mechanism requires that some of the cobalt be deoxygenated in the membrane. The $P_{1/2}$ value for CoSDPT in solution is reported[14] to be $6.715 \times 10^3$ mmHg at 295 K. A more stable adduct forms in the polymer,[15] and its $P_{1/2}$ value determines the partial pressure of $O_2$ that can be attained on the lower pressure side before metal-facilitated enhancement ceases.

**Acknowledgment.** This research was supported by the Army CRDEC through the University of Florida Technology Center and the National Science Foundation (Grant 86 18766).

**Registry No.** $O_2$, 7782-44-7; polystyrene, 9003-53-6.

(14) Drago, R. S.; Cannady, J. P.; Leslie, K. A. *J. Am. Chem. Soc.* **1980**, *102*, 6014.
(15) Drago, R. S.; Gaul, J. H. *Inorg. Chem.* **1979**, *18*, 2019.

# Some Thermal and Photochemical Reactions of [4.4.4.5]Fenestranes

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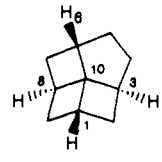
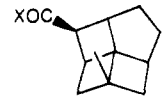
**Abstract:** Thermolysis of **8b** at 100 °C in benzene leads to isomerization to **12** and **14**, and **9b** furnishes **13** rather than **12**. Products **12** and **13** are regarded as resulting from a concerted $[{}_\pi 2_s + {}_\pi 2_s + {}_\pi 2_s]$ cycloreversion. In methanol **14** is replaced by solvent adduct **20**, and it is suggested that both **14** and **20** are secondary products resulting from further reaction of initially formed **16**. Photolysis of **8b** ($\lambda > 280$ nm) in benzene containing methanol gives small amounts of **20** and **21**, along with aldehyde **28**. The former arise through $\beta$-cleavage of the ketone, and **28** results from $\alpha$-cleavage, followed by bond scission and hydrogen transfer. Mechanistic explanations for these various reactions are supported by both molecular mechanics and MNDO calculations. Formation of these products demonstrates the role of the short, weak bonds to the central carbon atom C(10) in controlling reactions of these [4.4.4.5]fenestranes.

One incentive for preparation of novel strained systems is the opportunity to assess the effects of their structures on chemical transformations. For derivatives of [4.4.4.5]fenestrane (**1**), both



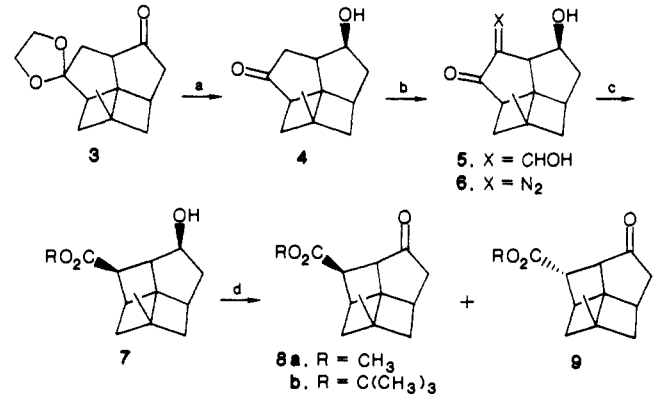

**1**




**2a**, X = *p*-$BrC_6H_4NH$
**b**, X = $CH_3O$

MNDO calculations[2] and the crystallographic structure of **2a**[3] indicate that the bond angles at the central quaternary carbon C(10) are opened from the normal value of ~109° to 128-129° and that bonds to this atom are unusually short, averaging 1.508 Å.[4] Keese has pointed out that, among systems with increased $sp^3$ bond angles, the fenestranes are essentially unique in that these changes occur almost solely through compression and involve little or no twisting.[5] We have now examined transformations in [4.4.4.5]fenestranes for evidence for the chemical effects of this skeletal distortion and report here studies of photolysis and thermolysis in this series. The results reveal a significant role in these reactions for the short, weak bonds to the central carbon atom of these compounds. In previous studies,[2] semiempirical MNDO calculations have provided rather accurate structural parameters for several fenestrane systems, and with this in mind we have employed both MNDO and molecular mechanics procedures as an aid in guiding and interpreting various aspects of this work.

Scheme I[a]




[a] Key: (a) $LiAlH_4$; TsOH, $H_2O$; (b) $HCO_2Et$, $CH_3O^-$;[3,7] **5**, $MsN_3$, $Et_3N$;[3,8,9] (c) **6**, *hν*, ROH;[3,10] (d) $OxCl_2$, DMSO, $Et_3N$.[11]

Preparation of the desired substrates proceeded as detailed in Scheme I, starting with the previously described[3] keto ketal **3**. The structure of major (~10:1) reduction product **4** was assigned as shown since in models of **3** approach of hydride to the carbonyl group appears less hindered from below; rigorous proof for this stereochemistry comes from an X-ray structure noted below.[6] As

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(2) Keese, R.; Luef, W., unpublished results. Luef, W. D. *Inauguraldissertation*, Universität Bern, Berne, Switzerland, 1985.
(3) Rao, V. B.; George, C. F.; Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1985**, *107*, 5732.
(4) A general review, including a discussion of nomenclature, is available: Venepalli, B. R.; Agosta, W. C. *Chem. Rev.* **1987**, *87*, 399. In the present work [4.4.4]fenestrane refers to tricyclo[4.2.0.0$^{1,4}$]octane, [4.4.5.5]fenestrane to (1,11-*syn*,1$\alpha$,3$\beta$,6$\alpha$,9$\beta$)tetracyclo[4.4.1.0$^{3,11}$.0$^{9,11}$]undecane, and [4.4.4.5]-fenestrane to (1,10-*syn*,1$\alpha$,3$\beta$,6$\alpha$,8$\beta$)tetracyclo[4.3.1.0$^{3,10}$.0$^{8,10}$]decane.
(5) Luyten, M.; Keese, R. *Tetrahedron* **1986**, *42*, 1687. Luef, W.; Keese, R. *Helv. Chim. Acta* **1987**, *70*, 543.
(6) Selective formation of **4** is in contrast with the behavior of *cis*-bicyclo[3.3.0]octan-2-one, where reduction with hydride reagents under a variety of conditions yields largely the endo alcohol: Fujita, K.; Hata, K.; Oda, R.; Tabushi, I. *J. Org. Chem.* **1973**, *38*, 2640.

