Carbenes in a Rigid Matrix. Substituent Effects on the Temperature Dependence of α-Carbonylcarbene Reactions

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The temperature dependence of methoxycarbonyl- (1a and b) and benzoyl-carbenes (2a and b) reactions in alcohols has been examined in order to elucidate the scope and limitation of low-temperature photolysis as a tool for detecting triplet carbenes. The results reveal that the method cannot be applied to all carbenes but gives important information on the reactivity and/or multiplicity of ground-state carbenes. Low-temperature photolysis of $PhCN_2CO_2Me$ in an ethanol matrix, for example, resulted in a dramatic increase in C–H insertion products, probably derived from the triplet (1a) *via* an abstraction–recombination mechanism, at the expense of the singlet product, *i.e.* the O–H insertion compound, which was shown to be the main product of photolysis at ambient temperature. In marked contrast, (1b) generated in a propan-2-ol matrix at −196 °C did not result in a major increase in the C–H insertion product. Similar and more contrasting substituent effects on the temperature dependence were observed in the benzoylcarbene system (2). Thus, the Wolff rearrangement of (2a) was almost completely suppressed in a rigid matrix at −196 °C, whereas that of (2b) was not appreciably suppressed even at −196 °C. These differences were explained by considering the effects of the substituent on the ground-state multiplicity of carbene and/or on the relation of the activation energy differences of the singlet and triplet reactions with energy differences between two states.

CARBENE chemistry is of interest to both mechanistic and synthetic organic chemists, mainly in relation to the spin states of carbenes and their intrinsic reactivity. Since it was recognized [1] that most reacting nascent carbene is in the singlet state, for it is not necessarily true that carbene is generated and hence reacts in the ground state, several methods have been devised to generate triplet carbene. A low-temperature photolytic technique is currently attracting considerable interest as a new tool for such studies, which can be successfully applied to arylcarbene systems.[2,3] Moss *et al.*, for example, have reported [3] that when photolysis of diazophenylmethane is conducted in frozen but-2-ene matrices (−196 °C), the stereospecificity of cyclopropanation is reduced and an increase in C–H insertion occurs. Triplet phenylcarbene in rapid thermal equilibrium with, or formed by decay, from the singlet, has been suggested as the key intermediate in low temperature matrix experiments and C–H ' insertion ' products are supposed to be arising *via* an abstraction–recombination (a–r) mechanism. We have also found [2] that phenylcarbene generated in alcoholic matrices results in a decrease in the O–H insertion product, a characteristic product of singlet carbene, with a concomitant increase in C–H insertion products, which are also believed to be derived from the triplet *via* the a–r mechanism. The technique is also expected to have synthetic importance because so-called matrix-fostered carbene reactions, *i.e.*, C–H ' insertion ' into olefins or alcohols, do not occur in liquid-phase carbene reactions.[1] Thus, in order to elucidate the scope and limitation of the method, we have performed temperature studies of the photolysis of some α-diazocarbonyl compounds in alcohol. α-Diazocarbonyl compounds are valuable in organic synthesis due to their ready accessibility and to the wide range of reactions.[1,4] Furthermore, the photochemistry of α-diazocarbonyl compounds has received much attention recently from those interested in using them as labeling reagents for the active sites of enzymes.[5] To achieve effective labeling, the carbene produced photolytically must insert into the surrounding molecules; nevertheless, most reactions of diazocarbonyl compounds suffer from loss of reagent during photolysis because of Wolff rearrangement, which consumes an important fraction of the oxocarbene products. Thus, the present method is also expected to improve the value in synthesis of the carbene (1) and (2) derived from α-diazocarbonyl compounds by changing their multiplicity.

