(methyl methacrylate) with either UV source has little net effect on the composition of the surface. The polymer decomposes primarily into small molecules (exclusively monomer with laser ablation[15]) and the increase in the O/C ratio is small or zero. Even though these three polymers show somewhat different degrees of surface reaction with oxygen, they all show a high degree of specificity after far-UV oxidation, e.g., in the attachment of silver atoms to the surface.[16]

In summary, far-UV CW irradiation of poly(ethylene terephthalate) and polyimide in air leads to a rapid oxidation of the surface region, whereas laser ablation leads to a surface that is depleted in oxygen. Poly(methyl methacrylate) appears to be less reactive in terms of surface modification than either of these polymers.

Registry No. Poly(ethylene terephthalate) (SRU), 25038-59-9; poly(methyl methacrylate) (homopolymer), 9011-14-7; (*p,p'*-diaminodiphenyl oxido)·(pyromellitic dianhydride) (copolymer), 25038-81-7; poly(pyromellitic dianhydride)·(*p,p'*-diamiodiphenyl oxide) (SRU), 25036-53-7.

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Synthesis and Structure Determination of Isoaplysin-20

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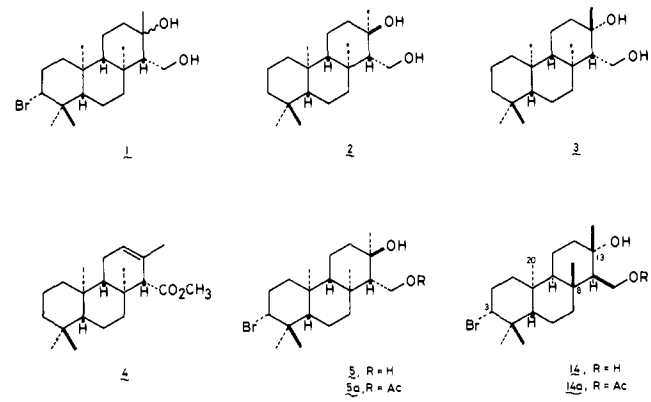
Received March 26, 1984

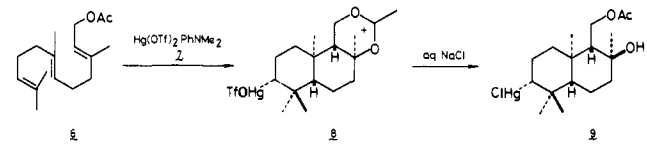
In 1977, Yamamura and Terada reported the isolation of a small amount of bromine-containing tricyclic diterpenoid, named isoplysin-20, from a sea hare, *Aplysia kurodai*.[1] They proposed the structure **1** to this new class of diterpenoid based on the spectral analysis, in which the stereochemistry at C-13 remained unclear. Imamura and Rûveda followed the structural study and prepared two kinds of debromo compounds (**2** and **3**) from methyl isocopalate (**4**). By comparison of the ^{1}H NMR spectra with those of the natural product, they concluded that the structure of isoaplysin-20 must be represented by the formula **5**[2] (Chart I).

We have synthesized polycyclic terpenoids with some ambiguity in their proposed structures by means of mercury(II) trifluoromethanesulfonate/amine complex induced olefin cyclization.[3] As mentioned in our earlier communication,[4] (*E,E*)-farnesyl acetate (**6**) cyclizes by this method to a C-8 hydroxylated product, **9**, as the major product in a stereospecific manner. This is recognized as a result of intramolecular participation of the neighboring acetoxyl group as represented in Scheme I. Therefore, we expected that (*E,E,E*)-geranylgeranyl acetate (**10**) would lead to the corresponding C-13 hydroxylated tricyclic product analogously. This was the case, indeed, and we prepared bromine-containing tricyclic compounds. However, the major carbinol product **5a** showed different spectral properties from those of the acetate of natural isoaplysin-20. The cyclization of **10** was not completely stereospecific, and small amounts of minor products were also obtained. One of the minor products showed an entirely superimposable ^{1}H NMR spectrum with that of the natural product derivative. Single-crystal X-ray diffraction experiment gave the

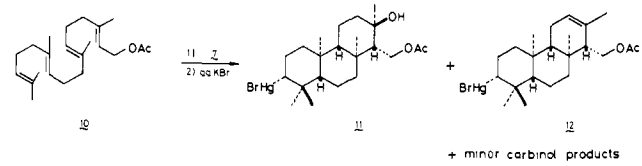
Chart I



Scheme I



Scheme II



precise structure of this synthetic material (**14a**); therefore the correct structure of isoaplysin-20 is shown in formula **14** with a chair/boat/chair perhydrophenanthrene skeleton.

