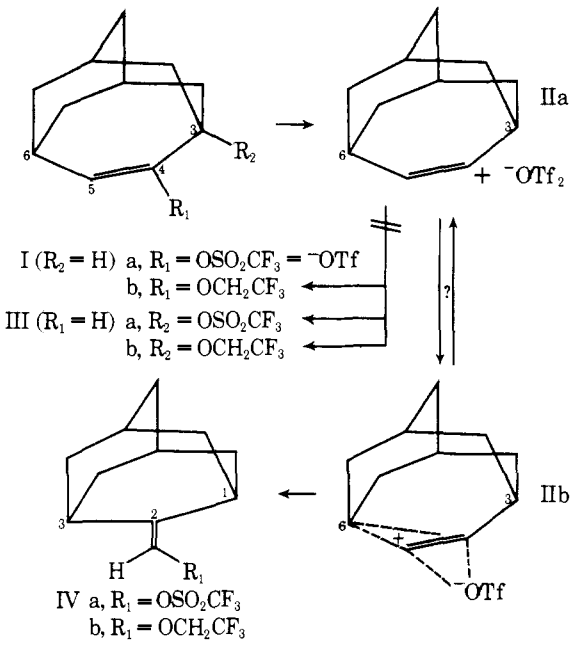

and the effect of "hiding" the developing cationic orbital between (or inside) the "cage" and $CF_3SO_3^-$.

These data alone do not clarify why antiperiplanar C_6 migration is so dominant over synperiplanar H migration. Influential factors may include substituent geometry, ring structure, and destabilization of charge on C_3 if H migration were to occur. Pyridine buffer and product structural features do not accommodate an addition-rearrangement-elimination mechanism, which, moreover, is practically unknown in related neutral media solvolyses.

A preliminary search for the independent or interconverting primary and secondary vinyl carbenium ions was inconclusive. Mixing either Ia or IVa with SbF_5-SO_2ClF at −80 °C gave an orange solution which showed only broad, partially resolved proton NMR absorptions between 2 and 5 ppm (δ).[13] Neither mixture showed significant NMR change upon warming to −10 °C.

Experiments are planned to determine activation parameters, and if the carbon-bound oxygen atom in IVa is different from that in Ia, whether C_5 undergoes inversion during the Ia to IVa rearrangement, and if the photolysis of I (R_1 = iodine) will be a source of "free" 4-homoadamanten-4-yl carbenium ion.

