detected (see Figure 7). As is described above, α,β-DNP can form only the partially overlapped dimer. An enantiomer with the *R* chirality seems to be bound preferentially to the primary OH side of the γ-CDx cavity.

Summary

The present study reveals that the hydrophobic guest molecules having molecular sizes larger than the cyclodextrin cavity size tend to be bound to the relatively hydrophobic part (primary OH side) of the cavity unless the primary OH side is capped. The intermolecular pyrene dimer as well as the intramolecular dinaphthylpropane dimers are included in the primary OH side of the γ-CDx cavity, which recognizes the enantiomers of these guest molecules. The *S* chiral pyrene dimer is preferentially bound to γ-CDx, whereas the *R* chiral stacked dimers of α,α- and α,β-DNPs are recognized as the preferable guests by γ-CDx. Extension of the present study may allow designation of the appropriate systems for asymmetric syntheses and chiral recognition using cyclodextrins.

Acknowledgment. Experimental assistance provided by K. Yoshiyasu is acknowledged.

Reaction of Dicarbomethoxycarbene with Acetaldehyde and Simple Ketones[1]

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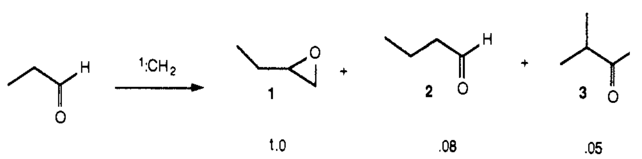
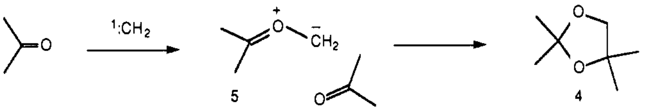
Abstract: Singlet dicarbomethoxycarbene reacts with acetaldehyde to give dioxolane **8**, the ultimate product of formation of ylide **10** and subsequent addition of a second molecule of aldehyde. Photosensitized generation of the carbene gives increased hydrogen abstraction and decreased products derived from the ylide. Replacement of the aldehyde with a ketone changes the course of the reaction and dioxolanones (**11**, **20**, and **26**) become the major products. Suggestions are made for the mechanisms of the singlet and triplet reactions and for the peculiar behavior of acetone in which generation of singlet and triplet carbene gives the same product slate.

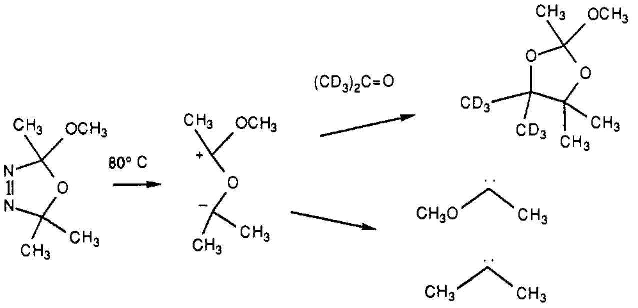
The addition to the carbon–carbon double bond is surely the most familiar reaction of divalent carbon.[2] Given that a significant portion of organic chemistry is concerned with reactions of the carbonyl group, it is striking how little investigated is the reaction of carbenes with the carbon–oxygen double bond. Kirmse's famous book[2a] devotes but three pages to the subject, and relatively little has been published since. Important exceptions include the report by Rose and Fuqua of the reactions of methylene with propionaldehyde in the gas phase[3] and Huisgen and de March's relatively recent and thorough description of the reaction of dicarbomethoxycarbene with aromatic aldehydes.[4]

Methylene reacts with propionaldehyde to give three main products, epoxybutane (**1**), *n*-butyraldehyde (**2**), and isobutyraldehyde (**3**). The major product is **1**, and Rose and Fuqua estimated that the carbonyl group is 13–18 times as reactive as the α and β carbon–hydrogen bonds, respectively. This observation supported an earlier report of Bradley and Ledwith,[5] who found that in solution the carbonyl group of acetone was ca. 15 times as reactive toward methylene as was the carbon–hydrogen bond. These workers found that the dominant product in solution was the dioxolane **4**, and proposed a sensible mechanism involving capture of the ylide **5** by a second molecule of acetone.





In 1983 it was noted by Běkhazi and Warkentin that oxadiazolines lost nitrogen on heating to generate carbonyl ylides.[6] These ylides both fragmented to carbenes and were trapped by acetone. The daughter carbenes reacted with acetone to give new ylides which also could be trapped by acetone.



Reactions of carboalkoxycarbenes with aldehydes had been described as early as 1885,[7] and the structure of the dioxolane products proposed in 1910,[8] but it remained for Huisgen and de March[4] to describe the reaction in detail and to trap the ylide **6** with a number of reagents, including the aldehyde itself to give dioxolane **7**.

In recent years carbonyl ylides have been detected spectroscopically from the reactions of a variety of carbenes, usually

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(1) Support for this work by the National Science Foundation through Grant CHE 83 18345 is gratefully acknowledged. Portions are taken from the A. B. Thesis of T.M.F., Princeton University, 1974.

(2) (a) Kirmse, W. *Carbene Chemistry*; Academic: New York, 1971. In these three pages Kirmse also notes a number of copper-catalyzed reactions with carbonyl compounds. (b) Moss, R. A.; Jones, M., Jr., Eds. *Carbenes*; Wiley: New York, 1973, 1975; Vol. 1, 2.

(3) Rose, T. L.; Fuqua, P. J. *J. Am. Chem. Soc.* **1976**, *98*, 6988.

