Figure 3. Emission spectra of TMD dissociated by the laser: ● coincident with the laser; O 140 μs after the laser pulse. The left-hand curve is acetone fluorescence; the right-hand curve is acetone phosphorescence (from ref 8).

of its kind in TMD thermolysis. Previous workers,[5,12,13] detected the triplet mostly by indirect methods. The observed emission spectrum, even in oxygen free solutions, was always shifted to the blue relative to genuine triplet phosphorescence. The high time resolution afforded by the pulsed infrared laser technique is of crucial importance in our work, and allowed us to distinguish between the 420-nm emission, dominant at short time intervals, and the weaker 460-nm emission, that is fully developed only after $\sim 10^{-4}$ s.

We can thus conclude that the 420-nm emission cannot be due to either acetone phosphorescence or to acetone fluorescence. One possibility is that it is a mixture of the two.[14] Since on a $10^{-8} - 10^{-7}$ time scale, all singlet states formed emit radiation instantaneously, whereas only a small fraction of triplet molecules have a chance to emit, this interpretation implies a strong preference for triplet production. The shift from 410 to 420 nm implies that the triplet accounts for $\sim 20\%$ of the total light yield. In order to produce that much light in a short time internal (say 10^{-7} s) initial triplet acetone concentration should be at least 10^3 times that of the excited singlet. Indeed, triplet acetone formation is reported to be dominant in TMD thermal decomposition.[12] The quantitative aspects of our observations obviously require further investigation.

Another possibility that was previously suggested by us[2] is that the 420-nm emission is due to a third, different species. The involvement of an intermediate chemical species (leading to triplet formation) in dioxetane thermolysis has often been indicated in the literature.[15] The nature of this species is far from being clarified, and in particular it may not be emissive. We tentatively proposed acetone excimer as a candidate,[2] but this assignment is rather dubious as this species has not been observed inspite of considerable effort. We are now using energy transfer methods in an attempt to further elucidate this point.

The mechanism of TMD decomposition by direct absorption of a large number of infrared photons appears to be complex, and a full discussion is beyond the scope of this communication. Figures 1 and 2 indicate that both uni- and bimolecular processes are involved. The ambiguity concerning the identity of the 420-nm emission precludes detailed mechanistic interpretation at this stage. However, the fact that it appears within 20 ns of laser pulse onset, and that it partially follows laser intensity modulations to ~ 5 ns, strongly suggests the involvement of a unimolecular process. In fact, many multiphoton dissociation reactions are believed to be dominated by uni-

molecular decomposition,[1] so that TMD would be no exception in this respect. As Figure 2 clearly shows, the 420-nm emission persists a few microseconds after laser pulse termination. The source of this emission must be collisional activation and the fact that the spectrum of the product of this bimolecular process is indistinguishable from that of the unimolecularly formed species may help in resolving the mechanism.

In conclusion, we have shown that the high sensitivity and excellent time resolution provided by the infrared laser dissociation method make it a powerful tool for mechanistic studies of reactions of electronically ground state molecules. In view of these properties, this method will probably be utilized in the elucidation of many other complex organic reactions.

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Synthesis of *P*-Mesityldiphenylmethylenephosphine: A Stable Compound with a Localized P=C Bond

Sir:

It is well known that second and higher row elements are in general reluctant to form multiple bonds in which they are involved in a pπ-hybridized state.[1] Thus, simple compounds containing multiple phosphorus–carbon bonds, such as methylidynephosphine (HC≡P)[2] and methylenephosphine (H_2C=PH),[3] are not stable at room temperature.

Three approaches have been applied to stabilize double bonds involving phosphorus in the pπ-hybridized, two-coordinate state. The first one, delocalization, involves thermodynamic stabilization and has been particularly successful as exemplified by the phosphamethinecyanines[4] and by phosphabenzene and its derivatives.[5] The second one involves generation of positive charge on phosphorus to give contracted 3p orbitals which can overlap with 2p orbitals more effectively. Besides being an additional factor in the aforementioned phosphamethinecyanines,[4] this effect is clearly demonstrated in the amidophosphinium cations;[6] the stabilization thus achieved is also thermodynamic in nature. The third approach, kinetic stabilization of more or less isolated double bonds by steric hindrance, has so far been limited to a few cases of P=N[7] and heterosubstituted P=C[8] bonds. We wish to report the synthesis of *P*-mesityldiphenylmethylenephosphine (**1a**), the first thermally stable compound with a localized, all-car-

