

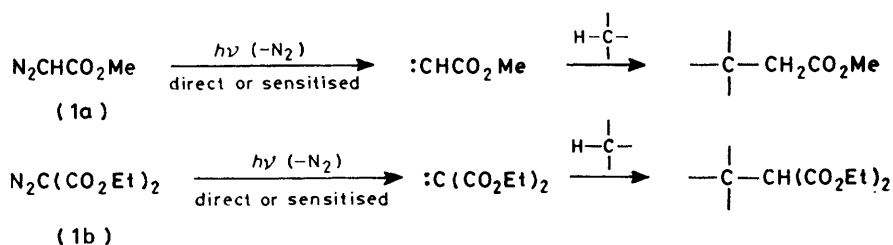
The Reactivity of Carbenes from Photolysis of Diazo-compounds towards Carbon-Hydrogen Bonds. Effects of Structure, Temperature, and Matrix on the Insertion Selectivity

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Direct and/or sensitized photolyses of diazo-acetate (1a) and -malonate (1b) in hydrocarbons and ether were investigated at various temperatures in order to learn more about the nature of the C-H insertion process and the structural factors governing positional selectivity within the matrix. Photolysis of the diazo-compounds in a rigid matrix resulted in a marked decrease in the insertion selectivity, which may be interpreted as indicating that the matrix imposes severe steric demand especially on the direct C-H insertion process of the singlet carbene. The addition of a sensitizer in matrix photolysis causes a marked increase in the selectivity in the case of (1a), as is observed in the comparable liquid-phase experiment, but it causes a decrease in the case of (1b). This is interpreted as suggesting that the excited triplet (1b) itself is involved in C-H insertion under these conditions. More extensive temperature studies show that, as the temperature decreases, the C-H insertion selectivity of $\text{:CHCO}_2\text{R}$ decreases regularly regardless of the reaction phase, whereas that of $\text{:C(CO}_2\text{R)}_2$ increases in the liquid phase but decreases in the solid phase. This difference in the temperature dependence is explained by assuming that the singlet carbene is responsible for the C-H insertion of $\text{:CHCO}_2\text{R}$ throughout the temperature range studied, while both singlet and triplet are involved in the insertion of $\text{:C(CO}_2\text{R)}_2$.

THE importance of the method of generation of a carbene on its chemical behaviour has become evident in recent years. Among examples which may be cited, arylcarbene, when generated by the photolysis of aryldiazo-compounds at ambient temperatures in alcohols, gives the O-H insertion products almost exclusively, but, when the photolysis is carried out at -196°C , C-H insertion products gain at the expense of the O-H insertion product.¹ Similarly, the major reaction of

as liquid-phase experiments. Thus, the results have been interpreted³ as indicating that matrix not only selects the multiplicity of arylcarbenes, but it also imposes a severe steric demand on carbene processes within it. There is still some ambiguity, however, as to which multiplicities are responsible for the dominance of the primary C-H insertion product in the solid-phase experiments. Attempts to determine the multiplicity are generally met with the problems that absorption of



arylcarbenes generated in olefinic matrices is C-H insertion into rather than addition to olefins.² The main factor that has been proposed to account for these differences is spin multiplicity. Therefore, the C-H 'insertion' products in a rigid matrix have been assumed to be derived from triplet carbene apparently *via* an abstraction-recombination mechanism. The method was thus expected to serve as a useful adjunct in the investigation of the relationship between the multiplicity and reactivity patterns of the carbene. Similar temperature studies on the C-H insertion selectivity of arylcarbene in hydrocarbons with various C-H bonds show,³ however, that the selectivity decreases dramatically in the matrix environment; primary C-H insertion is highly favoured over secondary and/or tertiary C-H insertion. This is completely unexpected behaviour since triplet carbenes have been shown to be much more selective intermediates in the C-H insertion reaction than the corresponding singlets for gas- as well

