Supporting Information

Formation of secondary organic aerosol marker compounds from the photooxidation of isoprene and isoprene-derived alkene diols under low-NO_x conditions

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1. Preparation and characterization of C_5-alkene diols

1.1. Chemicals

The chemicals used for the preparation of the C_5-alkene diols were purchased from the following suppliers: methyl lithium (1.6 *M* in diethyl ether) and isoprene (purity, 99%) from Sigma-Aldrich (St. Louis, MI, USA); bromine (99+%, extra pure), 3,4-epoxytetrahydrofuran (purity, 96%) and sodium acetate (ACS reagent) from Acros Chemicals (Geel, Belgium); and barium hydroxide, octahydrate (analytical grade) from Merck (Darmstadt, Germany).

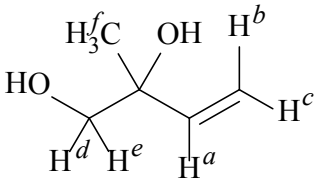
1.2. Experimental Procedures and ^{1}H-NMR Characterization

The numbers in the procedures below refer to the numbers in Scheme 1 (main text). ^{1}H-NMR spectra were recorded on a Bruker Ultrashield 400 spectrometer (Bruker Corporation, Billerica, MA, USA) with a working frequency of 400 MHz.

1,2-Dihydroxy-2-methyl-3-butene (diol 1) (1).[1] In a 100 mL round-bottom flask, a solution of 10 mL of 2-methyl-2-vinyloxiran (97 mmol) and 50 mL water was placed for 1 h at 80 °C. Subsequently, a few drops of 1 N sulfuric acid were added and the reaction mixture was kept overnight at 80 °C. After neutralizing with 1 N NaOH, the reaction mixture was saturated with NaCl and extracted three times with 20 mL of diethyl ether. The combined diethyl ether extracts were dried over Na_2SO_4 and the diethyl ether was evaporated under nitrogen, so that a yellowish

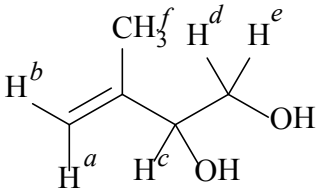
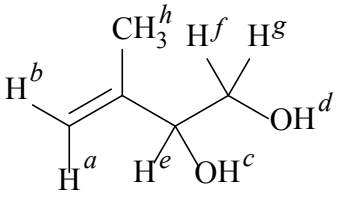
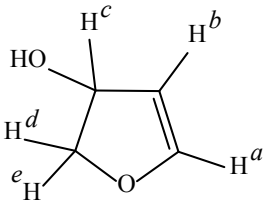
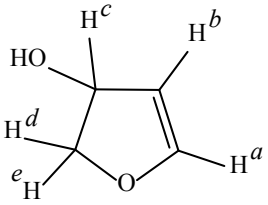
oil was left. Vacuum distillation (< 100 mbar) of this residue yielded two fractions, a first fraction distilling at 53 – 54 °C and a second one distilling at 55 – 58 °C. The first fraction was used in the smog chamber experiments. According to GC/MS with prior trimethylsilylation, the purity of this fraction is 99%.

Table S1. ^{1}H-NMR data for product **1**.

N	Compound	Solvent	Proton	Chemical shift, δ, in ppm (coupling constant, *J*, in Hz)	Ref.
1		$CDCl_3$	H^a H^b H^c H^d H^e H^f	5.89 (dd, 1H, 17.4, 10.8) 5.33 (dd, 1H, 17.4, 1.2) 5.18 (dd, 1H, 10.8, 1.2) 3.51 (d, 1H, 11.0) 3.44 (d, 1H, 11.0) 1.27 (s, 3H)	[2]

