protonation of *p*-hydroxyphenoxyl radical.[26] This comparison indicates some similarity between the quinone triplet and the phenoxyl radical which parallels that between alkoxyl radicals and ketone triplets.[3]

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Regioselectivity in the Addition of Singlet and Triplet Carbenes to 1,1-Dimethylallene. A Probe for Carbene Multiplicity

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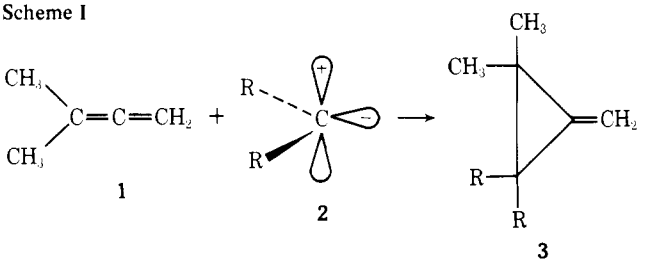
Abstract: Singlet carbenes add preferentially to the more substituted bond of 1,1-dimethylallene (**1**), to give methylenecyclopropanes **3** as the major product. In contrast, many triplet carbenes add with differing regioselectivity, giving the thermodynamically preferred isopropylidenecyclopropanes, **10**. A mechanism involving an intermediate trimethylenemethane, **8**, has been suggested for this product. This regioselectivity probe has been applied to diphenylcarbene and the nitrophenylcarbenes and suggests a reaction occurring through the triplet state in direct photolysis of the diazoprecursors. Benzophenone-sensitized photolysis of ethyl phenyldiazoacetate (**32**) in **1** gave the methylenecyclopropane **33** as the major product. This fact, along with the observed largely stereospecific addition to *cis*-2-butene, suggests a singlet reacting carbene despite the initially generated triplet state. Singlet monoarylcarbenes add to **1** with increasing selectivity as a function of electron-donating ability of the substituent. This feature implies that electron-donor groups stabilize the singlet state. Benzophenone-sensitized decomposition of aryldiazomethanes, **40**, also gave large amounts of methylenecyclopropanes **41.** This was interpreted in terms of predominant singlet reaction despite the initially generated triplet state. Even in the case of electronegative substitution in **40**, singlet pathways remained important. These results suggest that the solution chemistry of triplet phenylcarbene is quite different from that of the matrix-generated triplet.

The chemical literature over the past 25 years contains vast amounts of information on divalent carbon intermediates (carbenes).[2] The possibility of dual multiplicities was recognized quite early in the history of carbene chemistry.[3] To date, the primary method for distinguishing carbene multiplicities has been based on the Skell hypothesis, that is, singlets will add to olefins in a stereospecific fashion while triplet additions will be stepwise and give loss of stereospecificity.[3]

We have been interested in the mechanistic and synthetic aspects of the addition of carbenes to 1,1-dimethylallene (**1**), as a preparative entry into substituted methylenecyclopropanes.[4] From a mechanistic standpoint, it is felt that a singlet electrophilic carbene, **2**, should add in a concerted manner preferentially to the more substituted bond of **1** to give the methylenecyclopropane **3** as in Scheme I. This prediction is supported by the addition of dihalocarbenes to **1** in which methylenecyclopropanes **3** (R = halogen) are the sole products.[5] Our studies[4] have shown that monoarylcarbenoids also

Scheme I



add predominantly to the more substituted bond of **1**. These carbenoids are not as selective as the dihalocarbenes and small, but significant, amounts of the isopropylidenecyclopropanes resulting from the addition to the less substituted bond of **1** are formed.

In contrast, we have observed that triplet methylcarboethoxycarbene, generated by the benzophenone-sensitized decomposition of ethyl diazopropionate (**4**), affords only the

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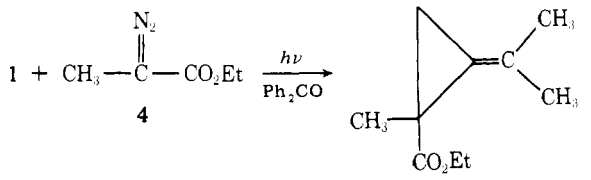
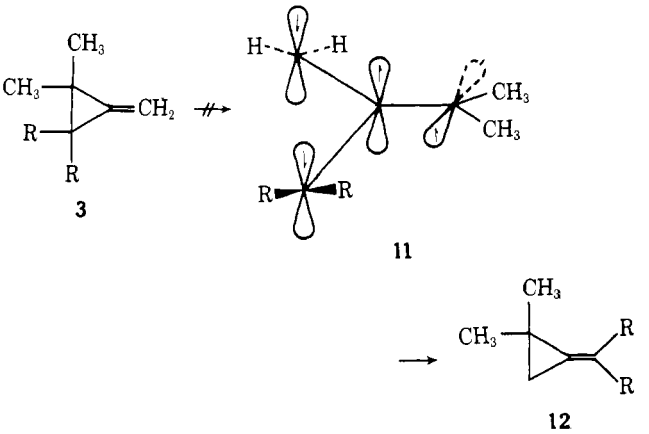


4 5

isopropylidenecyclopropane **5**.[4a] This completely different regioselectivity can be rationalized as follows. It is felt that a triplet carbene should add to **1** in a stepwise manner giving a trimethylenemethane intermediate such as **7** or **8**. This type of radical addition to the central carbon of 1,1-dimethylallene has precedent.[6] The orthogonal π orbitals of the allene should lead to the formation of **7**, a perpendicular triplet trimethylenemethane. However, rotation to the ground state[7] planar triplet, **8**, could be concerted with or subsequent to the addition of the carbene. Closure of **8**, after spin inversion, could give, in principle, three products. However it is felt that one product, **10**, should be formed preferentially for the following reasons. Rotation of the isopropylidene group to give **11** should be unfavorable relative to rotation giving **9** if the groups R are radical stabilizing. The relative stabilities of **9** and **11** (generated in the thermal rearrangement of **3**) have previously been discussed.[4] Since **9** should be formed in preference to **11**, then the alkylidenecyclopropane **12** should not be a product from **8**. Closure of **9** is expected to give **10**, and not the methylenecyclopropane **3**, on the basis of thermodynamic stabilities. We have shown that methylenecyclopropanes of general structure **3** rearrange thermally to give the thermodynamically preferred isopropylidenecyclopropanes **10** quantitatively.[4] Hence the observed formation of **5** can be rationalized by Scheme II.[8]

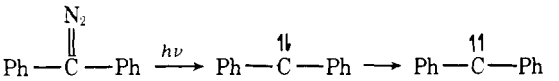
If the general mechanism shown in Scheme II is valid, then the prediction is that singlet and triplet carbenes will give different regioselectivities in the addition to 1,1-dimethylallene. With this in mind, the reaction of **1** with a variety of carbenes was carried out. The goal of these studies was to further de-



3 11 12

velop this new probe for carbene multiplicities based on regiospecificity in addition to **1**, to complement the Skell criterion, which, although quite useful, has been criticized.[9] We also wanted to evaluate regioselectivity as a function of substitution in the carbene as a probe for factors contributing to carbenic stability.

