ArF and KrF Laser-Induced Gas-Phase Photolysis of Selenophene and Tellurophene: Extrusion of Te and Se and Intramolecular 1,3-H Shift Competing with β-C−C Cleavage in C_4H_4 Residue

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ArF (193 nm) and KrF (248 nm) laser-induced photolysis of gaseous selenophene and tellurophene (C_4H_4M, M = Se and Te) has been examined. It is shown that, unlike thiophene and furan, selenophene and tellurophene cleave both M−C bonds and yield the elemental heteroatom (Se, Te), 1-buten-3-yne, and ethyne. The proposed mechanism involves an intermediate $^{\bullet}HC{=}CH{-}CH{=}CH^{\bullet}$ diradical that decomposes via two competitive pathways, namely, 1,3-H shift to 1-buten-3-yne and β-cleavage to two molecules of ethyne. It is shown that the relative importance of the channels depends both on the energy of the photon and on the heteroatom. Specifically, the 1,3-H shift/β-cleavage ratios are 2.3 (193 nm, M = Se), 3.6 (248 nm, M = Se), 1.4 (193 nm, M = Te), and 10.5 (248 nm, M = Te). The inertness of the Te residuum and the high preference for the 1,3-H shift in KrF laser photolysis of tellurophene suggest that this photolysis can serve as a source of the C_4H_4 diradical for mechanistic studies.

Introduction

The photolysis of furan[1] and thiophene[1e,2] has been extensively studied in order to elucidate the mechanism of these reactions. It has been demonstrated for both compounds that the initial photochemical event is the formation of the Dewar isomers[1e,g,2e] and that the nature of the final products depends on the photolytic conditions.

With furan, the rearranged products, 2-cyclopropenecarboxaldehyde and 2,3-butadienal (trapped as furan Diels−Alder adducts), are produced in the liquid phase,[1f] whereas the ring-contracted products, carbon monoxide and cyclopropene (Hg-sensitized photolysis[1a−d]), along with other unsaturated hydrocarbons (direct photolysis[1g,h]), are the principal products in the gas phase.

With thiophene, the Dewar isomer (trapped as furan Diels−Alder adducts) is produced in a solution of thiophene in furan, whereas unsaturated hydrocarbons and carbon disulfide, arising via the postulated $^{\bullet}CHCHCHCHS^{\bullet}$ and C_2H_2S intermediates[2a] or the detected HCCS radical,[2b−d] are produced[2a] in both direct and Hg-sensitized photolysis in the gas phase.

These photolyses involve the extensive formation of polymers, and their final products reveal the cleavage of only one of the two C−X bonds.

Surprisingly, the photolysis of the congener rings containing Se and Te remains essentially unknown. Thus, the only reported data are the transient absorption spectra in the flash photolysis of gaseous selenophene[3] and those from the UV laser photodeposition of Te from tellurophene in solution.[4]

In this work, we examined the photolysis of selenophene and tellurophene in the gas phase using monochromatic laser radiation at 193 and 248 nm and revealed that these compounds photolytically cleave in a completely different way than do their O- and S-atom-containing congeners. We report that selenophene and tellurophene decompose via the same mechanism into the heteroatom, ethyne, and 1-buten-3-yne and that the ratio of these hydrocarbons is controlled by the energy of the photon and by the heteroatom.

Results and Discussion

The UV absorption spectrum of gaseous selenophene shows an absorption band at 190 nm and a continuous absorption[5] between 210 and 260 nm, and that of gaseous tellurophene exhibits three major bands at 196, 220, and 275 nm, the maxima being shifted compared to those for the *n*-hexane solution.[6] Both compounds show sufficient absorption in the region of ArF and KrF laser emission (Figure 1) and can be photolyzed by laser radiation at 193 and 248 nm.

Laser irradiation of gaseous selenophene and tellurophene at these wavelengths results in the formation of three hydrocarbons as the exclusive volatile products, namely, 1-buten-3-yne, ethyne, and butadiyne, and in the deposition of thin selenium and tellurium films.