1,2-Dihydroxy-3-methyl-3-butene (diol 2) (2).[3] In a 50 mL round-bottom flask, a solution of 1.6 *M* methyl lithium in hexane (10.1 mL, 16.1 mmol) was placed together with dry tetrahydrofuran (2 mL) and the mixture was stirred for 10 min at 10 °C. Subsequently, the flask was placed in a cooling bath (acetone-dry ice) at a temperature of –78 °C. To the white suspension formed, 3,4-epoxytetrahydrofurane (0.4 mL, 5.8 mmol) was added in portions. The reaction mixture was left stirring in the cooling bath overnight, while warming up to room temperature. Thereafter, the formed orange suspension was cooled down to –20 °C and quenched with methanol (12 mL). After 10 min stirring at ambient temperature, the solvents were removed under reduced pressure. The residue was triturated with several portions of diethyl ether and the combined ethereal extracts were filtered through a thin layer of SiO_2 and evaporated. According to the ^{1}H NMR spectrum, the residue is a mixture of the target compound **2** and 2,3-dihydrofuran-3-ol (**3**) as a side product in a ratio 10:1 – 1:7 (depending on the experiment). To purify the target compound, preparative thin layer chromatography (PTLC) (SiO_2, eluent: diethyl ether) was used: the target compound with R_f ~0.41 is not visible in UV and is found in the colorless stripe just below the visible band. Methanol was used to remove the target compound from the silica. To visualize the target compound on TLC (eluent: diethyl ether), use is made of I_2 or phosphomolybdic acid reagents. According to GC/MS with prior trimethylsilylation, the purity of the target compound **2** is 99.9%.

Table S2. ^{1}H-NMR data for products **2** and **3**.

N	Compound	Solvent	Proton	Chemical shift, δ, in ppm (coupling constant, *J*, in Hz)	Ref.
2		CD_3OD	H^a H^b H^c H^d H^e H^f	5.01 (m, 1H, 0.98) 4.89 (br.s, 1H) 4.06 (dd, 1H, 7.1, 4.6) 3.57 (dd, 1H, 11.2, 7.1) 3.49 (dd, 1H, 11.2, 4.6) 1.74 (br.s, 3H)	
2		DMSO-d_6	H^a H^b H^c H^d H^e H^f H^g H^h	4.91 (m, 1H) 4.77 (m, 1H) 4.75 (d, 1H, 4.4)* 4.48 (t, 1H, 5.9)* 3.88 (dd, 1H, 11.2, 4.8) 3.37 (m, 1H) 3.28 (m, 1H) 1.65 (s, 3H)	[1] – in $CDCl_3$ [4] – in D_2O
3		CD_3OD	H^a H^b H^c H^d H^e	6.61 (br.d, 1H, 2.5) 5.18 (m, 1H) 4.90-4.89 (m, 1H) 4.19 (dd, 1H, 10.8, 7.0) 4.12 (dd, 1H, 10.8, 2.5)	
3		DMSO-d_6	H^a H^b H^c H^d H^e	6.62 (br.d, 1H, 2.6) 5.11 (m, 1H) 4.81-4.76 (m, 1H) 4.11 (dd, 1H, 10.5, 6.5) 3.97 (dd, 1H, 10.5, 2.7)	

* This proton is exchangeable with D_2O.

1,4-Dihydroxy-2-methylbut-2-ene (6):

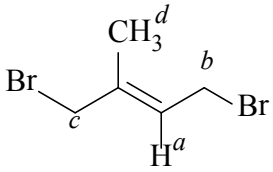
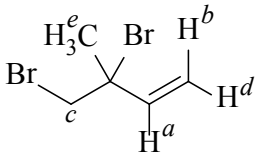
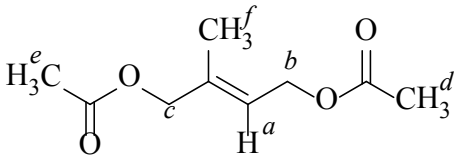
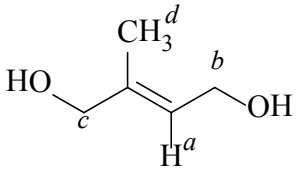
1,4-Dibromo-2-methylbut-2-ene (**4**).[5] To a solution of isoprene (15.3 mL, 153 mmol) in chloroform (15 mL) cooled with an acetone-dry ice cooling bath, a solution of bromine (8.0 mL, 155 mmol) in chloroform (35 mL) (also pre-cooled in an Erlenmeyer flask at 0 °C) was added. The bromine solution was added dropwise with a Pasteur pipette in a period of 2 h, while the temperature of the cooling bath was maintained below – 65 °C (in [1]: below – 25 °C). Upon addition of the entire bromine solution the cooling bath was removed and the reaction mixture