$R\ddot{C}CO\text{-}OMe$ (1) $R\ddot{C}COPh$ (2)

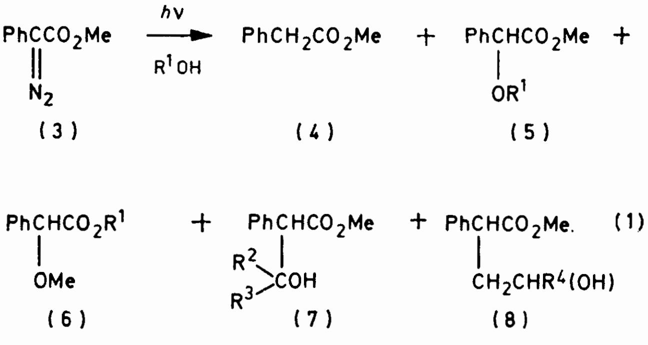
a ; R = Ph
b ; R = H

RESULTS AND DISCUSSION

Solutions of methyl α-diazo-α-phenylacetate (3) in ethanol and propan-2-ol were photolysed in Pyrex tubes (λ >300 nm) as detailed in the Experimental section. Sensitized photolyses of (3) in ethanol were performed in Pyrex tubes containing Michler's ketone (MK) with CS-0-52 filter (λ >350 nm). G.l.c. analysis of the product mixture revealed the presence of methyl phenylacetate (4), O–H insertion products (5), Wolff rearrangement products (6), and C–H insertion products (7) and (8) [equation (1)]. Traces of methyl benzoylformate, a product belived to be derived from triplet carbene with molecular oxygen, were also detected. The product distributions were determined by g.l.c. analysis using the cut and weigh method (Table 1). Direct photolysis of (3) in alcohol at room temperature gave the O–H insertion compound (5), as the major product; this is believed to be derived from the singlet state of (1a). When photolysis was performed in a rigid matrix at −196 °C, the

C–H insertion products dramatically increased at the expense of the O–H insertion product.

When (3) was irradiated in frozen ethanol saturated with oxygen, the emission of blue-white light was observed during warming the sample in the dark, with an increase in the formation of the benzoylformate (g.l.c.).



a; $R^1 = Et$, $R^2 = Me$, $R^3 = R^4 = H$
b; $R^1 = Pr^i$, $R^2 = R^3 = R^4 = Me$

The emission of light is due to the reaction of triplet carbene with oxygen, since this emission has frequently been observed [2a,6] during warming rigid glasses after irradiation of aryl diazo-compounds in air-saturated frozen matrices and has been used to detect the presence of triplet carbene in the low-temperature photolysis of diazo-compounds. This indicates that the key intermediate leading to the C–H insertion products in the solid-phase experiments is also the triplet carbonylcarbene (1a), and thus we suggest an a–r mechanisms rather than direct insertion to rationalize the formation of the C–H ' insertion ' products (7) in the matrix experiments, as proposed for similar reactions of other arylcarbenes with alcoholic [2] and olefinic [3] matrices. In order to obtain more precise insight into the mechanisms by which the matrix controls C–H insertion processes, a more extensive temperature study has been performed on propan-2-ol, f.p. −88.5 °C, and the logarithms of the OH insertion : abstraction ratio, (5) : (4) + (7) + (8), were plotted against T^{-1} (Figure 1). It should be noted that the ratio decreases steadily as the temperature decreases through liquid to solid runs and that there is no such discontinuity (or inversion) in the graph as observed [7] for plots of insertion selectivity of $\mathrm{Ph\ddot{C}H}$ into alkanes *versus* T^{-1}. Assuming a triplet a–r reaction for the formation of alcohols in the low-temperature reaction, this can be taken as reflecting a temperature effect [3d] operating on an equilibrated singlet and triplet arylcarbene system. Furthermore, MK-sensitized photolysis of (3) in liquid ethanol did not result in an appreciable change in the product distribution, also indicating that a rapid and reversible singlet–triplet equilibrium [1] is possible in this carbene system. All these phenomena are known [2] to be characteristic of an arylcarbene which is a ground-state triplet.