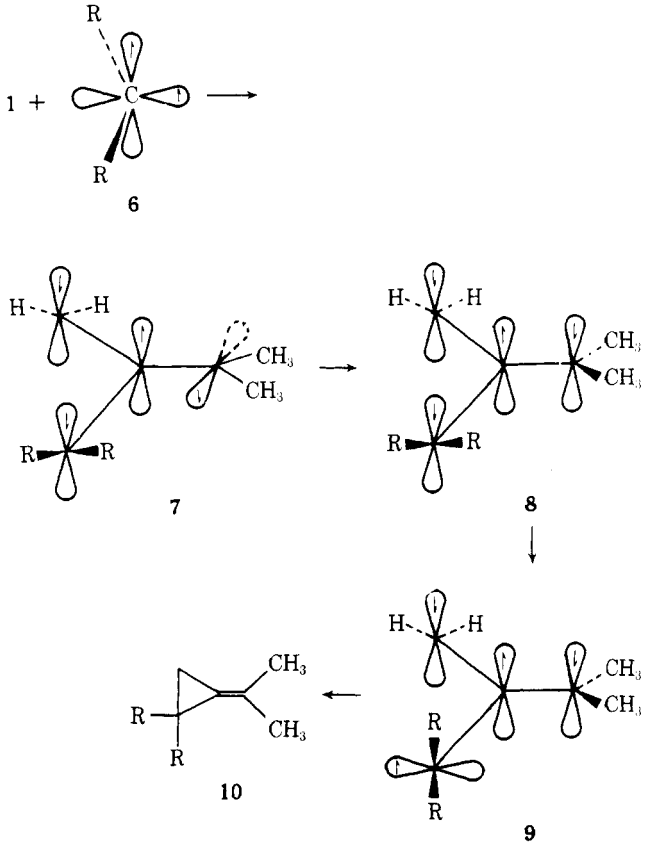
Reaction of Diphenylcarbene with 1. The properties of diphenylcarbene have been investigated in some detail.[10] Direct irradiation of diphenyldiazomethane generates an intermediate with radical-like properties.[10a] Electronic spectra[10b] as well as EPR spectra[10c,d] of this intermediate have been recorded. These results have been interpreted in terms of intersystem crossing to give the ground-state triplet carbene as shown below. The reaction of diphenyldiazomethane (**13**) with 1,1-



13 14 15

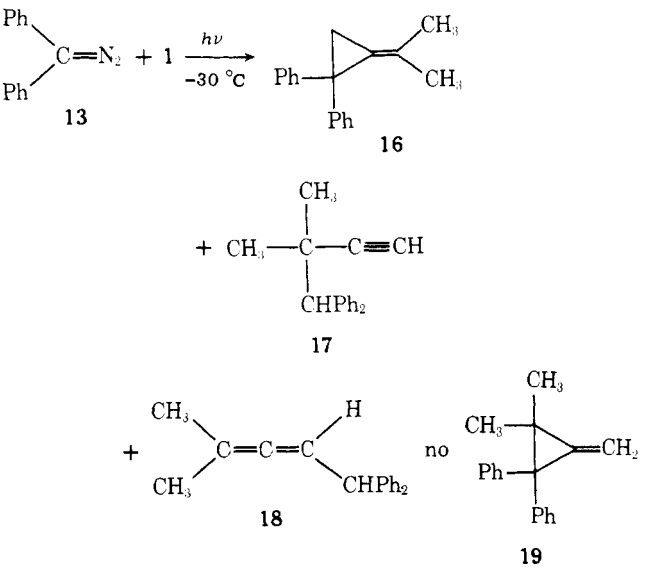
dimethylallene (**1**) has previously been reported to give **16**.[11] We were not certain if any of the methylenecyclopropane **19** was produced since rearrangement of **19** to **16** was expected to occur at a reasonable rate at room temperature.[12] Consequently the photoreaction of **13** in **1** as solvent was repeated at −30 °C, where the thermal rearrangement of **19** would be slow enough to allow its detection. The reaction gave hydrocarbons **16**, **17**, and **18** in a 6:2:1 ratio. No methylenecyclopropane **19** could be detected even at low temperature. The origin of **16** is consistent with the mechanism suggested in Scheme II and lends credence to the suggested regiospecificity criterion for carbene multiplicity.

Scheme II



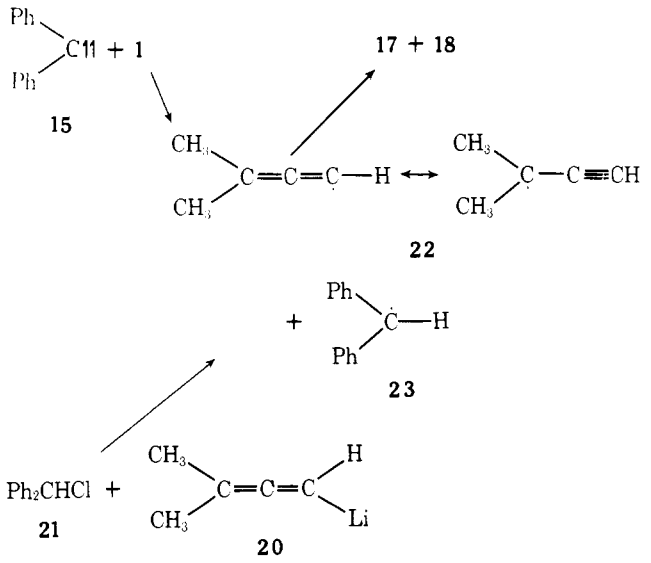
6 7 8 9 10

Scheme III

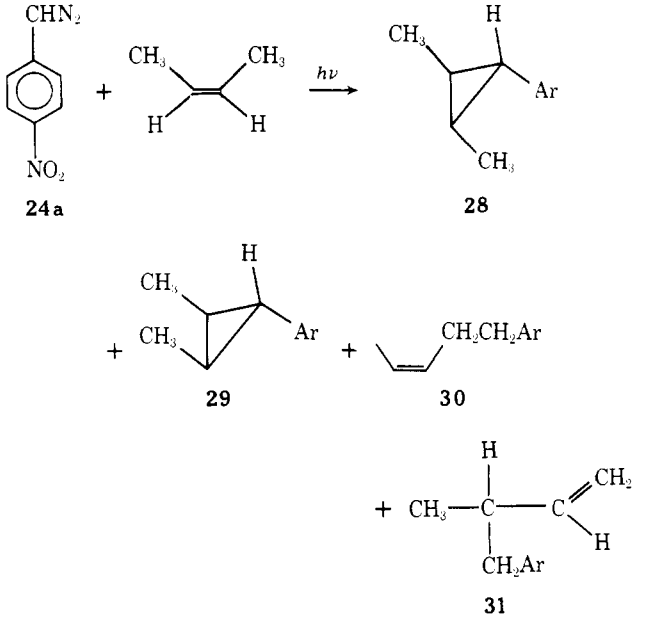


13 16 17 18 19

Scheme IV



Scheme VI

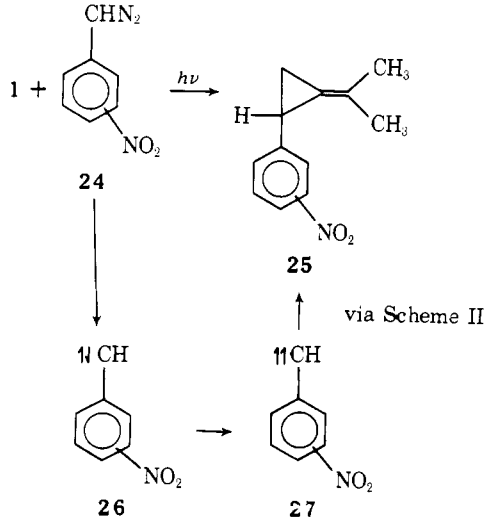


By the regiospecificity criterion, diphenylcarbene reacts with **1** via the triplet state. Herein lies one of the advantages of this probe—cyclopropanation products with **1** tend to be produced in preference to formal C–H insertion products. Attempts to apply the Skell stereospecificity criterion, using 2-butenes, to diphenylcarbene are foiled since the major products (90%) in reaction with 2-butenes are formal C–H insertion products.[13]