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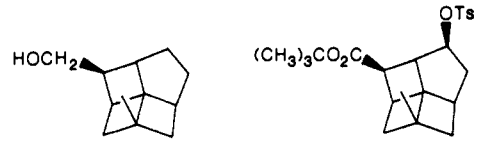
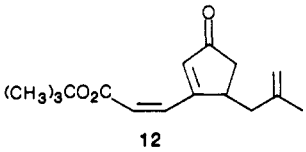
expected for the more congested isomer, **4** is less polar than the accompanying minor alcohol and moves more rapidly on chromatography. In this and subsequent steps, the major product was purified and characterized, but in general the diastereomeric mixture of alcohols was carried forward, since this asymmetric center is absent in the ultimately desired substrates. Protection of the hydroxyl group offered no advantage in conversion of **4** to **6**. Ring contraction of **6** in methanol or *tert*-butyl alcohol gave a mixture of hydroxy esters with **7** predominating. This mixture was oxidized to **8** and **9**. Reduction of **8b** using sodium borohydride gave **7b** unaccompanied by its epimer. Characteristics in the nuclear magnetic resonance (NMR) spectra of **8a,b** and **9a,b** assured that the same stereochemistry predominated regardless of whether methanol or *tert*-butyl alcohol was employed in the ring contraction. The indicated stereochemistry is that expected in analogy with ring contraction of the diazo ketone lacking the hydroxyl group of **6**, where in methanol the major product is **2b**;[3] a chemical correlation of the two series corroborated this conclusion. Keto ester **8a** was reduced with borohydride in methanol, and the resulting hydroxy ester was converted to the tosylate. Vigorous reduction of the tosylate by lithium aluminum hydride in hot tetrahydrofuran then furnished the (hydroxymethyl)fenestrane **10**, which proved to be identical with the alcohol previously obtained on reduction of **2b**.[3] These stereochemical assignments for **8** and **9**, as well as for the hydroxyl group of **4**, were confirmed by an X-ray crystallographic structure determination on **11**, the tosylate of **7b**.




10




11

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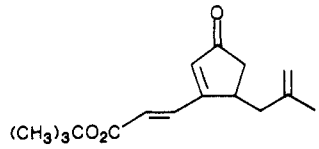
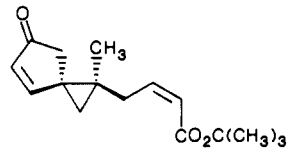
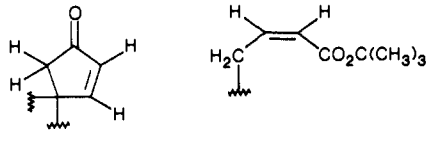
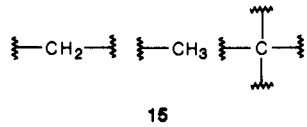



13



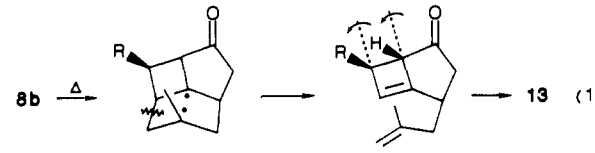

14

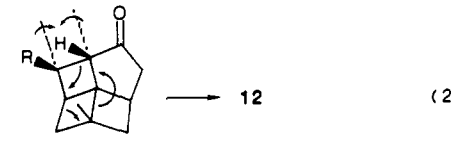



15

**Thermolysis.** At 100 °C in benzene **8b** undergoes isomerization to two products. The first of these (15%) is keto ester **12**, the structure of which was apparent from its infrared (IR) and proton NMR spectra, which are reported in the Experimental Section. Isolation of only **12** implied that formation of the *Z* double bond is stereospecific, and this conclusion was verified through thermolysis of the epimeric ester **9b**, which yielded only the corresponding *E* isomer **13**.[12] Such stereospecificity suggests that a symmetry-allowed process operates in formation of **12** and **13**, and we consider two possible mechanisms. The first, shown in eq 1, involves stepwise homolysis of the C(1)–C(10) bond in **8b**,



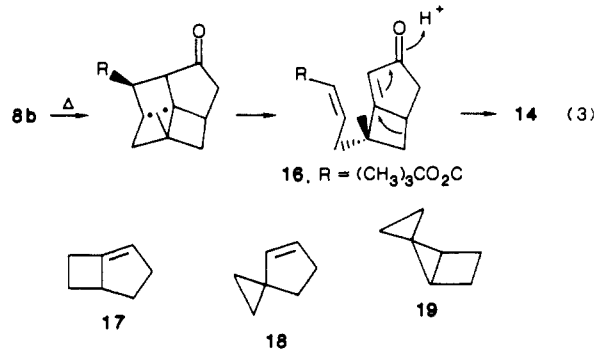




**8b**, R = $(CH_3)_3CO_2C$

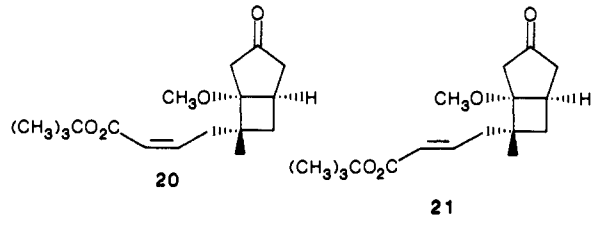
fragmentation, and then opening of the cyclobutene. Numerous studies have shown that the thermal ring opening of cyclobutenes follows a conrotatory path,[13] and in the present case, owing to the fused five-membered ring that will incorporate one of the double bonds being formed, conrotatory opening can only occur with outward rotation of the ester grouping, as shown. This path then predicts formation of **13** from **8b**, contrary to observation. The second mechanism, however, is more satisfactory. This is a symmetry-allowed $[{}_{\pi}2_s + {}_{\pi}2_s + {}_{\pi}2_s]$ thermal cycloreversion proceeding directly from **8b** to the product (eq 2) and requiring that the motion of the hydrogen atom and ester group at C(6) and C(7), respectively, be disrotatory inward.[14] The fenestrane skeleton imposes on the six reacting carbon atoms [C(1) and C(6)–C(10)] a rigid-boat cyclohexane geometry that is ideal for such concerted fragmentation,[14] and this pathway leads specifically to the observed products **12** and **13** from **8b** and **9b**, respectively. We conclude then that formation of these isomers is a concerted [2 + 2 + 2] cycloreversion involving one of the weak central bonds and two peripheral cyclobutane bonds of the fenestrane.

The constitution of the second product (45%) from thermolysis of **8b** was surprising. Apart from stereochemistry, we could deduce structure **14** for this substance from its spectroscopic properties, which reflect the structural features illustrated in **15**. IR and NMR spectra imply a 4,4-disubstituted cyclopentenone and a 4-substituted *tert*-butyl (*Z*)-crotonate,[15] a methyl group appears at $\delta$ 1.19 (s, 3 H), and an isolated aliphatic methylene group exhibits an AB quartet at 1.425 ($\nu$ 0.01, $J$ = 5.6 Hz); the NMR spectrum also indicates that the crotonate is bonded to saturated carbon bearing no hydrogen. The structural features in **15** account for all hydrogen atoms, and the quaternary carbon atom is deduced by difference. These data lead directly to **14**. This conclusion was substantiated, and the stereochemistry about the cyclopropane ring was established, by an X-ray crystallographic study of the derived red 2,4-dinitrophenylhydrazone. A purely homolytic pathway to **14** presents problems that are noted below, and the simplest mechanism that we have considered for this transformation combines homolytic and heterolytic steps, as shown in eq 3. Homolysis of the C(8)–C(10) bond in **8b** and fragmentation lead to **16**,[16] a derivative of highly strained[17] bicyclo[3.2.0]-

