bonate) and evaporated *in vacuo*. The last traces of ether and acetone were removed by dissolution in carbon tetrachloride and evaporation *in vacuo*. The pmr spectrum of the resulting white solid was superimposable in all respects on that of **7**.[6a]

When **6** was treated by exactly the same procedure (except the solvolysis was allowed to proceed for 4 days), the pmr spectrum of the oily solid indicated *ca.* 70% of **8** and 30% of unreacted **6**. No peaks were observed which could be attributed to **7**.

**Kinetic Methods.** Commercial platinum plate electrodes were used in the hydrolysis experiments. The bridge was carefully calibrated. Solvolysis rates were determined on *ca.* $10^{-3}$ *M* solutions of **5** or **6** in 60% aqueous acetone, and were followed for 1-2 half-lives. The computer program used for computation of the rates was that mentioned previously.[1]

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# Mechanism of the Wolff Rearrangement. IV. The Role of Oxirene in the Photolysis of α-Diazo Ketones and Ketenes

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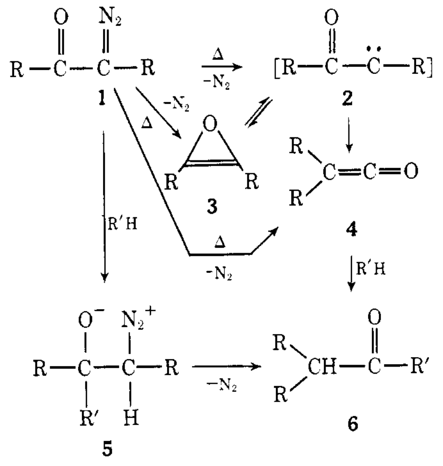
**Abstract:** Oxirenes, the family of unsaturated epoxides, have been detected as reactive transients in the photochemical Wolff rearrangement sequence of α-diazo ketones and in the photolysis of ketenes.[1-3] Photolyses of 3-diazo-2-propanone, 3-diazo-2-butanone, azibenzil, and α-diazoacetophenone, carbon-13 labeled in the carbonyl group, yield the corresponding ketene in which the carbon-13 atom is scrambled. The extent of scrambling was determined by mass spectrometric analysis of the CO and the carbene insertion products from the secondary *in situ* photolysis of the ketene or from its solvolysis product. The yield of scrambling, indicative of oxirene participation, is dependent on the substituents in the diazo ketone, phase, solvent, and to some extent wavelength of excitation. The highest yield of oxirenes obtains from the gas-phase photolysis of symmetrically substituted diazo ketones. Oxirene is shown to be a characteristic photoproduct; the thermolysis of azibenzil does not give oxirene. From a consideration of the kinetic behavior of the $O(^3P) + CH_3C{\equiv}CCH_3$ and other triplet systems, it is also concluded that oxirene formation occurs *via* a singlet reaction surface. The photolysis of dimethylketene and diphenylketene, carbon-13 labeled in the carbonyl group, yields labeled carbene and unlabeled CO as products. The extent of isotopic scrambling in these cases is decidedly lower than from the corresponding diazo ketones. It is proposed that the reaction path to oxirene is *via* the vibrationally excited ground-state ketene formed through internal conversion of the electronically excited molecule.

The conversion of α-diazo ketones into acids and their derivatives was discovered by Wolff[4,5] and independently by Schroeter.[6,7] The decomposition–rearrangement sequence has proved to be of great synthetic value.[8,9] A notable feature of the Wolff rearrangement (WR) is that it can be brought about catalytically, thermally, or photochemically;[10-13] however, in spite of its facility and widespread application, still, after some sixty years of intensive research, no unified mechanistic picture of this reaction has emerged.

Scheme I shows the different mechanistic pathways which have been proposed for the thermal WR. All mechanisms consider the migration of the R group to be an intramolecular process which does not involve ionic or free radical intermediates. This postulate is based on the well-documented experimental observation that during migration, the stereochemical information content of the R group is retained.[10]

**Scheme I**



R' = OH, OAc, $NH_2$, etc.

The path **1** → **2** → **4** → **6** was first proposed by Wolff[4,5] and is still favored, although there are few direct proofs for the intermediacy of **2**. Huisgen and coworkers[14-16] succeeded in isolating oxazole deriva-

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tives, the 1,3-addition products of the ketocarbenes, in the catalyzed and uncatalyzed thermolysis of diazo ketenes. The ketenes or secondary products derived from them have been isolated in several cases of diazo ketone thermolysis in aprotic solvents.[10]

Another alternative was proposed by Eistert,[17] and has been discussed recently by Wilds, *et al.*[18] These authors pointed out the possibility of an initial protonation step, leading to the betaine **5**. This then would rearrange synchronously to **6**.

Kaplan and Meloy[19] have proposed a one-step, concerted rearrangement[20] **1** → **4**, suggesting that, due to stereoelectronic reasons, only the cis configuration of diazo ketones should undergo the WR. In cases where the cis ⇄ trans interconversion is slow relative to the product-forming reactions, the rate of interconversion should determine the product distribution.

Recently, Bartz and Regitz[23] offered evidence against the Eistert mechanism in the presence of alcohols and amines. Two other groups[24,25] prefer the keto carbene–ketene mechanism on the basis of kinetic measurements of thermolysis in protic solvents. The intermediacy of the oxirene structure **3** in the WR has been rejected on the basis of isotopic labeling studies.

The history of oxirene is similar to that of many other unstable small ring compounds. Its isolation was claimed and withdrawn and its intermediacy proposed several times during the past hundred years.[26–28] The first step of the peroxidation of acetylenes was discussed in terms of oxirene formation;[29–33] this concept is based on analogy to oxirane formation in the peracid oxidation of olefins and has no other justification. Oxirenes have been proposed as intermediates in the photolysis of *trans*-1,4-diphenyl-3,4-epoxybutan-1-one[34] and in the pyrolytic mass spectrometric decomposition of 1,2-dinitronaphthalene.[35]

Nearly 30 years ago, Huggett and coworkers[36] investigated the role of oxirene in the WR of diazoacetophenone using the isotopic labeling technique and found that no scrambling took place during rearrangement. Later, Franzen[37] applied radioactive labeling techniques in the photochemical and thermal WR of azibenzil. It was concluded that oxirene is not an intermediate in the reaction.

The first observation of a photochemical WR is due to Süs,[38] but the general value of this photorearrangement was first recognized by Horner, *et al.*,[39–41] who found that rearrangement takes place generally in substances which contain the diazocarbonyl structure. Since its discovery, the photochemical WR has become a widely used method in organic synthesis. In the photochemical WR, in addition to the problem of different pathways discussed above another question arises concerning the character of the excited state responsible for the rearrangement **1** → **2**. As in the thermal process, ketenes could be isolated or trapped in inert solvents but the most crucial question that remains is the intermediacy of keto carbenes, for which there is no direct evidence.

One would expect the rearrangement to be possible only from an excited singlet state of **1**, or **2**, since the first excited state of ketenes lies at high energies rendering triplet **1** → triplet **4** endoenergetic. Indeed, recently several groups found indications that the reactive intermediate in the photochemical WR is a singlet,[42–45] with some possible exceptions.

