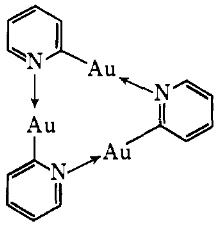
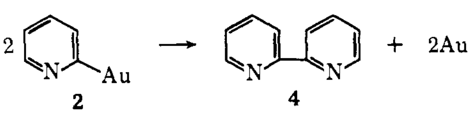
basic solvents such as pyridine (best), DMSO, and DMF. The pure compound is a bright yellow, crystalline solid, stable to air and water but somewhat sensitive to light. *Anal.* Calcd for $C_5H_4AuN$: C, 21.83; H, 1.47; Au, 71.61; N, 5.09. Found: C, 22.07; H, 1.34; Au, 71.34; N, 4.97. When the compound is heated, decomposition is first noted about 120°, followed by melting with complete decomposition at 150°.

The simplest structure consistent with the coordination requirements of gold(I) is a planar, cyclic trimer (**3**). Although this structure requires a central nine-membered ring, the linear bonding of the gold atom and the 60° angle between the nitrogen atom, ring center, and $C_2$ allow it to be strain free. Low solubility and apparent dissociation of the trimeric structure in solution have prevented accurate molecular weight measurements, and a higher polymeric structure cannot be completely excluded at this time.


**3**

The decomposition of 2-pyridylgold(I) at its melting point (or at lower temperatures under vacuum) quantitatively produces metallic gold and 2,2′-bipyridine (**4**).


**2** **4**

This mode of decomposition is of potential industrial importance since it permits deposition of pure gold films under very mild thermal conditions. The reaction also provides a high-yield route, *via* 2-pyridylgold(I) derivatives, from 2-bromopyridines to 2,2′-bipyridines. These latter reagents are of major importance in analytical and coordination chemistry.[2,3]

Six simple derivatives of 2-pyridylgold(I), prepared in the same manner as the parent compound, are listed in Table I. Yields were about 90% in all cases. The 6-methyl derivative is of particular interest since steric coordination hindrance by the methyl group was considered possible. However, the compound formed without difficulty and shows no unusual solubility or thermal instability properties. When pyrolyzed under vacuum, all derivatives gave the expected decomposition products, metallic gold and the symmetrical bipyridine. None of these derivatives shows significantly better solubility than 2-pyridylgold(I), but, in contrast to the parent compound, all are stable indefinitely to light.

**Table I.** Derivatives of 2-Pyridylgold(I)[a]

| Substituent | Mp,[b] °C | Bipyridine yield, %[c] |
|---|---|---|
| 3-Methyl | 217–220 dec | 69 |
| 4-Methyl | 184 dec | 76 |
| 5-Methyl | 159 dec | 84 |
| 6-Methyl | 169–171 dec | 73 |
| 4,6-Dimethyl | 185–190 dec | 77 |

[a] Satisfactory elemental analyses have been obtained for all compounds. [b] Slight decomposition commences about 15° below the listed decomposition temperatures. [c] Crude 2-pyridylgold(I) derivatives were used in these experiments.

---

(2) W. Brandt, F. P. Dwyer, and E. C. Gyarfas, *Chem. Rev.*, **54**, 959 (1954).

(3) C. M. Harris and S. E. Livingstone in "Chelating Agents and Metal Chelates," F. P. Dwyer and D. P. Mellor, Ed., Academic Press, New York, N. Y., 1964, Chapter 3.

(4) Electrochemicals Department, Experimental Station, E. I. du Pont de Nemours and Co., Wilmington, Del. 19898.

(5) This work is to be presented in part at the 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 1970.

**Lawrence G. Vaughan**[4,5]
*Central Research Department, Experimental Station*
*E. I. du Pont de Nemours and Company*
*Wilmington, Delaware 19898*

*Received November 14, 1969*

## Mass Spectrometry in Structural and Stereochemical Problems. CXC.[1] Electron Impact Induced Triple Hydrogen Migration in Vinyl Alkyl Ethers[2]

*Sir:*

The many detailed studies[3] of hydrogen migrations, which occur in organic compounds after electron impact, have aided enormously in our understanding of the mechanistic pathways and fragmentation reactions in the mass spectrometer. While most well-known hydrogen transfers result in a net gain or loss of one hydrogen in the charged fragment, unidirectional[4] and reciprocal[5] double hydrogen rearrangements are also well documented through deuterium labeling. Triple hydrogen transfers have so far been recorded only in higher alkyl esters of trimellitic anhydride[6] and no real insight has as yet been gained into them because of the absence of any isotopic labeling. We record now the second example of a unidirectional triple hydrogen migration, whose course could be defined through extensive deuterium labeling.