(7) Ainsworth, C. *Organic Syntheses*; Wiley: New York, 1963; Collect. Vol. IV, p 536.
(8) Reagan, M. T.; Nickon, A. *J. Am. Chem. Soc.* **1968**, *90*, 4096. Lowe, G.; Ridley, D. D. *J. Chem. Soc., Chem. Commun.* **1973**, 328. Taber, D. F.; Ruckle, R. E., Jr.; Hennessy, M. J. *J. Org. Chem.* **1986**, *51*, 4077.
(9) Regitz, M. *Angew. Chem.* **1967**, *79*, 786; *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 733. Regitz, M. *Synthesis* **1972**, 351.
(10) Wiberg, K. B.; Furtek, B. L.; Olli, L. K. *J. Am. Chem. Soc.* **1979**, *101*, 7675.
(11) Mancuso, A. J.; Huang, S.-L.; Swern, D. *J. Org. Chem.* **1978**, *43*, 2480.
(12) Assignment of stereochemistry in these esters follows from their NMR spectra; $J_{\alpha,\beta}$ is 12.6 Hz in **12** and 16.3 Hz in **13**.
(13) Extensive references are given by: Marvell, E. N. *Thermal Electrocyclic Reactions*; Academic: New York, 1980; Chapter 5.
(14) Woodward, R. B.; Hoffmann, R. *Angew. Chem.* **1969**, *81*, 797; *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781. The example adduced by Woodward and Hoffmann to illustrate this process was boat cyclohexane.
(15) IR 1725 (s), 1716 (s), 1645 (w) $cm^{-1}$; NMR $\delta$ 7.46 (d, $J$ = 5.7 Hz, 1 H), 6.14 (d, $J$ = 5.7 Hz, 1 H), 2.56 (d, $J$ = 19.2 Hz, 1 H), and 2.24 (d, $J$ = 19.2 Hz, 1 H) for the ketone and 6.10 (ddd, $J$ = 7.3, 7.3, 11.6 Hz, 1 H), 5.76 (ddd, $J$ = 1.8, 1.8, 11.5 Hz, 1 H), 2.97 (ddd, $J$ = 1.8, 7.0, 16.1 Hz, 1 H), 2.74 (ddd, $J$ = 1.5, 7.5, 16.4 Hz, 1 H), and 1.48 (s, 9 H) for the ester.



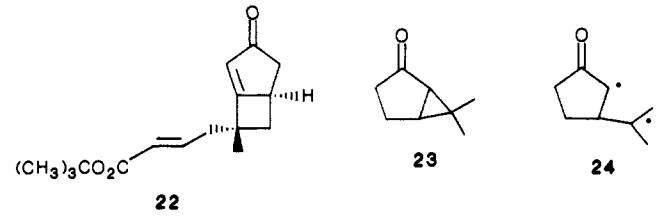

hept-1-ene (**17**). Under catalysis by adventitious acid, **16** could then undergo a 1,2 alkyl shift, as shown, to form **14**.[18] This mixed mechanism was attractive for several reasons. Any simple pathway leading to **14** must incorporate a ring contraction to furnish the spiro-fused cyclopropane, but 1,2 alkyl shifts in radical systems are rare or nonexistent.[19] In fact, although **17** is quite strained, this hydrocarbon itself is thermally stable to 150 °C. On thermolysis it gives products totally different from **18**, which is the parent hydrocarbon of the spiro system present in **14**.[20,21] A homolytic pathway from **16** to **14** by way of a spiropentane-containing isomer can be written, but this is also unlikely, as the parent spiropentane hydrocarbon **19** rearranges in the reverse direction at 150 °C to form **17**.[21] In contrast to these objections, the acid-catalyzed shift in eq 3[18] is mechanistically unexceptional. These conclusions concerning the feasibility of various rearrangements in derivatives of **17**–**19** are buttressed by molecular mechanics and MNDO calculations; these suggest that isomerization of **17** to **18** is exothermic and that isomerization of **17** to **19** is endothermic by ~25 kcal/mol.[22,23] Most importantly, two experimental observations support the mechanism proposed in eq 3. Thermolysis of **8b** in benzene at 100 °C as before, but in a stirred solution containing solid sodium bicarbonate, yielded **12** but no **14**, and when the reaction was carried out in methanol rather than benzene as solvent, the product was **20**, the compound



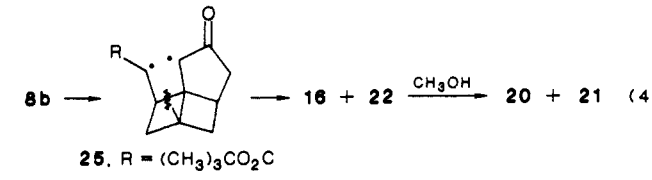

expected[24] from conjugate addition of methanol to **16**. The structure of **20** could be assigned from examination of its IR and NMR spectra, which are given in the Experimental Section. We conclude then that the initial major thermal product from **8b** is **16** and that this does not survive the reaction conditions but can be trapped as **14** or **20**.

We turn now to details of the formation of **16** from **8b**. It is noteworthy that both of the isolated products **14** and **20** are *Z* $\alpha,\beta$-unsaturated esters; *E* ester **21** was independently available, as we discuss below, but was not found on thermolysis of **8b** in methanol. Formation of **16** then is stereospecific, but a concerted pathway providing the observed stereochemistry from cleavage of the cyclobutane would necessarily be a symmetry-forbidden $[{}_{\pi}2_s + {}_{\pi}2_s]$ process.[14,25] However, the strained, rigid skeleton of **8b** provides just the sort of system that should favor a low-energy diradical pathway for this reaction.[14,26] Scission of the weak C(8)–C(10) bond in **8b** (eq 3) furnishes a diradical that is still relatively rigid, and its direct fragmentation without prior conformational inversion to the chair 1,4-cyclohexanediyl will lead to **16**.[27] This transformation then can be understood as a stereospecific diradical reaction in which the exceptional feature is the structurally favored fragmentation of a boat cyclohexanediyl. We note finally that the thermal rearrangements of **8b** to **12** and to **16** involve rupture of either C(1)–C(10) or C(8)–C(10), the two short central bonds expected to be weakest.[28]

**Photolysis.** Turning now to photochemistry, we found that irradiation of **8b** through Pyrex ($\lambda > 280$ nm) in benzene containing ~7% methanol led to three isolated products. Two of these were the *Z*- and *E*-unsaturated esters **20** and **21** (~5% each). We infer that initially **16** and its *E* isomer are formed and that these



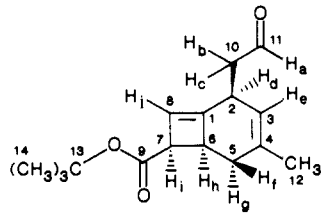

are trapped as above by Michael addition of methanol. In the photochemical reaction then both geometric isomers of the unsaturated ester are formed; this appears mechanistically reasonable and ultimately attributable to the exceptional strain in the [4.4.4.5]fenestrane system. Irradiation of **8b** leads to an $n\pi^*$ state of the ketone carbonyl and then cleavage of the C(6)–C(7) bond to form diradical **25** (eq 4). Such $\beta$-cleavage is not unusual in




the photochemistry of cyclopropyl ketones, where its occurrence is attributed to strain and its effective competition with $\alpha$-cleavage depends on specific substitution pattern;[29] photolysis of 6,6-dimethylbicyclo[3.1.0]hexan-2-one (**23**), for example, leads to **24**.[30] The strain inherent in **8b** apparently is sufficient to permit such $\beta$-cleavage of a cyclobutane, although simple acylcyclobutanes do not behave in this fashion. To account for formation of both **20** and **21**, it is necessary only that rotation and inversion at the unhindered side chain radical center of **25** be more rapid than fragmentation to the diene.

