unpublished scheme.[10] Treatment of the Grignard reagent of 2-bromo-4-methoxytoluene with formaldehyde provided 2-methyl-5-methoxybenzyl alcohol which was converted to 2-methyl-5-methoxybenzyl chloride with thionyl chloride.

2-Methyl-5-methoxybenzyl chloride: IR (neat) 2720, 1600 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 6.6–7.2 (m, 3 H), 4.52 (s, 2 H), 3.78 (s, 3 H), 2.35 (s, 3 H); MS, *m/e* 175 (M + 2, 15%), 170 (M, 49%), 135 (100%), 91 (26%). Anal. Calcd for C$_9$H$_{11}$ClO: C, 63.33; H, 6.45. Found: C, 63.27; H, 6.50.

Apparatus. The experimental setup was a modification of that described in the literature.[11] A 30-cm portion of a quartz tube with a 2-cm outside diameter packed with pieces of quartz chips was mounted vertically in a Hoskins FD303A electric furnace. The reaction temperature was measured by a thermocouple inside a thermowell that extended into the middle of the heated zone. A 12-cm portion above the furnace served as the preheating zone, the temperature in the middle of which was 250–300 °C. An addition funnel was attached to the upper end of the quartz tube, and the lower end was joined to two cold traps in series which in turn was connected to a vaccum pump.

General Procedures. The furnace was heated to the desired temperature, and vacuum was applied, at which time the starting materials in the addition funnel were added. The rate of addition was determined by dividing the amount of the added materials by the elapsed time and was about 0.2 g/min. Products and unreacted starting materials were collected in the cold traps. The amounts of unreacted starting materials and products were determined by GLC with internal standards. Their structures were confirmed by GC/MS.

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Direct Observation of a Diiodo Derivative and Phosphonium Intermediates in Iodolactonization by Fast Atom Bombardment Mass Spectrometry

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Received August 28, 1986

It has been recognized, since Bougault[1] first reported the conversion of β,γ- or γ,δ-unsaturated acids into iodo lactones, that γ,δ-unsaturated acids frequently react with iodine to form iodo lactones instead of the simple addition products. This iodolactonization reaction has shown great value in organic synthesis in different aspects,[2] especially for stereocontrolling purposes[3] and structural determination. Arnold et al.[4] proposed a general mechanism for the reaction of halogen and γ,δ-unsaturated acids and esters. Later on, based on a kinetic study, Amaral and Melo[5] presented a more detailed mechanism, in which the fast formation of an iodine–double bond complex intermediate was supposed. This explains the fact that in chloroform, 1 mol of unsaturated acid reacts with 2 mol of iodine. Zhao
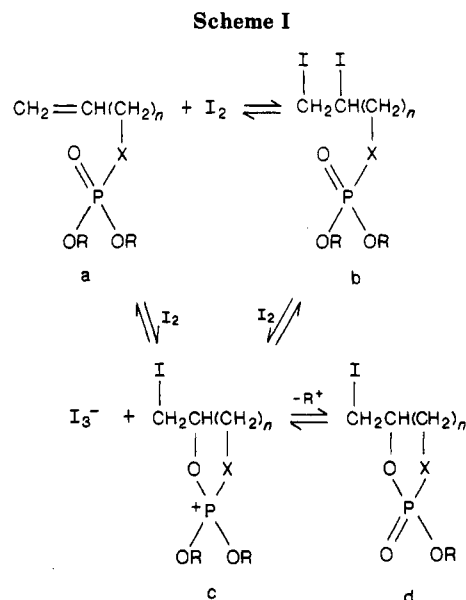
Scheme I

and co-workers[6] traced the iodine-induced cyclization reaction of δ,ϵ-unsaturated phosphonate by ^{31}P NMR, and found that two intermediates resulted: the diiodo derivative and the cyclic phosphonium ion. However, these labile short-lived intermediates do not allow any separation and purification, and they are not amenable to full characterization.

Fast atom bombardment mass spectrometry (FAB MS), which was introduced by Barber et al.[7] in 1981, has shown promise in the direct characterization of liquid-phase systems. In FAB MS, the sample is dissolved in a liquid matrix (usually glycerol) and then bombarded by a beam of energetic particles (such as Ar^0 and Xe^0 of 5–10 keV). With this technique, Saito and Kato[8] detected short-lived glutathione-conjugate intermediates in a rapid conjugation reaction of carcinogenic–mutagenic arylnitroso compounds with glutathione, which was performed within a mass spectrometer. Daves et al.[9] directly observed the transmetalation intermediates, which is central to palladium-mediated reaction of organomercurials, in reaction mixtures.

