The ^{13}C chemical shifts of **12** are also consistent with this assignment. The C_2 chemical shift for the endo isomer is 62.33 ppm and 70.06 ppm for the exo isomer. These compare with values of 73.66 and 72.88 ppm for the corresponding carbons of *endo*- and *exo*-4-isopropyl-3,5-dioxabicyclo(5.1.0)octanes, **4** and **5**, respectively. This is consistent with the Gorenstein interpretation of the γ *effect*, that is, the γ *effect* is a function of the dihedral angle between the carbon in question and the γ-carbon.[10] For the exo isomer **13** the orientation between C_2 and the methine (CH) carbon of the isopropyl group is anti whereas for the endo isomer **12** it is gauche. Accordingly the endo isomer gives a C_2 resonance upfield from the exo isomer **13**. The C_2 chemical shifts for **4** and **5** are nearly the same because they have the same anti orientations to the isopropyl methine carbons.

The exo isomer **13** gave coupling constants of J_{2a-1a} = 9.56, J_{2e-1a} = 7.34, and J_{2a-2e} = −13.45 Hz. These values are consistent with values reported for *exo*-4-phenyl-8,8-dichloro-3,5-dioxabicyclo[5.1.0]octane[12] which is known to exist in a CC conformation.

Experimental Section

NMR spectra were recorded on a Brücker 250 spectrometer. Samples were run in deuterochloroform as 10% solutions. All chemical shifts are reported in parts per million downfield from internal Me_4Si. Spectra were reproduced by LAOCOON III. The ^{13}C NMR spectra were recorded at 25.15 MHz on a Varian HA-100D spectrometer. All chemical shifts are reported in parts per million downfield from interal Me_4Si. All mass spectra were determined on a AE1-9 high-resolution spectrometer. Equilibration were run in deuteriochloroform at 25 °C unless otherwise noted, and equilibrium was approached from both sides using samples enriched in one isomer. Amberlite IR-120 (plus) was used as the catalyst.

cis-1,2-Bis(hydroxymethyl)cyclopentane[13] and 2-isopropyl-1,3-dioxacyclohept-5-ene[3] were synthesized as described in the literature. *cis*-1,2-Bis(hydroxymethyl)cyclobutane was prepared by $LiAlH_4$ reduction of *cis*-1,2-cyclobutanedicarboxylic anhydride and used without further purification.

***endo*- and *exo*-4-Isopropyl-3,5-dioxabicyclo[5.2.0]decane.** The general procedure for the preparation of these compounds has been described previously.[1,3] The mixture of endo and exo isomers was prepared in 73% yield by the reaction of isobutyraldehyde and *cis*-1,2-bis(hydroxymethyl)cyclopentane, bp 80–85 °C (20 torr). The isomers were separated by GLC (8 ft 10% polyphen, Chromosorb W), and the endo isomer was the first peak: ^1H NMR $CH_a(4)$ δ 4.13, $CH_a(2)$ 3.88, $CH_e(2)$ 3.66, $CH_e(1)$ 2.11, CH_2(ring) broad multiplet at δ 1.7, CH(isopropyl) 1.90, CH_3 0.92. The exo isomer was the second peak: ^1H NMR $CH_a(4)$ δ 4.17, $CH_a(2)$ 3.49, $CH_e(2)$ 3.91, $CH_a(1)$ 3.48, CH(isopropyl) 1.80, CH_3 0.93. A mass spectrum gave m/e 141 (parent minus isopropyl).

***endo*- and *exo*-4-Isopropyl-8,8-dichloro-3,5-dioxabicyclo-[5.1.0]octane.** The synthetic procedure used to synthesize these compounds is the same as described in reference[6] except that 2-isopropyl-1,3-dioxacyclohept-5-ene was used as the olefin. The mixture of endo and exo isomers was prepared in 30% yield. The fraction boiling at 92–95 °C (3 torr) was collected and separated by GLC (8ft Carbowax 20 M, 15% on Chromosorb W). The exo isomer was the first peak: ^1H NMR $CH_a(4)$ δ 4.30, $CH_a(2)$ 3.80, $CH_e(2)$ 4.67, $CH_a(1)$ 2.38, CH(isopropyl) 1.88, C(methyl) 0.98; ^{13}C NMR $C_{(1,7)}$ δ 35.03, $C_{(2,6)}$ 70.06, $C_{(4)}$ 116.0, $C_{(8)}$ 97.63, C(isopropyl) 33.40, C(methyl) 18.24; mass spectrum m/e 225 (parent peak).

The endo isomer was the second peak: ^1H NMR $CH_a(4)$ δ 4.35, $CH_a(2)$ 4.08 (or 4.15) $CH_e(2)$ 4.15 (or 4.08), $CH_a(1)$ 2.02, CH(isopropyl) 1.75, CH_3 0.87; ^{13}C NMR C(1,7) δ 33.59, C(2,6) 62.33, C(4) 108.48, C(isopropyl) 32.73, C(methyl) 17.31; mass spectrum, m/e 225 (parent peak).

