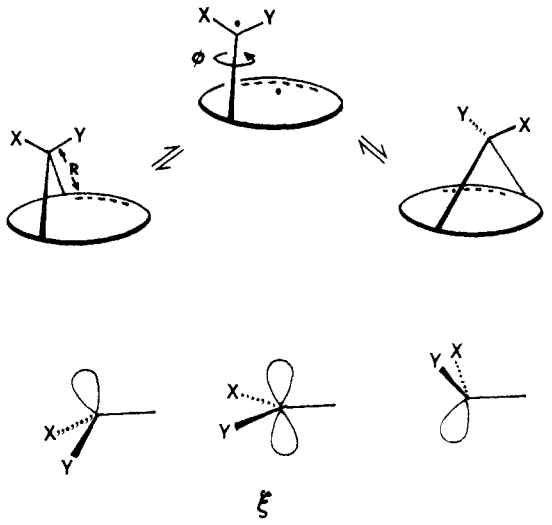

Figure 2. Principal coordinates for describing a formal [1,*n*]-sigmatropic shift in a bicyclic molecule.

present proposal from those in (b) and (c) of Scheme I where, barring an unlikely coincidence of barrier heights, temperature dependence of the product ratio would be expected.

Work carried out in this laboratory has recently shown that 1-phenyl- and 2-phenylbicyclo[2.1.1]hexenes do rearrange with a strong preference for inversion and that the product ratio is, within experimental error, temperature independent.[7] The parent compound showed temperature-dependent stereoselectivity and is, therefore, a candidate for one of the more traditional mechanisms ((b) or (c) in Scheme I).

Looking further afield, one can hypothesize that the phenomenon proposed here could explain the observed preference for inversion in the formal [1,5]-sigmatropic shifts of 7,7-dimethylbicyclo[4.1.1]octadiene[8] and norcaradiene derivatives.[9] It might also have a role in the mysterious inversion observed in pyrazoline deazetizations.[10]

What is still unclear is how much the phenomenon would be attenuated for intermediates with larger numbers of degrees of freedom. If it persists in cyclopropane,[11] cyclobutane,[12] and cyclopentane[13] stereomutations or in reactions such as the vinylcyclopropane[14] rearrangement, then a considerable amount of reinterpretation of reaction stereochemistry will be necessary. Experiments are under way in this laboratory to probe these questions.

Acknowledgment. Thanks go to Richard H. Newman-Evans whose careful experimental work on the rearrangement of bicyclo[2.1.1]hexenes inspired this study. Support of the work by the NIH (Grant GM 27022) is gratefully acknowledged.

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Synthetic and Structural Studies in the [4.4.4.5]Fenestrane Series

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Abstract: Photolysis of dienone **16** furnishes **20**, which by way of diazoketone **22c** is cyclized through carbene insertion to **24**. Reductive removal of the carbonyl group of **24** followed by deketalization gives **30**, and photochemical Wolff rearrangement of the derived α-diazoketone **31b** in methanol gives **32** and **33**. X-ray crystallographic analysis of the related *p*-bromoanilide **37** confirmed these assignments and provided structural information. The two angles that reflect flattening at the central quaternary carbon atom are 128° and 129°. These are the first examples of [4.4.4.5]fenestranes (tetracyclo[4.3.1.$0^{3,10}$.$0^{8,10}$]decanes) to be prepared.

Synthetic efforts in recent years have resulted in preparation of several ring systems related to the unknown hydrocarbon tetracyclo[3.3.1.$0^{3,9}$.$0^{7,9}$]nonane ([4.4.4.4]fenestrane, windowpane), of which the most frequently discussed[2-5] isomer is **1**. There are

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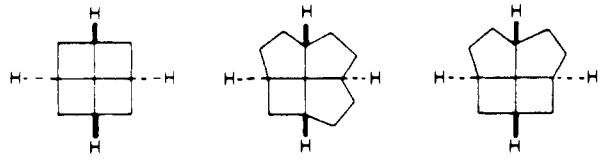
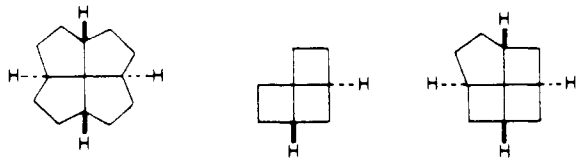
now known representatives of the [4.5.5.5]-(**2**),[6,7] [4.4.5.5]- (**3**),[6] [5.5.5.5]- (**4**),[8] and [4.4.4]fenestranes (**5**),[4,9] as well as homologous tetracyclic systems composed of larger rings.[10] Structural interest



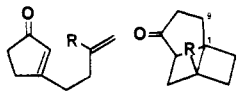
1 2 3



4 5 6

in these systems arises from the severe strain and distortion expected at the central quaternary carbon atom of **1**. Thus, two recent calculations of the strain energy of **1** are 183 kcal/mol (upper limit, molecular mechanics)[4] and 160 kcal/mol (ab initio, 4-31G basis set);[5] these values may be compared with 108 kcal/mol, which is 4 times the 27 kcal/mol strain energy of cyclobutane. The isomer of **1** with four cis methine hydrogen atoms is predicted[2,4] to be even more excessively strained. Our exploration of routes to **1** has now led to synthesis of derivatives of [4.4.4.5]fenestrane (**6**), the smallest and most strained of the tetracyclic fenestranes prepared to date.[11]

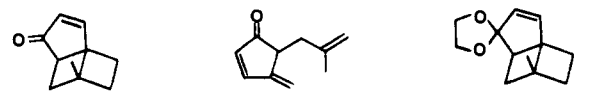
Our interest in these compounds originated in studies of regiochemical control of the intramolecular [2 + 2] photochemical cyclization of substituted 1,5-hexadienes.[12,13] The discovery that irradiation of **7a,b** led to ketones **8a,b** suggested a simple synthesis of [4.4.4]fenestranes through ring contraction of the cyclopentanone ring of **8**. This was successful,[9] and we then turned



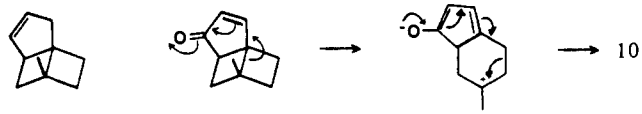
7 8

a, R = H
b, R = CH_3

to the problems of adapting this approach to the preparation of tetracyclic fenestranes. We first attempted to functionalize readily available **8b** at C(9), where the fourth ring should eventually close. Efforts to convert **8b** into the unsaturated ketone **9** led invariably to the fragmentation product **10**.[14] Thus, **8b** yielded an α-phenylseleno derivative[15] without difficulty, but oxidative elimination,[15] even at 0 °C, gave only **10**. Similarly, a double bond could be introduced into the ethylene ketal of **8b** through bromination–dehydrobromination,[16] but efforts to deketalize **11** yielded **10** rather than **9**. It appears then that the strain relief provided by cleavage of the central bond of **9**, as shown or by a similar radical mechanism, leads to fragmentation even under quite mild conditions. Equally unrewarding were attempts to make use of olefin **12**, which was available through treatment of the tosylhydrazone of **8b** with butyllithium.[17] When applied to **12**, a variety of methods generally useful for allylic oxidation led either to no reaction or to unpromising mixtures of products.

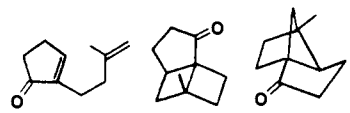


9 10 11



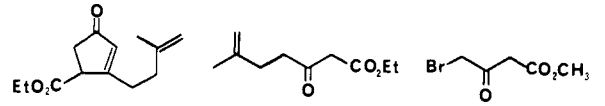
12

An attractive alternative strategy should be the introduction of functionality at C(9) prior to formation of the strained system of **8**, and with this in mind, we first prepared the isomeric cyclopentenone **13**. Straight [2 + 2] photochemical closure of this substrate, in analogy with the conversion of **7** to **8**, would furnish the C(9)-substituted product **14**. Unfortunately for the present

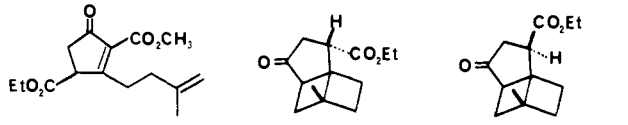


13 14 15

purposes, however, we found that **13** cyclizes regiospecifically in the crossed fashion, yielding **15** as the only [2 + 2] product.[13] As we have discussed elsewhere,[13] this behavior seems to be a general property of 2-acylhexadiene systems. We then turned to the straightforward solution to our problem offered by ketoester **16**.



