] into 3*H*-pyrroles (2-aza diene) and/or

Scheme I



4 **I**$^-$ **6** **7** **8**

(*E*)-/(*Z*)-**5**

a: R^1 = but-3-enyl, R^2 = Me, R^3 = Ph, R^4 = H
b: R^1 = but-3-enyl, R^2 = Me, R^3 = Ph, R^4 = Me
c: R^1 = pent-4-enyl, R^2 = Me, R^3 = Ph, R^4 = H
d: R^1 = pent-4-enyl, R^2 = Me, R^3 = Ph, R^4 = Me
e: R^1 = but-3-enyl, R^2 = Ph, R^3 = Me, R^4 = H
f: R^1 = but-3-enyl, R^2 = Ph, R^3 = Me, R^4 = Me
g: R^1 = pent-4-enyl, R^2 = Ph, R^3 = Me, R^4 = H
h: R^1 = pent-4-enyl, R^2 = Ph, R^3 = Me, R^4 = Me
i: R^1 = Me, R^2 = Ph, R^3 = but-3-enyl, R^4 = H
j: R^1 = R^2 = Me, R^3 = Ph, R^4 = but-3-enyl
k: R^1 = R^2 = Me, R^3 = Ph, R^4 = pent-4-enyl

1*H*-pyrroles, which can then cyclize into 2-azabicyclo-[2.2.1]hept-2-ene and/or 7-azabicyclo[2.2.1]hept-2-ene derivatives, respectively. The nature of the expected tricyclic adducts will allow one to establish which of these processes is the favored one.[11]

Results

The 2*H*-pyrroles **8a–k** were prepared according to the general procedure shown in Scheme I.[12]

The condensation of ketones **4** with dimethylhydrazine generated the corresponding hydrazones which were deprotonated with *n*-BuLi and allowed to react with an alkyl bromide (R^1Br). After addition of MeI, the corresponding *N,N,N*-trimethylhydrazonium iodides **5** were formed. On

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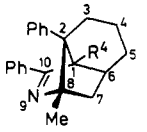
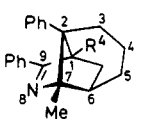
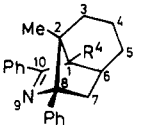
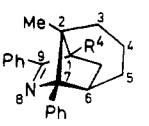
(9) Laurent, A.; Mison, P.; Nafti, A.; Pellissier, N. *Tetrahedron Lett.* **1979**, *20*, 1587–1590; **1982**, *23*, 655–658.

(10) Patterson, J. M.; Ferry, J. D.; deHann, J. W.; Boyd, M. R. *J. Am. Chem. Soc.* **1975**, *97*, 360–362.

(11) For the first example of intramolecular cycloaddition of 1*H*-pyrrole derivative, see: Jung, M. E.; Rohloff, J. C. *J. Chem. Soc., Chem. Commun.* **1984**, 630–632. For analogous reaction with cyclopentadiene derivatives, see, e.g.: Snowden, R. L. *Tetrahedron* **1986**, *42*, 3277–3290 and references cited therein.

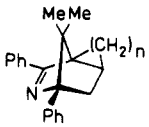
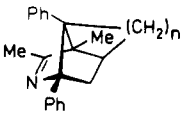
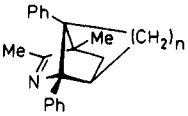
(12) Laurent, A.; Mison, P.; Nafti, A.; Pellissier, N. *Tetrahedron*, **1979**, *35*, 2285–2292.

Table II. Product Distributions in the Thermolyses of 2-Pent-4-enyl-2*H*-pyrroles 8c,d,g,h and of the Resulting Azatricyclodecene Derivatives 14b + 15b, 16a + 17a, and 16b + 17b in C_6H_6 (Isolated Yields)

	products				
reactants	 **14a,b**	 **15a,b**	 **16a,b**	 **17a,b**	reactn conditions [±2 °C]
8c (R^4, = H)	12% **14a**[a]	7% **15a**[a]	20% **16a**[a]	7% **17a**[a]	0.4 M, 188 °C, 24 h[b]
8c	16%	10%	23%	11%	0.8 M, 200 °C, 33 h[c]
8c	11%	4%	38%	6%	1.3 M, 216 °C, 24 h
8d (R^4 = Me)	19% **14b**[a]	19% **15b**[a]	25% **16b**[a]	18% **17b**[a]	0.3 M, 208 °C, 24 h[d]
8d	14%	23%	32%	13%	1.3 M, 212 °C, 42 h
8d			41%	16%	1.1 M, 245 °C, 65 h
8g (R^4 = H)			62% **16a**[a]	38% **17a**[a]	0.2 M, 165 °C, 63 h
8h (R^4 = Me)			50% **16b**[a]	50% **17b**[a]	0.4 M, 190 °C, 70 h
14b/15b (2:3)			50% **16b**[a,c]	50% **17b**[a,e]	0.4 M, 208 °C, 86 h
16a/17a (2:1)			>95% **16a**[a,e]	<5% **17a**[a,e]	0.3 M, 227 °C, 24 h
16b/17b (3:2)			>95% **16b**[a,e]	<5% **17b**[a,e]	0.3 M, 227 °C, 24 h

[a] Proportions as determined from the ^{1}H NMR spectrum of the crude reaction mixture. [b] Ca. 50% of a mixture of 2*H*-pyrroles was recovered. [c] 12% of **8c** was recovered together with 2% of **23**. [d] 20% of unreacted **8d** was recovered. [e] 40–70% of polymeric material is formed in these reactions.

Table III. Product Distributions in the Thermolyses of 4-But-3-enyl- (8j) and 4-Pent-4-enyl-2*H*-pyrroles (8k) and of the Tricyclic Products 18–20 (Isolated Yields)

	products			
reactants				reactn conditions [±2 °C]
8j (n = 2)			5% **19**[a]	0.3 M, 202 °C, 16 h[b]
8j		30% **18**[a]	30% **19**[a]	0.3 M, 215 °C, 63 h[c]
8j		36% **18**	33% **19**	0.6 M, 225 °C, 62 h[d]
8k (n = 3)	42% **20**[a]	5% **21**[a]	5% **22**[a]	0.3 M, 210 °C, 87 h[e]
8k	52%	3%	13%	0.6 M, 210 °C, 140 h[f]
8k	13%	14%	10%	0.4 M, 242 °C, 40 h[f]
18 (n = 2)		59% **18**[a]	41% **19**[a]	0.1 M, 220 °C, 354 h
18/19 (2:3)		60% **18**[a]	40% **19**[a]	0.2 M, 235 °C, 111 h[g]
20 (n = 3)	33% **20**[a]	33% **21**[a]	33% **22**[a]	0.1 M, 234 °C, 88 h[g]

[a] Proportions as determined from the ^{1}H NMR spectrum of the crude reaction mixture. [b] Ca. 75% of unreacted **8j** was recovered together with 15% of **24**. [c] 33% of **8j** and 7% of **24** were recovered. [d] 4% of **8j** was recovered. [e] 40% of **8k** was recovered. [f] Ca. 9% of **8k** was recovered. [g] 30–70% of polymeric material is formed in these reactions.

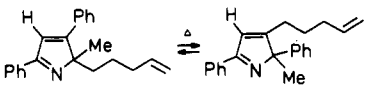
treatment with dimsylsodium, the corresponding 2*H*-azirines **6** were generated. The latter, which do not have to be isolated, reacted with the enolates of ketones **7** and afforded the corresponding 2*H*-pyrroles **8**. Our technology allowed one to introduce a large variety of substituents in a regiospecific fashion. The unsaturated side chain can be introduced at the position C(2) (**8a–h**) by using R^1Br = but-3-enyl bromide or pent-4-enyl bromide, at position C(3) (**8i**) by using **6i** (3-but-3-enyl-2-methyl-2-phenyl-2*H*-azirine), or at position C(4) (**8j,k**) when using **6f** (3-phenyl-2,2-dimethyl-2*H*-azirine) and **7j,k** (pent-4-enyl and hex-5-enyl phenyl ketones). Satisfactory overall yields were obtained in all cases except for derivatives **8f–h** (see Experimental Section). The structures of **8** were deduced from their mode of formation, their spectral data, and elemental analyses.

The thermolyses of 2*H*-pyrroles **8** gave mixtures of tricyclic compounds possessing the 2-azanorbornene moiety whose structures (**10–22**) and corresponding isolated yields are reported in Tables I–III. The reactions were carried out in benzene solutions (sealed Pyrex tube) and could be followed by ^{1}H NMR spectroscopy. The reactions were terminated when a conversion rate better then 80% was reached. The product distributions shown in Tables I–III correspond to mixtures that are not completely equilibrated. This was confirmed by isomerization experiments of the products obtained (Table I–III).

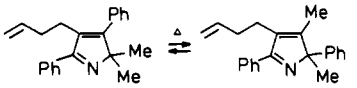
On heating a 3:1 mixture of **10a/11a** to 211 °C for 49 h, **10a** was formed in 95% yield. The isomerization of **11a** into **10a** demonstrates that branching the 2-azanorbornene moiety between C(5) and C(7) (2-azanorborn-2-ene numbering) by a two-membered chain leads to more stable tricyclic systems (3-azatricyclo[4.3.0.$0^{4,9}$]non-2-ene) than branching between C(6) and C(7) (2-azanorborn-2-ene numbering), which gives 7-azatricyclo[3.3.1.$0^{2,6}$]non-7-ene derivatives. This is also the case for the isomeric pair **12a** and **13a**. Indeed, on heating 3:7 mixture of **12a/13a** pure **12a** (92% isolated) was obtained. When **12a** was heated to 227 °C for 24 h, the ^{1}H NMR spectrum showed some decomposition but no trace of the isomeric adduct **10a**. This suggested either than **12a** is more stable than **10a** or that a substantial energy barrier is associated with the isomerization **10a** ⇄ **12a**.

A 8:1:1 mixture of **10b/11b/12b** was isomerized into a 64:24:13 mixture of the same products after 48 h at 235 °C. Pure **11b** heated to 227 °C for 72 h gave a 63:30:7 mixture of **10b/11b/12b**. This product ratio was similar to that obtained in the pyrolysis of **8b** (Table I). Moreover, the latter product ratio did not vary signficantly on further heating, thus showing that **10b**, **11b**, and **12b** have similar stabilities. Less than 5% of **13b** was present in this mixture. As for **10a**, **11a**, **12a**, and **13a**, the 3-azatricyclo-

[4.3.0.0^{4,9}]non-2-ene derivatives **10b** and **12b** are more stable than the isomeric 7-azatricyclo[3.3.1.0^{2,6}]non-7-enes **11b** and **13b**. However, it should be noticed that the difference in stability is somewhat reduced for the 1-methyl-substituted derivatives (series **b**) than for the derivatives unsubstituted at the bridgehead center C(1). This can be attributed to differential torsional effects involving the H–C(1) vs Me–C(1) and C–C(6) bonds (numbering of **10a,b** and **12a,b**). This interpretation is also valid in the case of **18**/**19**. A 2:3 mixture of **18**/**19** was isomerized into a 3:2 mixture of **18**/**19** on heating to 235 °C for 111 h (see Table III). Pure **18** yielded a 3:2 mixture of **18**/**19** after 354 h at 220 °C. We have seen that the isomerization **10a** ⇄ **11a** and **12a** ⇄ **13a** (R^4 = H) occurred concurrently with the formation of these cycloadducts, whereas the equilibration **12a** ⇄ **10a** which exchanges the methyl and phenyl substituents at positions C(4) and C(9) (numbering of **10a,b** and **12a,b**) could not be achieved under forcing conditions (235 °C, 7 days). In the case of the **b** series (R^4 = Me), both type of isomerizations, i.e., **10b** ⇄ **11b** and **12b** ⇄ **13b** on one hand and **10b** + **11b** ⇄ **12b** + **13b** on the other hand, have similar free activation enthalpies between 227 and 235 °C.



8c **23**



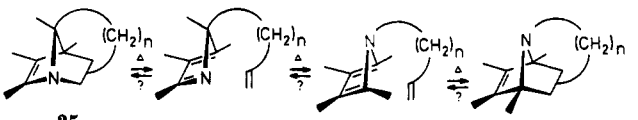
8j **24**

In the case of the thermolysis of **8c** (200 °C, 33 h), 12% of unreacted starting material and 2% of the 2*H*-pyrrole **23** were isolated together with the tricyclic products **14a**, **15a**, **16a**, and **17a** (Table II). This indicates that [1,5]-sigmatropic shifts leading to isomeric pyrroles are competitive with the intramolecular cycloadditions. A confirmation of this hypothesis was given with the thermolysis of **8j**. On heating **8j** to 202 °C for 16 h, 15% of the 2*H*-pyrrole **24** was formed together with a small amount of adduct **19** (75% of **8j** was recovered, see Table III). On heating to 215 °C for 63 h, 5:1:5:5 mixture of **8j**/**24**/**18**/**19** was formed. Heating to higher temperature (225 °C, 62 h) gave a 4:3:2 mixture of **18**/**19** and an unidentified compound (Table III). No trace of the 2*H*-pyrrole **24** could be detected. The structure of the latter compound was confirmed by independent synthesis (see Experimental Section). The relative amounts of **14a**, **15a**, **16a**, and **17a** depended on the conditions of the thermolysis of **8c**. Our results (Table II) suggested that **16a** and **17a** are more stable than **14a** and **15a** since the product ratio (**14a** + **15a**)/(**16a** + **17a**) varied between 26:34 to 15:44 when the temperature was changed between 200 and 216 °C. Furthermore, when a 2:1 mixture of **16a**/**17a** was heated to 227 °C for 24 h, only **16a** was detected in the ^{1}H NMR spectrum of the crude reaction mixture together with some polymeric material.

