

Table II. Reduction of α -Iodo Esters with Bu_3SnH

entry	iodide	con- ditions ^a	ratio ^b (erythro:threo)	products (erythro:threo)	yield, %
1	1	A	>25:1	5:6	78 ^c
2	1	B	1:>25	5:6	86 ^d
3	2	A	1:4	5:6	61 ^e
4	2	B	1:>25	5:6	85 ^d
5	3	A	>25:1	7:8	79 ^e
6	3	B	1:24	7:8	87 ^d
7	4	A	1:2.3	7:8	76 ^e
8	9	A	5:1	10:11	82 ^e
9	9	B	1:4	10:11	80 ^e
10	12	A	10:1	13:14 ^f	53 ^e
11	12	B	1:>25	13:14 ^f	93 ^d
12	15	A	1:2.2	16 ^g	88 ^e
13	15	B	1:2.3	16 ^g	89 ^e

^aA: HSnBu_3 (2 equiv), MgI_2 (2 equiv), CH_2Cl_2 (0.04-0.05 M), -50°C , 1 h, then 0°C , 30 min. B: HSnBu_3 (2 equiv) catalytic AIBN, toluene (0.1 M), -78°C , $h\nu$ (sunlamp, 275 W). ^bRatios determined by ^1H NMR spectroscopy unless otherwise indicated. ^cIsolated yield of pure erythro isomer. ^dIsolated yield of pure threo isomer. ^eTotal isolated yield. ^fRatio determined by gas chromatographic analysis. ^gRelative stereochemistry not determined.

Interestingly, the use of catalytic amounts of MgI_2 or $\text{MgBr}_2\cdot\text{Et}_2\text{O}$ resulted in no loss of diastereoselection (entries 3 and 5) while AlCl_3 provides good ratios only if a full equivalent is added (entry 7). In addition, no radical initiator is required for these reactions to proceed, the initiation step probably occurring via a single electron transfer process between Bu_3SnH and the electron-deficient chelate.¹¹

Contrary to many radical reductions, the configuration of the substrate iodide has a significant effect on the stereochemical outcome of the reaction (Table II). Iodides in which the alkoxy group and iodo moiety are anti (1, 3, 9, 12) show a marked preference for producing erythro products when MgI_2 is present while compounds in which the alkoxy and iodo groups are syn (2, 4)¹² show a modest preference for the threo isomer in the presence of MgI_2 . The syn and anti iodides react identically in the absence of MgI_2 producing selectively the threo products (entries 2 and 4).^{5b} One could rationalize these results by suggesting that the chelated form of the syn iodide is less reactive than the anti iodide in the initial phase of the reaction (C-I breakage) due to developing $\text{A}_{1,2}$ strain in the transition state. In the case of syn iodides, the unchelated pathway would therefore be more energetically favored.

The described chemistry provides a novel approach to control of stereochemistry in acyclic radical reactions¹³ and is of potential synthetic utility due to its mildness and the ready availability of the starting materials. We are currently investigating the mechanistic aspects of this transformation, the results of which will be published in a full account of this work.

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Supplementary Material Available: Experimental procedures and spectral data (^1H NMR, ^{13}C NMR, IR, MS, analysis and/or HRMS) for compounds 1-16 (11 pages). Ordering information is given on any current masthead page.

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(12) Obtained by isomerization of 1 (LiI·3H₂O, THF, reflux, 16 h).

(13) Although the presence of a free radical in this reaction has not been firmly established, one will note that the inclusion of deuterated methanol in the reaction medium could not compete with Bu_3SnH as a hydrogen donor, indicating that a radical is probably involved in the reaction.