16 17 18



19 20 21

In line with a procedure developed for related compounds,[18] condensation of β-keto ester **17**[19] with methyl 4-bromoacetoacetate

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(10) Georgian, V.; Saltzman, M. *Tetrahedron Lett.* **1972**, 4315. This last class of fenestranes also includes the diterpene laurenene; Corbett, R. E.; Couldwell, C. M.; Lauren, D. R.; Weavers, R. T. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1791.
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(13) Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1983**, *105*, 1299.
(14) Trienone **10** was first encountered (ref 9) as the sole product of thermal decomposition (210 °C) of the α-diazoketone derived from **8b**. It was suggested that **9** was a probable intermediate.
(15) Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97* 5434, and references cited therein.
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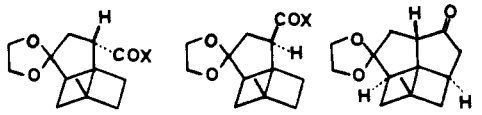
(18)[18] furnished **19** in high yield. Treatment of **19** with sodium iodide and acetic acid in hot diglyme[18] then effected selective removal of the carbomethoxy group to provide **16**. As expected from the behavior of **7b**,[9,12] photochemical cyclization of **16** ($\lambda > 340$ nm, hexane solvent) was regiospecific and furnished a 2:1 mixture of keto esters **20** and **21** in 82% yield. Examination of molecular models suggested that the transition state leading to **20** is less congested sterically and that this, the desired isomer, should be the major product. This conclusion was supported by equilibration studies. It is clear in models that **21** is more hindered than **20**, largely because of interaction between the ester and methyl groups. On treatment with base, **21** is epimerized to an equilibrium mixture of **20** and **21** in a ratio ~2:1. Additional support and final proof of the stereochemistry of these esters comes from reactions discussed below.

Major ester **20** could be separated and purified by flash[20] chromatography, but it was more convenient on a preparative scale to separate the crystalline ketal acids **22a** and **23a**, formed on ketalization and saponification of the mixture, since most of **22a** crystallizes spontaneously from the mixture. Acid **22a** was



22 23 24

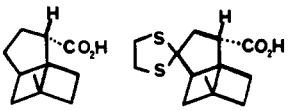
a, X = OH; b, X = Cl; c, X = CHN_2; d, X = OEt

converted to the acyl chloride **22b** with oxalyl chloride in benzene and thence to the diazoketone **22c** using diazomethane and triethylamine. Treatment of **22c** with rhodium(II) acetate[21] in dichloromethane caused rapid decomposition and formation of the tetracyclic product **24** (64% from **22a**). A parallel sequence with **23a** furnished **23c**, similar decomposition of which furnished no tractable products. Models indicate that only the ketocarbene from **22c** should insert to form the [4.4.5.5]fenestrane system, and that as a straightforward consequence of the structure of **22c**, this reaction should yield the stereochemistry depicted in **24**. Support for the structure of **24** came from its conversion to the symmetrical hydrocarbon **25**. Deketalization of **24** gave diketone **26**, which was treated sequentially with lithium aluminum hydride,

25 26

tosyl chloride in pyridine, and again lithium aluminum hydride to give **25**. As required by symmetry, the ^{13}C NMR spectrum of **25** consists of only 8 lines; in contrast, the spectrum of **26** shows the expected 12 signals.

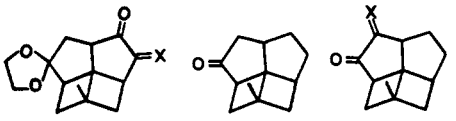
Preliminary study of the carbene insertion reaction in two other series of compounds related to **22** showed that it is quite sensitive to the specific structure of the diazoketone. In one of these series, the ketal of **22** is replaced by a simple methylene group. Acid **27** was available through conversion of the epimeric mixture of **20** and **21** to the tosylhydrazone, reduction with catecholborane,[22] and saponification of the esters thus obtained.[23] In the other series,



27 28

an ethylene thioketal takes the place of the ketal in **22**. Thioketalization of **20** and **21** followed by ester hydrolysis provided thioketal carboxylic acid **28** along with its minor epimer. Diazoketones from **27** and **28** were prepared and decomposed as described for **22c**. In neither case were useful yields of monomeric products obtained. One possible explanation of this sensitivity of the insertion reaction to substitution in the five-membered ring is that the conformation of this ring is critical for the desired process to compete with other reactions of the carbene and that the predominant conformation of **22c** is particularly favorable for closure to **24**. In the thioketal series, it is also possible that competitive ylide formation takes place between sulfur and the ketocarbene.[24]

Ketone ketal **24** is nicely substituted to permit sequential contraction of each of the five-membered rings to reach the [4.4.4.4]fenestrane skeleton. For the present purposes, however, it is necessary to contract only one ring and simply remove the functionality from the other. Our first experiments involved conversion of **24** into the related ketal α-diazoketone and then photochemical Wolff rearrangement. Neither step was encouraging. Base condensation[25] of **24** with ethyl formate and then treatment of the intermediate hydroxymethylene ketone **29a** with tosyl azide[26] gave the α-diazoketone **29b** in only poor yield (12%).

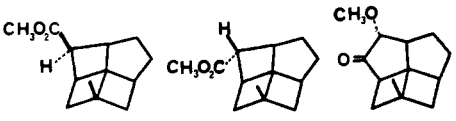


29 30 31

a, X = CHOH; b, X = N_2

The direct procedure employing 2,4,6-triisopropylbenzenesulfonyl azide under phase-transfer conditions[27] offered no improvement. Irradiation ($\lambda > 310$ nm) of **29b** in methanol led to a mixture of products with little carbonyl absorption in the infrared spectrum.

In seeking a solution to this problem, we noted that the two functional groups in **24** occupy different relative positions on the ring system and that it is the location of the ketal that is analogous to that of the carbonyl groups of **8a,b**. Since these tricyclic ketones[4,9] had been condensed with formic ester, converted to the diazoketones, and successfully subjected to ring contraction, it seemed worthwhile now to transfer attention to the analogous site of **24**. The carbonyl group of **24**, therefore, was removed as in conversion of **26** to **25** through hydride reduction, tosylation, and hydride reduction, and the resulting monoketal was hydrolyzed to **30**. Formylation (**31a**) and then tosyl azide now gave diazoketone **31b** successfully. Photolysis[28] of **31b** in methanol gave 20% of a 3:1 mixture of esters **32** and **33**, respectively, along with 23% of α-methoxy ketone **34**. Competitive insertion of the intermediate



32 33 34

ketocarbene into solvent methanol can account for formation of

(19) Previous preparation of **17** has required carboethoxylation of the related methyl ketone (43%): Mageswaren, S.; Sultanbawa, M. U. S. *J. Chem. Soc. Perkin Trans. 1* **1976**, 884 and references cited therein. We found it more convenient to alkylate the dianion of acetoacetic ester with methylallyl chloride (78%) using a known procedure: Huckin, S. N.; Weiler, L. *J. Am. Chem. Soc.* **1974**, *96*, 1082.

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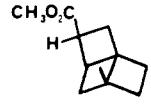
Table I. Final Coordinates of **37**, p-$BrC_6H_4N(H)COC_{11}H_{15}$ ($\times 10^4$), and Equivalent Isotropic Thermal Parameters ($Å^2 \times 10^3$) with Esd's in Parentheses

	molecule A				molecule B			
atom	x/a	y/b	z/c	U_{eq}*	x/a	y/b	z/c	U_{eq}*
C(1)	11135 (8)	2003 (6)	1968 (3)	50 (2)	3763 (8)	2469 (6)	9146 (3)	46 (2)
C(2)	12469 (9)	1861 (7)	1363 (7)	65 (3)	4731 (9)	2706 (7)	9700 (3)	58 (3)
C(3)	10882 (8)	1866 (7)	970 (3)	55 (3)	6531 (8)	3067 (7)	9224 (3)	53 (3)
C(4)	10106 (10)	3124 (7)	555 (3)	63 (3)	7999 (9)	2087 (7)	9050 (4)	68 (3)
C(5)	8074 (9)	2915 (6)	810 (3)	56 (3)	8333 (8)	2513 (7)	8300 (3)	59 (3)
C(6)	8011 (8)	2595 (3)	1536 (3)	44 (2)	6429 (8)	2544 (6)	8139 (3)	49 (2)
C(7)	6990 (8)	1386 (5)	2055 (3)	41 (2)	5534 (7)	3713 (5)	7695 (3)	41 (2)
C(8)	8807 (8)	581 (6)	2088 (3)	47 (2)	4588 (8)	4209 (5)	8312 (3)	42 (2)
C(9)	10238 (9)	760 (7)	2503 (3)	62 (3)	2772 (8)	3621 (6)	8716 (3)	48 (2)
C(10)	9680 (8)	1820 (6)	1590 (3)	42 (3)	5491 (8)	3053 (6)	8693 (3)	42 (2)
C(11)	11370 (10)	3283 (8)	2198 (4)	81 (4)	3078 (10)	1034 (7)	9224 (4)	63 (3)
C(12)	6054 (8)	1685 (6)	2670 (3)	43 (2)	4292 (8)	3313 (5)	7290 (3)	42 (2)
C(1)′	4326 (8)	462 (5)	3720 (3)	41 (2)	1959 (8)	4390 (5)	6657 (3)	45 (2)
C(2)′	3933 (8)	1559 (6)	3995 (3)	48 (2)	1171 (10)	3212 (6)	6563 (4)	66 (3)
C(3)′	3064 (8)	1335 (6)	4622 (3)	50 (3)	−253 (10)	3308 (6)	6234 (4)	73 (3)
C(4)′	2591 (8)	36 (6)	4962 (3)	46 (2)	−900 (9)	4577 (6)	5988 (3)	53 (3)
C(5)′	3014 (8)	−1086 (6)	4700 (3)	49 (2)	−93 (9)	5745 (6)	6070 (3)	59 (3)
C(6)′	3856 (8)	−839 (6)	4075 (3)	47 (2)	1312 (9)	5642 (6)	6389 (3)	55 (3)
N	5235 (7)	590 (4)	3087 (2)	46 (2)	3332 (7)	4362 (4)	7015 (2)	48 (2)
O	6059 (6)	2831 (4)	2775 (2)	58 (2)	4084 (6)	2130 (4)	7239 (2)	61 (2)
Br	1366 (1)	−262 (1)	5820 (1)	58 (1)	−2899 (1)	4727 (1)	5558 (1)	77 (1)