(16) These first two steps are discussed in more detail below.
(17) Schleyer, P. v. R.; Maier, W. *J. Am. Chem. Soc.* **1981**, *103*, 1891.
(18) Alternatively, protonated **16** can undergo an initial 1,2 hydride shift, followed by ring contraction of the cyclobutane in the opposite direction. The product, including predicted stereochemistry, is again **14**, although the order of carbon atoms is changed.
(19) Wilt, J. W. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, Chapter 8.
(20) Moss, R. A.; Whittle, J. R. *J. Chem. Soc. D* **1969**, 341.
(21) Roth, W. R.; Enderer, K. *Ann.* **1970**, *733*, 44.
(22) Molecular mechanics gives $H_f$ = 42.5 (**17**), 31.6 (**18**), and 66.4 kcal/mol (**19**); MNDO gives $H_f$ = 24.3 (**17**), 23.7 (**18**), and 53.3 kcal/mol (**19**). The published molecular mechanics $H_f$ for **17** is 44.5 kcal/mol.[17]
(23) Molecular mechanics calculations made use of MMPMI, an adaptation by J. J. Gajewski and K. E. Gilbert (Midland, M. M. *J. Am. Chem. Soc.* **1986**, *108*, 5042) of MM2 (Allinger, N. L.; Yuh, Y. H. *QCPE* **1981**, *13*, 395) with $\pi$-subroutines from MMI/MMPI (Allinger, N. L.; et al. *QCPE* **1976**, *11*, 318). MNDO calculations made use of a revision by K. E. Gilbert and J. J. Gajewski of MNDO (Thiel, W. *QCPE* **1978**, *11*, 353).
(24) House, H. O.; DeTar, M. B.; VanDerveer, D. *J. Org. Chem.* **1979**, *44*, 3793.
(25) Goldstein, M. J.; Benzon, M. S. *J. Am. Chem. Soc.* **1972**, *94*, 5119 and references cited therein.
(26) Paquette, L. A.; Thompson, G. L. *J. Am. Chem. Soc.* **1971**, *93*, 4920.
(27) Paquette, L. A.; Schwartz, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 3215. This paper is a report of thermolysis of the three dimethyl bicyclo[2.2.0]butane-2,3-dicarboxylates, reactions interpreted as involving diradical intermediates that do relax to chair cyclohexanediyls before fragmentation. The stereochemical result, formally $[{}_{\pi}2_s + {}_{\pi}2_a]$, is the opposite of that observed in formation of **16**.
(28) (a) Wiberg, K. B.; Olli, L. K.; Golembeski, N.; Adams, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 7467. (b) Wolff, S.; Agosta, W. C. *J. Chem. Soc., Chem. Commun.* **1981**, 118. Wolff, S.; Agosta, W. C. *J. Org. Chem.* **1981**, *46*, 4821.
(29) Cowan, D. O.; Drisko, R. L. *Elements of Organic Photochemistry*; Plenum: New York, 1976; Chapter 4, and references cited therein.
(30) Dauben, W. G.; Schutte, L.; Schaffer, G. W.; Gagosian, R. B. *J. Am. Chem. Soc.* **1973**, *95*, 486.

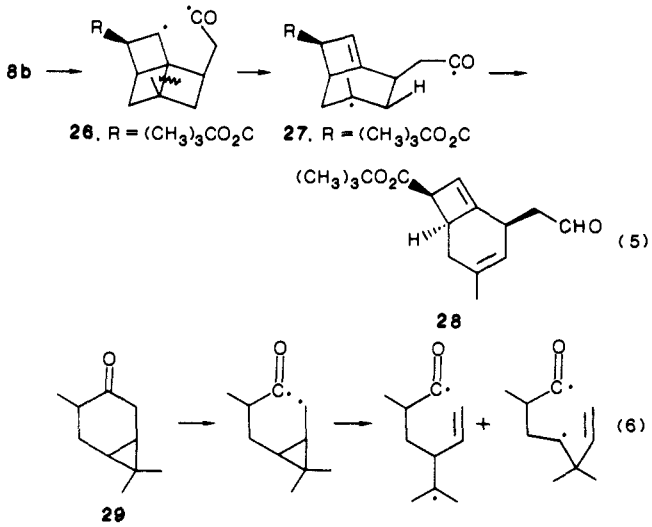
Table I. $^1H$ and Off-Resonance Decoupled $^{13}C$ NMR Spectra of **28**



| $^1H$ chem shift, $\delta$ | mult | coupling const, Hz | assgnt | $^{13}C$ chem shift, $\delta$ | mult | assgnt |
|---|---|---|---|---|---|---|
| 9.83 | dd | $J_{ab} = J_{ac} = 1.6$ | $H_a$ | 201.58 | d | C(11) |
| 5.67 | d | $J_{dj} = 2.3$ | $H_j$[a] | 171.84 | s | C(9) |
| 5.27 | br s | | $H_e$ | 153.59 | s | C(1) |
| 3.69 | dd | $J_{di} = J_{hi} = 4.0$ | $H_i$[a] | 135.56 | s | C(4) |
| 3.33 | br m | $J_{bd} = 7.1$, $J_{cd} = 6.0$ | $H_d$ | 122.19, 122.02 | d | C(8), C(3) |
| | | $J_{dg} \sim 0.75$, $J_{dh} = 1.5$ | | | d | |
| | | $J_{di} = 4.0$, $J_{dj} = 2.3$ | | 80.43 | s | C(13) |
| 3.04 | dddd | $J_{dh} = 1.6$, $J_{fh} = 7.5$ | $H_h$ | 48.34 | d | C(7) |
| | | $J_{gh} = 9.9$, $J_{hi} = 4.5$ | | 46.08 | dt | C(10) |
| 2.66 | ddd | $J_{ab} = 1.6$, $J_{bd} = 7.1$, $J_{bc} = 17.5$ | $H_b$ | 40.20 | d | C(2) |
| 2.52 | ddd | $J_{ac} = 1.6$, $J_{cd} = 6.0$, $J_{bc} = 17.5$ | $H_c$ | 32.43 | t | C(5) |
| 2.12 | dd | $J_{fh} = 7.6$, $J_{fg} = 16.5$ | $H_f$ | 31.11 | d | C(6) |
| 1.99 | dddd | $J_{dg} > 0.8$, $J_{eg} > 0$ | $H_g$ | 28.24 | q | C(14) |
| | | $J_{fg} = 16.5$, $J_{gh} = 9.7$ | | 24.37 | q | C(12) |
| 1.69 | br s | | $CH_3$ | | | |
| 1.46 | s | | $(CH_3)_3C$ | | | |

[a] From COSY spectrum, $J_{ij} \neq 0$; see text.