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References and Notes

(1) This statement is true only for those ions having ground-state vibrational energy. Compare R. Yamaguchi, S. Aritmatsu, and M. Kawanisi, *Chem. Lett.*, 121 (1973).
(2) M. McKervey, *Chem. Soc. Rev.*, **3**, 479 (1974).
(3) 4-Homoadamantanone, from adamantanone and diazomethane, is converted to liquid Ia (> 90%) (silica gel-pentane; M^+, 296. Anal. Calcd for $C_{12}H_{15}F_3O_3S$: C, 48.65; H, 5.08. Found: C, 48.82; H, 5.08. NMR (δ), 6.1 dd (1 H, vinyl), 1.7–2.7 (14 H)) by the method of ketones. P. Stang and T. Dueber, *Org. Synth.*, **54**, 79 (1974).
(4) An authentic sample of liquid IVa (silica gel-pentane elution before Ia) was prepared from adamantan-2-carboxaldehyde (J. Sharp, H. Wynberg and J. Strating, *Recl. Trav. Chim. Pays-Bas*, **89**, 18 (1970); or, in our hands from adamantanone reacting with the Wittig reagent of CH_3OCH_2Cl followed by HCl) by the silyl ether method for aldehydes. P. Stang, M. Mangum, D. Fox, and P. Haak, *J. Am. Chem. Soc.*, **96**, 4562 (1974)): M^+, 296. Anal. Found: C, 48.71; H, 5.10. NMR (δ), 6.5 s (1 H, vinyl), 3.1 m (C_1–H), 2.45 m (C_3–H), 1.7–2.2 (12 H).
(5) All reactions were carried out in a glass-lined, stainless steel reactor sealed with Teflon gaskets. Product mixtures were monitored by thermal conductivity VPC.
(6) M. Imhoff, R. Summerville, P. v. R. Schleyer, A. Martinez, M. Hanack, T. Dueber, and P. Stang, *J. Am. Chem. Soc.*, **92**, 3802 (1970).
(7) Authentic IVb was not available. Our liquid IVb analyzed as follows: M^+, 246; NMR (δ), 6.0 s (1 H, vinyl), 4.1 q (2 H), 3.1 m (C_1–H), 2.3 m (C_3–H), 1.7–2.2 (12 H); VPC R_f IVb > IVa > Ia on OV-275 at 140 °C.
(8) Monocyclic vinyl triflates do not ring contract in S_N1 solvolyses unless the product is also secondary: W. Pfeifer, C. Bahn, P. v. R. Schleyer, S. Bocher, C. Harding, K. Hummel, M. Hanack, and P. Stang, *J. Am. Chem. Soc.*, **93**, 1513 (1971). In fact, exocyclic primary vinyl cations generated by vinyl iodide photolysis rearrange to endocyclic secondary ones: P. Kropp and S. McNeely, 170th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1975, Abstracts, ORGN 4.
(9) (a) P. Stang and T. Dueber, *J. Am. Chem. Soc.*, **95**, 2683 (1973); (b) R. Summerville, C. Senkler, P. v. R. Schleyer, T. Dueber, and P. Stang, *ibid.*, **96**, 1100, 1110 (1974); (c) Z. Rappoport and Y. Apeloig, *ibid.*, **97**, 821, 836 (1975); (d) T. Clarke, D. Kelsey, and R. Bergman, *ibid.*, **94**, 3626, 3627 (1972); (e) Z. Rappoport, E. Noy, and Y. Houminer, *ibid.*, **98**, 2238 (1976).
(10) See ref 9b and L. Radom, P. Hariharan, J. Pople, and P. v. R. Schleyer, *ibid.*, **95**, 6531 (1973).
(11) Compare S. Liggero, R. Sustmann, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **91**, 4571 (1969); P. Peterson and R. Kamat, *ibid.*, **91**, 4521 (1969); G. Modena, et al., *J. Chem. Soc., Perkin Trans. 2*, 493 (1973).
(12) This has been shown to be the most desirable geometry for vinyl carbenium ion stabilization: Z. Rappoport and Y. Apeloig, *J. Am. Chem. Soc.*, **96**, 6428 (1974); D. Kelsey and R. Bergman, *ibid.*, **92**, 228 (1970).
(13) This experiment was suggested and performed by Dr. David Forsyth. Further work is in progress.

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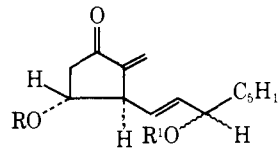
The Ene Reaction as a Route to 3-Hydroxycyclopentanone Derivatives. Application to the Prostaglandins

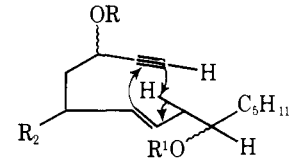
Sir:

We have previously demonstrated an efficient route to the prostaglandins via 2-methylenecyclopentanones (**1**) which were synthesized by formaldehyde trapping of the proper regiospecifically generated enolate.[1,2]



1

We now wish to report an entirely different approach to **1**: the thermal ene reaction of an appropriate acyclic enyne (e.g., **2** → **3**).[3]



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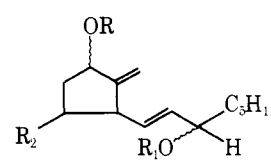
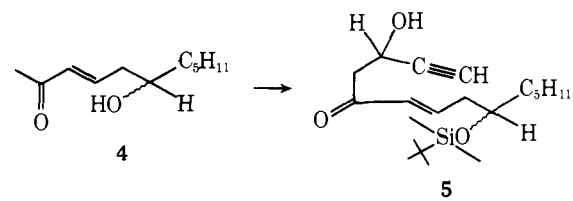