Photoreaction of Meldrum's Diazo in Poly(methyl methacrylate) Matrices

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Most photochemical reactions are carried out in solution. In the liquid phase, excited molecules normally are able to explore a variety of accessible conformations before reacting. In the solid state, much of this motion is suppressed. In recent years there has been an extensive effort, nicely reviewed by Scheffer,¹ to study photochemical reactions in organic crystals, where the molecular conformation prior to excitation is the same for each molecule. Very special features appear in the photoreaction of organic molecules dissolved in rigid polymer films. This is a field pioneered by Smets and his group in Belgium² and reviewed recently.^{3,4} The fundamental characteristic of photoreactions in glassy polymer films is their sensitivity to the distribution of free volume in the film: Below the glass transition temperature (T_g), large-scale motion of the polymer is suppressed. As a consequence, if a reaction of a guest molecule involves a change in conformation, the reaction will occur faster in molecules adjacent to sites of substantial free volume, and the reaction rate and quantum efficiency (Φ_r) will decrease as the reaction proceeds. This is clearly the case with a wide variety of photochromic molecules studied by Smets and others, and this principle has been employed by Horie^{5a} and by Torkelson^{5b} as a means of mapping out the free volume distribution in amorphous polymer films below T_g . It is not surprising that most photoreactions have substantially lower Φ_r values in rigid films than in solution. There are a few rare examples of reactions that have higher Φ_r values in polymer films, one set involving proton tautomerism in benzoylacetylides,⁶ held in the proper geometry by intramolecular hydrogen bonding, and one involving ring closure of an imine oxide to an oxazirine.⁷

This paper describes the photochemistry of Meldrum's diazo (1) in poly(methyl methacrylate) (PMMA) films at 22°C . 1 is of interest to organic chemists because of the question of whether its Wolff rearrangement involves the singlet carbene as a discrete intermediate.^{8,10} 1 and its derivatives are also of interest in the microelectronic area since they display many of the ideal characteristics ($\lambda_{\text{max}} \approx 250$ nm, transparent photoproducts) of photoactive additives for deep UV photoresists. Effective resists have been reported for 1 in Novolac films,¹¹ and irradiation of 1 in PMMA films causes those films to dissolve much faster upon

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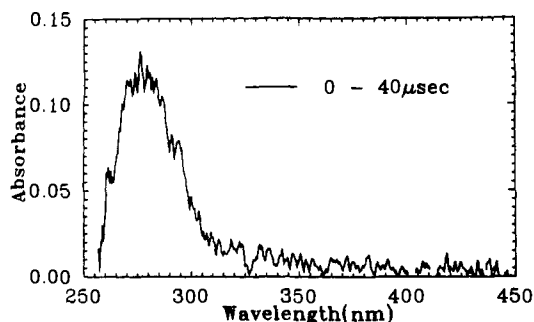
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Table I. Quantum Yields of **1** in PMMA Films and in Solution^a

diazo compound	Φ in PMMA film	Φ in solution
1	1.00 ^b	0.27 (methanol)
1	1.00 ^c	0.37 (chloroform)

^aThe error in Φ estimated from the plot of absorbance vs time¹⁵ is ca. 2%, whereas the sample to sample reproducibility is better than 10%. ^bFilms spin coated from toluene, vacuum dried at 60 °C, then baked 10 min at 125 °C, and cooled slowly. ^cFilms cast from CH₂Cl₂ and vacuum dried in a desiccator for 72 h.

**Figure 1.** Transient UV absorption spectrum of the ketene intermediate **2** as detected by laser flash photolysis with streak camera detection.

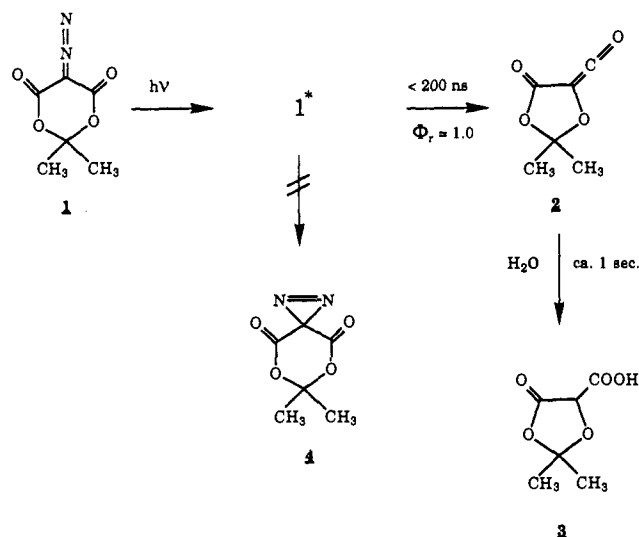
exposure to organic solvents.¹² Thus our report here, that Φ for **1** increases from 0.37 in methanol (0.27 in chloroform) to 1.0 in PMMA films, has a special added significance.