During the verification of iodolactonization products of unsaturated phosphoamidate I, phosphonates II and III, and phosphate IV by FAB MS, we observed the diiodo derivative and monoiodo phosphonium intermediates in the mass spectra of the reaction mixtures, which is the direct evidence for the mechanism of iodine-induced cyclization of unsaturated organophosphorus compounds.

$$(RO)_2PX(CH_2)_nCH=CH_2$$

with O double-bonded to P
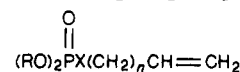
	X	*n*	R
I	NH	1	Et
II	CH$_2$	1	Et
III	CH$_2$	2	*n*-Pr
IV	O	2	Et

Results and Discussion

The iodine-induced cyclization of unsaturated organophosphorus compounds I–IV is described in Scheme I based on the mechanism proposed by Zhao et al.[6] The overall process involves two intermediates: iodine addition

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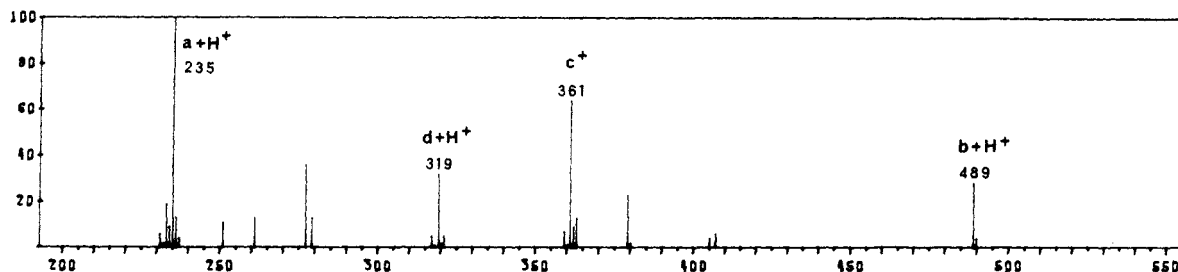
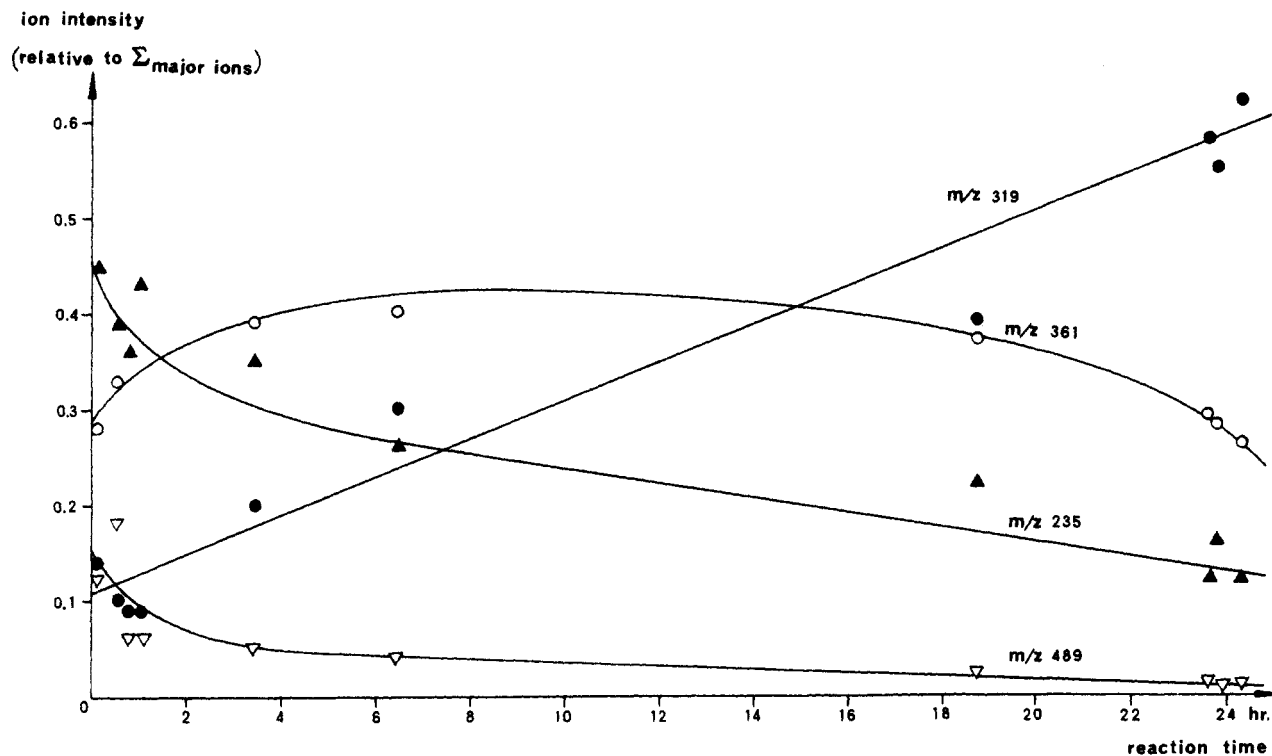**Figure 1.** FAB mass spectrum of reaction mixture of compound III.

