J. Am. Chem. Soc. **1984**, *106*, 7167–7175

of concentrated ammonium hydroxide was added. The solution was stirred for 5 h, condensed to dryness, and partitioned between 50 mL of CH_2Cl_2 and 50 mL of H_2O. A bad emulsion formed. After sitting 14 h, the CH_2Cl_2 layer was separated and the aqueous layer was extracted with 20 mL of CH_2Cl_2. The combined organic extracts were washed with 100 mL of water, dried ($MgSO_4$), filtered, and evaporated under reduced pressure to give a colorless oil. This material was crystallized from ethanol/water to give, after washing with three 1-mL portions of 7:3 ethanol/water and drying (160 °C/0.01 mm), 0.0442 g (70.7%) of **8**: mp >269 °C dec; ^1H NMR ($CDCl_3$) δ 1.945–2.262 (m, 4 H, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{CH_2N}$), 2.303 (s, 3 H, $ArCH_3$), 2.337 (s, 3 H, $ArCH_3$), 2.359 (s, 6 H, $ArCH_3$), 3.033 (s, 3 H, $ArOCH_3$), 3.233 (s, 6 H, $ArOCH_3$), 3.303–3.367 (m, 6 H, $\mathrm{NC}\mathit{H}_2\mathrm{CH_2C}\mathit{H}_2\mathrm{N}$), 3.355 (AB, J = 13.7 Hz, 2 H, $ArCH_2N$), 3.555 (s, 3 H, $ArOCH_3$), 3.608–3.716 (m, 2 H, $\mathrm{NC}\mathit{H}_2\mathrm{CH_2C}\mathit{H}_2\mathrm{N}$), 5.853 (AB, J = 13.7 Hz, 2 H, $ArCH_2N$), 7.031–7.092 (m, 8 H, ArH); MS (70 eV, 220 °C), *m/e* 704 (M^+, 11), 674 ($M^+ - 30$, 100). Anal. Calcd for $C_{42}H_{48}N_4O_6$: C, 71.57; H, 6.86; N, 7.95. Found: C, 71.39; H, 6.82; N, 7.93.

Registry No. 1, 83604-21-1; **1**·NaBr complex, 92184-73-1; **1**-Li-·picrate, 92184-75-3; **1**-Na·picrate, 92184-77-5; **1**-K·picrate, 92184-79-7; **1**-Rb·picrate, 92184-81-1; **1**-Cs·picrate, 92184-83-3; **1**·NH_4^+·picrate, 92185-55-2; **1**·$CH_3NH_3^+$·picrate, 92185-56-3; **1**·$(CH_3)_3CNH_3^+$·picrate, 83604-22-2; **2**, 83604-24-4; **2**-Li·picrate, 92184-85-5; **2**-Na·picrate, 92184-87-7; **2**-K·picrate, 92269-44-8; **2**-Rb·picrate, 92184-89-9; **2**-Cs·picrate, 92184-91-3; **2**·NH_4^+·picrate, 92185-57-4; **2**·$CH_3NH_3^+$·picrate, 92185-58-5; **2**·$(CH_3)_3CNH_3^+$·picrate, 92185-59-6; **3**, 83604-25-5; **3**·NaBr complex, 83604-26-6; **3**-Li·picrate, 92184-93-5; **3**-Na·picrate, 92184-95-7; **3**-K·picrate, 92184-97-9; **3**-Rb·picrate, 92184-99-1; **3**-Cs·picrate, 92185-00-7; **3**·NH_4^+·picrate, 92185-60-9; **3**·$CH_3NH_3^+$·picrate, 92185-61-0; **3**·$(CH_3)_3CNH_3^+$·picrate, 92185-62-1; **4**, 84379-21-5; **4**·NaBr complex, 92185-01-8; **4**-Li·picrate, 92185-03-0; **4**-Na·picrate, 92185-05-2; **4**-K·picrate, 92185-64-3; **4**-Rb·picrate, 92185-07-4; **4**-Cs·picrate, 92185-09-6; **4**·NH_4^+·picrate, 92185-65-4; **4**·$CH_3NH_3^+$·picrate, 92185-66-5; **4**·$(CH_3)_0CNH_3^+$·picrate, 92185-67-6; **5**, 84379-22-6; **5**-Li·picrate, 92185-11-0; **5**-Na-picrate, 92185-13-2; **5**-K·picrate, 92185-15-4; **5**-Rb·picrate, 92185-17-6; **5**-Cs·picrate, 92185-19-8; **5**·NH_4^+·picrate, 92185-68-7; **5**·$CH_3NH_4^+$·picrate, 92185-69-8; **5**·$(CH_3)_3CNH_3^+$·picrate, 92185-70-1; **6**, 84379-24-8; **6**·NaBr complex, 92185-20-1; 6-Li·picrate, 92185-22-3; **6**-Na·picrate, 92185-24-5; **6**-K·picrate, 92185-27-8; **6**-Rb·picrate, 92185-29-0; **6**-Cs·picrate, 92185-31-4; **6**·NH_4^+·picrate, 92185-71-2; **6**·$CH_3NH_3^+$·picrate, 92185-72-3; **6**·$(CH_3)_3CNH_3^+$·picrate, 92185-73-4; **7**, 84379-23-7; **7**·NaBr complex, 92185-32-5; 7-Li·picrate, 92185-34-7; 7-Na·picrate, 92185-36-9; 7-K·picrate, 92185-38-1; 7-Rb-picrate, 92185-40-5; 7-Cs·picrate, 92185-42-7; 7·NH_4^+·picrate, 92185-74-5; 7·$CH_3NH_3^+$·picrate, 92185-75-6; 7·$(CH_3)_3CNH_3^+$·picrate, 92185-76-7; 8, 92185-77-8; 8-Na·picrate, 92185-44-9; 8-K·picrate, 92185-46-1; 9, 83604-23-3; 9-Li·picrate, 92219-68-6; 9-Na·picrate, 92185-48-3; 9-K·picrate, 92185-50-7; 9-Rb·picrate, 92185-52-9; 9-Cs·picrate, 92219-70-0; 9·NH_4^+·picrate, 92219-71-1; 9·$CH_3NH_3^+$·picrate, 92185-78-9; 9·$(CH_3)_3CCNH_3^+$·picrate, 89482-94-0; **10**, 83604-32-4; **12i**, 89827-45-2; **13**, 92185-79-0; **14**, 83604-34-6; **15**, 83604-35-7; **16**, 83604-38-0; **17**, 83604-39-1; **18**, 71128-89-7; **19**, 84379-25-9; **20**, 84379-26-0; **21**, 84379-27-1; **22**, 84379-28-2; **23**, 84379-29-3; **24**, 84379-30-6; **25**, 91-04-3; **26**, 7259-92-9; **27**, 84379-31-7; **28**, 92185-80-3; **29**, 92185-81-4; **30**, 84379-43-1; **3u**, 84379-37-3; **32**, 84379-38-4; **33**, 92185-82-5; **34**, 92185-83-6; **35**, 84379-39-5; **36**, 83587-11-5; **37**, 84379-40-8; **38**, 84395-43-7; **39**, 92185-84-7; **40**, 83587-10-4; **41**, 29455-11-6; **42**, 37780-40-8; **43**, 92185-85-8; **44**, 84379-33-9; **45**, 84379-42-0; **46**, 84379-34-0; **47**, 84379-35-1; **48**, 84379-36-2; **49**, 92185-86-9; **50**, 84379-32-8; **51**, 92185-87-0; **52**, 17454-52-3; **52**-Li-picrate, 64799-51-5; **52**-Na·picrate, 64799-49-1; **53**-K·picrate, 64851-30-5; **52**-Rb·picrate, 64822-96-4; **52**-Cs·picrate, 64799-34-4; **52**·NH_4^+·picrate, 92185-88-1; **52**·$CH_3NH_3^+$·picrate, 92185-89-2; **52**-$(CH_3)_3CNH_3^+$·picrate, 92185-90-5; HUA′UA′UCH$_2$BCH$_2$OH, 92185-91-6; BrAAABr, 92185-92-7; HUAUAUCH$_2$BCH$_2$OH, 92185-93-8; $COCl_2$, 75-44-5; 1,2-bis(bromomethyl)benzene, 91-13-4; dibenzofuran, 132-64-9; 2-bromoanisole, 578-57-4; 4-(2-hydroxphenyl)dibenzofuran, 92185-94-9; 2,2′,2″-trihydroxy-[1,1:3′,1″]terphenyl, 92185-95-0; 2,4,4,6-tetrabromocyanohexadienone, 20244-61-5; 1-amino-3-bromopropane hydrobromide, 5003-71-4; 4-methyl-2-aminoanisole, 120-71-8; 1,3-dibromopropane, 109-64-8; 1,3-bis(2-methoxy-5-methylphenyl)-1,3-bis(2-propenyl)urea, 92185-96-1; 3-chloropropane isocyanate, 13010-19-0; 2,6-dibromo-4-methylphenol, 2432-14-6.

Chemical Consequences of Single-Electron Oxidation of Phenylmesityldiazoethane

Charles B. Little and Gary B. Schuster*

Contribution from the Department of Chemistry, Roger Adams Laboratory, University of Illinois, Urbana, Illinois 61801.
Received September 12, 1983

Abstract: Both thermolysis and photolysis of 1-phenyl-2-mesityldiazoethane (PMDE) lead exclusively to products derived from facile hydrogen or mesityl migration subsequent to, or concurrent with, loss of N_2. No detectable amounts of ketazine or any dimeric hydrocarbons are formed in these reactions—a result that is attributable to the steric hindrance about the diazo carbon in PMDE. Quite in contrast, the one-electron oxidation of this diazoalkane yields *no* monomeric products by simple hydrogen or mesityl migration; instead, ketazine and dimeric products are formed by two distinct paths. Dimerization of diazo radical cations followed by competing secondary reactions of the resulting dication is the favored path accounting for the major products. In a very much slower reaction, $PMDE^{+\cdot}$ attacks neutral PMDE to yield ketazine.

The ease with which diazoalkanes lose nitrogen to form transient carbenes has made this class of compounds the object of intensive mechanistic investigations.[1] Unfortunately, carbenes are such high-energy transients that their subsequent reactions are often indiscriminate and hence of little synthetic value.[2] The synthetic utility of diazoalkanes is realized more often in metal-salt-catalyzed reactions in which the nature of reactive intermediates derived from the diazoalkane is seldom understood.[3] However, a number of reports have appeared in the last decade which indicate that a general electron-transfer mechanism may explain much of the chemistry observed in catalyzed diazoalkane decompositions.[4] In many cases, diazo radical cations were proposed as discrete intermediates.