(4) de March, P.; Huisgen, R. *J. Am. Chem. Soc.* **1982**, *104*, 4952, 4953.

(5) Bradley, J. N.; Ledwith, A. *J. Chem. Soc.* **1963**, 3480.

(6) Běkhazi, M.; Warkentin, J. *J. Am. Chem. Soc.* **1983**, *105*, 1289.

(7) Buchner, E.; Curtius, Th. *Ber. Dtsch. Chem. Ges.* **1885**, *18*, 2371.

(8) Dieckmann, W. *Ber. Dtsch. Chem. Ges.* **1910**, *43*, 1024.

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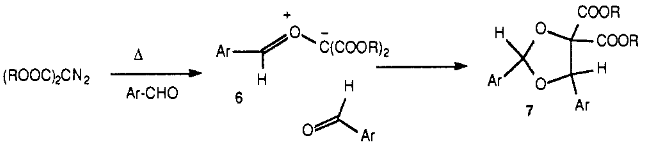
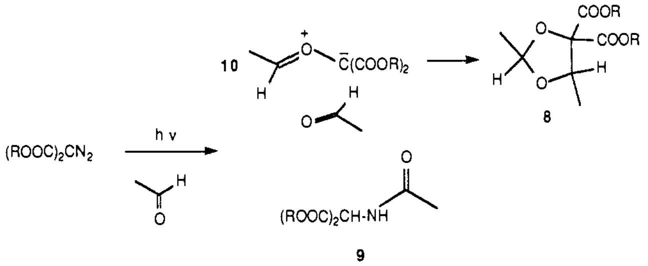


aromatic, with carbonyl compounds.[9]

We have encountered reactions of dicarbomethoxycarbene with ketones in which carbonyl ylides are formed only to suffer intramolecular capture, a different fate from those previously reported.[10] We describe here the direct and sensitized photolyses of dimethyl diazomalonate in three ketones and contrast these reactions to those in acetaldehyde. In the text and tables that follow the yields of products, which range from ca. 0.5% to 47%, are based on gas chromatographic analyses *of the volatile material.* Relative percentages are based on a similar analysis. Although it is conceivable that the product ratios could be distorted by further reaction of these compounds with carbenes, the small amounts of products are born in a vast excess of solvent which is generally a quite receptive carbene trap, and we doubt that secondary reactions can be a serious problem.

When dimethyl diazomalonate is irradiated in neat acetaldehyde with a 450-W medium-presure mercury arc filtered through uranium glass ($\lambda > 340$ nm), the major products are the two stereoisomers of dioxolane **8** (50 relative %) and dimethyl malonate (50 relative %). Photosensitization with benzophenone results in the elimination of **8** and the increase in relative yield of dimethyl malonate to 83%. In addition, 17% of a new product **9**, was formed. Most of this can be explained in quite conventional fashion: the singlet carbene forms ylide **10**, which is captured intermolecularly by another molecule of acetaldehyde to give **8**. In the sensitized reaction, increased hydrogen abstraction by the triplet carbene results in more malonate, and the inability of the radical-like triplet to form an ylide eliminates compounds such as **8**. Compound **9** is worthy of note, although we are not yet able to shed much light on the mechanism of its origin. It appears as a major product only in photosensitized reactions in aldehydes, and clearly is produced by some process of reduction of the diazomalonate. It is interesting in that its formation suggests some participation of excited diazo compound in the overall reaction.[11]



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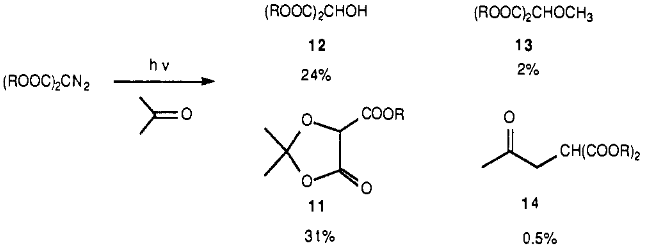
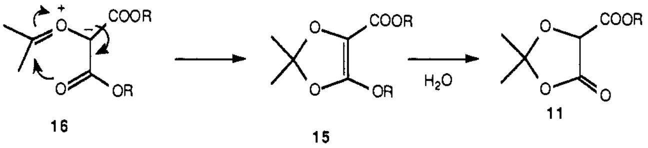
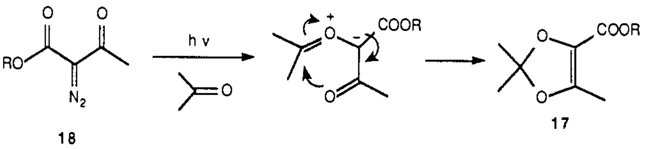
So far there is little difference from the reactions of the singlet carbomethoxycarbene studied by Huisgen and de March[4] or from what one might expect of a triplet carbene in the sensitized reaction. Intuition fails, however, when the seemingly trivial change is made from acetaldehyde to simple ketones as substrates for the carbene. Most important is the observation that compounds analogous to **8** are not formed, but are replaced by molecules formed by intramolecular capture of an ylide. For instance, direct irradiation of diazomalonic ester in acetone leads to **11** as the major product (31% yield). In addition the carbene is captured by water to give 24% of hydroxymalonic ester **12** and by methanol to give the related ether **13**. A very small amount (<1%) of **14**, the product of apparent carbon–hydrogen insertion, is also formed.