3

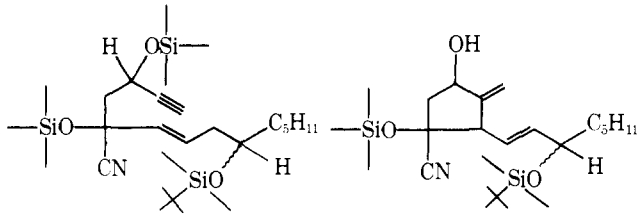
We were encouraged to examine the possibility of this transformation because arrays such as **2** are now easily accessible: the vinylogous aldol[4] **4** was protected as its *tert*-butyldimethylsilyl[5] derivative which was then submitted to the kinetic aldol reaction[6] with propynal. The usefulness of the



4 **5**

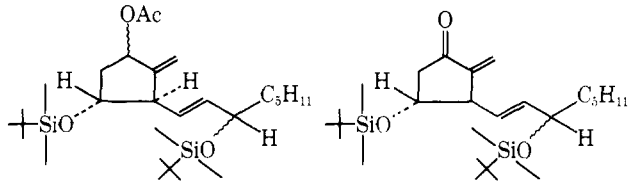
kinetic aldol process is well illustrated by this example which, in spite of the acidity of the acetylene hydrogen, gives acceptable (60–70%) yields of **5**.[7]

Simultaneous cyanohydrin formation and protection of the two free hydroxyls as their trimethylsilyl ethers was achieved conveniently by reaction of **5** with trimethyl silyl cyanide[8] (catalytic amount of potassium cyanide and dicyclohexyl-18-crown-6 in carbon tetrachloride at 75 °C) to yield, in quantitative yield, **6** (mixture of diastereoisomers: δ 5.4–6.5 (m; trans HC=CH), 4.4–4.9 (m; $Me_3SiOCHC{\equiv}C$), 3.65–3.9 (m; $HCOSi\text{-}t\text{-}BuMe_2$) 2.1–2.45 (m; $CH_2C{=}C$, $C{\equiv}CH$), 0.9–1.6 (m; C_5H_{11}, $Me_3SiOC(CN)CH_2$) 0.9 (s; $Si\text{-}C(CH_3)_3$), 0.15 (s; $OSi(CH_3)_3$, $O\,Si\text{-}t\text{-}Bu(CH_3)_2$), 0.05 (s, $OSi\,(CH_3)_3$). Thermal cyclization of **6** was effected remarkably easily (10% in deoxygenated toluene 250 °C, 27 min)[9] to produce, after selective desilylation of the ring secondary hydroxyl[10] (10^{-4} N HCl in tetrahydrofuran, 50 min at room temperature), the methylenecyclopentanol **7**, in 60% yield (*m/e:* (P + 1) − HCN 425).



6 **7**

Acetylation of the newly liberated hydroxyl (acetic anhydride–pyridine) was followed by treatment with sodium borohydride in methanol and protection of the new hydroxyl as its *tert*-butyl dimethylsilyl ether which gave **8** in 50% yield from **7**. In this molecule, the important trans relationship between the vinyl carbinol chain and the adjacent cyclopentanol hydroxyl (C_{11} and C_{12} of the eventual prostaglandins) has been established stereoselectively by taking advantage of the expected[11] formation of a *trans* 2-alkylcyclopentanol in the reduction of a 2-alkylcyclopentanone with sodium borohydride. The cyclopentanone function required for this operation was generated in situ, under the conditions of the borohydride reduction, from the silylated cyanohydrin which thus allowed the survival of a latent carbonyl function in what would otherwise have been an incompatible environment.