long wavelength light by most of the precursor aryldiazo-compounds makes the sensitization experiment difficult and, more importantly, most arylcarbenes are known⁴ to undergo rapid and reversible singlet-triplet equilibrium. Mono- and bis-alkoxycarbonylcarbenes seemed a good choice for determining the multiplicity of a reacting carbene within a matrix as there is evidence which demonstrates that benzophenone-sensitized photolysis of the precursor diazo-compounds, *i.e.* diazo-acetate and -malonate, does result in the almost exclusive formation of triplet carbene in the liquid^{4,5} as well as solid phases.⁶ Thus, to learn more about the nature of the C-H insertion process and the structural factors governing positional selectivity within a rigid matrix, we carried out temperature studies of the direct and sensitized photolysis of methyl diazoacetate (1a) and diethyl diazomalonate (1b) in hydrocarbons and ether and found that temperature dependence was highly dependent on the carbene structure.

RESULTS AND DISCUSSION

Insertion Selectivity of Mono- and Bis-alkoxycarbonyl-carbenes into C-H Bonds of Isobutane and n-Pentane.—A solution of diazo-compounds in n-pentane or isobutane with or without benzophenone was irradiated at

TABLE 1

Relative yield of C-H insertion products in photolysis of diazoacetate (1a) in n-pentane and isobutane

Substrate	Conditions	Ratio	Relative ratio ^a	Relative yield ^b
n-Pentane	20 °C-hν	Secondary/ primary	2.2	1.00
	20 °C-hν-Ph ₂ CO		6.4	0.45 ^c
	-196 °C-hν	Tertiary/ primary	0.75	0.15 ^d
	-196 °C-hν-Ph ₂ CO		1.5	0.24 ^d
Isobutane	20 °C-hν	Tertiary/ primary	2.5	1.00
	20 °C-hν-Ph ₂ CO		7.2	0.47 ^c
	-196 °C-hν	Tertiary/ primary	1.8	0.08 ^d
	-196 °C-hν-Ph ₂ CO		3.8	0.49 ^d

^a Corrected for number of hydrogens. Averages of triplicate runs are tabulated; reproducibility was $< \pm 5\%$. ^b Relative total yields of C-H insertion product are indicated. Total yield in direct photolysis at 20 °C is 55–65%. Note that the diazo-esters employed in the photochemical reactions in an attempt to generate carbene have suffered from loss of reagent during photolysis because of Wolff rearrangement (see for examples, V. Chowdhry and F. H. Westheimer, *J. Amer. Chem. Soc.*, 1978, **100**, 309). ^c Roughly equal amounts of (7) and (8) are detected. ^d Decrease in the total yield in the matrix run is presumably due to the aggregation of the precursor diazo-ester molecules in the crystalline matrix. Such aggregation is known to result in the formation of XYC=CXY and/or XYCH-CHXY instead of the expected C-H insertion products (see ref. 1b and references cited therein). Note also that the total yields in ethyl ether which forms a glass-like matrix upon cooling do not change appreciably over the temperature range studied, including liquid and solid runs (see Table 3).

different temperatures as described in the Experimental section and the solution was analysed by g.l.c., each product being identified by comparison of its retention time with that of an authentic sample. The relative

of the product during the irradiation. Tables 1 and 2 give the observed distributions of the esters derived from C-H insertion [equations (1) and (2)] in both liquid- and solid-phase photolysis of (1). In all cases the results are averages of two or three experiments under comparable conditions. Other products detected were the double hydrogen-abstraction product (7) and the free-radical dimerization product (8). Direct photolysis in the liquid phase complements earlier suggestions^{5a,7} that the order of reactivity of each carbene is tertiary C-H > secondary C-H > primary C-H and that bis-alkoxycarbonylcarbene is more discriminating in the

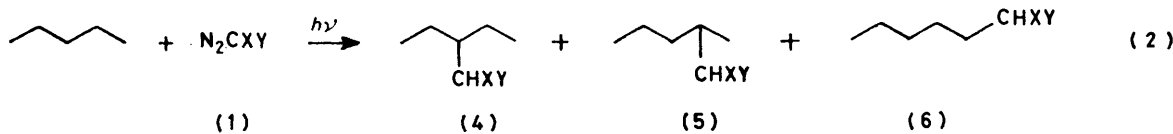
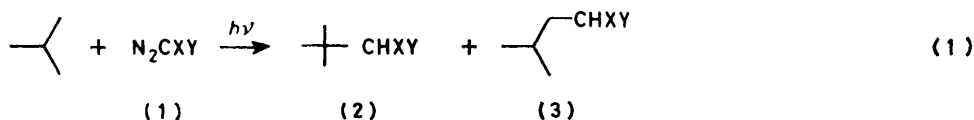
TABLE 2