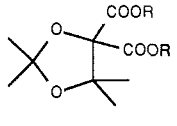
Compounds **12** and **13** presumably arise from trapping of the singlet carbene by traces of water and methanol, which are known to be most effective singlet scavengers, even in very small concentration.[12] Water must be active as well in the conversion of **15**, the first-formed product of internal cyclization of ylide **16**,



to **11**. In support of this notion we have shown that **17**, the known[10] analogue of the putative **15**, but resistant to hydrolysis, is formed as the major product when diazoacetoacetic ester **18**



is irradiated in acetone. No trace of **19**, the compound analogous to the major products formed in acetaldehyde can be found. This sort of negative evidence must always be treated with caution, but we estimate that 5% of **19** would have easily been seen.



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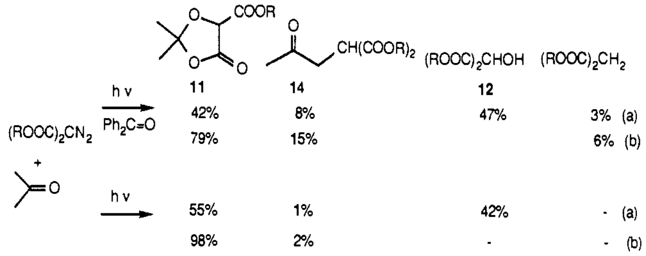
So the first serious mechanistic question appears: why does the replacement of the aldehydic hydrogen by a methyl group, a seemingly innocuous transformation, completely change the path of reaction? The second question arises almost immediately; unlike reaction in acetaldehyde, photosensitization in acetone makes almost no difference in the product distribution. Small amounts of dimethyl malonate are formed (3%) as would be expected of a reaction involving a radical-like triplet, the ether **13** has disappeared, and there is an increase (to 8%) in the relative percentage of **14**, the product of apparent carbon–hydrogen insertion. Otherwise the direct and photosensitized reactions are remarkably similar. Although Roberts has shown that acetone is a modestly effective photosensitizer of diazomalonate,[13] the products, dominated as they are by compounds formed from ylides, seem to demand the singlet as the primary reacting state of the carbene (see relative yields in the figure).



	11	14	(ROOC)$_2$CHOH 12	(ROOC)$_2$CH$_2$	
h v, Ph$_2$C=O	42%	8%	47%	3%	(a)
	79%	15%		6%	(b)
h v	55%	1%	42%	-	(a)
	98%	2%	-	-	(b)

(a) relative % yield of volatile material; (b) normalized to exclude product of reaction with water

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(9) For a recent example, see: Barcus, R. L.; Hadel, L. M.; Johnston, L. J.; Platz, M. S.; Savino, T. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 3928. For a description of the parent carbonyl ylide, see: Prakash, G. K. S.; Ellis, R. W.; Felberg, J. D.; Olah, G. A. *J. Am. Chem. Soc.* **1986**, *108*, 1341.

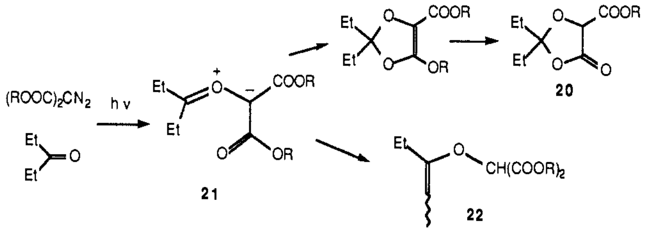
(10) Examples of intramolecular addition are known when copper catalysis is used to promote the reaction. See, for instance: Alonso, M. E.; Garcia, M. del C.; Chitty, A. W. *J. Org. Chem.* **1985**, *50*, 3445.

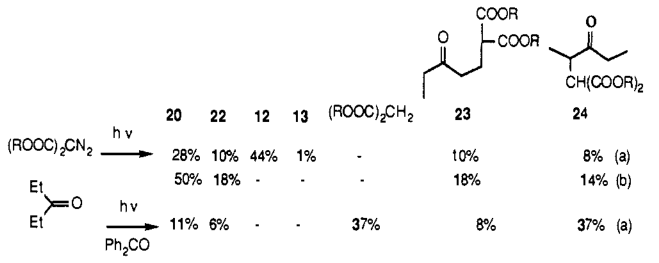
(11) Wulfman, D. S.; Poling, B.; McDaniel, R. S. *Tetrahedron Lett.* **1975**, 4519. Tomioka, H.; Kitagawa, H.; Izawa, Y. *J. Org. Chem.* **1979**, *44*, 3072.

(12) Griller, D.; Liu, M. T. H.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5549.

(13) Roberts, P. J. A. B. Thesis, Princeton University, 1981.

But not all ketones behave this way! For instance, although direct irradiation in 3-pentanone gives a product spectrum rather closely resembling that formed from acetone, large differences appear when the photolysis is photosensitized. In the singlet reaction the major adduct is **20** (13%, 28 relative %), presumably derived from an ylide (**21**), as is **11**. An additional 5% (10 relative %) of ylide-derived products is produced in the form of **22**. So the product spectrum is quite similar to that formed from acetone in either the direct or photosensitized photolysis. Products of carbon-hydrogen insertion (**23** and **24**) amount to 9%, and **12** and **13** are produced as well. In this system the sensitized reaction is quite different. Compounds **20** and **22**, the products of **21**, are reduced to 4% and 2% (11% and 6% relative yield), respectively. Insertion products **23** and **24** have increased to a total of 16% (45% relative yield) and it is the α position that is greatly favored by a factor of 4.6. Adventitious water and methanol no longer seriously compete and are replaced with 13% (37% relative yield) of the double-abstraction product, dimethyl malonate.

