Table II. ^{13}C NMR Chemical Shifts ($CDCl_3$) of Side Chain and Angular Methyl Carbons

carbon	chemical shift, ppm: xestospongesterol (2)	chemical shift, ppm: isoxestospongesterol (3)
C-18	11.84	11.83
C-19	19.40	19.40
C-20	36.34	36.20
C-21	18.89	18.89
C-22[b]	30.88	30.61
C-23[b]	38.78	37.29
C-24	39.18	39.48
C-25	146.96	148.15
C-26[b]	28.62	20.22
C-27	118.37	116.96
C-28[a]	28.94	27.68
C-29[a]	28.68	27.20
C-30	15.06	14.37
C-31[a]	15.63	13.60

[a] Assignment proved by selective decoupling. [b] These assignments were confirmed by comparing the observed chemical shifts with those calculated by the procedures described by Kelecom [A. Kelecom, *Bull. Soc. Chim. Belg.*, **89**, 343-352 (1980)].

$CHCl_3$), which was shown to be identical with the natural material (cf. Table I).

Isomerization of the double bond was achieved by the procedure of Dervan and Shippey[15] through conversion (*m*-chloroperbenzoic acid, CH_2Cl_2, 0 °C, 24 h) of isoxestospongesterol i-methyl ether (**8**) to the epoxide **9** ($M^+ = 470$; NMR consistent with structure) and exposure (100 °C, 2 h) to excess hexamethyldisilane and potassium methoxide in hexamethylphosphoramide, followed by removal of the i-methyl ether protecting group. The resulting xestospongesterol (**2**), mp 133-134 °C, $[\alpha]^{28}{}_D$ -46.6° (*c* 0.07, $CHCl_3$) was identical in all respects (cf. Table I) with the natural sponge sterol.

The two most plausible biosynthetic paths involve well-documented[4] processes: one-step SAM [(*S*)-adenosylmethionine] biomethylation of a double bond (e.g., **10**, **11**, **13**, **15-17**) and proton elimination from a carbon adjacent to the resulting carbonium ion (e.g., **12** → **13** or **16**). The key precursor is either codisterol or 24-epicodisterol (**11**), both of them naturally occurring[16,17] and easily derivable[4] by SAM biomethylation of desmosterol (**10**). A second SAM biomethylation of C-26 would provide the carbonium ion **12**, which through proton loss from either C-24 (**12** → **13**) or C-27 (**12** → **16**) can initiate two further, alternative biomethylation processes. Indirect evidence for either scheme to (iso)xestospongesterol (**2**, **3**) is provided by our recent isolation of the postulated biosynthetic intermediates **15**[18] and **16**.[17] While the highly alkylated desmosterol (**10**) analogues **13** and **17** have not yet been encountered in nature, their intermediacy seems highly likely, since we have not only found in marine sponges the products of SAM biomethylation at C-24 (i.e., **17** → **2** or **3**; **13** → **15**) but also the products **14**[19] and **18**[20] arising from SAM attack at C-25. In summary, the continuing isolation of highly branched marine sterols has no terrestrial counterpart and most likely is associated with a special biological function[21] in these marine organisms. However, as the various "missing links" are isolated and identified, their biosynthesis fits beautifully into the currently accepted[4] scheme of sequential single-step biomethylations of olefinic precursors.

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(15) P. B. Dervan and M. A. Shippey, *J. Am. Chem. Soc.*, **98**, 1265-1267 (1976).

(16) I. Rubinstein and L. J. Goad, *Phytochemistry*, **13**, 481-484 (1974).

(17) W. C. M. C. Kokke, C. S. Pak, W. Fenical, and C. Djerassi, *Helv. Chim. Acta*, **62**, 1310-1318 (1979).

(18) L. N. Li and C. Djerassi, to be published.

(19) L. N. Li, U. Sjöstrand, and C. Djerassi, *J. Am. Chem. Soc.*, **103**, 115-119 (1981).