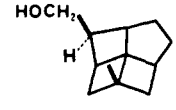
* $U_{eq} = {}^1/_3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i a_j$.

34,[28,29] and this suggests that ring contraction of the carbene is relatively slow. In the NMR spectrum of **34**, the appearance of the tertiary carbinyl proton [δ 3.80 (dd, $J_1 = 4.1$, $J_2 = 1.5$ Hz, 1 H)] implies the stereochemistry shown for the methoxyketone; J_1 is attributed to a cis vicinal coupling with the adjacent bridgehead hydrogen, and J_2 is assumed to be an unassigned long-range coupling in the rigid system.

Major component **32** of the epimeric mixture of [4.4.4.5]fenestrane esters was obtained pure with difficulty by either gas or flash[20] chromatography; these techniques also furnished mixtures enriched in minor component **33**, from which its ^1H and ^{13}C NMR spectra could be determined. The major isomer could be assigned the stereochemistry of **32** with good precedent,[4,9,30] since methanol addition from the less-hindered rear side of the intermediate ketene should be favored. The assignment was strongly supported by the ^1H and ^{13}C NMR spectra of **32** and **33**. In the 300-MHz ^1H spectrum of **32**, all signals could be assigned except those of the ethylene fragment of the five-membered ring; in the spectrum of **33**, a few additional signals remained obscure. The NMR data are in good accord with those obtained earlier for the two epimeric tricyclic esters of structure **35**[9] and for other [4.4.4]fenestranes.[4,9] Ester **32** was further characterized by hydride reduction to the corresponding primary alcohol **36**. Esters **32** and **33** show no



35



36

unusual thermal instability; they survive gas chromatography for a half hour at 130 °C with only a few percent decomposition. Finally, **32** was converted to a crystalline derivative for X-ray structural analysis; treatment[31] with the complex formed from trimethylaluminum and p-bromoaniline in dichloromethane yielded the p-bromoanilide **37**.[32] Slow crystallization of **37** from acetonitrile furnished a sample suitable for crystallographic studies.

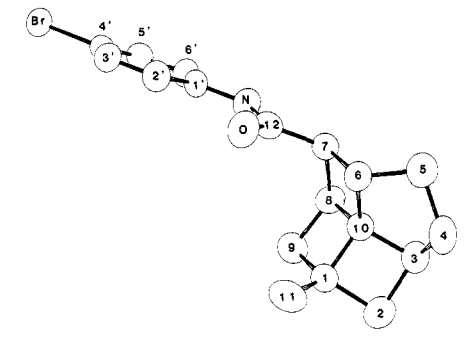
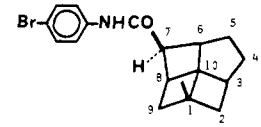
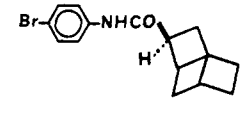


Figure 1. ORTEP diagram of **37**, p-$BrC_6H_4N(H)COC_{11}H_{15}$, showing 50% probability ellipsoids. Only molecule A of the two molecules in the asymmetric unit is shown with the hydrogens omitted for clarity. Molecule B differs only by a small change in the orientation of the p-bromoanilide group. Numbered atoms are carbons.

The molecular structure of **37** shown in Figure 1, as determined



37



38

by X-ray crystallography, has two molecules in the asymmetric unit of the triclinic space group $P\bar{1}$ that are nearly identical. An examination of the non-hydrogen bond distances and angles shows only two parameters that differ by more than three standard deviations. The primary difference between the two molecules is the orientation of p-bromoanilide portion of each molecule with respect to the fenestrane ring system. Torsion angles N–C(12)–C(7)–C(8) are −73.9 (7)° for molecule A and 64.1 (5)° for molecule B. Fractional coordinates for the two molecules are listed in Table I; bond distances and angles are given in Table II.

The three cyclobutane rings and one cyclopentane ring share the central quaternary carbon C(10). Bond distances involving C(10) are shortened; they average 1.508 (20)[34] in both molecules with C(1)–C(10) and C(8)–C(10) showing a difference in values

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(29) Meier, H.; Zeller, K.-P. *Angew. Chem.* **1975**, *87*, 43; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 32 and references cited therein.
(30) Meinwald, J.; Gassman, P. G. *J. Am. Chem. Soc.* **1960**, *82*, 2857 and references cited therein.
(31) Basha, A.; Lipton, M.; Weinreb, S. M. *Tetrahedron Lett.* **1977**, 4171.
(32) Prior to preparation of **37**, various other compounds were examined, including the p-bromobenzoate, 3,5-dinitrobenzoate, and α-naphthyl carbamate derived from alcohol **36**. None of these proved suitable for crystallographic analysis.
(33) For simplicity, the numbering of **37** is applied to the analogous carbon atoms of **38** in this discussion.
(34) Errors quoted for averaged quantities are (sample variance)$^{1/2}$.

Table II. Bond Distances (Å) and Angles for **37**, p-$BrC_6H_4N(H)COC_{11}H_{15}$, with Esd's in Parentheses

	molecule A	molecule B
	Bond Distances	
C(1)–C(2)	1.563 (9)	1.566 (10)
C(1)–C(9)	1.574 (8)	1.580 (8)
C(1)–C(10)	1.514 (9)	1.544 (8)
C(1)–C(11)	1.502 (11)	1.501 (9)
C(2)–C(3)	1.583 (10)	1.572 (8)
C(3)–C(4)	1.548 (9)	1.544 (10)
C(3)–C(10)	1.494 (8)	1.498 (9)
C(4)–C(5)	1.559 (10)	1.565 (10)
C(5)–C(6)	1.528 (9)	1.543 (9)
C(6)–C(7)	1.570 (7)	1.566 (8)
C(6)–C(10)	1.493 (8)	1.491 (9)
C(7)–C(8)	1.602 (8)	1.597 (8)
C(7)–C(12)	1.503 (8)	1.502 (9)
C(8)–C(9)	1.553 (10)	1.558 (8)
C(8)–C(10)	1.529 (7)	1.497 (8)
C(12)–O	1.223 (7)	1.232 (7)
C(12)–N	1.342 (6)	1.357 (7)
N–C(1)′	1.417 (7)	1.394 (9)
C(1)′–C(2)′	1.378 (9)	1.401 (9)
C(1)′–C(6)′	1.376 (7)	1.383 (8)
C(2)′–C(3)′	1.385 (8)	1.379 (12)
C(3)′–C(4)′	1.365 (8)	1.386 (9)
C(4)′–C(5)′	1.388 (9)	1.387 (10)
C(4)′–Br	1.905 (6)	1.894 (7)
C(5)′–C(6)′	1.374 (8)	1.354 (11)
	Bond Angles	
C(2)–C(1)–C(9)	124.4 (6)	123.9 (5)
C(2)–C(1)–C(10)	86.2 (5)	85.8 (5)
C(2)–C(1)–C(11)	115.3 (5)	115.0 (5)
C(9)–C(1)–C(10)	87.2 (5)	86.5 (4)
C(9)–C(1)–C(11)	114.5 (6)	115.6 (6)
C(10)–C(1)–C(11)	122.6 (6)	122.8 (5)
C(1)–C(2)–C(3)	90.6 (5)	91.0 (5)
C(2)–C(3)–C(4)	127.2 (6)	128.1 (5)
C(2)–C(3)–C(10)	86.2 (5)	87.2 (5)
C(4)–C(3)–C(10)	98.4 (5)	98.2 (5)
C(3)–C(4)–C(5)	102.1 (5)	102.0 (5)
C(4)–C(5)–C(6)	102.5 (5)	102.4 (5)
C(5)–C(6)–C(7)	128.3 (5)	128.6 (5)
C(5)–C(6)–C(10)	100.0 (5)	99.0 (5)
C(7)–C(6)–C(10)	88.5 (4)	87.3 (4)
C(6)–C(7)–C(8)	89.7 (4)	89.9 (4)
C(6)–C(7)–C(12)	118.2 (5)	118.0 (5)
C(8)–C(7)–C(12)	116.8 (5)	115.0 (5)
C(7)–C(8)–C(9)	126.2 (5)	124.4 (5)
C(7)–C(8)–C(10)	86.1 (4)	86.0 (4)
C(1)–C(9)–C(8)	91.0 (5)	90.3 (4)
C(9)–C(8)–C(10)	87.5 (5)	89.0 (4)
C(1)–C(10)–C(3)	96.1 (5)	94.7 (4)
C(1)–C(10)–C(6)	128.3 (6)	128.0 (5)
C(1)–C(10)–C(8)	94.3 (4)	94.0 (4)
C(3)–C(10)–C(6)	115.4 (5)	116.1 (5)
C(3)–C(10)–C(8)	129.2 (5)	128.7 (5)
C(6)–C(10)–C(8)	95.6 (4)	96.8 (5)
C(7)–C(12)–N	114.1 (5)	113.7 (5)
C(7)–C(12)–O	122.3 (5)	123.3 (5)
O–C(12)–N	123.6 (5)	122.8 (6)
C(12)–N–C(1)	130.0 (5)	131.2 (5)
N–C(1)′–C(2)	123.4 (5)	123.4 (5)
N–C(1)′–C(6)	117.2 (5)	118.6 (6)
C(2)′–C(1)′–C(6)	119.3 (5)	117.9 (6)
C(1)′–C(2)′–C(3)	119.5 (5)	120.5 (6)
C(2)′–C(3)′–C(4)	120.1 (6)	120.0 (7)
C(3)′–C(4)′–C(5)′	121.3 (5)	119.4 (7)
C(3)′–C(4)′–Br	119.9 (5)	120.7 (5)
C(5)′–C(4)′–Br	118.8 (4)	119.9 (5)
C(4)′–C(5)′–C(6)′	117.6 (5)	120.1 (6)
C(5)′–C(6)′–C(1)′	122.1 (6)	122.0 (6)