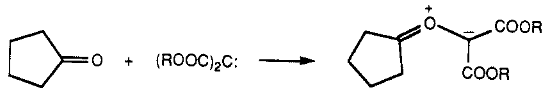




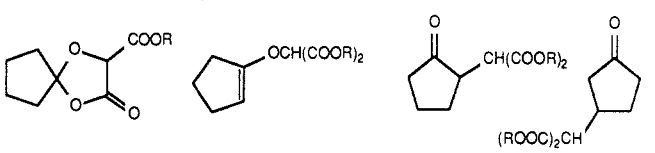
	20	22	12	13	$(ROOC)_2CH_2$	23	24	
$(ROOC)_2CN_2$ + 3-pentanone, hv	28%	10%	44%	1%	-	10%	8%	(a)
	50%	18%	-	-	-	18%	14%	(b)
hv, Ph_2CO	11%	6%	-	-	37%	8%	37%	(a)

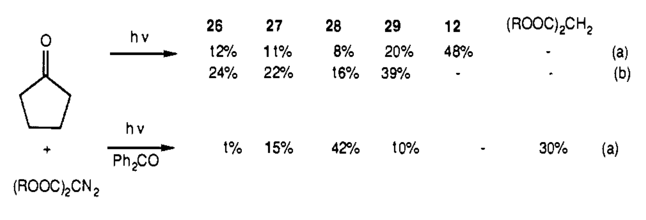
(a) relative % yield of volatile material; (b) normalized to exclude products of reaction with water

Reaction in cyclopentanone is similar to that in 3-pentanone. Direct irradiation is dominated by products (**26** and **27**) derived from an ylide (**25**).


25

These are substantially decreased when the reaction is photosensitized. Compounds of carbon-hydrogen insertion, **28** and **29**, are also produced in the singlet reaction and once again it is the product of α insertion that is most greatly increased in the triplet reaction, this time by a factor of 4.2.





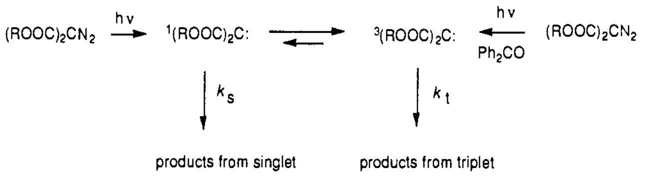
	26	27	28	29	12	$(ROOC)_2CH_2$	
cyclopentanone + $(ROOC)_2CN_2$, hv	12%	11%	8%	20%	48%	-	(a)
	24%	22%	16%	39%	-	-	(b)
hv, Ph_2CO	1%	15%	42%	10%	-	30%	(a)

(a) relative % yield of volatile material; (b) normalized to exclude the product of reaction with water

These experiments show that 3-pentanone and cyclopentanone share the ability with acetone to turn the reaction from external capture of a carbonyl ylide to internal cyclization. Yet it is only in acetone that the mode of generation of the carbene, producing initially either the singlet or triplet state, is irrelevant. The remainder of this paper will suggest explanations and provide evidence for our ideas.

In acetone, where the mode of generation of the carbene affects the composition of the product slate only minimally, it appears that the singlet carbene is always the reactive species. This is reminiscent of the behavior of most arylcarbenes where it also is the more reactive singlet that reacts even though the triplets are generally the more stable species.[14] The singlet and triplet are often close enough in energy to be in thermal equilibrium and even though the triplet is generally favored, it is the more reactive singlet state that generates the observable products. In olefins it is possible to observe separately the properties of both singlet and triplet dicarbomethoxycarbene.[15] Thus an alkene is a sufficiently effective trap to react with either singlet or triplet carbene before equilibrium is established. We suggest that in acetone this is no longer the case. Here it is only the products of the singlet state that are observed regardless of the spin state in which the carbene is generated. This requires that the carbonyl group of acetone be most reactive toward the singlet carbene and that the singlet be accessible from the triplet. The singlet triplet gap has not been determined for dicarbomethoxycarbene, but carboethoxycarbene is known to have a triplet ground state.[16a] Calculations on the parent carboxycarbene (hydroxycarbonylcarbene) suggest a triplet ground state some 7 kcal/mol lower than the lowest singlet.[16b] Our mechanistic explanation would require that the gap in dicarbomethoxycarbene be quite small. There is evidence from a study of the Wolff rearrangement that singlet and triplet carbomethoxycarbene can equilibrate thermally,[17] but our work provides the first clue that this is the case for dicarbomethoxycarbene.

We still need an explanation for why the larger ketones behave differently from acetone. With 3-pentanone and cyclopentanone it appears that the triplet state can compete with the singlet and that the carbonyl oxygen is no longer able to scavenge effectively the singlet state of the carbene. We suggest that the change in available carbon-hydrogen bonds from which the triplet can abstract hydrogen tips the balance. In both 3-pentanone and cyclopentanone there are secondary α C–H bonds available whereas in acetone there are only primary. Typical ratios for secondary/primary free radical abstractions are ca. 9.[18] It would take only a small effect to change the reacting state in a reaction in which the two spin states are close enough in energy to be both observable, as appears to be the case here. For this explanation to be correct, triplet dicarbomethoxycarbene must show a high preference for secondary over primary α carbon-hydrogen bonds. Methyl ethyl ketone provides such a test, although primary in-



$k_s >> k_t$ for ylide formation vs. primary α abstraction

$k_s << k_t$ for ylide formation vs. secondary α abstraction

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(14) For a recent example and appropriate references, see: Gasse, P. B.; Zupancic, J. J.; Lapin, S. C.; Hendrich, M. P.; Schuster, G. B. *J. Org. Chem.* **1985**, *50*, 2352.