Figure 2. Change in ion intensities in the mass spectrum of III at prolonged reaction time.

Table I. Major Ions of Reaction Mixtures of I–IV in Positive Ion FAB Mass Spectra[a]

	a		b		c		d	
	mass	obsd m/z	mass	obsd m/z	mass	obsd m/z	mass	obsd m/z
I	193	194 (100)	447	448 (11)	320	320 (26)	291	292 (9)
II	192	193 (100)	446	447 (55)	319	319 (50)	290	291 (19)
III	234	235 (100)	488	489 (29)	361	361 (67)	318	319 (33)
IV	208	209 (100)	462	463 (20)	335	335 (37)	306	307 (30)

[a] Relative abundance given in parentheses.

product b and phosphonium ion c.

Positive ion FAB mass spectra were recorded by using aliquots taken from reaction mixtures immediately after the mixing of the reaction components. A typical spectrum thus obtained for compound III is shown in Figure 1. All the species from a to d were observed in the spectrum, where the reactant a appeared as a + H⁺ at m/z 235 and iodo lactone product d as d + H⁺ at m/z 319. The diiodo derivative b gave a prominent ion b + H⁺ at m/z 489, while the monoiodo phosphonium ion c appeared as c⁺ at m/z 361. The elemental composition of b + H⁺ and c⁺ were supported by high-resolution accurate mass measurement. Similar ion peaks observed in the spectra for reaction mixtures of other compounds are summarized in Table I.

In positive ion FAB MS, usually the sample molecules are ionized by protonation[10] and MH⁺ are often observed.

This is the case with a, b and d. According to Scheme I, c exists as an ionic species in the reaction medium. This preformed phosphonium ion could be directly sputtered from the condensed phase, and c⁺ was observed.

It has been known that dimerization could occur during the bombardment process if the sample solution is too concentrated. The addition product between a and I₂ would have the same mass as b. To decide whether the observed ion corresponds to a species existing in solution or to a product formed during the bombardment, a simple experiment was made. A reaction mixture of compound II was diluted a hundred times, and the same volume of the diluted solution was subjected to FAB analysis. The spectrum thus obtained is roughly the same as that in Table I.

If the diiodo derivative is a FAB-induced adduct a + I₂ + H⁺, statistically 2a + H⁺ should also be present. However, no such dimer was noticed in all four spectra. Furthermore, spectra taken at prolonged reaction time showed

(10) Barber, M.; Bordoli, R. S.; Elliot, G. J.; Sedgwick, R. D.; Tyler, A. N. *Anal. Chem.* **1982**, *54*, 645A.

alteration in relative intensities of ion peaks as depicted in Figure 2, which showed constant decrease for a + H^{+} and b + H^{+} and increase for d + H^{+} within the reaction time of 24 h. These semiquantitative data are consistent with the ^{31}P NMR traced experiment[6] and are in agreement with the expected change of the concentration of the four species in the reaction mixture.

These results suggested that the principal ions obtained are the direct response of the major species existing in the liquid reaction medium and are not FAB-induced artifacts or fragments.

We fail to get similar results for γ,δ-pentenoic acid, which is the typical example of iodolactonization. It is likely that the ease of the direct detection of a–d by FAB MS is due to the existence of the dialkoxyphosphinyl moiety, which has been proved to have very high sensitivity for FAB MS analysis.[11] Hence, the FAB mass spectra provide direct evidence for the existence of the cyclic phosphonium ion intermediate and further evidence for the iodine addition product intermediate in the iodine cyclization reaction of unsaturated organophosphorus compounds.