A 3:2 mixture of **16b**/**17b** was isomerized to **16b** on heating to 227 °C for 24 h. Under these conditions less than 5% of the isomeric adducts **14b** and **15b** was formed, thus indicating that **16b** is the most stable isomer. A similar proposal was made as above for **16a**. It is interesting to note here that under conditions of thermodynamic control and for both series of cycloadducts **10**–**13** (Table I) and **14**–**17** (Table II), the 2-azanorborn-2-ene derivatives prefer to be annulated between centers C(5) and C(7) than between centers C(6) and C(7).

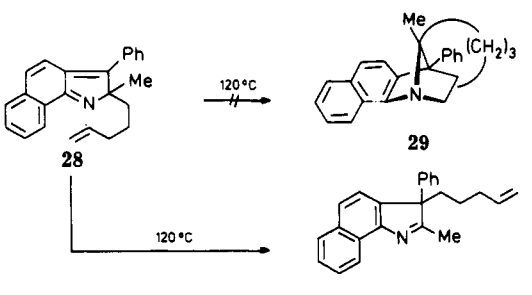
At the beginning of the thermolysis of **8k**, adduct **20**, which involves annulation between the C(4) and C(5) centers of the 2-azanorbornene moiety, was the preferred product of reaction. For instance, on heating **8k** to 210 °C for 87 h (60% conversion), a 8:1:1 mixture of **20**/**21**/**22** was formed. Prolonged heating (210 °C, 140 h, Table III) gave a 52:3:13:9 mixture of **20**/**21**/**22**/**8k**. This suggested that **21** and **22** arise probably from the competitive isomerization of **20**, **20** being the preferred cycloadduct under conditions of kinetic control. This hypothesis was confirmed by the following experiments. On heating **8k** to 242 °C for 40 h, a 13:14:10:9 mixture of **20**/**21**/**22**/**8k** was formed. Furthermore, on heating pure **20** to 234 °C for 88 h, a 1:1:1 mixture of **20**/**21**/**22** was obtained together with a polymeric material. Because of the competitive decomposition of **20**–**22** under the conditions of their formation, we could not evaluate their relative stabilities.

For all the thermolyses reported here, no trace of products **25** resulting from the intramolecular Diels–Alder additions of the 2*H*-pyrroles **8** (or **23**, **24**) could be detected. The products are tricyclic derivatives with the 2-azabicyclo[2.2.1]hept-2-ene moiety. Their formation can be interpreted in terms of intramolecular cycloadditions of 3*H*-pyrrole intermediates (see, e.g. Schemes II–V) arising from the starting 2*H*-pyrroles[8] through one or several successive [1,5]-sigmatropic shifts.[9,10] This hypothesis is in agreement also with the isomerization reactions described above and with the isolation of **23** in the thermolysis of **8c** and the observation of **24** during the thermolysis of **8d**. It is interesting to note that no trace of the expectedly more stable (aromatic)[13] *N*-alkyl- or *N*-alkenyl-1*H*-pyrrole derivatives **26** or of the corresponding 7-azabicyclo[2.2.1]hept-2-ene derivatives **27** resulting from their intramolecular Diels–Alder additions could be isolated.



25 **8** **26** **27**

With the hope to favor the intramolecular Diels–Alder addition over the [1,5]-sigmatropic shifts, we prepared the 2*H*-indole **28** which is an ortho-quinonic system. The latter 2*H*-pyrrole was envisioned to yield the naphthalene derivatives **29** on heating. However, we found that **28** was transformed nearly quantitatively to 3*H*-indole **30** on heating to 120 °C, thus showing that the [1,5]-sigmatropic shift of the pentenyl side chain is a faster process than the intramolecular cycloaddition of the 2*H*-pyrrole **28**. The "extra driving force" due to the gain in aromaticity for the cycloaddition **28** ⇄ **29** is also present in the case of the isomerization **28** ⇄ **30** and thus contributes to the facile formation of **30**.



28 **29** **30**

(13) Acheson, R. M. *An Introduction to the Chemistry of Heterocyclic Compounds*, 3rd ed.; Wiley: New York, 1976; p 91.

Table IV. Rate-Enhancement Effect of Added Aminium Salt and Lewis Acids for the Cyclizations of 2*H*-Pyrroles 8c and 8d

reactant	solv	catalyst	% mol equiv	conc of 8, M	temp, °C	reactn time,[a] h	product
8c	C_6H_6	none		0.8	200	33	**14a–17a**[b]
	CH_2Cl_2	$(4\text{-}BrC_6H_4)_3NSbCl_6$	67	0.15	135	20	**14a–17a**
8d	C_6H_6	none		1.3	212	42	**14b–17b**
	C_6H_6	$Eu(thd)_3$	25	0.4	180	43	**14b–17b**
	C_6H_6	$Yb(fod)_3$	9	0.5	190	72	**14b–17b**
	C_6H_6	$Eu(fod)_3$	10	0.8	192	63	**14b–17b**
	C_6H_6	$Ni(acac)_2$	35	0.4	193	40	**14b–17b**
	C_6H_6	$ZnBr_2$	68	0.4	155	63	*c*
	CH_2Cl_2	$(4\text{-}BrC_6H_4)_3NSbCl_6$	25	0.2	135	62	*d*

[a] Until complete disappearance of the starting material (control by ^1H NMR). [b] 14% of a mixture of 2*H*-pyrroles was recovered under these conditions. [c] Half-life of **8d** was ca. 20 h under these conditions. [d] 25% of conversion after 16 h.

Attempts to accelerate the intramolecular cycloadditions of **8** with Lewis acid[14] or an aminium salt[15] were met with success. Our results for the reactions of the 2*H*-pyrroles **8c** and **8d** are summarized in Table IV. In the presence of the cation-radical $(4\text{-}BrC_6H_4)_3N^{\bullet+}SbCl_6^-$,[14] the temperature and the time required for the transformation of **8c** were reduced significantly compared with the thermal reaction in the absence of catalyst (135 °C, 20 h, instead of 200 °C, 33 h). A similar accelerating effect was observed for the thermolysis of **8d** in the presence of the aminium salt. Significant rate enhancements of the cyclization of **8d** were observed in the presence of 20% $Eu(thd)_3$[16] or of 68% $ZnBr_2$ (Table IV). Interestingly, the same tricyclic products as those formed in the absence of catalyst were formed in similar proportions. No trace of adduct **25** arising from the direct intramolecular cycloadditions of the 2*H*-pyrrole **8c** and **8d** could be seen. Therefore, it appears that not only the intramolecular Diels–Alder additions have been accelerated by the aminium salt and the Lewis acids but also the [1,5]-sigmatropic shifts responsible of the formation of the 3*H*-pyrrole intermediates. Examples of rate enhancements of [1,5]-sigmatropic rearrangements by protic or Lewis acids have been reported in the literature.[17] It is also known that the Diels–Alder additions of 1-aza dienes are accelerated by substitution of the nitrogen atom.[2,18]

The structures of the tricyclic adducts **10–22** were deduced from their elemental analysis and their spectral data (see Experimental Section). The ^{13}C NMR spectra showed only one signal for the olefinic carbon atom between 174 and 183 ppm which is typical of the C=N function.[19] Thus, 1-azabicyclo-[2.2.1]hept-2-ene (see **25**) and 7-azabicyclo[2.2.1]hept-2-ene (see **27**) structures were excluded. The quarternary carbon atoms of the phenyl substituents attached to the carbon atom of the C=N moieties resonate between 132 and 136 ppm, whereas the para carbon atoms resonate between 128 and 131 ppm. In contrast, when the phenyl substituents are attached to sp^3-hybridized carbon atoms, the signals of the quarternary and para carbon atoms are found between 138 and 144 ppm and between 125 and 127 ppm, respectively (compare **18**, **19**, **21**, **22** vs **10–17**, **20**). The distinction between compounds **10**, **11** (and **14**, **15**) and **12**, **13** (and **16**, **17**), which differ by the relative positions of a phenyl and methyl substituents at C(1) and C(7) of the norborn-2-ene moiety, was based on the comparison of their ^{13}C NMR spectra and more specifically on the comparison of difference in α- and β-substitution effects between phenyl and methyl groups. It is known[19] that the α-substituent effect is larger for a phenyl than for a methyl group. The opposite is true for the β-substituent effects. The distinction between C(5)–C(7) and C(6)–C(7) bridging (**10a** vs **11a**, **12a** vs **13a**, **14a** vs **15a**, **16a** vs **17a**) was obvious from the ^1H NMR spectra for the series of adducts with R^4 = H. In the case of bridging between C(5) and C(7), the bridgehead protons at C(4) resonate as broad singlets (^3J(H–C(4), H-endo-C(5)) $\simeq$ 0), while in the case of bridging between positions C(6) and C(7), the bridgehead protons at C(4) resonate as broad doublets because of the vicinal coupling with H-exo-C(5) (^3J(H–C(4), H-exo-C(5)) $\simeq$ 4.5 Hz).[20] In the case of the derivatives with $R^4 = CH_3$, the distinction between **11b** vs **10b**, **13b** vs **12b**, **15b** vs **14b**, **17b** vs **16b**, **19** vs **18** and **22** vs **21** was given by the comparison of their ^{13}C NMR characteristics with those of the corresponding nonmethylated derivatives (series **a**, R^4 = H). Substitution of C(4) with a methyl group induces typical[19] β-substituent effects on C(5) which resonate as doublets in **10b**, **12b**, **14b**, **16b**, **18**, and **21** and as triplets in **11b**, **13b**, **15b**, **17b**, **19**, and **22**. The structures of **10b**, **14b**, **15b**, and **20** have been established independently by single-crystal X-ray diffraction studies.[21] They were in agreement with the structures derived from our NMR analysis, thus confirming

(14) For examples of Lewis acid catalyzed cycloadditions: Yates, P.; Eaton, P. *J. Am. Chem. Soc.* **1960**, *82*, 4436–4437; Vieira, E.; Vogel, P. *Helv. Cheim. Acta* **1982**, *65*, 1700–1706 and references cited therein. Fringuelli, F.; Pizzo, F; Taticchi, A.; Wenkert, E. *J. Org. Chem.* **1983**, *48*, 2802–2808 and references cited therein. Denmark, S. E.; Dappen, M. S.; Cramer, C. J. *J. Am. Chem. Soc.* **1986**, *108*, 1306–1307 and references cited therein. Mach, K.; Antropiusova, H.; Sedmera, P.; Hanus, V.; Turecek, F. *J. Chem. Soc., Chem. Commun.* **1983**, 805–806. Dieck, H. T.; Diercks, R. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 778–779. Dieck, H. T.; Dietrich, J. *Ibid.* **1985**, *24*, 781–783. Sakurai, H. *Pure Appl. Chem.* **1982**, *54*, 1–22.

(15) For examples of hole-catalyzed cycloadditions, see: Bellville, D. J.; Wirth, D. D.; Bauld, N. L. *J. Am. Chem. Soc.* **1981**, 103, 718–720. Bauld, N. L.; Bellville, D. J.; Pabon, R.; Chelsky, R.; Green, G. *Ibid.* **1983**, *105*, 2378–2382. Laszlo, P.; Lucchetti, J. *Tetrahedron Lett.* **1984**, *25*, 1567–1570. See also: Julliard, M.; Chanon, M. *Chem. Rev.* **1983**, *83*, 425–506. Gassman, P. G.; Singleton, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 7993–7994. Groenewold, G. S.; Gross, M. L. *Ibid.* **1984**, *106*, 6569–6575, 6575–6579.

(16) For examples of rare earth complex catalyzed cycloadditions, see: Danishefsky, S. J.; Larson, E.; Askin, D.; Kato, N. *J. Am. Chem. Soc.* **1985**, *107*, 1246–1255; Bednarski, M.; Maring, C.; Danishefsky, S. *Tetrahedron Lett.* **1983**, *24*, 3451–3454.

(17) Schiess, P.; Stalder, H. *Tetrahedron Lett.* **1980**, *21*, 1417–1420.

(18) Serckx-Poncin, B.; Hesbain-Fresique, A.-M.; Ghosez, L. *Tetrahedron Lett.* **1982**, *23*, 3261–3264.

(19) Breitmaier, E.; Voelter, W. *^{13}C-NMR Spectroscopy*, 2nd ed.; Verlag Chemie: New York, 1978.

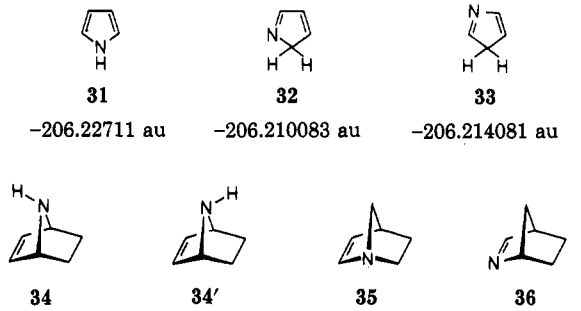
(20) Joela, H. *Org. Magn. Reson.* **1977**, *9*, 338–340 and references cited therein. Gassend, R.; Limouzin, Y.; Maire, J. C. *Ibid.* **1974**, *6*, 259–263. Sanchez-Obregon, R.; Salmon, M.; Walls, F. *Ibid.* **1972**, *4*, 885–888. Meinwald, J.; Meinwald Y. C. *J. Am. Chem. Soc.* **1963**, *85*, 2514–2515; Tori, K.; Kitahonoki, K.; Takano, Y.; Tanida, H.; Tsuji, T. *Tetrahedron Lett.* **1964**, 559–564; Masar, S. E.; Krieger, H. *Suom. Kemistil B* **1969**, *B42*, 1–5; Paasivirta, J. *Ibid.* **1971**, *B44*, 131–135. Moen, R. V.; Makowski, H. S. *Anal. Chem.* **1971**, *43*, 1629–1633; Chollet, A.; Hagenbuch, J. P.; Vogel, P. *Helv. Chim. Acta* **1979**, 62, 511–524. Gagnaire, D.; Payo-Subiza, E. *Bull. Soc. Chim. Fr.* **1963**, 2627–2631. Mahaim, C.; Vogel, P. *Helv. Chim. Acta* **1982**, *65*, 866–886. Kienzle, R. *Ibid.* **1975**, *58*, 1180–1183.

