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Thermal Degradation of Terpenes: Camphene, Δ^3-Carene, Limonene, and α-Terpinene

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Emissions from wood dryers have been of some concern for a number of years, and recent policy changes by the Environmental Protection Agency have placed emphasis upon the gaseous emissions that lead to the formation of particulate matter as small as 2.5 μm diameter. In this qualitative study, camphene, Δ^3-carene, limonene, and α-terpinene were thermally degraded in the presence of air to determine the number and kind of oxidative degradation products that might be expected under drying conditions used in processing wood products. Various chromatographic methods were used to isolate the products for proof of structure by NMR and/or GC–MS. The degradation products resulted from dehydrogenations, epoxidations, double bond cleavages, allylic oxidations, and rearrangements. A number of compounds not previously associated with the thermal degradation of these terpenes were identified.

Introduction

Monoterpenes and their derivatives are commonly found in trace amounts in the troposphere. In addition to being emitted by many species of vegetation (biogenic sources), they are also introduced into the atmosphere in a variety of activities associated with wood processing industries (anthropogenic sources). It has been estimated that the annual global volatile organic compounds (VOC) flux is 1150 Tg C, of which 11% is thought to be monoterpenes (*1*). Whereas such compounds are normally recovered from wood pulping processes and used in a variety of chemical markets, they are not generally recovered in solid wood or wood composite manufacture.

Emissions from wood dryers have been of some concern for a number of years (*2*). Although these emissions may include particulates, of more interest are the hydrocarbons that make up the bulk of the effluent. The hydrocarbons are of concern, not because of intrinsic toxicity or corrosiveness, but because of their potential for the production of both particulates and oxidants downwind from the source (*3*).

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The hydrocarbon emissions are typically divided into two categories: (a) the condensed hydrocarbons of higher molecular weight that are responsible in part for the blue-haze plume characteristic of dryer emissions and (b) the lower molecular weight hydrocarbons (C_2–C_{10}), generally referred to as volatile hydrocarbons. Both nongaseous (condensed) and gaseous (volatile) hydrocarbons emitted by wood dryers have been analyzed by a number of workers (*2–8*). In general, the nongaseous fraction consists of a mixture of resin acids and fatty acids and their esters as well as some sesquiterpenoid compounds and undefined oxidation products. The gaseous fraction is primarily made up of monoterpenes present in the wood and some of their oxidation products. Comparatively little is known about the yields, structures, and biological properties of oxidation products of monoterpenes.

Cronn et al. (*3*) studied the gaseous emissions from a number of veneer dryers at mills in the northwest and southern U.S. From a plywood veneer dryer in the southern U.S. using a mixture of loblolly and shortleaf pines, it was found that terpenes accounted for 98.9% of the total gaseous hydrocarbon emissions. The authors also found that for loblolly and shortleaf pines the total emissions were predominated by terpenes (86–93% and 56–62%, respectively). For slash pine, the nongaseous fraction constituted the bulk of emissions with only 42% gaseous. It was estimated that the terpenic hydrocarbons were emitted at a rate of about 4 lb/h, which would be the equivalent to the emissions of 125 acres of coniferous forest at noon (*9*).

Some definitive work has also taken place regarding the fate of these hydrocarbons in the atmosphere. Graedel (*10*) reports that the oxidation of the terpenes in the lower atmosphere is initiated by reaction with the ozone molecule or hydroxyl radical. After measuring the rate constants for these reactions, he was able to calculate the tropospheric lifetimes for a number of terpenes after assuming constant atmospheric concentrations for ozone and the hydroxyl radical. The lifetimes ranged from under 1 min to slightly less than 8 h, leading one to expect that most would react near the point of emission.

Most of the studies on the atmospheric oxidation of terpenes have been carried out utilizing smog chambers, although a few suspected oxidation products have been detected in ambient air. Smog chamber experiments have been performed using ozone, hydroxyl radical, and NO_x. Terpenes studied include α-pinene (*5, 11*), β-pinene (*5, 12, 13*), Δ^3-carene (*6, 12*), limonene (*5, 6, 14*), and terpinolene (*6, 14*) among others. It seems to be typical that, when the terpenes react with ozone, hydroxyl radical, or NO_x, the products generated form aerosols; it is in these aerosol particles that the products are identified. The degradation products are usually oxygenated, and it has been estimated that 80% of the terpenoid carbon is converted to particulate matter within several hours (*15*).