The minor products **17** and **18** are also of interest mechanistically. The same two products are produced when 3,3-dimethylallenyllithium (**20**)[6] reacts with benzhydryl chloride (**21**). We have previously presented evidence[6] that **20** reacts with benzyl halides by an electron transfer–radical recombination mechanism. The same type of mechanism seems likely in the reaction of **20** with **21.** It is suggested that the same radical pair, **22** and **23,** can be produced by hydrogen atom abstraction by **15** from **1**, leading ultimately to **17** and **18.**

Reaction of Nitrophenylcarbenes with 1. Photolysis of both *p*-nitrophenyldiazomethane and *m*-nitrophenyldiazomethane with **1** gave isopropylidenecyclopropanes **25** and no methylenecyclopropanes. Again these products suggest the involvement of triplet carbenes **27** by the regioselectivity criterion. This observation is also consistent with the results of Goh[14] in which direct irradiation of *m*-nitrophenyldiazomethane in *cis*-2-butene gave more than 13% nonstereospecific addition. The involvement of the triplet species was suggested,

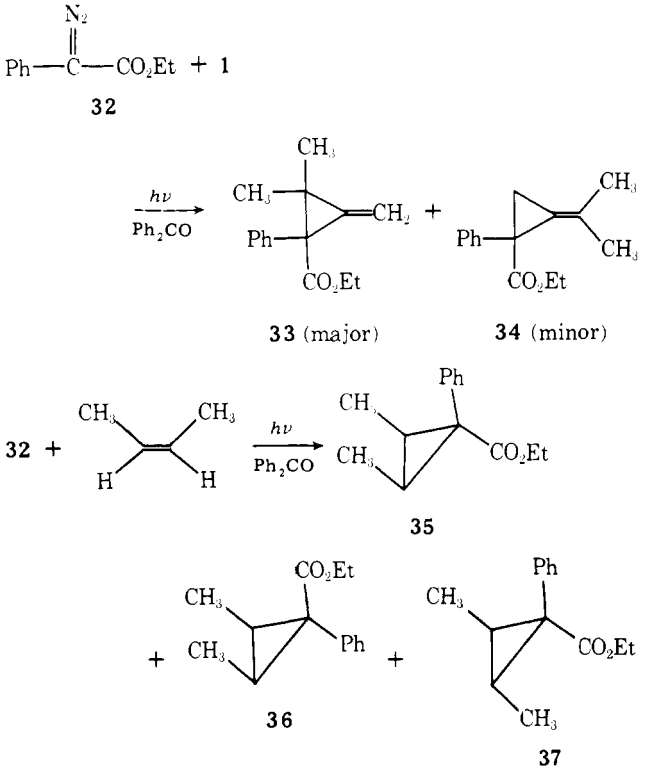
Scheme V



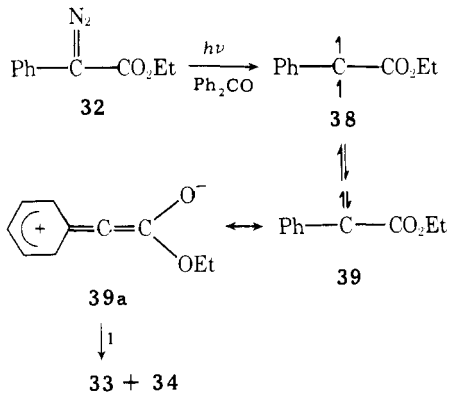
and, according to unpublished work,[14] *p*-nitrophenylcarbene showed similar characteristics. In support of these suggestions, we have found that direct irradiation of *p*-nitrophenyldiazomethane with *cis*-2-butene gave the nonstereospecific cyclopropanation product **28** as the major product (52%) along with minor products **29, 30,** and **31** in comparable amounts. The stereochemistries of **28** and **29** were assigned by the method discussed by Closs.[9a] Cyclopropane **28** showed nonequivalent methyl groups at δ 1.23 and 0.84 in the ^{1}H NMR. The equivalent methyl groups in **29** appear at δ 1.23 and are not in the shielding region of the aromatic ring and hence are assigned the stereochemistry shown. This stereochemistry in **29** is unusual in that singlet aryl carbenes usually add to *cis*-2-butene to give a slight excess of the syn isomer. The formation of both **28** and **29** would be consistent with a stepwise mechanism. Therefore the conclusion based on all criteria is that the products are, for the most part, derived from triplet nitrophenylcarbenes. Apparently the nitro group in either the meta or para position is quite influential at inducting intersystem crossing.

Reaction of Phenylcarboethoxycarbene with 1. We have previously reported[4a] that direct irradiation of ethyl diazophenylacetate (**32**) in **1** gave predominantly **33**, consistent with a singlet electrophilic intermediate. We now report, to our initial surprise, that the benzophenone-sensitized decomposition of **32** in **1** gave the same product mixture. This regioselectivity would be consistent with a singlet electrophilic carbene in the photosensitized reaction of **32**. As a further check, the Skell criterion was applied to the decomposition of **32.** The benzophenone-sensitized irradiation of **32** gave mostly stereospecific addition to *cis*-2-butene. Greater than 96% of the products were cyclopropanes **35** and **36** while less than 4% of **37** was formed. The benzophenone-sensitized decomposition of **32** in *trans*-2-butene was completely stereospecific, giving only **37**. Direct photodecompositions of **32** in both *cis*- and *trans*-2-butene were also completely stereospecific. The stereochemical assignments in **35, 36,** and **37** were based on ^{1}H NMR in which methyl groups syn to the phenyl group are shielded. Product **35** shows equivalent methyl groups at δ 0.96 while **36** shows equivalent methyl groups at δ 1.32. The nonequivalent methyl groups of **37** appear at δ 1.30 and 0.77. The chemistry of phenylcarboethoxycarbene therefore appears to be from the *singlet* manifold regardless of the initially generated state. This suggests that triplet–singlet interconversion, **38** → **39,** occurs readily under the reaction conditions. The type

Scheme VII



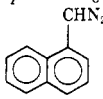
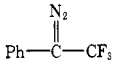
Scheme VIII



of conversion shown in Scheme VIII is quite unusual. Most cases of carbene multiplicity interchanges involve the singlet to triplet mode. In cases where the triplet is the ground state, this process is readily rationalized. The type of multiplicity interchange seen in the present case (triplet to singlet) has rare precedent. Roth[15] has suggested a similar process for triplet-generated acetylcarbene as inferred by CIDNP studies on the reaction of this carbene with chloroform. Our studies suggest that similar processes control the chemistry of phenylcarboethoxycarbene. The data to not allow one to choose the ground state of this carbene. This observation of singlet derived products could also be consistent with a triplet ground state but with the singlet form **39** being the more reactive of a rapidly interconverting triplet-singlet pair. Contributions of conjugated forms such as **39a** should add to the stability of the singlet state and make triplet to singlet interconversion a more facile process.