was stirred at ambient temperature overnight. Thereafter, $NaHSO_4$ (2.8 g, 23.0 mmol) was added to the resulting transparent yellow-greenish solution and stirred thoroughly. Filtration and evaporation of volatiles under reduced pressure yielded a light brown oil (15.4 g, 44%), which was introduced in the next step without further purification. According to ^{1}H-NMR, it is a mixture of 1,4-dibromo-2-methylbut-2-ene (**4)** and its isomer 3,4-dibromo-3-methylbut-1-ene in a ratio 8:1.[6]

2-Methyl-2-vinyl-1,3-dioxolane (**5**).[1] To the powdered potassium acetate (15.7 g, 160 mmol) in a 250 mL round-bottom flask glacial acetic acid (62 mL) and dibromide **1** (15.4 g, 68 mmol) were added subsequently. The open flask was then placed in a DrySyn® bath (Asynt Ltd, Cambridgeshire, UK) at 100 °C with stirring for 18 h. Thereafter, the reaction was poured into water (100 mL) and extracted with diethyl ether (3 x 150 mL). The combined ethereal layers were washed three times with water, then with brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure yielding diacetate **5** as a yellowish oil (8.4 g, 66%), which was introduced in the next step without further purification.

1,4-Dihydroxy-2-methylbut-2-ene (**6**).[1, 5, 6] To 95% ethanol (50 mL) in a 100 mL round-bottom flask equipped with a reflux condenser, $Ba(OH)_2 \bullet 8H_2O$ (21 g, 66 mmol) was added and the solution was placed in a DrySyn® bath at 70 °C. The diacetate **5** was then added with stirring and the reaction mixture was stirred for 5 h. After cooling, the solution was vacuum-filtered, and the precipitate was washed with ethanol for a combined liquid volume of 400 mL. The ethanol was then removed under reduced pressure giving 1.57 g of crude 1,4-diol **6** as a yellow oil. To separate the target compound in a pure form, 0.25 g of the crude reaction mixture was subjected to PTLC on Silicagel (eluent: ethyl acetate) yielding 0.12 g (41%) of 1,4-diol **3** as a slightly yellowish oil. The diol **6** (R_f 0.25) cannot be detected with UV light but can be visualized by phosphomolybdic acid, ninhydrin or iodine reagents. According to GC/MS with prior trimethylsilylation, the target compound **6** (*E* isomer) also contains the *Z* isomer and the isomeric ratio *E*/*Z* is 93:7.

Table S3. ^{1}H-NMR data for products **4**, **5**, and **6**.

	Compound	Solvent	Proton	Chemical shift, δ, in ppm (coupling constant, J, in Hz)	Ref.
4		$CDCl_3$	H^a H^b H^c H^d	5.89 (br.t, 2H, ~8.0) 3.96 (d, 2H, ~8.0) 3.95 (s, 2H) 1.85 (s, 3H)	[5,6]
		$CDCl_3$	H^a H^b H^c H^d H^e H^f	6.07 (dd, 1H, 17.2, 10.6) 5.32 (d, 1H, 17.2) 5.29 (s, 2H) 5.21 (d, 1H, 10.6) 1.98 (s, 3H)	[5,6]
5		$CDCl_3$	H^a H^b H^c H^d H^e H^f	5.54 (br.t, 1H, 6.9) 4.56 (d, 2H, 6.9) 4.42 (s, 2H) 2.01 (s, 3H) 1.98 (s, 3H) 1.66 (s, 3H)	[5]
6		$CDCl_3$	H^a, H^b H^c H^d H^e H^f	4.05-3.93 (m, 4H) 3.05 (dd, 1H, 3.8, 2.8) 2.71 (d, 1H, 2.8) 2.70 (d, 1H, 3.8) 1.40 (s, 3H)	[1,5]