The occurrence of terpenes in wood has been thoroughly investigated (*16*) with considerable work directed toward those in southern pines (*17, 18*). It has been shown that the hydrocarbon effluent from drying kilns closely resembles the hydrocarbon content of the wood and smog chamber experiments on those hydrocarbons illustrate the fates of those hydrocarbons in the atmosphere. However, although reference is made to terpene oxidation products in the effluents, little work has been done to identify those products. This work takes a qualitative look at the nature of oxidation products that might be generated in the drying of wood products with the anticipation that knowing some of the

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products actually generated under such contitions and, in the least, the nature of oxidation reactions occurring will facilitate the identification of materials emitted from wood dryers.

Experimental Methods

Terpenes were used as obtained from Aldrich Chemical Co.: (+)-camphene, 95% (91% by GC); Δ^3-carene, 90% (89% by GC); *R*-(+)-limonene, 97% (99% by GC); and α-terpinene, 85% (86% by GC). The thermal degradations were carried out by placing 4.0 g of terpene (0.029 mol) into a 4-L screw-cap bottle. Thus, the bottle contained 0.036 mol of O_2 to give a ratio of terpene to O_2 of 1:1.24. The bottle was then sealed and heated at 120 °C in a gas chromatograph oven for varying lengths of time, depending on the reactivity of the terpene. Upon cooling, the reaction vessel was rinsed with CH_2Cl_2 and acetone to remove oxidation products and any unreacted terpene. No attempt was made to analyze gaseous products that may have escaped upon opening the reaction vessel. After removal of the solvent under reduced pressure, the reaction mixture was subjected to flash chromatography (*19*) over silica, eluting with increasingly polar mixtures of hexane/ethyl acetate. The eluted fractions were monitored using TLC on silica plates and visualized by their UV absorbance and/or their color reaction with anisaldehyde spray (*20*). The combined fractions usually required further purification by column and/or preparative thin-layer chromatography, also using silica gel as the adsorbent. Because several separate chromatographic procedures were typically used in order to obtain materials for identification and each purification step resulted in loss of sample, quantitative results are not reported.

Unheated terpene samples were also subjected to flash chromatography and compared to the heated samples using GC–MS in order to be certain that the products isolated were not artifacts resulting from the exposure of the terpenes to silica.

Results and Discussion

The title monoterpenes were selected for their occurrence in wood dryer emissions (*3*) and/or their structural characteristics (mono- vs bicyclic, conjugated vs nonconjugated, etc.). After beginning the study, it was learned that similar work with α- and β-pinene had already been carried out (*21*), so work on these two common monoterpenes was minimized. Punsuvon (*21*) heated α-pinene in the presence of air at temperatures of 90–130 °C and reported that between 23 and 37% of the α-pinene had been rearranged or oxidized. Products included β-pinene, α-pinene oxide, α-campholene aldehyde, verbenol, pinocamphone, myrtenol, and verbenone. Similar air oxidation of β-pinene resulted in the loss of 22% of this compound, and myrtenol was identified as a major product. In our study, the amount of oxidation of the terpenes roughly paralleled the atmospheric lifetimes of the terpenes reported in the literature (*1*). The percent degradation of the terpenes (estimated by GC on the reaction mixtures) and the length of heating time at 120 °C were as follows: α-terpinene, 100% in 4 h; limonene, 50% in 24 h; Δ^3-carene, 7% in 24 h and 36% in 72 h; and, camphene, 38% in 72 h. Although none of the degradation products identified were new compounds, many of them had not been reported as thermal degradation products of the respective terpenes, being generated instead in smog chamber studies by various oxidizing agents or isolated as natural products themselves. The products isolated from the thermal degradation of Δ^3-carene are examples of this (*22–24*).

The use of ambient air in this study means that any of the oxidizing agents used in the smog chamber studies previously referenced—ozone, hydroxyl radical, and nitrate radical—might be present. This makes it difficult to assign any particular product or series of products to a specific oxidation process but does more closely mimic wood-drying ovens or kilns.