In 1971, Yamamoto and co-workers[5] reported that reactions of diphenyldiazomethane (DDM) can be induced by metal ions

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[1] Patai, S., Ed. "The Chemistry of Diazonium and Diazo Groups"; Wiley: New York, 1978.

[2] Moss, R. A.; Jones, M., Jr. In "Reactive Intermediates"; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1981; Vol. 2, Chapter 3. In contrast, diazonium ions have great synthetic utility. See Chapter 8 in ref 1 above.

[3] Wulfman, D. S.; Poling, B. In "Reactive Intermediates"; Abramovitch, R. A., Ed.; Plenum Press: New York, 1980; Vol. 1, Chapter 5.

[4] Despite the similarities between electrochemical and metal-catalyzed decompositions of diazo alkanes, the electrochemistry of diazo alkanes remains little studied by comparison. See Chapter 10 in ref 1 above.

[5] Shirafuji, T.; Yamamoto, Y.; Nozaki, H. *Tetrahedron* **1971**, *27*, 5353.

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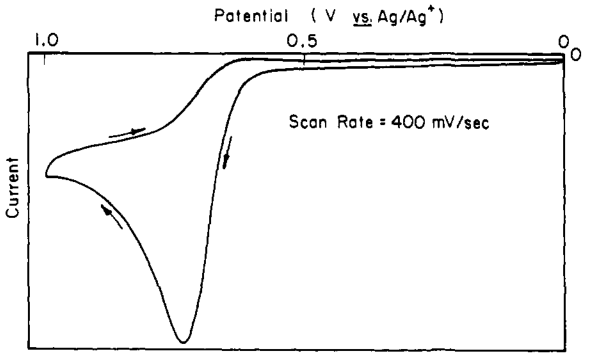
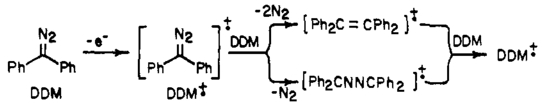


Figure 1. Cyclic voltammogram obtained by oxidizing PMDE at a platinum button electrode (0.1 M TBAP in CH_3CN).

that have a stable, lower oxidation state and that products are determined largely by the reduction potential of the metal ion. Two years later, Kochi and co-workers[6] found that several diazoalkanes are decomposed by Cu(II) and Cu(I) salts; they concluded that one-electron transfer occurs between diazoalkanes and Cu(II) salts, but that this only serves to convert the nominal catalyst to a Cu(I) species which then yields products by forming a complex with the remaining diazoalkane.

More recently, Bethell and co-workers[7] found that copper(II) perchlorate initiates a chain reaction with DDM that results in formation of tetraphenylethylene (TPE) as the major product with minor amounts of ketazine and other products. Their mechanism calls for DDM$^{+\cdot}$ to undergo ambident attack on a neutral DDM molecule to give either TPE$^{+\cdot}$ or ketazine radical cation which continues the chain (eq 1).

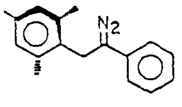


(1)

A few reports have appeared recently in which organic electron acceptors have been used to oxidize diazoalkanes, thus precluding a specific role for metals in these cases.[8] Bethell and co-workers[7] found that tris(*p*-bromophenyl)aminium perchlorate initiates the same reaction with DDM that they found with copper(II) perchlorate. Jones[9] recently found that a series of such triarylaminium radical cations react with diazoacetophenone at rates that correlate with their reduction potentials; unfortunately, only intractable tars could be isolated from these reactions. Finally, Gaspar[10] found that TPE appears to mimic some copper catalysts in decomposing DDM in thoroughly degassed solutions to give benzophenone ketazine in >75% yield.

What seems to be a common feature of these studies is that the diazoalkanes used could form stable products only by intermolecular reactions (dimerization, trapping of H_2O, etc.). There has been a notable absence of studies to probe the possibility that intramolecular processes (e.g., cyclization or rearrangement) might be accelerated or inhibited in a suitably situated diazo radical cation.

Herein we describe the results of our investigation of the thermal, photochemical, and oxidative reactions of 1-phenyl-2-mesityldiazoethane (PMDE). In these reactions, PMDE was expected to undergo facile migration of hydrogen or the mesityl group in competition with bimolecular reactions which are characteristic of other more commonly studied diazoalkanes, such

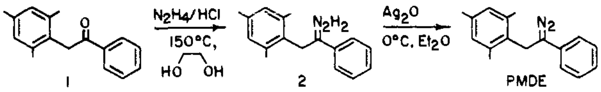


PMDE

as DDM.[11] By comparing the products of thermolysis and photolysis with the products of oxidation, we hoped to gain further insight into the nature and chemical reactivity of diazoalkane radical cations.

Results

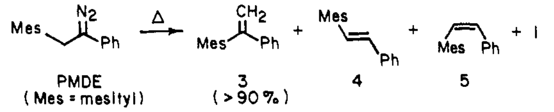
(I) Synthesis. PMDE was prepared from mesitylene in five steps via the known deoxybenzoin **1**, as in eq 2. In the solid form



(2)

(mp 81 °C), this bright red diazoalkane is stable to air and laboratory light. In solution it is likewise stable so long as the solution is rigorously degassed. Solutions left open to the air decompose over a period of days to give the corresponding ketone—even in the dark.

(II) Thermolysis. When PMDE is thermolyzed in purified solvents (see Experimental Section), the major product (>90%), **3**, is the result of mesityl migration (eq 3); ketone **1** and trace

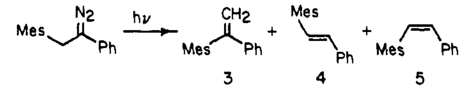


(3)

amounts of the isomeric stilbenes **4** and **5** comprise the remainder of the products. No detectable quantities of ketazine or dimeric products are formed.

The rate of this reaction was determined by following the disappearance of the optical absorption of PMDE ($\lambda_{max} = 516$ nm, $\epsilon = 35$). The reaction is cleanly first order over at least four half-lives, highly reproducible, and unaffected by solvent polarity or by the addition of weak, ground-state electron acceptors.[12]

(III) Photolysis of PMDE. Irradiation of PMDE in acetonitrile was carried out in order to investigate further the preference for mesityl migration revealed by the thermolysis of this diazoalkane. The products of irradiation consist of olefins derived from both mesityl and hydrogen migration, but in a much lower ratio (61:39) than in the thermolysis (>90:10) (eq 4). This ratio does not vary



(4)

with the percent conversion of PMDE.[13] Of the two possible hydrogen-migration products (**4** and **5**), the cis isomer predominates, but control experiments established that the trans isomer is converted to the cis isomer under the conditions of the photolysis. Conversion of PMDE to the monomeric olefins is quantitative. Again, as in the thermolysis, no ketazine or other dimeric products are formed.

(IV) Electrochemical Oxidation. Cyclic Voltammetry. In argon-purged acetonitrile solutions containing 0.1 M tetra-*n*-bu-

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(6) Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 3300.

(7) Bethell, D.; Handoo, K. L.; Fairhurst, S. A.; Sutcliffe, L. H. *J. Chem. Soc., Perkin Trans. 2* **1979**, 707.

(8) This reaction is of limited value since most organic electron acceptors are just electron deficient olefins (e.g., tetracyanoethylene, TCNQ) which readily undergo 1,3 dipolar cycloaddition with the diazo moiety. See: Oshima, T.; Yoshioka, A.; Nagai, T. *J. Chem. Soc., Perkin Trans 2* **1978**, 1283 and references cited therein.

(9) Jones, C. *J. Org. Chem.* **1981**, *46*, 3370.

(10) Ho, C.-T.; Conlin, R. T.; Gaspar, P. P. *J. Am. Chem. Soc.* **1974**, *96*, 8109.

(11) In a preliminary study we prepared 1,2-diphenyldiazoethane from desoxybenzoin by a method analogous to that used for PMDE. We found that it is unstable toward ketazine formation under all conditions (especially as a neat oil) and that it gives only miniscule amounts of rearrangement products, making it unsuitable as a model system. Ketazine formation is a general feature of diazoalkane chemistry (see ref 1 above).

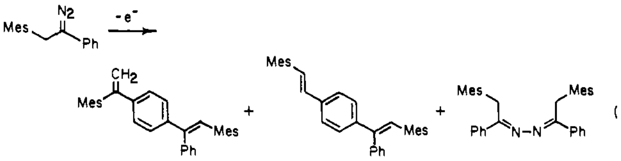
(12) For example, $k_{uni} = 3 \times 10^{-4}$ s^{-1} for thermolysis of 10^{-2} M solutions at 119 °C in benzene, acetonitrile, and benzonitrile. The same rate constant was obtained in benzonitrile solutions containing *p*-dinitrobenzene (6×10^{-3} M), 9,10-dicyanoanthracene (9×10^{-3} M) or tetraphenylethylene (2×10^{-3} M).

(13) Products were determined by GC analysis. When photolysis was carried out to <100% conversion, excess PMDE was destroyed with diethyl acetylenedicarboxylate (ref 41). Treatment of a PMDE solution in this manner before photolysis showed that no olefins were present.

tylammonium perchlorate (TBAP) as the supporting electrolyte, PMDE is irreversibly oxidized at a platinum button electrode. As shown in the cyclic voltammogram reproduced in Figure 1, no cathodic wave is observed at scan rates up to 400 mV/s; nevertheless, the oxidation potential of PMDE can be estimated from the peak potential to be ca. 0.7 V vs. Ag/Ag$^+$, or ca. 1.0 V vs. SCE.[14]

Controlled-Potential Electrolysis. PMDE was exhaustively oxidized at a platinum sheet electrode at a potential of 0.8 V vs. Ag/Ag$^+$ in acetonitrile containing 0.1 M TBAP. As the oxidation proceeds, a deeply colored, reddish-violet substance is formed transiently at the surface of the electrode; the stirring action in the cell then causes it to stream out from the electrode and fade away. This substance is formed only as long as PMDE remains and as long as a potential is being applied to the electrode.

Seven products detected in this reaction account for ca. 80%[15] of the starting material oxidized (eq 5). One of the minor products is the ketazine **6**, identified by comparison with an authentic sample prepared from the ketone **1**. The six remaining products are all isomeric dehydro dimers (MW 442, $C_{34}H_{34}$ hydrocarbons) as shown by high-resolution GC/MS. Two of these isomers are always the major products and are always formed in nearly equal amounts. These were identified as the rearranged dehydro dimers **7** by their spectra, GC/MS analysis of their ozonization products, and finally synthesis of authentic material as described in the Experimental Section. The four remaining dehydro dimers are isomers of the unrearranged product **8**. The structures of these products were similarly deduced from their spectra and their ozonization products and confirmed by synthesis of authentic material.