1.3. Characterization by gas chromatography/mass spectrometry with prior trimethylsilylation

Gas chromatography/mass spectrometry with prior trimethylsilylation was used to determine the purity of the synthesized C_5-alkene diols (results given above) and for additional characterization of the different positional or geometric isomers by electron ionization (EI) mass spectrometry. Chromatographic and methane chemical ionization (CI) mass spectral data obtained on trimethylsilylated C_5-alkene diols have been reported by Kleindienst et al.[7]. However, on the basis of the methane CI mass spectra no difference could be noted between the different

positional C_5-alkene diols; hence, the results reported here complement these earlier data. Figure S1 presents total ion chromatograms (TICs) obtained for the trimethylsilylated C_5-alkene diols and the corresponding first-order EI mass spectra. From the TICs it can be seen that the isomeric C_5-alkene diols have distinctly different retention times: diol 1, 18.54 min; diol 2, 19.40 min, diol 3 – *Z* form, 24.68 min, and diol 3 – *E* form, 25.96 min. The EI mass spectra of the trimethylsilyl (TMS) derivatives of diols 1 and 2 are very similar, showing ions at *m/z* 73, 143, 147, and 231, and are consistent with the behaviors of positional isomers. A very weak molecular ion at *m/z* 246 is revealed in the EI mass spectra of the TMS derivative of diol 2. The ion at *m/z* 231 can be explained by the loss of a methyl group from one of the two TMSO groups. The ion at *m/z* 147 is a common ion observed in EI mass spectra of TMS derivatives of polyhydroxy compounds containing at least two TMSO groups and results from an interaction between these groups.[8–11] The ion at *m/z* 143 in the TMS derivatives of diols 1 and 2 can be explained by loss of a terminal $–CH_2–$OTMS substituent through an allylic α-cleavage (Scheme S1). It is noted that the EI mass spectrum of the TMS derivative of diol 3 is distinctly different from those of diols 1 and 2. Compared to the TMS derivatives of diols 1 and 2, the relative abundance of *m/z* 143 is much lower, due to the fact that the TMS derivative of 3 can less readily lose a terminal $–CH_2–$OTMS group (Scheme S1). Another characteristic ion of the TMS derivative of diol 3 (E isomer) is *m/z* 191, which has been observed in TMS derivatives of polyhydroxy compounds and formally corresponds to a $C_7H_{19}O_2Si_2^+$ ion.[8] The formation of the latter ion, however, cannot be explained in a straightforward manner and involves the loss of an internal C_4H_7 radical moiety (55 *u*). Furthermore, it can be seen that the *E* and *Z* isomers of diol 3 can be differentiated; a characteristic ion of the TMS derivative of diol 3 (Z isomer) is *m/z* 156, which is formed by the loss of trimethylsilanol and can further eliminate a methyl radical resulting in *m/z* 141 (Scheme S1).