(20) L. N. Li, U. Sjöstrand, and C. Djerassi, to be published.

(21) R. M. K. Carlson, C. Tarchini, and C. Djerassi in "*Frontiers of Bioorganic Chemistry and Molecular Biology*", S. N. Anachenko, Ed., Pergamon, Oxford, 1980, pp 211-224.

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Silver(I) Photocatalyzed Addition of Acetonitrile to Norbornene

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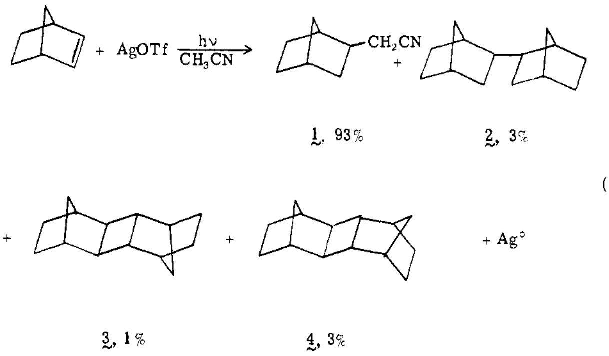
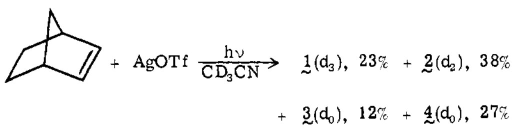
We have recently reported that the cationic polymerization of cyclic ethers can be photoinitiated with metal ions such as Ag(I) and Cu(I).[1] The metal ion serves as a one-electron oxidant upon ligand-to-metal charge-transfer excitation and ultimately forms a metallic precipitate, thus rendering electron transfer irreversible. The contrasting failure of strong organic electron acceptors to effect charge-transfer photoinitiated polymerization of cyclic ethers presumably is due to rapid back electron transfer from the acceptor anion radical to a cationic species.[2] We have now extended our investigations to the photochemical behavior of Ag(I)-alkene complexes and here report the efficient conversion of norbornene to *exo*-2-(cyanomethyl)bicyclo[2.2.1]heptane (**1**) upon irradiation of the Ag(I)-norbornene complex in acetonitrile solution. The novel mechanism of this reaction involves ligand-to-metal charge-transfer photoinitiation and, ultimately, free radical chain addition of the cyanomethyl radical to norbornene.

Irradiation of an acetonitrile solution of norbornene (0.25 M) and silver trifluoromethanesulfonate (AgOTf, 0.002-0.02 M) with a medium pressure mercury lamp in a Vycor lamp well results in the formation of **1**, minor amounts of the norbornene dimers **2-4**, and a silver mirror (eq 1).[3] Conversions of norbornene to **1** in preparative scale reactions were typically 35-40%, even when the initial norbornene-Ag(I) ratio was 15:1. Irradiation in acetonitrile-d_3 yields the same norbornene-containing products, albeit in greatly different relative yields (eq 2). Mass spectral analysis



(1)



(2)

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(1) (a) Woodhouse, M. E.; Lewis, F. D.; Marks, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 996. (b) Submitted for publication.

(2) Achiba, Y.; Kimura, K. *Chem. Phys. Lett.* **1976**, *39*, 515.

(3) Spectroscopic properties of **1-4** were identical with those of independently synthesized samples.

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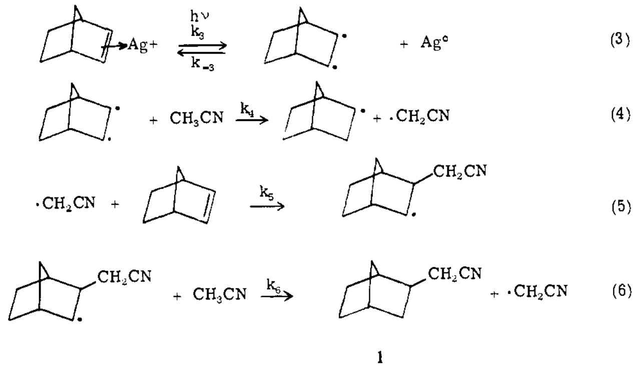
of photoproducts indicated the incorporation of deuterium in products **1** and **2**, but not in **3** or **4**. The generality of this reaction is supported by the observation that propionitrile can be added to norbornene and acetonitrile to several cyclic and acyclic alkenes. The scope of this reaction is under continuing investigation.

