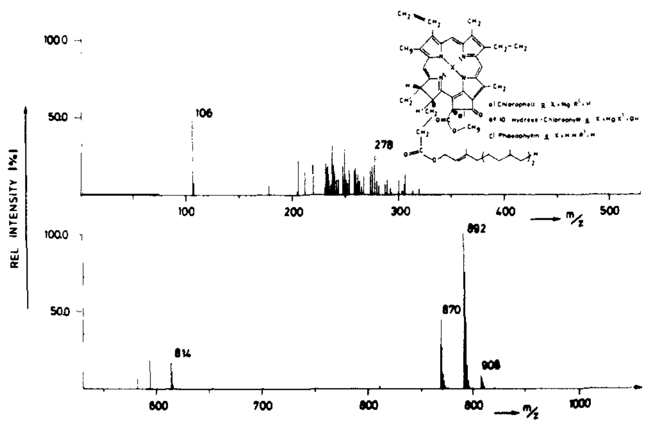

Figure 1. Laser desorption multiphoton-ionization mass spectrum of chlorophyll *a* from *Spirulina geitlerie*.

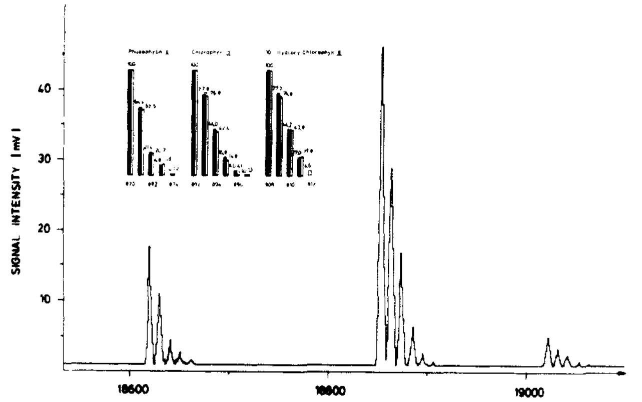

Figure 2. Raw data between data points 18 532 and 19 100, sampled with 10 ns per point. Insert upper left: comparison of calculated and measured peak pattern for the molecular ions from *Spirulina geitlerie*. Shaded area: calculated values.

belongs to the molecular ion of chlorophyll *a*, being also the base peak of the spectrum. The group at m/z 908 is assigned to the molecular ion of 10-hydroxychlorophyll *a*, which is an oxidation product formed during the extraction procedure.[14] The molecular ion of phaeophytin *a* is found at m/z 870. The replacement of the magnesium might occur either during the workup procedure or during the vaporization. The main fragmentation, the loss of the phytyl chain, leads to the signal at m/z 614. No cleavage reaction of the macrocycle nor loss of additional side groups of the macrocycle is observed.

Figure 2 shows the raw data of the high-mass region with the three different molecular ions. All isotopic peaks are clearly resolved and give the possibility to prove the identity of the molecular ions because of their isotopic distribution. The insert in Figure 2 shows the calculated isotopic distribution compared to the measured peak pattern of the molecular ions. The very good agreement between the two sets of data demonstrates again the softness of the vaporization process, showing that no hydrogen transfer or abstraction occurs during heating. This is unique for our method in contrast to all other vaporization methods.

This first results with this new method of vaporization in combination with multiphoton-ionization mass spectrometry point to new possibilities for the investigation of large thermally unstable molecules.

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Cation Radical Chain Cyclopropanation

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The pioneering discovery of the [2 + 1] olefin cyclodimerization reaction,[1] followed by the development of cation radical cycloadditions of dienes to triplet oxygen,[2] and the emergence of the cation radical Diels–Alder[3-5] reaction have now clearly established cycloaddition as an intrinsically preferred reaction mode of organic π cation radicals. Extended basis set ab initio SCF MO theoretical reaction path calculations[6,7] suggest that such reactions are activationless, with respect to potential energy in the gas phase, and experimental measurements confirm that even in solution the activation energy for the cycloaddition step is typically only 0–5 kcal at most[8] (compared to 62.5 and 32.4 kcal for the corresponding [2 + 2] and neutral Diels–Alder reactions.).[9,10] Despite such phenomenal rate enhancements, many of these reactions are quite reliably suprafacially stereospecific and typically exhibit enhanced stereoselectivities relative to corresponding neutral reactions.[5,11] Since cycloadditions play an especially powerful role in organic synthesis, further classes of hole-catalyzed/initiated cycloaddition reactions are being sought. The purpose of the present paper is to report the observation of facile, hole-catalyzed *cyclopropanation* of a variety of conjugated dienes, styrenes, and electron-rich alkenes using ethyl diazoacetate and a triarylaminium salt catalyst/initiator of appropriate oxidation potential.