TABLE 1

Product distributions in the photolysis [a] of (3) in alcohols

ROH	T/°C	Additives	Relative product yield [b] (%) (4)	(5)	(6)	(7)	(8)
EtOH	20	None	9.8	77.2	0.7	12.4	
	−77	None	7.0	84.7	Trace	8.3	
	−77	MK [c]	13.4	82.5	Trace	3.9	
	−196	None	10.0	14.2	Trace	63.0	12.8
Pr^{i}OH	20	None	6.8	67.0	Trace	19.4	
	−196	None	13.8	4.7	Trace	42.1	15.7

[a] Irradiations were carried out as described in the Experimental section. [b] Determined by g.l.c. analysis of portions removed from the irradiation mixture. Total product yields are *ca.* 70—80%. A trace of benzoylformate was detected. [c] Degassed solution saturated with Michler's ketone was irradiated.

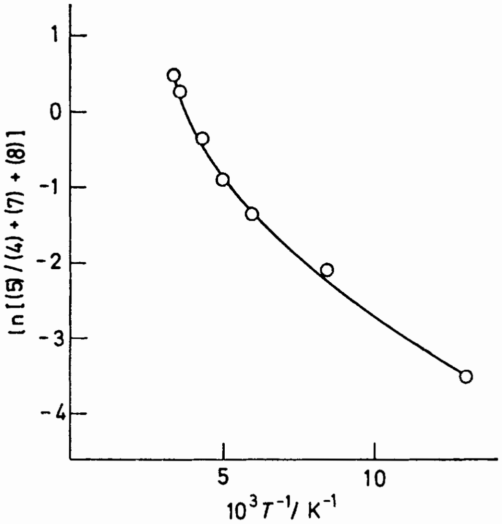
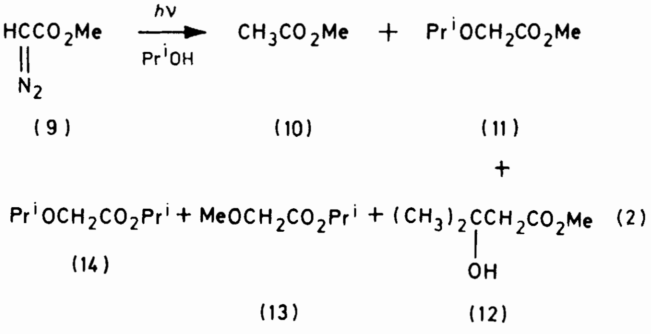


FIGURE 1 Product ratio as a function of temperature in the photolysis of (3) in propan-2-ol

The behaviour of the carbene (1b) derived from methyl diazoacetate (9) in alcohol, on the other hand, is completely different. Thus, photolysis of (9) in propan-2-ol afforded [8] the double hydrogen abstraction product (10), O–H (11) and C–H insertion products (12), and Wolff rearrangement (13) and ' exchange ' products (14) [equation (2)]. The product distributions appear in Table 2. The addition of Ph_2CO in the room temperature photolysis of (9) resulted in an marked change in the product distribution; thus, a dramatic increase in CH_3CO_2Me and considerable suppression of (13) and (14) were noted. But the addition of piperylene, an efficient