With regard to the role of oxirene in the photochemical WR, it has been shown in a recent series of preliminary communications[1–3] from this laboratory that contrary to earlier claims, the oxirene structure is an intermediate in the photochemical WR of several diazo ketones and diazo esters. Thus, the gas-phase irradiation of 3-diazo-2-butanone-*2*-$^{13}C$ (**7**) resulted in complete scrambling of the heavy isotope. Scrambling was observed in the photolysis of the asymmetrical diazo ketone, 3-diazo-2-propanone-*2*-$^{13}C$ (**8**), to the extent of 16%. Similar results were found[2] in the gas-phase irradiation of methyl and ethyl diazoacetates, **9** and **10**. The compounds were labeled with $^{13}C$ in the carboxylate group and the amounts of scrambling indicated 32% oxirene participation with **10** and 28% with **9**.

Subsequently, experiments were extended to the liquid phase.[3] Photolysis of azibenzil-$^{13}C$ (**11**) labeled in the carbonyl position in both a polar and a nonpolar solvent led to over 50% oxirene participation. In the nonpolar solvent the scrambling, as determined from the CO product of the secondary photolysis of diphenylketene, yielded somewhat higher yields for oxirene formation than those obtained in polar sol-

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**Table I.** Photolysis of 3-Diazo-2-butanone-*2*-$^{13}C$ (7) in Cyclopentane[a]

| Concn, μmol 7 | $N_2$ | CO | % $^{13}CO$ in CO | Propene concn, μmol | % $^{13}CC_2H_6$ in propene | % oxirene intermediate From CO | From propene |
|---|---|---|---|---|---|---|---|
| 80.5 | 69.4 | 40.8 | 37 | | | 71 | |
| 71.4 | 65.3 | 41.8 | 39 | | | 64 | |
| 72.4 | 56.7 | 31.6 | 38 | 9 | 24 | 65 | 84 |
| 59.1 | 53.1 | 32.6 | 39 | 9 | 22 | 62 | 76 |

[a] Vycor filtered light, 3.5 hr photolysis time.

**Table II.** Gas-Phase Photolysis of 3-Diazo-2-butanone-*2*-$^{13}C$ (7)[a]

| 7, Torr | Irradiation time, min | Concn, μmol $N_2$ | CO | $C_3H_6$ | $CH_3C{\equiv}CCH_3$ | $CH_3CO$-$CH{=}CH_2$ | $CH_3CH_2$-CHO | $CH_3CHO$ |
|---|---|---|---|---|---|---|---|---|
| Nm[c] | 60 | +CO | 95 | | 0.71 | | 0.3 | 3.3 |
| Nm[c] | 180 | +CO | 175 | | 0.43 | | 0.6 | 0.9 |
| 7[b] | 90 | +CO | 15.6 | 2.7 | 0.13 | | 0.3 | 0.4 |
| Nm[c] | 105 | +CO | 111 | 27.8 | 0.46 | | 0.5 | 0.4 |
| Nm[c] | 120 | +CO | 107 | | | 3.3 | 0.3 | 0.6 |
| 6 | 90 | 25.1 | 12.1 | 9.3 | 0.34 | 1.5 | 0.4 | 0.4 |
| 6 + 6NO | 90 | 16.8 | 7.9 | 5.4 | 0.36 | 2.1 | 1.5 | 0.6 |
| 6 | 90 | 17.0 | 8.8 | 6.3 | 0.37 | 1.0 | 0.2 | 0.2 |
| Nm[c] | 90 | 72.5 | 42.0 | 35.3 | 0.42 | 4.6 | | 1.0 |

[a] The compound 7 could not be readily separated from the 1-propanol solvent used in its synthesis and contained up to ~50% 1-propanol. Photolysis with Vycor filtered light. [b] Cell 5 × 6 cm, otherwise 5 × 15 cm. [c] Not measured.

vents where the ketene was trapped rather than photolyzed. It could not be determined whether this was due to experimental error or to additional oxirene participation in the photolysis of diphenylketene.

In a communication contemporary with the azibenzil photolysis report, Russell and Rowland[46] observed oxirene formation in the gas-phase photolysis of ketene-*1*-$^{14}C$. Montague and Rowland[47] also concluded that chemically activated ketene produced by the addition of singlet methylene to carbon monoxide rearranges to oxirene.

In the present article we wish to give a detailed account of our studies on the role of the oxirene structure in the photolysis and thermolysis of a number of α-diazo ketones and ketenes. Some of the systems were studied in the gas phase as well as in the condensed phase permitting the evaluation of the effect of phase shift on the intervention of oxirene. The result of an auxiliary study on the reaction of oxygen atoms with acetylenes is also briefly described.

In order to elucidate the mechanism of these processes a theoretical study of relevant structures and reactions was also undertaken, the details of which are presented in the accompanying article.[48]

## Results

**(a) 3-Diazo-2-butanone-*2*-$^{13}C$.** The parent compound 7 was prepared by conventional means from acetyl-*1*-$^{13}C$ chloride (Merck, 56.8% $^{13}C$). The position and extent of the labeling were determined by ir, nmr, and mass spectrometry. The mass spectrum did not show a molecular ion; the *m/e* 70 (M − 28) and 71 peaks indicated 56.8% $^{13}C$ content.

Degassed 1.4 × $10^{-2}$ *M* cyclopentane solutions of 7 were irradiated at room temperature with Vycor filtered light. The noncondensable gases were separated from the condensable products and both fractions were subjected to high resolution mass spectrometric analysis. The results are shown in Table I; it is apparent that oxirene participation is important, occurring to the extent of about 70%.

The photolysis of 7 in a polar solvent, dioxane–water (2:1), was then investigated. A 0.15 *M* solution of 7 in dioxane–water was irradiated and the resulting isobutyric acid was analyzed by high resolution mass spectrometry. The fragmentation pattern allowed an

$$C_4H_8O_2 \longrightarrow C_3H_7^+ \quad m/e\ 43;\ \ COOH\ m/e\ 45$$

$$^{13}CC_3H_8O_2 \longrightarrow C_3H_7^+ \text{ and } {}^{13}CC_2H_7 \quad m/e\ 44;$$
$$COOH \text{ and } {}^{13}COOH\ m/e\ 46$$

unequivocal determination of the extent of scrambling. This corresponded to 61.5% oxirene participation.