Treatment of (*E,E,E*)-geranylgeranyl acetate (**10**)[5] with mercury(II) trifluoromethanesulfonate/*N,N*-dimethylaniline complex (**7**) (1.2 equiv) in nitromethane at −20 °C for 2 h,[4] and subsequent exposure to an aqueous solution of KBr (excess) at room temperature for 12 h afforded a *tert*-alcohol product, **11** (mp 222–223 °C, 16% yield), together with an olefinic compound, **12** (mp 188.5–190 °C, 17% yield)[6] (Scheme II). The stereochemistry of **11** was rigidly established by the conversion to the demercuration product **2** ($NaBH_4$/aqueous NaOH/C_2H_5OH),[7] which was identified with the compound reported by Rŷeda.[2] The organomercury compound **11** was then subjected to the bromination according to the procedure reported by Hoye (Br_2/LiBr/O_2/pyridine)[8] to give **5a** in 65% yield (mp 166.5–167 °C). The orientation of C-3 bromine was clearly shown to be α-equatorial based on its ^{1}H NMR spectrum (H-3: δ 3.94, dd, J = 12 and 4 Hz). However, this spectrum showed a different pattern in the methyl region (δ 0.86 (6 H), 0.94 (3 H), 1.05 (3 H), and 1.16 (3 H)) from that of natural isoaplysin-20 acetate (δ 0.92 (3 H), 0.97 (3 H), 1.03 (6 H), and 1.20 (3 H)). Thus, the structure of isoaplysin-20 is not **5**, which was proposed by Rûveda.[2]

Now we turned our attention to the minor products of the above hydroxylative cyclization. After separation of the major carbinol product **11**, the presence of some minor stereoisomeric constituents were detected in the crystallization mother liquor. This mixture was subjected to bromination as mentioned before and exhaustive purification by using HPLC.[9] Two kinds of tricyclic compounds, **13** (mp 147 °C, 1.6% yield from **10**)[10] and **14a** (mp 178 °C, 1.8%

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(9) Acetonitrile/water (7:3) on a Develosil ODS-5 column and then hexane/ethyl acetate (3:1) on a Develosil Silica 30-3 column using an Altex RI detector.

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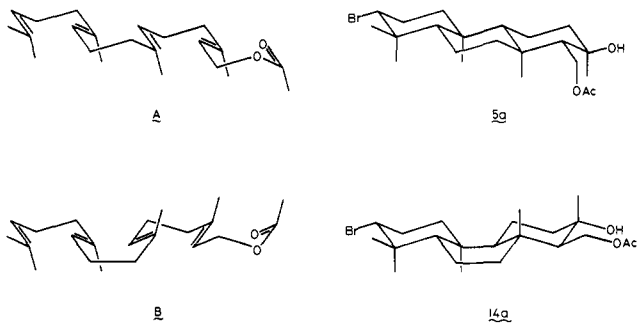
Chart II



yield from **10**), were isolated as crystals. The latter product, **14a**, afforded ^{1}H NMR, IR, and mass spectra entirely superimposable with those of natural isoaplysin-20 acetate. Hydrolysis of **14a** ($NaOH/C_2H_5OH$, 0 °C, 10 min) gave a diol, **14**, which was again identified with the natural isoaplysin-20 in all respects. Since no more sample of isoaplysin-20 is available, the correct structure was established through the X-ray crystallography of our synthetic material **14a**, which was crystallized from methanol.

It should be noted that the perhydrophenanthrene system of this compound involves in an anti/syn/anti ring juncture, which forces the ring system to take a chair/boat/chair conformation. Observed dihedral angles show that some distortion is presented in all three rings, and, particularly, the ring B takes a skew-boat rather than a boat conformation. The bond distances of C-9/C-10 (1.579 (8) Å) and C-8/C-14 (1.575 (8) Å) are rather long. The lengthening of these distances is mainly due to the intramolecular H-1α/H-11α and C-16/C-17 repulsions.