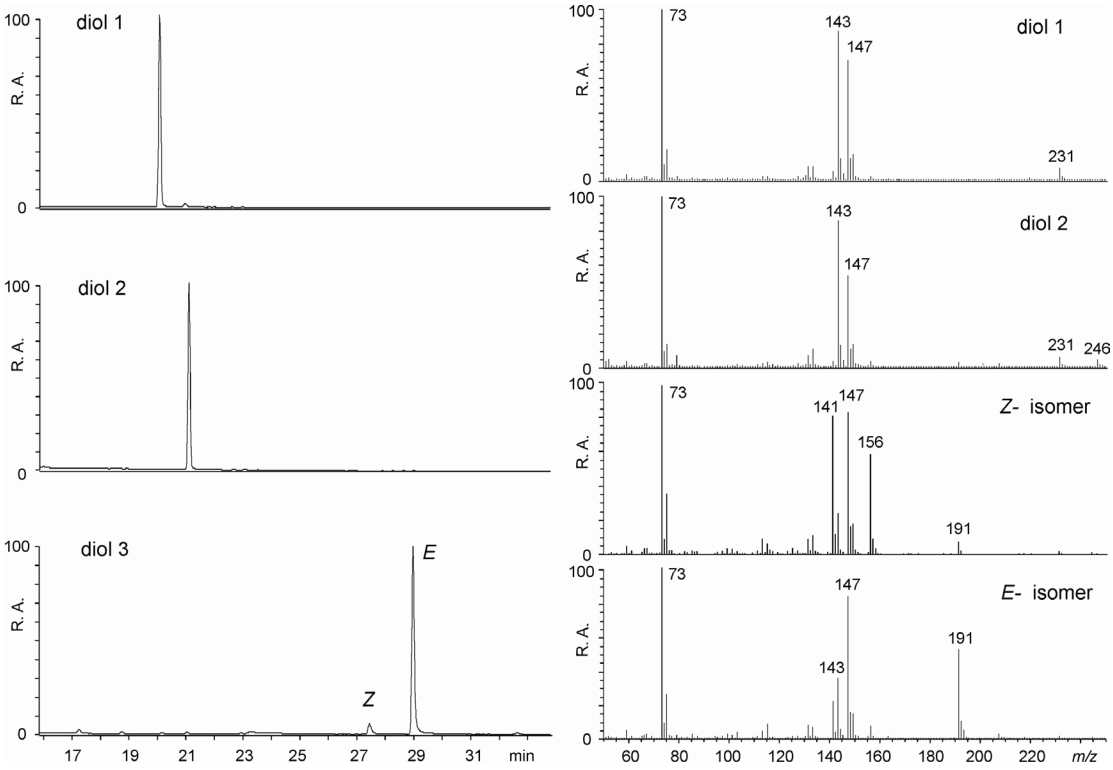
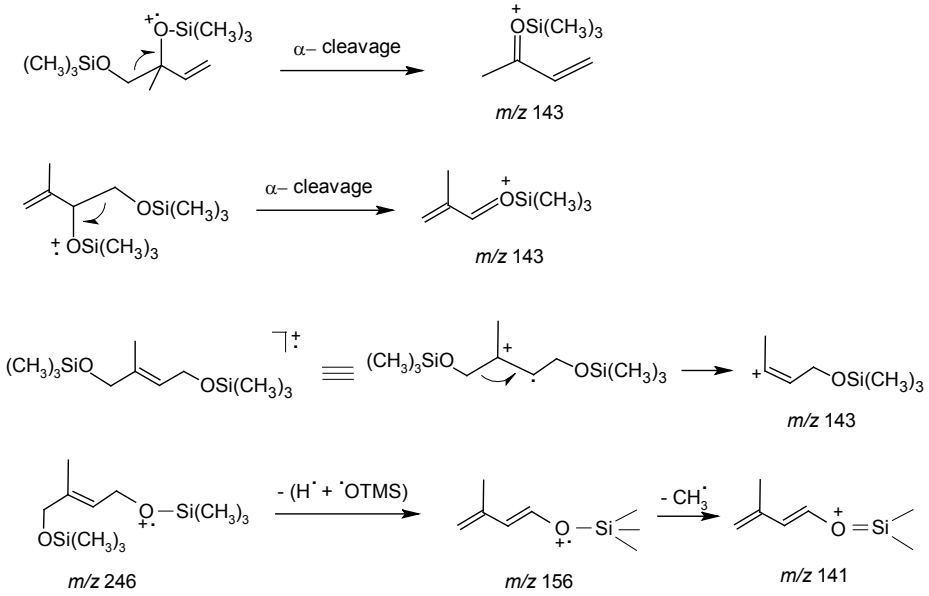


Figure S1. GC/MS data obtained for the trimethylsilylated C_5-alkene diols [total ion chromatograms and corresponding electron ionization (EI) mass spectra]: diol 1, diol 2, and diol 3. The EI mass spectra given for diol 3 correspond to the *Z* and *E* isomers.