Relative yield of C-H insertion products in photolysis of diazomalonnate (1b) in n-pentane and isobutane

Substrate	Conditions	Ratio	Relative ratio ^a	Relative yield ^b
n-Pentane	20 °C-hν	Secondary/ primary	5.1	1.00
	20 °C-hν-Ph ₂ CO		7.2	0.24
	-196 °C-hν	Tertiary/ primary	2.8	0.06
	-196 °C-hν-Ph ₂ CO		0.8	0.21
Isobutane	20 °C-hν	Tertiary/ primary	43.5	1.00
	20 °C-hν-Ph ₂ CO		50.9	0.47
	-196 °C-hν	Tertiary/ primary	11.5	0.11
	-196 °C-hν-Ph ₂ CO		4.2	0.20

^a Corrected for number of hydrogens. Averages of duplicate runs are tabulated; reproducibility was $< \pm 4\%$. ^b Relative total yields of C-H insertion products are indicated. Total yield in direct photolysis at 20 °C is 50–60%. See also footnotes c and d on Table 1.

C-H insertion than monoalkoxycarbonylcarbene. The principal features in the sensitized run in liquid phase are an increase in the insertion selectivity, a complementary sharp decrease in the total yield, and the appearance of products expected from a free radical, *i.e.* (7) and (8). These phenomena are in keeping with the Jones' indication^{5a} that direct irradiation produces



a; X = H, Y = CO₂Me

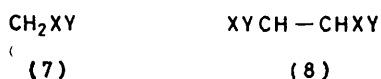
b; X = Y = CO₂Et

reactivities for insertion of each carbene into tertiary, secondary, and primary C-H bonds at different temperatures were also determined by g.l.c. on the basis of the yields of the products. Total absolute yields for the products were *ca.* 50–65% in direct photolytic runs at room temperature but varied with the reaction conditions. Control experiments ruled out the interconver-

an intermediate, *i.e.* singlet carbene, which gives only insertion products with little free-radical products, while sensitized decomposition produces an intermediate, *i.e.* triplet carbene, that gives the 'insertion' products *via* an abstraction-recombination (a-r) mechanism which also accounts for the formation of (7) and (8). This also implies that part of the apparent selectivity of triplet

carbene can be attributed to the selectivity of the abstraction reaction.

The results of solid phase photolysis are particularly noteworthy. Thus, direct photolysis of diazoacetate (1a) in rigid hydrocarbon matrices at -196°C resulted in a dramatic decrease in the insertion selectivity, whereas sensitized photolysis of (1a) in a rigid matrix again resulted in a marked increase in selectivity as observed for the comparable liquid-phase experiments (Table 1). The marked decrease in selectivity in the direct run is identical behaviour to that observed³ previously for arylcarbene systems, which has a ground state triplet and may be interpreted as indicating that the matrix also imposes a steric demand on the C-H insertion process of this carbene. This is, however, in



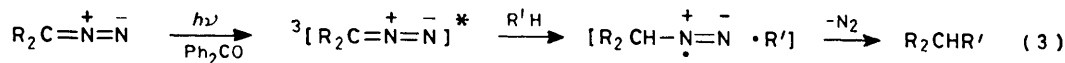
- a; X = H, Y = CO_2Me
b; X = Y = CO_2Et