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(1) (a) Srinivasan, R. *J. Am. Chem. Soc.* **1967**, *89*, 1758. (b) Srinivasan, R. *J. Am. Chem. Soc.* **1967**, *89*, 4812. (c) Srinivasan, R. *Pure Appl. Chem.* **1968**, *16*, 65. (d) Poquet, E.; Dargelos, A.; Chaillet, M. *Tetrahedron* **1976**, *32*, 1729. (e) Rendal, W. A.; Clement, A.; Torres, M.; Strausz, O. P. *J. Am. Chem. Soc.* **1986**, *108*, 1691. (f) Rendall, W. A.; Torres, M.; Strausz, O. P. *J. Org. Chem.* **1985**, *50*, 3034. (g) Price, D.; Ratajczak, E.; Sztuba, B.; Sarzynski, D. *J. Photochem.* **1987**, *37*, 273. (h) Hiraoka, H.; Srinivasan, R. *J. Chem. Phys.* **1968**, *48*, 2185.

(2) (a) Wiebe, H. A.; Heicklen, J. *Can. J. Chem.* **1969**, *47*, 2965. (b) Krishnamachari, S. L. N. G.; Ramsay, D. A. *Discuss. Faraday Soc.* **1981**, *71*, 205. (c) Venkatasubramanian, R.; Krishnamachari, S. L. N. G. *Indian J. Pure Appl. Phys.* **1991**, *29*, 697. (d) Cooper, D. L. *Chem. Phys. Lett.* **1981**, *81*, 479. (e) Rendall, W. A.; Torres, M.; Strausz, O. P. *J. Am. Chem. Soc.* **1985**, *107*, 723. (f) Krishnamachari, S. L. N. G.; Veinkitachalam, T. V. *Chem. Phys. Lett.* **1978**, *55*, 116.

(3) Krishnamachari, S. L. N. G.; Veinkitachalam, T. V. *Chem. Phys. Lett.* **1979**, *67*, 69.

(4) Ouchi, A.; Yamamoto, K.; Koga, Y.; Pola, J. *J. Mater. Chem.* **1999**, *9*, 563.

(5) Trombetti, A.; Zauli, C. *J. Chem. Soc. A* **1967**, 1106.

(6) Fringuelli, F.; Taticchi, A. *J. Chem. Soc., Perkin Trans. 1* **1972**, 199.

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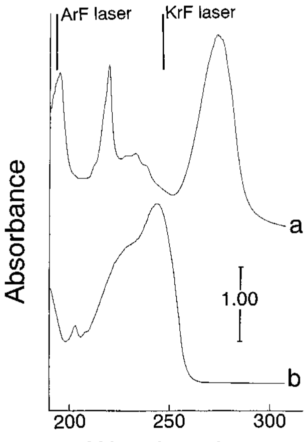

Figure 1. UV absorption spectrum of (a) gaseous tellurophene (0.5 kPa) and (b) gaseous selenophene (0.1 kPa).

The measured amounts of the three hydrocarbon products account for all of the depletion of both selenophene and tellurophene. This shows that no hydrocarbon undergoes photolysis after its formation. (Ethyne and 1-buten-3-yne do not absorb at 248 nm, and their independent photolysis with 193-nm radiation revealed that irradiation times at least 2 orders of magnitude longer than those used for the photolysis of tellurophene and selenophene were required for a noticeable decay in either of them.)

Selenophene. The 193- and 248-nm photolyses of selenophene yield 1-buten-3-yne and ethyne as major products and butadiyne as a minor product. Concomitantly, a pink film is deposited from the gas phase onto the reactor surface. An examination of the laser-fluence-dependent depletion of selenophene at each laser irradiation wavelength shows that the slope of this dependence for a double-logarithmic plot is close to unity (Figure 2). This confirms that both photolyses are one-photon processes. The initial quantum yield of both processes was assessed as 0.5−0.6.

The hydrocarbon product distribution (in relative mole %) in the ArF laser photolysis (fluence, 6.6−55 mJ cm^{-2})—1-buten-3-yne, 47−53; ethyne, 41−47; and butadiyne, 5−6—is essentially independent of the laser fluence and the photolysis progress. The product distribution in the KrF laser photolysis is also independent of the photolysis progress, but somewhat different for fluences lower than 55 mJ cm^{-2} (1-buten-3-yne, 58−66; ethyne, 27−35; and butadiyne, 5−7) and for fluences higher than 100 mJ cm^{-2} (1-buten-3-yne, 40−50; ethyne, 40−50; and butadiyne, 8−10).