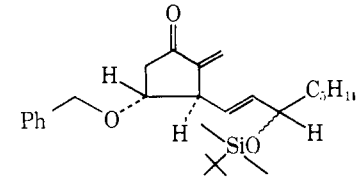


8 **9**

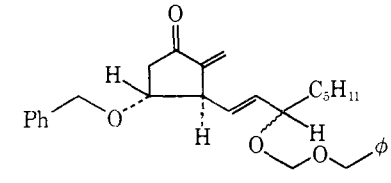
Transformation to the desirable 2-methylenecyclopentanone system and confirmation of the stereoselectivity of the borohydride reduction were carried out by deacetylation (potassium carbonate–aqueous methanol, room temperature) followed by Jones oxidation (−20 → −10 °C). The expected isomer **9** was isolated in 75–80% yield after purification by silica gel chromatography (1:10 ether–pentane) (*m/e:* (P + 1) 467); NMR δ 6.0–6.15 (dd, 1 H, $H_2C{=}C{-}C{=}O$), 5.75 (m, 2 H), 5.1–5.25 (m, 1 H), 3.9–4.35 (m, 2 H), 3.1–3.4 (m, 1 H, $C{=}C{-}CH{-}C{=}C$), 1.95–2.8 (m, 2 H, $O{=}C\text{-}CH_2CHO$-); ir ν 1740, 1642.

The structure and stereochemistry of **9** were corroborated by correlation with the previously synthesized methylene cyclopentanone **11**.[1] This was achieved by protection of the alcohol function of **7** (ethyl vinyl ether), borohydride reduction and benzylation (benzyl iodide on lithium salt) to **10** followed, after desilylation, by introduction of the requisite benzyloxymethyl group on the side chain hydroxyl and, finally, by Jones oxidation (−20 °C). Chromatography on silica gel (1:3 ether–pentane) easily separated the desired **11** from its cis isomer (ratio ~3.5:1). The more rapidly eluted methylene cyclopentanone **11** had an identical NMR spectrum as that of the substance prepared previously.[12]

The ene reaction would seem to be an excellent route to 2,3-disubstituted-4-hydroxycyclopentanones in general, and prostaglandins in particular.



10



11

Acknowledgment. We thank the National Institutes of Health and the National Science Foundation for their support of this work.

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(2) G. Stork and M. Isobe, *J. Am. Chem. Soc.*, **97**, 6260 (1975).
(3) The formation of a methylenecyclopentane system by the thermal cyclization of 6-octen-1-yne has been described by W. D. Huntsman and R. P. Hall, *J. Org. Chem.*, **27**, 1988 (1962).
(4) G. Stork and G. A. Kraus, *J. Am. Chem. Soc.*, **98**, 2351 (1976).
(5) Cf. E. J. Corey and A. Venkateswarlu, *J. Am. Chem. Soc.*, **94**, 6190 (1972).
(6) G. Stork, G. A. Kraus, and G. Garcia, *J. Org. Chem.*, **39**, 3459 (1974).
(7) The spectral properties (NMR, ir) of the compounds reported here were in agreement with the postulated structures. The various compounds were purified by chromatography on silica gel (ratio 10–20:1) with ether–pentane (ratios 1:3, 1:4, 1:7, 1:10, 1:7, and 1:3 for compounds **5**, **7**, **9**, **10**, and **11**, respectively). The mass spectra referred to are chemical ionization spectra.
(8) D. Evans, L. K. Truesdale, and G. L. Carroll, *J. Chem. Soc., Chem. Commun.* 55 (1973).
(9) The sealed tube was previously washed with pyridine.
(10) The slower hydrolysis of the silylated cyanohydrin may reflect either steric hindrance to hydrolysis or a rate-determining oxygen protonation step in this case, or both.
(11) J. B. Umland and B. W. Williams, *J. Org. Chem.*, **21**, 1302 (1956).
(12) This compound is actually a mixture of "C_{15}" epimers (prostaglandin numbering), as are all the other "15"-hydroxy compounds.

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Austin, a Novel Polyisoprenoid Mycotoxin from *Aspergillus ustus*

Sir:

The discovery of the highly toxic and carcinogenic aflatoxins[1] has generated considerable interest in other toxins produced by fungi contaminating stored foodstuffs. Steyn has reported austamide[2] and substances biogenetically related to it as toxic metabolites from a strain of *Aspergillus ustus*. Vleggaar, Steyn, and Nagel have described austdiol as the major toxin from the same source.[3] We now report the highly unusual structure **1** for the major toxin elaborated by a strain of *A. ustus* found on stored black-eyed peas (*Vigna sinensis*).[4] We propose the trivial name austin for this metabolite.