TABLE 1. Thermal Degradation Products of Camphene

Product	Method
(1-Methylethyl)benzene [cumene]	GC-MS actual
1-Methyl-2-(1-methylethyl)benzene [o-cymene]	GC-MS library
3,3-Dimethylbicyclo[2.2.1]heptan-2-one [camphenilone]	NMR
4,6,6-Trimethylbicyclo[3.1.1]hept-3-en-2-one [verbenone]	GC-MS; NMR

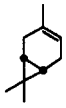
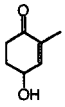
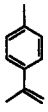
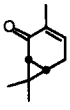
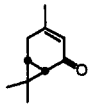
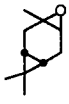
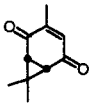
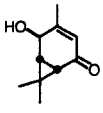
The degradation products of the terpenes are shown in Tables 1 (camphene), 2 (Δ^3-carene), 3 (limonene), and 4 (α-terpinene). The method of identification is also shown as NMR (compound was isolated and analyzed by ^{1}H NMR, ^{13}C NMR, and various 2D NMR techniques), GC–MS actual (compound identified by GC–MS by comparing retention time and mass spectrum to those of the actual compound), and GC–MS library [compound was identified by comparing mass spectrum to mass spectral terpene database (540 compounds) and/or NIST database (10 000 compounds)].

The products identified in this study indicate that the thermal degradation of the terpenes leads to four types of oxidative reactions. First, six-membered rings containing one or two double bonds readily undergo dehydrogenation to form aromatic systems. This was observed with α-terpinene (Figure 1) and limonene in the formation of *p*-cymene and thymol, respectively. In addition, both camphene and Δ^3-carene yielded aromatic compounds among their degradation products, resulting from rearrangement accompanied by dehydrogenation.

A second common reaction is the oxidative cleavage of carbon–carbon double bonds. This was observed with the formation of camphenilone from camphene and the generation of two keto aldehydes by cleavage of the double bonds in α-terpinene (Figure 2). Smog chamber studies on numerous terpenes using ozone and/or hydroxyl radical showed the major degradation products to be those resulting from oxidative cleavage of the olefinic bond (*22, 25, 26*), similar to the results from this study.

The third reaction that was characteristic of the thermal degradations was epoxide formation. This was observed with Δ^3-carene, limonene (Figure 3), and α-terpinene. The Δ^3-carene and limonene products were the expected 1,2-epoxy derivatives, but the products isolated and identified from α-terpinene were 1,4- and 1,8-ethers (1,4-cineole and eucalyptol, respectively). Epoxides are readily generated in the laboratory using peracids (*27*). Their formation under atmospheric conditions has been attributed to the presence of nitrate radicals and peroxy radicals (*28*).

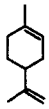
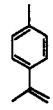
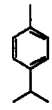
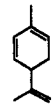
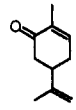
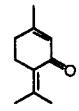
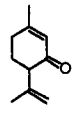
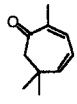
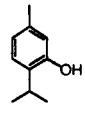
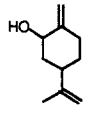
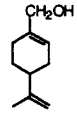
TABLE 2. Thermal Degradation Products of Δ^3-Carene

Product	Method
	
 4-Hydroxy-2-methyl-2-cyclohexenone	NMR
 4-Methyl-1-(1-methylethenyl)benzene [p-cymenene]	GC-MS library
1-Methyl-2-(1-methylethyl)benzene [o-cymene]	GC-MS library
 3,7,7-Trimethylbicyclo[4.1.0]hept-3-en-2-one [3-caren-2-one]	GC-MS; NMR
 4,7,7-Trimethylbicyclo[4.1.0]hept-3-en-2-one [3-caren-5-one]	GC-MS; NMR
 3,4-Epoxy-3,7,7-trimethylbicyclo[4.1.0]heptane [3-carene oxide]	NMR
 3,7,7-Trimethylbicyclo[4.1.0]hept-3-en-2,5-dione [3-Carene-2,5-dione]	GC-MS; NMR
 trans-2-Hydroxy-3-caren-5-one	NMR

Allylic oxidation to form alcohols, ketones, and aldehydes represents the fourth oxidation reaction observed under the conditions investigated. The majority of the identified degradation products from Δ^3-carene (Figure 4) and limonene resulted at least in part from such oxidation. Singlet oxygen reacting with alkenes can lead to oxidation of the carbon adjacent to the carbon–carbon double bond (allylic oxidation) (*28*). Jay and Stieglitz have identified the allylic oxidation product verbenone in smog chamber studies with α-pinene and ozone (*29*).