(21) The phenyl substituents at the sp^2-hybridized carbon centers were bending toward the endo face of the 2-azabicyclo[2.2.1]hept-2-ene moiety of these molecules, in agreement with MO calculations on the nonplanarity of 2-azabicyclo[2.2.1]hept-2-ene double bond: Carrupt, P. A.; Vogel, P.; Mison, P.; Eddaïf, A.; Pellissier, N.; Faure, R.; Loiseleur, H. Nouv. J. *Chimie* **1986**, *10*, 277–283.

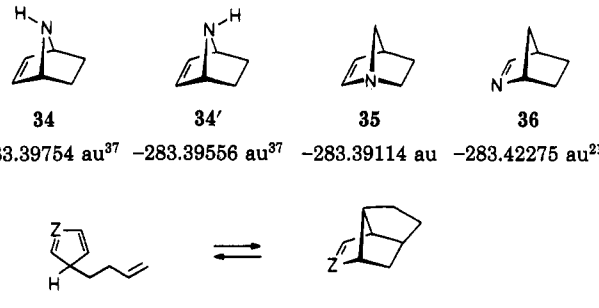
its validity in the cases of the other adducts.

Discussion

The thermolyses of the 2*H*-pyrroles 8 did not give any trace of the expected 1-azanorbornene derivatives **25**. This observation raises the two following questions: (1) Are the intramolecular cycloadditions **8** ⇄ **25** processes too slow in comparison with the competitive [1,5]-sigmatropic shifts leading to 3*H*-pyrrole intermediates and their intramolecular Diels–Alder additions to yield the observed 2-azanorbornene derivatives reported in Tables I–III? (2) Are the 1-azanorbornenes **25** stable under our reaction conditions; in other words, could they be formed and isomerized into the more stable 2-azanorbornenes? Since the [1,5]-sigmatropic rearrangements are occurring concomitantly with the intramolecular cycloadditions (see, e.g., the observation of **8c** ⇄ **23** and **8j** ⇄ **24**), a third question is now raised: (3) Why is there no trace of the aromatic 1*H*-pyrroles **26** or of their corresponding adducts **27** (7-azanorbornenes) in the reaction mixtures? Answers to this first set of questions will be given by a simple thermochemical analyses[22] and with help of MO calculations (ab initio, STO 3G basis set,[23] fully optimized geometries with respect to all bond lengths and bond angles) on the model compounds **31–36** (the calculated total energies are shown with each formula).



31 −206.22711 au **32** −206.210083 au **33** −206.214081 au



34 −283.39754 au[37] **34′** −283.39556 au[37] **35** −283.39114 au **36** −283.42275 au[21]

37, Z = CH
39, Z = N

38 $\Delta H_r°$(estn) = −16.5 kcal/mol
40 $\Delta S_r°$(estn) = −13 eu

From the standard heat of formation in the gas phase of cyclopentadiene ($\Delta H_f°$ = 31.94 kcal/mol[24]) and the usual values for the group increments contributing to $\Delta H_f°$,[22,24] one calculates $\Delta H_f°$ = 40.14 kcal/mol for 5-but-3-enylcyclopentadiene (**37**) in the gas phase. Similarly, from the standard heat of formation of bicyclo[2.2.1]hept-2-ene ($\Delta H_f°$ = 21.13 kcal/mol[25]), and considering an extra ring strain of 6 kcal/mol for the five-membered ring inserted between centers C(5) and C(7), one calculates a gas-phase standard heat of formation of 23.63 kcal/mol for **38**, the cycloadduct of **37**. Therefore, the heat of reaction **37** ⇄ **38** amounts to $\Delta H_f°$ = −16.5 kcal/mol.

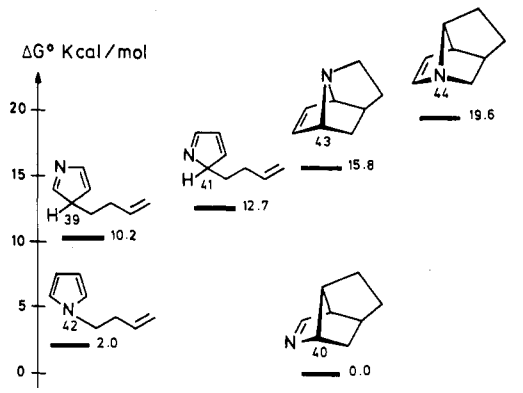


Figure 1. Estimated free enthalpies (gas phase, 210 °C, 1 atm) of pyrroles **39**, **41**, and **42** and of the corresponding intramolecular cycloadducts **40**, **43**, and **44**.

The standard entropy change of **37** ⇄ **38** can be approximated to $\Delta S_r°$ = −13 eu, the standard entropy change for the cyclization of pent-1-ene to cyclopentane.[22] If one assumes the standard thermochemical parameters to be applicable at temperatures different than 25 °C (due to the cancellation effect of the errors on $\Delta H_r°$ and $-T\Delta S_r°$), one calculates at 210 °C, $\Delta G_r°_{483K}$(**37** ⇄ **38**) = −10.2 kcal/mol. We take the same value for the free enthalpy of reaction **39** ⇄ **40**. To a first approximation this is reasonable as the same number of C—N and C=N bonds is maintained in **39** and **40**.

For the unsubstituted pyrroles, our ab initio STO-3G calculations (assuming $\Delta\Delta E = \Delta\Delta H$) gave the following relative stabilities: $\Delta\Delta H_f°$(**31**) = 0.0, $\Delta\Delta H_f°$(**32**) = 10.7 and $\Delta\Delta H_f°$(**33**) = 8.2 kcal/mol. Experimental results have shown that 2*H*-pyrrole derivatives are generally more stable than the corresponding 3*H*-pyrrole derivatives.[1,27] Thus, our calculations give estimates that deviate somehow from the expectations. Nevertheless, this has no consequence in the context of the problem treated here. Our calculations, however, agree with the observation that 1*H*-pyrroles are significantly more stable than 2*H*- and 3*H*-pyrroles.[13] If one accepts the same relative stabilities for the but-3-enyl-substituted pyrroles **39**, **41**, and **42**, one obtains the free enthalpies shown in Figure 1 for these derivatives. We assume here the same standard entropies for **41** and **42** as for **39**. Furthermore, we suppose that there is no differential stability effects due to the varying position of the side chain. Similarly, for the azanorbornenes **34–36**, our MO calculation give the following relative stabilities: $\Delta\Delta H_f°$(**34**) = 15.8 kcal/mol, $\Delta\Delta H_f°$(**35**) = 19.6 kcal/mol, and $\Delta\Delta H_f°$(**36**) = 0.0 kcal/mol. Using the value $\Delta G_r°_{484K}$ (**39** ⇄ **40**) = −10.2 kcal/mol and assuming the same change of entropy for equilibria **39** ⇄ **40**, **41** ⇄ **44**, and **42** ⇄ **43** and the same relative stabilities between **40**, **43**, and **44** as between **36**, **34**, and **35**, respectively, one obtains the free enthalpies shown in Figure 1 for **40**, **43**, and **44** and the following free enthalpies of reaction, $\Delta G_r°_{484K}$(**41** ⇄ **44**) = +6.9 kcal/mol and $\Delta G_r°_{484K}$(**42** ⇄ **43**) = +13.8 kcal/mol.

Since our thermolyses of **8** were carried out in benzene, a nonpolar solvent, we assume that the thermochemical parameters evaluated for the gas phase are reasonable approximations for those in the solution. It thus appears that the cycloadducts with the 2-azanorborn-2-ene moiety (Tables I–III) are the only products that can be formed

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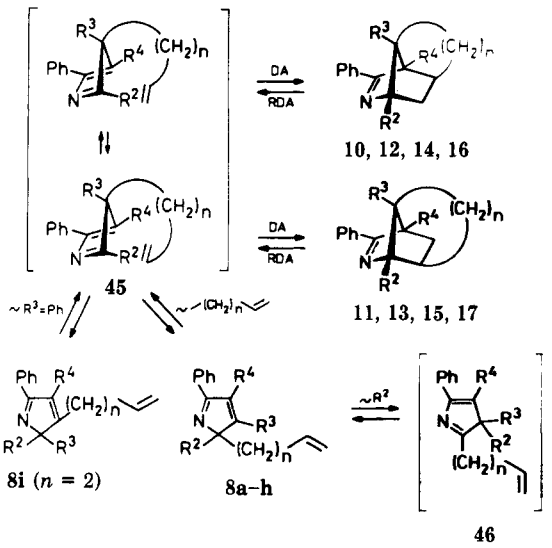
(24) Cox, J. D.; Pilcher, G. In *Thermochemistry of Organic and Organometallic Compounds*; Academic: London, 1970.
(25) Walsh, R.; Wells, J. M. *J. Chem. Thermodyn.* **1976**, *8*, 55–60.
(26) The geometries were fully optimized with respect to all bond lengths and bond angles by using Davidon's method: Davidon, W. C. *Math. Programming* **1975**, *9*, 1–9.
(27) Wong, J. L.; Ritchie, M. H.; Gladstone, C. M. *J. Chem. Soc., Chem. Commun.* **1971**, 1093–1094.

Scheme II



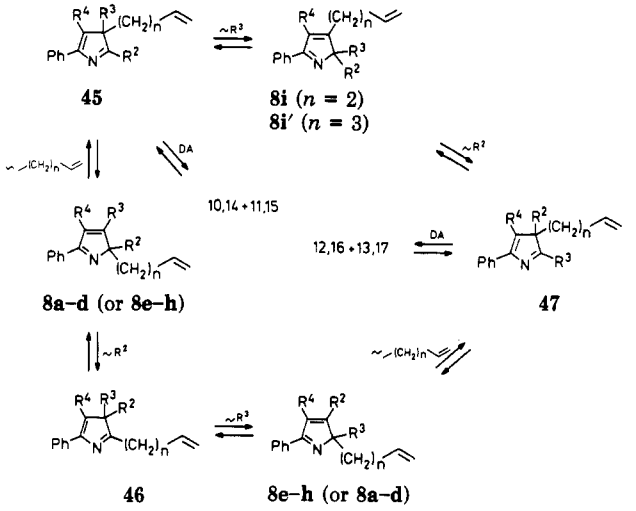
R^2 = Ph, R^3 = Me, or R^2 = Me, R^3 = Ph; R^4 = H or Me

under our thermolysis conditions from the corresponding 2*H*-pyrroles **8**. The fact that cycloadducts **25** and **27** are not observed is, in the light of our analysis, perfectly explained (answers questions 1–3). Even if the intramolecular Diels–Alder additions **8** → **25** should be very fast, these reactions are estimated to be too endergonic ($\Delta G_r^\circ \gg 0$). We do not see how methyl and phenyl substituents in derivatives **8** could change the ΔG_r° values of **41** ⇄ **44** in a dramatic fashion and make it approaching zero or becoming negative.

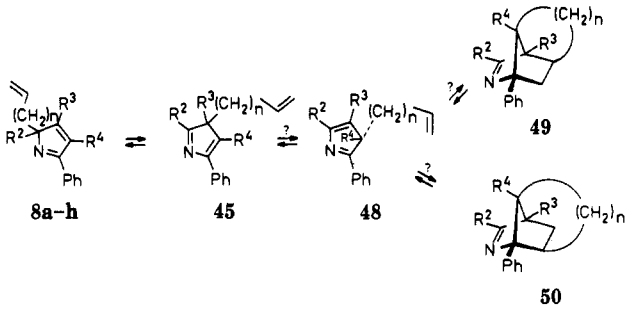
Our calculations suggest that 1*H*-pyrrole **42** is slightly less stable than the isomeric cycloadduct **40**, thus explaining the lack of **26** in our thermolysis mixtures. However, the estimated stability difference is a small one, and thus for some, derivatives **26** and **40** could coexist under thermodynamically controlled conditions. In other words it is possible that derivatives **26** have not been detected because their rates of formation were too low[1,5] compared with those of the [1,5]-sigmatropic shifts that rearrange **8** into the corresponding 3*H*-pyrrole intermediates[9,28] and their subsequent intramolecular cycloaddition to the observed 2-azanorbornene derivatives (Table I–III). The interconversion of 7-azatricyclo[3.3.1.$0^{2,6}$]non-7-enes to 3-azatricyclo[4.3.0.$0^{4,9}$]non-2-enes (see, e.g., **11a** → **10a** at 211 °C, **13a** → **12a** at 196 °C) as well as the interconversion of 8-azatricyclo[4.3.1.$0^{2,7}$]dec-8-enes to 9-azatricyclo[4.4.0.$0^{2,8}$]dec-9-enes (see, e.g., **17** → **16** at 227 °C, **19** ⇄ **18** at 220 °C) can be interpreted in terms of cycloreversions with the formation of 3*H*-pyrrole intermediate **45**, which can react according to the two possible orientations of the ethylenic dienophile (Scheme II).