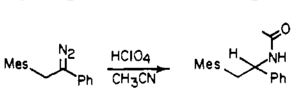
(5)

7 (plus Z isomer) 8 (Double Bond isomers) 6

In every experiment involving oxidation of PMDE (vide infra), **7** and **8** were always produced in the same ratio (72:28). However, the relative yields of the ketazine **6** and the hydrocarbons **7** and **8** varied from run to run. In bulk electrolyses, the yield of **6** never exceeded the combined yield of **7** and **8**.

(V) Chemical Oxidation. Copper(II) Perchlorate. The anhydrous, tetrasolvated reagent Cu $(ClO_4)_2 \cdot 4CH_3CN$ used in this study was prepared from the commercially available hexahydrate by a new procedure. Published procedures were found to be inconvenient or inadequate.[7,16] The reduction potential of the anhydrous salt in acetonitrile is reported to be +1.0 V vs. SCE and is thus capable of oxidizing PMDE in this solvent.[7]

When an acetonitrile solution of anhydrous copper(II) perchlorate is rapidly added to an acetonitrile solution of PMDE at room temperature, a deeply colored transient forms then quickly fades just as in the electrochemical experiment. When an excess of the oxidant is used, the hydrocarbon dehydro dimers **7** and **8** are formed nearly quantitatively with only trace amounts of monomeric olefins and other products being detected.[17] With less than one equivalent of oxidant, the fraction of PMDE that is consumed to form dehydro dimers approximately equals the fractional equivalent of the oxidant used. In this circumstance, the remainder of the PMDE decomposes by a perchloric acid catalyzed pathway to give the unrearranged acetamide **9** (eq 6)



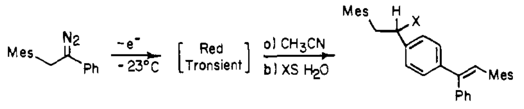
(6)

9

identified by its ^{1}H NMR, IR and mass spectra, as well as by independent synthesis of au [illegible] aterial.[18] Perchloric acid catalyzed decomposition of [illegible] s not responsible for the formation of any dimeric p [illegible]

Ketazine **6** is not found in more than trace amounts when the oxidant and diazo solutions are mixed rapidly as described above. However, the yield of ketazine is increased at the expense of the dehydro dimers **7** and **8** when the oxidant solution is added slowly to the PMDE solution. Ketazine yields can be further raised by adding more dilute oxidant solutions to more concentrated solutions of PMDE. Furthermore, such conditions lead to catalytic formation of ketazine—yields as high as 70% are obtained with as little as 0.2 equiv of oxidant. Slow inverse addition of PMDE to oxidant produces no ketazine whatsoever. Thus, at room temperature the only experimental variable that is found to influence ketazine yield is the instantaneous [diazo]:[oxidant] ratio.[20]

At low temperatures (−40 to −20 °C) in acetonitrile the red transient color observed on oxidation of PMDE at room temperature persists for hours (thus facilitating its spectroscopic investigation, vide infra). The major products isolated in such a reaction after the red color has discharged are the dehydro dimeric solvent incorporation products **10** (two isomers) instead of the hydrocarbons **7** and **8** (eq 7). Removing the low temperature bath and warming quickly to room temperature results in very rapid discharge of the red color with formation once again of **7** and **8**, instead of **10**, as the major products. Finally, addition of excess water immediately after formation of the red color at low temperatures causes the instant discharge of the color and formation of the dehydrodimeric alcohols **11** (two isomers) along with only minor amounts of the acetamide **10** (eq 7). Thus even at low temperatures, dehydro dimer formation is fast and efficient; no monomeric products attributable to oxidation of PMDE could be seen.



(7)

a) X = NHCOCH$_3$ (10)
b) X = OH (11)

The formation of the solvent incorporation product **10** led us to suspect that the nitrile solvent might be participating in the oxidation of PMDE in such a way as to inhibit migration or enhance dimer formation (by forming a complex or an ylide adduct, for example). In investigating this possibility, we determined that some non-nitrile solvents in which copper(II) perchlorate is soluble will support the oxidation reactions we have described (e.g., nitromethane) while others will not (e.g., acetone). These results are indicative not of solvent participation in the reaction, but rather of the sensitivity of the Cu(II) reduction potential to solvation effects.[21]

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[14] Kratochvil, B.; Lorah, E.; Garber, C. *Anal. Chem.* **1969**, *41*, 1793.

[15] This value represents a maximum because recovery of products from the bulk electrolysis reactions was never quantitative. The remainder of the products recovered are **4** and traces of **3** and **5**. Often as much as 20% of starting PMDE could not be accounted for.

[16] (a) Hathaway, B. J. *Proc. Chem. Soc. London* **1958**, *1958*, 344. (b) Baillie, M. J.; Brown, D. H.; Moss, K. C.; Sharp, D. W. A. *J. Chem. Soc. A* **1968**, 104.

[17] Mass balances of 95% or greater were routinely obtained in reactions with copper(II) perchlorate, due to the ease of recovering products from the copper-containing residues after the reaction solvent is evaporated. Bulk electrolysis, by comparison, is quite inferior for complete product studies.

[18] The monomeric acetamide **9** was not detected in bulk electrolyses presumably because it could not be removed from the large excess of supporting electrolyte (see ref 15). Synthesis of authentic material from ketone **1** established that formation of **9** by acid catalysis is not also accompanied by any rearrangement.

[19] $HClO_4$ in acetonitrile converts PMDE quantitatively to **9**. This result contrasts with the finding that $HClO_4$ catalyzed decomposition of DDM produces tetraphenylethylene: Bethell, D.; Callister, J. D. *J. Chem. Soc.* **1963**, 3801.

[20] Copper(I) perchlorate can catalyze formation of ketazines in a slow reaction. This source of **6** in our experiments was ruled out on the basis of the following control experiment: 0.2 equiv of copper(I) perchlorate was added to PMDE at the same slow rate as copper(II) perchlorate; the yield of ketazine from the two reactions was comparable, but the Cu(I) reaction required >2 h while the Cu(II) reaction was complete at the end of the addition of oxidant (ca. 5 min). No dehydrodimers were produced from copper(I) perchlorate. Bethell obtained similar results with DDM (ref 7).

(VI) Chemical Oxidation. Tris(*p*-bromophenyl)aminium Hexachloroantimonate. This stable, free radical salt is a strong enough oxidant to bring about the decomposition of PMDE ($E_{red} = +1.05$ V vs. SCE).[22] We have used it to initiate the same reaction of PMDE that we observed with copper(II) perchlorate as the oxidant. In all respects the chemistry is the same, with one exception: acid-catalyzed decomposition of PMDE is more pronounced with this reagent unless great care is taken to keep the reagent pure and to keep solvents dry. Above all, any contact of the aminium salt solutions with stainless steel must be avoided to prevent the rapid decomposition of the reagent with formation of HCl.

The use of this reagent confers one major advantage over the copper salts we used more frequently: the reduction potential of this organic oxidant should not be as sensitive to solvation effects as copper(II) perchlorate is. Thus we were able to confirm (by low-temperature UV) that the red transient can indeed be formed from PMDE in acetone. This result firmly establishes that neither solvent nor the particular choice of oxidant is of any consequence in the formation of the red transient or dehydro dimers so long as the electron transfer can proceed.

(VII) Spectroscopic Investigation of the Red Transient. Since a major aim of this work was to explore the chemistry of diazo radical cations, we considered that direct spectroscopic observation of such a species would be a high priority. Accordingly, our suspicion that the red transient might be $PMDE^{+\cdot}$ led us to examine it in some detail.

Addition of oxidant (copper(II) perchlorate or the aminium salt) to a PMDE solution at −30 °C produces an intense absorption centered at 520 nm (ϵ ca. 1200). The rate of decay of this red species is cleanly first order and is unaffected by excess oxidant or excess PMDE. Furthermore, the first-order decay constant is the same in both acetonitrile and nitromethane ($k_{obsd} = 2 \times 10^{-3}$ s^{-1}).

We were unable to detect an ESR signal for any organic radical from PMDE oxidation. When excess copper(II) perchlorate is added to 1 M PMDE in heptyl cyanide at −35 °C, the only signal observed is that of the excess Cu(II) ion even though the red color is intense and persistent. Deoxygenation of reactant solutions by argon purging before mixing has no effect.[23] Such a result does not rule out the presence of radicals in low concentrations, but it does argue against a radical structure for the red transient.

Discussion

(I) Thermolysis and Photolysis. The formation of olefin **3** in high yield upon thermolysis of PMDE is surprising for two reasons. First, it is formed to the exclusion of ketazine or any other dimeric products. Second, such predominance of aryl over hydrogen migration is unprecedented in the literature of carbene chemistry. And while photolysis yields a different mix of monomeric olefins, it likewise yields no bimolecular reaction products.

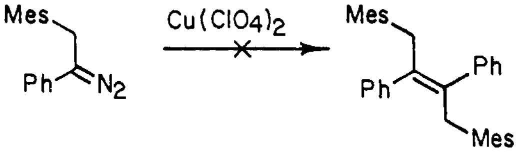
We attribute the failure of PMDE to form the ketazine to the steric hindrance introduced by the ortho methyl groups of the mesityl ring. This effectively reduces the rate of bimolecular reactions while introducing no barrier to facile migrations. A similar steric effect presumably is responsible for the failure of dimestiyldiazomethane to form ketazine during thermolysis or photolysis,[24] even though DDM does form ketazine under the same conditions.[25]

The presumption of a carbene intermediate in thermolysis of PMDE, however, does not adequately explain the clear predominance of mesityl migration that we observe. Electron-releasing substituents on aryl groups migrating to carbene centers have been shown to enhance migratory aptitudes marginally but never to the point of making aryl migration the exclusive process.[26] On the basis of ample literature precedent, our expectation is that a true carbene formed from PMDE at elevated temperatures would be far more indiscriminate in formation of products than is seen in this thermolysis.

Precisely this indiscriminate behavior is shown in the photolysis of PMDE, wherein the mesityl migration product accounts for no more than ca. 60% of products formed. The simplest explanation for this divergence in chemistry is that photolysis involves formation of carbenes while thermolytic decomposition occurs by mesityl-assisted loss of N_2 in a (concerted?) migration that does not involve carbenes. Furthermore, this latter process readily explains the predominance of mesityl migration in thermolysis of PMDE: space-filling models show that restricted rotation caused by the ortho methyl groups keeps the mesityl ring "face toward" the diazo carbon, thus facilitating formation of a stable phenonium ion from which loss of N_2 is expected to be more facile than in the open form of the diazoalkane. This interpretation, finds support in a recent study by Nickon and Bronfenbrenner.[27] They report that aryl migration to a diazoalkane carbon is severely inhibited if a steric interaction prevents the aryl ring from adopting a "face toward" orientation.

These findings show only that migrations of the putative carbene and the diazoalkane to give monomeric products are faster than the bimolecular reactions of these species. Quite the opposite result obtains when PMDE is oxidized to its radical cation.