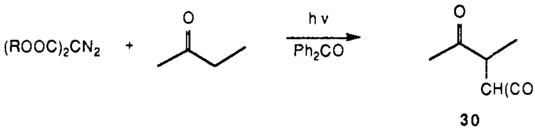
(15) Jones, M., Jr.; Ando, W.; Hendrick, M. E.; Kulczycki, A., Jr.; Howley, P. M.; Hummel, K. F.; Malament, D. S. *J. Am. Chem. Soc.* **1972**, *94*, 7469.

(16) (a) Hutton, R. S.; Roth, H. D. *J. Am. Chem. Soc.* **1978**, *100*, 4324. (b) Kim, K. S.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1980**, *102*, 5389.

(17) Tomioka, H.; Okuno, H.; Izawa, Y. *J. Org. Chem.* **1980**, *45*, 5278.

(18) For example, see: Bridger, R. F.; Russell, G. A. *J. Am. Chem. Soc.* **1963**, *85*, 3754.

sertion will be favored by at least the statistical ratio of 3/2. Yet it is only **30** that is observed in the photosensitized decomposition



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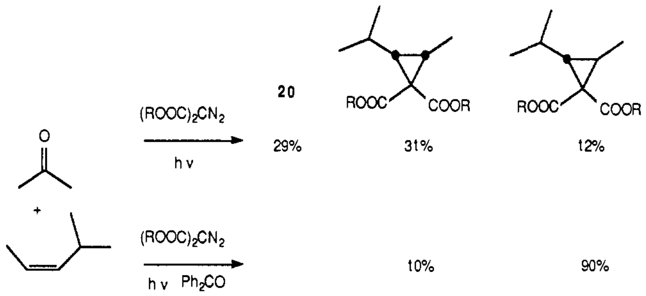
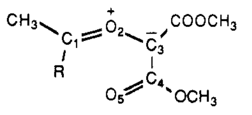
of diazomalonic ester in methyl ethyl ketone. Thus the unique behavior of acetone can be explained by an equilibrium favoring triplet carbene, but nonetheless providing enough singlet so that when only a poor reaction of the triplet is available (abstraction of primary α hydrogen, but not secondary α) it is the singlet that reacts because of the ease of ylide formation. When a more reactive secondary α C–H bond is available as in 3-pentanone or methyl ethyl ketone, the triplet becomes detectable, although products of the singlet persist. When an even better triplet trap is used no products of the singlet appear. In the photosensitized decomposition of dimethyl diazomalonate in a 1:2 mixture of acetone and *cis*-4-methyl-2-pentene no dioxolanone is formed and the 90/10 trans/cis ratio of the cyclopropanes formed indicates that the cycloaddition has come exclusively from the triplet.[15] The direct photolysis in the same mixture of acetone and olefin is more difficult to interpet as acetone is known to function as a sensitizing agent.[13] Both singlet and triplet products are formed in approximately 85/15 ratio.



This still leaves open the question of why the ketones all form dioxolanones (**11**, **20**, and **26**) but the aldehydes do not. We have investigated this question computationally, using the MNDO approximation.[19] The calculated activation energies for intramolecular cyclizations of **10** and **16** (18.4 and 19.8 kcal/mol, respectively) give no hint of the cause for the divergent behavior of the two ylides. The calculated minimum energy structures for the ylide formed from acetaldehyde and dicarbomethoxycarbene (**10**) and that from acetone and dicarbomethoxycarbene (**16**) are



10 R = H

16 R = CH3

similar, but in **16** the angle between the plane containing ylide carbon–oxygen bonds (C_1–O_2–C_3) and that formed by the old carbene carbon and the carbonyl group of one ester (C_3–C_4–O_5) is 20° wider than in the more nearly flat **10**. In addition, the intermolecular cycloaddition of **16** is sure to be retarded by the "new" methyl groups present in **16** and acetone, but missing in **10** and acetaldehyde. Recall the Bradley and Ledwith found that reaction of acetone with the smallest carbene, (singlet) methylene, did lead to external capture of an ylide to give **4**.[5] Therefore we suggest that steric factors are important and that the difference in reactivity found between acetaldehyde and the ketones lies in the differing accessibilities of the initially formed ylides to further external cycloaddition.

Experimental Section

General. Routine NMR spectra were recorded on a General Electric QE300 or Bruker WM250 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 283B IR spectrometer. Precise mass and chemical ionization (CI) mass spectra were performed by the Midwest Center for Mass Spectrometry, Lincoln, NB. Elemental analyses were performed by Atlantic Microlabs Inc., Atlanta, GA. The melting point was determined on a Thomas-Hoover Uni-Melt apparatus and is uncorrected.

Preparative gas chromatography was performed on a Varian Aerograph A90P gas chromatograph using a 6 ft × $^1/_4$ in. aluminum column packed with 15% OV17 on Chromosorb P. Quantitative gas chromatography was performed on a Hewlett-Packard 5890A thermal conductivity gas chromatograph equipped with a Hewlett-Packard 3390A integrator using the following columns: A, 530 μm × 25 m 50% phenylmethylsilicone capillary column; B, 320 μm × 30 m Supelcowax 10 capillary column; C, 750 μm × 60 m 1:1 FFAP:PPE capillary column; D, 6 ft × $^1/_8$ in. stainless steel column packed with 3% OV17 on Chromosorb W-HP.