In connection with our study[7] of the mass spectrometric behavior of alkyl vinyl ethers,[8] we encountered a striking feature (see Table I) in the fragmentation of those ethers with an alkyl chain longer than five carbon atoms, namely the loss of the elements of ethanol (substantiated by a metastable peak) from the molecular ion.[9] Since deuterium labeling showed that the vinyl group

---

(1) For preceding paper see R. T. Gray, J. Diekman, G. L. Larson, W. K. Musker, and C. Djerassi, *Org. Mass Spectrom.*, in press.

(2) Financial assistance from the National Institutes of Health (grant No. AM-04257) is gratefully acknowledged.

(3) For leading references see (a) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1967; (b) W. Benz, "Massenspectrometrie Organischer Verbindungen," Akademische Verlagsgesellschaft, Frankfurt, 1969, pp 128–150.

(4) For leading references see C. Djerassi and C. Fenselau, *J. Amer. Chem. Soc.*, **87**, 5756 (1965).

(5) L. Tökes, G. Jones, and C. Djerassi, *ibid.*, **90**, 5465 (1968); G. Eadon and C. Djerassi, *ibid.*, **91**, 2724 (1969).

(6) S. Meyerson, I. Puskas, and E. K. Fields, *Chem. Ind.* (London), 1845 (1968).

(7) M. Katoh and C. Djerassi, *Chem. Commun.*, 1385 (1969).

(8) For earlier studies see F. W. McLafferty, *Anal. Chem.*, 31, 2072 (1959); S. Meyerson and J. D. McCollum, "Advances in Analytical Chemistry and Instrumentation," Vol. 2, C. N. Reilley, Ed., Interscience Publishers, New York, N. Y., 1963, p 211; M. E. Audier, *Org. Mass Spectrom.*, **2**, 283 (1969).

(9) No metastable ion was encountered for the hypothetical sequence $M^+ \rightarrow M - C_2H_4O \rightarrow M - C_2H_6O$ using the defocusing technique.

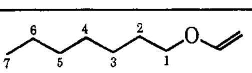
**Table I.** Relative Intensity of Some Characteristic Fragment Ions of *n*-Alkyl Vinyl Ethers (ROCH=CH$_2$) at 70 and 12 eV[a]

| R | M − $C_2H_3O$ | M − $C_2H_4O$ | M − $C_2H_5O$ | M − $C_2H_6O$ |
|---|---|---|---|---|
| $C_4H_9$ | 37.3 (10.7) | 55.0 (89.3) | 7.7 (0) | 0 |
| $C_5H_{11}$ | 25.0 (21.9) | 67.6 (73.0) | 4.2 (1.5) | 1.3 (3.6) |
| $C_6H_{13}$ | 16.8 (7.8) | 21.9 (17.7) | 16.4 (12.1) | 39.2 (62.4) |
| $C_7H_{15}$ | 5.9 (11.6) | 27.9 (16.1) | 18.3 (12.9) | 47.6 (59.3) |
| $C_8H_{17}$ | 10.3 (6.0) | 9.7 (10.3) | 15.5 (11.8) | 64.5 (73.5) |
| $C_9H_{19}$ | 5.0 (2.1) | 25.0 (16.4) | 7.0 (10.7) | 62.0 (70.8) |
| $C_{10}H_{21}$ | 10.7 | 8.9 | 10.3 | 70.0 |

[a] Nominal 12-eV values are given in parentheses.

was lost in this fragmentation, it followed that three hydrogen atoms had to migrate from the alkyl chain ($C_5$>). In order to establish the origin of these itinerant hydrogens, *n*-heptyl vinyl ether (I) was labeled with deuterium in every position of the alkyl chain. The results, summarized in Table II, demonstrate the absence of hydrogen randomization in the alkyl chain, since essentially no hydrogen was lost from positions 1, 2, and 7. Since summation of all deuterium transfers in the labeled substrates (Table II) did not amount to 300%, a deuterium isotope effect had to operate, whose existence and magnitude is quite compatible with previously demonstrated[10] deuterium isotope effects in mass spectrometry.

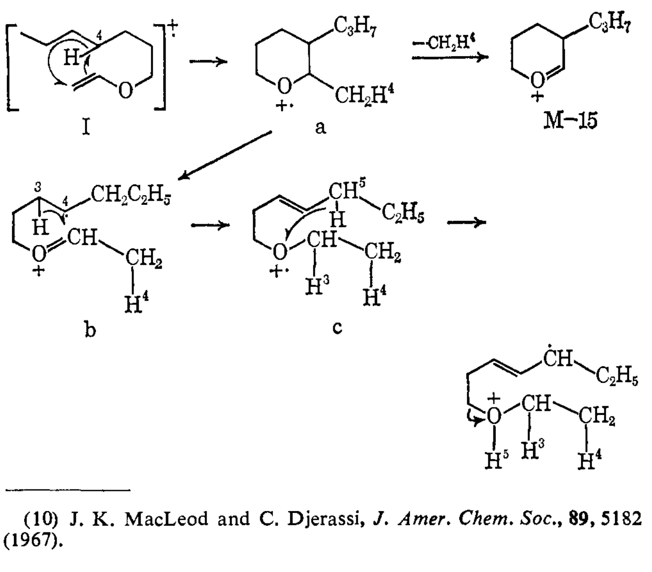
**Table II.** Origin of Hydrogen Transfer in M − $C_2H_6O$ Fragment in *n*-Heptyl Vinyl Ether at 70 eV[a,b]