sharp contrast with the results obtained in alcoholic matrices. Thus, methoxycarbonylcarbene generated in an alcoholic matrix at -196°C failed⁸ to show the predominant triplet carbene chemistry in spite of e.s.r. evidence⁶ that it has a triplet ground state. Most arylcarbenes, on the other hand, have been shown¹ to undergo C-H insertion in alcoholic matrices presumably *via* the triplet. This difference has been explained⁸ by assuming that at -196°C the matrix is not cool enough to quench singlet methoxycarbonylcarbene to the triplet owing to its high reactivity. These facts seem to suggest that the singlet is not quenched in the -196°C hydrocarbon matrix and hence is responsible for the dominance of the primary C-H insertion product in the solid-phase run. This assignment may be rationalized by the following considerations for the mechanisms of C-H insertion. There is experimental⁹ as well as theoretical¹⁰ evidence which supports a mechanism involving direct attack of carbene on the C-H bond itself through a triangular transition state, as suggested by Doering¹¹ and Skell.¹² Obviously such a transition state suffers from the lower steric accessibility of tertiary and/or secondary C-H bonds than that of the alternative mechanism proposed by DeMore and Benson,¹³ in which insertion and abstraction of carbene both begin with an incipient abstraction. Moreover, this steric hindrance should be much greater in a rigid environment than in the liquid phase. Consequently, a primary C-H insertion process is favoured over tertiary and/or secondary C-H insertion, despite the fact that the latter is energetically more favourable. The marked reduction in the absolute yield of C-H insertion products in this run indicates that singlet C-H insertion is highly unfavourable because of steric hindrance and hence most carbenes probably undergo other available intermolecular and/or intramolecular processes.⁴ Further support for the above assignment was lent by the sensitized photolysis

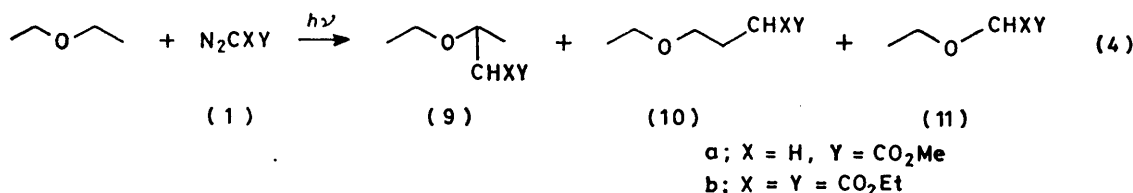
of (1a), indicating that a more selective intermediate, *i.e.* the triplet carbene, intervenes even in a rigid matrix. Although triplet sensitization within a rigid matrix is relatively limited,¹⁴ the fact⁶ that the e.s.r. signal intensities of triplet methoxycarbonylcarbene upon photosensitized decomposition of (1a) at 10–40 K have been shown to be an order of magnitude higher than those in direct runs clearly indicates that triplet sensitization occurs in this case even at the lower temperatures. Furthermore, sensitized photolysis of (1a) in an alcoholic matrix at -196°C has resulted⁸ in a marked increase in the C-H insertion product, which might be derived from triplet carbene *via* an a-r mechanism. It is quite surprising to note that triplet carbene can exhibit considerable discrimination towards C-H insertion even in a rigid matrix in spite of the evidence that molecular motions are¹⁵ probably severely restricted within the matrix cage and hence the carbene seems not to have enough freedom to select C-H bonds to react. Presumably, small molecules like methoxycarbonylcarbene can diffuse to some degree within the cage of the matrix. Moreover, the triplet carbene would afford C-H 'insertion' products *via* the a-r mechanism whose transition state may be less sterically affected and more energetically favoured compared with that for the singlet carbene insertion discussed above. A marked increase in the total yield of the C-H insertion products in the sensitized run indicates that hydrogen abstraction by the triplet carbene from C-H bonds of lower bond energy occur relatively easily even at low temperature and, more importantly, subsequent coupling of the radical pairs to the apparent C-H 'insertion' products is quite efficient in the matrix environment because of the limited diffusion. This is in marked contrast with the results of sensitized experiments in the liquid phase, in which diffusion of the radical pairs is efficient, forming the escape product, *e.g.* (7a) as the main product. Further, triplet carbene appears to have no other available pathway as does the singlet.