(II) Oxidation. One-electron oxidation of PMDE not only fails to give any monomeric products, it even fails to give the dimeric products we might expect on the basis of what little literature precedent there is, viz, the head-to-head dimers (eq 8).[28] Instead,



(8)

ketazine **6** and the dehydro dimers **7** and **8** are the exclusive products of oxidation. The different conditions under which these products are formed, as well as the basic similarity in the structures of the dehydro dimers, supports a simple mechanistic scheme that reveals a feature of diazoalkane chemistry that may prove to be of general value.[29]

Since the products of oxidation depend only on the conditions of the reaction (temperature, nucleophilic solvent, water content

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[21] The Cu(II) reduction potential is 0.5 V higher in acetone than in acetonitrile. See: Coetzee, J. F.; McGuire, D. K.; Hedrick, J. L. *J. Phys. Chem.* **1963**, *67*, 1814. For comparison with acetonitrile solvent, see: Kolthoff, I. M.; Coetzee, J. F. *J. Am. Chem. Soc.* **1957**, *79*, 1852. That copper(II) perchlorate does not oxidize PMDE in acetone is confirmed by the finding that addition of excess PMDE does not affect the ESR signal of the Cu(II) ion. Addition of just a few percent of acetonitrile to such a solution results in disappearance of the Cu(II) signal with concomitant red transient formation.

[22] Reynolds, R.; Line, L. L.; Nelson, R. F. *J. Am. Chem. Soc.* **1974**, *96*, 1087. The nomenclature follows that used by Walter: Walter, R. I. *J. Am. Chem. Soc.* **1955**, *77*, 5999.

[23] In a positive control experiment, we were able to reproduce Bethell's ESR spectrum (ref 7) of benzophenone ketazine radical cation by thoroughly argon purging solutions of DDM and copper(II) perchlorate and transferring them, under argon, to a quartz ESR tube.

[24] Zimmerman, H. E.; Paskovich, D. H. *J. Am. Chem. Soc.* **1964**, *86*, 2149.

[25] (a) Bethell, D.; Whittaker, D.; Callister, J. D. *J. Chem. Soc.* **1965**, 2466. (b) Kirmse, W.; Horner, L.; Hoffman, H. *Justus Liebigs Ann. Chem.* **1958**, *614*, 19.

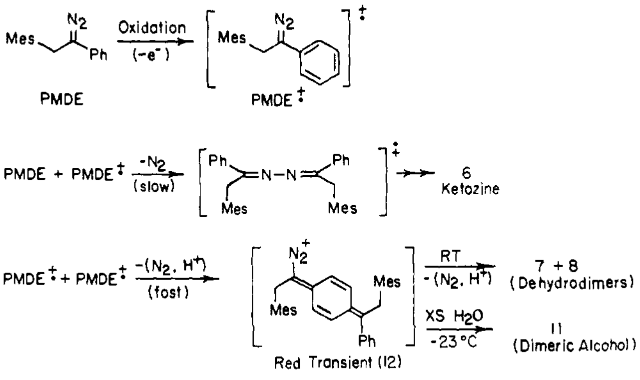
[26] (a) Jones, W. M. In "Rearrangements in Ground and Excited States"; deMayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, Chapter 3. (b) Seghers, L. H. P. Ph.D. Dissertation, The Ohio State University, Columbus, OH, 1977; *Diss. Abstr. Int. B* **1977**, *38*, 696. (c) Schaefer, H. F., III. *Acc Chem. Res.* **1979**, *12*, 288.

[27] Nickon, A.; Bronfenbrenner, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 2022.

[28] To our knowledge the oxidative decomposition of simple arylalkyldiazomethanes has not been studied systematically. In addition to diaryldiazomethanes (ref 7 and Chapter 10 in ref 1), aryldiazomethanes also give head-to-head dimers (stilbenes) under oxidative conditions: Shankar, B. K. R.; Shechter, H. *Tetrahedron Lett.* **1982**, *1982*, 2277 and references cited therein.

[29] We note that the mechanism proposed here for PMDE oxidation can apply equally well to previous results with other diazoalkanes. In particular, ambident attack of $DDM^{+\cdot}$ on DDM to give both ketazine and TPE catalytically is not required by the evidence cited in ref 7 above. The dication that would result from $DDM^{+\cdot}$ dimerization in this case (TPE^{2+}) could not easily form neutral products by elimination of two protons, as we observe in PMDE oxidation, and so could propagate the chain decomposition of DDM that is observed.

Scheme I



of the solvent) and not on the means of oxidation (electrochemical, inorganic or organic oxidant), we presume that the initial event in all cases is the formation of the free diazo radical cation PMDE$^{+\cdot}$. One option that evidently is not available to this reactive intermediate is mesityl or hydrogen migration with loss of N_2. Formation of $3^{+\cdot}$, $4^{+\cdot}$, or $5^{+\cdot}$ by this process will certainly lead to the formation of substantial amounts of the neutral olefins, contrary to our findings. Evidently, a significant barrier exists to prevent migration in the radical cation that is not operating for the neutral diazoalkane or the photochemically generated carbene. The data at hand do not suggest an explanation for the origin of this barrier; nevertheless it appears to be the determining factor in product formation from PMDE$^{+\cdot}$ since dehydro dimers predominate even under high-dilution conditions that would favor unimolecular reactions over bimolecular reactions.

In principle, then, PMDE$^{+\cdot}$ may form dimeric products by reaction either with a neutral PMDE or with another PMDE$^{+\cdot}$. Our results suggest that it does both but at very different rates and with very different outcomes. The basic features of the mechanism are outlined in Scheme I.

Formation of ketazine **6** is a consequence of the slow reaction between PMDE$^{+\cdot}$ and PMDE. This reaction generates, eventually, the ketazine radical cation $\mathbf{6}^{+\cdot}$, which is a strong enough oxidant to oxidize PMDE to propagate a chain reaction. This follows from the observation that ketazine is formed catalytically as well as the observation that ketazine is only formed in significant amounts when low oxidant concentrations and high diazoalkane concentrations favor reaction between PMDE$^{+\cdot}$ and PMDE and disfavor dimerization of PMDE$^{+\cdot}$.

The evidence shows that rapid dimerization of PMDE$^{+\cdot}$ to give, eventually, the isolated dehydrodimers is the principle result of oxidation of PMDE. These products are the result of a net two-electron oxidation and so cannot be formed from reaction between PMDE$^{+\cdot}$ and PMDE unless this initial reaction product is further oxidized. Our results discount this possibility because this subsequent oxidation must also occur in the presence of excess PMDE, which itself would have consumed any oxidant capable of further oxidizing the PMDE$^{+\cdot}$–PMDE reaction product.[30]

Evidently, PMDE$^{+\cdot}$ dimerizes to give a single precursor to all of the dehydrodimeric products. The steric hinderance of the mesityl group prevents close approach of two diazo carbons, so coupling occurs between this position in one PMDE$^{+\cdot}$ and the para position of the conjugated benzene ring of another PMDE$^{+\cdot}$. Similar arguments have been invoked to explain the abnormal pinacol coupling of sterically hindered aryl ketones.[31a,b] Furthermore, ring coupled products have been detected in electrochemical oxidations of some aryldiazoalkanes[31c,d] and of some triarylamines.[31e]

The initial dication formed from PMDE$^{+\cdot}$ dimerization could, in principle, proceed along numerous reaction paths. However, the data indicate that its nearly exclusive reaction is loss of a proton and N_2 to give the conjugated alkene diazonium ion **12**. This ion is thus the immediate precursor to all of the major products of the reaction and is also likely to be the observed red transient species.

Diazonium ions related to **12** are thought to lose N_2 spontaneously in solution to give vinyl cations;[32] some, however, can be stabilized toward loss of N_2 at lower temperatures (−20 °C or below) but still readily undergo other reactions, such as solvolysis[32a,b] (or perhaps, as in our case, tautomerization to give a protonated diazoalkane). Thus **12** accounts for exclusive formation of **7** and **8** at room temperature where spontaneous loss of N_2 would likely be followed by rapid mesityl or hydrogen migration.[32d] It also accounts for formation of the unrearranged products **10** and **11** at low temperature since spontaneous loss of N_2 from **12** might no longer be faster than solvolysis (by excess H_2O) or tautomerization to give a protonated diazoalkane which then captures solvent.

Finally, several other lines of evidence suggest that the red transient observed upon oxidation of PMDE is actually the alkene diazonium ion **12**. First, similar diazonium ions are frequently reported to be colored compounds.[32b,c] Second, the red transient is long-lived at −20 °C or below, just as has been observed for diazonium ions similar to **12**.[32] And third, rate-limiting tautomerization of **12** to the protonated diazoalkane form readily explains the solvent-independent, unimolecular decay of the red transient at low temperatures.

Conclusions

Because of the unique structure of PMDE, its oxidative decomposition is clearly distinguishable from its nonoxidative decomposition: the former gives dimeric products only, while the latter gives monomeric products only.

This exclusivity in mode of decomposition and product formation provides some insight into the structure and reactivity of diazoalkane radical cations. In the neutral diazoalkane, steric hindrance prevents bimolecular reactions, but 1,2 shift of hydrogen or the mesityl group remains a facile process. In the diazoalkane radical cation, however, this 1,2 shift is effectly prohibited; instead, the chemistry is typical of aryl radicals, which show a high propensity to dimerize.

Among the various dimeric products from oxidation of PMDE, there is a similarity of structure which suggests that a common precursor exists. A likely candidate for such a precursor is the cation **12**, with which we associate the red transient color formed upon oxidation of PMDE.

The finding that intramolecular processes are supressed in diazoalkane radical cations may have some bearing on the mechanism of metal-salt-catalyzed "carbenoid" reactions of diazoalkanes.[3]

Experimental Section

General Remarks. Acetonitrile (Aldrich Gold Label spectrophotometric grade) was refluxed over and distilled from CaH_2 under an atmosphere of dry N_2. The first and last 10% were discarded. Unless otherwise noted, all acetonitrile used was prepared in this manner.

Benzene used for thermolyses was washed repeatedly with concentrated sulfuric acid until the washes were colorless then washed with

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(30) This alternative cannot be positively excluded, however, because dropwise addition even of dilute oxidant solutions can result in high local concentrations of oxidant even after PMDE in the region of the drop has been consumed. Still, we cannot envision formation of an intermediate capable of giving both ketazine *and* ring-coupled dehydrodimers from the initial reaction between PMDE$^{+\cdot}$ and PMDE.