The probable mechanism for the formation of photoproduct **1** is given in eq 3–6. In support of photoinitiation via excitation of a ground-state Ag(I)–norbornene complex (k_3), we find that excitation at 313 nm, where the complex is the only absorbing species, effects the formation of **1–4**. The quantum yield for formation of **1** is dependent upon norbornene concentration, a linear plot of Φ^{-1} vs. $[\text{norbornene}]^{-1}$ yielding a limiting value of $\Phi = 0.50$. Alkenes which fail to form light-absorbing ground-state complexes do not undergo this reaction. That the mode of excitation may be ligand-to-metal charge transfer is supported by the formation of metallic silver and the nature of the organic products (vide infra). A conceivable alternative role for Ag(I) would be as a catalyst for norbornene singlet → triplet intersystem crossing.[4] Triplet sensitization of norbornene in acetonitrile is known to yield products **1–4**[5] (eq 7); however, the product ratios are different from those obtained in the present Ag(I) initiated reaction (eq 1), and the triplet mechanism would not account for the formation of Ag^0. Moreover, the triplet reaction is quenched by low concentrations of oxygen,[4] whereas the Ag(I) initiated reaction actually requires low concentrations of oxygen (1–5 torr over the solution) and does not occur in thoroughly deoxygenated solutions. Oxygen may react with atomic Ag to yield $Ag^+ O_2^-$,[6] facilitating chain initiation by preventing back electron transfer (k_{-3}). Oxygen serves as an essential electron carrier in the charge-transfer initiated cyclodimerization of *N*-vinylcarbazole.[7]



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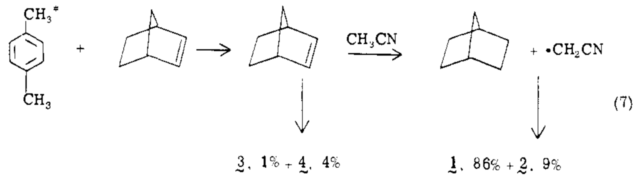

Following ligand-to-metal charge transfer, the norbornene cation radical reacts with acetonitrile to form the norbornyl cation and the cyanomethyl radical (eq 4). Hydrogen atom abstraction from acetonitrile by organic cation radicals has been reported by Whitten et al.[8] The reaction of the cyanomethyl radical with norbornene leads to formation of **1** by a free radical chain process (eq 5 and 6). In support of this mechanism, we find that the quantum yield of **1** is substantially reduced in the presence of high oxygen concentrations[9] or acetonitrile-d_3. The solvent isotope effect is consistent with a chain process for the formation of **1**, involving C–D abstraction in both initiation (eq 4) and propagation (eq 6) steps, competing with nonchain processes for the formation of **2–4**. Furthermore, when the terminal alkene, 2-ethyl-1-butene, is added to a solution of norbornene and AgOTf, irradiation leads to a mixture of **1** and an acetonitrile adduct of the terminal alkene. Irradiation of 2-ethyl-1-butene and AgOTf under the same conditions gives a substantially lower yield of adduct.

