the enzymic reaction.[21] We conclude, therefore, that the thermal rearrangement of chorismate to prephenate follows the same stereochemical course as the enzymic reaction and proceeds through a transition state of chairlike geometry.

Registry No. Chorismate, 617-12-9; *trans*-prephenate, 97645-23-3; (*E*)-[9-³H,²H]chorismate, 89437-80-9; (*Z*)-[9-³H,²H]chorismate, 89496-34-4.

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(21) From independent analysis of the stereochemical location of ³H at carbon-3 of the labeled phosphoenolpyruvate used (Grimshaw, C. E., unpublished work) and from the known isotope effect in the reaction catalyzed by 3-phosphoshikimate-1-carboxylvinyl transferase,[20] we predicted that our (*E*)-chorismate sample would yield phenphenate having a 66:34 distribution at the prochiral positions of the methylene carbon, and the (*Z*)-chorismate sample would yield a 69:31 distribution in the location of ³H, if the reaction were completely stereospecific. While the results from Figure 2 suggest a bias to high values of the percentage of ³H at the *pro-S* position (the cause of which is unknown), the agreement between the results for the enzymic and nonenzymic reactions (Table I) makes the assignment of transition-state geometry unambiguous.

Construction of Linearly Fused Tricyclopentanoids by Intramolecular [6 + 2] Cycloadditions of Fulvenes with Enamines
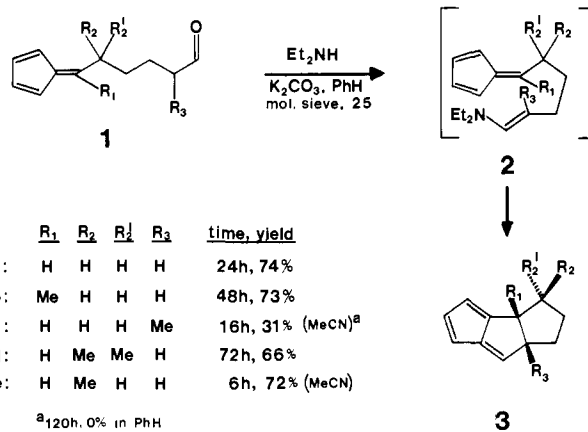
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The synthesis of linearly fused tricyclopentanoids is a popular subject for the demonstration of modern synthetic methods.[1] Among the two-score methods applied to the preparation of hirsutene and its more elaborate relatives,[2] those reported by the groups of Little and Curran involve the simultaneous annulation of two new five-membered rings onto a preexisting cyclopentane.[3] We have developed a similar strategy based upon intramolecular [6 + 2] cycloadditions. We previously reported the [6 + 4] cycloadditions of dienamines to fulvenes,[4] as well as intramolecular analogues.[5] The electrophilicity of the 6-position of a fulvene toward nucleophilic dienamines suggested to us that the intramolecular [6 + 2] reaction of a fulvene with an enamine might succeed through the intervention of a zwitterionic intermediate.[6] Here we report the successful realization of this plan.

The new reaction sequence for conversion of **1** to **3** is shown in Scheme I.[7] Fulvenes substituted at the exocyclic 6-position by 6-(ω-formylalkyl) groups are converted into the corresponding enamines,[8] which undergo the intramolecular [6 + 2] cycloaddition and spontaneous loss of diethylamine to form tricyclopentanoid

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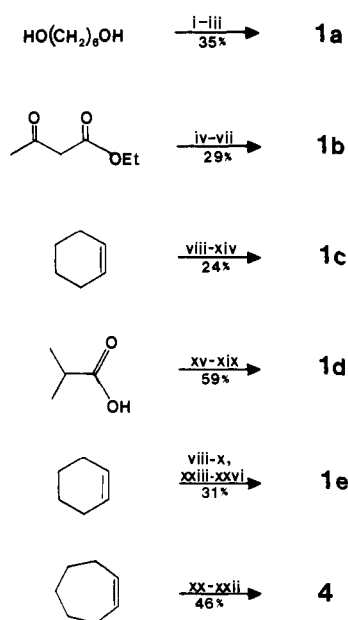(5) Wu, T.-C.; Mareda, J.; Gupta, Y. N.; Houk, K. N. *J. Am. Chem. Soc.* **1983**, *105*, 6996.
(6) Although we have found that enamines do react with dimethylfulvene, we have been unable to characterize the products, which rapidly decompose.
(7) All new compounds were characterized by 300-MHz NMR and high-resolution mass spectrometry. The conversion of **1** to **3** also occurs with base catalysis. With potassium *tert*-butoxide, formation of **3a** occurs in several minutes at 25 °C, but the product is rapidly destroyed under these conditions. Triethylamine converts **1** to **3** at a rate about ten times slower than the reaction with diethylamine.
(8) Stork, G.; Brizzolara, A.; Landesman, H.; Szmuszkovicz, J.; Terrell, R. *J. Am. Chem. Soc.* **1963**, *85*, 207.