(31) (a) Fuson, R. C.; Kerr, R. O. *J. Org. Chem.* **1954**, *19*, 373. (b) Fuson, R. C.; Hornberger, C., Jr. *J. Org. Chem.* **1951**, *16*, 631. (c) Pragst, F.; Hübner, W.; Jugelt, W. *J. Prakt. Chem.* **1970**, *312*, 105. (d) Jugelt, W.; Lamm, W.; Pragst, F. *J. Prakt. Chem.* **1972**, *314*, 193. (e) Seo, E. T.; Nelson, R. F.; Fritsch, J. M.; Marcoux, L. S.; Leedy, D. W.; Adams, R. N. *J. Am. Chem. Soc.* **1966**, *88*, 3498.

(32) (a) The chemistry of vinyl cations has been reviewed (with the appropriate caveats): Rappoport, Z. In "Reactive Intermediates"; Abramovitch, R. A., Ed.; Plenum Press: New York, 1983; Vol. 3, Chapter 7, especially pp 484–489. (b) Bott, K. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 259. (c) Reimlinger, H. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 482. (d) Since unassisted loss of N_2 to give free vinyl cations is not a universally accepted mechanism, we consider that concerted migration and loss of N_2 (followed by loss of a proton) to give **7** and **8** is equally plausible. See: Kirmse, W. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 251.

saturated aqueous $NaHCO_3$ and distilled water. After being predried over $CaCl_2$, this purified benzene was refluxed over and distilled from active sodium wire under dry N_2 with benzophenone ketyl as indicator.

We succeeded in preparing the anhydrous reagent copper(II) perchlorate as the tetrasolvate by refluxing a dilute acetonitrile solution of the hexahydrate in a Soxhlet apparatus with the thimble filled with CaH_2. Refluxing was continued until gas evolution from the thimble ceased. Removal of solvent on a rotary evaporator at room temperature followed by high vacuum overnight afforded $Cu(ClO_4)_2 \cdot 4CH_3CN$ as a pale blue hygroscopic powder in quantitative yield: mp 192–194 °C (lit.[33] 196 °C).

Tris(*p*-bromophenyl)aminium hexachloroantimonate was prepared according to the procedure of Ledwith, et al.[34] This salt was reprecipitated from CH_2Cl_2 with ether to remove decomposition byproducts whenever required.

All other commercially available materials and reagents were used as received or were purified before use according to literature procedures.

All ^1H NMR spectra were obtained in deuteriochloroform solution (unless otherwise stated) with tetramethylsilane as internal standard at ambient temperature either on a Varian EM390 spectrometer (90 MHz), a Varian HR 220 spectrometer (220 MHz), or a Nicolet NT360 spectrometer (360 MHz).

All IR spectra were obtained either on a Perkin-Elmer Model 237B grating infrared spectrophotometer or on a Nicolet Model 7003 Fourier transform IR spectrophotometer. All UV–vis spectra were obtained on a Perkin-Elmer Model 552 UV–vis spectrophotometer using electronically matched 10-mm cells with the appropriate solvent blank.

When kinetic measurements were to be made on the UV–vis spectrophotometer, 10-mm UV cells sealed by a Teflon stopcock were used. The temperature of the cell was controlled by a specially constructed cell holder capable of regulating to within ±0.2 °C in the range −50 to +150 °C. The appropriate fixed wavelength was monitored while the output of the spectrometer was fed to an analog-to-digital converter. The digital data was then analyzed by the method of rigorous least squares.[35]

GC analyses were carried out on either a Varian 2700 or a Varian 3700 gas chromatograph, both of which were equipped with a linear temperature programmer and a flame ionization detector. A Hewlett-Packard 5900 integrator was used for quantitative analyses. Preparative GC was performed on the Varian 3700 by diverting the column effluent to a heated collection port with a 10:1 glass splitter. Two sets of operating conditions were found to be adequate for most product analyses: (A) 3 ft × 0.125 in. silanized glass column, 10% OV-101 on Chromosorb W-HP, oven = 165–295 °C @ 15 °C/min, injector = 290 °C, detector = 310 °C, He = 33 mL/min. (B) 6 ft × 0.125 in. silanized glass column, 10% OV-101 on Chromosorb W-HP, oven = 200–250 °C @ 8 °C/min, injector = 250 °C, detector = 300 °C, He = 30 mL/min. Other conditions and columns were sometimes required and are noted for specific cases.

All mass spectrometry was performed on one or more of the following instruments: Varian-MAT CH-5, Varian 311A, Varian 731, or Varian VG-7070E. Unless otherwise noted, the ionization technique employed was electron impact at 10 and 70 eV.

ESR spectroscopy was performed on a Varian Associates E-4 (X band) spectrometer equipped with a variable-temperature probe. When solvents of high dielectric constant were used, the standard 4-mm quartz tube was replaced by a flat quartz cell (0.1-mm film thickness) obtained from Dr. P. Morse.

Bulk electrolyses and cyclic voltammetry were performed using a Parr Model 173 Potentiostat/Galvanostat; output was obtained on a Tektronix 915 X–Y recorder.

All melting points were determined by the powder-packed capillary tube method and are reported uncorrected. Elemental analyses were performed by Analysis Laboratories, Department of Chemistry, University of Illinois, Urbana, IL.

Synthesis. α-Mesitylacetophenone (1). Mesitylacetonitrile[36] in ether was added slowly to excess phenylmagnesium bromide, then heated at reflux for 6 h. Aqueous workup yielded **1** in 98% crude yield and 63% purified yield after repeated recrystallization from ethanol: mp 163.5–164.0 °C (lit.[37] 161–162 °C); NMR δ 2.23 (s, 6 H), 2.29 (s, 3 H), 4.30 (s, 2 H), 6.85 (s, 2 H), 7.50 (m, 3 H), 8.07 (m, 2 H).

α-Mesitylacetophenone Hydrazone (2). In a modification of a general procedure by Nagata and Itazaki,[38] 9.5 g of **1** (40 mmol) was stirred with 100 g of anhydrous hydrazine (3.1 mol, 95%; J. T. Baker Co.) and 40.1 g of hydrazine dihydrochloride (0.4 mol, 99%; Aldrich Co.) in 500 mL of ethylene glycol at 150° C under dry N_2 for 12 h. After it was cooled to room temperature, the reaction mixture was continuously extracted with *n*-hexane for 9 h. The hexane solution was washed with H_2O until the washes were neutral to pH indicator paper then dried over $MgSO_4$. Removal of solvent yielded an oily yellow solid, which was recrystallized from *n*-hexane to give 5.0 g (50% based on starting ketone) of off-white powder, apparently as a mixture of syn and anti isomers: mp 80–85 °C; NMR δ 2.19 (s, 3 H), 2.25 (s, 6 H), 3.70 (s, 1 H), 3.87 (s, 1 H), 6.77 (s, 2 H), 7.0–7.5 (m, 5 H). In addition, the broad signal for the NH_2 protons exhibits concentration-dependent chemical shifts and disappears upon addition of D_2O.

Anal. Calcd for $C_{17}H_{20}N_2$: C, 80.91; H, 7.99; N, 11.10. Found: C, 81.06; H, 8.16; N, 11.39.

1-Phenyl-2-mesityldiazoethane (PMDE). This diazoalkane was prepared by Ag_2O oxidation of **2** by an adaptation of three literature procedures.[39] In a typical procedure, **2** (1.1 g, 4.4 mmol), Ag_2O (1.04 g, 4.5 mmol), and $MgSO_4$ (1.4 g) were added to a base-washed (concentrated NH_4OH) and oven-dried, 250-mL three-neck round-bottom flask. A magnetic stir bar and 125 mL of anhydrous ether were added. The flask was then purged for 10 min with dry N_2 while being cooled in an ice water bath. Five drops of freshly prepared, saturated ethanolic KOH were then added, and the flask was sealed under a positive nitrogen atmosphere. Within 20 min, the red color of the diazo compound had appeared. In 1 h the reaction appeared to be over as judged from the conversion of Ag_2O to a metallic silver mirror on the walls of the flask.

The deep red solution was decanted to a separatory funnel, washed with distilled H_2O then twice with brine, dried ($MgSO_4$), filtered, and evaporated to yield 1.00 g of crude diazo compound (~95%). Recrystallization from pentane (8 mL) yielded 0.25 g: mp 81.0–81.5 °C dec. The mother liquor was evaporated and the residue recrystallized from hexane to yield 0.48 g: mp 81.0–81.5 °C; total yield, 0.73 g (70% based on hydrazone); NMR δ 2.28 (s, 9 H), 3.68 (s, 2 H), 6.80–7.40 (m, 7 H); IR (Nujol mull) 2033 cm^{-1} (s); UV max (CH_3CN) 516 nm (ε 35); mass spectrum, *m/e* 250 (3.5%, P), 222 (95%, P − 28), 207 (100%, P − 28 − 15).

Anal. Calcd for $C_{17}H_{18}N_2$: C, 81.56; H, 7.25; N, 11.19. Found: C, 81.39; H, 7.27; N, 11.34.

Mercuric oxide, a more common reagent used in hydrazone oxidations,[40] was found to be inferior for this preparation because it is exceedingly slow and causes extensive overoxidation to the ketone.

PMDE does not survive column chromatography on silica gel or alumina, nor does it survive gas chromatography; it melts with decomposition and does not sublime under high vacuum. Analysis for impurities by GC is possible if the PMDE is first destroyed with diethyl acetylenedicarboxylate (DEAD).[41]

1-Phenyl-1-mesitylethylene (3). This olefin was prepared as a colorless oil by the method of House et. al.,[42] the final purification being accomplished by chromatography on basic alumina.

1-Phenyl-2-mesitylethanol (PME). Lithium aluminum hydride reduction of ketone **1** in ether proceeded quantitatively to give PME as a colorless oil. NMR δ 2.25 (s, 9 H), 2.95 (t, 2 H), 4.74 (dd, 1 H), 6.67 (s, 2 H), 7.25 (s, 5 H).

***trans*-2,4,6-Trimethylstilbene (4).** This olefin was formed in 55% purified yield by dehydration of PME in 50% H_2SO_4 followed by recrystallization from ethanol: mp 54.5–55.5 °C (lit.[43] 55–56 °C). Mass spectrum, *m/e* 222 (80%, P), 207 (100%, P − 15).

***cis*-2,4,6-Trimethylstilbene (5).** This material was prepared by benzil-sensitized photoisomerization of **4** using a high-intensity tungsten lamp with a Corning CS-3-73 filter (cutoff 402 nm). A solution of **4** (364 mg) and benzil (392 mg) in 35 mL of CH_3CN was irradiated at room temperature in a Pyrex cell until GC analysis (6 ft × 0.125 in. 3% SE-30 on Chromosorb W, oven = 225 °C) showed complete conversion (13 h). Removal of solvent and chromatography of the residue on basic alumina (eluted with *n*-hexane) yielded 320 mg of fine white powder (100% conversion, 89% recovery based on **4**): mp 72.0–73.0 °C; NMR δ 2.11 (s, 6 H), 2.30 (s, 3 H), 6.52 (s, 1 H), 6.56 (s, 1 H), 6.75–7.20 (m, 2 H);

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[33] Hathaway, B. J.; Underhill, A. E. *J. Chem. Soc.* **1960**, 3705.