The major product (36%) from irradiation of **8b** is aldehyde **28**. This structural assignment rests on NMR measurements presented in Table I and mechanistic considerations offered later. The NMR data include proton spin–spin decoupling experiments that permit assignment of all observed couplings and yield virtually the complete connectivity of the compound, and also an off-resonance decoupled $^{13}C$ spectrum in excellent accord with expectation for **28**. We note that two vicinal couplings are absent from the reported proton spectrum. Although $H_d$ shows six measurable couplings, $J_{de} = 0$, presumably indicating flattening of the cyclohexene ring and a small dihedral angle between $H_d$ and $H_e$. The other vicinal coupling absent in Table I involves $H_i$ and $H_j$; in other cyclobutenes this coupling is typically 0–1.5 Hz,[31] and a two-dimensional (COSY) spectrum of **28** reveals that $H_i$ and $H_j$ are in fact coupled. Formation of **28** requires $\alpha$-cleavage of the ketone toward the adjacent four-membered ring, subsequent homolysis of the C(1)–C(10) bond, and then hydrogen transfer (eq 5). This mechanistically satisfactory sequence provides good




support for the structural assignment and also raises an interesting point. Typically, type I cleavage of cyclobutyl ketones takes place preferentially away from the four-membered ring or else gives both possible products, as formation of a cyclobutyl radical is somewhat disfavored.[32] Cleavage of **8b** on either side of the ketone carbonyl would provide relief of strain, since the [4.4.4]fenestrane skeleton resulting in either case is considerably less strained than the [4.4.4.5] system.[33] Additional stabilization, however, is available from conversion of **26** to **27**,[34] and it is possible that the existence of this favorable second step influences the direction of $\alpha$-cleavage. Similar selectivity exists in the photochemistry of certain $\beta,\gamma$-cyclopropyl ketones, such as *cis*- and *trans*-caranone (**29**), that undergo specific, stepwise $\alpha$-cleavage toward the cyclopropane followed by opening of the three-membered ring (eq 6), even though this requires initial scission of the less substituted $\alpha$-bond prior to the energetically favorable second step.[35,36] In the cyclopropyl ketones this happens presumably because the cyclopropane ring weakens the appropriate bond $\alpha$ to the carbonyl group by conjugative or inductive effects;[35] the behavior of **8b** suggests that the bond suffering initial $\alpha$-cleavage here [C(5)–C(6)] is also relatively weak.

## Experimental Section

**General Information.** Most procedures and equipment have been described previously.[3] High-field NMR spectra were obtained on a GE GN-500 (500 MHz for hydrogen) spectrometer. High-resolution mass spectra were obtained in EI or CI modes, as convenient. For CI spectra, the ionizing gas was isobutane for positive-ion spectra and $N_2O/CH_4$ for negative-ion spectra. All purified products were obtained as colorless oils unless otherwise indicated. Tables of fractional coordinates and anisotropic thermal parameters have been deposited with the Crystallographic

(31) For example: Trost, B. M.; McDougal, P. G. *J. Org. Chem.* **1984**, *49*, 458. Birkofer, L.; Eichstädt, D. *J. Organomet. Chem.* **1986**, *307*, 279.

(32) Fallis, A. G. *Can. J. Chem.* **1975**, *53*, 1657. Hobbs, P. D.; Magnus, P. D. *J. Am. Chem. Soc.* **1976**, *98*, 4594.

(33) Molecular mechanics calculations[28a] give a difference in strain energy of 19 kcal/mol between the two systems, probably as an upper limit. In good agreement, we calculate a difference of ~17 kcal/mol based on MNDO[23] $H_f$ values for **1** (36.5 kcal/mol) and [4.4.4]fenestrane (16.5 kcal/mol) and approximate corrections for the difference in molecular composition.

(34) We estimate fragmentation of **26** to **27** to be ~6 kcal/mol exothermic. Conversion of a cyclobutyl radical to an unstrained *tert*-alkyl radical provides ~3 kcal/mol (McMillen, D. F.; Golden, D. M.; Benson, S. W. *Int. J. Chem. Kinet.* **1972**, *4*, 487. Castelhano, A. L.; Griller, D. *J. Am. Chem. Soc.* **1982**, *104*, 3655.), and MNDO $H_f$ values[23,33] suggest that bicyclo[4.2.0]oct-6-ene (13.4 kcal/mol) is ~3 kcal/mol more stable than [4.4.4]fenestrane (16.5 kcal/mol).

(35) Heckert, D. C.; Kropp, P. J. *J. Am. Chem. Soc.* **1968**, *90*, 4911.

(36) Carson, M. S.; Cocker, W.; Evans, S. M.; Shannon, P. V. R. *Tetrahedron Lett.* **1968**, 6153. Takakis, I. M.; Agosta, W. C. *J. Am. Chem. Soc.* **1979**, *101*, 2383.

Data Centre, Cambridge CB2 1EW, England. Crystallographic data are also available as supplementary material.

**Preparation of 5β-Hydroxy-1-methyl[4.4.5.5]fenestran-8-one (4).** To a well-stirred suspension of $LiAlH_4$ (0.2 g) in anhydrous ether (150 mL) at 0 °C was added a solution of keto ketal **3**[3] (0.63 g, 2.7 mmol) in ether (20 mL). The reaction mixture was stirred at 0 °C for 0.5 h followed by warming to room temperature and stirring for another 2 h. Unreacted $LiAlH_4$ was destroyed by careful addition of moist ether. The ether layer was separated, and solid residue was washed with ether (3 × 30 mL). Standard workup yielded the ethylene ketal of **4**, which was directly used in the next step.

A solution of this ketal in 3% aqueous acetone (30 mL) was stirred with *p*-toluenesulfonic acid (50 mg) at room temperature for 20 h. Acetone was removed on a rotary evaporator, and the residue was taken up in ether (250 mL). This was washed with saturated $NaHCO_3$ solution followed by brine to obtain a crude product that was further purified by flash chromatography (20% hexane in ether) to yield pure **4** as a colorless solid: mp 90–91 °C; 0.31 g (overall yield 60%); IR 3610 (br), 3400 (br) 2955 (s), 2920 (s), 2850 (s), 1750 (s), 1453 (m), 1170 (w), 1080 (m) $cm^{-1}$; NMR δ 3.91 (ddd, *J* = 4.42, 7.42, 11.28 Hz, 1 H, C*H*OH) 2.69 (ddd, *J* = 0.81, 4.33; 8.26 Hz, 1 H), 2.57 (dd, *J* = 7.98, 16.45 Hz, 1 H), 2.52–2.16 (m, 5 H), 2.33 (ddd, *J* = 1.4, 9.30, 16.58, 1 H), 2.04 (ddd, *J* = 1.35, 4.64, 13.02 Hz, 1 H), 1.85–1.61 (m, 3 H), 1.06 (s, 3 H, $CH_3$). Anal ($C_{12}H_{16}O_2$) C, H.

**Preparation of 7-Diazo-5β-hydroxy-1-methyl[4.4.5.5]fenestran-8-one (6).** Keto alcohol **4** (0.35 g, 1.87 mmol) in ethyl formate (1.5 mL) and ether (10 mL) was added dropwise to a suspension of NaH (0.17 g of 50% oil dispersion, 4 mmol) in ether (50 mL) containing methanol (2 drops) at 0 °C. The reaction mixture was brought to room temperature slowly and stirred for 20 h. The dark brown mixture thus obtained was diluted with water (30 mL) and the ether layer separated. The aqueous layer was acidified and extracted with ether (2 × 30 mL); standard workup yielded hydroxymethylene compound **5** (0.29 g, 73%) as a gum.