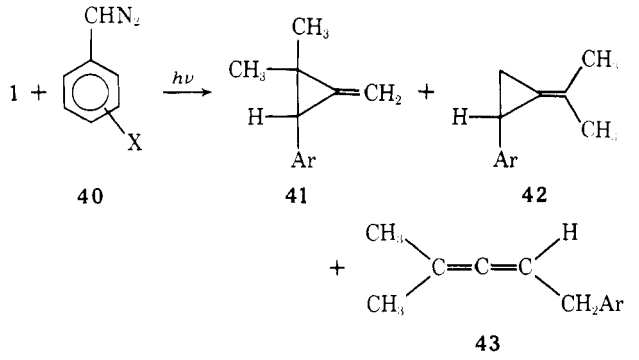
Reaction of Monoarylcarbenes with 1. A series of monoaryldiazomethanes **40** was irradiated with **1** under direct irradiation and under benzophenone photosensitization. Table I gives the results of these studies in terms of the methylenecyclopropane **41** to isopropylidenecyclopropane **42** ratio. Products were all photostable under the reaction conditions. Photolysis of pyrazoline intermediates, derived from thermal cycloaddition of **40** and **1**, has been ruled out since pyrazoline formation is not observable under nonphotolytic conditions. However, photochemical pyrazoline formation cannot be ruled out. In certain cases, small amounts of a formal insertion product, allene **43**, could be detected. Factors contributing to the formation of analogous products have previously been discussed.[4]

Table I. Reaction of Aryldiazomethanes with 1,1-Dimethylallene. Product Ratios **41:42**

	aryldiazomethane	product ratio **41:42** direct irradiation (% yield)	product ratio **41:42** Ph_2CO sensitized (% yield)
40a	p-$CH_3OC_6H_4CHN_2$	12.0 (80)	11.0[a]
40b	p-$CH_3C_6H_4CHN_2$	6.5 (74)	5.6[a]
40c	p-$FC_6H_4CHN_2$	5.8 (55)	4.1 (55)
40d	$C_6H_5CHN_2$	4.3 (59)	1.9 (54)
40e	m-$CH_3C_6H_4CHN_2$	4.2 (75)	2.3[a]
40f	p-$ClC_6H_4CHN_2$	3.5[a]	1.5[a]
40g	p-Br-$C_6H_4CHN_2$	2.3 (80)	0.9 (59)
40h	m-$FC_6H_4CHN_2$	2.0 (78)	0.7 (74)
40i	m-$CF_3C_6H_4CHN_2$	2.0 (86)	0.5[a]
40j	p-$CF_3C_6H_4CHN_2$	1.7 (74)	0.6[a]
40k	p-$CO_2MeC_6H_4CHN_2$	1.4 (65)	
40l	m-CN-$C_6H_4CHN_2$	1.3[a]	
40m	3,5-di$ClC_6H_3CHN_2$	1.3 (85)	0.4 (82)
40n	p-CN-$C_6H_4CHN_2$	1.0 (73)	0.5[a]
44		2.0[a]	0.15[a]
45		1.1 (79)	0.3[a]

[a] Absolute yield not determined.

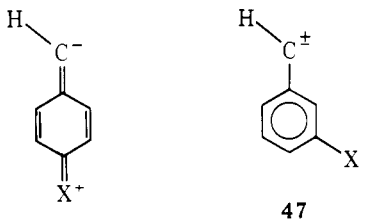
Scheme IX



Consider first the direct irradiation experiments. In all cases, the methylenecyclopropane **41** is produced in larger amounts than the isopropylidenecyclopropanes **42**.[16] However, the product ratio is quite substituent dependent. Electron-donating substituents such as p-methoxy, p-methyl, and p-fluoro lead to a much more regioselective reaction, while selectivity becomes quite low in the case of electronegative substituents. This is illustrated graphically in Figure 1. A plot of log (**41**/**42**) vs. σ (σ^+ for electron donor groups) gives a fairly linear correlation (r = 0.96).

We interpret this behavior as indicative of greater singlet carbene stability in the case of the more regioselective carbenes. It is suggested that the increased stability is derived from delocalization as in **46**. In a similar manner, carbenes such as **47** are destabilized (less selective) owing to less favorable electronic interactions in the singlet.

The arylcarbene regioselectivity in addition to **1** gives an indication of the ability of various substituents to stabilize



46

a, X = F
b, X = OCH_3

47

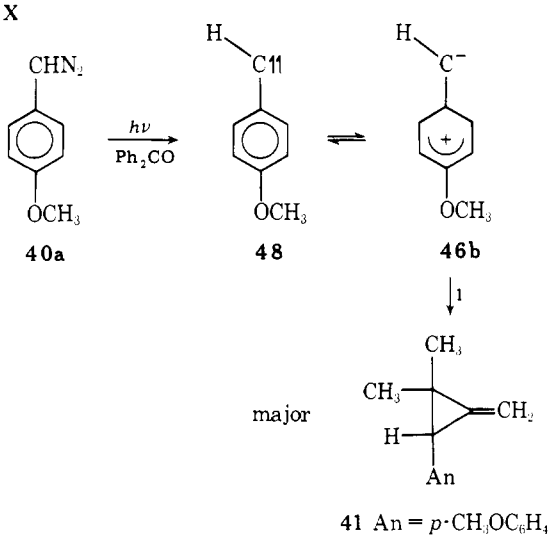
X = CF_3, CN, F, 3,5-di-Cl

singlet arylcarbenes. Previously, a limited number of arylcarbene selectivities had been measured in addition to olefins.[9,17] Although the carbenes showed selectivities favoring the more substituted olefins, no great differences were seen in the carbenes studied as a function of substituent. These results gave no indication of stabilizing or destabilizing substituent effects. Where, then, does the present study fit into the overall scheme of quantitative carbene studies? The 1,1-dimethylallene regioselectivity study complements the M_{CXY} approach introduced by Moss,[18] the recent thermal decomposition rate studies of Shechter,[19] and the log $k_r - \sigma$ approach (in which ρ values are determined for addition of carbenes to substituted styrenes) used by others.[20] All of these tools give pertinent information as to the features contributing to carbenic stabilities. The advantage of the regioselectivity tool is that real differences can be noted for substituted arylcarbenes even though the more tedious M_{CXY} tool (which works well for dihalo- and related carbenes) would probably lead to nondiscernible M_{CXY} values for substituted arylcarbenes.

Consider next the benzophenone-sensitized reactions of aryldiazomethanes with **1**. The methylenecyclopropane **41** to isopropylidenecyclopropane **42** ratios are more difficult to explain. The ratios are all *smaller* than in the direct irradiation experiments, indicative of increased triplet involvement by the regioselectivity criterion. However, the **41** to **42** ratio is not zero. Previously discussed triplet carbenes had given exclusively isopropylidenecyclopropanes. Now, in some cases, the isopropylidenecyclopropanes **42** are the minor products. For example, with electron donor substituents the methylenecyclopropanes **41** are the major products.