[34] Bell, F. A.; Ledwith, A.; Sherrington, D. C. *J. Chem. Soc. C* **1969**, 2719.

[35] Computer programs were written by Dr. John Hurst of this Department based on a published algorithm for rigorous least squares adjustment: Wentworth, W. E. *J. Chem. Ed.* **1965**, *42*, 96.

[36] Fuson, R. C.; Rabjohn, N. "Organic Syntheses"; Wiley: New York, 1955; Collect. Vol. III, p 557.

[37] Hauser, C. R.; Humphlett, W. J. *J. Org. Chem.* **1950**, *15*, 359.

[38] Nagata, W.; Itazaki, H. *Chem. Ind.* **1964**, *27*, 1194.

[39] (a) Schroeder, W.; Katz, L. *J. Org. Chem.* **1954**, *19*, 718. (b) Colter, A. K.; Wang, S. S. *J. Org. Chem.* **1962**, *27*, 1517. (c) Ciganek, E. *J. Org. Chem.* **1965**, *30*, 4366.

[40] See Chapter 15 in ref 1 above, especially p 666.

[41] The product of this reaction is unknown. When solutions of quenched diazo compound are assayed by GC, a very broad peak is observed at very long retention times that does not interfere with normal product analysis.

[42] House, H. O.; Chu, C.-Y. *J. Org. Chem.* **1976**, *41*, 3083.

[43] Fuson, R. C.; Denton, J. J.; Best, C. E. *J. Org. Chem.* **1943**, *8*, 64.

mass spectrum, *m/e* 222 (90%, P), 207 (100%, P − 15).

Anal. Calcd for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.69; H, 8.30.

***N*-(1-Phenyl-2-mesitylethyl)acetamide (9). Method A.** Formic acid (1 mL, 27 mmol), ammonium formate (2.7 g, 43 mmol), and ketone **1** (1.0 g, 4.2 mmol) were heated at 190 °C under N_2 in a flask set up for downward distillation.[44] After the first 3 h, no more liquid distilled over, but ammonium carbonate continued to sublime on the upper surfaces of the reaction vessel; it was occasionally removed by gentle tapping. Heating was continued for a total of 19 h, after which time the cooled reaction mixture was partitioned between H_2O and benzene. After the layers were separated, the aqueous layer was extracted once with benzene. The benzene extracts were combined and washed successively with H_2O, aqueous $NaHCO_3$, and brine. Removal of solvent yielded 1.06 g of crude product as an oily solid. Preparative TLC (silica gel, eluted with 15% ethyl acetate in hexane) yielded 0.74 g of the intermediate formamide as a white solid (66% based on starting ketone): mp 125.0–126.0 °C; NMR δ 2.14 (s, 6 H), 2.21 (s, 3 H), 3.1 (m, 2 H), 5.2 (dd, 1 H), 6.12 (br s, 1 H), 6.75 (s, 2 H), 6.85 (s, 2 H), 7.3 (m, 5 H), 8.10 (s, 1 H); IR (Nujol mull) 1665 cm^{-1} (s).

Hydrolysis of the formamide was effected by boiling with concentrated HCl.[44] Treatment of the resulting amine hydrochloride with $NaHCO_3$ followed by extraction into benzene and filtration to remove the remaining salts gave 0.2 g of the free amine as a colorless oil after vacuum drying. NMR δ 1.50 (s, 2 H, NH_2), 2.30 (s, 9 H), 2.89 (dd, 2 H), 4.15 (t, 1 H), 6.80 (s, 2 H), 7.29 (m, 5 H).

The amine (107 mg, 0.4 mmol) in 0.8 mL of pyridine was added by syringe to freshly distilled acetic anhydride (0.6 g, 6 mmol) over a 7-min period. The resulting solution was stirred under dry N_2 at room temperature overnight. Removal of solvent left the crude acetamide as a light tan powder (100% crude yield); recrystallization of 10 mg from hexane/ethanol yielded **9** as a fine, white powder: mp 152–153 °C; NMR δ 1.93 (s, 3 H, $COCH_3$), 2.15 (s, 6 H), 2.24 (s, 3 H), 3.1 (dd, 2 H), 5.17 (dd, 1 H), 5.9 (br s, 1 H), 6.75 (s, 2 H), 7.2 (m, 5 H); IR (Nujol mull) 1647 cm^{-1}; mass spectrum (high-resolution FAB), calcd for $C_{19}H_{24}NO$ (P + 1) *m/e* 282.1858, found 282.1856 (50%, P + 1), 240 (10%), 223 (100%), 133 (25%, $MesCH_2^+$).

Anal. Calcd for $C_{19}H_{23}NO$: C, 81.10; H, 8.26; N, 4.98. Found: C, 80.97; H, 8.16; N, 4.79.

Method B. 9 was also formed, quantitatively, when PMDE in 2 mL of CH_3CN was treated with 1 mL of CH_3CN containing one drop of 70% $HClO_4$. Removal of solvent yielded a substance that was identical in all respects (IR, ^1H NMR, GC retention time) with the material synthesized above.

Method C. The alcohol PME was treated with $HClO_4$ in acetonitrile as in method B. In 2 h at room temperature PME was converted quantitatively to **9** by the Ritter reaction.

α-Mesitylacetophenone Ketazine (6). This material was prepared from α-mesitylacetophone (**1**) and its hydrazone **2** by an adaptation of a general ketazine synthesis.[45] Thus, **1** (0.50 g, 2.1 mmol), **2** (0.53 g, 2.1 mmol), and tosic acid (0.1 g) were heated at reflux in 50 mL of xylene for 12.5 h. After it was cooled, the organic layer was washed with saturated $NaHCO_3$ and brine, then dried ($MgSO_4$), and evaporated. The residue was recrystallized once from ethanol/xylene and once from ethanol/toluene to yield 0.60 g (60%) of **6** as a bright-yellow, flocculent solid: mp 181–182 °C; NMR δ 2.19 (s, 6 H), 2.21 (s, 3 H), 3.81 (s, 2 H), 6.62 (s, 2 H), 7.1–7.7 (m, 5 H); mass spectrum, *m/e* 472 (28%, P), 133 (100%, $MesCH_2^+$).

Anal. Calcd for $C_{34}H_{36}N_2$: C, 86.40; H, 7.68; N, 5.93. Found: C, 86.71; H, 7.56; N, 5.86.

(2,4,6-Trimethylbenzyl)triphenylphosphonium Chloride. This phosphonium salt was prepared from 2,4,6-trimethylbenzyl chloride (1.55 g, 9.2 mmol, 98%, Aldrich) and triphenylphosphine (2.43 g, 9.3 mmol, 99%-Aldrich) by reaction at room temperature in 8 mL of benzene for 5 days.[46] The fine white powder obtained by filtration and washing with benzene weighed 1.5 g (38% based on the benzyl chloride): mp 228–230 °C.

Anal. Calcd for $C_{28}H_{28}PCl$: C, 78.04; H, 6.55; P, 7.19; Cl, 8.23. Found: C, 77.70; H, 6.45; P, 7.27; Cl, 8.35.

Another 0.8 g of the salt was obtained by warming the benzene supernatant overnight. Nitromethane was added to the supernatant from this second crop and heated on a steam bath overnight. From this solution another 1.6 g of the phosphonium salt was obtained, bringing the overall yield to 98%.

1-(1-Phenyl-2-mesitylethenyl)-4-(1-mesitylethenyl)benzene (7). Chromic acid oxidation of 4-methylbenzophenone according to a published procedure[47] gave 4-benzoylbenzoic acid in 75% purified yield, treatment of which with $SOCl_2$ and DMF (cat.) in $CHCl_3$ gave 4-benzoylbenzoyl chloride as white plates after one recrystallization: mp 93.0–94.5 °C (lit.[48] 93 °C).

Fresh, anhydrous $AlCl_3$ (0.8 g, 6 mmol) was vigorously slurried with 10 mL of CS_2 under dry N_2 while a solution of 4-benzoylbenzoyl chloride (0.5 g, 2.2 mmol) and mesitylene (1.0 mL, 7.2 mmol) in 3 mL of CS_2 was added dropwise by syringe over 25 min. Upon addition of the first drop, an insoluble orange material began to separate out. After 18 h at room temperature, the Friedel–Crafts complex was decomposed by cautious addition of wet benzene, followed by dilute HCl. Washing the organic layer successively with H_2O, aqueous $NaHCO_3$, and brine, drying ($MgSO_4$), and finally evaporating it yielded a pale yellow oil which solidified overnight under vacuum: mp 121–124 °C. Recrystallization from hexane/ether gave fine, white crystals of 4-mesitoylbenzophenone: mp 131–132 °C; NMR δ 2.16 (s, 6 H), 2.31 (s, 3 H), 6.91 (s, 2 H), 7.53 (m, 4 H), 7.88 (m, 5 H); mass spectrum *m/e* 328 (65% P), 223 (65%, P − 105), 147 (50%, $MesCO^+$), 119 (35%, Mes^+), 105 (100%, $PhCO^+$).

Anal. Calcd for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14. Found: C, 84.06; H, 5.96.

To a 50-mL three-neck round-bottom flask fitted with a reflux condenser and a Teflon stopcock septum adaptor was added 444 mg (1.03 mmol) of finely powdered (trimethylbenzyl)triphenylphosphonium chloride and 15 mL of anhydrous ether. The slurry was magnetically stirred as vigorously as possible while 0.6 mL of *n*-BuLi (1.32 mmol, 2.2 M in ether) was added dropwise with a gas-tight syringe over 5 min[46]; the orange color of the ylide appeared and persisted after the first drop of the base was added. The bright orange solution was stirred for 0.5 h at room temperature then for 1 h at reflux and cooled to room temperature again. CH_2Cl_2 (0.5 mL, B & J Distilled in Glass) was then added to destroy excess base, whereupon the bright orange solution became brown.

To this ylide solution was added a solution of 196 mg (0.6 mmol) of 4-mesitoylbenzophenone in 3 mL of CH_2Cl_2 over 5 min with a gas-tight syringe. The resulting solution was refluxed gently and monitored by TLC until reaction had ceased (44 h); during this time, solvent was added to replace that lost due to evaporation.