These relative amounts are not affected by the addition of an inert gas (13−26 kPa of hydrogen or nitrogen). XPS measurements of the deposited films confirmed the presence of elemental selenium (binding energy of the 3d electrons, 55.5 eV), and the UV spectrum of the films showed a broad absorption band with the maximum at 190 nm typical for amorphous selenium.[7]

Tellurophene. The 193- and 248-nm photolyses of tellurophene yield the same three hydrocarbons as those of selenophene (1-buten-3-yne, ethyne, and butadiyne) and produce black films on the reactor surface. An examination of the laser-fluence-dependent tellurophene depletion at each laser irradiation wavelength reveals that these two photolyses are also one-photon processes, as the slope of the dependence for a double-logarithmic plot is close to unity in each case (Figure 3). The initial quantum yield of both photolyses was estimated as ca. 0.6.

The relative amounts of the hydrocarbon products essentially do not change with the photolysis progress, they depend slightly on the laser fluence, and they depend significantly on the laser wavelength. Thus, the hydrocarbon distribution (in relative mole %) in the ArF laser photolysis at fluences of 7−40 mJ cm^{-2}—1-buten-3-yne, 36−42; ethyne, 54−60; and butadiyne, ~4—differs significantly from that observed for the KrF laser photolysis at fluences of 8−60 mJ cm^{-2}—1-buten-3-yne, 81−84; ethyne, 15−17; and butadiyne, 1−2.

As with the photolysis of selenophene, these relative amounts are also not subject to changes when the photolyses are conducted in 13−26 kPa of hydrogen or nitrogen.

XPS measurements of the deposited films are in accord with the elemental tellurium having a Te 3d$_{5/2}$ electron binding energy of 573.2 eV.

Photolysis Mechanism. The observed products of the laser photolysis of C_4H_4M (M = Se and Te) compounds can be rationalized by a mechanism for a 2-fold cleavage of the C−M bonds that involves transient formation of a $^{\bullet}HC{=}CH{-}CH{=}CH^{\bullet}$ diradical undergoing both 1,3-H shift (into 1-buten-3-yne) and β-C−C cleavage (into two molecules of ethyne). The intermediacy of the seemingly elusive C_4H_4 diradical gains support from the thermochemical data,[8] from the identification of the *cis*-butadienediyl diradical as a stable product on the singlet potential energy surface for the interconversions of C_4H_4 species (MINDO/3 calculations, ref 9), and from ab initio investigations of ethyne reactions.[10] A plausible route for the minor formation of butadiyne involves cleavage of the ethyne C−H bond and subsequent recombination of the two $HC_2^{\bullet}$ radicals. The steps for the formation of the major products are given in Scheme 1.

The relative importance of the 1,3-H shift and the β-C−C cleavage in the C_4H_4 diradical is reflected by the 1-buten-3-yne/(0.5 × ethyne) ratios. This ratio is 2.3 ± 0.3 for the 193-nm photolysis of selenophene, 3.6 ± 0.3 (low-fluence range) and 2.0 ± 0.2 (high-fluence range) for the 248-nm photolysis of selenophene, 1.4 ± 0.2 for the 193-nm photolysis of tellurophene, and 10.5 ± 0.5 for the 248-nm photolysis of tellurophene. These values show that the 1,3-H shift is, in all instances, more feasible than the β-C−C cleavage, that the 1,3-H shift is enhanced with the 248-nm photons, and that this enhancement is more pronounced with tellurophene than with selenophene.

The observed preference for the 1,3-H shift over the β-C−C cleavage in the postulated C_4H_4 diradical under photolytic conditions differs from the relative importance of these pathways theoretically predicted for a thermally equilibrated system,[9] for which the (one-step) conversion of the *cis*-butadienediyl diradical to ethyne is energetically more feasible than the (multistep) conversion to

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[7] Vasko, A. *J. Non-Cryst. Solids* **1990**, *3*, 225.

[8] Zhang, M.-Y.; Wesdemiotis, C.; Marchetti, M.; Danis, P. O.; Ray, J. C.; Carpenter, B. K.; McLafferty, F. W. *J. Am. Chem. Soc.* **1989**, *111*, 8341 and references therein.