In a preliminary communication[1] it was reported that the gas-phase photolysis of 7 at *ca.* 5 Torr pressure gave complete scrambling of the isotopic carbon atom indicating 100% oxirene formation in the decomposition sequence. Furthermore, it was also noted that the two minor products, ethylene and ethane, showed the expected isotopic distribution; the ethylene was partially labeled and the ethane contained no labeling. Additional products of the reactions were methane, propane, methyl vinyl ketone, propionaldehyde, acetaldehyde, and 2-butyne. The yields of some of these products are tabulated in Table II. Particularly interesting is the small but persistent yield of 2-butyne, because of the possibility that it arises *via* oxygen atom loss from dimethyloxirene. That this is the case was confirmed by nitric oxide scavenging and isotopic labeling experiments. When the photolysis of 7 was carried out in the presence of 6 Torr of added NO the yield of 2-butyne was not altered, suggesting a molecular mode of formation. The yields of $N_2$, CO, and $C_3H_6$ were also unaffected while those of the methyl vinyl ketone and aldehydes increased, because of suppression by NO of free radical attack upon them. Isotopic analysis of the 2-butyne showed the same

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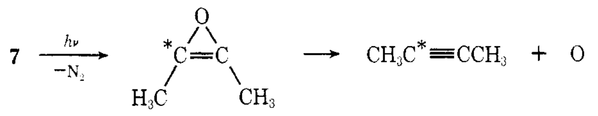
**Table III.** Gas- and Solution-Phase Photolysis of Dimethylketene-*1*-$^{13}C$ (12)[a]

| Concn, $\mu$mol<br>12 | Concn, $\mu$mol<br>CO | $^{12}CO/^{13}CO$ | % oxirene from CO | Propene concn, $\mu$mol | $^{13}CC_2H_6^+/C_3H_6^+$ | % oxirene from Propene |
|---|---|---|---|---|---|---|
| 13.2 | 6.0 | 0.78 | 22.5 | 8.7 | 4.0/96.0 | |
| 17.2 | 7.5 | 0.61 | 4.0 | 12.9 | 4.8/95.2 | 2.5 |
| 12.8 | 6.9 | 0.785 | 23.0 | 9.5 | 5.1/94.9 | 3.4 |
| 20.5 | 9.6 | 0.745 | 19.0 | 14.1 | 5.5/94.5 | 4.8 |
| 22.4 | 8.7 | 0.725 | 16.8 | In cyclopentane solution | | |
| 28.1 | 12.4 | 0.60 | 2.0 | | | |
| 28.0 | 2.6 | 0.72 | 16.0 | | | |

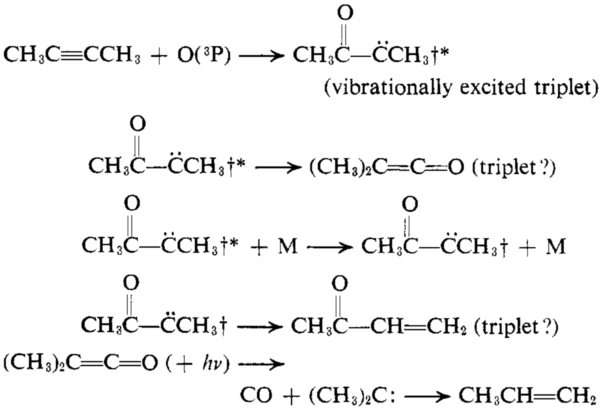
[a] With Vycor filtered light.

amount of $^{13}C$ as the starting material. Thus, the most reasonable mechanism for the formation of this product is



The reaction is computed to be slightly endoenergetic[48] and it is also spin and orbital symmetry forbidden.

Methyl vinyl ketone apparently forms from the $CH_3C(=O)\ddot{C}CH_3$ carbene (or $CH_3C(O\cdot)\dot{C}CH_3$ diradical) in competition with the WR. In order to investigate these reactions we generated the carbene by reacting $O(^3P)$ atoms with dimethylacetylene. The oxygen atoms were produced *in situ* by the triplet mercury photosensitization of nitrous oxide in the presence of dimethylacetylene. The principal products of the reaction were $N_2$, CO, methyl vinyl ketone, and propylene. Product yields, relative to nitrogen, are plotted against total pressure in Figure 1. It is seen that the yield of methyl vinyl ketone increases and those of CO and propylene decrease with increasing total pressure, but their sum remains unaffected. The appropriate reactions appear to be



$$CH_3C{\equiv}CCH_3 + O(^3P) \longrightarrow CH_3\overset{\displaystyle O}{\overset{\|}{C}}{-}\ddot{C}CH_3{\dagger}^* \quad \text{(vibrationally excited triplet)} \tag{1}$$

$$CH_3\overset{\displaystyle O}{\overset{\|}{C}}{-}\ddot{C}CH_3{\dagger}^* \longrightarrow (CH_3)_2C{=}C{=}O \text{ (triplet?)} \tag{2}$$

$$CH_3\overset{\displaystyle O}{\overset{\|}{C}}{-}\ddot{C}CH_3{\dagger}^* + M \longrightarrow CH_3\overset{\displaystyle O}{\overset{\|}{C}}{-}\ddot{C}CH_3{\dagger} + M \tag{3}$$

$$CH_3\overset{\displaystyle O}{\overset{\|}{C}}{-}\ddot{C}CH_3{\dagger} \longrightarrow CH_3\overset{\displaystyle O}{\overset{\|}{C}}{-}CH{=}CH_2 \text{ (triplet?)} \tag{4}$$

$$(CH_3)_2C{=}C{=}O\ (+\ h\nu) \longrightarrow CO + (CH_3)_2C{:} \longrightarrow CH_3CH{=}CH_2 \tag{5}$$

Steady-state kinetics predict the following relation: $(CH_3COCH{=}CH_2]/[CO] = k_3(M)/k_2(I)$. Plotting the product ratios against total pressure yields a straight line from the slope of which, with the usual assumption of unit collision efficiency, the value of $k_2$ is *ca.* $5 \times 10^9$ sec$^{-1}$. These results would predict that at very high pressures, that is in the condensed phase, ketene formation would be suppressed and the only major product should be methyl vinyl ketone. This is clearly not the case in the photolysis of 7, where the condensed-phase photolysis afforded over 50% yield of CO and 15% of propylene, both presumably from the photolysis of dimethylketene. Thus, it may be concluded that in the photolysis of 7 the carbene is present in a different, most likely singlet, electronic state.

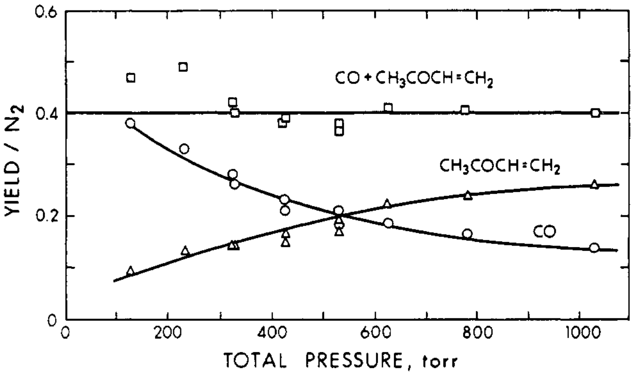


Figure 1. Yield ratios for $CO/N_2$ (○), $CH_3COCH{=}CH_2/N_2$ (△), and their sums (□), as a function of total pressure, from the reaction of $O(^3P)$ atom with dimethylacetylene.

In the condensed-phase photolysis of 7 the oxirene participation appeared to be somewhat higher in cyclopentane solution where the yields were deduced from the ketene photolysis products CO or $C_3H_6$ than from dioxane–water solvent where the yields were obtained from the analysis of the hydrolyzed ketene, isobutyric acid. To examine the possibility of isotopic scrambling during the dimethylketene photolysis we have investigated this reaction separately.