The solution was cooled, diluted with 20 mL of ether, and poured into water. After the layers were separated, the aqueous layer and the dark brown residue were extracted with ether. The ether layers were combined, washed with brine, dried ($MgSO_4$), and evaporated. Preparative TLC of the resulting brown residue yielded 7.5 mg of unreacted 4-mesitoylbenzophenone and 142 mg of the mono-Wittig adduct 1-mesitoyl-4-(1-phenyl-2-mesitylethenyl)benzene (87% based on diketone consumed). One recrystallization from CH_3OH gave pure, white powder: mp 163–166 °C dec; NMR δ 2.13 (s, 6 H), 2.23 (s, 6 H), 2.31 (s, 3 H), 2.35 (s, 3 H), 6.8–7.8 (complex aromatic and vinyl, 13 H). Though the NMR showed only one product initially, GC/MS detected another minor isomer (with identical mass spectrum). The two isomers reached a steady-state concentration of ca. 50 mol % after several months in acetone solution: mass spectrum, *m/e* 444 (45%, P), 429 (10%, P − 15), 223 (100%), 147 (50%, $MesCO^+$), 119 (30%, Mes^+).

The mono-Wittig adduct (30 mg, 0.1 mmol) in 15 mL of anhydrous ether was treated with MeLi (0.25 mL, 1.5 M "low halide", 0.4 mmol) by dropwise addition with stirring. After 0.5 h the resulting yellow solution was quenched with wet THF/ether. The organic phase was separated, washed with H_2O and then brine, dried ($MgSO_4$), and evaporated to leave a bright yellow oil (37 mg). TLC separated the product alcohol from the starting material as a very pale yellow oil (21 mg, 68%). This intermediate was dehydrated directly in refluxing benzene (30 mL) with tosic acid (5 mg). After 30 min, the solution was cooled, washed successively with $NaHCO_3$ (aqueous), H_2O, and brine, then dried ($MgSO_4$), and evaporated to give **7** (16 mg, 80%) as a mixture of two isomers by GC analysis (conditions A, long retention time:short retention time = 93:7). This product likewise isomerized over a period of months to approximately a 50:50 mixture—indistinguishable from the mixture that results from oxidation of PMDE. The isomers, separated by preparative GC, gave similar NMR spectra and identical mass spectra: NMR (long retention time isomer) δ 2.05 (s, 6 H), 2.15 (s, 6 H), 2.22 (s, 3 H), 2.32 (s, 3 H), 5.10 (d, 1 H, *J* = 1 Hz), 5.97 (d, 1 H, *J* = 1 Hz), 6.65–7.40 (complex aromatic and vinyl, 14 H); NMR (short retention time isomer) 2.04 (s, 6 H), 2.06 (s, 6 H), 2.24 (s, 3 H), 2.30 (s, 3 H), 5.03 (d, 1 H, *J* = 1.2 Hz), 5.87 (d, 1 H, *J* = 1.2 Hz), 6.75–7.38 (complex

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(44) This is an adaptation of a general procedure for reductive formylation of ketones: Ingersoll, A. W. "Organic Syntheses"; Wiley: New York, 1943; Collect. Vol. II, p 503.

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(47) Wertheim, E. *J. Am. Chem. Soc.* **1933**, *55*, 2540.

(48) Norris, J. F.; Ware, V. W. *J. Am. Chem. Soc.* **1939**, *61*, 1418.

aromatic and vinyl, 14 H); Mass spectra *m/e* 442 (50%, P), 221 (100%), 206 (55%), 145 (30%).

1-(1-Phenyl-2-mesitylethenyl)-4-(2-mesitylethenyl)benzene (8). 4,4′-Dibenzoylbibenzyl (7.7 g, 20 mmol) was heated at reflux for 15 min with Br_2 (1 mL, 20 mmol) in 25 mL of $PhNO_2$.[49] After the first minute of refluxing, the heavy bromine vapors had disappeared and HBr evolution had begun. When cooled, the solution deposited a solid that was collected and washed first with $PhNO_2$ then with benzene. Elimination of HBr from this solid was completed by boiling in xylene for 10 min. The very insoluble product was extracted in a Soxhlet apparatus for 10 h with CH_2Cl_2. The shiny, tan plates of 4,4′-dibenzoylstilbene so produced weighted 2.16 g (34%): mp 236–237 °C (lit.[49] 234–235 °C).

Large-scale ozonization of 4,4′-dibenzoylstilbene provides a direct, convenient, and high-yield route to 4-benzoylbenzaldehyde that is recommended over other procedures.[50] Thus, 4,4′-dibenzoylstilbene (2.0 g, 5.2 mmol) in 250 mL of CH_2Cl_2 and 0.5 mL of CH_3OH was cooled to 0 °C while purging with dry N_2 through a gas sparger. Ozone was passed through the solution for 10 min, and then N_2 purging resumed for 30 min; GC assay of an aliquot at this point revealed that starting material had been consumed. Excess dimethyl sulfide (5 mL) was then added dropwise and the solution slowly warmed to room temperature. Removal of solvent (by water aspirator) and dimethyl sulfoxide (high vacuum) gave 4-benzoylbenzaldehyde in quantitative yield and pure by GC/MS analysis (GC conditions A). Mass spectrum, *m/e* 210 (20%, P), 181 (10%, P − 29), 105 (100%, $PhCO^+$).

The Wittig reagent was prepared, as before in the synthesis of **7**, from 482 mg of (trimethylbenzyl)triphenylphosphonium chloride (1.1 mmol) and 0.6 mL of *n*-BuLi(2.2 M, 1.3 mmol). To this was added 68 mg of 4-benzoylbenzaldehyde (0.3 mmol) in 3 mL of CH_2Cl_2 over 10 min. After refluxing 20 h, the reaction mixture was diluted with ether and then poured into H_2O. The organic layer was treated as before except that the product was not isolated by TLC but rather was subjected directly to GC/MS analysis (GC conditions A). By single-ion monitoring we detected only four substances at *m/e* 442. Retention times of these substances are identical with those of the minor dehydrodimers formed in oxidations of PMDE.

Oxidation of PMDE—Copper(II) Perchlorate. Typically, 3 mL of a stock solution of PMDE (ca. 10^{-5} to 10^{-3} M) was pipetted to a 10-mL pear-shaped flask, sealed with a rubber septum, and purged with argon for 15 min (using Teflon needles). The desired amount of oxidant was then delivered from a stock solution by microliter syringes.

When the solution had become colorless, the solvent was removed on a rotary evaporator at room temperature, the residue partitioned between benzene and water to remove soluble copper salts,[51] and the benzene layer evaporated. The residue was analyzed by GC (conditions A). Products of these reactions were identified by the coincidence of their GC retention time and their mass spectra with those of authentic materials whose syntheses have been described above. Authentic samples of **10** and **11**, however, were not prepared; these materials were characterized by spectroscopic and chemical means (vide infra).

In addition, all products that could be isolated were characterized by ^1H NMR. Thus, 1 mg of **9** and 1 mg of each of the two isomers of **7** were collected by preparative GC from a large-scale oxidation in CH_3CN at room temperature. Their 360-MHz ^1H NMR spectra are identical with those reported above for the synthetic materials. Since the diene **8** was synthesized only as a GC/MS standard, ^1H NMR spectra of the authentic individual isomers were not available for comparison. However, the two isomers of **8** that could be separated cleanly by preparative GC from a large-scale oxidation of PMDE gave 220-MHz ^1H NMR spectra that are consistent with their assigned structure: Isomer A δ 2.12 (s, 6 H), 2.26 (s, 3 H), 2.28 (s, 3 H), 2.32 (s, 6 H), 6.79–6.36 (16 H, complex aromatic and vinyl. Isomer B δ 2.07 (s, 6 H), 2.24 (s, 3 H), 2.29 (s, 3 H), 2.35 (s, 6 H), 6.76–7.46 (16 H, complex aromatic and vinyl).

The assignment of structures **10** and **11** was straightforward. The dimeric amides **10** were separated cleanly by preparative GC (conditions A) from a large-scale oxidation at −23 °C. Spectral data for the two isomers are virtually identical, so data for only one isomer is reported: mass spectrum (high-resolution FD) calcd for $C_{36}H_{39}NO$ *m/e* 501.3032, found 501.3034, (by low-resolution EI) *m/e* 442 (5%, P −59), 368 (80%, P − 133), 326 (100%, P − 133 − 42); NMR (CCl_4) δ 1.87 (s, 3 H, $COCH_3$), 1.97 (s, 6 H), 2.04 (s, 6 H), 2.18 (s, 3 H), 2.24 (s, 3 H), 3.05 (m, 2 H), 5.1 (m, 1 H), 5.6 (br s, 1 H), 6.64 (s, 1 H, vinyl H), 6.85–7.27 (complex aromatic, 14 H); IR (Nujol mull) 1640 cm^{-1} (s).

The alcohols **11** were produced by adding 50 μL of H_2O to a large-scale oxidation reaction at −23 °C immediately after an excess of oxidant had been added. The mixture of isomers was obtained pure by preparative TLC of the crude reaction mixture. No GC conditions could be found to resolve the isomers well enough to obtain each of them in pure form by prep GC. However, the two isomers gave identical GC/mass spectra: *m/e* 442 (100%, P − 18), 326 (40%, P − 134). No molecular ion could be detected by EI or FAB, but high-resolution FD yielded *m/e* 460.2776 (100%, P; calcd for $C_{34}H_{36}O$ *m/e* 460.2766). An NMR spectrum of the mixture of isomers showed complex resonances for methylene and methine protons at the same chemical shifts and with similar coupling patterns as in the monomeric alcohol PME. The structure of **11** is further established by the observation that the mixture of isomers can be dehydrated in refluxing benzene with tosic acid to give complete conversion to the four isomers of the diene **8**. Finally, stirring 1 mg of **11** in 1 mL CH_3CN containing 1 drop of 70% $HClO_4$ for 2 h effects complete conversion to the amides **10** by the Ritter reaction.

Further structural information on **7** and **8** was gained by ozonizing the individual isomers in 5 mL of CH_2Cl_2 at −78 °C. Typically, a solution was purged with dry N_2 while cooling then purged with ozone until it was pale blue. After 1 min, N_2 purging was resumed until the solution was again colorless. Dimethyl sulfide (ca. 0.25 mL) was added and the solution slowly warmed to room temperature. Solvent was evaporated and the residue dissolved in acetone for GC/MS analysis (conditions A and B).

Ozonization of the two isolated isomers of **8** resulted in complete consumption and nearly quantitative formation 4-benzoylbenzaldehyde, identified by comparison of its GC/mass spectrum with that of authentic material. Similarly, the two isomers of **7** were completely consumed by ozone and gave identical product mixtures. The only complication in this case was that the major product (ca. 90%) was due to incomplete ozonization. This product was assigned its structure by analogy to the ozonization product obtained from 1-phenyl-1-mesitylethylene[52] and on the basis of its GC/mass spectrum: *m/e* 342 (80%, P), 313 (65%, P − 29), 105 (100%, $PhCO^+$). The minor product (ca. 5%) was the complete ozonization product 4-mesitoylbenzophenone, identified by comparison of its GC/mass spectrum with that of authentic material.