While one might suggest other rationalizations to explain the photosensitized reactions, one attractive explanation comes to mind. The similarity of the sensitized reaction product ratios with the direct irradiation product ratios in the cases of *p*-methoxyphenyldiazomethane, *p*-methylphenyldiazomethane, and *p*-fluorophenyldiazomethane (**40a–c**) suggests that the benzophenone-sensitized reactions are giving predominantly *singlet-derived* products. Since the ground states of many arylcarbenes have been suggested to be triplet,[21] this would require a rapid triplet to singlet interconversion in all of the cases studied, with the singlet being more reactive with **1** than the triplet. It is felt that electron donor substituents facilitate singlet formation as illustrated for *p*-methoxyphenyldiazomethane. With singlet destabilizing substituents such as CF_3, CN, *m*-Cl, etc., increased amounts of triplet-derived **42** are formed from the initially generated triplet state. Yet, even with these substituents, intersystem crossing to the singlet state remains important.

Scheme X



major

41 An = *p*-$CH_3OC_6H_4$

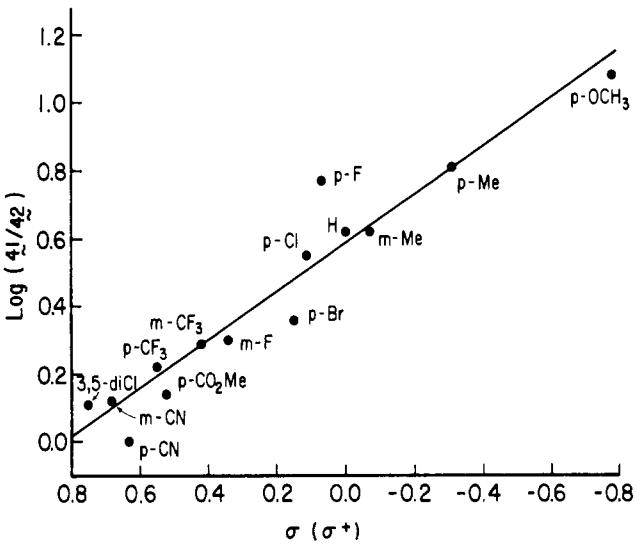


Figure 1. A plot of log (**41**/**42**) produced by photolysis of aryldiazomethanes in 1,1-dimethylallene vs. σ (σ^+).

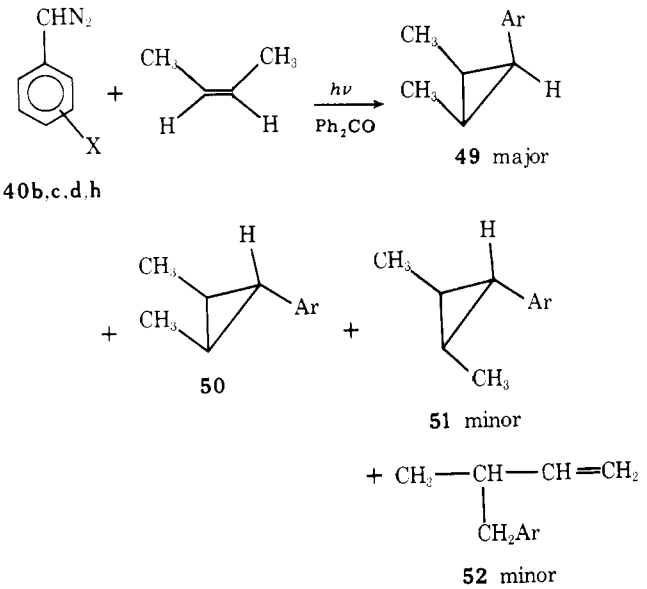
Table II. Yields of Products from the Benzophenone-Sensitized Decomposition of **40** in *cis*-2-Butene

	aryldiazomethane	product ratios **51**	**49 + 50**	**52**	total yield (%)
40b	*p*-$CH_3C_6H_4CHN_2$	2	98	trace	(80)
40c	*p*-$FC_6H_4CHN_2$	3	94	3	(72)
40d	$C_6H_5CHN_2$	7	89	4	(76)
40h	*m*-$FC_6H_4CHN_2$	20	60	10[a]	(64)

[a] Approximately 10% 5-(3-fluorophenyl)-2-pentene also produced.

We considered these results quite surprising and wanted further supporting evidence for the mechanistic suggestions. Table II gives the result of a limited study of benzophenone-sensitized reactions of aryldiazomethanes with *cis*-2-butene. Only minor amounts of the olefinic product **52** are produced. The reactions are all largely stereospecific as shown in Scheme XI, giving **49** and **50** as major products. As before, stereochemical assignments in cyclopropanes **49**, **50**, and **51** were based on the shielding effect of the syn aryl group on adjacent methyl groups in the ^1H NMR. Stereospecificity decreases with increasingly electronegative substituents. The trend is the same as the decreasing regioselectivity seen in the sensitized additions to **1**. The Skell stereoselectivity criterion again is in agreement with the regioselectivity probe and suggests that the solution chemistry of many monoarylcarbenes contains predominantly singlet character even when the triplet state is the initially generated state.

Intersystem crossing in carbenic systems is a topic of continuing interest.[22] The suggestion that singlet and triplet phenylcarbenes can interconvert has limited precedent. Closs and Moss[9a] have observed small amounts of nonstereospecific cyclopropanation products in the addition of phenyldiazomethane to *cis*- and *trans*-2-butene. The small amounts of cyclopropanation products produced from diphenyldiazo-



methane and *cis*-2-butene were largely stereospecific.[13] Baer and Gutsche[23] have found very similar behavior in the direct and photosensitized decomposition of *o*-butylphenyldiazomethane. Moritani, Yamamoto, and Marahashi[24] found significant amounts of stereospecific cyclopropanation products in the benzophenone-sensitized reaction of 1-phenyldiazoethane with *cis*-2-butene. All of these results imply that a certain amount of intersystem crossing can occur with interconversion from the triplet to the singlet state occurring in the latter two examples.

The present results imply a pronounced difference in the chemistry of triplet phenylcarbene generated in solution and the same species generated in a matrix. Moss[25] has shown that in the latter medium triplet phenylcarbene gives predominantly olefinic products by formal abstraction-recombination mechanisms. In contrast, the solution chemistry of triplet phenylcarbene at room temperature appears to involve largely intersystem crossing and resultant singlet chemistry. With singlet stabilizing substituents, the degree of singlet involvement can be increased to the point where triplet reactions are unimportant. With electronegative substituents, increasing amounts of triplet chemistry can be seen. These studies demonstrate the importance of intersystem crossing in determining the chemistry of solution-generated arylcarbenes and the influence of substituents on this intersystem crossing.

Conclusions

1,1-Dimethylallene reacts with singlet and triplet carbenes with different regioselectivities. This probe, along with the Skell stereospecificity criterion, indicates that phenylcarboethoxycarbene and many monoarylcarbenes react by way of the singlet state even when the triplet is the initially generated state. Diphenyl- and nitrophenylcarbenes react from the triplet state when the singlet is the initially generated state. Monoarylcarbene regioselectivity in reaction with 1,1-dimethylallene is very substituent dependent. The implication is that electron-donor substituents stabilize the singlet state and hence increase selectivity.

Experimental Section

Preparation of Diazo Compounds. The preparations of diphenyldiazomethane (**13**),[26] *m*-nitrophenyldiazomethane,[14] *p*-nitrophenyldiazomethane,[27] ethyl diazophenylacetate (**32**),[28] and *p*-methoxyphenyldiazomethane (**40a**)[9] have previously been described. Aryldiazomethanes **40b**,[9] **40d**,[9] **40f**,[f] **44**,[29] and **45**[30] have also previously been prepared but were prepared in the present case by the modified procedures described below.