The behaviour of bisethoxycarbonylcarbene in a rigid matrix was also examined in connection with the difference in the reactivity patterns between mono- and bis-alkoxycarbonylcarbene frequently noted⁴ in the liquid-phase experiments. The results listed in Table 2 showed that bisethoxycarbonylcarbene also gave a marked decrease in the insertion selectivity as the reaction phase changed from liquid to solid. This can be explained similarly in terms of the steric strain advanced above. In sharp contrast with the behaviour of $:\text{CHCO}_2\text{Me}$, however, the presence of Ph_2CO in the matrix photolysis of (1b) caused a much more marked increase in the relative yield of the primary C-H insertion product. This is completely unexpected and quite amazing. Several explanations may be offered for this difference. First, a triplet carbene with two ethoxycarbonyl groups may be more crowded than the singlet due to a larger bond angle and hence suffer from greater hindrance to the accessibility of tertiary and/or secondary C-H bonds. But this possibility was rejected since the

comparable chemical behaviour of $\text{:CHCO}_2\text{R}$ clearly indicates that the C-H insertion process for the triplet carbene was more affected by the energy factor than the steric one even in a rigid matrix. A second and more probable explanation is that the free triplet carbene is



not involved in the C-H insertion process in the sensitized photolysis of (1b) within the matrix. It is of particular interest to note here that, while the sensitized photodecomposition of diazoacetate has been demonstrated¹⁶ to proceed *via* energy transfer, the sensitized photolysis of diazomalonate has been explained¹⁷ in terms of chemical sensitization, initiated by a ketyl radical which decomposes the diazo compound either by hydrogen



transfer or by radical addition. The chemical sensitization mechanism proposed in the liquid phase is apparently not applied to account for the results in the solid run since this process requires diffusion of a large molecule, which is highly improbable in a rigid matrix. A more probable intermediate would be, then, the excited triplet (1b) itself. Thus, hydrogen abstraction by an excited diazo-carbon, followed by loss of nitrogen and coupling of the resulting radical pairs, resulted in the formation of the C-H 'insertion' product [reaction (3)]. Apparently, initial hydrogen abstraction by the excited precursor diazo-compound would suffer from steric hindrance more severely than that from the free triplet carbene because the diazo-carbon undergoing abstraction is blocked by a large diazo-group, whereas the carbene will be much less affected by the highly diffusible nitrogen leaving group. Moreover, it has been proposed¹⁸ recently that the C-H insertion product in the photolysis of (1b) in cyclohexene solution can be explained in terms of direct attack by the photoexcited diazo-compound without invoking the free carbene intermediate even at ambient temperature. From this, one can expect that the photoexcited diazo-compound would survive long enough to abstract hydrogen at this low temperature before it loses nitrogen.

Selectivity for Insertion and Displacement in Diethyl Ether. Temperature and Matrix Effects.—The effects of temperature and sensitizer on product distribution for the photolysis of (1a and b) in ethyl ether are listed in Table 3. The trends of temperature and sensitizer on the C-H insertion selectivity were similar to those observed in hydrocarbons; a decrease in the selectivity in the rigid matrix and the reverse effect of sensitizer on the selectivities of mono- and bis-alkoxycarbonyl-

carbenes within the matrix were observed. An important pathway in the reaction with the ether is C-O displacement to give (11) [equation (4)]. Among several *a priori* mechanisms for the displacement reaction, a widely quoted one¹⁹ is electrophilic attack of singlet

carbene on the lone pair of electrons to form an ylide intermediate which then undergoes the Stevens rearrangement and/or Hoffmann-type β -elimination. The suppression of this process by the sensitizer supports this explanation. It should be noted that the process was also suppressed in a rigid matrix at low temperature. This also supports the above assignment since a singlet carbene reaction is generally suppressed at lower tem-

peratures. In order to explore the detailed effect of temperature upon both insertion and displacement processes, we have examined more extensive temperature studies and results are shown in Figures 1 and 2 as a function of T^{-1} . As the temperature decreases, the ratio of displacement to C-H insertion, (11)/[(9) + (10)],