Scheme I

	R₁	R₂	R₂′	R₃	time, yield	
a:	H	H	H	H	24h, 74%	
b:	Me	H	H	H	48h, 73%	
c:	H	H	H	Me	16h, 31%	(MeCN)ᵃ
d:	H	Me	Me	H	72h, 66%	
e:	H	Me	H	H	6h, 72%	(MeCN)

ᵃ120h, 0% in PhH

fulvenes. The yields given are for the overall conversion of **1** to **3**.

The reaction is actually a cycloaddition analogue of Hafner's elegant electrocyclic synthesis of dihydropentalenes.[9] It is also related to the strategy used in Büchi's β-vetivone synthesis,[10] where addition of a cuprate to the 6-position of fulvene generates a cyclopentadienide which attacks a ketone to form a spiro [6.5] system. Whereas the tricyclopentanoids are formed exclusively as the cis isomers (see below), the higher homologue, **4**, gives a ~2:1 ratio of cis and trans products, **5**.
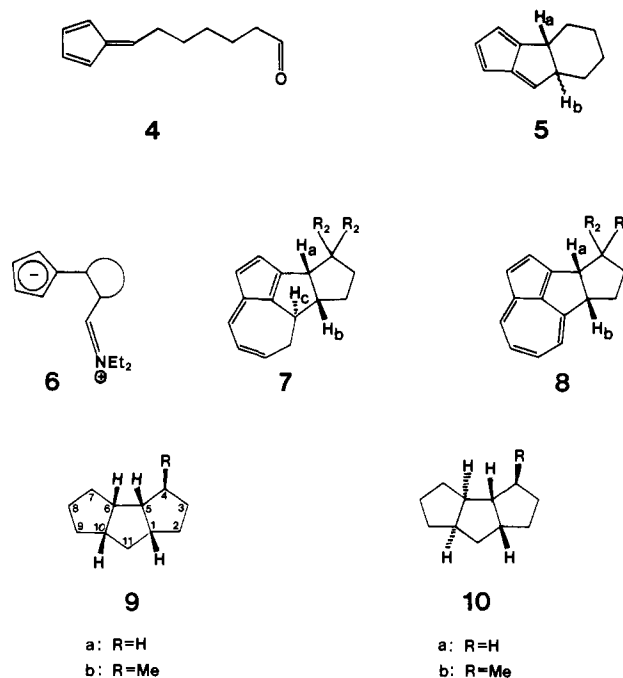
The reaction is subject to steric hindrance, as evidenced by the failure of **1c** to give any adduct under normal conditions. However, in the more polar solvent, acetonitrile, even this reaction proceeds readily, albeit in modest yield. Similarly, the reaction of **1e** is rapid in acetonitrile. These results suggest that these [6 + 2] cycloadditions involve zwitterionic intermediates, **6**. It is possible that the formation of **6** is reversible, but only *cis*-**6a–e** cyclizes, since the trans-fused adducts will be considerably more strained than the cis. The exclusive formation of **3e** from **1e** can also be rationalized as a result of equilibration of **6** to give the most stable intermediate before the second cyclization, or by steric control of the first step of the reaction sequence.