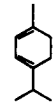
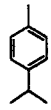
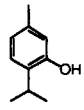
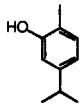
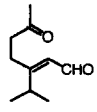
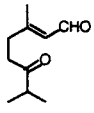
In addition to the above oxidation reactions, some degradation products resulted from carbon skeleton rearrangements. These products also incorporated at least one of the previously described oxidation reactions, and it is unclear whether the monoterpene or its oxidation product underwent the rearrangement. In such manner camphene yielded verbenone, Δ^3-carene produced *o*-cymene and 4-hydroxy-2-methyl-2-cyclohexenone, and eucarvone was generated from limonene (Figure 5).

TABLE 3. Thermal Degradation Products of Limonene

Product	Method
	
 4-Methyl-1-(1-methylethenyl)benzene [p-cymenene]	GC-MS library
 1-Methyl-4-(1-methylethyl)benzene [p-cymene]	GC-MS actual
 2-Methyl-5-(1-methylethenyl)-1,3-cyclohexadiene [p-mentha-1,5,8-triene]	GC-MS library
 2-Methyl-5-(1-methylethenyl)-2-cyclohexen-1-one [carvone]	GC-MS; NMR
 3-Methyl-6-(1-methylethylidene)-2-cyclohexen-1-one	GC-MS library
 3-Methyl-6-(1-methylethenyl)-2-cyclohexen-1-one	GC-MS library
 2,6,6-Trimethyl-2,4-cycloheptadienone [eucarvone]	GC-MS library
 5-Methyl-2-(1-methylethyl)phenol [thymol]	GC-MS actual
 2-Methylene-5-(1-methylethenyl)cyclohexanol [p-mentha-1(7),8-dien-2-ol]	GC-MS library
 4-(1-Methylethenyl)-1-cyclohexenylmethanol [perillyl alcohol]	GC-MS library

It is not possible to accurately mimic the conditions of drying of wood flakes for manufacture of oriented strand board, drying wood veneers used in production of plywood, or even drying of lumber in a simple bench-scale experiment. However, knowledge of the reactions of these comounds at

TABLE 4. Thermal Degradation Products of α-Terpinene

Product	Method
	
 1-Methyl-4-(1-methylethyl)benzene [p-cymene]	GC-MS; NMR
 5-Methyl-2-(1-methylethyl)phenol [thymol]	GC-MS actual
 2-Methyl-5-(1-methylethyl)phenol [carvacrol]	GC-MS actual
1-(1-Methylethyl)-4-methyl-7-oxabicyclo-[2.2.1]heptane [1,4-cineole]	NMR
1,3,3-Trimethyl-2-oxabicyclo[2.2.2]octane [eucalyptol]	GC-MS; NMR
 3-(1-Methylethyl)-6-oxo-2-heptenal	NMR
 3,7-Dimethyl-6-oxo-2-octenal	GC-MS: NMR

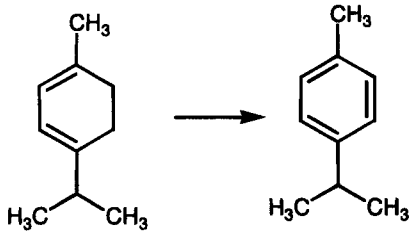


FIGURE 1. *p*-Cymene from α-terpinene.

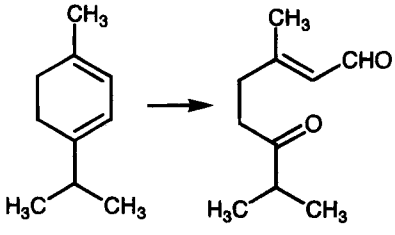


FIGURE 2. 3,7-Dimethyl-6-oxo-2-octenal from α-terpinene.

120 °C (representing modest temperatures) together with the availability of 1.24 mol of O_2/mol of terpene (representing low levels of available oxygen) do provide a reasonable reference point from which to consider what can happen in all these wood-drying operations. For example, a typical oriented strand board plant might dry 20 green ton/h of

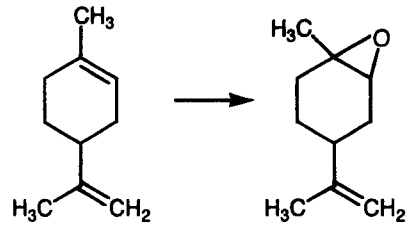


FIGURE 3. Limonene oxide from limonene.