Previous work has established the ability of aminium salts (and other hole catalyst/initiator systems) to generate small concentrations of chain-carrying cation radicals from ionizable substrates such as conjugated dienes, styrenes, and electron-rich alkenes. The cycloadditions of these cation radicals to neutral ethenic and dienic systems respectively engenders cyclobutanation and Diels–Alder cycloaddition. It was anticipated that addition of these same classes of chain-carrying cation radicals to diazo compounds would yield either pyrazolines, via 1,3-dipolar cycloaddition, or cyclopropanes, via cheleotropic carbene transfer with simultaneous or stepwise loss of dinitrogen. In fact, exclusive and efficient cyclopropanation has now been established.

Ethyl diazoacetate (**1**) was selected as the diazo component primarily because it was expected that the carbethoxy substituent would minimize competing ionization of the diazo component. This component was initially paired with several readily ionizable π components [*trans*-anethole (**2**), 1,1′-dicyclopentenyl (**3**), and 2,5-dimethyl-2,4-hexadiene (**4**); Scheme I].[12] In order to suppress the cyclodimerizations of **2**–**4**, reactions were carried out by using a 5:1 ratio of **1**/**2**–**4** (1.0 M in **1**) in dichloromethane solvent at 0 °C. The reactions were initiated by addition, over a 5-min period, of 10 mol % of tris(4-bromophenyl)aminimum hexachloroantimonate (**5**) relative to **2**–**4**, in ca. one-third of the solvent.

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[12] The oxidation potentials of **2** and **3** in acetonitrile vs. SCE are 1.11 and 1.30 V, respectively, compared to 1.05 V for tris(*p*-bromophenyl)amine.

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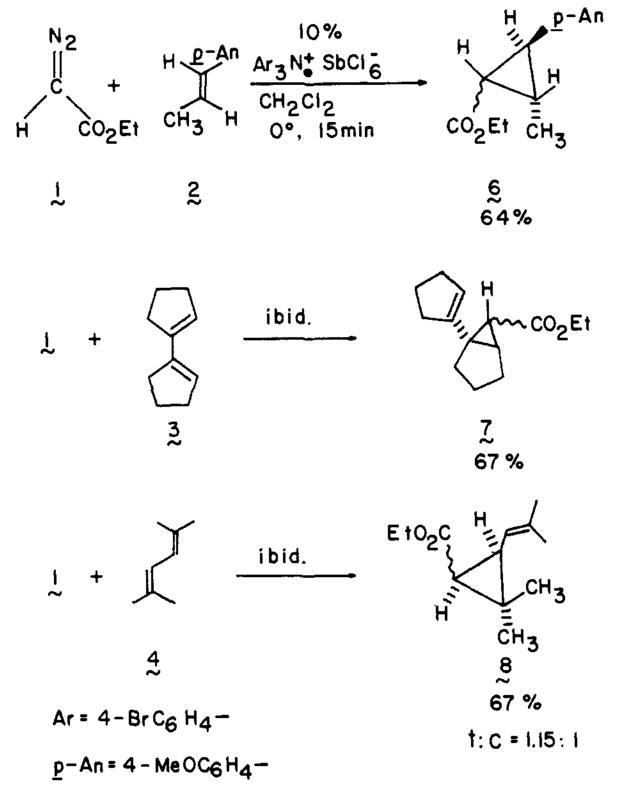
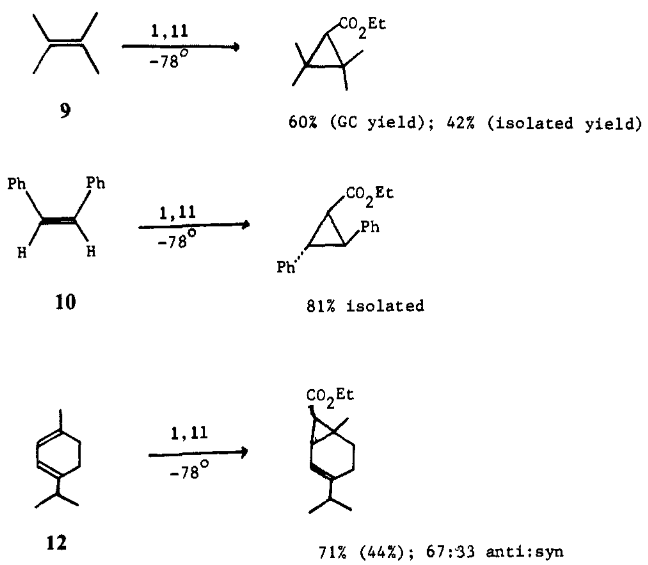
Scheme I