Table I. Spectral Data of **1a**, **4**, and **5**

Compd	¹H NMR[a]	¹³C NMR[b]	³¹P NMR[c]	UV[d]
1a	7.60–6.75 (m, 10 H, H^d), 6.69 (s, 2 H, H^c), 2.27 (s, 6 H, H^a), 2.19 (s, 3 H, H^b)	193.37 (d, $^1J_{PC}$ = 43.5 Hz, C^e), 144.9–125.5 (m, C arom), 22.67 (d, $^3J_{PC}$ = 10.3 Hz, C^a), 22.06 (d, $^3J_{PC}$ = 8.8 Hz, C$^{a'}$), 20.96 (s, C^b)	233.06	254 (3.20) 268 (3.01) 324 (2.84)
4	7.44–6.83 (m, 10 H, H^d), 6.78 (s, 1 H, H^f), 6.74 (s, 2 H, H^c), 2.23 (s, 3 H, H^b), 2.07 (s, 6 H, H^a)	144.1–127.0 (C arom + C^f), 133.85 (C^e), 20.90 (C^b), 20.40 (C^a)		267 (3.06) 273 (3.02) 290 (2.70)
5	7.9–7.0 (m, 10 H, H^d), 6.68 (s, 2 H, H^c), 2.18 (s, 3 H, H^b), 2.00 (s, 6 H, H^a)	146–125.5 (C arom), 167.30 (C^e), 20.57 (C^b), 18.30 (C^a)		242 (3.62) 275 (3.29) 360 (2.92)

^{a} CDCl$_3$, δ from Me$_4$Si. ^{b} CDCl$_3$, δ from Me$_4$Si. ^{c} CDCl$_3$, δ from external 85% H$_3$PO$_4$; shift toward lower field is indicated by positive sign in accordance with the newly recommended convention. ^{d} THF, λ in nm (log ε).

Scheme I
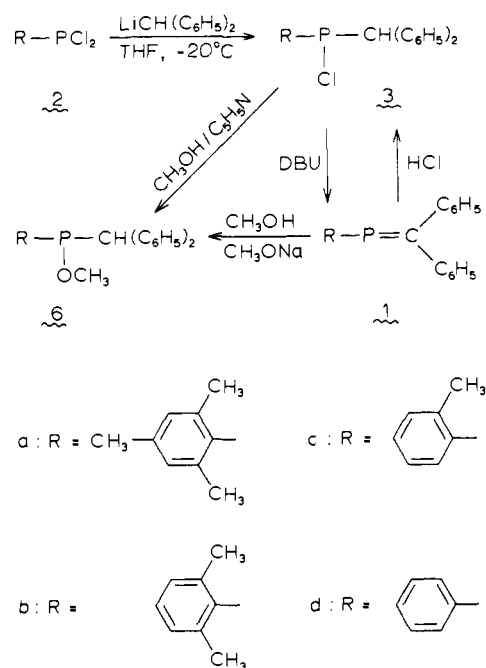
bon-substituted phosphorus–carbon double bond, in which steric hindrance most likely makes the most important contribution to stability.

The synthesis of **1a** was performed according to the reaction sequence shown in Scheme I (all reactions were carried out under an argon atmosphere). The reaction of mesityldichlorophosphine (**2a**)[9] with ~50% excess of diphenylmethyllithium in THF at −20 °C afforded **3a** (mp 90–95 °C, from diethyl ether) in 50% yield. Dehydrohalogenation of **3a** with 1 equiv of DBU (1,5-diazabicyclo[5.4.0]undec-5-ene) in THF (room temperature, 1 h) afforded **1a** almost quantitatively.

1a is thermally stable and can be distilled (bp 140 °C (10⁻³ Torr)) without decomposition; it solidifies to give slightly yellow crystals (mp 51–58 °C; attempted recrystallization has been unsuccessful so far). Mass spectrum: calcd for C$_{22}$H$_{21}$P, m/e 316.1381; found, m/e 316.1388 (100%). The spectral data of **1a** and, for comparison, those of its carbon and nitrogen analogues **4**[10] and **5**,[11] respectively, are presented in Table I.