TABLE 3

Relative yield of C-H insertion (9) and (10) and displacement products (11) in photolysis of diazo-acetate (1a) and -malonate (1b) in ethyl ether^a

Diazo-compound	Conditions	Relative ratio	
		Secondary/primary ^b	(11)/[(9) + (10)] ^c
Diazoacetate (1a)	20 °C- $h\nu$	7.3	0.93
	20 °C- $h\nu$ -Ph ₂ CO	10.2	0.28
	20 °C- $h\nu$ -Q ^d	6.9	0.89
	-196 °C- $h\nu$	2.5	0.06
	-196 °C- $h\nu$ -Ph ₂ CO	7.9	0.12
Diazomalonate (1b)	20 °C- $h\nu$	91.5	1.31
	20 °C- $h\nu$ -Ph ₂ CO	110	0.12
	20 °C- $h\nu$ -Q ^d	36.8	1.06
	-196 °C- $h\nu$	28.5	0.32
	-196 °C- $h\nu$ -Ph ₂ CO	9.9	0.11

^a Total yields of (9)–(11) are 65–70% over the temperature ranges studied for direct runs. Addition of the sensitizer reduces the yield to *ca.* 40%. ^b Corrected for number of hydrogens. Averages of triplicate runs: reproducibility was $\pm 3\%$. ^c Product ratio. ^d Five-molar excess of piperylene is added.

decreases rather steeply in the liquid phase but less steeply in the solid for each carbene system. The temperature dependence of the C-H insertion selectivity, on the other hand, was completely different in the two carbene systems. Thus, as the temperature decreases, the selectivity of methoxycarbonylcarbene decreases regularly regardless of the reaction phases, whereas that of bisethoxycarbonylcarbene increases in the liquid

phase but decreases when the reaction phase changes from liquid to solid. The fact that singlet $\text{:CHCO}_2\text{Me}$ is involved in the C-H insertion process even in a rigid hydrocarbon matrix suggests that the singlet is also involved in the C-H insertion of ether throughout the temperature range studied and that a steady decrease in the selectivity might reflect increasing steric strain

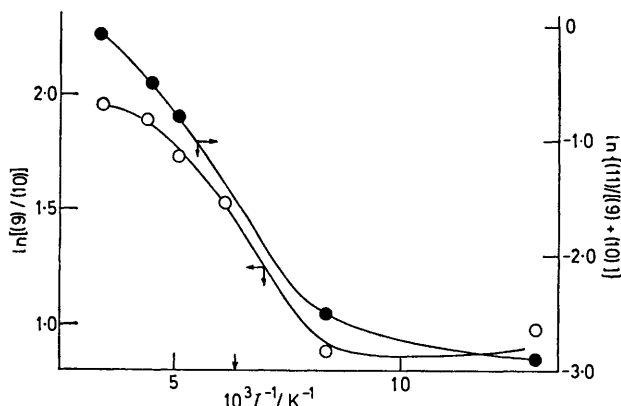


FIGURE 1 Ratios of secondary/primary (○) and displacement/insertion (●) as a function of temperature in the photolysis of (1a) in ethyl ether. The point marked \downarrow represents the freezing point of ether

superimposed on the triangular transition state as the solvent viscosity increases with a decrease in temperature. It is noteworthy that the alternative process, *i.e.* displacement of the singlet $\text{:CHCO}_2\text{R}$ was almost completely damped at lower temperature. This suggested that the latter process has a higher activation energy. Alternatively, the reason for this difference in the temperature dependence of two competitive processes probably lies

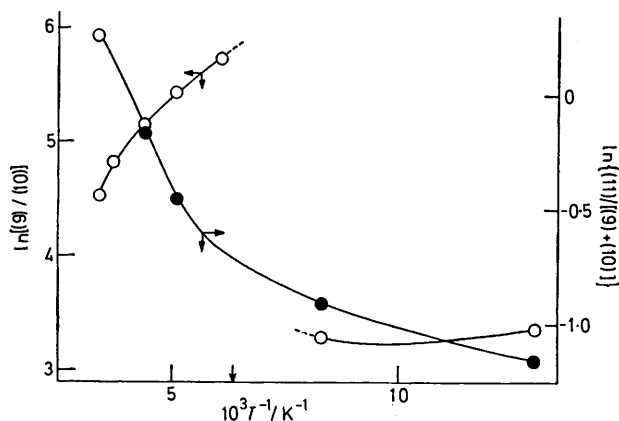


FIGURE 2 Ratios of secondary/primary (○) and displacement/insertion (●) as a function of temperature in the photolysis of (1b) in ethyl ether. The point marked \downarrow represents the freezing point of ether