[9] Kollmar, H.; Carrion, F.; Dewar, M. J. S.; Bingham, R. C. *J. Am. Chem. Soc.* **1981**, *103*, 5292.

[10] Gey, E.; Wiegratz, S.; Kühnl, W.; Ondruschka, B.; Saffert, W.; Zimmermann, G. *J. Mol. Struct. (THEOCHEM)* **1989**, *184*, 69.

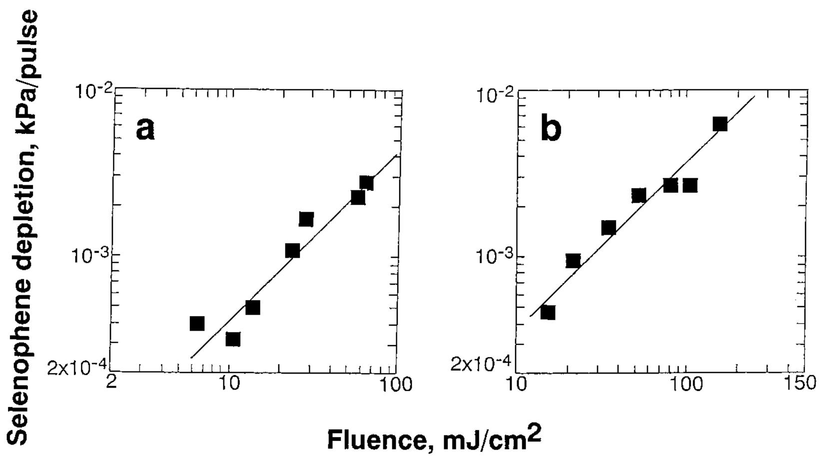


Figure 2. Depletion of selenophene in (a) ArF and (b) KrF laser photolysis as a function of laser fluence.

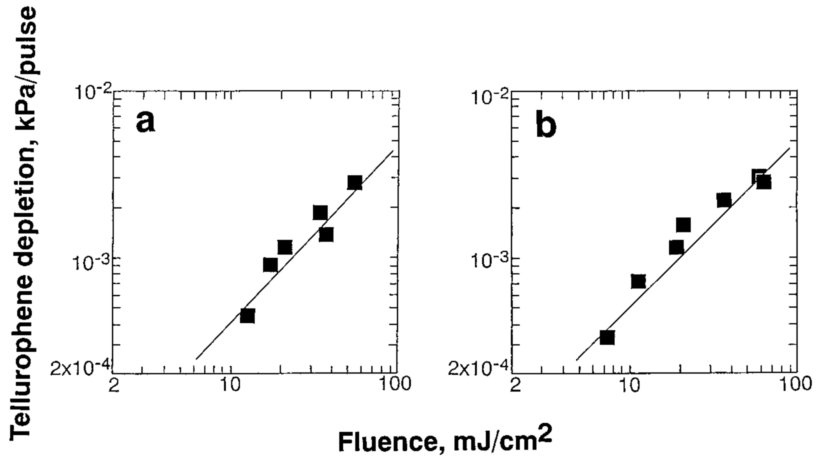
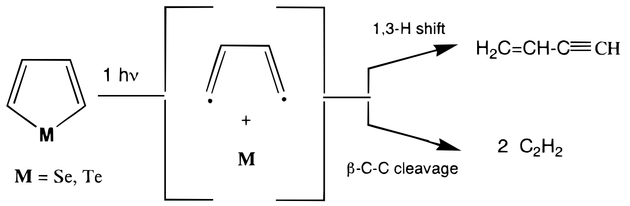


Figure 3. Depletion of tellurophene in (a) ArF and (b) KrF laser photolysis as a function of laser fluence.

Scheme 1



1-buten-3-yne, which takes place via several stable intermediates (cyclobutadiene and bicyclo[1.1.0]butenes). It can be only reconciled with another, much less feasible (higher-energy), pathway to 2 C_2H_2, as predicted[9] from the vibrationally excited (*trans*-butadienediyl) C_4H_4 diradical. The latter reaction can conceivably take place with hot molecules produced in the intense laser beam, but an explanation of the observed relative occurrences of both laser-photolytic pathways is not straightforward because of the possible involvement of both nonequilibrium laser-induced conditions and energy-randomized thermal processes. The accomplished electronic transitions ($\pi-\pi^*$ excitation of the diene system or a system involving the M atom,[5,6,11] possible interference of nearby Rydberg states[12]) and also post-excitation events can differ with each M and wavelength.