Oxidation of PMDE—Tris(*p*-bromophenyl)aminium Hexachloroantimonate. Reactions using this free radical salt were carried out as described for copper(II) perchlorate with only two major exceptions. First, all manipulations were performed in glass or Teflon equipment; the oxidant solutions were delivered through Teflon needles. Second, only CH_3CN and CH_2Cl_2 could be used conveniently as solvents because the high residual water content of other common solvents in which it is soluble (e.g., acetone) cause rapid decomposition of the reagent.

This reagent was found to be less convenient to use than copper(II) perchlorate. It was used largely as an alternative to copper(II) perchlorate when the copper salt was sparingly soluble in a solvent we wished to use for oxidation of PMDE.

Oxidation of PMDE—Electrochemical. The cyclic voltammetry cell used has been described previously.[53] The working electrode was a platinum button, the counter electrode was a platinum helix and the reference electrode was a silver wire submerged in 0.01 M $AgNO_3$/0.1 M TBAP separated from the anodolyte by a fine glass frit. The background current measured for a 0.1 M TBAP solution in CH_3CN was <0.2 μA over the range explored (0.0–1.0 vs. Ag/Ag^+). PMDE was then added and the cyclic voltammogram in Figure 1 was obtained.

Bulk electrolyses were performed in a custom made H-type cell.[54] The reference electrode was a Ag/Ag^+ electrode as described above. Typically, a 4 × 10^{-3} M solution of PMDE in 0.1 M TBAP was degassed in the cell by five freeze–pump–thaw cycles. The cell was then flooded with purified argon at atmospheric pressure before electrolysis was begun. After electrolysis was completed, solvent was evaporated and the residue extracted with hexane.

This technique proved to be inconvenient for quantitative studies because of the difficulty of separating the variety of oxidation products from the very large quantity of electrolyte present. The product mixtures obtained by this method, however, are comparable to those obtained by copper(II) perchlorate and the aminium salt.

Thermolysis of PMDE. After the UV cell holder had equilibrated at the desired temperature, a stopcock-sealed UV cell containing 3 mL of PMDE solution (5 × 10^{-3} 5 × 10^{-2} M in purified solvents) was inserted. Data collection (OD at 516 nm) was begun immediately and was continued until thermolysis was complete. The first 5 min was routinely omitted from the data analysis to allow for warmup of the solution.

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(50) Zderic, J. A.; Kubitschek, M. J.; Bonner, W. A. *J. Org. Chem.* **1961**, *26*, 1635.

(51) This water wash did not alter product yields but did allow us to avoid injecting copper salts onto GC columns.

(52) Bailey, P. S.; Lane, A. G. *J. Am. Chem. Soc.* **1967**, *89*, 4473.

(53) Slocum, G. H. Ph.D. Dissertation, The University of Illinois, Urbana, IL, 1983.

(54) Details available upon request. See ordering information on any current masthead page.

The ^1H NMR spectrum of the thermolysis products was superimposable on the spectrum of olefin **3**. GC analysis (conditions A and B) revealed that **4**, **5**, and **1** were also present but in a combined yield of <10%. Subjecting authentic olefins **3**–**5** to the thermolysis conditions showed that they do not interconvert.

The only circumstance under which any product besides **3** was formed in substantial yield was when unpurified solvents were used in thermolyses. For example, thermolysis in reagent benzene from a freshly opened bottle yielded ca. 20% of **4**. Repeating the experiment after purifying the benzene as described above resulted in <5% yield of **4**.

Photolysis of PMDE. Precisely measured quantities of PMDE stock solutions were irradiated in two sealed Pyrex cells in a Rayonet reactor at room temperature. One cell was removed after 0.5 h and the other was left in the reactor until the diazo color had bleached (2 h).

The percent conversion in the partially photolyzed samples was determined by observing the reduction in absorbance at 516 nm. This value agreed, to within 1%, with the value determined by quenching excess PMDE with DEAD[41] and quantifying the total yield of **3**–**5** by GC (conditions A and B).

Similarly, GC analysis of the completely photolyzed solutions established that **3**–**5** accounted for 99% of PMDE converted. No other products were detected. The ratio **3**:(**4** + **5**) was found to be invariant; only the relative amounts of **4** and **5** varied since **4** is efficiently photoisomerized to **5**.

Acknowledgment. We thank J. Carter Cook and Dr. Richard Milberg for their assistance with the mass spectrometric analyses. This work was supported by the National Science Foundation. GBS is a Dreyfus Teacher-Scholar.

Registry No. 1, 5350-76-5; **1** (formamide), 92345-71-6; **1** (amine), 92345-72-7; **2**, 92345-67-0; **3**, 1667-02-3; **4**, 17024-58-7; **5**, 20488-50-0; **6**, 92345-73-8; **6** radical cation, 92345-86-3; (*Z*)-**7**, 92365-81-6; (*E*)-**7**, 92345-78-3; **8**, 92345-79-4; **9**, 92345-70-5; (*E*)-**10**, 92345-81-8; (*Z*)-**10**, 92345-82-9; (*E*)-**11**, 92345-83-0; (*Z*)-**11**, 92345-84-1; PMDE, 92345-68-1; PME, 92345-69-2; Ag_2O, 20667-12-3; $Cu(ClO_4)_2$, 13770-18-8; mesitylacetonitrile, 34688-71-6; (2,4,6-trimethylbenzyl)triphenylphosphonium chloride, 54757-04-9; 4-methylbenzophenone, 134-84-9; mesitylene, 108-67-8; 4-mesitoylbenzophenone, 92345-74-9; (2,4,6-trimethylbenzylidene)triphenylphosphine, 92345-75-0; (*E*)-1-mesitoyl-4-(1-phenyl-2-mesitylethenyl)benzene, 92345-76-1; (*Z*)-1-mesityl-4-(1-phenyl-2-mesitylethenyl)benzene, 92365-82-7; 1-mesitylhydroxymethyl-4-(1-phenyl-2-mesitylethenyl)benzene, 92345-77-2; 4,4′-dibenzoylbibenzyl, 47658-53-7; α-bromo-4,4′-dibenzoylbibenzyl, 92345-80-7; Red Transient (12), 92345-87-4; bromobenzene, 108-86-1; 2,4,6-trimethylbenzyl chloride, 1585-16-6; 4-benzoylbenzoic acid, 611-95-0; 4-benzoylbenzoyl chloride, 39148-58-8; 4,4′-dibenzoylstilbene, 53178-88-4; 4-benzoylbenzaldehyde, 20912-50-9; tris(*p*-bromophenyl)aminium hexachloroantimonate, 40927-19-3; $PMDE^{+\cdot}$, 92345-85-2.

The Stabilized Iminium Ylide–Olefin [3 + 2] Cycloaddition Reaction. Total Synthesis of *Sceletium* Alkaloid A_4

Pat N. Confalone* and Edward M. Huie

Contribution No. 3453 from the Central Research and Development Department E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware 19898.

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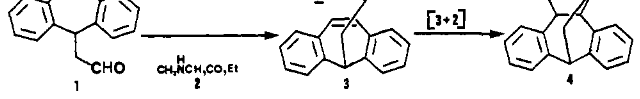
Abstract: A new method for performing an intramolecular [3 + 2] cycloaddition generating two carbon–carbon bonds utilizing a stabilized iminium ylide (**3**) has been developed. In practice, an olefin aldehyde is condensed with a secondary amino acid ester, generating **3** in situ which undergoes a [3 + 2] cycloaddition. Effectively, a proline is annulated to an internal olefin. Application of this method to the total synthesis of *Sceletium* alkaloid A_4 is discussed.

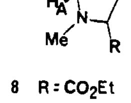
We recently reported that the reaction of the aldehyde **1** and sarcosine ethyl ester (**2**) afforded the cycloadduct **4** under dehydrating conditions.[1] This transformation presumably proceeds via the stabilized iminium ylide **3** which underwent an intramolecular [3 + 2] cycloaddition. *This reaction mode is predicted to be very powerful since it simultaneously constructs two carbon–carbon bonds, forms complex ring systems with stereocontrol, and effectively annulates a proline moiety to an internal olefin.*[2]



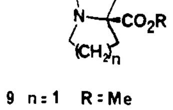
In order to further exemplify this chemistry, we examined the reaction of a number of olefin aldehydes with secondary amino acid esters and applied these results to the total synthesis of a naturally occurring substance, *Sceletium* alkaloid A_4.

O-Allylsalicylaldehyde (**5**)[3] was treated with **2**, proline methyl ester (**6**), and pipecoline ethyl ester (**7**) to afford the polycyclic adducts **8**, **9**, and **10**, respectively, in corresponding yields of 97%, 98%, and 99%, In practice, the reaction is carried out by reacting the olefinic aldehyde with the amino acid ester in refluxing toluene and driving off water by means of a Dean–Stark trap.[4] The amino acid ester hydrochloride may also be used if 1 equiv of diiso-

5



8 R = CO_2Et
15 R = CO_2H
16 R = H



9 n = 1 R = Me
10 n = 2 R = Et

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(1) Confalone, P. N.; Huie, E. M. *J. Org. Chem.* **1983**, *48*, 2994.

(2) Other examples of related reactions: (a) Huisgen, R.; Gotthardt, H.; Bayer, H. O. *Angew. Chem. Int. Ed. Engl.* **1964**, *3*, 135. (b) Livinghouse, T.; Smith, R. *J. Chem. Soc., Chem. Commun.* **1983**, 210. (c) Grigg, R.; Gunaratne, H. Q. N. *Tetrahedron Lett.* **1983**, *24*, 4457. (d) Texier, F.; Carrie, R. *Bull. Soc. Chim. Fr.* **1974**, 310. (e) Huisgen, R.; Schees, W.; Sziemies, G.; Huber, H. *Tetrahedron Lett.* **1966**, 397. (f) Achiwa, K.; Sekiya, M. *Heterocycles* **1983**, *20*, 167. (g) Padwa, A.; Hoffmanns, G.; Tomas, M. *Tetrahedron Lett.* **1983**, *24*, 4304. (h) Tsuge, O.; Ueno, K.; Ueda, I. *Heterocycles* **1981**, *16*, 1503. (i) Grigg, R.; Aly, M. F. Sridhasan, V.; Thianpatanagul, S. *J. Chem. Soc. Chem. Commun.* **1984**, 180, 182.

(3) For a typical procedure, see: *Org. Synth.* **1955**, *3*, 418.

(4) Removal of water was not essential but improved the yields by preventing ester hydrolysis. Reactions were faster and gave higher yields at high concentrations (1 M) of both substrates.