for the two molecules, 1.514 (9) and 1.544 (8) Å, for C(1)–C(10), and 1.529 (7) and 1.497 (8) Å for C(8)–C(10), respectively, for A and B. The perimeter C–C bonds for the cyclobutane rings are correspondingly lengthened with an average value of 1.574 (15) Å. There is less strain evident in **38**, where the carbon–carbon distances in the cyclobutane rings range from 1.515 (3) to 1.571 (3) Å and average 1.542 (18) Å.[4] The angles C(1)–C(10)–C(6) and C(3)–C(10)–C(8), which reflect the enforced flattening at C(10) are 128° and 129°, respectively. Earlier theoretical estimates of this angle in the symmetric parent [4.4.4.5]fenestrane are 124° (molecular mechanics)[4] and 128.7° and 129.1° (MNDO).[35] The same molecular mechanics calculations also yielded too small a value for the angle C(3)–C(10)–C(6)[33] in the [4.4.4]fenestrane system (130° compared with 132.5° observed in **38**), and it was noted at the time that this discrepancy suggests that the calculations overestimate the bond angle strain at this point.[4] Comparison of the bond angles of **37** and **38**[4] indicates that the largest change effected by closure of the five-membered ring is, not surprisingly, reduction of C(3)–C(10)–C(6), which passes from 132.5° in **38** to 116° in **37**. In compensation, the three internal cyclobutane angles at C(10) all increase 5–6° in **37**.

In the three cyclobutane rings of **37**, the dihedral angles defining their planarity have a range of values. C(6)–C(7)–C(8)–C(10) is quite planar with deviations from a least-squares plane of 0.005 Å for molecule A and 0.003 Å for molecule B. This corresponds to a dihedral angle of 1.2° and 0.8°, respectively, where the dihedral is taken as the angle between the plane containing the central carbon atom and the two atoms to which it is bonded within a cyclobutane ring and the three-atom plane not including the central atom. Ring C(1)–C(9)–C(8)–C(10) has dihedral angles of 2.5° and 5.5° for A and B, while C(1)–C(2)–C(3)–C(10) has dihedral angles of 10.2° and 12.5°, respectively. C(2) is trans with respect to C(6), and C(9) is cis to C(6), while in the essentially planar C(6)–C(7)–C(8)–C(10), C(7) is cis to C(1). The cyclopentane ring is in the half-chair conformation; C(5) deviates from the plane C(3)–C(10)–C(6) by –0.29 Å and is trans to C(1), and C(4) deviates from the plane by 0.48 Å for both A and B.

The p-bromoanilide portion of the molecule is normal with respect to bond distances and angles with the carbonyl oxygen being syn to C(6). The dihedral angle between least-squares planes through the aromatic ring and the amido group has the values of 8.2° and 8.4° for molecules A and B. The hydrogen atoms were refined, but they showed a range of values, 0.8–1.10 Å, with esd's near 0.05 Å.

In the crystal, there are two hydrogen bonds and two intermolecular contacts less than normal van der Waals separations. The nitrogen in molecule A acts as a donor to the carbonyl oxygen of the neighboring molecule B, $(-x,-y,-z)$, similarly B to A. The respective H···O*, N···O*, distances, and N–H···O* angle are 2.16 (6) Å, 3.00 (1) Å, and 170.1 (3.2)° and 2.15 (6) Å, 3.01 (1) Å, and 163.5 (3.4)°. Normal van der Waals Br···H contacts are 3.15 Å. In the crystal, close intermolecular contacts occur between molecule A and its symmetry equivalent, $(-x,-1.0-y,-z)$, H(9b)···Br = 2.74 (7) Å, and between molecule A and B, $(-1.0-x,-y,-z)$, H(3)′···Br = 3.00 (7) Å. The closest H···H intermolecular contacts are in the range of 2.32–2.46 Å.

Experimental Section

General Information. All the operations were performed under an atmosphere of nitrogen using recently dried solvents. Ether refers to diethyl ether. Melting points were determined by using sealed capillary tubes and are corrected; boiling points are uncorrected. IR spectra were obtained on a Perkin-Elmer 237B spectrometer as solutions in CCl_4, and absorption values are given in inverse centimeters (s, strong; m, medium; w, weak; br, broad). NMR spectra were recorded on Varian Model T-60A (60 MHz) and on a Nicolet/Oxford NT-300 (300 MHz) instruments. Unless otherwise stated, all spectra are at 300 MHz in $CDCl_3$ with tetramethylsilane as the internal standard, and absorptions are reported as δ values and J values in hertz (s, singlet; d, doublet; t, triplet; q, quartet; br, broad). Mass spectra were recorded on a Varian MAT CH7 instrument at 70 eV.

All preparative VPC was carried out by using a Varian Aerograph Model 920 gas chromatograph with one of the following columns: A, 25% QF-1, 2 ft × $^1/_4$ in.; B, 10% OV-101, 2 ft × $^1/_4$ in.; C, 10% OV-101, 5 ft × $^1/_4$ in. Analytical VPC was carried on a Varian Aerograph Model 1400 instrument with 5% OV-101, 5 ft × $^1/_8$ in. column. Flash column

(35) Keese, R.; Luef, W. Personal communication. We thank Prof Keese for permission to mention these unpublished results.

chromatography[20] was performed with 230–400-mesh silica gel (Merck, Type 600). Unless otherwise stated, all pure compounds were obtained as colorless oils. Standard workup means that the combined organic extracts were washed with saturated aqueous NaCl solution, dried over anhydrous $MgSO_4$, and filtered, and solvent was removed on rotary evaporator.

Preparation of Ethyl 3-Oxo-6-methylhept-6-enoate (17). Ethyl acetoacetate (26 g, 0.2 mol) was converted to its dianion and reacted with 1-chloro-2-methyl-2-propene (19 g, 0.21 mol) following the earlier described procedure.[19] The reaction mixture was stirred at room temperature for 16 h, and workup and distillation (76–77 °C, 0.2 mm) yielded pure product **17** (29 g, 79%). Spectroscopic properties were in substantial agreement with those reported.[19]

4-Carbethoxy-2-carbomethoxy-3-(3-methyl-3-butenyl)-2-cyclopenten-1-one (19). The anion generated from **17** (36.8 g, 0.2 mol) and NaH (4.8 g, 0.2 mol) in dimethoxyethane (250 mL) was reacted with methyl 4-bromoacetoacetate (20 g, 0.1 mol)[18] at −10 °C. Workup as described,[18] and extraction with ether yielded unreacted **17** (17.0 g, 92%) and product **19** as a gummy solid (26.8 g, 96%): IR 2995 (m), 2960 (m), 1728 (s), 1652 (m), 1598 (m), 1550 (m), 1450 (m), 1225 (s), and 1180 (s); NMR (60 MHz, CCl_4) δ 4.72 (br s, 2 H), 4.16 (q, J = 7 Hz, 2 H, CH_2CH_3), 3.8 (s, 3 H, OCH_3), 2.0-3.2 (m, 7 H), 1.8 (s, 3 H, CH_3), and 1.3 (t, J = 7, 3 H, CH_2CH_3). This was used without further purification in the following reaction.