The observed occurrences of the 1,3-H shift and the β-C$-$C cleavage are related to the photon energy and the mass of the M atom. The energy delivered by the 193- and 248-nm photons corresponds, respectively, to ca. 620 and 480 kJ einstein^{-1}, while the dissociation energy of both the Se$-$C[13] and the Te$-$C bonds[14] can be speculated to be ca. 250 kJ mol^{-1}. It is thus conceivable that absorption of the 248-nm photons is barely sufficient to break both M$-$C bonds, whereas absorption of the 193-nm photons delivers ca. 100 kJ mol^{-1} more energy than needed for this cleavage. We assume that the remarkably greater enhancement of the 1,3-H shift when using the 193-nm photons instead of the 248-nm photons with tellurophene compared to that with selenophene may reflect a different energy partitioning between the C_4H_4 radical and the two different M atoms, as it can be assumed that the greater amount of energy being carried away by the heavier Te atom leaves the C_4H_4 diradical less energetic and hence less prone to the higher-energy β-C$-$C cleavage.

The absence of an effect of excess nitrogen and hydrogen gases on the relative importance of the 1,3-H shift and β-C$-$C cleavage indicates that the C_4H_4 diradical is

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[11] (a) Schäfer, W.; Schweig, A.; Gronowitz, S.; Taticchi, A.; Fringuelli, F. *J. Chem. Soc., Chem. Commun.* **1973**, 541. (b) Kuder, J. E. In *Organic Selenium Compounds: their chemistry and biology*; Klayman, D. L., Günther, W. H. H., Eds.; Wiley: New York, 1973.

[12] Nyulaszi, L.; Veszpremi, T. *Acta Chim. Hung.* **1993**, *130*, 811 and references therein.

[13] Batt, L. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1986; Vol. 1.

[14] (a) Mullin, J. B.; Irvine, S. J. C. *J. Vac. Sci. Technol., A* **1986**, *4*, 700. (b) McAllister, T. *J. Cryst. Growth* **1989**, *96*, 552.

too short-lived to undergo stabilizing collisions with N_2 and H_2. This view is in accord with the fact that the photolyses in the presence of hydrogen do not lead to any detectable amounts of hydrocarbons (e.g., *n*-butane, 1-butene, propene, and ethene) that might have been formed through reactions (e.g., H-abstraction, radical disproportionation, recombination, and cleavage) of the C_4H_4 diradical with H_2.

The results reported here on the preference of the 1,3-H shift over β-C−C-cleavage in the C_4H_4 diradical produced from photolytically activated selenophene and tellurophene reveal interesting aspects of the laser photolysis of heavy-atom-containing organic compounds. The results also suggest that the mechanism of the 1,3-H shift after electronic excitation may be different than the multistep channel[9] operating in the ground electronic state. The observed dependence of the competition between the two photochemical paths on the photon energy and the mass of the heavy atom can be used for various synthetic applications in which some photochemical event can be enhanced or diminished by proper choice of the heteroatom and photolysis wavelength. The system itself is suited for photochemical generation of the $^{\bullet}HC{=}CH{-}CH{=}CH^{\bullet}$ diradical and for studies of reactions of this diradical with specifically designed reactive scavengers. The leaving Te and Se atoms are inert residues and will not interfere with a deliberately added reactant that will react exclusively with the $^{\bullet}HC{=}CH{-}CH{=}CH^{\bullet}$ diradical and will not be exposed to other intervening steps.

Conclusion

ArF and KrF laser-induced photolyses of selenophene and tellurophene are revealed to occur via the extrusion of the Se and Te atoms and via the two different fragmentation channels (1,3-H shift and β-C−C cleavage) of the postulated $^{\bullet}HC{=}CH{-}CH{=}CH^{\bullet}$ diradical. The relative importance of these channels is dependent on the excitation energy of the photon (193 or 248 nm) and on the heteroatom.

The decomposition mode of tellurophene and selenophene is different from that of furan and thiophene, which cleave just one of the two available O−C or S−C bonds.