quencher for both triplet carbene[9] and the triplet excited state of (9), did not alter the distribution of (11)—(14), although it quenched the formation of (10). These results indicate that (11)—(14) are derived from the singlet state. It has been suggested[8] that (13) and (14) are derived directly from the excited singlet state of (9). Support is lent to this suggestion by the recent evidence[10,11] that singlet carbonylcarbene is eliminated as an intermediate in the Wolff rearrangement and that the migration concerted with loss of nitrogen from the singlet excited diazocarbonyl compound is favoured *in some cases* (see below, however). Then, not only O–H insertion giving (11) but also C–H insertion giving (12) are thought to be derived from the singlet carbene itself at least directly. It has been shown[12] in the reaction of vinylidene with alcohol that hydrogen bonding between the alcohol and the free electron pair orients the singlet centre in close proximity to the C–H bond α to hydroxy and thereby facilitates insertion. A similar hydrogen-bonding complex is expected[12] in the case of (1b), which explains the singlet carbene insertion into the C–H bond of alcohol. Since intersystem crossing from the triplet state of the diazo-compound to the higher-lying excited singlet state is most unlikely, sensitization circumvents the formation of the excited singlet (9), the precursor of (13) and (14), and results in almost exclusive formation of the triplet state, which subsequently dissociates nitrogen to give the triplet carbene, as characterized by the formation of CH_3CO_2Me. The appreciable formation of (11) and (12) from the singlet carbene even for sensitized decomposition, then, suggests that intersystem crossing of the triplet carbene to the singlet is significant. Similar phenomena have been observed in other similar carbene systems, *e.g.*, $CH_3CO\dot{C}H$,[10] $NC\dot{C}H$,[10] and $Et_2NCO\dot{C}H$.[11] This also implies that the carbene has a singlet ground state or that the singlet state of carbene cannot lie significantly above the corresponding triplet ground state. The temperature dependence of carbene (1b) is quite different from that observed for (1a). Thus, direct photolysis of (9) at −196 °C did not result in an appreciable increase in the C–H insertion product (12) at the expense of (11), suggesting that triplet carbene chemistry does not occur prominently in this system. The sensitized photolysis of (9) at −196 °C, on the other hand, resulted in an increase in the formation of (12), indicating that triplet carbene (1b) generated in rigid matrix did insert into the C–H bonds of alcohol, probably *via* the a–r mechanism. Although triplet sensitization within a rigid matrix is relatively limited,[13] there is evidence[14,15] to show that such energy transfer is possible, even at much lower temperature. Further, there is no obvious trend in the graph of ln (11)/(12) *versus* T^{-1} (Figure 2), as has been observed for the similar plot for (1a). Apparently, the displacement of the phenyl group on the carbene carbon by hydrogen markedly changed the temperature dependence of the product distribution.

TABLE 2

Product distributions in the photolysis[a] of (9) in propan-2-ol

T/°C	Additives	Yield[b] (%)				
		(10)	(11)	(12)	(13)	(14)
25	None	5.1	35.0	8.7	32.5	10.5
	Ph_2CO[c]	61.0	5.5	4.0	3.0	1.1
	Q[d]	0	30.4	8.7	35.5	11.9
−196	None	1.1	27.5	12.8	11.3	Trace
	Ph_2CO[c]	4.8	27.2	22.7	3.5	Trace

[a] Irradiations were carried out as described in the Experimental section. [b] Total product yields determined by g.l.c. [c] A five-fold excess of Ph_2CO was used. Dimethyl succinate was also formed (*ca.* 5%) in this run. [d] A 20-fold excess of piperylene was added.

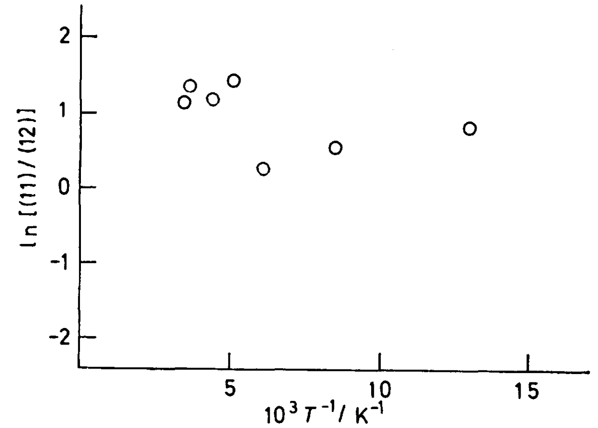


FIGURE 2 Product ratio as a function of temperature in the photolysis of (9) in propan-2-ol