Acetaldehyde, 3-pentanone, and cyclopentanone were purchased from Aldrich Chemical Co., and distilled from calcium sulfate (Drierite) and stored over 4-Å molecular sieves. Acetone (Aldrich) was distilled from its sodium iodide complex and stored over 4-Å molecular sieves. Dimethyl diazomalonate (MDM) and ethyl diazoacetoacetate (EDA) were prepared by the method of Rosenberger and Yates.[20]

General Photolysis Conditions. In a 5-mL volumetric flask was placed 14–18 mg of diazo compound. The flask was then filled to the mark with the appropriate solvent. The solutions were transferred to 10 mm × 160 mm Pyrex tubes which were degassed by three freeze–pump–thaw cycles. The samples were irradiated with a 450-W medium-pressure Hanovia mercury arc lamp filtered through a uranium glass absorption sleeve (λ > 340 nm) for 8–14 h, after which time the signal at 2160 cm^{-1} present in the diazo compound had disappeared. The excess solvent was removed at the water pump.

Triplet reactions were performed by adding 45–60 mg of benzophenone as sensitizer to reaction mixtures made as described above.

Yields were determined by the internal standard method. After removal of solvent the residue was placed in a 2-mL volumetric flask, 4–6 mg of diethyl malonate (internal standard) was added, and the mixture was diluted to the mark with the reaction solvent. In the case of acetaldehyde, the mixtures were diluted with acetone. Response factors were determined from dimethyl malonate, **8**, **9**, **11**, **12**, **20**, **23**, **26**, and **29**. It was assumed that the other compounds had response factors similar to those of closely related compounds. Thus, in yield determination, the response factor for **24** was set equal to that for **23**. The calculated yields are reported to the nearest milligram in most cases. Samples for analysis were obtained by scaling the above reactions to a total volume of 25 mL and separating the crude reaction mixture by preparative gas chromatography.

Direct Decomposition of MDM in Acetaldehyde. A solution of 22 mg of MDM in acetaldehyde was irradiated for 8 h. Analysis by gas chromatography using column C at 125 °C yielded 1 mg (6%) of dimethyl malonate and 2 mg (6%) of 2,4-dimethyl-5,5-bis(methoxycarbonyl)-1,3-dioxolane (**8**). Analytical samples were obtained by preparative gas chromatography at 125 °C. The syn and anti isomers of **8** were assigned on the basis of NOE experiments.

syn-**8**: ^{1}H NMR (CDCl$_3$) δ 5.19 (q, 1 H, J = 5 Hz), 4.53 (q, 1 H, J = 6 Hz), 3.81 (s, 3 H), 3.78 (s, 3 H), 1.51 (d, 3 H, J = 5 Hz), 1.36 (d, 3 H, J = 6 Hz).

anti-**8**: ^{1}H NMR (CDCl$_3$) δ 5.59 (q, 1 H, J = 5 Hz), 4.89 (q, 1 H, J = 7 Hz), 3.81 (s, 3 H), 3.79 (s, 3 H), 1.38 (d, 3 H, J = 5 Hz), 1.27 (d, 3 H, J = 7 Hz); IR (neat) 3010, 2990, 1765, 1755, 1450, 1300, 1270, 1240, 1100, 875 cm^{-1}. Anal. Calcd for $C_9H_{14}O_4$: C, 49.54; H, 6.47. Found: C, 49.57; H, 6.50.

Sensitized Decomposition of MDM in Acetaldehyde. A solution of 18 mg of MDM and 39 mg of benzophenone in acetaldehyde was irradiated for 8 h. Analysis by gas chromatography using column B temperature programmed at 90–200 °C with an initial time of 10 min, a ramp rate of 10 °C/min, and a final time of 15 min yielded 2 mg (15%) of dimethyl malonate and ca. 0.6 mg (3%) of dimethyl acetamidomalonate (**9**, mp 130–132 °C (lit.[21] mp 128 °C)). Analytical samples were obtained by preparative gas chromatography at 180 °C.

9: ^{1}H NMR (CDCl$_3$) δ 6.52 (bs, 1 H), 5.20 (d, 1 H, J = 6 Hz), 3.81 (s, 6 H), 2.07 (s, 3 H).

Direct Decomposition of MDM in Acetone. A solution of 17 mg of MDM in acetone was irradiated for 10 h. Analysis by gas chromatography using column A temperature programed at 70–200 °C with an initial time of 5 min, a ramp rate of 5 °C/min, and a final time of 15 min yielded 6 mg (31%) of 2,2-dimethyl-5-(methoxycarbonyl)-1,3-dioxolan-4-one (**11**), 4 mg (24%) of dimethyl hydroxymalonate (**12**), ca. 0.2 mg (ca. 1%) of dimethyl methoxymalonate (**13**), and ca. 0.1 mg (ca. 0.5%) of methyl 2-(methoxycarbonyl)-4-oxopentanonate (**14**). Analytical

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samples were obtained by preparative gas chromatography at 125 °C.

11: ^{1}H NMR ($CDCl_3$) δ 4.93 (s, 1 H), 3.85 (s, 3 H), 1.70 (s, 3 H), 1.61 (s, 3 H); IR (neat) 3020, 2995, 1825, 1780, 1395, 1155, 990, 899 cm^{-1}. Anal. Calcd for $C_7H_{10}O_5$: C, 48.28; H, 5.79. Found: C, 47.84; H, 5.90.