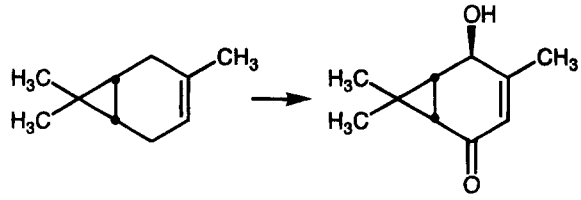


FIGURE 4. *trans*-2-Hydroxy-3-caren-5-one from 3-carene.

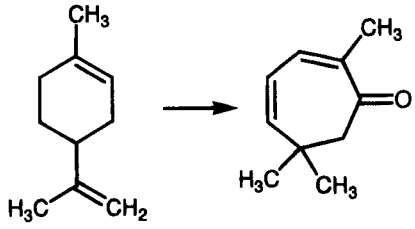


FIGURE 5. Eucarvone from limonene.

wood flakes (at 90% moisture content dry basis) in a rotary dryer with 40 000 cfm of air at an inlet temperature of between 400 and 550 °C. The temperature in the dryer would be expected to drop to an outlet temperature of 100–130 °C over a residence time of about 15 min. Evaporation of water from the flake holds the temperature of the wood flake low until the free water is removed (about 30% moisture content). However, the wood temperature rises as it is dried over the range of 30–5% moisture content in the later part of the drying period.

When drying wood veneers for manufacture of plywood, a typical plant might dry 20 green ton of veneer (at 90% moisture content), with air flowing over the veneer at temperatures between 180 and 200 °C over a drying period of 8–15 min. As in drying wood flakes, temperatures of the wood veneers do not increase until the wood reaches the fiber saturation point, and this zone gradually moves back from the surface to the center of the veneer as it dries. Because air is only vented periodically from the drying chamber, the volatilized compounds are exposed to high temperatures but also probably low oxygen levels until they are vented to the atmosphere. Probably the most severe oxidation conditions may be associated with veneer drying even though the initial temperatures are much lower than for flake dryers because of the comparatively long time periods the volatilized terpenes are held in the vapor state at high temperatures.

When drying lumber with "high temperature" schedules, kiln temperatures above 100 °C can be employed over a period of 24–30 h. Alternatively, low-temperature drying of nominal 2 in. framing lumber can involve a gradual increase in temperature from about 70 to 90 °C over a total drying time of 130 h. As in wood veneer drying, the lumber kiln is vented intermittently to control the relative humidity throughout the process. Because of the increased mass of porous material involved, residence time for the terpenes within the drying wood, probably with limited oxygen, is comparatively long.

To interpret these results relative to actual wood-drying operations, one must consider what proportion of volatile terpenes remain within the porous wood structure and what

proportion has been volatilized and entered the dryer air stream at various levels through the course of the drying process. The rate at which the air stream is vented to the atmosphere is also important. The conditions studied here most closely represent the conditions seen by the terpenes in lumber and veneer drying proceses.

The compounds selected for study provide models for the structures of many other terpenes that may be subjected to thermal oxidative rearrangement in processing wood or other plant materials. Some generalizations may be useful in providing clues to the type of products one might look for in the vent gases from wood-drying operations, and such an endeavor is the next logical step to take. Dehydrogenation to form aromatic systems is a reaction shared by all of the model systems studied. When a monocyclic six-membered ring system with existing unsaturation is present, as in α-terpinene and limonene, aromatization appears to be the most common oxididation process. Oxidative cleavage of double bonds to form the carbonyl compounds was observed with three of these model compounds. Surely, where aldehydes are formed, the corresponding carboxylic acids would be expected and could probably be isolated as the methyl esters by altering the workup procedure. All of the model terpenes also showed some form of allylic oxidation, and this suggests that such compounds should be expected in the dryer effluents. Although not observed in our study, the formation of epoxides, as seen with 3-carene and α-terpinene, would probably lead to diols under wood-drying conditions with the presence of acids and high moisture found there.

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Literature Cited

(1) Guenther, A.; Hewitt, C. N.; Erickson, D.; Fall, R.; Geron, C.; Graedel, T.; Harley, P.; Klinger, L.; Lerdau, M.; McKay, W. A.; Pierce, T.; Scholes, B.; Steinbrecher, R.; Tallamraju, R.; Taylor, J.; Zimmerman, P. *J. Geophys. Res.* **1995**, *100*, 8873–8891.

(2) Adams, D. F.; Monroe, F. L.; Rasmussen, R. A.; Bamesburger, W. L. *Volatile Emissions form Wood*; Fifth Washington State University Symposium on Particle Board: Pullman, WA, June 1971.