The 3*H*-pyrroles **45** are most probably derived from **8a–h** via a single [1,5]-sigmatropic shift of the butenyl or pentenyl side chain. Although no adduct analogous to **20** (Table III) and corresponding to the intramolecular cycloaddition of the isomeric 3*H*-pyrroles **46** could be seen in the product mixture of the thermolyses of **8a–h**, one cannot exclude the hypothesis of competitive isomerizations of **8a–h** to **46** via [1,5]-sigmatropic shifts of a phenyl or a methyl group. In the case of **8i**, the phenyl group migration **8i** ⇄ **45** (R^2 = Me, R^3 = Ph) is probably faster than the methyl group migration (in accord with other

Scheme III



Scheme IV



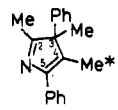
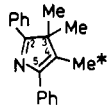
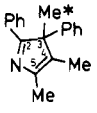
experimental results[9]) since the adducts **10a** and **11a** were the major products under conditions of kinetic control.

The observation that **10b**, **11b**, **12b**, and **13b** (exchange of the methyl and phenyl substituents between positions C(1) and C(7) of the 2-azanorborn-2-ene moiety) can be equilibrated under conditions only slightly more severe than those of their formation implies that the 3*H*-pyrrole intermediates **45** and **46** can rearrange to various isomeric 3*H*-pyrroles competitively with their cycloadditions, as outlined in Scheme III. Similar processes must also occur in the thermal isomerizations **14**, **15** ⇄ **16**, **17** and **20** ⇄ **21**, **22**. This type of equilibria has already been evidenced in the study of thermal isomerizations of other 2*H*-pyrrole derivatives.[9,17]

In the case of isomerization of **11a** to **10a** (221 °C, $\tau_{1/2}$ = 12 h), a free activation enthalpy $\Delta G^\ddagger$ = 39.3 kcal/mol was evaluated. If one considers a free enthalpy of reaction of 10.2 kcal/mol (Figure 1) for the cycloadditions **45** → **10a** and **45** → **11a**, one can state that these cyclizations have energy barriers $\Delta G^\ddagger \simeq$ 29 kcal/mol. The 3*H*-pyrroles **45** and **47** were cyclized at most 100 times as fast as the cycloreversions of the adducts to **8**. If one assume the 2*H*- and 3*H*-pyrroles to have similar stabilities, one can thus estimate a free activation enthalpy $\Delta G^\ddagger \simeq$ 35–38 kcal/mol for cycloadditions of **8**. This energy barrier appears to be higher than that for the intramolecular Diels–Alder additions of the 3*H*-pyrrole intermediates **45**. Therefore, the rate-determining steps for the cyclizations of **8** are their isomerization via [1,5]-sigmatropic shift into the corresponding 3*H*-pyrrole intermediates **45** and/or **47**.

It is known that [1,5]-migrations of alkyl and phenyl groups in 2*H*-pyrroles to give the corresponding 1*H*-pyrroles have energy barriers significantly higher than those for the isomerization of 2*H*-pyrroles into other 2*H*-pyrroles derivatives or into 3*H*-pyrroles.[9,28] Thus, the lack

(28) See, however: Sammes, M. P.; Chung, M. W. L.; Katritzky, A. R. *J. Chem. Soc., Perkin Trans. 1*, **1985**, 1773–1779. Chiu, P.-K.; Sammes, M. P. *Tetrahedron Lett.* **1987**, *28*, 2775–2778.

	55 (model for 51)	56 (model for 53)	57 (model for 54)
$\Delta H_f°$(MINDO/3), kcal/mol	109.4	105.2	110.8
Φ_5, deg	89	89	
Φ_2, deg		5	75
$\epsilon_{LUMO} - \epsilon_{HOMO}$, eV	8.9	8.4	8.8

Me* = chain position

of 1*H*-pyrroles **26** under our thermolysis conditions could be attributed to a kinetic control rather than to the thermodynamic control suggested in Figure 1 (answers question 3).

In the thermolyses of **8a–i** (Tables I and II) we did not observe products **49** and **50**, which should result from rearrangement of **45** to another 3*H*-pyrrole derivative (**48**) (Scheme IV). This contrasts with the thermolyses of **8j** and **8k** for which this rearrangement was observed. A priori, there are two possible interpretations of these results. First of all, one can invoke a kinetic control that implies a higher energy barrier for the rearrangements and cycloadditions **45** ⇄ **48** ⇄ **49** + **50** than for the cyclization **45** → **10–17** (Scheme III). A second possible explanation is to invoke a better stability of the phenyl imines **10–17** compared with the methyl-substituted (R^2 = Me) derivatives **49** and **50**. It should be noted, though, that the hypothesis of thermodynamic control invoked to interpret the lack of products **49** and **50** in the thermolyses of **8a–h** does not apply in the case of the thermolyses of **8j,k** (see Table III, Scheme V).

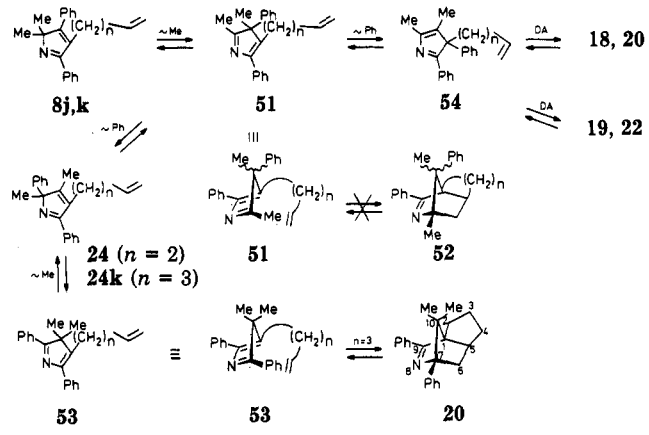
The thermolyses (210 °C) of **8k** is unique in the sense that it allowed one to isolate the 8-azatricyclo[5.2.1.$0^{1,5}$]-dec-8-ene derivative **20**, which corresponds to a 2-aza-norbornene system annulated between center C(5) and the adjacent bridgehead center C(4). **20** was found to be the preferred product under conditions of kinetic control. This result is not readily interpreted. A possible mechanism is shown in Scheme V.

The migration of methyl group in **8j,k** leads to corresponding 3*H*-pyrrole intermediates **51**. A subsequent migration of a phenyl group can give either the 2*H*-pyrroles **24** or the 3*H*-pyrroles **54**. **24** (n = 2) was observed during the thermolyses of **8j**. The homologous derivative **24k** could not be seen during the thermolysis of **8k**, because **24k** has the possibility to undergo a further [1,5]-sigmatropic shift of a methyl group, giving the intermediate **53**, which can cyclize readily to **20**. The competitive formation of the 3*H*-pyrrole intermediate **54** would explain the isolation of adducts **18** + **19** (n = 2) and **21** + **22** (n = 3). The mechanism proposed in Scheme V raises a number of questions. Since **53** is capable to cyclize to **20**, why does **51** not give adduct **52**, at least for n = 3 (thermolysis of **8k**)? One possible explanation could be that the concentration of **51** is always much smaller than that of **53** (hypothesis a). Another possible interpretation would be to invoke a faster cyclization rate of **53** than of **51** (hypothesis b). Because of the extra strain introduced with the formation of a four-membered ring, no adducts analogous to **20** and **52** are expected for the thermolysis of **8j** (and other 2*H*-pyrroles substituted with a butenyl side chain, n = 2).

In order to evaluate the above hypotheses a and b we have carried out MO calculations on the model compounds **55–57** (a methyl group replaces the butenyl or pentenyl side chain in **8j,k**).

The enthalpies shown with formulae **55–57** were obtained for completely optimized geometries with the

Scheme V



MINDO/3 technique.[29] We find that the 3*H*-pyrrole **56** with both phenyl groups attached to sp^2-hybridized carbon atoms is more stable than isomers **55** and **57**. This confirms hypothesis a implying that the 3*H*-pyrrole intermediates **53** are more stable than the corresponding isomers **51** (Scheme V). The calculated geometries of **55–57** showed that the phenyl groups at C(5) are not in the π-plane of the 3*H*-pyrroles (see the torsional angles Φ_5 (angle between planes of the pyrrole and phenyl rings at C(5)) shown with formulae **55** and **56**). This is due to gauche interactions between the phenyl groups at C(5) and the alkyl (methyl) substituents at C(4). In contrast, the phenyl group at C(2) in **56** is almost in the π-plane of the 3*H*-pyrrole (torsional angle Φ_2 = 5° (angle between planes of the pyrrole and phenyl rings at C(2))). This allows for a π-conjugation between this phenyl group and the diene moiety of the 3*H*-pyrrole. This stabilizing effect is obviously not present in **55** and **57**, thus explaining the better stability of **56** compared with **55** and **57**. For **57**, a torsional angle Φ_2 = 75° was calculated, thus showing that the phenyl group at C(2) in **57** cannot adopt a staggered conformation when C(3) is substituted with a methyl and a phenyl group. In the case of **56**, with two methyl groups at C(3), the phenyl group at C(2) can adopt a favorable staggered conformation. These results explain also why **20** is the product formed under conditions of kinetic control in the thermolysis of **8k**. The higher stability of intermediate **53k** compared with that of **54k** is the probable cause of the observed selectivity. As expected[30] because of the π-conjugation between the phenyl group at C(2) and the 3*H*-pyrrole, the LUMO–HOMO energy gap is calculated to be smaller in **56** than in **55** and **57**. Therefore and in agreement with hypothesis b, our calculations predict that the 3*H*-pyrrole intermediate **53k** must be more reactive than the isomeric intermediates **51k** and **54k** in their

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(30) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: New York, 1976; pp 150 ff.

intramolecular Diels–Alder additions.[31] This interpretation may also apply to explain the lack of products analogous to **20** (and **52**) during the thermolyses of **8a–h**. Indeed, the required intermediates **46** (Scheme II) are of the same type as **51**, i.e., same type of substitution as in **55**; they lack a conjugating phenyl group at C(2).

Conclusion

A general method for the synthesis of alkyl- and phenyl-substituted 2*H*-pyrroles bearing but-3-enyl and pent-4-enyl side chains has been developed. On heating, these compounds underwent [1,5]-sigmatropic shifts to yield 3*H*-pyrrole intermediates which afforded tricyclic systems possessing the 2-azanorbornene moiety via intramolecular Diels–Alder additions. No product resulting from the intramolecular cycloadditions of 1*H*- and 2*H*-pyrroles intermediates could be observed. The same transformations were found under hole-catalyzed and Lewis acid catalyzed conditions. In agreement with observations made for the acyclic 1-aza and 2-aza dienes, the 3*H*-pyrroles underwent intramolecular Diels–Alder reactions much faster than the corresponding 2*H*-pyrroles due to the higher exothermicity of the cycloadditions of the former than of the latter systems. MO calculations on model molecules confirmed this interpretation. It is in agreement also with that proposed by Jung and Shapiro[7] to interpret the reluctance of 1-aza dienes to undergo Diels–Alder cycloadditions.

Experimental Section

Melting points (uncorrected) were determined on a Tottoli apparatus (Buchi). Infrared spectra (IR) are reported in cm^{-1} (Perkin Elmer 297, in CH_2Cl_2). Routine ^1H NMR spectra in CCl_4 were obtained on a Varian EM 360 (60 MHz) spectrometer. The ^{13}C NMR spectra in $CDCl_3$ obtained on a Varian XL-100 (25.2 MHz, FT, proton noise decoupling or off-resonance partial decoupling). Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane (TMS), with either TMS (δ_H = 0.00, δ_C = 0.00 ppm) or the solvent's signal ($CDCl_3$, δ_C = 77.0 ppm) as an internal reference. Also reported are the apparent multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, sep = septuplet, br = broad), number of protons (when appropriate), apparent coupling constants (J, in Hz), and tentative structural assignment. The mass spectra (MS) were taken on a Varian MAT CH5 spectrometer in electron-impact ionization mode (70 eV). Exact masses were determined on a VG-Instrument 7070F instrument (70 eV; 140 °C; resolution, 10 000; sweeping rate, 10 s per decade). Preparative separation were carried out by column chromatography on silica gel (Merck 7734) or on basic alumina (WOELM), with elution solvents being petroleum ether (bp 45–60 °C), Et_2O and MeOH, or mixtures thereof.

Synthesis of 2-Methyl-1-phenylhex-5-en-1-one Dimethylhydrazone. See ref 32.

2-Methyl-1-phenylhept-6-en-1-one Dimethylhydrazone. *n*-BuLi (1.6 M in hexane, 62 mL, 99 mmol) was added dropwise to a stirred solution of 17.80 g (101 mmol) of the *N,N*-dimethylhydrazone of ethyl phenyl ketone[33] in 100 mL of THF at −10 °C and under nitrogen atmosphere. The reaction mixture was stirred at −10 °C for 5 h. After the mixture was cooled to −60 °C, 5-bromo-1-pentene (12 mL, d = 1.26, 101 mmol) was added dropwise. The mixture was stirred at −60 °C for 2 h, and then it was allowed to warm up to room temperature (overnight). Workup with ice-cold water, extraction with ether, and distillation in vacuo yielded 20.26 g (82%) of an oil, bp 90–95 °C (0.3 Torr), 79:21 mixture of *Z*- and *E*-isomers (before distillation the *E*-isomer was the major product). IR (film): 2860, 2810, 2770, 1640, 1615. ^1H NMR of *Z*-isomer: δ 1.03 (d, J = 6.5, 3 H); 0.9–2.9 (m, 7 H); 2.25 (s, 6 H); 4.6–5.1 (m, 2 H); 5.4–6.3 (m, 1 H); 7.0–7.7 (m, 5 H). ^1H NMR of *E*-isomer δ 1.17 (d, J = 7, 3 H); 0.9–2.5 (m, 6 H); 2.43 (s, 6 H); 3.67 (m, 1 H); 4.6–5.1 (m, 2 H); 5.3–6.1 (m, 1 H); 7.0–7.7 (m, 5 H).