The inertness of the selenium and particularly tellurium residuum suggests that the photolysis of selenophene and tellurophene can serve as an efficient method for the generation of the $^{\bullet}HC{=}CH{-}CH{=}CH^{\bullet}$ diradical in mechanistic studies.

Experimental Section

Laser photolysis experiments were carried out on gaseous samples of selenophene (2.7 kPa) and tellurophene (0.5 kPa) using an excimer laser (ArF and KrF radiation) operating with a repetition frequency of 10 Hz at 193 and 248 nm, respectively. The samples were irradiated in a reactor consisting of two orthogonally positioned tubes (both 3 cm in diameter), one (13 cm in length) furnished with KBr windows and the other (9 cm in length) equipped with quartz windows. The reactor had two sidearms, one fitted with a rubber septum and the other connecting to a standard vacuum manifold. The reactor accommodated metal, quartz, and KBr substrates, which, covered with solid material deposited in the course of photolysis experiments, were transferred for measurements of their properties by UV and photoelectron spectroscopy. The laser beam of different fluences was passed through a slit, and its output energy was measured by a joulemeter coupled with a 10-MHz storage oscilloscope.

The progress of the photolysis was monitored directly in the reactor by infrared spectroscopy and, after expansion of helium into the reactor, also by gas chromatography [chromatographs equipped with a 60 m × 0.25 mm i.d. Neutra Bond-1 capillary column and with a packed 2 m × 3 mm i.d. Unipak S SUS column, programmed temperature (30−150 °C), helium carrier gas]. The sampling was conducted using a gastight syringe. Both chromatographs were equipped with flame-ionization detectors (FID) and coupled with a chromatograph data processor. The depletion of selenophene and tellurophene was followed by infrared spectroscopy using diagnostic bands at 685 cm^{-1} (absorption coefficient, 3.3×10^{-2} kPa^{-1} cm^{-1}) and 688 cm^{-1} (absorption coefficient, 3.4×10^{-2} kPa^{-1} cm^{-1}), respectively. The photolytic products, i.e., ethyne, 1-buten-3-yne, and buta-1,3-diyne, were monitored by a combination of FTIR spectral and GC methods. The formation of ethyne and 1-buten-3-yne was followed by FTIR spectroscopy using diagnostic absorptions at 731 and 619 cm^{-1}. Absorption coefficients determined for authentic samples of ethyne and 1-buten-3-yne at these wavenumbers were 2.5×10^{-2} and 2.2×10^{-2} kPa^{-1} cm^{-1}, respectively. Relative amounts of ethyne, 1-buten-3-yne, and buta-1,3-diyne were also determined by gas chromatography (Unipak S SUS column), considering that the FID response factors of all three compounds are virtually the same.[15] The identification of all three products was performed by GC−MS analysis using the Unipak S SUS column.

For the examination of the dependence of selenophene and tellurophene depletion on the laser fluence, the entrance reactor window was cleaned before each experiment. This helped to circumvent the data irreproducibility caused by a gradual decay of laser power within the reactor, which was due to the Se and Te film buildup on the reactor window.

The UV spectra of gaseous selenophene, tellurophene, ethyne, 1-buten-3-yne, and buta-1,3-diyne were recorded as they were admitted to the reactor. UV spectra were also recorded for the solid films as they were deposited on the quartz substrates housed in the reactor prior to irradiation.

Properties of the photodeposited solids were also analyzed by X-ray photoelectron spectroscopy.

Selenophene (Aldrich, 97% purity) was a commercial sample. Tellurophene (>96% purity) was synthesized by a reported synthesis using bis(trimethylsilyl)-1,3-butadiyne and in situ generated sodium telluride.[16] 1-Buten-3-yne (98% purity) was obtained as previously reported.[17] Ethyne (>99.9% purity) was purchased from Toho Asechiren K. K.

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(15) Dietz, W. A. *J. Gas Chromatogr.* **1967**, *5*, 68.
(16) Lohner, W.; Praefcke, K. *Chem. Ber.* **1978**, *111*, 3745.
(17) Torneng, E.; Nielsen, C. J.; Klaeboe, P.; Hopf, H.; Priebe, H. *Spectrochim. Acta, A* **1980**, *36*, 975.