Scheme II



After a 15-min reaction time, excess sodium methoxide–methanol was added to quench cation radicals and the reaction mixture subjected to aqueous workup. The cyclopropane products (**6**–**8**; Scheme I) were purified by preparative TLC and preparative GC. Structure assignments are based upon GC/MS, IR, and ^{13}C and ^1H NMR (500 MHz, COSY).[13]

Less ionizable substrates, such as 2,3-dimethyl-2-butene (**9**) and *cis*- and *trans*-stilbene (**10**) could not be efficiently cyclopropanated with **5** as the initiator, but facile cyclopropanation of these substrates occurred (Scheme II), even at −78 °C, with the more potent single electron acceptor tris(2,4-dibromophenyl)aminium hexachloroantimonate (**11**).[14] The higher selectivities available at −78 °C make this procedure useful even for the relatively ionizable substrates, as illustrated by the selective cyclopropanation of α-terpinene (**12**; Scheme II).

That these triarylaminium salt initiated cyclopropanations are mechanistically cation radical chain processes is supported by application of the 2,6-di-*tert*-butylpyridine criterion[15] and by the fact that these same reactions occur using other hole-catalyst/initiator systems, including photosensitized electron transfer[16-18] and heterogeneous catalysis on 13X zeolite.[19] The premise that ionization of **1** is not competitive with ionization of **2**–**4**, and **10**–**12** is supported by the observation that **1** is stable in the presence of **5** (0 °C, 15 min, dichloromethane). The circumstance that hole-catalyzed/initiated cyclopropanation occurs via ionization of the π functionality to be cyclopropanated suggests that these reactions should be highly selective with respect to functional groups and especially so in view of the availability of initiators spanning a wide range of oxidation potentials.

Acknowledgment. We acknowledge support of this research by the Robert A. Welch Foundation.

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(13) The syn/anti isomers of 7 and 8 were separated by preparative GC. Decoupled 500-MHz ^1H NMR decisively reveal the stereochemistry of each isomer. Yields of 6–8 are corrected GC yields. Yields in Scheme II are isolated yields (silica gel chromatography).

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First Structural Characterization of a Boron-Centered Radical: X-ray Crystal Structure of $[Li(12\text{-}crown\text{-}4)_2]^+[BMes_3]^{\bullet-}$

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The reaction between triaryl boron compounds (BAr_3) and alkali metals (M = Li–Rb) in ether solvents to give the reduced salts $[M]^+[BAr_3]^-$ was first reported in 1924 by Krause.[2] The triarylboron anions, which are isoelectronic with the triarylmethyl radicals, may be paramagnetic provided they remain as unassociated species in solution.[3] It is apparent that the steric properties of the aryl substituent play a key role in determining the structure, as well as the magnetic and spectral characteristics, of these interesting compounds. For example, the sodium salts of the triphenylborane and related anions were found to be diamagnetic in ether or THF, presumably due to the association of ion pairs into ion clusters.[4] On the other hand, Chu and Weissmann[5] showed that the more crowded trimesitylboron ($BMes_3$ Mes = 2,4,6-$Me_3C_6H_2$–) reacts readily with sodium in THF to give an intense blue solution and inferred from magnetic susceptibility

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(3) More recently the work of Berndt and co-workers has shown that other types of boron-centered radical species such as $[B_2R_4]^{\bullet-}$ (R = *t*-Bu, *n*-pentyl) or cyclo-$[(BRRCRT)_2]^{\bullet-}$ are possible although no structures have yet emerged. Klusik, H.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 482. Klusik, H.; Berndt, A. *J. Organomet. Chem.* **1982**, *232*, C21; *234*, C17. Wehrmann, R.; Pues, C.; Klusik, H., Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 372.

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