A solution of **5** in $CH_3CN$ (10 mL) was cooled in ice bath, and triethylamine (0.5 mL) was added. To this cold solution under nitrogen was added methylsulfonyl azide[8,9] (0.2 g, 1.65 mmol) dropwise, and the mixture was stirred at room temperature for 5 h. Solvent was removed under vacuum, and the residue was purified by flash chromatography (20% hexane in ether) to obtain diazo compound **6** as yellow crystals: 0.15 g (53%); mp 146–147 °C; IR, 2080 $cm^{-1}$. This was used without further purification in the following reaction.

**Methyl 5β-Hydroxy-1-methyl[4.4.4.5]fenestrane-7β-carboxylate (7a).** Diazo compound **6** (0.13 g, 0.6 mmol) was dissolved in methanol (10 mL), and the solution was degassed and irradiated through Pyrex with a Hanovia 450-W mercury lamp for 3 h. Solvent was removed, and the residue was purified by careful flash chromatography (33% hexane in ether) to obtain a mixture of esters **7a** and its 7α-epimer in a 3:1 ratio (0.045 g (34%)). This mixture was best separated after oxidation. However, pure **7a** could be obtained by careful flash chromatography using 33% hexane in ether as eluent: IR 3400 (br), 2950 (s), 2920 (s), 1725 (s), 1430 (m), 1310 (m) $cm^{-1}$; NMR δ 4.16 (ddd, *J* = 4.4, 8.0, 10.4 Hz, 1 H), 3.72 (s, 3 H), 3.61 (dd, *J* = 4.8, 8.2 Hz, 1 H), 2.87 (dd, *J* = 7.24, 13.77, 1 H), 2.77 (dd, *J* = 7.05, 12.86, 1 H), 2.21–2.55 (m, 6 H), 1.92–2.1 (m, 2 H), 1.19 (s, 3 H); mass spectrum, *m/z* 221.1137 [(M − 1)$^+$, calcd for $C_{13}H_{17}O_3$, 221.1178].

***tert*-Butyl 5β-Hydroxy-1-methyl[4.4.4.5]fenestrane-7α- and -7β-carboxylate (7b). A.** A solution of diazo ketone **6** (0.104 g, 0.48 mmol) and 15% *tert*-butyl alcohol in benzene (30 mL) was degassed and irradiated in Pyrex with a Hanovia 450-W mercury lamp for 3 h. Solvent was removed under vacuum, and the residue was purified by flash chromatography. Careful and slow elution with 40% ether in hexane yielded the 7α-epimer (0.006 g (5%)) followed by the 7β-compound (**7b**) (0.047 g (37%)). For **7b**: IR 3600 (br), 3400 (br), 2950 (s), 2910 (s), 1725 (s), 1370 (s), 1263 $cm^{-1}$; NMR δ 4.13 (ddd, *J* = 4.42, 7.99, 10.05, 1 H), 3.50 (dd, *J* = 4.78, 8.33 Hz, 1 H), 2.85 (dd, *J* = 6.86, 13.26 Hz, 1 H), 2.76 (dd, *J* = 6.96, 12.79, 1 H), 1.5–2.5 (m, 8 H), 1.48 (s, 9 H), 1.19 (s, 3 H); mass spectrum, *m/z* 263.1643 [(M − H)$^-$, calcd for $C_{16}H_{23}O_3$ 263.1647]. For 7α-epimer: IR 3600 (b), 3300 (br), 2940 (s), 2910 (s), 1725 (s), 1370 (m), 1150 (s) $cm^{-1}$; NMR δ 4.22 (ddd, *J* = 4.32, 8.1, 10.17 Hz, 1 H), 3.43 (dd, *J* = 4.31, 7.6 Hz, 1 H), 3.04–3.05 (m, 1 H), 2.99 (dd, *J* = 6.96, 13.4, 1 H), 2.77 (dd, *J* = 8.49, 14.25, 1 H), 1.98–2.42 (m, 7 H), 1.46 (s, 9 H), 1.16 (s, 3 H); mass spectrum, *m/z* 265.1796 [(M + H)$^+$, calcd for $C_{16}H_{25}O_3$ 265.1804].

**B.** Hydroxy ester **7b** was also formed on reduction of keto ester **8b** described below with sodium borohydride in methanol, followed by purification of the derived acetate by flash chromatography and treatment with methanol containing potassium carbonate. There was no evidence for concomitant formation of the epimeric 7α-hydroxy ester.

**Methyl 5-Oxo-1-methyl[4.4.4.5]fenestrane-7β- and -7α-carboxylate (8a and 9a).** To a solution of oxalyl chloride (0.15 mL, 1.5 mmol) in $CH_2Cl_2$ (6 mL) at −78 °C was added a solution of dimethyl sulfoxide (0.3 mL) in $CH_2Cl_2$ (1 mL). The mixture was stirred at −78 °C for 3 min followed by the addition of the mixture of **7a** and its epimer (0.031 g, 0.14 mmol), as a $CH_2Cl_2$ (0.5 mL) solution. Triethylamine (1 mL) was added after this mixture was stirred for 15 min. The reaction mixture was stirred at −78 °C for 5 min followed by warming to room temperature, dilution with water (10 mL), and extraction with ether (2 × 30 mL). Standard workup and flash chromatography (20% ether in hexane) yielded pure keto esters **8a** (eluted first, 0.019 g (61%)) and **9a** (0.007 g (22%)). For **8a**: IR 2952 (m), 2925 (m), 1752 (s), 1733 (s), 1225 (w) $cm^{-1}$; NMR δ 3.77 (dd, *J* = 5.1, 8.64, 1 H), 3.73 (s, 3 H), 3.10 (d, *J* = 4.9 Hz, 1 H), 3.07 (dd, *J* = 14.33, 8.0 Hz, 1 H), 2.99 (dd, *J* = 13.92, 7.30 Hz, 1 H), 2.64 (dt, *J* = 3.54, 7.9 Hz, 1 H), 2.53 (ddd, *J* = 1.4, 11.1, 14.25 Hz, 1 H), 2.25–2.42 (m, 4 H), 1.25 (s, 3 H); $^{13}C$ NMR δ 209.44 (s), 172.28 (s), 51.83 (q), 47.49 (t), 44.01 (d), 41.10 (t), 39.88 (t), 38.72 (d), 36.74 (s), 35.70 (s), 33.40 (d), 27.33 (d), 23.75 (q); mass spetrum, *m/z* 220.1062 (M$^+$, calcd for $C_{13}H_{16}O_3$ 220.1099). For **9a**: IR 2960 (s), 2930 (s), 1753 (s), 1735 (s), 1430 (m), 1345 (m), 1240 (m) $cm^{-1}$; NMR δ 3.70 (s, 3 H), 3.59 (dd, *J* = 4.11, 8.49 Hz, 1 H), 3.08–3.14 (m, 1 H), 3.10 (dd, *J* = 7.3, 13.8 Hz, 1 H), 2.87 (d, *J* = 8.47 Hz, 1 H), 2.64 (dt, *J* = 3.7, 7.18 Hz, 1 H), 2.2–2.48 (m, 5 H), 1.25 (s, 3 H); mass spectrum, *m/z* 220.1109 (M$^+$, calcd for $C_{13}H_{16}O_3$ 220.1099).