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(9) Kaiser, R.; Hafner, K. *Agnew. Chem. Int. Ed. Engl.* **1970**, *9*, 892; **1973**, *12*, 335.
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Scheme II

Structure proofs for all adducts were based upon 300-MHz ^{1}H and ^{13}C NMR analysis and chemical transformations. Each compound gave characteristic fulvene and cyclopentane resonances. When bridgehead hydrogens were present, surprisingly low cis couplings were observed; in **3a** and **3d**, $J_{1,3}$ = 5.3 and 5.1 Hz, respectively. These small cis couplings are likely the result of strain and consequent distortions of the central ring, as shown by the more normal couplings found in less strained intermediates.[11] The reactions of **3a** or **3d** with 1-(diethylamino)butadiene in benzene proceeded by [6 + 4] cycloadditions to form the tetracyclic dihydroazulenes **7a** and **7d**, in 31% and 66% yield, respectively. The bridgehead couplings, J_{ab}, are 7.9 and 8.2 Hz in these adducts, closer to expectation for cis couplings in such systems.[11] The J_{bc} couplings of 5.2 and 6.0 Hz in **7a** and **7d** suggest the trans stereochemistry of these hydrogens, consistent with approach of the dienamine to the less hindered face of **3a** or **3b** in the [6 + 4] cycloadditions. Conversions of **7a** and **7d** to the brilliant blue tetracyclic azulenes **8a** (14%, J_{ab} = 6.2 Hz) and **8d** (20%, J_{ab} = 5.9 Hz) was effected by refluxing **7a** and **7b** in triglyme in the presence of sulfur. Small cis couplings are observed again in these strained compounds.

Catalytic hydrogenation (5% Pd–C, hexane) of **3a** gave two adducts, **9a** and **10a**, the parent linearly fused tricyclopentanoids, in a 60:40 ratio. These were separated by GLC (SE-30 column). The ^{13}C NMR spectra[12] of each compound gave only six resonances, consistent with C_s or C_2 symmetry. Only the spectra predicted[13] for the cis-syn-cis and cis-anti-cis structures are consistent with the observed spectra of **9a** and **10a**, respectively. The alternative C_s and C_2 all-trans compounds would be highly strained and give different ^{13}C spectra. Hydrogenation of **6e** gave two adducts, **9b** and **10b** in a 56:44 ratio. ^{13}C spectra excluded the structure which is the epimer of **10b** at C-4, since this epimer

(11) A coupling constant of 12 Hz has been reported for the bridgehead hydrogens in a cis-fused tricyclopentanoid precursor to coriolin: Trost, B. M.; Curran, D. P. *J. Am. Chem. Soc.* **1981**, *103*, 7380.

(12) ^{13}C NMR (CDCl$_3$). **9a**: 27.3 (t, C-3,8 or 4,7), 28.4 (t, C-3,8 or 4,7), 31.6 (t, C-2,9), 40.3 (dd, C-11), 47.2 (d, C-1,10), 47.4 (d, C-5,6). **10a**: 26.1 (t, C-3,8), 32.9 (t, C-4,7), 34.0 (t, C-2,9), 40.2 (t, C-11), 44.9 (d, C-1,10), 52.4 (d, C-5,6). **9b**: 20.9 (q, Me), 27.8 (t, C-7), 28.1 (t, C-8), 31.3 (t, C-2,9), 36.0 (d, C-4), 37.6 (t, C-3), 41.0 (dd, C-11), 46.5 (d, C-6), 48.3 (d, C-1,10), 55.3 (d, C-5). **10b**: 19.8 (q, Me), 26.4 (t, C-8), 31.8 (t, C-7), 33.1 (t, C-2), 34.4 (t, C-9), 35.8 (t, C-3), 41.0 (t, C-11), 41.7 (d, C-4), 44.4 (d, C-1), 44.8 (d, C-10), 50.4 (d, C-6), 61.2 (d, C-5). MM2 calculations indicate that **9a** and **10a** have essentially identical heats of formation. **Note Added in Proof**: Syntheses of **9a** and **10a** by alternative routes were recently reported: Kakiuchi, K.; Takeuchi, H.; Tobe, Y.; Odaira, Y. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1613. ^{13}C spectra reported there are the same, to within ±0.1 ppm, as those reported here.

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has been prepared by a different route in Professor Curran's laboratories.[3b] The spectra[12] confirm the structures shown and establish the stereochemistry of **6e**.