3-Phenylhept-6-en-2-one Dimethylhydrazone. *n*-BuLi (1.6 M in hexane, 48 mL, 77 mmol) was added dropwise to a stirred solution of the dimethylhydrazone of benzyl methyl ketone[33] (12.95 g, 74 mmol) in THF (75 mL) at −60 °C and under N_2 atmosphere. After 5 h 4-bromobut-1-ene (10.00 g, 74 mmol) was then added dropwise under stirring at −56 °C. The mixture was stirred for 2 h and then allowed to warm to 20 °C overnight. Workup with water, extraction with ether, and distillation in vacuo yielded 12.73 g (75%) of an oil, bp 85–87 °C (0.3 Torr), 95:5 mixture of the *E*- and *Z*-isomers. IR: 2860, 2820, 2770, 1640, 1625. ^1H NMR of the *E*-isomer: δ 1.6–2.3 (m, 4 H); 1.70 (s, 3 H); 2.38 (s, 6 H); 3.37 (t, J = 7, 1 H); 4.7–5.3 (m, 2 H); 5.3–6.5 (m, 1 H); 7.1–7.5 (m, 5 H). ^1H NMR of the *Z*-isomer: δ 1.7 (s, 3 H); 2.4 (s, 6 H); 5.1 (m, 1 H).

3-Phenyloct-7-en-2-one Dimethylhydrazone. The same procedure as above but with 11.41 g (77 mmol) of 5-bromopent-1-ene: yield, 12.96 g (73%) of an oil, bp 90–95 °C (0.2 Torr); 95:5 mixture of the *E*- and *Z*-isomers. IR (CCl_4): 2860, 2820, 2780, 1640, 1625. ^1H NMR of the *E*-isomer: δ 0.9–2.5 (m, 6 H); 1.62 (s, 3 H); 2.30 (s, 6 H); 3.30 (t, J = 7, 1 H); 4.5–5.2 (m, 2 H); 5.2–6.2 (m, 1 H), 6.9–7.5 (m, 5 H). ^1H NMR of the minor *Z*-isomer: δ 1.6 (s, 3 H); 2.3 (s, 6 H); 5.0 (m 1 H).

2-Methyl-1-phenylhex-5-en-1-one Trimethylhydrazonium Iodide (5a). See ref. 32.

2-Methyl-1-phenylhept-6-en-1-one Trimethylhydrazonium Iodide (5c). A mixture of 2-methyl-1-phenylhept-6-en-1-one dimethylhydrazone (8.01 g, 32.8 mmol) and methyl iodide (8 mL, d = 2.28, 128.5 mmol) was stirred at 20 °C for 22 h. After filtration, 12.05 g (95%) of a viscous solid was obtained. ^1H NMR ($CDCl_3$): δ 1.13 (d, J = 7, 3 H); 0.8–2.4 (m, 6 H); 2.4–3.0 (m, 1 H); 3.57 (s, 9 H); 4.7–5.3 (m, 2 H); 5.5–6.3 (m, 1 H); 7.2–8.0 (m, 5 H).

3-Phenylhept-6-en-2-one Trimethylhydrazonium Iodide (5e). A mixture of 3-phenylhept-6-en-2-one dimethylhydrazone (6.27 g, 27.2 mmol) and methyl iodide (8 mL, 128.5 mmol) was stirred at 20 °C overnight. After filtration, 10.06 g (99%) of a viscous solid was obtained. ^1H NMR ($CDCl_3$): δ 1.6–2.4 (m, 4 H); 2.43 (s, 3 H); 3.57 (t, J = 7, 1 H); 3.83 (s, 9 H); 4.7–5.4 (m, 2 H); 5.4–6.3 (m, 1 H); 7.1–7.8 (m, 5 H).

3-Phenyloct-7-en-2-one Trimethylhydrazonium Iodide (5g). A mixture of 3-phenyloct-7-en-2-one (7.87 g, 32.2 mmol) and methyl iodide (10 mL, 160.6 mmol) was stirred at 20 °C for 48 h. After filtration, 11.97 g (96%) of a viscous solid was obtained. ^1H NMR ($CDCl_3$): δ 0.9–2.3 (m, 6 H); 2.37 (s, 3 H); 3.93 (s, 9 H); 3.6 (t, J = 7, 1 H); 4.7–5.2 (m, 2 H); 5.3–6.2 (m, 1 H); 7.1–7.6 (m, 5 H).

2-Methyl-1-phenylpropan-1-one Trimethylhydrazonium Iodide (5j). See ref. 33.

2-But-3-enyl-2-methyl-3-phenyl-2*H*-azirine (6a). See ref. 32.

2-Methyl-2-pent-4-enyl-3-phenyl-2*H*-azirine (6c). Following the described procedure,[34] a solution of NaH (0.76 g, 31.7 mmol) in isopropyl alcohol (200 mL) was added to a solution of **5c** (12.05 g, 31.1 mmol) in isopropyl alcohol (100 mL). After the mixture stood for 15 h at 20 C, the solvent was evaporated in vacuo and the residue extracted with cyclohexane. After removal of the solvent in vacuo, the distillation yielded 5.44 g (87%) of **6c** as a colorless oil, bp 73–75 °C (0.08 Torr). IR (film): 1725, 1640, 990, 910. ^1H NMR: δ 0.5–2.3 (m, 6 H); 1.33 (s, 3 H); 4.5–5.2 (m, 2 H); 5.2–6.2 (m, 1 H); 7.1–7.7 (m, 3 H); 7.7–8.1 (m, 2 H).

3-Methyl-2-pent-4-yl-2-phenyl-2*H*-azirine (6g). The same procedure as above was used, with **5g** (11.97 g, 30.9 mmol) and 0.74 g (30.8 mmol) of NaH: yield, 6.0 g (98%) [**6g** was utilized crude for the next step (preparation of **8h**)]. IR (cyclohexane): 1765, 1640, 990, 910. ^1H NMR: δ 0.7–2.5 (m, 6 H); 2.30 (s, 3 H);

(31) Similar prediction was made by applying the Klopman–Salem equations: Klopman, G. *J. Am. Chem. Soc.* **1968**, *90*, 223–234. Salem, L. *Ibid.* **1968**, *90*, 553–566. See also: Houk, K. N.; Sims, J.; Duke, R. E., Jr.; Strozier, R. W.; George, J. K. *Ibid.* **1973**, *95*, 7287–7301. Houk, K. N.; Sims, J.; Watts, C. R.; Luskus, L. J. *Ibid.* **1973**, *95*, 7301–7315.

(32) Abbas, S. A.; Laurent, A.; Mison, P.; Pellissier, N. *Bull. Soc. Chim. Fr.* **1986**, 288–296.

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4.6–5.3 (m, 2 H); 5.3–6.2 (m, 1 H); 6.9–7.7 (m, 5 H).

3-But-3-enyl-2-methyl-2-phenyl-2*H*-azirine (6i).[35] *n*-BuLi (1.6 M in hexane, 1.25 mL, 1.8 mmol) was added dropwise to a stirred solution of 2,3-dimethyl-2-phenyl-2*H*-azirine[12] (255 mg, 1.8 mmol) in THF (5 mL) at −60 °C and under N_2 atmosphere. After the mixture was stirred at −60 °C for 30 min, a solution of allyl iodide (0.16 mL, d = 1.837, 1.8 mmol) in THF (3 mL) was added dropwise. After the mixture was stirred at −60 °C for 30 min, water (10 mL) was added and the mixture allowed to warm to 20 °C. The aqueous layer was extracted with ether. The organic phases were united and washed with water. After drying ($MgSO_4$), the solvent was evaporated in vacuo, yielding 277 mg (85%) of **6i** as an oil. IR (film): 1760, 1640, 995, 920. ^{1}H NMR: δ 1.55 (s, 3 H); 2.1–3.0 (m, 4 H); 4.8–5.2 (m, 2 H); 5.4–6.2 (m, 1 H); 6.8–7.5 (m, 5 H).

2,2-Dimethyl-3-phenyl-2*H*-azirine (6j). See ref 12.

2-But-3-enyl-2-methyl-3,5-diphenyl-2*H*-pyrrole (8a). See ref 32.

2-But-3-enyl-2,4-dimethyl-3,5-diphenyl-2*H*-pyrrole (8b). Propiophenone (1.45 g, 10.8 mmol) in DMSO (5 mL) was added to a stirred suspension of NaH (0.3 g, 12.5 mmol), washed three times with anhydrous petroleum ether in DMSO (10 mL) under N_2 atmosphere and at 20 °C. After the mixture was stirred at 20 °C for 2 h, **6b** (2 g, 10.8 mmol) in anhydrous DMSO (10 mL) was added dropwise. After being stirred at 20 °C for 24 h, the mixture was poured onto ice (30 g). The aqueous phase was extracted with ether (100 mL, three times). The organic extracts were combined and washed with H_2O (10 mL, 3 times). After drying ($MgSO_4$), the solvent was evaporated in vacuo. The residue was purified by column chromatography on silica gel (90 g; ether/petroleum ether, 1:4), yielding 2.2 g (66%) of **8b** as a colorless oil. ^{1}H NMR: δ 1.33 (s, 3 H); 1.97 (s, 3 H); 1.4–2.2 (m, 4 H); 4.6–5.1 (m, 2 H); 5.4–6.1 (m, 1 H); 7.0–7.5 (m, 8 H); 7.6–7.9 (m, 2 H).

2-Methyl-2-pent-4-enyl-3,5-diphenyl-2*H*-pyrrole (8c). Same procedure as for **8b**, using **6c** (2.01 g, 10.1 mmol) 0.26 g (10.8 mmol) of NaH and 1.22 g (10.2 mmol) of acetophenone. Purification by column chromatographic on silica gel (ether/petroleum ether, 1:9); yield, 2.24 g (74%) of **8c** as a colorless oil. ^{1}H NMR: δ 0.6 −1.3 (m, 2 H); 1.48 (s, 3 H); 1.6–2.6 (m, 4 H); 4.6–5.1 (m, 2 H); 5.3–6.1 (m, 1 H); 7.12 (s, 1 H); 7.2–7.8 (m, 8 H); 7.9–8.3 (m, 2 H).

2,4-Dimethyl-2-pent-4-enyl-3,5-diphenyl-2*H*-pyrrole (8d). The same procedure was used as for **8b**, with 1.79 g (9 mmol) of **6c**, 0.22 g (9.1 mmol) of NaH, and 1.21 g (9 mmol) of propiophenone. The reaction of the enolate with **6c** was 18 h at 20 °C and then 26 h at 35 °C. After purification through column chromatography on silica gel (ether/petroleum ether, 1:9) one obtains 1.90 g (67%) of **8d** as a colorless oil. ^{1}H NMR: δ 0.8–1.5 (m, 2 H); 1.30 (s, 3 H); 1.5–2.2 (m, 4 H); 1.93 (s, 3 H); 4.6–5.2 (m, 2 H); 5.2–6.1 (m, 1 H); 6.9–7.5 (m, 8 H); 7.5–8.0 (m, 2 H).

2-But-3-enyl-3-methyl-2,5-diphenyl-2*H*-pyrrole (8e). Acetophenone (5.80 g, 48.3 mmol) in DMSO (20 mL) was added to a stirred suspension of NaH (1.25 g, 52.1 mmol, washed three times with petroleum ether) in DMSO (50 mL) under N_2 atmosphere and at 20 °C. After the mixture was stirred at 20 °C for 4 h, **5e** (7.65 g, 20.5 mmol) in DMSO (20 mL) was added dropwise. After being stirred at 20 °C for 17 h and then at 35 °C for 26 h, the mixture was poured onto 130 g of ice. The aqueous phase was extracted with ether (150 mL, four times). The organic extracts were combined and the solvent was concentrated to 300 mL and treated with aqueous 10% HCl (pH 1, vigorous shaking). The aqueous layer was extracted with ether (150 mL, twice), and after neutralization with 10% NaOH (pH 12), the solution was extracted with ether (200 mL, 4 times). After drying ($MgSO_4$), the solvent was evaporated in vacuo, and the residue was purified by column chromatography on silica gel (ether/petroleum ether, 8:92), yielding 1.92 g (33%) of colorless crystals of **8e**, after recrystallization from hexane/ether, mp 95–95.5 °C. ^{1}H NMR: δ 1.5–2.8 (m, 4 H); 1.95 (d, J = 1, 3 H); 4.6–5.2 (m, 2 H); 5.4–6.2 (m, 1 H); 6.47 (q, J = 1, 1 H); 7.0–7.3 (m, 5 H); 7.3–7.6 (m, 3 H); 7.7–8.2 (m, 2 H).