Procedure A. Vacuum Pyrolysis Method.[31] The substituted benzaldehyde was added to a suspension of 1.05 equiv of tosylhydrazine in methanol. After 30 min, the precipitated tosylhydrazone was collected. In the cases where no tosylhydrazone crystallized, the solutions were treated directly with 1.1 equiv of sodium methoxide. The solid tosylhydrazones were redissolved in methanol containing 1.1 equiv of sodium methoxide. The solvents were removed by rotary evaporator and the solid residue was evacuated at 0.05 mm for 8 h. The residue was then pyrolyzed under vacuum in an oil bath at 80–160 °C with the receiver cooled in a dry ice–acetone bath. The red aryldiazomethane began to collect at an oil-bath temperature of about 100 °C. The aryldiazomethanes were redistilled at 0.1 mm. At this pressure, distillations occurred with little decomposition at or below room temperature. Aryldiazomethanes **40b** (52%), **40c** (59%), **40d** (76%), **40e** (55%), and **40h** (84%) were prepared by this method.

Procedure B. Ethylene Glycol Pyrolysis Method. Sodium (2 equiv) was dissolved in ethylene glycol and 1 equiv of the appropriate tosylhydrazone was added. When dissolution was complete, hexane was added. The tightly stoppered (hexane boils at 69 °C at 760 mm), stirred mixture was heated in an oil bath at 80–90 °C for 5-min intervals. The hexane extracts were periodically withdrawn and replaced with fresh hexane until the red-orange aryldiazomethane was no longer formed. The combined hexane extracts were washed with dilute sodium hydroxide solution and dried over sodium sulfate. The solvent was removed by rotary evaporator leaving the crude aryldiazomethane which was not further purified except for **40i** and **40j** which were distilled. Aryldiazomethanes **40i** (79%), **40j** (88%), **40f** (71%), **40g** (80%), **40k, 40l** (45%), **40m** (90%), **40n** (63%), and **44** (77%) were prepared by this method.

Preparation of 1-phenyl-2,2,2-trifluorodiazoethane (**45**) by mercuric oxide oxidation of trifluoroacetophenone hydrazone was not successful in our hands.[30] Hence the oxidation was carried out using $Pb(OAc)_4$.[32] A solution of 4.9 g of $Pb(OAc)_4$ in 18 mL of methylene chloride was cooled to −40 °C. A solution of 1.88 g of trifluoroacetophenone hydrazone in 5 mL of methylene chloride was added dropwise. The mixture was warmed to −10 °C and recooled to −40 °C and 1.5 g of triethylamine was added. An aqueous workup using ether extraction followed. Solvents were removed by rotary evaporator. Distillation gave 1.60 g (86%) of **45**, bp 28–30 °C (1.1 mm).

Photolysis of Diphenyldiazomethane (13) with 1,1-Dimethylallene (1). A solution of 80 mg of diphenyldiazomethane in 6.5 mL of **1** under nitrogen was freeze degassed at 0.05 mm and sealed in a Pyrex tube under vacuum. The tube was immersed in an ethanol–water mixture at −25 to −30 °C. The solution was irradiated with Pyrex-filtered light from a 450-W Hanovia medium-pressure lamp at this temperature for 75 min until the red color disappeared. The tube was opened at low temperature and the allene solvent was removed at −30 °C under vacuum. An NMR solution was prepared using cold $CDCl_3$. The NMR showed no trace of a methylenecyclopropane methyl singlet due to **19** which would be expected at approximately δ 0.85.[4] The entire product was chromatographed on 15 g of silica gel with pentane elution. Isopropylidenecyclopropane **16** eluted first followed by mixtures of **18** and **17**. Acetylene **17** eluted last. The total yield of chromatographed products was 63 mg (65%). Compounds **17** and **18** were identified by spectral comparison with authentic samples prepared as described below. The ratios of **16:17:18** were 6:2:1 as determined by gas chromatography on the crude photolysis mixture. NMR of **16** ($CDCl_3$): δ 7.25 (10 H, bs), 1.94 (6 H, m), 1.76 (2 H, m).

Reaction of Benzhydryl Chloride with 3,3-Dimethylallenyllithium. 3,3-Dimethylallenyllithium (**20**) was prepared as previously described[4b] from 0.75 g of **1** and 3 mL of 1.84 M methyllithium. Benzhydryl chloride (0.56 g) was added and the mixture was refluxed for 30 min. After an aqueous workup, the entire product was chromatographed on silica gel. Samples of **18** and **17** eluted in that order, which were spectrally identical with the photolysis products. The total yield of **17** and **18** was 0.36 g (55%). Approximately 200 mg of 1,1,2,2-tetraphenylethane also eluted after **18**. The ratio of **17** to **18** was 2:1 as determined by gas chromatography. NMR of **17** ($CDCl_3$): δ 7.8–7.1 (10 H, m), 3.64 (1 H, s), 2.34 (1 H, s), 1.28 (6 H, s). NMR of **18** ($CDCl_3$): δ 7.5–7.0 (10 H, m), 5.47 (1 H, m), 4.73 (1 H, d, J = 7 Hz), 1.58 (6 H, d, J = 3 Hz).

Photolysis of *p*-Nitrophenyldiazomethane (24a) in 1,1-Dimethylallene. A solution of 45 mg of **24a**[27] in 6 mL of 1,1-dimethylallene was freeze degassed at 0.05 mm and sealed in a Pyrex tube under vacuum. The tube was placed in a Griffin-Srinivasan photochemical reactor equipped with 350-nm lamps. The tube was irradiated for 40 min,

Table III. NMR Spectra (δ) of **41** and **42**

	compd	Ar	CH_2	HCAr	CH_3	other
41	(*p*-F)[a]	7.4–6.8	5.54	2.40	1.35, 0.83	
41	(*m*-CH_3)[a]	7.3–6.7	5.53	2.36	1.32, 0.83	2.32 (3 H, s)
41	(*m*-CF_3)[a]	7.7–7.2	5.67	2.53	1.38, 0.85	
41	(*p*-CF_3)[b]	7.6–7.2	5.59	2.50	1.37, 0.85	
41	(*p*-CO_2CH_3)[a]	8.1–7.1	5.61	2.40	1.38, 0.86	3.89 (3 H, s)
41	(*m*-CN)[b]	7.9–7.4	5.75	2.53	1.40, 0.85	
41	(3,5-diCl)[b]	7.4–7.0	5.65	2.42	1.37, 0.89	
41	(*p*-CN)[a]	7.9–7.3	5.68	2.53	1.40, 0.87	
42	(*p*-F)[a]	7.4–6.8	1.70, 1.10	2.52	1.93, 1.80	
42	(*m*-CH_3)[a]	7.3–6.7	1.70, 1.10	2.50	1.90, 1.78	2.33 (3 H, s)
42	(*m*-CF_3)[b]	7.7–7.2	1.70, 1.15	2.63	1.96, 1.82	
42	(*p*-CF_3)[b]	7.7–7.2	1.70, 1.14	2.60	1.94, 1.78	
42	(*p*-CO_2CH_3)[a]	8.1–7.1	1.70, 1.15	2.49	1.93, 1.78	3.89 (3 H, s)
42	(*m*-CN)[a]	7.7–7.3	1.73, 1.16	2.57	1.95, 1.82	
42	(3,5-diCl)[b]	7.4–7.0	1.70, 1.15	2.54	1.93, 1.80	
42	(*p*-CN)[a]	7.9–7.3	1.73, 1.15	2.58	1.94, 1.80	

[a] CCl_4. [b] $CDCl_3$.

during which time the color faded substantially. The solvent was removed under vacuum. The NMR of the crude residue showed only isopropylidenecyclopropane **25** (*p*-NO_2) and no trace of methyl singlets due to the isomeric methylenecyclopropane. Distillation at 0.05 mm gave 34 mg (61%) of **25** (*p*-NO_2). NMR of **25** (*p*-NO_2) ($CDCl_3$): δ 8.24–7.00 (4 H, AA′BB′ quartet), 1.90 (3 H, m), 1.78 (3 H, m), 2.60 (2 H, m), 1.70 (1 H, m), 1.10 (1 H, m).