(3) Cronn, D. R.; Truitt, S. G.; Campbell, M. J. *Atmos. Environ.* **1983**, *17*, 210–211.

(4) Fehsenfeld, F.; Calvert, J.; Fall, J.; Goldan, P.; Guenther, A. B.; Hewitt, C. N.; Lamb, B.; Liu, S.; Trainer, M.; Westberg., H.; Zimmerman, P. *Global Biogeochem. Cycles* **1992**, *6*, 389–430.

(5) Grosjean, D.; Williams, E. L., II; Seinfeld, J. H. *Environ. Sci. Technol.* **1992**, *26*, 1526–1533.

(6) Hakola, H.; Arey, J.; Aschmann, S. M.; Atkinson, R. *J. Atmos. Chem.* **1994**, *18*, 75–102.

(7) Fraser, H. S.; Swann, E. P. *Information Report VP-X-101*; Department of the Environment, Canadian Forestry Service, Western Forest Products Laboratory: Vancouver, BC, 1972.

(8) Monroe, F. L.; Rasmussen, R. A.; Bamesburger, R. A.; Adams, D. F. *Report to Plywood Research Foundation*; Washington State University: Pullman, WA, 1972.

(9) Zimmerman, P. R. Final Report to the Environmental Protection Agency, Contract 68-02-2071, 1979.

(10) Graedel, T. E. *Rev. Geophys. Space Phys.* **1979**, *17*, 937–947.

(11) Schwartz, W. E.; Jones, P. W.; Riggle, C. J.; Miller, D. F. The Organic Composition of Model Aerosols. Presented at Eastern Analytical Symposium, New York City, November 1978.

(12) Gay, B. W., Jr.; Arnts, R. R. *Proceedings of the International Conference on Photochemical Oxidant Pollution and its Control*; EPA-600/3-77-001b; U.S. EPA: Washington, DC, 1977; pp 745–751.

(13) Palen, E. J.; Allen, D. T.; Pandis, S. N.; Paulson, S. E.; Seinfeld, J. H.; Flagan, R. C. *Atmos. Environ.* **1992**, *26A*, 1239–1251.

(14) Scheutzle, D.; Rasmussen, R. A. *J. Air Pollut. Control Assoc.* **1978**, *28*, 236–214.

(15) Duce, R. A. *Pure Appl. Geophys.* **1978**, *116*, 244–273.

(16) Dev, S. In *Natural Products of Woody Plants*, Vol. II; Rowe, J. W., Ed.; Springer-Verlag: Berlin, 1989; pp 691–807.

(17) Zinkel, D. F., Russell, J., Eds. *Naval Stores: Production, Chemistry, Utilization*; Pulp Chemicals Association: New York, 1988.

(18) Zinkel, D. F. In *Natural Products of Woody Plants*, Vol. II; Rowe, J. W., Ed.; Springer-Verlag: Berlin, 1989; pp 953–978.

(19) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.

(20) Stahl, E., Ed. *Thin-Layer Chromatography: A Laboratory Handbook*; Springer-Verlag: New York, 1969.

(21) Punsunvo, V. Ph.D. Dissertation, Mississippi State University, 1994.

(22) Hakola, H.; Arey, J.; Aschmann, S. M.; Atkinson, R. *J. Atmos. Chem.* **1994**, *18*, 75–102.

(23) Bruns, W. D. P.; Carson, M. S.; Cocker, W.; Shannon, P. V. R. *J. Chem. Soc. C* **1968**, 3073–3079.

(24) Flynn, T.; Southwell, J. A. *Phytochemistry* **1987**, *26*, 1673–1686.

(25) Grosjean, D.; Williams, E. L., II; Grosjean, E.; Andino, J. M.; Seinfeld, J. H. *Environ. Sci. Technol.* **1993**, *27*, 2754–2758.

(26) Arey, J.; Atkinson, R.; Aschmann, S. M. *J. Geophys. Res.* **1990**, *95*, 18539–18546.

(27) Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis;* John Wiley and Sons: New York, 1967.

(28) Larson, R. A.; Weber, E. J. *Reaction Mechanisms in Environmental Organic Chemistry*; Lewis Publishers: Ann Arbor, 1994.

(29) Jay, K.; Stieglitz, L. *Air Pollut. Ecosyst.* **1988**, 542–547.

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