**(b) Dimethylketene-*1*-$^{13}C$ (12).** The dimethylketene-*1*-$^{13}C$ contained 63.3% $^{13}C$ at the C-1 position. Photolyses were conducted in the gas and liquid phase and the degree of isotopic scrambling was determined. The results are given in Table III. There are some rather obvious inconsistencies in the data, notably the discrepancy between the degree of labeling found in CO analyses and in the propylene analyses and also the scatter in the values. The cause of these is not known, but as will be noted below somewhat similar problems were encountered in working with diphenylketene as well. We take the upper limit for oxirene participation as ~20% in the gas phase and ~16% in the condensed phase, both being considerably lower than the corresponding values obtained from the photolysis of 7.

**(c) 3-Diazo-2-propanone-2-$^{13}C$ (8).** The parent compound contained 55% $^{13}C$ labeling. Gas-phase photolysis of *ca.* 10 Torr of 8 afforded $N_2$ and smaller amounts of CO along with some $H_2$ and $CH_4$. The major component of the condensable fraction was ethylene with acetylene (20%) and a few per cent each of ethane, propane, and propylene. Mass spectrometric analysis of the CO indicated a minimum value for isotopic scrambling of 16%. Also 27% of the ethylene and 23% of the acetylene were $^{13}C$ labeled

**Table IV.** Photolysis of Azibenzil-$^{13}$*CO* (**11**) in Cyclopentane

| Filter | Concn, μmol<br>**11** | <br>$N_2$ | <br>CO | $^{12}CO/^{13}CO$ | % oxirene from CO | % yield of **13** | *m/e* 236/237[a] | % oxirene from **13** |
|---|---|---|---|---|---|---|---|---|
| Quartz | 9 | 12 | 9 | 1.85 | 71 | 40 | 2.10 | 53 |
| | 11 | 13 | 11 | 1.63 | 59 | 40 | 1.76 | 67 |
| Vycor | 10 | 10 | 7 | 1.80 | 69 | 40 | 2.10 | 53 |
| | | | | 1.40 | 47 | 40 | | 67 |
| Pyrex | 13 | 12 | 9 | 1.81 | 70 | 40 | 1.52 | 78 |
| | 13 | 14 | 10 | 1.85 | 72 | 40 | | |

[a] Natural diphenylmethylcyclopentane (**13**) has *m/e* 236/237 = 4.6.

**Table V.** Photolysis of Diphenylketene-*1*-$^{13}$*C* (**14**) in Cyclopentane

| Filter | Yield of CO, % | $^{12}CO/^{13}CO$ | % oxirene from $^{13}CO$ | Yield of **13**, % | *m/e* 236/237 | % oxirene from **13** | Irradiation time, hr |
|---|---|---|---|---|---|---|---|
| Quartz | 60 | 1.22 | 35.0 | | | | 5.5 |
| | 50 | 1.20 | 34.8 | 25 | 2.64 | 34.8 | 6.5 |
| | 57 | 1.16 | 37.4 | | | | 20 |
| Vycor | Na | 1.03 | 19.4 | 27 | 2.88 | 29.4 | 3.5 |
| | Na | 1.10 | 29.7 | | | | 3.5 |
| Pyrex | 63 | 1.24 | 36.6 | 25 | 2.32 | 44.8 | 6 |
| | 46 | 1.03 | 19.9 | | | | 8 |

which raises the minimum value for oxirene formation to 27%. A preliminary study carried out on the $CH_3C{\equiv}CH + O(^3P)$ reaction indicated a reaction path similar to that found for the butyne-2 + $O(^3P)$ system.

**(d) Azibenzil-$^{13}$*CO* (11).** Cyclopentane solutions (1.6 × $10^{-2}$ *M*) of **11** (61.0% $^{13}$C) were irradiated in sealed quartz tubes at 15° for 3 hr, using Quartz, Vycor, and Pyrex filters. The isotopic composition of the CO indicated scrambling of the $^{13}$C to an extent corresponding to 64 ± 10% oxirene participation in the reaction. This value appears to be independent of the wavelength of the exciting radiation, Table IV. Two hydrocarbon products were isolated and identified as diphenylcyclopentylmethane (**13**) and tetraphenylethane. Both showed a substantial amount of $^{13}$C labeling, and the tetraphenylethane was a mixture of substances with none, one, and with two $^{13}$C atoms. In the Vycor filtered irradiation, the amount of scrambling in **13** was also measured by means of nmr spectroscopy and found to correspond to approximately 75% oxirene participation.

In order to secure data comparable to that of Franzen,[37] the photolysis of azibenzil was repeated in dioxane–water (2:1), using a 2200-Å filter. A 2 × $10^{-2}$ *M* solution of **11** was irradiated for 30 min under the same conditions as used with cyclopentane as solvent. The resulting diphenylacetic acid was isolated and subjected to high resolution mass spectroscopic and nmr analysis. By monitoring the intensities of the *m/e* 212 and 213 molecular ions the overall isotopic concentration was found to correspond to that of the starting material, 61%. The position of the $^{13}$C in the molecule was determined from the $[C_{13}H_{11}]^+$ and $[^{13}CC_{12}H_{11}]^+$ ion intensities. Subtraction of the mass spectrum of authentic diphenylacetic acid from the sample yielded the $^{13}$C distribution between C-1 and C-2 in the diphenylacetic acid; this corresponded to approximately 50% oxirene participation in the reaction. Unfiltered photolysis in dioxane–$H_2O$ yielded acid with scrambling corresponding to approximately 30% oxirene participation, as deduced from the mass spectrum. The nmr spectrum ($CDCl_3$) indicated about 10% $^{13}$C at C-2; this corresponds to ~35% oxirene.

In contrast to the scrambling observed in the photochemical WR of azibenzil in dioxane–water, none could be detected in the thermal WR. Thermolysis of a 0.2 *M* solution of azibenzil in dioxane–water at 100° for 20 min resulted in brisk evolution of gas and the discharge of the yellow color. The resulting diphenylacetic acid, obtained in 59% yield, had a mass spectrum in which the intensity ratio of *m/e* 167/[212 + 213] was identical with that of the authentic, unlabeled acid. This indicates that oxirene is not involved in the thermolysis of azibenzil.

Again as with **7**, the extent of scrambling in the photolysis of **11** was dependent on the technique used for analysis. Trapping of the diphenylketene gave a significantly lower yield of oxirene than photolysis did and consequently it was necessary to examine the photolysis of the diphenylketene for isotopic scrambling.

**(e) Diphenylketene-*1*-$^{13}$*C* (14).** Photolyses of **14** were carried out in a manner identical with those of azibenzil, using *ca.* 5 × $10^{-3}$ *M* solutions in cyclopentane. Diphenylketene-*1*-$^{13}$*C* was generated by pyrolysis *in vacuo* of azibenzil (neat) at 100°. Comparison of the *m/e* 165 (100) and 166 (66) peaks in the mass spectrum of the labeled ketene with the corresponding peaks in natural diphenylketene generated in a similar way, *m/e* 165 (100) and 166 (63), showed that no scrambling had occurred in the pyrolysis. Quenching of the labeled ketene in water yielded diphenylacetic acid-$^{13}$*C* in which the heights of *m/e* 167 (100) and 68 (24) peaks were virtually identical in magnitude to the same peaks in the natural acid, *m/e* 167 (100), 168 (22), providing additional evidence that no scrambling occurred in the thermolysis. The labeled ketene contained 61% $^{13}$C. The results[49] are shown in Table V. It is seen that oxirene participation occurs to the extent of ~30%, which is half of that obtained from the photolysis of **11** under identical conditions.