Experimental Section

The preparation of compounds I–IV will be published elsewhere. The reaction was carried out in chloroform. The molar ratio of the reactant to iodine was 1:2. The reaction mixture was kept at room temperature and protected from light.

FAB mass spectral data were obtained on a KYKY ZhP-5 double focusing mass spectrometer (Scientific Instrument Factory, Beijing) equipped with a standard KYKY fast atom gun (from the same supplier). A neutral argon beam was used at the energy of 7 keV and gun monitor current of 1.2 mA. The accelerating voltage was 6 kV, and the resolution was kept at 1500. The spectra were recorded on UV-sensitive paper. The m/z values and relative intensities were manually counted and measured, respectively. The accurate mass measurement was carried out by peak-matching technique on the same instrument at the resolution of 4000.

An aliquot of 0.5 μL of the reaction mixture was transferred into a drop of glycerol (~1 μL) on the probe target by microsyringe. Spectra were taken 30 s after insertion of the probe to let the ion current become optimized and stabilized.

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Unsymmetrical Alkenes by Carbene Coupling from Diazirine Decomposition in the Presence of Diazo Compounds

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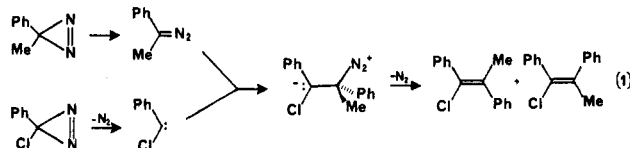*Department of Chemistry, Trinity University, San Antonio, Texas 78284*

Thermal and photochemical decomposition of diazirines results in the formation of azines with carbene dimers formed in much lower amounts.[1] Azine production has

(1) (a) Liu, M. T. H. *Chem. Soc. Rev.* 1982, *11*, 127. (b) Schmitz, E. *Adv. Heterocycl. Chem.* 1979, *24*, 63.
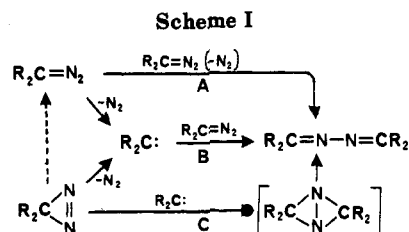
Scheme I

been viewed as a bimolecular reaction between two diazo compounds, formed by diazirine isomerization, followed by elimination of dinitrogen (path A, Scheme I),[2,3] as a coupling between a carbene and a diazo compound (path B),[4] and as an addition of a carbene to a diazirine followed by rearrangement (path C).[5,6] By inference, alkene products are formed through carbene coupling. However, these mechanisms are apparently inconsistent with experimental results obtained by Liu and Ramakrashnan[7] who showed that, although thermal decomposition of either 3-chloro-3-phenyldiazirine or 3-methyl-3-phenyldiazirine resulted in nearly quantitative azine formation, decomposition of an equimolar mixture of these two diazirines produced the carbene dimer from this reactant combination without azine. The mixed carbene dimer was proposed to have resulted from nucleophilic attack of 1-phenyldiazoethane, presumed to have been formed from 3-methyl-3-phenyl-diazirine, on chlorophenylcarbene (eq 1). Since alternate explanations for these observations are possible, the present investigation was undertaken to determine the validity of this mechanistic interpretation and to evaluate the feasibility of alkene synthesis by reactions between diazo compounds and carbenes thermally generated from diazirines.

3-Halo-3-phenyldiazirines were prepared from benzamidine hydrochloride by Graham's procedure.[8] The decomposition of these thermally unstable halophenylcarbene precursors was performed in refluxing carbon tetrachloride. Diazirine decomposition in the presence of a representative selection of diazo compounds produced the carbene coupling products (eq 2) in remarkably high yields (Table I). Since diazo compounds such as ethyl
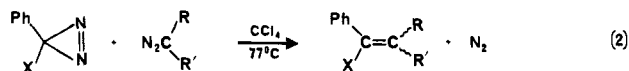
diazoacetate are stable to decomposition at these temperatures, the coupling products must have arisen by electrophilic addition of the thermally generated halophenylcarbene to the diazo compound with subsequent loss of dinitrogen to form the observed products. No evidence for unsymmetrical azines was obtained.

The effectiveness of this transformation is demonstrated by the high yields of products obtained from nearly stoi-

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