The cis and trans tricyclic compounds **5** were obtained as an inseparable mixture. The chemical shifts of the vinyl protons of the major isomer are essentially identical with those observed for the cis adduct **3**, leading to the tentative conclusion that the major isomer of **5** has the cis stereochemistry.

Synthetic routes to the 6-(ω-formylalkyl)fulvenes, **1a–e** and **4**, involved the sequences listed in Scheme II. Each of these compounds was prepared in excellent overall yields using the commercial reagents given in ref 14.[14–21] Thus, the substituted linearly fused tricyclopentanoid skeleton can be easily assembled in 4–8 steps from readily available starting materials in 7–39% overall yield by this reaction sequence.

(14) Reagents and yields. **1a**: (i) PCC, Celite, CH$_2$Cl$_2$, 62%; (ii) C$_5$H$_6$, 35% aqueous CH$_3$NH$_2$, THF,[15] 69%; (iii) PCC, Celite, CH$_2$Cl$_2$, 82%. **1b**: (iv) NaOEt/EtOH; 4-bromobutyraldehyde ethylene acetal[16], reflux,[17] 76%; (v) decarboxylation, 8% KOH, 1:1 THF/H$_2$O, 81%; (vi) C$_5$H$_6$, KOH, CH$_3$OH–THF,[18] 52%; (vii) 0.5% HCl, 2:1 THF/H$_2$O, 91%. **1c**: (viii) O$_3$, EtOH–CH$_2$Cl$_2$ (1:5); (CH$_3$CO)$_2$O, Et$_3$N,[19] 70%; (ix) HOCH$_2$CH$_2$OH, *p*-TsOH, PhH reflux, 95%; (x) LDA, THF; MeI, HMPA, 97%; (xi) DIBAL, toluene, 0 °C,[20] 67%; (xii) 1% HCl, 2:1 THF/H$_2$O, 99%; (xiii) C$_5$H$_6$, 35% aqueous CH$_3$NH$_2$, THF[15] 68%; (xiv) PCC, CH$_2$Cl$_2$, Celite, 81%. **1d**: (xv)2 equiv of LDA, THF; 4-bromobutyraldehyde ethylene acetal,[16] HMPA,[21] 86%, (xvi) LAH, ether, 95%; (xvii) PCC, CH$_2$Cl$_2$, Celite, 90%; (xviii) C$_5$H$_6$, *n*-BuLi, THF, 0 °C, 82%; (xix) 0.2% HCl, 2:1 THF/H$_2$O, 99%. **4**: (xx) O$_3$, CH$_2$Cl$_2$/CH$_3$OH (5:1); *p*-TsOH; NaHCO$_3$; (CH$_3$)$_2$S, 74%; (xxi) C$_5$H$_5^-$Li$^+$, THF, 0 °C, 64%; (xxii) 0.1 N HCl, 2:1 THF/H$_2$O, 99%. **1e**: (xxiii) DIBAL, CH$_2$Cl$_2$, 0 °C, 1h, 89%; (xxiv) PCC, NaOAc, Celite, CH$_2$Cl$_2$, 82%; (xxv) C$_5$H$_6$, BuLi, THF, 0 °C, 71%; (xxvi) 0.06 N HCl, 9:6:1 THF/H$_2$O/acetone 89%.

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Ozonolysis of Olefins Adsorbed on Polyethylene: A New Access to Ozonides by Cycloadditions of Carbonyl Oxides to Ketones

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It is well recognized that in the absence of specific electronic, steric, or concentration effects, ketones are too unreactive to undergo intermolecular cycloadditions with carbonyl oxides to form ozonides.[1] As a consequence, ozonolyses of acyclic tetrasubstituted ethylenes in nonparticipating solvents usually do not lead to the corresponding ozonides. A case in point is tetramethylethylene (**1**). It has been reported that upon ozonolysis of **1** in chloroethane[2] or in pentane[3] as solvent, ozonide **4** could not be obtained, i.e., the primary fragments **2** and **3** of the ozone cleavage reaction did not recombine. Recently, it has been shown that cycloadditions of carbonyl oxides with aldehydes, and hence ozonide formation,

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