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(12) Clark, G. B.; Fraser-Reid, B.; Palenik, G. J. *J. Chem. Soc.* **1970**, 1641.
(13) Allinger, N. L.; Zalkow, V. B. *J. Am. Chem. Soc.* **1961**, *83*, 1144.
(14) Pihlaja, K.; Pasanen, P. *J. Org. Chem.* **1974**, *39*, 1948. (b) Pihlaja, K.; Nehander, H. *Acta Chem. Scand. Ser. A* **1977**, *B31*, 265. (c) Allinger, N. L.; Freibert, L. A. *J. Am. Chem. Soc.* **1960**, *82*, 2393.

A Mass Spectrometry Study of Levoglucosenone

Yuval Halpern and Joseph P. Hoppesch*

Borg-Warner Chemicals Central Research Laboratory, Des Plaines, Illinois 60018

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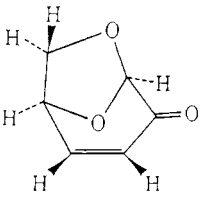
Levoglucosenone has attracted the attention of researchers the world over. Even though its structure is known,[1] no satisfactory determination of its molecular weight has been reported. The compound was reported by Tsuchiya and Sumi[2] as the major constituent of the tar fraction from the pyrolysis of acid-treated cellulose. Woodley[3] reported it as a major compound in the tar fraction from the pyrolysis of both cellulose and levoglucosan. Originally the empirical formula $C_5H_6O_2$ was assigned to the compound on the basis of the appearance of m/z 98 in the mass spectra recorded. Lipska and McCasland,[4] on the basis of IR, MS, and NMR concluded the material to be 1,5-anhydro-2,3-dideoxy-β-D-pent-2-enofuranose. Lam et al.[5] identified the material as *cis*-4,5-epoxy-2-pentanal. In 1973, however, Halpern, Riffer, and Broido[1] showed by carbon-13 NMR that the material was comprised of six carbon atoms. Therefore, the ion m/z 98, which was the primary reason for determination of the empirical formula $C_5H_6O_2$ by previous researchers, was now believed to be an ion resulting from fragmentation of the molecular ion. Halpern et al.[1] identified the compound as 1,6-anhydro-3,4-dideoxy-Δ^3-β-D-pyranosen-2-one (1). This has been accepted as the correct structure for levoglucosenone.



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The role of levoglucosenone in the pyrolysis of cellulose in relation to the fire retardancy of cellulosic materials, as well as its physical and chemical properties, have been studied extensively.[6-19] Determination of the correct

(1) Halpern, Y.; Riffer, R.; Broido, A. *J. Org. Chem.* **1973**, *38*, 204.
(2) Tsuchiya, Y.; Sumi, K. *J. Appl. Polym. Sci.* **1970**, *14*, 2003.
(3) Woodley, F. A. *J. Appl. Polym. Sci.* **1971**, *15*, 835.
(4) Lipska, A. E.; McCasland, G. E. *J. Appl. Polym. Sci.* **1971**, *15*, 419.
(5) Lam, L. K. M.; Fung, D. P. C.; Tsuchiya Y.; Sumi, K. *J. Appl. Polym. Sci.* **1973**, *17*, 391.
(6) Ohnishi, A.; Kato, K.; Takagi, E. *Polym. J.* **1975**, *7* (4) 431.
(7) Ohnishi, A.; Takagi, E.; Kato, K. *Bull. Chem. Soc. Jpn.* **1975**, *48* (6), 1959.
(8) Fung, D. P. C. *Wood Sci.* **1976**, *9* (1), 55.
(9) Shafizadeh, F.; Chin, P. P. S. *Carbohydr. Res.* **1976**, *46*, 149.
(10) Shafizadeh, F.; Chin, P. P. S. *Carbohydr. Res.* **1977**, *58*, 79.

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molecular weight (126) has, however, encountered difficulties. Various molecular weight determinations have yielded differing results. Early work using the Rast method revealed a value of 165.[1] By osmometry, a freshly prepared sample yielded a value of 131.[1] Mass spectrometry methods repeatedly suggested m/z 98 as the molecular ion corresponding to $C_5H_6O_2$.[3,13] Domburgs et al.[13] reported a peak at m/z 126 when the mass spectrometry analyses were conducted with fresh samples obtained by preparative gas chromatography. Aged samples revealed m/z 98 as the ion of highest mass.

We have concluded that the reactive nature of this compound has complicated its analysis. Since mass spectrometry analyses have not been definitive, we experimented with combined gas chromatography–mass spectrometry (GC–MS) using both electron impact and chemical ionization techniques. It is the purpose of this note to publish the methodology, the electron and chemical ionization data, and the elemental compositions determined by accurate mass measurements.