Similar and clearer substituent effects were observed in the benzoylcarbene system (Tables 3 and 4). Thus, it has been reported[16] that photolysis of α-diazo-α-phenylacetophenone in a variety of organic glasses at −196 °C results in a very small amount of diphenylketen (0—12%) which is the main product in the room-temperature photolysis and the major formation of the triplet benzoylphenylcarbene (2a), which, upon thawing the matrices in the dark, produces deoxybenzoin (74—80%) and benzil (0—12%). We also have observed a similar change in the product distribution in ethanol (Table 3). In marked contrast, the Wolff rearrangement product (20) was essentially the principal product in the photolysis of (19) at temperatures ranging from 10 to −196 °C including liquid and solid runs. It is interesting to note here that MK-sensitized photolysis of (19) at ambient temperature resulted in a marked increase in acetophenone, a double-hydrogen abstraction product from triplet (2b), but did

TABLE 3

Product distributions in the photolysis[a] of (15) in ethanol

T/°C	Yield[b] (%)		
	(16)	(17)	(18)
25	*ca.* 100	0	0
−196	52.4	30.2	17.4

[a] See footnote *a* in Table 1. [b] Total yields determined by g.l.c. No C–H insertion product was detected.

not completely suppress the formation of (20), suggesting[17] that intersystem crossing of the triplet (2b) to the singlet may compete with radical abstraction of hydrogen. The intervention of singlet α-oxocarbene itself in the Wolff rearrangement of (19) has been suggested by the findings that the intermediate generated photolytically from dimethylsulphonium phenacylide[18a] and α-oxodiazirine[18b] behaved very much like that produced by photolysis of (19).

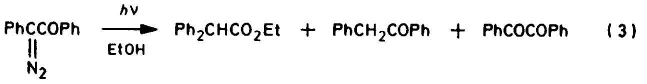
These results indicate that the low-temperature matrix cannot always induce triplet carbene chemistry but that the present method gives us important information on the reactivity and/or ground-state multiplicity of carbene. Although there is still some ambiguity as to the mechanism by which the matrix induces triplet carbene chemistry, the most probable explanation is that the nascent singlet carbene generated by direct photolysis, restricted in the matrix, decays to the lower-lying triplet faster than other available reactions. It is tempting, then, to interpret these results as evidence for singlet ground state of (1b) and (2b). Thus, if one assumes that the carbene has the singlet ground state separated by somewhat more than 5 kcal mol^{-1} from the upper triplet state, one would not expect a large increase in the triplet carbene products since the nascent and hence singlet carbene generated in the direct photolysis within a matrix has no lower-lying state to decay to. This is consonant with sensitized experiments which point to the presence of intersystem crossing from the triplet carbene to the singlet in these carbenes (1b)[10b] and (2b).[17] As with most 'negative' results, however, there may be several possible explanations for the failure to observe the triplet carbene chemistry. Moreover, the presence of intersystem crossing from the triplet to the singlet is not sufficient to establish the existence of singlet ground states for these carbenes, since this also implies that the singlet state of carbene cannot lie significantly above the corresponding triplet ground state. Recently, for example, Roth *et al.*[15] have shown by e.s.r. that (1b) has a ground state triplet or a triplet state that lies a maximum of 10 cal mol^{-1} above the singlet state. Interestingly, the e.s.r. signals follow the Curie law in the temperature range 10—40 K but vanish at higher temperature, indicating that conversion of the triplet state to a more reactive singlet state capable of undergoing intra- and inter-molecular reactions is rapid even at *ca.* 40 K. This is in marked contrast with the observations for arylcarbene systems in which triplet carbenes were shown[16] to be fairly stable even at 77 K. No large increase in the triplet carbene products in the matrix reaction of (1b), then, indicates that a 77 K matrix is not cool enough to populate the triplet (1b) by quenching the singlet reactions. Alternatively, the activation energy for hydrogen abstraction by the triplet (1b) is so high compared with that for the singlet reactions that the difference is much greater than the singlet–triplet splitting of (1b). Moreover, sensitized experiments as well as e.s.r. results clearly predict that the splitting of (1b) [and (2b)] is fairly small.