2-But-3-enyl-3,4-dimethyl-2,5-diphenyl-2*H*-pyrrole (8f). The same procedure was used as for **8e**, with 10.06 g (27 mmol) of **5e**, 1.37 g (57 mmol) of NaH, and 7.60 g (56.6 mmol) of propiophenone. The condensation reaction was done at 20 °C for 20 h and then at 40 °C for 69 h. Column chromatography on silica gel (ether/petroleum ether, 8:92) afforded a first fraction containing **8f**; yield, 0.2 g (3%), colorless oil. IR (film): 1640, 1540, 1495, 1450, 1340, 995, 915. ^{1}H NMR: δ 1.4–3.0 (m, 4 H), 1.73 (br s, 3 H); 1.93 (br s, 3 H); 4.6–5.1 (m, 2 H); 5.4–6.1 (m, 1 H); 7.1–7.3 (m, 5 H); 7.3–7.5 (m, 3 H); 7.6–7.9 (m, 2 H). A second fraction was eluted with ether/petroleum ether (3:7) and yielded 1.42 g (33%) of 1-amino-1-phenyl-pent-4-ene. ^{1}H NMR: δ 1.1–1.4 (m, 2 H); 1.4–2.3 (m, 4 H); 3.53 (t, J = 6.5, 1 H); 4.8–5.2 (m, 2 H); 5.4–6.2 (m, 1 H); 7.0–7.5 (m, 5 H). IR (film): 3340, 1640, 1490, 1450, 1030, 910. ^{13}C NMR: δ 30.6 (t); 38.4 (t); 55.5 (d); 114.5 (t); 126.1 (2 C, d); 126.7 (d); 128.2 (2 C, d); 137.9 (d); 145.9 (s).

3-Methyl-2-pent-4-enyl-2,5-diphenyl-2*H*-pyrrole (8g). The same procedure was used as for **8e**, with 8.00 g (20.7 mmol) of **5q**, 0.96 g (40 mmol) of NaH, and 4.80 g (40 mmol) of acetophenone. The condensation was carried out at 20 °C for 24 h and then at 35 °C for 24 h. Column chromatography on silica gel (ether/petroleum ether, 1:19) yielded 0.13 g (2%) of **8g** as a colorless oil. ^{1}H NMR: δ 1.0–2.5 (m, 6 H); 1.88 (d, J = 2, 3 H); 4.6–5.1 (m, 2 H); 5.2–6.1 (m, 1 H); 6.40 (q, J = 2, 1 H); 7.1–7.2 (m, 5 H); 7.3–7.5 (m, 3 H); 7.8–8.1 (m, 2 H).

3,4-Dimethyl-2-pent-4-enyl-2,5-diphenyl-2*H*-pyrrole (8h). The same procedure was used as for **8b**, with 6.48 g (32.6 mmol) of **6g**, 0.60 g (25 mmol) of NaH, and 3.35 g (25 mmol) of propiophenone. The condensation reaction was carried out at 20 °C for 18 h and then at 40 °C for 48 h. Chromatography on silica gel (ether/petroleum ether, 1:9) yielded 126 mg (2%) of **8h** as a colorless oil. ^{1}H NMR: δ 0.8–2.7 (m, 6 H); 1.80 (br s, 3 H); 2.00 (br s, 3 H); 4.7–5.2 (m, 2 H); 5.4–6.1 (m, 1 H); 7.1–7.3 (m, 5 H); 7.3–7.6 (m, 3 H); 7.7–7.9 (m, 2 H). Elution with ether/petroleum ether (2:3) afforded a second fraction, yielding 1.6 g (35%) of 1-amino-1-phenylhex-5-ene. ^{1}H NMR: δ 1.0–1.7 (m, 4 H); 1.20 (s, 2 H, NH_2); 1.7–2.3 (m, 2 H); 3.73 (t, J = 6, 1 H); 4.7–5.1 (m, 2 H); 5.4–6.1 (m, 1 H); 7.1–7.4 (m, 5 H). IR (film): 3340, 1640, 1490, 990, 905. ^{13}C NMR: δ 25.7 (t); 33.6 (t); 38.9 (t); 55.9 (d); 114.4 (t); 126.0 (2 C, d); 126.5 (d); 128.1 (2 C, d); 138.2 (d); 146.3 (s).

3-But-3-enyl-2-methyl-2,5-diphenyl-2*H*-pyrrole (8i). The same procedure was used as for **8b**, with 1.21 g (10 mmol) acetophenone, 0.24 g (10 mmol) of NaH, and 1.46 g (8 mmol) of azirine **6i**. The condensation reaction was carried out at 20 °C for 48 h and then at 35 °C for 23 h. Chromatography on silica gel (ether/petroleum ether, 12:88) yielded 535 mg (23%) of **8i** as a colorless oil. ^{1}H NMR: δ 1.63 (s, 3 H); 2.1–2.4 (m, 4 H); 4.7–5.2 (m, 2 H); 5.4–6.1 (m, 1 H); 6.52 (br s, 1 H); 7.1–7.3 (m, 5 H); 7.3–7.5 (m, 3 H); 7.8–8.1 (m, 2 H).

4-But-3-enyl-2,2-dimethyl-3,5-diphenyl-2*H*-pyrrole (8j). The same procedure as for **8b**, with 2.99 g (20.6 mmol) of 2,2-dimethyl-3-phenyl-2*H*-azirine (**6j**),[12] 0.50 g (20.8 mmol) of NaH, and 3.60 g (20.6 mmol) of 1-phenylhex-5-enone (**7j**). The condensation reaction was carried out at 50 °C for 18 h: yield, 4.66 g (75%), colorless crystals after column chromatography elution with ether/petroleum ether (1:9) and recrystallization from petroleum ether; mp 81–82 °C. ^{1}H NMR: δ 1.27 (s, 6 H); 1.6–2.1 (m, 2 H); 2.1–2.5 (m, 2 H); 4.4–4.9 (m, 2 H); 5.1–5.9 (m, 1 H); 6.9–7.2 (m, 2 H); 7.2–7.5 (m, 6 H); 7.5–7.8 (m, 2 H).

1-Phenylhex-5-en-1-one (7j). 5-bromo-pent-1-ene (13.0 g, 87 mmol) in anhydrous ether (50 mL) was added dropwise to 2.1 g (87.5 mmol) of magnesium turnings in anhydrous ether (5 mL) under stirring, N_2 atmosphere, and gentle reflux. After 3 h, the mixture was cooled to 20 °C, and benzonitrile (8.9 g, 86 mmol) in anhydrous ether (50 mL) was added slowly. After boiling under reflux for 17 h, the mixture was cooled to 0 °C, and 10% aqueous HCl was added dropwise under stirring until acidic pH. The aqueous phase was saturated with NaCl and extracted with ether (100 mL, three times). The organic extracts were combined, then washed with brine (30 mL, three times), and dried ($MgSO_4$). After solvent evaporation the residue was distilled in vacuo, yielding 9.6 g (64%) of **7j** as a colorless oil, bp 83–84 °C (0.45 Torr). IR (film): 1685, 1640. ^{1}H NMR: δ 1.4–2.3 (m, 4 H); 2.83 (t, J = 7, 2 H); 4.6–5.2 (m, 2 H); 5.3–6.2 (m, 1 H); 7.2–7.6 (m, 3 H); 7.7–8.1 (m, 2 H).

2,2-Dimethyl-4-pent-4-enyl-3,5-diphenyl-2*H*-pyrrole (8k). The same procedure was used as for **8b**, with **6j** (4.35 g, 30 mmol),

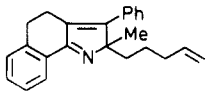
(35) Belloir, P. F.; Laurent, A.; Mison, P.; Bartnik, R.; Lesniak, S. *Tetrahedron Lett.* **1985**, *26*, 2637–2640.

0.74 g (31 mmol) of NaH, and 5.64 g (30 mmol) of 1-phenylhept-6-en-1-one (**7k**). The enolate formation required 3 h. The condensation required 72 h at 20 °C and 46 h at 35 °C. The crude product was recrystallized from petroleum ether, yielding 6.4 g (68%) of colorless crystals, mp 82–84 °C. ^{1}H NMR: δ 1.28 (s, 6 H); 1.0–1.5 (m, 2 H); 1.5–2.0 (m, 2 H); 2.0–2.5 (m, 2 H); 4.5–5.0 (m, 2 H); 5.1–5.9 (m, 1 H); 7.0–7.6 (m, 8 H); 7.6–8.0 (m, 2 H).

1-Phenylhept-6-en-1-one (7k).[36] The same procedure was used as for the preparation of **7j**, with 2.4 g of Mg (100 mmol) and 12.7 mL (95 mmol) of 6-bromohex-1-ene. The Grignard reagent was made in 4 h; 9.8 g (95 mmol) of benzonitrile was used, and the reaction time was 17 h: yield, 10.9 g (61%) of **7k** as a colorless oil, bp 93–95 °C (0.8 Torr). IR (film): 1685, 1640. ^{1}H NMR: δ 1.1–2.3 (m, 6 H); 2.87 (t, J = 7, 2 H); 4.7–5.2 (m, 2 H); 5.4–6.3 (m, 1 H); 7.3–7.7 (m, 3 H); 7.8–8.2 (m, 2 H).

4-But-3-enyl-2,3-dimethyl-2,5-diphenyl-2*H*-pyrrole (24). The same procedure was used as for **8b**, with 2,3-dimethyl-2-phenyl-2*H*-azirine[12] (1.03 g, 7 mmol), 0.17 g (7 mmol) of NaH, and 1.30 g (7 mmol) of 1-phenylhex-5-en-1-one **7j**. The enolate formation required 1 h. The condensation required 5 h at 20 °C and 40 h at 50 °C: yield, 43 mg (2%) of **24**, as an oil, obtained after column chromatography (elution with ether/petroleum ether, 1:4). ^{1}H NMR: δ 1.57 (s, 3 H); 1.73 (s, 3 H); 1.7–2.7 (m, 4 H); 4.4–5.1 (m, 2 H); 5.2–6.0 (m, 1 H); 6.9–7.9 (m, 10 H).

2*H*-Indole 28. The same procedure was used as for **8b**, with **6c** (1.99 g, 10 mmol), 0.25 g (10 mmol) of NaH, and 1.51 g (10 mmol) of α-tetralone. The enolate formation needed 3 h. The condensation required 42 h at 20 °C and 22 h at 40 °C with the presence of air: yield, 1.67 g (51%) of a 2:3 mixture of **28** and **28′** after column chromatography (elution with ether/petroleum ether, 1:4).



28′

Characteristics of 28. Oil. ^{1}H NMR: δ 0.7–1.7 (m, 2 H); 1.40 (s, 3 H); 1.7–2.4 (m, 4 H); 4.6–5.2 (m, 2 H); 5.3–6.2 (m, 1 H); 6.77 (s, 2 H); 7.1–7.6 (m, 8 H); 8.3–8.6 (m, 1 H).

Characteristics of 28′. ^{1}H NMR: δ 0.8–1.6 (m, 2 H); 1.38 (s, 3 H); 1.7–2.3 (m, 4 H), 2.6–3.1 (m, 4 H); 4.7–5.1 (m, 2 H); 5.3–6.1 (m, 1 H); 7.0–7.6 (m, 8 H); 8.0–8.3 (m, 1 H).

Thermolysis of 8a. A mixture of **8a** (606 mg, 2.1 mmol) and anhydrous benzene (2 mL) was sealed in a Pyrex tube under N_2 atmosphere. The tube was heated to 210 °C for 24 h. After cooling, the tube was opened and the solvent evaporated in vacuo. ^{1}H NMR of the residue showed a 79:21 mixture of **10a** and **11a**, which were separated by column chromatography on neutral alumina (10 g). Elution with petroleum ether/ether (9:1) yielded 332 mg (55%) of **10a** as a colorless oil. Then elution with petroleum ether/ether (4:1) gave 80 mg (13%) of **11a** as a colorless oil.

4-Methyl-2,9-diphenyl-3-azatricyclo[4.3.0.0^{4,9}]non-2-ene (10a). ^{1}H NMR: δ 1.0–1.4 (m, 2 H); 1.30 (s, 3 H); 1.4–2.3 (m, 5 H); 3.50 (br s, 1 H, HC(1)); 6.7–7.0 (m, 2 H); 7.0–7.3 (m, 3 H); 7.3–7.5 (m, 3 H); 7.7–8.1 (m, 2 H).

6-Methyl-2,8-diphenyl-7-azatricyclo[3.3.1.0^{2,6}]non-7-ene (11a). ^{1}H NMR: δ 0.7–1.8 (m, 3 H); 1.57 (s, 3 H); 1.8–2.2 (m, 4 H); 3.4 (br d, J = 5, 1 H, HC (1)); 7.07 (s, 5 H); 7.1–7.5 (m, 3 H); 7.6–7.9 (m, 2 H).

Thermal Isomerization of 11a into 10a. A 76:24 mixture of **10a/11a** (80 mg, 0.3 mmol) in C_6H_6 (1.5 mL) was heated to 211 °C for 49 h in a sealed Pyrex tube. After solvent evaporation 78 mg (95 %) of **10a** was isolated. ^{1}H NMR showed the absence of **11a**. On heating **10a** (87 mg, 0.3 mmol) in 0.9 mL of C_6H_6 at 208 °C during 65 h in a sealed tube, **10a** remained unchanged; some polymeric materials were obtained.

Thermolysis of 8b. **8b** (1.10 g, 3.7 mmol) in 2.5 mL of C_6H_6 in a sealed pyrex tube was heated to 228 °C for 24 h. The ^{1}H NMR spectrum of the crude product (1.04 g) showed a 60:33:7 mixture of **10b/11b/12b**. Column chromatography on neutral alumina (15 g) yielded a first fraction (petroleum ether/ether, 9:1) containing 554 mg (50%) of **10b** as colorless crystals, after recrystallization from $CHCl_3$. A second fraction (petroleum ether/ether, 85:15) yielded 305 mg (28%) of **11b** after recrystallization from petroleum ether.