The spectral data confirm the structures of **1a**. In particular, the low ³¹P chemical shift is only compatible with a two-coordinate, pπ-hybridized state of phosphorus; comparison with other pπ-hybridized phosphorus compounds[5,8] suggests that an increasing degree of delocalization is accompanied by a shift of the ³¹P chemical shift to higher fields. The ¹³C chemical shift of C^e confirms its sp²π-hybridized state; the value is surprisingly low which may be characteristic for carbon atoms next to pπ-hybridized phosphorus.[12] The ¹³C chemical shifts of the three methyl groups were puzzling at first; they were assigned by comparison with those of **1b** (δ 22.77 ppm (d, ^3J = 11.7 Hz, C^a), 22.19 ppm (d, ^3J = 8.8 Hz, C^a), C^b missing).[13] The magnetic nonequivalence of the two o-methyl groups points to considerable steric hindrance toward rotation around the mesityl–phosphorus bond. Steric hindrance is apparently also the predominant factor in the stabilization of **1a** and **1b**, as attempts to prepare **1c** and **1d** from **3c** and **3d**, respectively, have only led to the formation of polymeric material so far,[13] indicating that conjugation with the aromatic rings is not sufficient to stabilize the compounds. The infrared spectrum of **1a** is very similar to that of **4** and **5**, except for a strong absorption of **1a** at 900 cm⁻¹ (CCl$_4$), which is tentatively assigned to the P=C stretching vibration.

A preliminary investigation of the chemical reactivity of the new compound reveals the expected polarity of the P=C bond with phosphorus as the more positive partner. Anhydrous HCl does not lead to observable salt formation, but reconverts **1a** to **3a**. However, the bond polarity is apparently not very pronounced, as methanol adds to the double bond only on catalysis, e.g., by sodium methoxide, yielding **6a**; the latter may also be obtained from **3a** with methanol–pyridine. The reactions of **1a** leading to **3a** and to **6a** may be considered as chemical corroboration of the structure of **1a**.

The chemical and physical properties of the new class of compounds are under investigation.

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Hypervalent Organoiodine Chemistry.[1]
# Syn Elimination of Alkyl Iodoso Compounds

Sir:

We report here evidence that the oxidation of alkyl iodides in nonpolar media gives an oxidized iodine intermediate (the iodoso compound) which can lead to olefins by a syn elimination process. It is known that amine oxides,[2] sulfoxides,[3] and selenoxides[4] undergo thermal pericyclic eliminations of hydroxylamine, sulfenic acid (RSOH), and selenenic acid (RSeOH), respectively, to form olefins. Alkyl iodide oxides (iodoso compounds), although unknown as stable compounds,[5] should also be capable of a similar syn elimination of hypoiodous acid (IOH).

Alkyl iodides are inert to a number of oxidizing agents such as ozone, periodate, and hydrogen peroxide which serve to convert sulfides and selenides to their oxides. However, treatment with *m*-chloroperbenzoic acid (*m*-CPBA, 1.5 equiv) in dichloromethane or carbon tetrachloride leads to oxidation of the iodide. Primary alkyl iodides are converted to the cor-


$$R\diagup\diagdown I \xrightarrow[CH_2Cl_2O^*]{m\text{-}CPBA} R\diagup\diagdown OH$$

R = $CH_3(CH_2)_{13}$ 62%
CH_2Ph 75%
Ph 73%
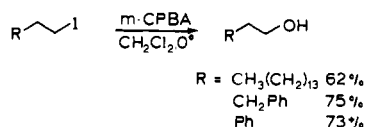
responding alcohols in good yields; only trace amounts of *m*-chlorobenzoate esters are formed. Labeled 2-phenyl-1-iodoethane-*1,1-d₂* leads to partially scrambled products (35% of 2-phenylethanol-*2,2-d₂*). This observation, together with the formation of complex mixtures of alcohols and benzoates from neophyl, cyclohexylmethyl and 2-dodecyl iodides, suggests that carbonium ion intermediates are involved.

The oxidation of alkyl iodides bearing strongly electron-attracting substituents such as carbomethoxy and sulfonyl at the α carbon proceeds differently than those reported above. For example, 2-phenylsulfonyl-2-iodopropane (**1**)[6] and ethyl 2-iododecanoate (**2**)[6] are converted in a high yield reaction to
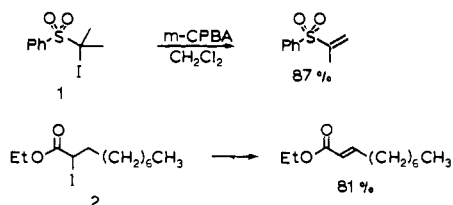

the unsaturated compounds. Approximately 2 equiv of peracid are required for complete oxidation since at least one of the products (I_2) is oxidized under these conditions.