Photolysis of *m*-Nitrophenyldiazomethane in 1,1-Dimethylallene. A solution of 45 mg of *m*-nitrophenyldiazomethane[14] in 5 mL of 1,1-dimethyl allene was irradiated as described above for *p*-nitrophenyldiazomethane for 80 min. The NMR of the crude residue showed **25** (*m*-NO_2) along with signals due to an unidentified product at δ 4.29 and 1.18. The yield was 36 mg (65%). NMR of **25** (*m*-NO_2) ($CDCl_3$): δ 8.3–7.0 (4 H, m), 1.90 (3 H, m), 1.80 (3 H, m), 1.70 (1 H, m), 1.10 (1 H, m).

Photolysis of *p*-Nitrophenyldiazomethane in *cis*-2-Butene. A solution of 50 mg of **24a** in 12 mL of *cis*-2-butene was sealed under vacuum and irradiated for 50 min in a Griffin-Srinivasan photochemical reactor at 350 nm. The crude residue after solvent removal was distilled at 0.05 mm, giving 45 mg (76%) of a mixture of **28, 29, 30,** and **31** in a 52:20:17:11 ratio, respectively, as determined by gas chromatography. Samples of each product were isolated by preparative gas chromatography using a 6-ft 5% SE-30 on Chromosorb G column at 135 °C. Structural assignments were made by NMR. NMR of **28** ($CDCl_3$): δ 8.3–7.20 (4 H, AA′BB′ quartet), 1.85 (1 H, doublet of doublets, J = 8, 5.5 Hz), 1.3–0.94 (5 H, m with bs at 1.23), 0.84 (3 H, AB doublet). NMR of **29** ($CDCl_3$): δ 8.2–7.0 (4 H, AA′BB′ quartet), 1.35–1.10 (9 H, m with bs at 1.23). NMR of **30** ($CDCl_3$): δ 8.3–7.2 (4 H, AA′BB′ quartet), 5.75–5.15 (2 H, m), 2.79 (2 H, t, J = 7 Hz), 2.40 (2 H, q, J = 7 Hz), 1.53 (3 H, d, J = 6 Hz). NMR of **31** ($CDCl_3$): δ 8.26–7.16 (4 H, AA′BB′ quartet), 5.76 (1 H, m), 5.02 (1 H, bs), 4.88 (1 H, broad doublet, J = 5 Hz), 2.84–2.36 (3 H, m), 1.04 (3 H, d, J = 7 Hz).

Benzophenone-Sensitized Photolysis of Ethyl Diazophenylacetate in 1,1-Dimethylallene. A solution of 65 mg of ethyl diazophenylacetate and 500 mg of benzophenone in 8 mL of **1** was degassed and sealed in a Pyrex tube at 0.1 mm. The solution was irradiated with Pyrex-filtered light from a 450-W Hanovia medium-pressure lamp at −10 °C for 40 min. The NMR of the crude photolysis products, after solvent removal, showed **33** and **34** in approximately a 4:1 ratio. Spectral data of **33** and **34** have previously been reported.[4a]

Photolysis of Ethyl Diazophenylacetate (32) in *cis*-2-Butene. A solution of 210 mg of **32** in 5 mL of *cis*-2-butene was sealed under vacuum and irradiated for 3 h using a 450-W Hanovia source. Distillation of the residue, after solvent removal, gave 226 mg (94%) of a mixture of **35** and **36**, bp 77 °C (0.14 mm). Samples of each product were isolated by preparative gas chromatography and structures were assigned by NMR. The ratio of **35** to **36** was 91:9 as determined by gas chromatography. NMR of **35** ($CDCl_3$): δ 7.5–7.0 (5 H, m), 4.04 (2 H, q, J = 7.5 Hz), 1.94 (2 H, m), 1.10 (3 H, t, J = 7.5 Hz), 0.96 (6 H, d, J = 6 Hz). NMR of **36** ($CDCl_3$): δ 7.5–7.0 (5 H, m), 4.10 (2 H, q, J = 7 Hz), 1.56 (2 H, m), 1.32 (6 H, d, J = 6 Hz).

Photolysis of 32 in *trans*-2-Butene. A solution of 140 mg of **32** in 7 mL of *trans*-2-butene was irradiated for 2 h using a 450-W Hanovia source. Distillation of the residue, after solvent removal, gave 139 mg (86%) of **37**, bp 62 °C (0.07 mm). NMR of **37** ($CDCl_3$): δ 7.5–7.0 (5 H, m), 4.09 (2 H, t, J = 7.5 Hz), 1.81 (1 H, q, J = 6 Hz), 1.40 (1 H, m), 1.30 (3 H, m), 1.14 (3 H, t, J = 7.5 Hz), 0.77 (3 H, d, J = 6 Hz).

Benzophenone-Sensitized Photolysis of 32 in *cis*-2-Butene. A solution of 70 mg of **32** and 500 mg of benzophenone in 8 mL of *cis*-2-butene was irradiated for 80 min at room temperature. Gas chromatographic analysis showed **35, 36,** and **37** in an 86:10:4 ratio. Samples of each product were isolated by preparative gas chromatography and identified by NMR spectral comparison with samples prepared as described above.

Benzophenone-Sensitized Photolysis of 32 in *trans*-2-Butene. A solution of 70 mg of **32** and 500 mg of benzophenone in 9 mL of *trans*-2-butene was irradiated for 30 min at room temperature. Gas chromatographic analysis showed **37** and no **35** and **36.** A sample of **37** was isolated by preparative gas chromatography and identified by NMR spectral comparison with the product produced in the direct irradiation described above.

Photolysis of Aryldiazomethanes 40 in 1,1-Dimethylallene. General Procedure for the Direct Irradiation. A solution of the appropriate aryldiazomethane **40** (60–80 mg) in approximately 7 mL of **1** was freeze degassed and sealed in a Pyrex tube at 0.1 mm. The tube was irradiated with Pyrex-filtered light from a 450-W Hanovia medium-pressure source until the color due to **40** disappeared (approximately 3 h). The crude mixtures were analyzed by gas chromatography for **41** and **42** in the cases of the more volatile products where rearrangement of **41** to **42** did not occur thermally on the column. Reactions of **40b–f,h–j** and **45** were so analyzed. In the case of **40a,g,k,l,m,n** and **44,** the crude photolysis mixture, after removal of the solvent under vacuum, was analyzed by NMR integration of the signals due to the two products. Allenes **43** were produced in trace amounts from **40a–e** and increasing amounts (up to 10%) from **40f–n.** Product mixtures were then isolated by distillation at 0.05 mm. Yield of products so isolated are given in Table I. NMR spectral data for **41** and **42** (*p*-H, *p*-CH_3, *p*-OCH_3, *p*-Cl, *p*-Br, *m*-F, 1-naphthyl) have been reported.[4] Data for the remaining products **41** and **42** are given in Table III.