| | 1-$d_2$ | 2-$d_2$ | 3-$d_2$ | 4-$d_2$ | 5-$d_2$ | 6-$d_2$ | 7-$d_3$ |
|---|---|---|---|---|---|---|---|
| M − $C_2H_6O$ | 99 | 96 | 32 | 47 | 28 | 61 | 97 |
| M − $C_2H_5OD$ | 1 | 4 | 63 | 53 | 62 | 37 | 1 |
| M − $C_2H_4OD_2$ | | | 5 | | 11 | 2 | 1 |

[a] Only minor changes were noted at low voltage (nominal 15 eV). [b] All values are %.

The bulk of the hydrogen transfer involves positions 3, 4, and 5, which can be rationalized readily through postulating the intermediacy of ionized 2-methyl-3-propyltetrahydropyran (a) and is also completely consistent with our previous observation[7] that over 80% of the hydrogen lost in the important M − $CH_3$ ion of all *n*-alkyl vinyl ethers originated from C-4 of the alkyl chain (together with the methylene portion from the vinyl group).



We visualize the triggering reaction to be the firmly established[7] eight-membered hydrogen transfer from C-4 in *n*-heptyl vinyl ether (I) with concomitant cyclization to ionized 2-methyl-3-*n*-propyltetrahydropyran (a). The latter now undergoes the thoroughly documented[11] α fission of tetrahydropyrans, which can lead either to the M − $CH_3$ ion[7] or to species b. Hydrogen transfer from C-3 of b is mechanistically attractive (six-membered transition and stabilization of C-4 radical site) and has in fact been demonstrated[12] in tetrahydropyran itself by deuterium labeling. The third required shift, from C-5, then occurs from an allylically activated position.

The proposed reaction scheme can also account for the observation (Table II) that C-6 is implicated in the triple hydrogen transfer, albeit to a lesser extent. If the hydrogen atom from C-5 rather than C-3 is transferred in the hypothetical intermediate b, then C-6 becomes an activated position and can participate in the hydrogen transfer in a manner analogous to the step c → d. This qualitative rationalization of the triple hydrogen transfer in higher *n*-alkyl vinyl ethers is supported by the observation that the mass spectrum of the hitherto unknown 2-methyl-3-propyltetrahydropyran[13] exhibited the same features (M − $CH_3$, M − $C_2H_6O$, etc.) as the vinyl ether I. The scheme also accounts for the fact (see Table I) that the M − $C_2H_6O$ loss becomes significant only with an *n*-hexyl chain, since this is the first member of the series in which all three migrating hydrogens originate from secondary positions.

In view of their intrinsic interest as well as their significant mechanistic implications, we are continuing in our laboratory the examination of other triple hydrogen transfer processes.

**Acknowledgment.** We are indebted to Mr. C. E. Conover for performing the mass spectral measurements with an MAT CH-4 mass spectrometer equipped with a molecular beam inlet system, and to Mitsubishi Chemical Industries Co. for fellowship funds and leave of absence to M. K.

---

[10] J. K. MacLeod and C. Djerassi, *J. Amer. Chem. Soc.*, **89**, 5182 (1967).

[11] See ref 3a, p 253.

[12] R. Smakman and T. J. de Boer, *Org. Mass Spectrom.*, 1, 403 (1968).

[13] Its synthesis will be described in our full paper dealing with the mass spectrometry of alkyl vinyl ethers.

**Masanobu Katoh, Carl Djerassi**
*Department of Chemistry, Stanford University*
*Stanford, California 94305*

*Received November 25, 1969*

---

## Conversion of Cholestanol to 12-Ketocholestanol and to $\Delta^{14}$- and $\Delta^{8(14)}$-Cholestenol by Remote Oxidation

*Sir:*

A recent communication[1] from this laboratory described the conversion of straight-chain hydrocarbon alcohols such as hexadecanol to products of "remote oxidation" such as 14-ketohexadecanol. The sequence—esterification with *p*-benzoylbenzoic acid, photolysis, dehydration, ozonolysis, and hydrolysis—led to

---

[1] R. Breslow and M. Winnik, *J. Amer. Chem. Soc.*, **91**, 3083 (1969).