Results and Discussion

Mass spectra were consistent with the structure of levoglucosenone (1). Measurements made by using high resolution techniques revealed an accurate mass of 126.0327 for the molecular ion corresponding to an empirical formula of $C_6H_6O_3$. The base peak ($C_5H_6O_2$) yielded an accurate mass of 98.0381. The errors in measurement were 12 ppm and 9 ppm, respectively. The neutral loss of 27.9946 corresponds to the elimination of carbon monoxide. The molecular weight of 126 was established by the molecular ion m/z 126 in the 70-eV spectrum and by the protonated molecular ion m/z 127 in the chemical ionization spectra. The quasimolecular ion m/z 127 resulted from a proton donation by the isobutane reagent ion $C_4H_9^+$.

In conclusion, we have shown that the molecular weight of levoglucosenone is indeed 126 and can be determined accurately by GC–MS techniques. The mass spectra recorded in this work support the accepted structure for levoglucosenone and add an important proof to its identity.

Experimental Section

Preparation of Levoglucosenone. For the reported study, levoglucosenone was prepared by the pyrolysis of kraft paper. The paper was moistened with a solution of 5% phosphoric acid and placed in a glass tube continually purged with helium. The tube was heated to 300 °C. The tar fraction of interest was protected from light, taken up in chloroform, and immediately analyzed.

Mass Spectrometry Analyses. The data reported herein were obtained on a VG Analytical Model 7350 (70/70) mass spectrometer and a Hewlett-Packard Model 5840 gas chromatograph. Using splitless injection, the samples were analyzed on SE-54 capillary columns. The columns were 25-m fused silica having an internal diameter of 0.3 mm. These columns were siloxane deactivated and coated with SE-54 at a phase ratio of 150. The temperature program involved an initial temperature of 50 °C with a 5-min hold followed by a 10 °/min program to 250 °C. The retention time observed for the levoglucosenone under these conditions was 9.8 min. This retention time corresponded to 288 scans. Mass spectra were recorded by using electron ionization (70 eV) and also by chemical ionization with isobutane as the reagent gas.

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Registry No. 1, 37112-31-5.

(11) Brimacombe, J. S.; Hunely, F.; Tucker, L. C. N. *Carbohydr. Res.* **1978**, *60*, C11.
(12) Pecka, J.; Cherny, M. *Collect. Czech. Chem. Commun.* **1978**, *43*, 1720.
(13) Domburg, G.; Berzina, I.; Kirshbaum, I.; Gavars, M. *Khim. Drev.* **1978**, (6) 105.
(14) Shafizadeh, F.; Furneaux, R. H.; Stevenson, T. *Carbohydr. Res.* **1979**, *71*, 169.
(15) Domburg, G.; Berzina, I.; Kupce, E.; Kirshbaum, I. Z. *Khim. Drev.* **1980** (3), 99.
(16) Wolf, R. *Ind. Eng. Chem. Prod. Res. Dev.* **1981**, *20*, 413.
(17) Lipska, A. E. U.S. Pat. 3926947, 1975.
(18) Domburg, G.; Kirshbaum, I.; Kulkevic, A.; Vedernikov, N. U.S.S.R. Pat. 595319, 1978.
(19) Domburg, G.; Kirshbaum, I.; Berzina, I. U.S.S.R. Pat. 639885, 1978.

Communications

Ti(O-*i*-Pr)$_4$-Mediated Nucleophilic Openings of 2,3-Epoxy Alcohols. A Mild Procedure for Regioselective Ring-Opening

Summary: The presence of Ti(O-*i*-Pr)$_4$ during the openings of 2,3-epoxy alcohol 1 with a variety of nucleophiles markedly increases the rates and regioselectivities of these processes. The magnitude of these effects was found to be nucleophile dependent.

Sir: The facility and selectivity of enzymic reactions is often attributed to the efficient preassembly of the reactants in a highly ordered manner. Juxtaposition of reactants through their coordination to the same metal center has provided an effective nonenzymic approach for achieving similar rate and selectivity benefits. This strategy is well exemplified by rhodium-catalyzed asymmetric hydrogenation[2] and by titanium-catalyzed asymmetric epoxidation.[3] The latter process depends crucially on the facile exchange of titanium alkoxides with alcohols in solution. In 1981 we reported that early transition-metal alkoxides, especially Ti(OR)$_4$, can also effect highly selective intramolecular rearrangements of certain epoxy alcohols.[4,5] These results were rationalized by invoking

(1) Holder of a NSERC postdoctoral fellowship (1982–1984).
(2) Halpern, J. *Science (Washington, D.C.)* **1982**, *217*, 401 and references cited therein.
(3) Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 5974. (b) Sharpless, K. B.; Woodard, S. S.; Finn, M. G. *Pure Appl. Chem.* **1983**, *55*, 1823. (c) For related hydroxyl-directed epoxidations of olefinic alcohols, see: Sharpless, K. B.; Verhoeven, T. R. *Aldrichimica Acta* **1979**, *12*, 63.
(4) Morgans, D. J.; Sharpless, K. B.; Traynor, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 462.

0022-3263/85/1950-1557$01.50/0