14: ^{1}H NMR ($CDCl_3$) δ 3.88 (t, 1 H, J = 7 Hz), 3.73 (s, 6 H), 3.05 (d, 2 H, J = 7 Hz), 2.19 (s, 3 H).

Sensitized Decomposition of MDM in Acetone. A solution of 15 mg of MDM and 52 mg of benzophenone in acetone was irradiated for 10 h. Analysis by gas chromatography using column A temperature programed at 70–200 °C with an initial time of 5 min, a ramp rate of 5 °C/min, and a final time of 15 min yielded ca. 0.2 mg (ca. 2%) of dimethyl malonate, 4 mg (25%) of **11**, 4 mg (25%) of **12**, and ca. 0.8 mg (5%) of **14**.

Direct Decomposition of EDA in Acetone. A solution of 15 mg of EDA in acetone was irradiated for 12 h. Analysis by gas chromatography using column A temperature programed at 70–200 °C with an initial time of 5 min, a ramp rate of 5 °C/min, and a final time of 15 min yielded 8 mg (47%) of 2,2,4-trimethyl-5-(ethoxycarbonyl)-1,3-dioxolan-4-ene (**17**).

17: ^{1}H NMR ($CDCl_3$) δ 4.28 (q, 2 H, J = 7 Hz), 2.17 (s, 3 H), 1.58 (s, 6 H), 1.30 (t, 3 H, J = 7 Hz).

Direct Decomposition of MDM in 3-Pentanone. A solution of 17 mg of MDM in 3-pentanone was irradiated for 10 h. Analysis by gas chromatography using column A temperature programed at 70–200 °C with an initial time of 5 min, a ramp rate of 5 °C/min, and a final time of 15 min yielded 3.5 mg (21%) of **12**, ca. 0.1 mg (ca. 0.6%) of **13**, 3 mg (13%) of 2,2-diethyl-5-(methoxycarbonyl)-1,3-dioxolan-4-one (**20**), 1 mg (4.7%) of methyl 2-(methoxycarbonyl)-3-oxoheptanoate (**23**), and 1 mg (3.8%) of methyl 2-(methoxycarbonyl)-5-oxoheptanoate (**24**). Analytical samples were obtained by preparative gas chromatography at 150 °C.

20: ^{1}H NMR ($CDCl_3$) δ 4.93 (s, 1 H), 3.86 (s, 6 H), 1.94 (q, 2 H, J = 7 Hz), 1.86 (q, 2 H, J = 7 Hz), 1.02 (t, 3 H, J = 7 Hz), 0.96 (t, 3 H, J = 7 Hz); IR (neat) 3005, 2995, 1820, 1779, 1475, 1450, 1212, 1152, 1025, 970, 940 cm^{-1}. Precise Mass (CI) Calcd for $C_9H_{15}O_5$: 203.0919. Found: 203.0917.

22 (cis/trans mixture): ^{1}H NMR ($CDCl_3$) (A) δ 4.92 (s, 1 H), 4.30 (q, 1 H, J = 7 Hz), 3.81 (s, 6 H), 2.22 (q, 2 H, J = 8 Hz), 1.50 (d, 3 H, J = 7 Hz), 1.09 (t, 3 H, J = 8 Hz); (B) δ 4.83 (s, 1 H), 4.75 (q, 1 H, J = 7 Hz), 3.82 (s, 6 H), 2.10 (q, 2 H, J = 7 Hz), 1.63 (d, 3 H, J = 7 Hz), 1.02 (t, 3 H, J = 7 Hz); IR (neat) 2990, 1772, 1686, 1448, 1275, 1201, 1130, 1028, 795 cm^{-1}. Precise Mass (CI) Calcd for $C_{10}H_{17}O_5$: 217.1076. Found: 217.1074.

23: ^{1}H NMR ($CDCl_3$) δ 3.73 (s, 6 H), 3.43 (t, 1 H, J = 7 Hz), 2.50 (t, 2 H, J = 7 Hz), 2.41 (q, 2 H, J = 7 Hz), 2.16 (q, 2 H, J = 7 Hz), 1.04 (t, 3 H, J = 7 Hz); IR (neat) 2990, 1758, 1730, 1450, 1165, 1120, 1020, 800 cm^{-1}. Precise Mass Calcd for $C_{10}H_{16}O_5$: 216.0997. Found: 216.0999.

24: ^{1}H NMR ($CDCl_3$) δ 3.81 (d, 1 H, J = 10 Hz), 3.75 (s, 3 H), 3.69 (s, 3 H), 3.29 (dq, 1 H, J = 10, 7 Hz), 2.65–2.57 (m, 2 H), 1.11–1.05 (m, 6 H); IR (neat) 3005, 2990, 1775, 1738, 1470, 1448, 1295, 1215, 1160, 1015, 925, 800 cm^{-1}. Precise Mass Calcd for $C_{10}H_{16}O_5$: 216.0997. Found: 216.0999.

Sensitized Decomposition of MDM in 3-Pentanone. A solution of 19 mg of MDM and 54 mg of benzophenone in 3-pentanone was irradiated for 10 h. Analysis by gas chromatography using column A temperature programed at 70–200 °C with an initial time of 5 min, a ramp rate of 5 °C/min, and a final time of 15 min yielded 2 mg (13%) of dimethyl malonate, 1 mg (4%) of **20**, ca. 0.5 mg (2%) of **22**, ca. 0.7 mg (3%) of **23**, and 3 mg (13%) of **24**.