TABLE 4

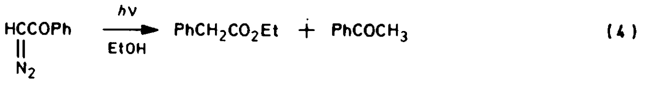
Product distributions in the photolysis[a] of (19) in ethanol

		Yield[b] (%)	
T/°C	Additives	(20)	(21)
10	None	73.8	Trace
	MK[c]	47.6	52.4
−196	None	72.9	3.6

[a] See footnote *a* in Table 1. [b] Total yields determined by g.l.c. [c] Relative yields in the Michler's ketone sensitized photolysis of (19) reported by Padwa.[17]


$$\underset{\underset{N_2}{\|}}{PhCCOPh} \xrightarrow[EtOH]{h\nu} Ph_2CHCO_2Et + PhCH_2COPh + PhCOCOPh \quad (3)$$

(15) (16) (17) (18)


$$\underset{\underset{N_2}{\|}}{HCCOPh} \xrightarrow[EtOH]{h\nu} PhCH_2CO_2Et + PhCOCH_3 \quad (4)$$

(19) (20) (21)

It is interesting to note here that the Wolff rearrangement process of (2b) is not appreciably suppressed even in the matrix photolysis of (19), in spite of the fact that a shift of the large phenyl group is generally inhibited in the rigid matrix. Thus, it has been shown[19] that Ph migration in $Ph\ddot{C}CHMePh$ is almost completely damped in a rigid matrix at −196 °C, even though the process has a much lower activation energy than the hydrogen shift. Furthermore, $Ph\ddot{C}CH_3$ generated in olefinic[3] and alcoholic[20] matrices produces styrene resulting from a hydrogen shift of the singlet as the principal product along with a sizeable amount of C–H insertion product, whereas phenyl migration in $Ph\ddot{C}COPh$ is largely suppressed in a rigid matrix, suggesting a similar matrix effect on the migratory aptitude. These results suggest that (2b) has a ground state singlet. It is important to point out that photolysis of (19) in the presence of O_2, a quencher for triplet carbene, results in no oxygen-incorporated products whereas the similar photolysis of (15) gives the products derived from carbon dioxide.[21]

These results suggest that (19) should have only limited synthetic value as a carbene precursor, using direct irradiation; no trace of O–H insertion product ($PhCOCH_2OEt$) is detected even in the sensitized photolysis of (19). On the other hand, a change in the reaction temperature much improves the synthetic value of (15) as a carbene source. An appreciable increase in the fraction of carbene products (11) and (12) at the expense of the Wolff rearrangement products (13) and (14) with decrease in temperature should also be noted for the photolysis of (9). This can be explained by assuming that migration of the methoxy-group possesses an appreciable activation energy and becomes less important at lower temperatures.[22] A similar explanation is applied to account for the fact that no trace of Wolff rearrangement product (6) is formed even in the matrix photolysis of (3), in spite of the fact that intramolecular reactions are generally favoured over intermolecular reactions within a rigid matrix.

EXPERIMENTAL

General.—I.r. spectra were obtained on a JASCO IR-G recording spectrometer. U.v. spectra were recorded on a Shimadzu UV 250 recording spectrometer. N.m.r. spectra were determined on a JEOL JNM-MH-100 spectrometer for $\mathrm{CDCl_3}$ solutions containing 5% $\mathrm{Me_4Si}$: chemical shifts are reported in δ units downfield from $\mathrm{Me_4Si}$. G.l.c. analyses were performed on a Yanagimoto instrument model G-80 using a 4.0 m × 4.0 mm external diameter column packed with 10% Carbowax 6000 on Diasolid L, a 2.0 m × 4.0 mm column packed with 5% silicon OV-17 on Diasolid L, and a 3.0 m × 4.0 mm column packed with 10% ODPN on Diasolid L.