Films of **1** in PMMA were prepared either by spin coating from toluene (1 μ m, 10 wt % **1**) or by solvent casting from CH₂Cl₂ (25 μ m, 1 to 10 wt. % **1**). The former were annealed above T_g as described previously,¹² whereas the latter were simply kept under vacuum for 3 days at 22 °C. For steady-state irradiation, films were exposed to 254-nm light in a Rayonet RPR-100 photochemical reactor, with intermittent monitoring of the UV absorption spectra (quartz or sapphire disks) or FTIR spectra (sapphire or NaCl windows) of the films. Pulsed experiments employed an excimer laser (248 nm) with either streak camera or simple photomultiplier tube transient absorption detection.

Irradiation of these films led to loss of detectable UV absorbance at $\lambda > 254$ nm. This was accompanied by disappearance of the diazo band in the IR spectrum (2170 cm⁻¹) and the growth of two new carbonyl peaks at 1810 and 1770 cm⁻¹. No ketene peak could be seen. We attempted to leach the photoproduct out of the films with warm CCl₄. While not quantitative, the extract showed peaks in the ¹H NMR spectrum at 1.6 and 1.7 ppm (two singlets) and another singlet at 4.95 ppm. These signals are characteristics of the 5-carboxy-1,3-dioxolan-4-one structure¹³ reported by Kammula⁹ from the irradiation of **1** in a benzene-methanol mixture.

Quantum yields were calculated by the method of Wilkinson.¹⁴ Table I indicates the remarkable increase in quantum yield for reactions carried out in the PMMA films. To confirm these results, we measured Φ for **1** in solution using the same equipment and data analysis as for film samples of comparable absorbances.

Pulsed excitation at 248 nm generates a transient whose UV spectrum is displayed in Figure 1. It is formed faster than our time resolution (200 ns) and decays nonexponentially, with a mean decay time (τ) = 1 s. We assign this species¹⁵ to the ketene **2**, which we failed to observe by FTIR. Why does the ketene decay? It might react with methanol or water in the film. Methanol is a byproduct of PMMA irradiation at 248–254 nm.¹⁶ Never-

Scheme I. Photochemistry of Meldrum's Diazo in PMMA

theless, the unit quantum efficiency for **1** and the fact that the decay profile of the transient is unaffected by a 10-fold variation in laser-pulse intensity eliminate this possibility. We conclude that the ketene is trapped by adventitious moisture in the film, and we confirm this conclusion by noting that the decay time of **2** is very sensitive to the moisture content of the film prior to flash photolysis.

Flash photolysis studies of diazonaphthoquinones in wet organic solvents^{17–20} and in Novolac films²¹ (which contain a lot of water) show that a ketene is formed which reacts rapidly with water to form a second transient, identified as a ketene hydrate, which in turn tautomerizes to a carboxylic acid.^{17,19} The ketene hydration rate in acetonitrile is second order in [H₂O], with rate coefficients on the order of 10⁵–10⁶ M⁻² s⁻¹.^{17,19} We do not observe a second transient for **1** in PMMA. A simplified mechanism for the reaction is presented in Scheme I, where we ignore the possible role of the carbene in the Wolff rearrangement and the hydrate in subsequent ketene reactions.