The study of the stereochemistry of this elimination reaction was initially attempted with the easily available compounds **3** and **4**. The results were ambiguous, however, since exclusive

3 R = CH_3
4 R = H

5
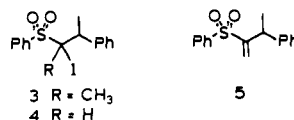
elimination toward the methyl group to give **5** was observed on oxidation of **3**, while **4** gave none of the expected vinyl sulfone product. A suitable system was the tetralin **6**, prepared as shown in Scheme I. Although base-catalyzed isotopic ex-

Scheme I[a]

8a R = H
8b R = D

7a

7b
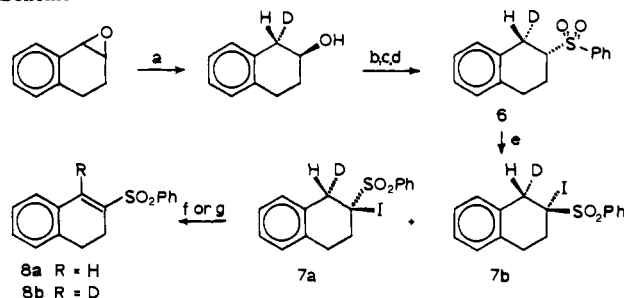
[a] Step a: $LiAlD_4$, $AlCl_3$, Et_2O (85%, ref 7). Step b: CH_3SO_2Cl, NEt_3 (96%). Step c: PhSH, *t*-BuOK, *t*-BuOH (61%). Step d: H_2O_2, *o*-$NO_2C_6H_4SeO_2H$, CH_2Cl_2 (81%, ref 8). Step e: LiN-*i*-Pr_2, THF, −78 °C; I_2, THF, −78 °C (84%). Step f: *m*-$ClC_6H_4CO_2H$ (2.0 equiv), CH_2Cl_2, 25 °C (67%). Step g: EtOH, EtOK (88%).

change of protons α to sulfones frequently occurs with retention of configuration,[9] the metalation–iodination steps (e in Scheme I) consistently led to a 1:1 mixture of **7a** and **7b**. An 87:13 ratio of **7a** to **7b** was obtained by partial dehydroiodination of the 1:1 mixture with 0.7 equiv of 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU). The configurational assignment for **7** was made on the basis of the following considerations: (1) a positive isotope effect for the presumed anti elimination (E_2),[10] (2) the presence of a four-bond long-range (W) coupling for the proton assigned as trans to the sulfonyl substituent,[11] and (3) the observation of a larger Eu(fod)₃ shift for the proton cis to the sulfonyl.[11b]

Treatment of the 87:13 mixture of **7a** and **7b** with *m*-CPBA gave vinyl sulfone **8** which was 89 ± 2% d_1 (**8b**) by ^{1}H NMR analysis. Base-catalyzed elimination (EtOH, EtOK) yielded vinyl sulfone which was 21% d_1.[12] The *oxidative elimination, therefore, proceeds with syn stereochemistry.*

We propose an iodoso compound as an intermediate along the reaction pathway. For most primary iodides, the iodoso compound rearranges to the hypoiodite, which is (oxidatively?) converted to the alcohol under the reaction conditions. This
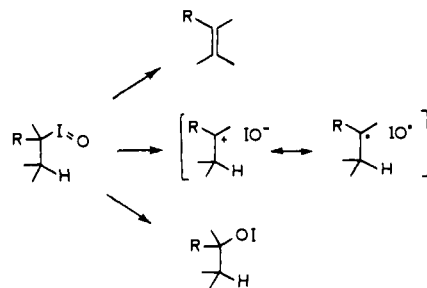
rearrangement may occur by either a 1,2-alkyl shift or via a radical or ion pair. If the carbonium ion is secondary and/or prone to Wagner–Meerwein rearrangements, more complex product mixtures are obtained.[13] When carbonium ion formation is suppressed by electron-withdrawing substituents (R = CO_2CH_3, SO_2Ph), a pericyclic syn elimination to the olefin predominates.