Ethyl 2-(3-Methyl-3-butenyl)-4-oxo-2-cyclopentene-1-carboxylate (16). Keto diester **19** (26.8 g, 0.096 mol) in diglyme (80 mL) was mixed with acetic acid (7 mL) and NaI (40 g, 0.27 mol). The mixture was heated at reflux under N_2 until the evolution of the gas ceased (~15 min) and then cooled to room temperature. Workup as described[18] and distillation yielded pure keto ester (12.6 g, 59%; bp 80–82 °C, 0.02 mm). An analytical sample was prepared by preparative VPC (column B, 140 °C): IR 3195 (w), 3000 (m), 2955 (m), 1745 (s), 1725 (s), 1450 (m), 1370 (m), 1328 (m), 1260 (m), 1180 (s), 1030 (m), and 890 (m); NMR δ 6.05 (d, J = 1.3 Hz, 1 H, CHCO), 4.78 (s, 1 H), 4.72 (s, 1 H), 4.22 and 4.31 (two q, J = 7.1 Hz, 2 H, OCH_2) 3.65-3.80 (m, 1 H, $CHCO_2Et$), 2.45-2.80 (m, 4 H, CH_2CH_2) 2.28-2.40 (m, 2 H, CH_2CO), 1.75 (s, 3 H, CH_3), 1.29 (t, J = 7.1 Hz, 3 H, CH_2CH_3). Anal. ($C_{13}H_{18}O_3$) C, H.

(1*S,4β,6α,9α)- and (1*R**,4α,6β,9α)-Ethyl 4-Methyl-7-oxotricyclo[4.3.0.0^{1,4}]nonane-9-carboxylate (20 and 21).** A solution of **16** (6.0 g) in hexane (300 mL) was degassed by bubbling N_2 and irradiated at 25 °C, using uranium glass filter with a 450-W Hanovia lamp. VPC analysis (150 °C) indicated the completion of the reaction after 60 h and formation of one major product. Hexane was removed and crude photolysate was distilled to yield **20** and **21** (4.9 g, 82%; bp 94–96 °C, 0.1 mm). From ^{1}H NMR, this product was a 2:1 mixture of epimeric esters **20** and **21**. Ester **20** could be purified by flash chromatography; **21** was obtained pure from **23a** by deketalization and reesterification. For **20**: IR 2965 (m), 2875 (w), 1745 (s), 1440 (w), 1365 (w), 1340 (w), 1265 (m), and 1050 (w); NMR δ 4.11 and 4.05 (two q, J = 7.1 Hz, 2 H, OCH_2), 3.30 (dd, J = 1.4, 8.0 Hz, 1 H), 2.85 (ddd, J = 1.5, 5.1, 9.0 Hz, 1 H), 2.71 (dd, J = 7.9, 18.2 Hz, 1 H), 2.50-2.58 (m, 2 H), 1.97–2.34 (m, 4 H), 1.90 (ddd, J = 1.5, 5.1, 7.1 Hz, 1 H), 1.22 (t, J = 7.1 Hz, 3 H, CH_2CH_3), and 1.15 (s, 3 H, CH_3); mass spectrum, m/z 222.1254 (M^+, calcd for $C_{13}H_{18}O_3$, 222.1256). For **21**: IR 2990 (m), 2950 (m), 2870 (w), 1743 (s), 1443 (w), 1362 (w), 1338 (w), 1225 (w), 1201 (w), and 1165 (m); NMR δ 4.24 and 4.23 (two q, J = 7.1 Hz, 2 H, OCH_2), 3.12 (dd, J = 11.9, 18.4 Hz, 1 H), 2.67-2.89 (m, 3 H), 2.45-2.59 (m, 2 H), 1.9-2.17 (m, 4 H), 1.35 (t, J = 7.1 Hz, 3 H, CH_2CH_3), 1.08 (s, 3 H, CH_3); mass spectrum, m/z 222.1251 (M^+, calcd for $C_{13}H_{18}O_3$, 222.1256).

Ketalization of 20 and 21. The mixture of **20** and **21** (4.0 g, 18 mmol) was taken in benzene (150 mL) containing ethylene glycol (1 mL), and pyridinium tosylate (50 mg) was added. The resulting solution was heated at reflux for 8 h with azeotropic removal of water using Dean-Stark apparatus. Dilution with water and extraction with ether (2 × 100 mL) followed by standard workup yielded a 2:1 mixture **22d** and **23d** (4.4 g, 92%): IR 2950 (s), 2895 (m), 2855 (m), 1728 (s), 1445 (w), 1375 (w), 1340 (m), and 1180 (m); NMR (60 MHz, CCl_4) δ 3.6-4.4 (m, 6 H), 1.6-2.9 (m, 10 H), 1.30 (t, J = 7.2 Hz, CH_2CH_3 of **23d**), 1.24 (t, J = 7.2 Hz, CH_2CH_3 of **22d**), 1.05 (s, CH_3 of **22d**), and 1.01 (s, CH_3 of **23d**). Anal. ($C_{15}H_{22}O_4$) C, H.

(1*S,4β,6α,9α)- and (1*R**,4α,6β,9α)-Ethylene Ketals of 4-Methyl-7-oxotricyclo[4.3.0.0^{1,4}]nonane-9-carboxylic Acids (22a and 23a).** A solution of ketal esters **22d** and **23d** (4.1 g, 0.015 mol) in 10% aqueous methanol (45 mL) was stirred with KOH (2.8 g) for 20 h at room temperature. Solvent was removed under vacuum, and residue was diluted with water (100 mL). This solution was extracted with ether (2 × 50 mL) followed by acidifying to pH 4 with 3 M HCl and extraction with CH_2Cl_2 (2 × 100 mL). Standard workup of the combined organic layer yielded crude acid mixture. This was taken in a solution of ether–hexane (1:1, 30 mL) when most of the **22a** crystallized out (~1 g). The remaining acid mixture was subjected to flash chromatography. Eluting with 50% ether in hexane yielded **22a** and **23a** as colorless crystalline compounds. For **22a**: mp 136.5–137.5 °C; yield, 39%; IR 3350-2500 (br), 2950 (m), 2895 (m), 1710 (s), 1115 (w), and 800 (w); NMR δ 10.8 (br, 1 H, COO*H*), 3.90–4.03 (m, 4 H, OCH_2CH_2O), 3.82 (t, J = 5.9 Hz, 1 H), 2.82 (t, J = 5.1 Hz, 1 H), 2.61 (t, J = 7.5 Hz, 1 H), 2.26-2.36 (m, 2 H), 2.09-2.20 (m, 2 H), 1.84-1.93 (m, 3 H), and 1.05 (s, 3 H, CH_3). Anal. ($C_{13}H_{18}O_4$) C, H. For **23a**: mp 109–110 °C; yield, 17%; IR 3400-2500 (br), 2980 (m), 2955 (m), 2910 (m), 1708 (s), 1454 (w), 1337 (m), 1268 (m), 1113 (m), 1040 (w), and 847 (w); NMR 9.5 (br, 1 H, COO*H*), 3.75-3.97 (m, 5 H, OCH_2CH_2O and CH), 2.62-2.72 (m, 2 H), 2.56 (t, J = 7.0 Hz, 1 H), 2.46 (t, J = 13.2 Hz, 1 H), 1.86-2.16 (m, 5 H), and 1.07 (s, 3 H, CH_3). Anal. ($C_{13}H_{18}O_4$) C, H.

Conversion of Acid 22a to Acyl Chloride 22b and Diazoketone 22c. To a well-stirred solution of **22a** (1.19 g, 5 mmol) in dry benzene (10 mL) was added oxalyl chloride (0.76 g, 6 mmol) dropwise under N_2. The resulting mixture was stirred for 2 h at room temperature. Solvent was removed under vacuum to obtain acid chloride **22b**: IR 3120 (w), 3055 (m), 2900 (s), 2901 (m), 1815 (s), 1485 (m), 1345 (m), 1200 (s), 1120 (m), 1070 (w), and 925 (m). An ethereal solution of this material was added dropwise to a solution of excess of CH_2N_2 and Et_3N (0.55 g, 5 mmol) cooled in ice. The reaction mixture was left stirring for 16 h at room temperature, and ether was removed on a steam bath. The residue was dissolved in pentane (100 mL) and dried over $MgSO_4$. The pentane solution was filtered and solvent removed on rotary evaporator to yield the diazomethyl ketone **22c** as pale yellow oil (1.3 g), which was directly used in the next reaction; IR 3120 (m), 2950 (s), 2903 (m), 2880 (m), 2105 (s), 1625 (s), 1440 (w), 1360 (s), 1110 (m), 1065 (m), and 1014 (m).