The mechanism of formation of the minor dimeric products **2–4** has not received detailed investigation. The Ag(I) initiated (eq 1) and triplet sensitized (eq 7) reactions yield similar dimer ratios **3**:**4** ~ 0.3. In contrast, Salomon and Kochi[10] report a dimer ratio **3**:**4** > 10 for the CuOTf-catalyzed cyclodimerization of norbornene in tetrahydrofuran solution. Furthermore, both Ag(I) initiated and triplet sensitized reactions yield dideuterated **2** in acetonitrile-d_3. Thus it is possible that the formation of minor products **2–4** in the Ag(I) initiated reaction occurs via a triplet mechanism. It is interesting to note that norbornene–CuOTf solutions are photostable in acetonitrile, presumably due to strong Cu(I)–nitrile coordination which excludes norbornene activation. Conversely, irradiation of norbornene and Ag(OTf) in tetrahydrofuran leads only to polymerized solvent.[1] Thus the intrinsic coordinative preferences of metal ions are found to impart substantial selectivity in terms of substrate binding and photochemical activation.[11]

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(4) Saito, T.; Yasoshima, S.; Masuhara, H.; Mataga, N. *Chem. Phys. Lett.* **1978**, *59*, 193.

(5) Schroeter, S. H. *J. Liebigs Ann. Chem.* **1974**, 1890.

(6) (a) Shimizu, N.; Shimakoshi, K.; Yasumori, I. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2929. (b) McIntosh, D.; Ozin, G. A. *Inorg. Chem.* **1977**, *16*, 59.

(7) Ledwith, A. *Acc. Chem. Res.* **1972**, *5*, 133.

(8) DeLaive, P. J.; Giannotti, C.; Whitten, D. G. *J. Am. Chem. Soc.* **1978**, *100*, 7413.

(9) High initial oxygen concentrations do not effect the final yield of products in preparative irradiations but do depress the initial rate of reaction.

(10) Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1974**, *96*, 1137.

(11) Acknowledgment is made to the donors of the Petroleum Research Fund (Grant10799-AC4), administered by the American Chemical Society, for generous support of this research.

On the Purported Fischer–Tropsch Alkylation of Benzene: Reaction of Benzene with Aluminum Trichloride Revisited

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In 1979 it was reported[1] that certain transition-metal carbonyls $M_m(CO)_n$ (M = W, Rh, Ru, Cr, Co) in the presence of $AlCl_3$ catalyzed the so-called Fischer–Tropsch alkylation of benzene. The reaction appears to be of great significance, since it is unprecedented and thought to be homogeneous. However, the fact that no labeling control experiments had been carried out and the assertion that no alkylbenzene formation was observed in the absence of the transition metal, in contrast to the well-established Lewis acid chemistry of benzene,[2-9] prompted a reinvestigation of the reported findings.

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* University of California.

(1) G. Henrici-Olivé and S. Olivé, *Angew. Chem.*, **91**, 83 (1979); *Angew. Chem., Int. Ed. Engl.*, **18**, 77 (1979).

(2) C. Friedel and J. M. Crafts, *J. Chem. Soc.*, 115 (1882); *Bull. Soc. Chim. Fr.*, **39**, 195, 306 (1883); *C. R. Hebd. Seances Acad. Sci.*, **100**, 692 (1885).

(3) C. H. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry", Van Nostrand Reinhold, New York, 1941.

(4) R. Pummerer and J. Binapfl, *Chem. Ber.*, **54**, 2768 (1921).

(5) E. Wertyporoch and H. Sagel, *Chem. Ber.*, **66**, 1306 (1933).

(6) M. G. Gonikberg and A. E. Gavrilova, *J. Gen. Chem. USSR (Engl. Transl.)*, **22**, 1429 (1952).

(7) G. E. Hall and E. A. Johnson, *J. Chem. Soc. C*, 2043 (1966). These authors report a detailed analysis of the higher boiling products from the reaction of $AlCl_3$ in boiling benzene.

(8) M. Siskin and J. Porcelli, *J. Am. Chem. Soc.*, **96**, 3640 (1974), and the references therein.

(9) P. Kovacic and A. Kyriakis, *J. Am. Chem. Soc.*, **85**, 454 (1963); J. E. Durham and P. Kovacic, *J. Polym. Sci., Polym. Lett. Ed.*, **14**, 347 (1976).

0002-7863/81/1503-3609$01.25/0