**(f) α-Diazoacetophenone-$^{13}$*CO* (15).** The total amount

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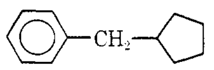
[49] Diphenylketene has been photolyzed in various solvents; see H. Hosaki, M. Nakano, and K. Kondo, *Tetrahedron*, **22**, 477 (1966).

**Table VI.** Photolysis of Diazoacetophenone-$^{13}CO$ (**15**) in Cyclopentane

| Filter (hr) | Concn, μmol **15** | Concn, μmol $N_2$ | Concn, μmol CO | $^{12}CO/^{13}CO$ | % scrambling[a] | Phenylcyclopentane, % yield (gc) | m/e 160/161 | % scrambling[b] |
|---|---|---|---|---|---|---|---|---|
| Quartz (2) | 27.4 | 26 | 10 | $1.2_2$ | 12 | 73 | $2.7_4$ | 21 |
| Quartz (2) | 41.0 | 41 | 21 | $1.2_2$ | 12 | 61 | $2.8_4$ | 20 |
| Quartz (17) | 13.7 | | 12 | | | 52 | $2.6_6$ | 23 |
| Vycor (22) | 20.6 | | 18 | $1.3_0$ | 20 | 61 | $2.6_5$ | 23 |
| Vycor (22) | 20.6 | | 20 | $1.3_3$ | 21 | 71 | $2.6_4$ | 23 |
| Pyrex (43) | 17.1 | 18 | 3 | $1.5_2$ | 27 | Nil | | |
| Pyrex (43) | 17.1 | | 4 | $1.5_7$ | 29 | Nil | | |
| Uranium glass (70) | 9.0 | | <1 | $2.9_2$ | 53 | Nil | | |
| Uranium glass,[c] sensitized (70) | 9.0 | | <1 | $3.1_0$ | 57 | Nil | | |

[a] % scrambling = $(54.6 - \%^{13}CO)/54.6 \times 100(\%)$. [b] % scrambling = $(\%\ m/e\ 161 = 15.0)/54.6 + 100(\%)$. [c] Sensitized with Michler's ketone, 4,4′-bis(dimethylamino)benzophenone.

of labeling in **15** was 63.2%, and in the carbonyl position 54.6%. Photolyses were conducted at 15° in cyclopentane solution using Vycor, Pyrex, and uranium glass filters. In the photolysis below 2800 Å the phenylmethylene from the secondary photolysis of the phenylketene underwent an insertion reaction with the solvent yielding phenylcyclopentylmethane (**16**). The isotopic scrambling was determined from the CO, as well as from **16**. In the Pyrex or uranium glass irradiation the yields of CO showed a marked fall-off and the formation of **16** was completely suppressed. The data are collected in Table VI. The degree of isotopic scrambling calculated from **16** is somewhat lower than that from CO. This discrepancy is probably due to errors in the mass spectrometric analyses. The amount of scrambling derived from the carbene insertion product



is constant, while that from CO appears to exhibit a definite trend with the wavelength of irradiation; the longer the wavelength the higher the yields. One sensitized experiment was done with uranium glass filtered radiation using Michler's ketone yielding a result similar to that in the direct photolysis.

The photolysis of **15** was also studied in methanol solution, and the isotopic scrambling determined from the mass spectrometric cracking pattern of the $PhCH_2COOMe$ product. The results are listed in Table VII.

**Table VII.** Photolysis of α-Diazoacetophenone-$^{13}CO$ (**15**) in Methanol

| Filter | Yield of $PhCH_2COOMe$, % | m/e 91/92 | % scrambling |
|---|---|---|---|
| Quartz | 100 | $3.2_6$ | 19 |
| Vycor | 100 | $3.7_8$ | 15 |
| Pyrex | 100 | $4.7_5$ | 8 |
| Uranium glass | 100 | $5.6_5$ | 9 |
| Uranium glass | 100 | $4.1_5$ | 12 |
| Uranium glass, sensitized[a] | ~30 | $4.0_0$ | 13 |
| Uranium glass, sensitized[a] | ~30 | $4.5_5$ | 9 |
| Uranium glass, sensitized[a] | ~30 | $3.7_6$ | 15 |

[a] Michler's ketone sensitized.

The extent of scrambling is small and is comparable to that obtained in cyclopentane solution at λ <2800 Å, and little variation appears with wavelength or on sensitization. Above λ 2800 Å, in addition to the WR product, methyl phenylacetate (**17**), the abstraction product of the ketocarbene, acetophenone, also appears in detectable yields. On photosensitization there is a marked increase in the yield of this latter product.

We also intended to examine the isotopic scrambling in the photolysis of phenylketene. Phenylketene-*1*-$^{13}C$ (**18**) was prepared by the Pyrex filtered photolysis of **15** in cyclopentane solution. The photolysis of **15** at this wavelength is quite rapid and could be brought to near completion in 1 hr irradiation. Under the same condition the ketene photolysis is slow and no significant decomposition would occur. The isotopic scrambling which occurred during conversion of **15** to **18** was determined by quenching **18** with methanol and analyzing the ester. The ketene solution was then photolyzed with quartz or Vycor filtered light and the carbene insertion product **16** subjected to mass spectrometric analyses. From the combined results the extent of scrambling which had taken place in the photolysis of **18** was evaluated to be about 3–4%.

## Experimental Section

**General.** Infrared spectra were measured on Perkin–Elmer 421 and 700 spectrophotometers in carbon tetrachloride. Nmr spectra were measured on Varian A-60 and HA-100 instruments. The mass spectra were measured on an AEI MS-2 or MS-9 instrument using the direct probe. Liquid products were analyzed with an AEI MS-12 coupled mass spectrometer–gas chromatograph, using a 15 ft × 1/8 in. 15% SE-30 on Chromosorb P-AW column at 240° and a 6 ft × 1/8 in. 5% SE-30 on Chromosorb column at 100°. Gases evolved from the photolyses were analyzed by gc using an 8 ft molecular sieve column at 80°. Liquid-phase photolyses were conducted at 15° with a Hanovia 450-W medium-pressure mercury lamp.

**Materials.** Compound **7** was prepared from acetyl-*1*-$^{13}C$ chloride (Merck, 56.8% $^{13}C$) and diazoethane by the method of Wilds and Meader.[50] The crude product was a 1:1 mixture of **7** and 1-propanol, the latter originating from the diazoethane solution. Pure **7** could be obtained by cautious bulb-to-bulb distillation as an orange-yellow oil; bp 35–40° (12 Torr); ir 1647 ($^{12}C{=}O$), 1606 ($^{13}C{=}O$), 2065 ($CN_2$) $cm^{-1}$; nmr ($CCl_4$) $\delta$ 2.14 (s and d, $J_{CH_3{}^{13}CO}$ = 5 Hz, $CH_3$–CO and $CH_3{}^{13}CO$), 1.94 (broad s, $CH_3C{=}N_2$); mass spectrum: m/e 28 (100), 39 (31), 40 (27), 41 (35), 42 (28), 55 (5), 56 (6), 70 $(M - 28)^+$, (31) 71 $(M + 1 - 28)^+$, (40).