(1α,3β,6α,9β)-4-Ethylene Ketal of 1-Methyltetracyclo[4.4.1.0^{3,11}.0^{9,11}]undecane-4,7-dione (24). Diazomethyl ketone **22c** (1.3 g) from the above reaction was dissolved in anhydrous CH_2Cl_2 (500 mL). To this well-stirred solution under N_2 was added rhodium(II) acetate[22] dimer (40 mg). Vigorous gas evolution was observed immediately and the solution turned a bright emerald green. Stirring was continued for 30 min, and the reaction mixture was diluted with 3% aqueous HCl (40 mL). Extraction with pentane (2 × 100 mL) followed by standard workup yielded the crude product which was flash chromatographed using 25% ether in hexane to obtain pure **24** (0.75 g, 64% overall yield from **22a**): mp 56–58 °C; IR 2950 (m), 2943 (m), 2908 (m), 1745 (s), 1440 (w), 1145 (w), 1080 (w), 1030 (m), and 945 (w); NMR δ 3.84-4.00 (m, 4 H, OCH_2CH_2O), 2.44-2.75 (m, 5 H), 1.80–2.30 (m, 5 H), 1.56-1.67 (m, 1 H), and 1.17 (s, 3 H, CH_3). Anal. ($C_{14}H_{18}O_3$) C, H.

Preparation and Decomposition of Diazoketone 23c. Diazomethyl ketone **23c** was prepared from ketal acid **23a** (0.24 g, 1 mmol) and reacted with rhodium(II) acetate (8 mg) following the procedure used for preparation of **24**. Vigorous gas evolution occurred immediately after adding rhodium acetate. Workup yielded crude residue which showed several spots on TLC (50% ether in hexane). Flash chromatography of this residue did not yield any identifiable products.

(1α,3β,6α,9β)-1-Methyltetracyclo[4.4.1.0^{3,11}.0^{9,11}]undecane-4,7-dione (26). A solution of ketone ketal **24** (0.117 g, 0.5 mmol) in 1% aqueous acetone (10 mL) was stirred with *p*-toluenesulfonic acid (30 mg) at room temperature. Progress of the reaction was monitored by TLC (33% ether in hexane) and was complete after 36 h. The reaction mixture was diluted with ether (100 mL) and washed with saturated $NaHCO_3$ solution. Standard workup and flash chromatography of the resulting residue with 33% ether in hexane as the eluent yielded pure **26** as a colorless crystalline solid (75 mg, 79%): mp 92-93 °C; IR 2950 (m), 1750 (s), 1420 (w), 1130 (w), and 865 (w); NMR δ 2.77-2.86 (m, 3 H), 2.58-2.72 (m, 4 H), 2.42-2.45 (m, 2 H), 2.17 (ddd, J = 1.3, 4.8, 13.1 Hz, 1 H), 2.03 (ddd, J = 1.2, 3.2, 13.0 Hz, 1 H), and 1.15 (s, 3 H, CH_3); ^{13}C NMR δ 215.9 (s), 213.79 (s), 53.74 (s), 47.62 (t), 44.29 (d), 41.04 (t), 40.44 (d), 39.77 (s), 39.28 (t), 35.65 (t), 30.85 (d), and 22.92 (q). Anal. ($C_{12}H_{14}O_2$) C, H.

(1α,3β,6α,9β)-1-Methyltetracyclo[4.4.1.0^{3,11}.0^{9,11}]undecane (25). Diketone **26** (95 mg, 0.5 mmol) was converted to diol and ditosylate following the procedure described below in the conversion of **24** to **30**. The ditosylate was reduced further by using $LiAlH_4$ (40 mg) in refluxing ether for 10 h. Workup as described below, and preparative VPC (column A, 70 °C) yielded pure hydrocarbon **25** (33 mg, 41% overall yield from **26**): IR 2960 (s), 2870 (s), 1445 (m), 1370 (w), 1280 (w), and 1210 (w); NMR 2.15-2.36 (m, 7 H), 1.89 (ddd, J = 5.7, 6.8, 12.3 Hz, 2 H), 1.4-1.6 (m, 4 H), 0.9-1.04 (m, 2 H), and 1.05 (s, 3 H, CH_3); ^{13}C NMR δ 66.97, 44.26, 40.77, 38.99, 37.71, 36.78, 34.92, and 24.31; mass spectrum, m/z 162.1415 (M^+, calcd for $C_{12}H_{18}$, 162.1408).

(1*S,4β,6α,9α)-4-Methyltricyclo[4.3.0.0^{1,4}]nonane-9-carboxylic Acid (27).** A solution of keto esters **20** and **21** (2.0 g, 9.0 mmol) and (*p*-toluylsulfonyl)hydrazine (1.7 g, 9.1 mmol) in absolute ethanol (6 mL) was acidified with concentrated HCl (3 drops) and left overnight while

stirring. TLC indicated the completion of the reaction. Solvent was removed, and residue dissolved in ether (30 mL) and passed through a plug of Florisil (8 g). Removal of ether yielded the tosylhydrazone as a viscous brown oil (3.1 g): IR 3225 (br) 2975 (s), 1725 (s), 1330 (m), 1240 (m), and 1152 (s). This was placed in a flame-dried, nitrogen-flushed flask containing $CHCl_3$ (12 mL), and catchecolborane (2.2 mL, 21 mmol) was added. The reaction mixture was stirred for 3 h, and methanol (2 mL) was added to destroy excess borane. The resulting solution was refluxed with NaOAc (1.0 g) and Me_2SO (3 mL) according to the procedure described.[22] Workup afforded a 2:1 mixture of epimeric esters (4-methyltricyclo[4.3.0.$0^{1,4}$]nonane-9-carboxylic acid ethyl ester) (1.1 g). A sample of this mixture was purified by preparative VPC (column B, 130 °C) for analytical purposes: IR 2950 (s), 2860 (m), 1728 (s), 1440 (m), 1370 (m), 1340 (m), 1150 (s), 1085 (w), and 1030 (m); NMR δ 4.11-4.22 (m, minor CH_2CH_3), 4.064, 4.058 (two q, J = 7.1 Hz, major CH_2CH_3), 2.6-2.8 (m, 2 H), 1.35-2.35 (m, 10 H), 1.30 (t, J = 7.1 Hz, minor CH_2CH_3), 1.22 (t, J = 7.1 Hz, major CH_2CH_3), 0.98 (s, major CH_3), 0.96 (s, minor CH_3). Anal. ($C_{13}H_{20}O_2$) C, H.

A solution of this mixture of esters (1.1 g) in 10% aqueous methanol (10 mL) was stirred with KOH (0.8 g) for 20 h. Removal of the solvent on rotary evaporator and acidic workup yielded crude acid, which was purified by flash chromatography with 50% ether in hexane to obtain pure **27** (0.34 g, 36%) as a viscous oil: IR 3350-2500 (br), 2950 (s), 2875 (m), 1704 (s), 1415 (m), 1195 (w), and 1130 (m); NMR δ 2.58-2.80 (m, 3 H), 1.1-2.4 (m, 10 H), 0.99 (s, 3 H, CH_3). Anal. ($C_{11}H_{16}O_2$) C, H.

Reesterification of **27** by way of the acyl chloride yielded the major isomer of the ester mixture described above.

Preparation and Decomposition of Diazomethyl Ketone from 27. Acid **27** (0.22 g, 1.2 mmol) was converted to the diazomethyl ketone (IR: 2100, 1650) by way of the corresponding acid chloride as described above.

To a well-stirred solution of the diazomethyl ketone (0.13 g, 0.64 mmol) in CH_2Cl_2 (10 mL) was added rhodium(II) acetate (15 mg). Vigorous evolution of gas started immediately and solution turned green. Stirring was continued for 1 h, and 3% aqueous HCl (10 mL) was added. Standard workup yielded residue (90 mg) which VPC analysis showed to be a mixture of several compounds in poor yield.

Preparation and Photolysis of Diazoketone 29b. To a solution of ketone ketal **24** (40 mg, 0.17 mmol), tetra-*n*-butylammonium bromide (15 mg), 18-crown-6 (3 mg), and 2,4,6-triisopropylphenylsulfonyl azide (105 mg, 0.34 mmol) was added 66% aqueous potassium hydroxide (3 mL). The mixture stirred vigorously for 30 min, further azide (105 mg) was added, and stirring continued for another 2 h. Extractive workup with ether as described[27] and preparative thin layer chromatography (Analtech "Uniplates", 20 × 20 cm precoated with silica gel GF, 2000 μL thick) with 50% ether in hexane yielded diazoketone **29b** (5.2 mg, 12%): IR 2950 (s), 2080 (s), 1675 (s), 1325 (m), 1265 (m), and 1095 (w); NMR δ (60 MHz, CCl_4), 3.8-4.0 (m, 4 H), 3.4-3.8 (m, 1 H), 1.3-3.1 (m, 8 H), and 1.1 (s, 3 H, CH_3). A degassed solution of **29b** (5 mg) in MeOH (3 mL) was irradiated through Pyrex with Hanovia 450-W mercury lamp for 3 h. Starting material disappeared, but no products could be isolated from the photolysate.