Photolysis of 40 in 1,1-Dimethylallene. General Procedure for the Benzophenone-Sensitized Irradiation. A solution of the appropriate aryldiazomethane **40** (50–60 mg) and approximately 500–600 mg of benzophenone in approximately 7 mL of **1** was degassed and sealed in a Pyrex tube at 0.1 mm. Irradiation times were of the order of 45 min for complete reaction of **40** as compared to 3 h for the direct irradiations. The more volatile products were analyzed by gas chromatography as previously described. In the other cases, benzophenone was removed by silica gel chromatography with pentane elution before NMR analysis for **41** and **42.** In a control experiment, doubling the amount of benzophenone did not change the ratio of **41** and **42** produced from **40d.** The yields given in Table I are isolated yields after removal of the benzophenone by silica gel chromatography.

Photolysis of 40 in *cis*-2-Butene. General Procedure for the Benzophenone-Sensitized Irradiation. *cis*-2-Butene (approximately 6 g) was condensed into a tube containing the appropriate aryldiazo-

methane (80 mg) and 700 mg of benzophenone. After sealing at 10 mm, photolysis was begun under the conditions described. The crude photolysis products were analyzed by gas chromatography after removal of the excess butene. Structures of products were assigned by NMR[9a] of samples isolated by gas chromatography following chromatography on silica gel or distillation to remove the benzophenone. Yields are given in Table II.

Benzophenone-Sensitized Photolysis of 40b in *cis*-2-Butene. A solution of 95 mg of *p*-toluyldiazomethane (**40b**) and 750 mg of benzophenone in 6.3 g of *cis*-2-butene was irradiated for 120 min. The total yield of products was 92 mg (80%). Structural assignments were made by NMR spectral comparison with previously published[9a] data on **49, 50,** and **51** (Ar = *p*-toluyl).

Benzophenone-Sensitized Photolysis of 40c in *cis*-2-Butene. A solution of 70 mg of *p*-fluorophenyldiazomethane (**40c**) and 650 mg of benzophenone in 6.4 g of *cis*-2-butene, after irradiation for 80 min, gave 61 mg (72%) of products. Structural assignments were based on NMR spectral data. NMR of **49** (Ar = *p*-F-C_6H_4) ($CDCl_3$): δ 7.25–6.80 (4 H, m), 1.92 (1 H, t, J = 8.5 Hz), 1.14 (2 H, m), 0.92 (6 H, AB doublet, J = 5 Hz). NMR of **50** (Ar = *p*-F-C_6H_4) ($CDCl_3$): δ 7.2–6.8 (4 H, m) 1.56 (1 H, m), 1.3–1.0 (8 H, m with bs at 1.14). NMR of **51** (Ar = *p*-F-C_6H_4) ($CDCl_3$): δ 7.4–6.8 (4 H, m), 1.70 (1 H, t, J = 6 Hz), 1.4–0.7 (8 H, m, with CH_3 doublet at 1.20 and CH_3 broad singlet at 0.80). NMR of **52** (Ar = *p*-F-C_6H_4) ($CDCl_3$): δ 7.6–6.8 (4 H, m), 5.80 (1 H, m), 5.00–4.80 (2 H, m), 2.55 (3 H, m), 1.00 (3 H, d, J = 6 Hz). A trace of 5-(4-fluorophenyl)-2-pentane, which was not separated by gas chromatography, could be seen in the spectrum of **50** (Ar = *p*-F-C_6H_4).

Benzophenone-Sensitized Photolysis of 40d in *cis*-2-Butene. A solution of 90 mg of phenyldiazomethane and 750 mg of benzophenone in 6.4 g of *cis*-2-butene, after irradiation for 15 min, gave 84 mg (76%) of products. Structural assignments were made by spectral comparison with previously published data on **49**,[9a] **50**,[9a] **51**,[9a] and **52**[25a] (Ar = Ph). A trace of 5-phenyl-2-pentene,[25a] which was not separated by gas chromatography, could be seen in the spectrum of **50** (Ar = Ph).

Benzophenone-Sensitized Photolysis of 40h in *cis*-2-Butene. A solution of 85 mg of *m*-fluorophenyldiazomethane (**40h**) and 700 mg of benzophenone in 6.0 g of *cis*-2-butene, after irradiation for 90 min, gave 66 mg (64%) of products. Structural assignments were based on NMR spectral data. NMR of **49** (Ar = *m*-FC_6H_4) ($CDCl_3$): δ 7.4–6.7 (4H, m), 2.01 (1 H, t, J = 8.5 Hz), 1.15 (2 H, m), 0.96 (6 H, AB doublet). NMR of **50** (Ar = *m*-FC_6H_4) ($CDCl_3$): δ 7.4–6.6 (4 H, m), 1.3–1.0 (8 H, m with bs at 1.18). NMR of **51** (Ar = *m*-FC_6H_4) ($CDCl_3$): δ 7.4–6.7 (4 H, m), 1.75 (1 H, t, J = 6 Hz). 1.3–0.7 (8 H, m, with CH_3, AB doublet at 1.18 and CH_3 broad singlet at 0.83). NMR of **52** (Ar = *m*-FC_6H_4) ($CDCl_3$): δ 7.5–6.8 (4 H, m), 5.80 (1 H, m), 5.16–4.84 (2 H, m), 2.6 (3 H, m), 1.00 (3 H, d, J = 6 Hz). A significant amount (approximately 10%) of 5-(3-fluorophenyl)-2-pentene, which was not completely separated from **50,** was produced in this reaction. NMR of 5-(3-fluorophenyl)-2-pentene ($CDCl_3$): δ 7.4–6.8 (4 H, m), 5.55 (2 H, m), 2.72 (2 H, m), 2.43 (2 H, m), 1.60 (3 H, d, J = 5 Hz).

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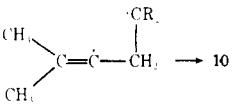
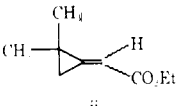
(8) A referee has suggested that addition of triplet carbenes to the unsubstituted double bond of **1** due to steric factors could account for the observed triplet regioselectivity. This would require the formation of i followed by closure



i

to give **10.** We cannot rule out this mechanism with the available data. However, we prefer the mechanism given in Scheme II in light of the propensity for other radicals to attack the central carbon of **1.** See ref 6. Additionally, energetic considerations also favor the formation of **8** (via **7**) over i, a vinyl radical. Radical i should be considerably less stable (approximately 30 kcal/mol) than the corresponding tertiary and allylic radicals represented by **7** and **8.** We have also previously reported[4a] that, in the benzophenone-sensitized reaction of ethyl diazoacetate with **1,** 30% of the cyclopropanation products were esters ii, in addition to 54% of the isopropyli-



ii

denecyclopropane. We feel that the formation of ii is best accounted for by the intervention of a trimethylenemethane and not by an intermediate such as i. While this does not prove the involvement of trimethylenemethanes in the present cases, the analogies are obvious. For these reasons we prefer the mechanism in Scheme II to the alternative mechanism involving i.
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