By consideration of this biomimetic olefin cyclization, the following assumption would be required for the reasonable reaction pathway. The major carbinol product **5a** must be derived by the consecutive four-ring formation via all chair folding (A) of (*E*,*E*,*E*)-geranylgeranyl chain including acetoxyl group participation, while **14a** should be formed from chair/boat/chair folding (B) (Chart II). . Even though the latter path (B) is more strained, this arrangement would release an apparent three successive 1,3-diaxial interaction originated from four methyl groups in A. Anyhow, this provides the clear experimental evidence to produce a perhydrophenanthrene derivative with the boat form B ring by means of the biomimetic cyclization of (*E*,*E*,*E*)-geranylgeraniol derivative.[11] The reaction pathway is somewhat similar to that of the Lewis acid or enzyme catalyzed cyclization of 2,3-oxidosqualene.[12]

Acknowledgment. We are indebted to Professor S. Yamamura of Keio University for a generous supply of spectral charts of natural isoaplysin-20 and its acetate, Dr. Y. Fujita of Kuraray Co. LTD for the gift of pure (*E*,*E*,*E*)-geranylgeraniol, and the Crystallographic Research Center, Institute for Protein Research, Osaka University, for computer calculations. This study is supported by the Grant-in-Aid for Special Project Research (1983), No. 582180024) from the Ministry of Education, Science and Culture of Japanese Government.

Supplementary Material Available: IR, ^{1}H NMR, ^{13}C NMR, mass spectra, analytical data, and details of X-ray analysis including an ORTEP drawing (14 pages). Ordering information is given on any current masthead page.

(10) The minor product **13** showed a different ^{1}H NMR spectrum in its methyl region (δ 0.94 (3 H), 1.05 (3 H), 1.24 (3 H), and 1.27 (6 H)) from those of **5a** and **14a**, and preparation of good crystals for X-ray diffraction analysis is still in effort.

(11) A nonenzymic biogenetic-type conversion of a geranylgeraniol-type tetraene oxide to 24,25-dihydroprotosterol and 24,25-dihydroparkeol, both of which possess the boat form B ring, has been recorded previously: van Tamelen, E. E.; Anderson, R. J. *J. Am. Chem. Soc.* **1972**, *94*, 8225.

(12) van Tamelen, E. E.; Leopold, E. J.; Marson, S. A.; Waespe, H. R. *J. Am. Chem. Soc.* **1982**, *104*, 6479. Review: van Tamelen, E. E. *Acc. Chem. Res.* **1975**, 152.

Are π-Complexes Intermediates in Halocarbene Cycloadditions?

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Received November 8, 1983

Halocarbenes are electrophilic species, undergoing faster cycloadditions with electron-rich alkenes than with electron-deficient alkenes. We recently showed that the room-temperature selectivities of carbenes in cycloadditions to a series of alkylethylenes[1] are linearly related to carbene stabilities.[2] This normal reactivity–selectivity relationship implies that variations in activation enthalpy control selectivity. However, it has been known since the work of Skell and Cholod in 1969 that the relative rates of CCl_2 cycloadditions to alkylethylenes parallel the differences in entropies of activation, while differences in activation enthalpies are negligible.[3] Giese and co-workers have thoroughly documented this "entropy control" of selectivity for cycloadditions of highly reactive carbenes (CCl_2, CBrCl, CBr_2). All halocarbenes exhibit identical selectivities at 360 K, while selectivity reversal occurs at higher temperatures.[4] Several experimental reports of zero or negative activation energies for carbene cycloadditions have also appeared.[5,6] It is usually concluded that an intermediate (π-complex, or "loose charge-transfer complex"[6]) is formed and that the conversion of this complex to products involves a barrier that is below the energy of the reactants.[4-6] A cage complex or proximity pair is also compatible with the observed kinetics.[6a] Zero or negative activation energies, and entropy control of reactivity also have been interpreted as evidence for the formation of intermediates in singlet oxygen reactions,[7] in quenching of ketone triplet excited states by alkenes,[8] in nitrile ylide cycloadditions,[9] and in a Diels–Alder reaction.[10]

In this and the following communication, we present a new interpretation of these results. We describe (1) calculations which suggest that the most reactive halocarbenes do not form stable π-complexes with alkenes, (2) computations of ΔH and ΔS at several points upon the potential energy surface, which show a simple relationship between ΔS and reaction progress, (3) models for ΔH and ΔS that parallel experimental data for carbene cycloadditions and provide a new explanation of how negative activation energies and entropy control of reactivity arise, and (4) a generalization of these results for other fast reactions.

Ab initio calculations were carried out on the cycloadditions of CCl_2 and CF_2 to ethylene. Structures of stationary points obtained at the 3-21G[11] level with gradient optimization[12] are shown in Figure 1. Energies at 3-21G, 6-31G*[13] and MP2/3-21G[14] levels are given in Table I.

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