(1α,3β,6α,9β)-1-Methyltetracyclo[4.4.1.$0^{3,11}$.$0^{9,11}$]undecan-4-one (30). To a well-stirred suspension of $LiAlH_4$ (50 mg, 1.3 mmol) in anhydrous ether (20 mL) was added a solution of **24** (0.29 g, 1.24 mmol) in ether (10 mL). The reaction mixture was stirred at room temperature for 2 h followed by destroying excess of $LiAlH_4$ by careful addition of moist ether. The ether layer was separated, and solid residue was washed with ether (3 × 20 mL). Standard workup yielded the ketal alcohol (0.29 g) as a low melting solid: IR 3650 (m), 3350 (br), 2970 (m), 2940 (s), 1450 (w), 1250 (m), 1075 (m), 1030 (m), 945 (m), and 860 (m); NMR (60 MHz, CCl_4) δ 3.3-3.9 (m, 6 H), 1.05-2.4 (m, 11 H), and 1.1 (s, 3 H, CH_3). This crude alcohol was directly used in the next step.

To the alcohol (0.29 g) in dry pyridine (2 mL) at 0 °C was added *p*-toluenesulfonyl chloride (0.25 g, 1.3 mmol) in pyridine (1 mL). The reaction mixture was stirred at room temperature for 16 h during which time a white solid separated. The residue was diluted with ether (50 mL) and extracted with 10% aqueous acetic acid (2 × 20 mL) followed by saturated $NaHCO_3$ solution. Standard workup yielded the ketal tosylate as a white crystalline solid (0.45 g, 93%, mp 111-112 °C), which was directly used in the next step without further purification: IR 2975 (s), 2945 (s), 2900 (m), 1605 (m), 1440 (m), 1275 (s), 1120 (m), 1185 (s), 1180 (s), 1100 (m), 1010 (m), 960 (s), and 930 (m); NMR (60 MHz, CCl_4) δ 7.69 (d, J = 8 Hz, 2 H), 7.33 (d, J = 8 Hz, 2 H), 3.3-4.3 (m, 5 H), 1.1-2.6 (m, 11 H), 2.5 (s, 3 H, CH_3), and 1.1 (s, 3 H, CH_3).

A mixture of this tosylate (0.45 g, 1.15 mmol) in anhydrous THF (30 mL) and $LiAlH_4$ (60 mg) was heated at reflux under N_2 for 3 h. Excess hydride was destroyed by adding moist ether to the cooled reaction mixture. The organic layer was then diluted with ether (100 mL) and washed with saturated $NaHCO_3$ solution (40 mL). Standard workup yielded the ethylene ketal of **30** (0.21 g, 82%): IR 2950 (s), 2920 (s), 2840 (m), 1450 (w), 1260 (m), 1210 (w), 1075 (m), and 860 (m); NMR (60 MHz, CCl_4) δ 3.4-4.1 (m, 4 H) 1.0-2.3 (m, 13 H), and 1.01 (s, 3 H).

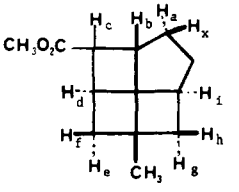
A solution of this ketal (0.21 g, 0.95 mmol) from the above reaction taken in 3% aqueous acetone (30 mL) was stirred with *p*-toluenesulfonic acid (30 mg) at room temperature. The progress of the reaction was monitored by VPC analysis (130 °C), and it was found to be complete after 20 h. Acetone was removed on rotary evaporator, and residue was dissolved in ether (100 mL). The organic layer was washed with saturated $NaHCO_3$ solution (30 mL) followed by standard workup to obtain crude compound, which was further purified by flash chromatography (10% ether in hexane) to yield pure ketone **30** (0.13 g, 78%), in an overall yield of 60% from **24**: IR 2965 (s), 2950 (s), 2870 (m), 1745 (s), 1450 (w), 1255 (w), and 1120 (w); NMR 2.70 (dd, J = 4.8, 7.65 Hz, 1 H), 2.40-2.49 (m, 4 H), 2.12-2.27 (m, 4 H), 2.03 (ddd, J = 1.4, 4.7, 12.9 Hz, 1 H), 1.64-1.73 (m, 1 H), 1.05-1.48 (m, 2 H), and 0.985 (s, 3 H, CH_3); mass spectrum, m/z 176.1212 (M^+, calcd for $C_{12}H_{16}O$, 176.1201).

Preparation and Photolysis of Diazoketone 31b. Ketone **30** (0.285 g, 1.6 mmol) in ethyl formate (1.2 mL) and ether (3 mL) was added dropwise to a suspension of NaH (90 mg of 50% oil dispersion, 1.87 mmol) in ether (10 mL) containing 3 drops of CH_3OH at 0 °C according to the published procedure.[25] The reaction mixture was stirred at 4 °C for 20 h. The resulting dark-brown mixture was diluted with water (20 mL) and the ether layer separated. The aqueous layer was acidified and extracted with ether (2 × 40 mL). Standard workup yielded hydroxymethylene compound **31a** (0.26 g, 80%) as a yellow gummy material, which solidified slowly: mp 109-110 °C; IR 2950 (m), 2920 (m), 1670 (s), 1440 (w), and 1375 (w).

This hydroxymethylene ketone (0.26 g, 1.27 mmol) was taken in CH_2Cl_2 (6 mL), and triethylamine (0.6 mL) was added. This solution was cooled in ice and treated with *p*-nitrobenzenesulfonyl azide (0.4 g, 1.75 mmol) in CH_2Cl_2 (5 mL) under N_2 atmosphere.[3] Workup afforded the diazoketone **31b** (90 mg, 35%) as a pale yellow oily liquid: IR 2955 (m), 2925 (m), 2860 (w), 2078 (s), 1675 (s), 1332 (m), 1300 (m), 1248 (m), 1205 (w), and 1190 (m); NMR (60 MHz, CCl_4) δ 3.3-3.6 (m, 1 H), 1.3-3.0 (m, 10 H), and 1.1 (s, 3 H, CH_3).

A methanol solution (3 mL) of this diazoketone (60 mg) was degassed and irradiated through Pyrex with a Hanovia 450-W mercury lamp for 3 h. The photolysate was diluted with water (10 mL) and extracted with pentane (2 × 30 mL); standard workup yielded an oily residue which contained three components by VPC (column B, 115 °C). The first component (trace) was not collected. The second component (20%) was identified as a 3:1 mixture of epimeric esters **32** and **33**, respectively: IR ($CDCl_3$) 2950 (s), 2920 (m), 2855 (m), 1723 (s), 1440 (m), 1350 (w), 1250 (m), and 1190 (m); mass spectrum, m/z 206.1316 (M^+, calcd for $C_{13}H_{18}O_2$, 206.1309). The third component (23%) was identified as **34**: IR ($CDCl_3$) 2950 (s), 2920 (s), 2855 (m), 1745 (s), 1445 (m), 1252 (m), 1205 (m), 1130 (m), and 1065 (w); NMR δ 3.80 (dd, J = 1.5, 4.1 Hz, 1 H, CH), 3.50 (s, 3 H, OCH_3), 2.81-2.86 (m, 1 H), 2.02-2.50 (m, 6 H), 1.62-1.79 (m, 2 H), 1.28-1.60 (m, 2 H), and 0.98 (s, 3 H, CH_3); ^{13}C NMR δ 215.06 (s), 90.44 (d), 57.91 (q), 52.63 (s), 40.67 (d), 40.32 (s), 39.71 (d), 38.64 (t), 38.56 (d), 37.36 (t), 36.35 (t), 35.65 (t), and 22.79 (q). Anal. ($C_{13}H_{18}O_2$) C, H.

Major ester **32** was purified by careful preparative VPC of the mixture of **32** and **33** (column C, 130 °C) or by careful flash chromatography (5% ether in pentane): IR ($CDCl_3$) 2955 (s), 2920 (m), 2860 (m), 1725 (s), 1445 (m), 1315 (w), 1292 (w), 1255 (m), 1200 (m), and 1174 (m); ^{13}C NMR δ 174.21 (s), 57.77 (s), 51.39 (q), 46.01 (d), 39.50 (t), 37.23 (t), 36.83 (d), 36.57 (t), 35.34 (d), 35.04 (t), 33.47 (s), 32.03 (d), and 23.70 (q); NMR δ 3.721 (s, OCH_3), 3.418 (dd, J_{cb} = 4.7, J_{cd} = 8.6 Hz, H_c), 2.885 (dd, J_{ef} = 13.6, J_{ed} = 7.2 Hz, H_e), 2.679 (dd, J_{gh} = 13.1, J_{gi} = 6.7 Hz, H_g), 2.396 (ddd, J_{fe} = 13.4, J_{fd} = 3.5, J_{fh} = 0.6 Hz, H_f), 1.85 (ddd, J_{hg} = 13.0, J_{hi} = 3.4, J_{hf} = 0.6 Hz, H_h), 2.487 (ddd, J_{dc} = 8.8, J_{de} = 7.0, J_{df} = 3.8 Hz, H_d), 2.535 (ddd, J_{bc} = 4.9, J_{bx} = 6.6, J_{ba} = 10.0 Hz, H_b), 2.2-1.98 (m, 3 H, H_i), 1.42-1.16 (m, 2 H), 1.116 (s, CH_3).