***tert*-Butyl 5-Oxo-1-methyl[4.4.4.5]fenestrane-7β- and -7α-carboxylate (8b and 9b).** Each of these ketones was obtained in virtually quantitative yield by the Swern oxidation of the corresponding alcohol following the procedure for **8a** and **9a**. Alternatively, the epimeric mixture of hydroxy esters was oxidized, and then flash chromatography (10% ether in hexane) yielded pure **8b** and **9b** in virtually quantitative yield. For **8b**: 2960 (s), 2925 (s), 1750 (s), 1720 (s), 1360 (m), 1225 (m) $cm^{-1}$; NMR δ 3.66 (dd, *J* = 5.0, 8.6 Hz, 1 H), 3.06 (d, *J* = 5.93, 1 H), 3.02–3.1 (m, 1 H), 2.97 (dd, *J* = 7.27, 13.78 Hz, 1 H), 2.13–2.63 (m, 6 H), 1.48 (s, 9 H), 1.28 (s, 3 H); mass spectrum, *m/z* 262.1556 (M$^+$, calcd for $C_{16}H_{22}O_3$ 262.1569). For **9b**: IR 2980 (m), 2920 (s), 1750 (s), 1725 (s), 1390 (m), 1370 (m), 1250 (m) $cm^{-1}$; NMR δ 3.47 (dd, *J* = 4.04, 8.46, 1 H), 3.08 (dd, *J* = 6.12, 12.93, 1 H), 3.07 (dd, *J* = 7.33, 13.72 Hz, 1 H), 2.82 (d, *J* = 8.48, 1 H), 2.56 (dt, *J* = 3.45, 6.91 Hz, 1 H), 2.18–2.45 (m, 5 H), 1.45 (s, 9 H), 1.23 (s, 3 H); mass spectrum, *m/z* 263.1635 [(M + 1)$^+$, calcd for $C_{16}H_{23}O_3$, 263.1647].

**Correlation of Keto Ester 8a with 7β-(Hydroxymethyl)-1-methyl-[4.4.4.5]fenestrane (10).** To a solution of **8a** (0.008 g, 0.036 mmol) in methanol (3 mL) at 0 °C was added $NaBH_4$ (0.03 g) slowly while stirring. The mixture was stirred for 30 min, warmed to room temperature, diluted with water (10 mL), and acidified to pH 4 with 5% HCl. Extractive workup with ether (2 × 30 mL) yielded the hydroxy ester, which was converted to the tosylate following a procedure previously described.[3] This tosylate was heated at reflux in THF (5 mL) with $LiAlH_4$ (0.015 g) for 4 h. The reaction mixture was cooled, and excess $LiAlH_4$ was destroyed by adding moist ether. Extraction with ether (2 × 25 mL) and standard workup yielded alcohol **10**, which was purified by flash chromatography (0.003 g). IR and NMR spectra of this material were identical with those of **10** previously reported.[3]

**Preparation of Tosylate 11.** To a solution of $NaBH_4$ (25 mg) in MeOH (3 mL) cooled in an ice/acetone bath was added dropwise a solution of **8b** (10 mg) in $C_6H_6$ (1 mL). The mixture was stirred for 20 min before excess hydride was destroyed by dropwise addition of 3% HCl. The reaction mixture was diluted with water and extracted with $Et_2O$. TLC (1:1 hexanes–$Et_2O$) indicated only one compound. A 300-MHz NMR spectrum was identical with that of **7b** described above.

The tosylate was prepared from the above alcohol and tosyl chloride (59 mg) in pyridine (0.5 mL). The product was purified by flash chromatography using 3:1 hexanes–$Et_2O$ ($R_f$ 0.31); NMR (300 MHz) δ 7.78 (d, *J* = 8.3 Hz, 2 H), 7.31 (d, *J* = 8.01, 2 H), 4.57 (ddd, *J* = 4.7, 8.2, 10.3 Hz, 1 H), 3.08 (dd, *J* = 4.7, 8.8 Hz, 1 H), 2.82 (dd, *J* = 7.2, 13.7 Hz, 1 H), 2.76 (dd, *J* = 8.2, 14.2 Hz, 1 H), 2.62 (dd, *J* = 4.8, 8.2 Hz, 1 H), 2.43 (s, 3 H), 2.35–2.25 (m, 2 H), 2.02–1.96 (m, 2 H), 1.83–1.75 (m, 2 H), 1.46 (s, 9 H), 1.14 (s, 3 H). Crystals (mp 63–64.5 °C) for X-ray crystallography were formed slowly from a hexane solution at −25 °C.

**Thermolysis of *tert*-Butyl 1-Methyl-5-oxo[4.4.4.5]fenestrane-7β-carboxylate (8b). A. Formation of 12 and 14 in Benzene.** A solution of keto ester **8b** (0.01 g, 0.038 mmol) in $C_6D_6$ (0.4 mL) was heated in a sealed tube at 100 °C for 16 h in an oil bath. Solvent was removed, and the residue was purified by flash chromatography (25% ether in hexane) to obtain **12** (0.0015 g, (15% yield)) and **14** (0.0045 g (45%)) as colorless oils. For **12**: IR 2980 (m), 2970 (m), 1725 (s), 1360 (m), 1140 (s) $cm^{-1}$; NMR δ 6.57 (d, *J* = 12.64 Hz, 1 H), 6.18 (m, 1 H), 5.99 (d, *J* = 12.60, 1 H), 4.81 (d, *J* = 0.57, 1 H), 4.72 (s, 1 H), 3.37–3.44 (m, 1 H), 2.57 (dd, *J* = 6.53, 18.95 Hz, 1 H), 2.44 (dd, *J* = 3.65, 14.66, 1 H), 2.19 (dd, *J* = 1.96, 18.92 Hz, 1 H), 1.90 (dd, *J* = 11.16, 14.28 Hz, 1 H), 1.73 (br s, 3 H), 1.47 (s, 9 H); mass spectrum, *m/z* 263.1651 [(M

+ 1)$^+$, calcd for $C_{16}H_{23}O_3$ 263.1647]. For **14**: IR 2970 (m), 1725 (s), 1716 (s), 1645 (w), 1575 (m), 1375 (m), 1155 (s) cm$^{-1}$; NMR $\delta$ 7.46 (d, $J$ = 5.7 Hz, 1 H), 6.14 (d, $J$ = 5.7 Hz, 1 H), 6.10 (ddd, $J$ = 7.3, 7.3, 11.6 Hz, 1 H), 5.76 (ddd, $J$ = 1.8, 1.8, 11.5 Hz, 1 H), 2.97 (ddd, $J$ = 1.81, 7.0, 16.1, 1 H), 2.74 (ddd, $J$ = 1.5, 7.5, 16.4 Hz, 1 H), 2.56 (d, $J$ = 19.2 Hz, 1 H), 2.24 (d, $J$ = 19.2 Hz, 1 H), 1.48 (s, 9 H), 1.43 (d, $J$ = 5.5, 1 H), 1.42 (d, $J$ = 5.6, 1 H), 1.19 (s, 3 H); mass spectrum, $m/z$ 263.1713 [(M + 1)$^+$, calcd for $C_{16}H_{23}O_3$ 263.1647].

**B. Formation of 12 in Benzene Containing $NaHCO_3$.** Thermolysis of **8b** as above in benzene, but containing solid $NaHCO_3$ (stirred, sealed ampule) yielded **12** as before, but no **14**.