Starting Materials.—Methyl α-diazo-α-phenylacetate (3) was prepared [23] by the formylation of methyl phenylacetate, followed by diazo-exchange with tosyl azide. Methyl diazoacetate (9) was prepared [24] by the acyl cleavage of methyl diazoacetoacetate and purified by distillation prior to use. α-Diazo-α-phenylacetophenone (15) was prepared [25] by the oxidation of benzil monohydrazone with mercury(II) oxide and purified by recrystallization from methanol prior to use. Benzoyldiazomethane (19) was prepared [26] by the reaction of benzoyl chloride with diazomethane and purified by recrystallization from Skellysolve F prior to use. All diazo-compounds showed satisfactory spectroscopic data. Commercial ethanol and propan-2-ol were dried over magnesium and purified by distillation. Piperylene was distilled prior to use.

Authentic Samples for Identification of Reaction Products.—α-Alkoxy-α-phenylacetates (5) and (6) were prepared [27] by the reaction of α-bromo-α-phenylacetate with sodium alkoxide, followed by ester exchange. B.p. and n.m.r. data are as follows: (5a), b.p. 132—134 °C at 18 mmHg, δ 1.20 (3 H, t, $\mathrm{OCH_2C}H_3$), 3.40 (3 H, s, $\mathrm{OCH_3}$), 4.16 (2 H, q, $\mathrm{OC}H_2\mathrm{CH_3}$), 4.74 (1 H, s, PhCH), and 7.33 (5 H, m, $\mathrm{C_6H_5}$); (5b), b.p. 136—138 °C at 23 mmHg, δ 1.20 [6 H, m, $\mathrm{OCH(C}H_3\mathrm{)_2}$], 3.58 (1 H, s, PhCH), 3.66 (3 H, s, $\mathrm{OCH_3}$), 4.96 [1 H, m, $\mathrm{O}CH\mathrm{(CH_3)_2}$], and 7.32 (5 H, m, $\mathrm{C_6H_5}$); (6a), b.p. 135—136.5 °C at 20 mmHg, δ 1.20 (3 H, t, $\mathrm{OCH_2C}H_3$), 3.40 (3 H, s, $\mathrm{OCH_3}$), 4.16 (2 H, q, $\mathrm{OC}H_2\mathrm{CH_3}$), 4.74 (1 H, s, PhCH), and 7.33 (5 H, m, $\mathrm{C_6H_5}$); (6b), b.p. 138—141 °C at 21 mmHg, δ 1.18 [6 H, dd, $\mathrm{OCH(C}H_3\mathrm{)_2}$], 3.42 (3 H, s, $\mathrm{OCN_3}$), 4.74 (1 H, s, PhCH), 5.08 [1 H, m, $\mathrm{O}CH\mathrm{(CH_3)_2}$], and 7.38 (5 H, m, $\mathrm{C_6H_5}$). β-Hydroxy-α-phenylbutyrates (7) were prepared [28] by the reaction of an Ivanov reagent with the corresponding carbonyl compound, followed by the esterification. B.p. and n.m.r. data are as follows: (7a), b.p. 86—88 °C at 0.6 mmHg, δ 1.05 (3 H, dd, $\mathrm{CHC}H_3$), 3.50 (1 H, m, $\mathrm{C}H\mathrm{CH_3}$), 3.64 (3 H, s, $\mathrm{OCH_3}$), 4.34 (1 H, m, $\mathrm{PhC}H$), and 7.24 (5 H, m, $\mathrm{C_6H_5}$); (7b), δ 1.08 [3 H, s, $\mathrm{C(CH_3)_2}$], 1.34 [3 H, s, $\mathrm{C(CH_3)_2}$], 3.52 (1 H, m, $\mathrm{PhC}H$), 3.64 (3 H, s, $\mathrm{OCH_3}$), and 7.28 (5 H, m, $\mathrm{C_6H_5}$). Methyl γ-hydroxy-α-phenylbutyrate (8a) was prepared [29] by the hydrolysis of γ-hydroxy-α-phenylbutyronitrile, followed by esterification, b.p. 101—122 °C at 0.55 mmHg, δ 2.20—2.70 (2 H, m, $\mathrm{CH_2}$), 3.60 (s, $\mathrm{OCH_3}$), 3.70—3.90 (1 H, m, $\mathrm{PhC}H$), 4.16—4.57 (2 H, m, $\mathrm{CH_2}$), and 7.28 (5 H, m, $\mathrm{C_6H_5}$). Methyl γ-hydroxy-α-phenylvalerate (8b) was prepared [30,31] by the reduction of methyl α-phenyllevulinate.