32 and 33

Ester **32** was further characterized by conversion into anilide **37** as described below and by reduction with lithium aluminum hydride in ether in the usual manner to yield 1α,3β,6α,7α,8β,10*S**)-7-(hydroxymethyl)-1-methyltetracyclo[4.3.1.$0^{3,10}$.$0^{8,10}$]decane (**36**): IR (CCl_4) 3630 (w), 3400 (br), 2955 (m), 2950 (s), 2910 (s), 1445 (w), 1260 (s), 1080

(m), and 1030 (m); NMR δ 3.96-3.82 (m, 2 H), 2.84 (dd, J = 7.50, 13.6 Hz, 1 H), 2.79-2.70 (m, 1 H), 2.70 (dd, J = 6.7, 13.0 Hz, 1 H), 2.34 (dd, J = 3.6, 13.7 Hz, 1 H), 2.20 (dt, J = 3.8, 7.6 Hz, 1 H), 2.07-1.96 (m, 3 H), 1.90-1.75 (m, 2 H), 1.4-1.1 (m, 3 H), and 1.07 (s, 3 H); mass spectrum CI, m/z 177.1257 [(M - 1)$^-$, calcd for $C_{12}H_{17}O$, 177.1279].

Although minor ester **33** could not be obtained pure, NMR spectra could be measured on enriched mixtures of **33** and **32**: ^{13}C NMR δ 173.84, 56.29, 51.39, 45.28, 32.50, 41.47, 36.73, 37.32, 37.44, 33.51, 33.36, 35.79, and 24.13; NMR δ 3.650 (s, OCH_3), 3.477 (dd J_{cb} = 4.5, J_{cd} = 7.8 Hz, H_c), 2.99 (dd, J_{ef} = 13.6, J_{ed} = 7.2 Hz, H_e), 2.68 (dd, J_{gh} = 13.0, J_{g}, = 7.1 Hz, H_g), 2.6-2.4 (m, H_b, H_d), 2.34 (ddd, J_{fe} = 13.5, J_{fd} = 3.3, J_{fh} = 0.9 Hz, H_f), 2.1-1.1 (m, 6 H), 1.110 (s, 3 H).

(1α,3β,6α,7α,8β,10S*)-*N*-(4-Bromophenyl)-1-methyltetracyclo-[4.3.1.0^{3,10}.0^{8,10}]decane-7-carboxamide (37). A 25% solution of trimethylaluminum (0.1 mL) was added to a CH_2Cl_2 (3 mL) solution of *p*-bromoaniline (41 mg) under N_2 atmosphere. This resulting mixture was stirred for 10 min at room temperature followed by adding ester **32** (5 mg) in CH_2Cl_2 (1 mL). Stirring was continued for 3 h, and the reaction was quenched by adding 5% aqueous HCl (5 mL). Extractive workup with ether yielded crude anilide, which was purified by flash chromatography by using 33% ether in hexane to obtain colorless crystalline anilide **37** (6 mg, 72%, mp 173-174 °C): mass spectrum CI, m/z 344.0656 [(M - 1)$^-$, calcd for $C_{18}H_{19}{}^{79}BrNO$, 344.0650]. Slow crystallization from acetonitrile in a cold room (~4 °C) over 2 weeks gave crystals, which were suitable for X-ray crystallography.

Crystal Data and Data Collection. *p*-$BrC_6H_4N(H)COC_{11}H_{15}$, M_r 346.27, triclinic, $P\bar{1}$, a = 7.619 (2) Å, b = 10.047 (2) Å, c = 21.691 (5) Å, α = 76.89 (2)°, β = 81.02 (2)°, γ = 89.64 (2)°. The unit cell volume is 1596.6 (6) Å^3, Z = 4, F(000) = 712, and the calculated density is ρ_{calcd} = 1.440 mg mm^{-3}. The cell chosen is the reduced basis.[36] A clear 0.35 mm × 0.075 mm × 0.03 mm crystal, bound by faces 010, 010, 001, 001, 101, 101, 101, and 101, was used for data collection. Data was collected on a Nicolet R3m automated diffractometer with an incident beam monochromator, λ = 1.541 78 Å (Cu Kα), at T = 295 K. Lattice parameters were determined from 22 centered reflections with 15 ≤ 2θ ≤ 55. The data collection range was -8 ≤ h ≤ 8, 0 ≤ k ≤ 10, and -23 ≤ l ≤ 23 with $\sin\theta/\lambda_{max}$ = 0.55 Å^{-1}. Three standards were monitored every 60 reflections and exhibited a linear 8% decrease over the data collection; a correction was made on this basis. A total of 4908 reflections was measured in the θ/2θ mode with a scan width of 2°; scan rate was a function of count rate (3°/min minimum, 30°/min maximum). There were 4367 unique reflections, R_{int} = 0.011 from merging equivalent reflections, 3248 observed with $F_o > 3\sigma(F_o)$. Lorentz and polarization corrections were applied and a numerical absorption correction was made, μ = 3.50 mm^{-1}, with maximum and minimum transmissions of 0.918 and 0.754, respectively.

Structure Solution and Refinement. The structure was solved by direct methods[37] with use of partial structure recycling.[38] The least-squares refinement program used program SHELXTL.[39] In the block-cascade least squares, the function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = 1/(\sigma^2(|F_o|) + g(F_o)^2)$ where $g(F_o)^2$ is included to account for random instrumental error (g is estimated to be 0.0004). There were 499 parameters refined, including the atom coordinates and the anisotropic temperature factors for all non-H atoms. The isotropic temperature factors for the hydrogens were fixed at 1.2 times the equivalent isotropic thermal parameters of the atom to which they were bonded. The final residuals were R = 0.057 and R_w = 0.055, with an error in an observation of unit weight of 1.33. The largest shift to error parameter in the final cycle was 0.07. The final difference Fourier excursions were -0.44 and 0.44 e Å^{-3} for the largest peaks which were located near the bromine atoms. Atomic scattering factors are from the International Tables for Crystallography.[40] The final values for the fractional coordinates of the hydrogen atoms, anisotropic temperature factors, and structure factor amplitudes are available as supplementary data.

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Supplementary Material Available: Fractional coordinates of hydrogen atoms, anisotropic temperature factors, and structure factor amplitudes for compounds (24 pages). Ordering information is given on any masthead page.

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Bicyclic, Boatlike Cope Rearrangements. Probe for Conformational Preference by the Nodal Carbon Atoms

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Abstract: 1,4-Bis(dideuteriomethylene)cyclohexane (**1d$_0$**) and -cycloheptane (**2d$_0$**) were rearranged thermally to 1,4-dimethylene-2,2,3,3-tetradeuteriocyclohexane (**1d$_4$**) and -cycloheptane (**2d$_4$**), respectively. The Arrhenius parameters for these intramolecular boatlike Cope rearrangements were determined for **1d$_0$**, $\log k_1 = (12.7 \pm 0.7) - (45\,600 \pm 1800)/\theta$, and for **2d$_0$**, $\log k_1 = (12.0 \pm 0.4) - (41\,900 \pm 1200)/\theta$. The activation enthalpy was expected to be as much as 9 kcal/mol higher than that of the boatlike Cope rearrangement of 1,5-hexadiene if the transition state of the boatlike Cope required planarity of the nodal (C_2 and C_5) carbon atoms of the allylic systems. The theoretical prediction of Dewar that the nodal carbon atoms should prefer a pyramidal conformation is confirmed. That the enthalpy of the transition state of the Cope rearrangement of **1d$_0$** and **2d$_0$** can be approximated by that of the conjugate noninteractive radicals, bicyclo[2.2.2]octa-1,4-diyl and bicyclo[3.2.2]nona-1,4-diyl, is supported by analysis of heats of formation. The relation of the Cope enthalpy surface of **1** to that of [2.2.2]propellane is explored.

As extensive as studies of the Cope rearrangement have been,[1] no attention to possible geometric demands of the "nodal" atoms appears prior to the contribution of Brown, Dewar, and Schoeller.[2] Their MINDO/2 studies reveal a diradical as transition state for both the boat- and chairlike Cope rearrangement in which, unexpectedly, the "nodal" atoms are partially tetrahedralized (pyramidalized) and their substituents are inclined inward toward

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