**C. Formation of 20 in Methanol.** Thermolysis of **8b** (5.0 mg) as above, but in methanol (1.75 mL) containing $NaHCO_3$ (50 mg), yielded **20** (50%), which was identified by comparison with the photochemically produced material described below.

**Thermolysis of *tert*-Butyl 1-Methyl-5-oxo[4.4.4.5]fenestrane-7$\alpha$-carboxylate (9b).** A solution of **9b** (7 mg) in benzene (1 mL) containing $NaHCO_3$ was heated 20 h at 100 °C. Flash chromatography yielded one product identified as **13** (1 mg) from its spectra: NMR $\delta$ 7.45 (d, $J$ = 16.2 Hz, 1 H), 6.27 (d, $J$ = 0.6 Hz, 1 H), 6.26 (d, $J$ = 16.1 Hz, 1 H), 4.86 (d, $J$ = 0.8 Hz, 1 H), 4.74 (d, $J$ = 0.6 Hz, 1 H), 3.37-3.26 (br m, 1 H), 2.60 (dd, $J$ = 6.5, 18.9 Hz, 1 H), 2.30 (dd, $J$ 1.3, 18.9 Hz, 1 H), 1.95-1.85 (m, 2 H), 1.77 (s, 3 H), 1.53 (s, 9 H); mass spectrum, $m/z$ 262.1586 (M$^-$, calcd for $C_{16}H_{22}O_3$ 262.1569).

**Photolysis of 8b.** A solution of **8b** (0.011 g) in benzene (2 mL), methanol (0.15 mL), and $K_2CO_3$ (0.002 g) was degassed and irradiated through Pyrex with a 450-W Hanovia mercury lamp. Reaction was closely monitored by TLC and found to be complete in 5 h. Solvent was removed, and the residue was purified by flash chromatography (20% ether in hexane) to obtain three products: **28**, 0.004 g (36%); **20**, 0.0006 g (5%); **21**, 0.0006 g (5%). For **20**: IR 1738, 1711 cm$^{-1}$; NMR $\delta$ 6.23 (dt, $J$ = 7.5, 11.6 Hz, 1 H), 5.82 (dt, $J$ = 1.41, 11.9 Hz, 1 H), 3.21 (s, 3 H), 3.11 (ddd, $J$ = 1.1, 7.37, 15.34 Hz, 1 H), 2.88-2.99 (m, 3 H), 2.74 (d, $J$ = 19.4, 1 H), 2.56 (d, $J$ = 20.95 Hz, 1 H), 2.53 (dd, $J$ = 1.44, 18.13 Hz, 1 H), 2.16 (dd, $J$ = 9.53, 12.1 Hz, 1 H), 1.49 (s, 9 H), 1.06 (s, 3 H), 0.82 (dd, $J$ = 8.16, 11.97 Hz, 1 H); mass spectrum, $m/z$ 293.1740 [(M - H)$^-$, calcd for $C_{17}H_{25}O_4$ 293.1753]. For **21**: NMR $\delta$ 6.92 (dt, $J$ = 7.7, 15.5 Hz, 1 H), 5.83 (dt, $J$ = 1.2, 15.4 Hz, 1 H), 3.19 (s, 3 H), 2.89 (dd, $J$ = 17.13, 8.55 Hz, 1 H), 2.73 (d, $J$ = 19.48, 1 H), 2.57 (d, $J$ = 8.52 Hz, 1 H), 2.51-2.58 (m, 1 H), 2.51 (dd, $J$ = 1.40, 7.96 Hz, 1 H), 2.40 (dd, $J$ = 7.71, 14.26 Hz, 1 H), 2.15 (d, $J$ = 18.64 Hz, 1 H), 2.07 (dd, $J$ = 9.61, 12.26 Hz, 1 H), 1.49 (s, 9 H), 1.05 (s, 3 H), 0.84 (dd, $J$ = 8.35, 12.21, 1 H); mass spectrum, $m/z$ 293.1740 [(M - H)$^-$, calcd for $C_{17}H_{25}O_4$ 293.1753]. For **28**: $^1$H and $^{13}$C NMR spectra given in the text; IR 3061 (w), 2979 (s), 2930 (s), 2819 (w), 2717 (w), 1725 (s), 1456 (m), 1392 (m), 1368 (m), 1151 (s), 1124 (m), 909 (s) cm$^{-1}$; mass spectrum, $m/z$ 263.1649 [(M + 1)$^+$, calcd for $C_{16}H_{23}O_3$ 263.1647].

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**Supplementary Material Available:** ORTEP diagrams of **11** and the 2,4-dinitrophenylhydrazone of **14** and listings of atomic coordinates, bond lengths, bond angles, anisotropic parameters, and H atom coordinates and isotropic parameters for **11** and of distances and angles for the 2,4-dinitrophenylhydrazone of **14** (12 pages). Ordering information is given on any current masthead page.

# Two Triplets Mediating Intramolecular Photochemical Abstraction of Hydrogen by Nitrogen in 4-Acyl-6-alkylpyrimidines

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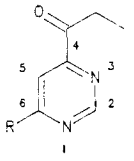
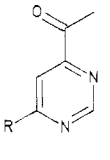
**Abstract:** Direct irradiation with $\lambda$ >340 nm of 4-acyl-6-alkylpyrimidines **1a** and **2c** or their triplet sensitization by aromatic ketones leads to an n$\pi$* triplet ($E_T$ ~ 70-71 kcal/mol). In **1a** this state is responsible for hydrogen abstraction from the C(4) side chain and isomerization to cyclopropanol **3** (eq 1). Ketone **2c** does not fragment under either these direct or sensitized conditions. However, triplet sensitization of **2c** by acetone ($E_T$ ~ 79-82 kcal/mol) or direct irradiation of **2c** through Vycor, $\lambda$ >200 nm, leads to hydrogen abstraction, cleavage of the C(6) side chain, and formation of **2a** (eq 2) in a reaction occurring from an upper n$\pi$* triplet ($E_T$ ~ 79-84 kcal/mol). Ketone **1c** yields mainly **5** and, depending upon conditions, a small amount of **1a** or **3** or both; the minor products arise by a novel monophotonic pathway (see eq 4).

We have found that in 4-acyl-6-alkylpyrimidines such as **1** and **2** intramolecular abstraction of hydrogen by nitrogen occurs from two distinct triplet states differing in energy by ~10 kcal/mol and that each of these states may be reached by appropriate triplet sensitization or direct irradiation. Despite its fundamental nature and biological implications,[1] photochemical abstraction of hydrogen by aromatic nitrogen has received much less attention than the related abstraction by carbonyl oxygen.[2] One complexity characteristic of functionalized nitrogen heteroaromatics is the



1



2

a, R = $CH_3$

b, R = H

c, R = $CH_2CH_2CH(CH_3)_2$

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(2) A review covering both reactions is available: Wagner, P. J. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic: New York, 1980; Vol. 3, Chapter 20. For more recent reports of hydrogen abstraction by nitrogen in 2(1*H*)-pyrimidinones, see the following: Nishio, T.; Katahira, K.; Omote, Y. *Chem. Lett.* **1982**, 1675. Nishio, T.; Kameyama, S.; Omote, Y. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1147. Photochemical electron-transfer reactions of nitrogen aromatics and related imine systems have received much greater attention and have been reviewed recently: Mariano, P. S. *Org. Photochem.* **1987**, *9*, 1.

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