Compound **12** was prepared as described for natural material.[51]

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(50) A. L. Wilds and A. L. Meader, *J. Org. Chem.*, **13**, 763 (1948).

(51) B. Rabjohn, Ed., "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1953, p 348.

From 0.32 g of α-bromoisobutyryl-*1*-$^{13}$*C* bromide (**19**), a solution of **12** was obtained in ethyl acetate. **12** was purified by two trap-to-trap distillations, from −65 to −196°. Final purification was achieved by preparative gc on an 8 ft × 0.25 in. silicone oil on Celite column. The purified ketene was a light yellow, volatile liquid; the mass spectrum indicated the presence of 63.3% $^{13}$C in the carbonyl group. The ratio of the *m/e* 41 and 42 peaks was the same as in the natural material, 79:21; thus it is concluded that no scrambling occurred during the preparation. The compound **19** was prepared by the method in ref 51 with slight modifications.

In the preparation of isobutyric acid-*1*-$^{13}$*C* the method of Dauben, *et al.*,[52] was followed.

In the preparation of compound **11** benzoic acid-*1*-$^{13}$*C* (Merck, 61% $^{13}$C) was converted to desoxybenzoin-$^{13}$*C* (**20**) by the method of Jenkins:[53] ir, 1682 ($^{12}$C=O), 1697 (sh), 1646 ($^{13}$C=O), 1656 cm$^{-1}$ (sh); nmr (CCl$_4$) δ 8.0 − 7.6 (m, 2 H), 7.41 − 7.0 (m, 8 H), 4.08 (s, 2 H, –CH$_2$–), 4.08 (d, –CH$_2$$^{13}$CO, $J_{\mathrm{CH_2{}^{13}C}}$ = 6.5 Hz); mass spectrum *m/e* 197 (M + 1)$^+$ (9.5), 196 (M)$^+$ (6.0), 106 (100), 105 (65), 91 (8). Compound **20** was converted into azibenzil-$^{13}$*CO*, mp (ether) 78°, with toluenesulfonyl azide by the method of Regitz.[54]

The properties of azibenzil-$^{13}$*CO* agreed with those reported in the literature.[53] The isotopic and normal carbonyl stretching vibrations appeared at 1600 and 1622 cm$^{-1}$, respectively. The molecular ion does not appear in the mass spectrum but the ratios *m/e* 122/123 and 77/78 of benzoic acid-$^{13}$*C*, supplied by Merck, used to prepare this diazo ketone, indicated that the total content of $^{13}$C in the molecule was 61.2%, while the phenyl ring contained 6.6% $^{13}$C. Thus, only 61.2 − 6.6 = 54.6% of the carbon atoms in the carboxy group are $^{13}$C. This was taken into account in evaluating the data.

Diphenylketene-*1*-$^{13}$*C* was generated by pyrolysis at 100° *in vacuo* of **11**: ir 2095 (C=C=O), 2043 cm$^{-1}$ (C=$^{13}$C=O); mass spectrum *m/e* 195 (67), 194 (43), 166 (66), 165 (100). Pyrolyses of natural azibenzil in a similar manner yielded natural diphenylketene: ir 2095 cm$^{-1}$ (C=C=O); mass spectrum *m/e* 195 (17), 194 (85), 166 (63), 165 (100). Diphenylacetic acid-*1*-$^{13}$*C* was prepared by quenching diphenylketene-*1*-$^{13}$*C* in water; mass spectrum *m/e* 167 (100), 168 (24). The natural acid was prepared in a similar way from natural diphenylketene; mass spectrum *m/e* 167 (100), 168 (22).

To prepare **15**, 680 mg of benzoic acid-*1*-$^{13}$*C* (Merck, 63.2 atom % $^{13}$C] was added to 3 ml of thionyl chloride. This mixture was heated at reflux for 20 min. The excess thionyl chloride was removed by codistillation with two 5-ml portions of benzene and the residue was taken up in 10 ml of ether. The ethereal solution was added dropwise over 22 min to an excess of stirred, cooled (0°) ethereal diazomethane. This mixture was stirred for 2.5 hr at 0°, followed by 1 hr at room temperature. Evaporation of the ether left a yellow solid, mp 44–46° after three recrystallizations from hexane: yield 230 mg (29%); ir (CCl$_4$) 1600 ($^{13}$C=O), 1637 ($^{12}$C=O) cm$^{-1}$.

**Irradiation in Cyclopentane.** Solutions of **7**, **11**, **14**, or **15** (0.5–2.0 × 10$^{-2}$ *M*) were irradiated in sealed quartz tubes *in vacuo* with Pyrex or Vycor filters. Noncondensable gases were collected from the tube after cooling to −196° and analyzed by glc and high resolution mass spectrometry. With **7**, propylene was separated from the solvent by distillation at −139° and was purified by preparative glc on a 7 ft silica gel column. With **11** and **15**, after the noncondensable gases were collected, the cyclopentane was distilled off at atmospheric pressure and the viscous, oily residue was analyzed in the MS-12 mass spectrometer. The product mixture from the photolysis of **14** was complex and was not resolved. Compound **13** was obtained in *ca.* 25% yield.

**Irradiations in Dioxane–Water.** Solutions of **7** and **11**, 0.02–0.15 *M*, were irradiated in dioxane–water (2:1) using a Vycor filter. The reaction mixture from **7** was treated with 1.5 ml of 1 *N* aqueous NaOH. The aqueous solution was separated from the organic layer, acidified with 2 ml of 1 *N* aqueous HCl and extracted three times with ether. The ether layer was dried over magnesium sulfate and evaporated through a 12-in. Vigreux column. Distillation at 100–110° (160 Torr) yielded 75% of the expected isobutyric acid, which was analyzed by mass spectrometry for $^{13}$C distribution.

The reaction mixture from the photolysis of **11** was worked up by evaporation of the dioxane–water mixture followed by trituration with chloroform, drying with sodium sulfate, and evaporation. The diphenylacetic acid was crystallized from 50% ethanol, mp 142–144°, yield 60%, and analyzed for $^{13}$C distribution by mass spectrometry.

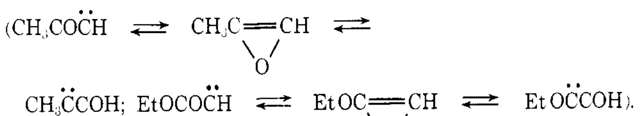
**Thermolysis of Azibenzil in Dioxane–Water.** A solution of 44 mg of azibenzil-$^{13}$*CO* in 2 ml of dioxane and 1 ml of water was heated at 100° for 20 min. Brisk evolution of gas started after 1 min of heating, and the deep orange solution turned to a light yellow color. The solution was poured into excess 5% aqueous NaHCO$_3$ and the mixture was extracted with 3 × 5 ml of ether. The residual aqueous layer was acidified with dilute HCl to pH 2 and the resulting white solid was extracted with ether (3 × 5 ml); the combined ether extracts were dried over magnesium sulfate and evaporated to yield diphenylacetic acid: mp 140–142°; mass spectrum *m/e* (167/[212 + 213]) = 79.4%/20.6%; natural diphenylacetic acid, obtained in the same way, exhibited an identical intensity ratio in its mass spectrum.