partly in the ramifications of stabilization by solvation. Thus, the ylide intermediate leading to the displacement product might be more assisted¹ by solvation than that leading to C-H insertion in which the separation of charge is not required.

The inversion of secondary/primary selectivity with temperature observed for $\text{:C(CO}_2\text{Et)}_2$ insertion was

similar to that observed³ for the arylcarbene system. This implies that not only temperature but also the matrix has an effect on the course of C-H insertion. Thus, in solution, secondary abstraction gains over primary abstraction as the temperature decreases because secondary abstraction is favoured by a lower activation energy. After the matrix is formed, a continued decrease of temperature hardens the matrix and the increasing rigidity then causes primary abstraction to gain relative to secondary abstraction. Taking into account the above assignment that singlet carbene is responsible for the decrease in selectivity in the low temperature liquid phase, in $\text{:C(CO}_2\text{Et)}_2$, it is the triplet that produces the secondary C-H insertion product more selectively. Obviously, hydrogen abstraction at a secondary carbon by the triplet proceeds with considerably more facility than at a primary carbon. Presumably, as the temperature decreases, triplet carbene chemistry gains because of the increasing steric hindrance to the singlet process. This is, however, not observed in the C-H insertion of $\text{:CHCO}_2\text{Me}$ which reacts *via* a singlet over the temperature range studied and is attributable to the reactivity difference between singlet and triplet carbenes for each carbene system. Apparently, the activation energy for the formation of the radical, *i.e.* $\cdot\text{CH(CO}_2\text{R)}_2$, from $\text{:C(CO}_2\text{R)}_2$ would be much lower than that of $\cdot\text{CH}_2\text{CO}_2\text{R}$ from $\text{:CHCO}_2\text{R}$. Therefore, one can expect that the triplet $\text{:C(CO}_2\text{R)}_2$ has comparable reactivity with the singlet and comes to participate in the reaction as the temperature decreases, whereas the reactivity of singlet $\text{:CHCO}_2\text{R}$ is so high compared with that of the triplet that it is not quenched by lowering the temperature. Support is lent to the above explanation by the quenching effect on the insertion selectivity. For example, addition of piperylene, an efficient quencher for both triplet excited state and triplet carbene, caused a marked decrease in the C-H insertion selectivity of $\text{:C(CO}_2\text{R)}_2$ at ambient temperature, whereas that of $\text{:CHCO}_2\text{R}$ was essentially unaltered by the quencher. This implies that a triplet state is involved at least in part in the C-H insertion process even in the direct photolysis of $\text{N}_2\text{C(CO}_2\text{R)}_2$. Furthermore, intervention of triplet carbene in the direct photolysis of (1b) has been indicated similarly by Ando *et al.*^{17a}

There remains some ambiguity as to which multiplicity is responsible for the dominance of the primary C-H insertion product in the solid-phase experiments in the case of bisethoxycarbonylcarbene. Apparently steric demand in the rigid matrix is much more severe for the direct singlet insertion process. However, the hydrogen-abstraction process for the triplet suffers from equally severe steric hindrance in this case because the carbene centre is blocked by the two ethoxycarbonyl groups.