Scheme S1. Possible EI fragmentation pathways of the trimethylsilylated C_5-alkene diols resulting in the formation of *m/z* 143, 156, and 141.

2. PTR-MS Results

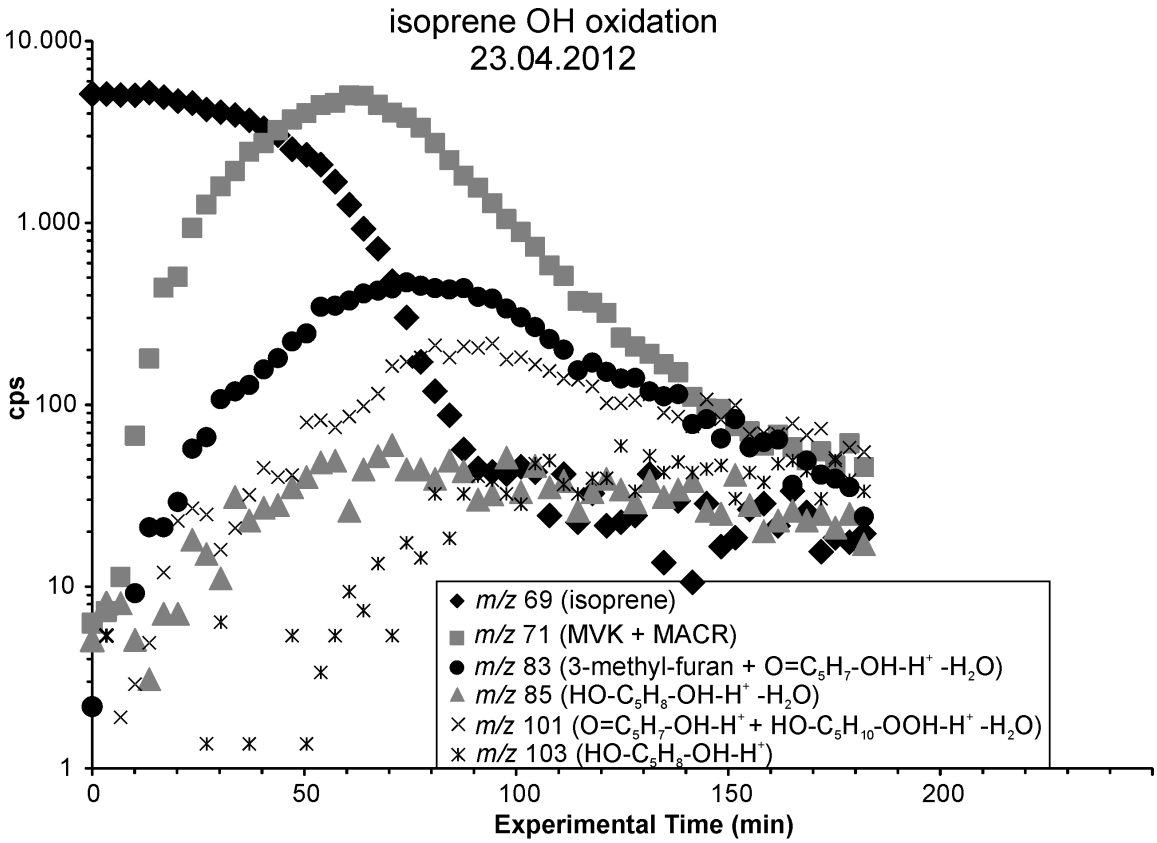


Figure S2. PTR-MS results for a selected isoprene experiment (Expt. 3; Table 1). Abbreviations: MVK, methyl vinyl ketone; MACR, methacrolein.

References

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