**Gas-Phase Photolysis of 3-Diazo-2-butanone and Dimethylketene.** In a typical run, *ca.* 10 mg of material was irradiated for 90 min in a quartz cell with a 140-W Hanovia medium-pressure mercury lamp equipped with a Vycor filter. The noncondensables at −196° were analyzed by gc on an 8-ft 5A molecular sieve column, the (−196–130°) fraction on a 7-ft medium-activity silica gel column, and the (−130 to −78°) fraction on a 10% tricresyl phosphate column.

## Discussion

In light of the experimental data presented here and in the previous preliminary communication,[1–3] the transient existence of the long-debated oxirene structure and its role in the photochemical WR sequence of α-diazo ketones and α-diazo esters can be regarded as firmly established. It now appears that the intervention of oxirenes in these reactions, as well as in the photochemical decompositions of ketenes, is a rule rather than an exception. The earlier literature claims to the contrary are evidently in error and should be disregarded.

For the sake of clarity we summarized the available data on isotopic labeling studies in Table VIII. From these it is clearly seen that a prominent feature of the oxirene-forming reaction is its restriction to excited singlet states, populated upon direct photoexcitation. In triplet photosensitization the WR does not occur[42–45] and in thermolysis, even when WR occurs, it proceeds without the intervention of the oxirene. Thus, while direct photolysis of diazocyclohexanone, diazoacetone, or ethyl diazoacetate yields the corresponding ketene as principal product, the triplet benzophenone sensitization of these molecules does not lead to ketene. Instead, it affords abstraction and nonstereospecific addition products with olefins, derived from triplet-state primary carbenes. It is conceivable that oxirene participation could occur without ketene formation; this would lead to secondary carbenes isomeric with the primary ones



To date no evidence exists for this type of rearrangement in triplet sensitization.

Thermal decomposition of ethyl diazoacetate gives products arising from the insertion and stereospecific addition of carbethoxymethylene. These products are indicative of a singlet state carbene which does not readily undergo WR, as manifested by the complete absence of ketene. Therefore if in the photochemical WR a singlet carbene is an intermediate it must be a

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(52) W. G. Dauben, J. C. Reid, and P. E. Yankwich, *Anal. Chem.*, **19**, 828 (1947).

(53) S. S. Jenkins, *J. Amer. Chem. Soc.*, **55**, 703 (1933).

(54) M. Regitz, *Chem. Ber.*, **98**, 1210 (1965).

**Table VIII.** Summary of Experimental Results

| Compound | Reaction | Phase | Conditions | % yield of oxirene |
|---|---|---|---|---|
| $CH_3COCN_2CH_3$ | Photolysis | Gas ~5 Torr | λ > 2200 Å | 100 |
| $CH_3COCN_2CH_3$ | Photolysis | c-$C_5H_{10}$ soln | λ > 2200 Å | ~70 |
| $CH_3COCN_2CH_3$ | Photolysis | Dioxane–water soln | λ > 2200 Å | ~61 |
| $(CH_3)_2C{=}C{=}O$ | Photolysis | Gas | λ > 2200 Å | ~20 |
| $(CH_3)_2C{=}C{=}O$ | Photolysis | c-$C_5H_{10}$ soln | λ > 2200 Å | ~16 |
| $PhCOCN_2Ph$ | Photolysis | c-$C_5H_{10}$ soln | λ > 2000 Å | 60–70 |
| $PhCOCN_2Ph$ | Photolysis | Dioxane–water soln | λ > 2200 Å | ~50 |
| $PhCOCN_2Ph$ | Photolysis | Dioxane–water soln | λ > 2800 Å | ~30–35 |
| $PhCOCN_2Ph$ | Thermolysis | Dioxane–water soln | 100° | Nil |
| $Ph_2C{=}C{=}O$ | Photolysis | c-$C_5H_{10}$ soln | λ > 2000 Å | 30 |
| $PhCOCN_2H$ | Photolysis | c-$C_5H_{10}$ soln | λ > 2000 Å | 12–21 |
| $PhCOCN_2H$ | Photolysis | c-$C_5H_{10}$ soln | λ > 2200 Å | 20–23 |
| $PhCOCN_2H$ | Photolysis | c-$C_5H_{10}$ soln | λ > 2800 Å | 27–29 |
| $PhCOCN_2H$ | Photolysis | c-$C_5H_{10}$ soln | λ > 3600 Å | ~53 |
| $PhCOCN_2H$ | Michler's ketone | c-$C_5H_{10}$ soln | Sensitized | ~57 |
| $PhCOCN_2H$ | Photolysis | $CH_3OH$ soln | λ > 2000 Å | 19 |
| $PhCOCN_2H$ | Photolysis | $CH_3OH$ soln | λ > 2200 Å | 15 |
| $PhCOCN_2H$ | Photolysis | $CH_3OH$ soln | λ > 2800 Å | 8 |
| $PhCOCN_2H$ | Michler's ketone | $CH_3OH$ soln | Sensitized | 12 |
| $PhHC{=}C{=}O$ | Photolysis | c-$C_5H_{10}$ soln | λ > 2220 Å | ~4 |
| $CH_3COCN_2H$ | Photolysis | Gas ~10 Torr | λ > 2200 Å | >27 |
| $C_2H_5OCOCN_2H$ | Photolysis | Gas ~5 Torr | λ > 2200 Å | >32 |
| $C_2H_5OCOCN_2H$ | Thermolysis | c-$C_5H_{10}$ soln | λ > 2200 Å | Nil |
| $CH_3OCOCN_2H$ | Photolysis | Gas ~5 Torr | λ > 2200 Å | >28 |

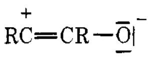
more energetic singlet than the one formed in thermolysis. (The moderately high-temperature, solution-phase thermolysis should lead to the lowest singlet state carbene.)

The thermolysis of azibenzil affords diphenylketene in at least 59% yield, but without the intervention of the oxirene. This result again suggests that if a singlet carbene is an intermediate, the one which follows the oxirene-forming reaction path is a more energetic singlet.

In the interpretation of the experimental data it is necessary at this point to take cognizance of the molecular orbital computational results presented in the accompanying article[48] which indicate that concerted decomposition to give ketene + $N_2$ in a single-step process as proposed in the literature[19] is not feasible even in photoexcitation, because of the large values of the computed activation energies involved. Both the thermal and photochemical modes of decomposition yield the ketocarbene as the primary reaction product.

The calculated state energy levels[48] suggest that in the photoexcitation of diazoethanone, diazopropanone, and diazobutanone, even with Pyrex filtered light ($\lambda_{min} \sim 2900$ Å ~ 100 kcal/mol) four different excited states can be reached. Using shorter wavelength radiation additional states can be populated.