1,4-Dimethyl-2,9-diphenyl-3-azatricyclo[4.3.0.0^{4,9}]non-2-ene (10b). Mp 83–86 °C. ^{1}H NMR: δ 0.8–1.3 (m, 2 H); 1.17 (s, 3 H); 1.33 (s, 3 H); 1.5–2.3 (m, 5 H); 6.8–7.1 (m, 2 H); 7.1–7.3 (m, 3 H); 7.3–7.5 (7, 3 H); 7.5–7.8 (m, 2 H).

1,6-Dimethyl-2,8-diphenyl-7-azatricyclo[3.3.1.0^{2,6}]non-7-ene (11b). Mp 120–122 °C. ^{1}H NMR (CCl_4): δ 1.07 (s, 3 H); 1.67 (s, 3 H); 1.0–2.4 (m, 7 H); 7.0–7.7 (m, 10 H).

Thermal Isomerization of 10b, 11b and 12b. On heating a 8:1:1 mixture of **10b/11b/12b** (104 mg, 0.35 mmol) in C_6H_6 (1 mL) to 235 °C for 48 h, 79 mg of a 63:24:13 mixture of **10b/11b/12b** was isolated. On heating **11b** (107 mg, 0.36 mmol) in C_6H_6 (1.5 mL) to 227 °C for 72 h, a 63:30:7 mixture of **10b/11b/12b** (107 mg) was obtained.

Thermolysis of 8c. A mixture of **8c** (1.50 g, 5 mmol) and anhydrous C_6H_6 (6 mL) was heated to 200 °C for 33 h in a sealed Pyrex tube. After solvent evaporation 1.5 g of a 27:17:38:18 mixture of **14a/15a/16a/17a** was obtained. Column chromatography on silica gel gave 350 mg (23%) **16a** as a colorless oil and then 173 mg of **17a** (11%) by elution with petroleum ether/ether (95:5). Elution with petroleum ether/ether (85:15) gave 243 mg (16%) of **14a** as a colorless oil. Elution with petroleum ether/ether (4:1) afforded 149 mg (10%) of **15a** as a colorless oil. 30 mg (2%) of 2*H*-pyrrole **23** and 175 mg (12%) of unreacted **8c** were eluted with petroleum ether/ether (9:1). On heating **8c** (117 mg, 0.39 mmol) in 5 mL of C_6H_6 at 180 °C for 24 h, ca. 20% of the cyclization was observed through ^{1}H NMR of the crude mixture. On heating 107 mg (0.36 mmol) of **8c** in 0.9 mL of C_6H_6 at 188 °C for 24 h, ca. 50% of conversion was observed (^{1}H NMR). The crude mixture was composed of **8c**, an isomeric 2*H*-pyrrole (which was not identified), and a 12:7:20:7 mixture of **14a/15a/16a/17a**. On heating 615 mg (2 mmol) of **8c** in 1.6 mL of C_6H_6 at 216 °C for 24 h, we isolated after column chromatography **14a** (11%), **15a** (4%), **16a** (38%), and **17a** (6%).

8-Methyl-2,10-diphenyl-9-azatricyclo[4.4.0.0^{2,8}]dec-9-ene (14a). ^{1}H NMR: δ 1.1–2.4 (m, 9 H); 1.55 (s, MeC(8)); 3.33 (br s, 1 H, HC(1)); 7.0–7.2 (m, 5 H); 7.2–7.6 (m, 3 H); 7.7–8.0 (m, 2 H).

7-Methyl-2,9-diphenyl-8-azatricyclo[4.3.1.0^{2,7}]dec-8-ene (15a). ^{1}H NMR: δ 0.8–1.5 (m, 2 H); 1.6–2.2 (m, 7 H); 1.70 (s, MeC(7)); 3.63 (br d, J = 4, 1 H, HC(1)); 6.9–7.2 (m, 5 H); 7.2–7.5 (m, 3 H); 7.6–7.9 (m, 2 H).

2-Methyl-8,10-diphenyl-9-azatricyclo[4.4.0.0^{2,8}]dec-9-ene (16a). ^{1}H NMR: δ 0.57 (s, 3 H); 1.1–2.5 (m, 9 H); 3.02 (br s, 1 H, HC(1)); 7.1–7.8 (m, 8 H); 7.8–8.1 (m, 2H).

Characteristics of 2-Methyl-7,9-diphenyl-8-azatricyclo-[4.3.1.0^{2,7}]dec-8-ene (17a). ^{1}H NMR: δ 0.93 (s, Me); 1.1–2.4 (m, 9 H); 3.07 (br d, J = 4, 1 H, HC(1)); 7.1–8.0 (m, 10 H).

Characteristics of 2-Methyl-3-pent-4-enyl-2,5-diphenyl-2*H*-pyrrole (23). ^{1}H NMR: δ 1.67 (s, 3 H); 0.8–2.9 (m, 6 H); 4.6–5.2 (m, 2 H); 5.2–6.2 (m, 1 H); 6.53 (t, J = 0.5, 1 H); 7.0–7.6 (m, 8 H); 7.7–8.2 (m, 2 H).

Thermal Isomerization of 16a and 17a. A 2:1 mixture of **16a** and **17a** (62 mg, 0.2 mmol) in C_6H_6 (0.6 mL) was heated to 227 °C for 24 h in a sealed tube. ^{1}H NMR of the crude residue showed the absence of **14a**, **15a**, and **17a**. Polymeric material was formed.

Thermolysis of 8d. **8d** (1.4 g, 4.4 mmol) in C_6H_6 (3.5 mL) was heated to 212 °C for 42 h in a sealed Pyrex tube. After solvent evaporation in vacuo, 1.38 g of a 15:26:31:15:13 mixture of **14b/15b/16b/17b/8d**. Column chromatography on silica gel (100 g) gave 448 mg (32%) of **16b** as a colorless oil and then 175 mg (13%) of **17b** by elution with petroleum ether/ether (93:7). Elution with petroleum ether/ether (85:15) gave a third fraction yielding 198 mg (14%) of **14b** after recrystallization from petroleum ether and a fourth fraction yielding 319 mg (23%) of **15b** after recrystallization from petroleum ether. **8d** (80 mg, 6%) was also recovered (petroleum ether/ether, 9:1). On heating 1.02 g (3.2 mmol) of **8d** in C_6H_6 (3 mL) to 245 °C for 65 h, 960 mg of a 85:15 mixture of **16b/17b** was obtained, containing less than 5% of **14b** and **15b** (^{1}H NMR). **14b** (41%) and **15b** (16%) were

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separated by column chromatography on neutral alumina (30 g). On heating 80 mg (0.25 mmol) of **8d** in C_6H_6 (1 mL) at 200 °C for 16 h, about 30% conversion was observed (^{1}H NMR). The thermolysis mixture contained **14b** and **15b** and already **16b** and **17b**. Heating 100 mg (0.31 mmol) of **8d** in C_6H_6 (1 mL) at 208 °C during 24 h afforded ca.80% conversion of **8d**. The product mixture was composed of **14b/15b/16b/17b** in roughly 19/19/25/18 (^{1}H NMR).

1,8-Dimethyl-2,10-diphenyl-9-azatricyclo[4.4.0.0^{2,8}]dec-9-ene (14b). Colorless crystals, mp 101–102 °C. ^{1}H NMR: δ 1.2–2.5 (m, 9 H); 1.50 (s, 3 H); 1.55 (s, 3 H); 7.0–7.3 (m, 5 H) 7.3–7.7 (m, 10 H).

1,7-Dimethyl-2,9-diphenyl-8-azatricyclo[4.3.1.0^{2,7}]dec-8-ene (15b). Colorless crystals, mp 127–128 °C. ^{1}H NMR ($CDCl_3$): δ 1.0–2.4 (m, 9 H); 1.28 and 1.63 (2 s, 2 Me); 7.0–7.5 (m, 10 H).

1,2-Dimethyl-8,10-diphenyl-9-azatricyclo[4.4.0.0^{2,8}]dec-9-ene (16b). Colorless oil. ^{1}H NMR: δ 0.33 (s, 3 H, MeC(2)); 1.20 (s, 3 H, MeC(1)) (compare with **14b**; the singlet at δ 0.33 is characteristic of a methyl group shielded by the anisotropy effect of the syn double bond); 0.8–2.4 (m, 9 H); 6.9–7.4 (m, 6 H); 7.4–7.8 (m, 4 H).

1,2-Dimethyl-7,9-diphenyl-8-azatricyclo[4.3.1.0^{2,7}]dec-8-ene (17b). Colorless oil. ^{1}H NMR: δ 0.78 (s, 3 H, MeC(2)); 1.1–2.4 (m, 9 H); 1.32 (s, 3 H, MeC(1)); 7.0–7.6 (m, 6 H); 7.6–7.9 (m, 4 H).

Thermal Isomerization of 14b and 15b. On heating 165 mg (0.52 mmol) of a 2:3 mixture of **14b** and **15b** in 1.4 mL of C_6H_6 for 86 h at 208 °C, we observed the formation of a 1:1 (^{1}H NMR) mixture of **16b** and **17b** with some polymeric material.

Thermal Isomerization of 16b and 17b. On heating 70 mg (0.22 mmol) of a 3:2 mixture of **16b** and **17b** in 0.7 mL of C_6H_6 for 24 h at 227 °C, we did not observed the presence of **17b** in the crude reaction mixture (^{1}H NMR). Only **16b** was identified with polymeric material.

Thermolysis of 8e. (a) **8e** (812 mg, 2.8 mmol) in 5 mL of C_6H_6 was heated to 168 °C for 67 h: yield, 800 mg; 35:65 mixture of **12a/13a** which were separated by column chromatography on silica gel (110 g). Elution with petroleum ether/ether (95:5) gave a first fraction containing 262 mg (32%) of **12a**. Elution then with petroleum ether/ether (93:7) gave 422 mg (53%) of **13a**. (b) On heating **8e** (82 mg, 0.29 mmol) in C_6H_6 (1.1 mL) to 168 °C for 40 h gave a 35:29:36 mixture of **8e/12a/13a**. No trace of **10a** and **11a** could be detected by ^{1}H NMR.

9-Methyl-2,4-diphenyl-3-azatricyclo[4.3.0.0^{4,9}]non-2-ene (12a). Colorless oil. ^{1}H NMR: δ 0.65 (s, 3 H, MeC(9)); 1.0–2.3 (m, 7 H); 3.20 (br s, HC(1)); 7.1–7.8 (m, 8 H); 7.8–8.1 (m, 2 H).

2-Methyl-6,8-diphenyl-7-azatricyclo[3.3.1.0^{2,6}]non-7-ene (13a). Colorless oil. ^{1}H NMR: δ 0.8–2.3 (m, 7 H); 1.00 (s, 3 H, MeC(2)); 3.02 (br d, J = 5, HC(1)); 7.1–7.8 (m, 8 H); 7.8–8.1 (m, 2 H).

Thermal Isomerization of 12a and 13a. On heating a 29:71 mixture of **12a** and **13a** (76 mg, 0.26 mmol) in 1.2 mL of C_6H_6 during 48 h at 196 °C, 70 mg of pure **12a** was isolated. ^{1}H NMR of the crude product showed less than 5% of **13a**. Heating of 72 mg (0.25 mmol) of **12a** in 0.7 mL of C_6H_6 during 24 h at 227 °C gave **12a** unchanged with some polymeric material.

Thermolysis of 8f: Synthesis of 1,9-Dimethyl-2,4-diphenyl-3-azatricyclo[4.3.0.0^{4,9}]non-2-ene (12b). **8f** (198 mg, 0.7 mmol) in C_6H_6 (1.5 mL) was heated in a sealed Pyrex tube to 168 °C for 69 h. After solvent evaporation, ^{1}H NMR of the residue showed only one reaction product (**12b**), which was purified by filtration on silica gel (15 g; ether/petroleum ether, 1:1): yield, 120 mg (61 %), colorless oil. ^{1}H NMR: δ 0.4–2.5 (m, 7 H); 0.52 (s, MeC(9)); 1.18 (s, MeC(1)); 7.0–7.5 (m, 8 H); 7.5–7.9 (m, 2 H).

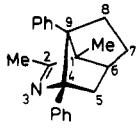
Thermolysis of 8g. (a) **8g** (40 mg, 0.1 mmol) in 0.6 mL of C_6H_6 was heated to 165 °C for 63 h. ^{1}H NMR of the crude product showed a 62:38 mixture of **16a/17a**. (b) **8g** (50 mg) in 1 mL of C_6H_6 were heated to 155 °C for 50 h. The same products were formed (6:4 **16a/17a**) with ca. 75% of unreacted **8g**.

Thermolysis of 8h. **8h** (126 mg, 0.4 mmol) in 1 mL of C_6H_6 was heated to 190 °C for 70 h. After solvent evaporation in vacuo a 1:1 mixture of **16b/17b** was obtained (≤5% of any other isomer, by ^{1}H NMR).

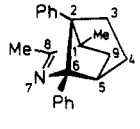
Thermolysis of 8i. **8i** (80 mg, 0.3 mmol) in 1.5 mL of C_6H_6 was heated to 169 °C for 69 h. A 76:24 mixture of **10a/11a** was formed. Traces of **12a** and **13a** were detected by ^{1}H NMR.