Concluding Remarks.—We believe that the present study constitutes a first attempt to determine the multiplicity of the reacting carbene within the matrix. The suggestion that the C-H insertion process of $\text{:CHCO}_2\text{R}$ proceeds *via* its singlet state throughout the

temperature range studied in spite of the fact that an alternative singlet process, *i.e.* displacement, is almost completely dampened, is most important in connection with the earlier proposal that triplet carbene is responsible for the dominance of the C-H insertion product in alcoholic¹ as well as olefinic² matrices. Rather, this implies only that the process initiated by electrophilic attack of singlet carbene on lone-pair electrons becomes less important compared with the alternative C-H insertion process as the temperature is lowered. This does not, therefore, support the earlier interpretation^{1,2} that singlet carbene generated in a matrix at low temperature, and restricted in the matrix, decays to the lower-lying triplet faster than the alternative reaction. We do not, however, intend to employ a similar interpretation to explain the temperature dependence of the chemical reactivity of carbene with quite different structures. But it sheds some light on the factor by which the matrix controls the several facets of carbene reactivity. One more noteworthy feature pointed out by the present study is that a non-carbene process in the C-H insertion is important in the photolysis of diazo-compounds even in a rigid matrix. This is consonant with the recent increasing evidence^{18,20} pointing to the intervention of the excited diazo-compound itself in the formally carbene reactions.

EXPERIMENTAL

I.r. spectra were obtained on a JASCO IR-G recording spectrometer. N.m.r. spectra were determined on a JEOL JNM-MH-100 spectrometer for CDCl₃ solutions containing 5% Me₄Si. G.l.c. for quantitative analyses was performed on a Yanagimoto model G80 instrument using a 4.0 m × 5.0 mm external diameter column packed with polyethylene glycol 20 M (5%) on Diasolid L.

Starting Materials.—Diethyl diazomalonate (1b), b.p. 65–67 °C at 0.6 mmHg, was prepared²¹ by the diazo-group transfer to malonate, and methyl diazoacetate (1a), b.p. 56–57 °C at 38 mmHg, was prepared²² by the acyl cleavage of methyl diazoacetoacetate. Both diazo-compounds were distilled prior to use. Commercial n-pentane and diethyl ether were purified by distillation. Isobutane was used simply by passing through a calcium chloride tube. Piperylene was distilled prior to use. Benzophenone of GR grade was used without purification.

Authentic Samples for Identification of Reaction Products.—Diethyl alkylmalonates (2a)–(6b), (9b), and (10b) were prepared by the reaction of diethyl malonate and appropriate alkyl bromide in the presence of sodium according to the literature^{5a} procedure. Methyl alkylacetates (2a)–(6a) and (10a) were prepared²³ by the hydrolysis of the corresponding malonates, followed by decarboxylation and esterification of the resulting alkylacetic acid with methanol. Methyl β-ethoxypropionate (9a) was prepared^{19a} by the coupling of β-hydroxypropionate and ethyl iodide in the presence of silver oxide, δ 1.08–1.22 (6 H, m), 3.70 (3 H, s), 2.40–2.56 (2 H, m), and 4.10–4.20 (1 H, m). Methyl ethoxymalonate (11b) was obtained^{17a} by the photolysis of (1b) in ethanol.

Photochemical Reactions and Analyses.—All irradiations were conducted using a Halos 300 W high-pressure mercury lamp with a water-cooled quartz jacket. In the general

procedure, diazo-compound (1) (0.5 mmol) was added to the appropriate hydrocarbon or ether (2.0 ml) in a Pyrex tube of 13 mm external diameter, into which a second Pyrex tube of 8 mm external diameter was inserted in order to maximize exposure and utilization of radiation, particularly in matrices where the problem is magnified. The tube was suspended in a transparent Pyrex Dewar flask filled with coolant and irradiated. Coolants were water (20 °C), ice-water (3 °C), dry ice-ethanol (–78 °C), liquid nitrogen-isopentane (–110 and –155 °C), and liquid nitrogen (–196 °C). When irradiation was performed in the solid phase, the matrices were thawed in the dark for 15 min every 2 h in order to homogenize them. Irradiations were continued until all the diazo-compound was destroyed. Product identification and relative yields were determined by standard g.l.c. techniques.

Sensitized as well as quenching experiments were performed under conditions similar to those above. More than a five-molar excess of benzophenone was added so as to assure the absorption of >95% of the incident light by the sensitizer. Control runs showed that no reaction occurred in the absence of light in the range of temperatures studied.

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