Decomposition of electronically excited diazo ketones gives rise to the formation of electronically excited ketocarbenes which undergo rapid internal transition to the ground state to yield vibrationally excited ground-state singlet carbenes. The carbenes convert to the more stable tautomeric zwitterion i. In this regard, however, a word of caution is necessary for the EHMO method used in the computations achieved notoriety in overestimating the stability of ionic structures. The zwitterion in turn can isomerize to ketene *via* a bridged cyclic intermediate ii in a simultaneous competing reaction to oxirene. The oxirene structure is inherently unstable with respect to C–O bond cleavage and reverts to the zwitterion, and ultimately to the ketene. The oxirene lies at a higher energy level than the transition state of the ketene forming step and while the latter is attainable in thermal excitation of the diazo ketone, the oxirene state is not. Thus, the difference in behavior between the thermal and photochemical systems is ascribed to the difference in the excess vibrational energy of the ground-state singlet ketocarbene intermediate.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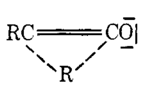
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The processes discussed above may be illustrated by the reactions in Scheme II.

All steps must be rapid because scavenging of ketocarbenes cannot be readily accomplished and in the photochemical systems oxirene formation competes efficiently with vibrational relaxation.

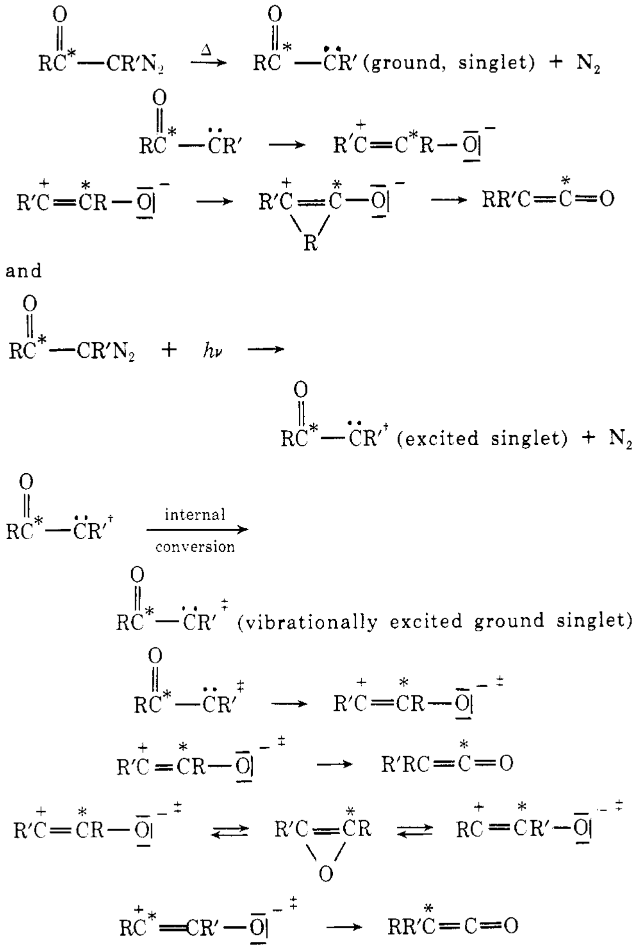
The highest yields of oxirene obtain from the symmetrically substituted diazo ketones, **7** and **11**, Table VIII. The cause of this is not clear but it is hoped that further studies using pairs of asymmetrically substituted diazo ketones, $RCOCR'N_2$ and $R'COCRN_2$, will help to elucidate this question.

The difference in yields using cyclopentane or dioxane–water as solvent can be attributed to secondary oxirene formation from the photolysis of the ketene in the former solvent, and its absence in the latter.

The influence of phase shift is evident from the data on **7** and can be interpreted as being due to either partial relaxation of the vibrationally excited zwitterion intermediate or reversion of the hot ketene molecule in the gas phase to oxirene, or both.

As shown above, the adduct from the reaction of $O(^3P)$ atoms with dimethylacetylene exhibits different kinetic features from those of the intermediate produced in the photolysis of **7**, although the computed total energies are approximately equal.[48] This was interpreted as being due to the difference in electronic

**Scheme II**

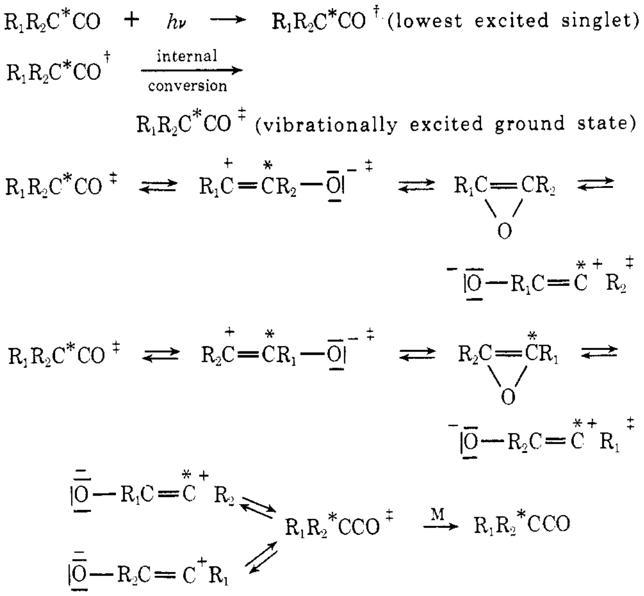


states; the former is in the lowest triplet and the latter is in the ground singlet state. The pressure dependence of the ketene to vinyl methyl ketone ratios is a clear manifestation of the substantial energy barrier for the ketene forming step in the triplet state.

The results obtained in the present study on diazoacetophenone are consistent with the earlier photochemical studies and point to the intervention of triplet ketocarbene in the long wavelength photolysis of **15.** This can arise from the primary decomposition of triplet excited **15,** formed *via* intersystem crossing.[55]

The yields of oxirene formation from the photolysis of ketenes are lower than from the photolysis of diazo ketones. The most plausible mechanism for the overall reaction is indicated by the sequence in Scheme III. Thus, the primary intermediate of the rearrangement sequence is the vibrationally excited ketene which is the end product of the sequence in the case of diazo ketones. Since deactivation and decomposition of the hot ketene always compete with rearrangement, the oxirene yields are expected to be lower.

**Scheme III**



It should also be mentioned that in the oxirene-forming rearrangement of the chemically activated hot ketene reported by Montague and Rowland[47] only singlet and not triplet methylene was found to be effective. This is in line with the general conclusions of the photochemical studies and theoretical predictions.[48] Further studies are in progress.[56]

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(55) With respect to the mechanistic interpretation given in ref 42 it should be pointed out that the experimental data can be explained in a plausible manner if the ground state of the carbene is taken to be a singlet.[48]

(56) After submission of our original manuscript two recent articles relevant to the present work came to our attention: (a) S. A. Matlin and P. G. Sammes, *J. Chem. Soc., Chem. Commun.*, 11 (1972), reported oxirene formation in the decomposition of a number of diazo ketones. The results are in accordance with and lend additional support to the data described above although slight differences appear to exist in the mechanistic interpretation. (b) H. E. Avery and S. J. Heath, *Trans. Faraday Soc.*, **68**, 512 (1972), reported a detailed study of the O($^3$P) + dimethylacetylene reaction. There again, the experimental results are concordant but the interpretations differ slightly.