Thermolysis of 8j. **8j** (490 mg, 1.6 mmol) in 2.5 mL of C_6H_6 was heated to 225 °C for 62 h. After solvent evaporation, a 3:2 mixture of **18/19** (460 mg) was obtained and separated by column chromatography on silica gel (30 g; petroleum ether/ether, 85:15). The first fraction yielded 175 mg (36%) of **18**, the second, 161 mg (33%) of **19**. **8j** (20 mg, 4%) was also isolated. **8j** (90 mg, 0.3 mmol) in 1 mL of C_6H_6 was heated to 202 °C for 16 h. ^{1}H NMR of the crude product showed that it is a mixture of **8j** (75%), **24** (15%), and **19** (ca. 5%). **8j** (89 mg, 0.3 mmol) in 1 mL of C_6H_6 was heated to 215 °C for 63 h. ^{1}H NMR of the crude product showed that it is a mixture of **8j/24** (40%, 5:1) and **18/19** (60%, 1:1).

1,2-Dimethyl-4,9-diphenyl-3-azatricyclo[4.3.0.0^{4,9}]non-2-ene (18). Colorless oil. ^{1}H NMR: δ 1.0–1.6 (m, 1 H); 1.25 (s, 3 H, MeC(1)); 1.6–2.5 (m, 6 H); 2.08 (s, 3 H, MeC(2)); 6.2–6.7 (m, 2 H); 6.7–7.1 (m, 3 H); 7.0–7.4 (m, 5 H).



18



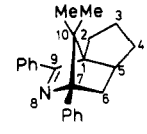
19

1,8-Dimethyl-2,6-diphenyl-7-azatricyclo[3.3.1.0^{2,6}]non-7-ene (19). Colorless crystals, mp 114–115 °C (petroleum ether). ^{1}H NMR: δ 0.90 (s, MeC(1)); 1.0–1.4 (m, 2 H); 1.4–2.5 (m, 5 H); 1.73 (s, MeC(8)); 6.6–7.0 (m, 2 H); 7.0–7.6 (m, 8 H).

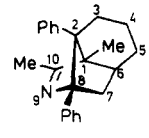
Thermal Isomerization of 18 and 19. On heating 52 mg (0.17 mmol) of **18** in 1.3 mL of C_6H_6 to 220 °C for 354 h, a 3:2 mixture of **18/19** was obtained (^{1}H NMR) together with a small amount of polymeric material. On heating 57 mg (0.19 mmol) of a 2:3 mixture of **18/19** to 235 °C for 111 h, in 1 mL of C_6H_6, a 3:2 mixture of **18/19** was obtained (^{1}H NMR) together with polymeric materials.

Thermolysis of 8k. (a) **8k** (1.15 g, 3.7 mmol) in 6 mL of C_6H_6 was heated to 210 °C for 140 h. A 18:55:5:18 mixture of **8k/20/21/22** (1.14 g) was formed. Column chromatography on silica gel (50 g) yielded a first fraction containing 100 mg (9%) of **8k** on elution with petroleum ether/ether (94:6). On elution with petroleum ether/ether (92:8), a second fraction yielded 602 mg (52%) of **20** after recrystallization from petroleum ether/ether. Elution with petroleum ether/ether (4:1) yielded 146 mg (13%) of **22**. Finally, elution with petroleum ether/ether (1:1) yielded 39 mg (3%) of **21** after recrystallization from petroleum ether. (b) On heating **8k** (1.02 g, 3.2 mmol) in 8 mL of C_6H_6 to 242 °C for 40 h, a 40:15:10:10 mixture of **8k/20/21/22** was obtained (^{1}H NMR). After column chromatography on silica gel (60 g) we isolated unreacted **8k** (9%) and **20** (13%), **21** (14%), and **22** (10%). (c) On heating **8k** (100 mg, 0.3 mmol) in 1 mL of C_6H_6 to 210 °C for 87 h a 40:42:5:5 mixture of **8k/20/21/22** was obtained (^{1}H NMR of the crude mixture). This indicates that **20** is formed under condition of kinetic control.

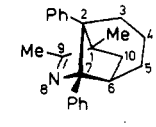
10,10-Dimethyl-7,9-diphenyl-8-azatricyclo[5.2.1.0^{1,5}]dec-8-ene (20). Colorless crystals, mp 105–107 °C. ^{1}H NMR: δ 0.50 (s, 3 H, 10-Me syn C=N); 0.90 (s, 3 H, 10-Me anti C=N); 1.2–2.6 (m, 9 H); 7.1–7.9 (7, 10 H).



20



21



22

1,10-Dimethyl-2,8-diphenyl-9-azatricyclo[4.4.0.0^{2,8}]dec-9-ene (21). Colorless crystals, mp 98–101 °C. ^{1}H NMR: δ 0.9–2.4 (m, 9 H); 1.33 (s, MeC(1)); 1.96 (s, MeC(10)); 6.3–6.6 (m, 2 H); 6.6–7.0 (m, 3 H); 7.0–7.5 (m, 5 H).

1,9-Dimethyl-2,7-diphenyl-8-azatricyclo[4.3.1.0^{2,7}]dec-8-ene (22). Colorless oil. ^{1}H NMR: δ 1.02 (s, MeC(1)); 1.1–1.7 (m, 4 H); 1.58 (s, MeC(9)); 1.7–2.4 (m, 5 H); 6.7–7.6 (m, 10 H).

Thermal Isomerization of 20. Pure **20** (36 mg, 0.1 mmol), in 1 mL of C_6H_6 was heated to 234 °C for 88 h and gave a 1:1:1 mixture on **20/21/22** together with polymeric materials.

Thermolysis of 28. A 3:2 mixture of **28** and **28′** (692 mg, ca. 2.1 mmol) in 5 mL of C_6H_6 was heated in sealed tube to 120 °C for 24 h. The ^{1}H NMR of the crude mixture (650 mg) showed that only **28** reacted. Column chromatography on silica gel (30 g) yielded a first fraction containing 310 mg of **30** (45%) on elution with petroleum ether/ether (9:2). A second fraction of 240 mg of unreacted **28′** (34%) was obtained with the same eluent.

Characteristics of 30. Oil, ^{1}H NMR: δ 0.4–1.3 (m, 2 H); 1.6–2.5 (m, 4 H); 2.07 (s, 3 H, Me); 4.6–5.1 (m, 2 H); 5.1–5.9 (m, 1 H); 6.8–7.3 (m, 6 H); 7.3–7.6 (m, 2 H); 7.6–7.9 (m, 2 H); 8.5–8.7 (m, 1 H).

Catalyzed Intramolecular Cycloaddition of 8c. **8c** (96 mg, 0.3 mmol) and 155 mg (0.2 mmol) of (4-Br-$C_6H_4)_3NSbCl_6$ in 2 mL of CH_2Cl_2 were heated to 135 °C for 20 h in a sealed Pyrex tube under N_2 atmosphere. After cooling, the tube was opened and the solution filtered through silica gel (petroleum ether/ether). The solvent was evaporated in vacuo and the residue analyzed by ^{1}H NMR (see Table IV).

Catalyzed Intramolecular Cycloaddition of 8d. (a) **8d** (115 mg, 0.4 mmol) and 78 mg (0.1 mmol) of (4-Br-$C_6H_4)_3NSbCl_6$ in 2.5 mL of CH_2Cl_2 were heated to 135 °C for 62 h and analyzed after workup (see above and Table IV). (b) **8d** (68 mg, 0.2 mmol) and 33 mg (0.05 mmol) of Eu(thd)$_3$ in 0.5 mL of C_6H_6 were heated to 180 °C for 43 h. The same workup conditions as above were used (see Table IV). (c) **8d** (166 mg, 0.5 mmol) and 49 mg (0.05 mmol) of Yb(fod)$_3$ in 1 mL of C_6H_6 were heated to 190 °C for 72 h. (d) **8d** (115 mg, 0.4 mmol) and 38 mg (0.04 mmol) of Eu(fod)$_3$ in 0.5 mL of C_6H_6 were heated to 192 °C for 63 h. (e) **8d** (66 mg, 0.2 mmol) and 18 mg (0.06 mmol) of Ni(acac)$_2$ in 0.5 mL of C_6H_6 were heated to 193 °C for 40 h. (f) **8d** (100 mg, 0.3 mmol) and 50 mg (0.2 mmol) of $ZnBr_2$ in 0.8 mL of C_6H_6 were heated to 155 °C for 63 h. After cooling, the tube was opened, and 50 mL of ether was added to the residue. Hydrolysis with 10% NaOH was performed. After drying, the solvent was evaporated in vacuo and the residue analyzed by ^{1}H NMR (see Table IV).

Ab initio MO calculations with the minimal STO-3G basis set were carried out by using the MONSTERGAUSS 81 program[23] on a CYBER 170-855 CDC computer. The geometries were fully optimized with respect to all bond lengths and bond angles by using Davidon's method with standard convergence criteria.[26] Due to the size of the molecules calculated and computer time limitations, we were forced to use the minimal STO-3G basis set. Systematic errors on the total energies should be canceled, in part at least, on comparing rigid isomers as it is done in our model studies.

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Registry No. (*E*)-**5a**, 110775-23-0; (*E*)-**5a** (hydrazone), 107112-63-0; (*Z*)-**5a**, 110775-27-4; (*Z*)-**5a** (hydrazone), 107112-62-9; (*E*)-**5c**, 110775-24-1; (*E*)-**5c** (hydrazone), 110775-58-1; (*Z*)-**5c**, 110775-28-5; (*Z*)-**5c** (hydrazone), 110775-55-8; (*E*)-**5e**, 110775-25-2; (*E*)-**5e** (hydrazone), 110775-56-9; (*Z*)-**5e**, 110775-29-6; (*Z*)-**5e** (hydrazone), 110775-59-2; (*E*)-**5g**, 110775-26-3; (*E*)-**5g** (hydrazone), 110775-57-0; (*Z*)-**5g**, 110775-30-9; (*Z*)-**5g** (hydrazone), 110775-60-5; (*E*)-**5j**, 75406-55-2; (*Z*)-**5j**, 75406-54-1; **6a**, 58130-08-8; **6c**, 62901-83-1; **6g**, 110775-31-0; **6i**, 100589-87-5; **6j**, 14491-02-2; **7j**, 22524-25-0; **7k**, 15177-05-6; **8a**, 92898-36-7; **8b**, 92898-34-5; **8c**, 92898-33-4; **8d**, 92898-27-6; **8e**, 110775-32-1; **8f**, 110775-33-2; **8g**, 110775-34-3; **8h**, 110775-35-4; **8i**, 110775-36-5; **8j**, 110775-37-6; **8k**, 110775-39-8; **10a**, 92898-37-8; **10b**, 92898-39-0; **11a**, 92898-38-9; **11b**, 92898-35-6; **12a**, 110775-48-9; **12b**, 92898-30-1; **13a**, 110775-49-0; **14a**, 110775-43-4; **14b**, 92898-32-3; **15a**, 110775-44-5; **15b**, 92898-31-2; **16a**, 110775-45-6; **16b**, 92898-28-7; **17a**, 110775-46-7; **17b**, 92898-29-8; **18**, 110775-50-3; **19**, 110775-51-4; **20**, 110849-70-2; **21**, 110775-52-5; **22**, 110775-53-6; **23**, 110775-47-8; **24**, 110775-40-1; **28**, 110775-41-2; **28′**, 110775-42-3; **30**, 110775-54-7; Eu(thd)$_3$, 15522-71-1; Yb(fod)$_3$, 18323-96-1; Eu(fod)$_3$, 17631-68-4; Ni(acac)$_2$, 3264-82-2; CH_2=$CH(CH_2)_3CH(Ph)NH_2$, 110775-38-7; CH_2=$CH(CH_2)_2CH(Ph)NH_2$, 109925-99-7; (4-Br$C_6H_4)_3NSbCl_3$, 24964-91-8; (*Z*)-EtC(Ph)=$NNMe_2$, 75406-34-7; $Br(CH_2)_3CH$=CH_2, 1119-51-3; (*Z*)-$PhCH_2C(Me)$=$NNMe_2$, 66930-29-8; $Br(CH_2)_2CH$=CH_2, 5162-44-7; ICH_2CH=CH_2, 556-56-9; PhCOEt, 93-55-0; PhCOMe, 98-86-2; PhCN, 100-47-0; $Br(CH_2)_4CH$=CH_2, 2695-47-8; (*E*)-EtC(Ph)=$NNMe_2$, 75406-33-6; (*E*)-$PhCH_2C(Me)$=$NNMe_2$, 66930-19-6; 2,3-dimethyl-2-phenyl-2*H*-azirine, 57573-53-2; α-tetralone, 529-34-0.

Supplementary Material Available: Spectra data and elemental analyses of compounds **8b–e,i–k**, **24**, **28**, **28′**, **10a**, **11a**, **10b**, **11b**, **14a**, **15a**, **16a**, **17a**, **14b**, **15b**, **16b**, **17b**, **12a**, **13a**, **12b**, **18–22** and **30** and ab initio STO-3G-optimized geometries of 1*H*- (**31**), 2*H*- (**32**), and 3*H*-pyrrole (**33**) and 1-azabicyclo[2.2.1]hept-2-ene (**35**) (17 pages). Ordering information is given on any current masthead page.

Doubly Clamped Cope Systems

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Cyclizations of *meso*-**15** and of *d,l*-**15** with phenyllithium lead to the "crossed Cope system" **6B**, the constitution of which is confirmed by 2D NMR and X-ray analysis (*d,l* configuration). Conformationally fixed biallyl skeletons of this type are shown not to undergo the typical rearrangement.

Introduction

The activation parameters of the Cope rearrangement are strongly influenced by substituents and by small rings condensed to the biallyl skeleton.[1] By formal replacement of small rings in the Cope system (cf. homotropilidene, **I**, B = CH_2) by larger, e.g., medium-sized or multimembered rings, we have attempted to examine other influences on the Cope rearrangement. The strain of a medium ring

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