Alkoxyacetates (11), (13), and (14) were prepared [32] by the reaction of bromoacetic acid with sodium alkoxide, followed by esterification. B.p. and n.m.r. spectra are as follows: (11), b.p. 146.5—147.5 °C, δ 1.20 [6 H, d, $\mathrm{OCH(C}H_3\mathrm{)_2}$], 3.76 (3 H, s, $\mathrm{OCH_3}$), and 4.08 (2 H, s, $\mathrm{CH_2}$); (13), b.p. 143.5—144 °C, δ1.26 [6 H, d, $\mathrm{OCHC(C}H_3\mathrm{)_2}$], 3.46 (3 H, s, $\mathrm{OCH_3}$), 4.00 (2 H, s, $\mathrm{CH_2}$), and 5.12 [1 H, m, $\mathrm{O}CH\mathrm{(CH_3)_2}$]; (14), b.p. 164.5—166.5 °C, δ 1.20 [6 H, d, $\mathrm{OCH(C}H_3\mathrm{)_2}$], 1.26 [6 H, d, $\mathrm{CO_2CH(C}H_3\mathrm{)_2}$], 3.48 [1 H, m, $\mathrm{OCH(CH_3)_2}$], 4.02 (2 H, s, $\mathrm{CH_2}$), and 5.10 [1 H, m, $\mathrm{CO_2C}H\mathrm{(CH_3)_2}$]. Methyl β-hydroxy-β-methylbutyrate (12) was prepared [33] by the Reformatsky reaction of methyl bromoacetate and acetone with zinc, b.p. 68.5—69.5 °C at 18 mmHg, δ 1.30 [6 H, s, $\mathrm{C(CH_3)_2}$], 2.52 (2 H, s, $\mathrm{CH_2}$), 3.72 (3 H, s, $\mathrm{OCH_3}$).

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, the appropriate amount of diazo-compound [(3) 85.2 mmol, (9) 0.06 mmol, (15) 0.02 mmol] was added to the appropriate alcohol (2.0 ml) in a 5 ml Pyrex tube. In the case of solid-phase photolyses, particularly, as an irradiation tube, a Pyrex tube of 13 mm external diameter, into which second Pyrex tube of 8 mm external diameter was inserted, was employed in order to maximize exposure and utilization of radiation 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—30 °C), ice-water (0 °C), solid $\mathrm{CO_2}$-acetonitrile (−45 °C), solid $\mathrm{CO_2}$-methanol (−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 every 2 h in order to homogenize them. Irradiations were continued until all the diazo-compound was destroyed. Products and absolute yields were determined by standard g.l.c. techniques. The sensitized experiment for (3) was performed using a saturated alcoholic solution of MK as solvent with a CS-0-52 filter ($\lambda > 350$ nm). The sensitized experiment for (9) at ambient temperature was performed with monochromatic light of 335 nm in the presence of a five-fold molar excess of benzophenone. For the sensitized experiments, it was assumed that >98% of the incident light was absorbed by the sensitizer. Control runs showed that no reaction occurred in the absence of light for the temperatures studied.

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