Since the diffusion of large molecules in glassy matrices is so slow, there are very few measurements of reaction rates in such systems. As a consequence we know very little about the influence of the matrix on multimolecular reaction rates. Under our conditions (60% relative humidity, 18 °C), the amount of moisture in a PMMA film can be estimated to be ca. 0.1 M.²² The long ketene lifetime in the presence of this water concentration indicates a rather low reactivity. Assuming that the reaction rate is second order in [H₂O], we estimate a rate coefficient value of 10² M⁻² s⁻¹. We hope that further studies will help to elucidate the origin of this low reactivity.²²

It remains to explain the increase of Φ in the film. One attractive explanation involves the interconversion of **1** to the corresponding diazirine **4**, which has been reported for long-wavelength irradiation (350 nm) of **1** in solution²³ and is a common

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photoprocess for α -diazo carbonyl compounds.^{10,24} If the radiationless decay channels in **1*** are coupled to this kind of C—C=N=N bond bending, the rigid matrix could suppress this motion and enhance the probability of N₂ extrusion and subsequent rearrangement.

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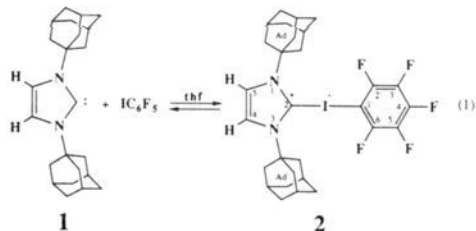
Synthesis of a Reverse Ylide from a Nucleophilic Carbene

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Carbene **1** reacts with iodopentafluorobenzene to give the 1:1 adduct **2**. In solution, **2** is in equilibrium with free carbene and iodopentafluorobenzene as evidenced by the observation of averaged NMR chemical shifts in the presence of either excess carbene or iodopentafluorobenzene. If solutions of **2** are allowed



to stand at room temperature for several hours, resonances for pentafluorobenzene and 1,3-di-1-adamantyl-2-iodoimidazolium ion are evident in the proton NMR spectrum. These observations suggest that either C—I bond may cleave in solution. We have made a similar observation of adduct formation between carbene **1** and iodotrifluoromethane, and decomposition products of 1,3-di-1-adamantyl-2-iodoimidazolium ion and fluoroform were observed on standing.²

Ylide **2** is stable in solid form and crystallizes from thf with 3 molecules of thf. Crystals of **2** gradually lose the thf of crystallization on warming and melt at 110 °C. At room temperature the ¹H NMR spectrum of **2** in thf-*d*₆ gives δ 1.76 (m, Ad_{4,6,10}, 12 H), 2.18 (m, Ad_{2,3,5,7,8,9}, 18 H), 7.03 (br s, NCH, 2 H). The NMR spectra of **2** in thf-*d*₈ at -50 °C are ¹H NMR δ 1.78 (m, Ad_{4,6,10}), 2.21 (m, Ad_{3,5,7}), 2.38 (m, Ad_{2,8,9}), 7.24 (s, NCH); ¹³C NMR [¹H] δ 30.90 (s, Ad_{3,5,7}), 36.70 (s, Ad_{4,6,10}), 44.36 (s, Ad_{2,8,9}), 57.79 (s, Ad₁), 87.35 (m, ICCF), 115.15 (br s, NCH), 137.23 (dm, ¹J_{CF} = 260.4 Hz, ICCCF), 140.65 (dm, ¹J_{CF} = 256.4 Hz,