Direct Decomposition of MDM in Cyclopentanone. A solution of 16.5 mg of MDM in cyclopentanone was irradiated for 10 h. Analysis by gas chromatography using column A temperature programed at 70–200 °C with an initial time of 5 min, a ramp rate of 5 °C/min, and a final time of 15 min yielded 5 mg (31%) of **12**, 2 mg (8%) of **26**, ca. 1.5 mg (7%) of **27**, 1 mg (5%) of **28**, and 3 mg (13%) of **29**. Analytical samples were obtained by preparative gas chromatography at 160 °C.

26: ^{1}H NMR ($CDCl_3$) δ 4.90 (s, 1 H), 3.85 (s, 3 H), 2.09–1.77 (m, 8 H); IR (neat) 2990, 1823, 1779, 1445, 1335, 1215, 1168, 972 cm^{-1}. Precise Mass (CI) Calcd for $C_9H_{13}O_5$: 201.0763. Found: 201.0755.

27: ^{1}H NMR ($CDCl_3$) δ 4.96 (s, 1 H), 4.45 (t, 1 H, J = 2 Hz), 3.83 (s, 6 H), 2.51–2.44 (m, 2 H), 2.33–2.26 (m, 2 H), 1.94–1.84 (m, 2 H); IR (neat) 2995, 2880, 1770, 1665, 1450, 1371, 1238, 1100, 1022, 822 cm^{-1}.

28: ^{1}H NMR ($CDCl_3$) δ 3.83 (d, 1 H, J = 6 Hz), 3.77 (s, 3 H), 3.72 (s, 3 H), 2.73 (m, 1 H), 2.38–2.05 (m, 4 H), 1.96–1.77 (m, 2 H); IR (neat) 2995, 1755, 1448, 1365, 1210, 1165, 1025 cm^{-1}.

29: ^{1}H NMR ($CDCl_3$) δ 3.76 (s, 3 H), 3.74 (s, 3 H), 3.38 (d, 1 H, J = 8 Hz), 2.91–2.82 (m, 1 H), 2.53 (dd, 1 H, J = 19, 8 Hz), 2.41–2.31 (m, 3 H), 2.02 (dd, 1 H, J = 19, 12 Hz), 1.68–1.61 (m, 1 H); IR (neat) 2995, 1755, 1450, 1338, 1165, 1025 cm^{-1}.

Sensitized Decomposition of MDM in Cyclopentanone. A solution of 16 mg of MDM and 56 mg of benzophenone in cyclopentanone was irradiated for 10 h. Analysis by gas chromatography using column A temperature programed at 70–200 °C with an initial time of 5 min, a ramp rate of 5 °C/min, and a final time of 15 min yielded 4 mg (28%) of dimethyl malonate, ca. 0.2 mg (1%) of **26**, 3 mg (15%) of **27**, 8 mg (39%) of **28**, and 2 mg (9%) of **29**.

Sensitized Decomposition of MDM in Methyl Ethyl Ketone. A solution of 15 mg of MDM and 50 mg of benzophenone in methyl ethyl ketone was irradiated for 14 h. Analysis by gas chromatography using column A temperature programed at 70–200 °C with an initial time of 5 min, a ramp rate of 5 °C/min, and a final time of 15 min yielded 3 mg (26%) of dimethyl malonate, ca. 1.5 mg (8%) of 2-ethyl-2-methyl-5-(methoxycarbonyl)-1,3-dioxolan-4-one, and 3 mg (31%) of methyl 2-(methoxycarbonyl)-3-methyl-4-oxopentanonate (**30**). Analytical samples were obtained by preparative gas chromatography at 145 °C.

2-Ethyl-2-methyl-5-(methoxycarbonyl)-1,3-dioxolan-4-one (mixture of syn and anti isomers): ^{1}H NMR ($CDCl_3$) δ 4.94, 4.93 (s, 1 H), 3.87 (s, 6 H), 1.95, (1.88) (q, 2 H, J = 6 Hz), 1.68 (1.57) (s, 3 H), 1.05 (0.98) (t, 3 H, J = 6 Hz).

30: ^{1}H NMR ($CDCl_3$) δ 3.82 (d, 1 H, J = 10 Hz), 3.78 (s, 3 H), 3.70 (s, 3 H), 3.31 (dq, 1 H, J = 10, 7 Hz), 2.28 (s, 3 H), 1.15 (d, 3 H, J = 7 Hz).

Direct Decomposition of MDM in Acetone/*cis*-4-Methyl-2-pentene. A solution of 15 mg of MDM in 3 mL of *cis*-4-methyl-2-pentene/acetone (2:1 (v/v)) was irradiated for 10 h. Analysis by gas chromatography using column D temperature programed at 80–200 °C with an initial time of 5 min, a ramp rate of 5 °C/min, and a final time of 15 min showed the products **20**, *cis*-1,1-bis(methoxycarbonyl)-2-methyl-3-isopropylcyclopropane, and *trans*-1,1-bis(methoxycarbonyl)-2-methyl-3-isopropylcyclopropane in the relative ratio of 2.4:2.6:1.

Computational Details. MNDO calculations were carried out with a slightly modified version of the MOPAC package (QCPE no. 455, version 2.08) running on a VAX 11/780 minicomputer. All structures were computed by using the restricted Hartree–Fock (RHF) method. Transition structures were located by using the reaction coordinate and the gradient norm minimization (SIGMA and NLLSQ) options in the MOPAC package. Stationary points were fully characterized by vibrational analysis to confirm that all eigenvalues for ground-state structures were greater than zero and transition structures had one and only one negative eigenvalue.

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