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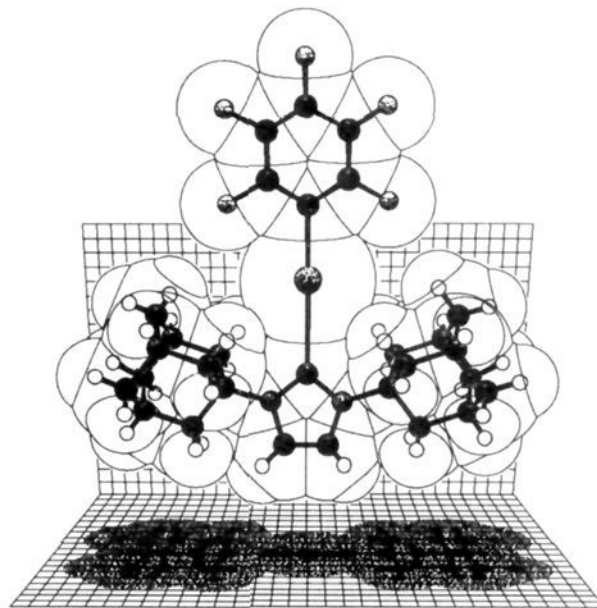


Figure 1. Space-filling KANVAS⁴ drawing of the X-ray structure of ylide **2**.

ICCCCF), 147.46 (dm, ¹J_{CF} = 235.6 Hz ICCF), 193.64 (br s, NCN); ¹⁵N NMR δ -161.07 (reference NH₄¹⁵NO₃); and ¹⁹F NMR δ -123.75 (br m, 2 F, ICCF), -159.44 (t, ICCCF), -163.63 (m, 2 F, ICCCF). A sample of vacuum-dried **2** gave a satisfactory elemental analysis (C₂₉H₂₃N₂IF₅; Calcd: C, 55.25; H, 5.12; N, 4.44; F 15.07. Found: C, 55.55; H 5.22; N 4.21; F, 14.45).

A crystal of **2** was grown from a 1:2 mixture of **1** and iodopentafluorobenzene in thf at -25 °C. The X-ray crystal structure of **2** is depicted in Figure 1.³ Selected bond lengths and angles are given in Table I.

The X-ray structure of **2** shows some change in the imidazole ring as a result of incorporation of IC₆F₅. The N—C—N angle has increased 2° from the characteristically small angle observed in **1**. The ring internal angles at nitrogen have decreased by an average of 1.4°. The C₂—N₁₍₃₎ bonds are slightly shortened (ΔR = 0.7 pm) and the N₁—C₅ and N₃—C₄ bonds are slightly lengthened (ΔR = 0.5 pm) relative to the corresponding bonds in **1**. The C₄=C₅ bond length is longer in **2** by 0.9 pm. These changes suggest an augmented imidazole π -delocalization in **2** as compared to **1**. This change in π -delocalization is also supported by the downfield shift in the imidazole ring proton in **2** versus **1** (δ 7.02 → 7.24).¹

The large C—I—C angle in **2** is consistent with 10—I-2 (hypervalent) bonding at the iodine center. There is considerable asymmetry in the two C—I bond distances but, as mentioned above, either C—I bond can be cleaved or retained in subsequent chemistry. The length of the C—I to the imidazole fragment is not the result of steric interactions. The C—I bond distance in the 1,3-di-1-adamantyl-2-iodoimidazolium ion (formed from carbene **1** and I₂) is 213.1 (11) pm.⁵ A flat potential surface for such

(3) Crystal data for **2** at 203 K with Mo K α radiation: *a* = 1135.3 (2) pm, *b* = 1333.3 (2) pm, *c* = 1422.0 (2) pm, α = 71.98 (1)°, β = 75.89 (1)°, γ = 82.51 (1)°, triclinic, *P*1, *Z* = 2, 5354 unique reflections with *I* > 3 σ (*I*). The final *R* factors were *R* = 0.035 and *R*_w = 0.037. The largest residual electron density in the final difference Fourier map was 0.62 e/Å³ near one of the thf units. Further details of the crystal structure are available in the supplementary material.

(4) This drawing was made with the KANVAS computer graphics program. This program is based on the program SCHAKAL of E. Keller (Kristallographisches Institut der Universität Freiburg, FRG), which was modified by A. J. Arduengo, III (E. I. du Pont de Nemours & Co., Wilmington, DE) to produce the back and shadowed planes. The planes bear a 50-pm grid and the lighting source is at infinity so that shadow size is meaningful.