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Temperature and Isotope Effects in the Reactions of Phenylcarbene with Acetone

Hideo Tomioka,* Yasuji Ozaki, Hiroyuki Nakamura, and Yasuji Izawa
Department of Industrial Chemistry, Faculty of Engineering, Mie University, Tsu, Mie 514

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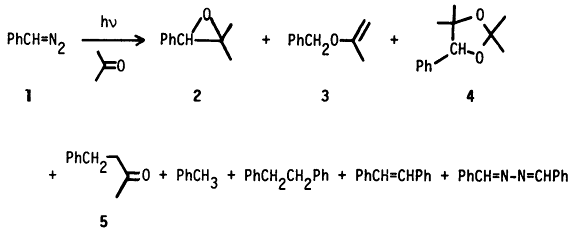
Synopsis. Phenylcarbene generated in acetone solution gives oxirane, vinyl ether and 1,3-dioxolane presumably *via* initial attack of the singlet state on the lone pair electrons of carbonyl oxygen leading to a carbonyl ylide, whereas a C–H insertion product arising from the triplet markedly increases in matrix environments.

In the past few years several research groups have studied the chemistry of carbenes in rigid matrices at low temperature.[1–4] In the case of carbenes with triplet ground states there are profound differences between the chemistry observed in fluid solution at ambient temperature and that obtaining in a matrix at −196 °C. For example, arylcarbene generated in olefinic solution at ambient temperature gives cyclopropanes almost exclusively which are mostly derived from the singlet state, whereas arylcarbene generated in olefinic matrices at −196 °C result in a dramatic increase in C–H insertion products at the expense of the cyclopropanes.[2] It has been proposed[1–4] that these C–H insertion products are formed *via* an abstraction-recombination of the triplet carbene on the basis of extensive spectroscopic and chemical evidence for the presence of the ground-state triplet carbene in the low temperature matrix photolysis of most aryldiazomethanes at −196 °C. Similar dependence of the product distribution upon the temperature at which the arylcarbene is generated has been observed in its reactions with alcohol,[1a] ether,[1f] amine,[1f] and halide,[1e] and pertinent information as to the relationship between the multiplicity and reaction pattern of the carbene is available from these studies.

In this work we have extended the matrix study of carbene reactions by investigating the mechanism of its reaction with ketone. In contrast to the intensive study lavished upon the reaction of carbenes with carbon-carbon double bonds,[5] only scant information is available concerning the reactions with the carbon-oxygen double bond. Interest in this reaction has intensified and a number of papers have appeared on the subject in the last few years.[6]

Results and Discussion

A solution of phenyldiazomethane (**1**) in degassed acetone was irradiated in a Pyrex tube at different temperatures. GLC analysis of the product mixture revealed the presence of oxirane (**2**), vinyl ether (**3**), 1,3-dioxolane (**4**) and 4-phenyl-2-butanone (**5**), along with toluene, bibenzyl, *cis*- and *trans*-stilbenes, and aldehyde azine as indicated in equation (1). The product distributions at different temperatures were determined by GLC analysis as summarized in Table 1. It is evident from the Table that the product distributions are highly dependent on the temperature at which the irradiation was carried out. Photolysis of **1** in acetone at 0 °C, for



(1)

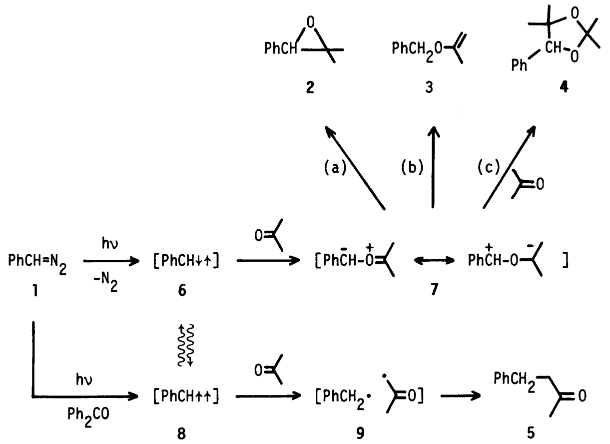
example, gave **4** as the main product along with **2** and **3**. When the photolysis was carried out below −150 °C, however, **5** became the main reaction product at the expense of 1,3-dioxolane.

The phenomena are similar to those observed[1–4] in the reaction of phenylcarbene with other substrates, *e.g.*, alcohol,[1a] and can be explained as follows. Phenylcarbene (**6**) is expected to react with acetone in its singlet state to form carbonyl ylide (**7**) as a result of electrophilic attack on the nonbonding electrons of the carbonyl oxygen, since it is well known[5] that most singlet carbenes can react as Lewis acids by sharing a pair of nonbonding electrons. The formation of a carbonyl ylide by reaction of carbene with acetone has been demonstrated recently by Wong, Griller, and Scaiano.[7] They generated singlet fluorenylidene, which was identified spectrophotometrically, and followed its capture by acetone to from a carbonyl ylide. The carbonyl ylide (**7**) thus formed collapses *via* three competing reaction pathways:[8] (a) ring-closure to give oxirane (**2**), (b) intramolecular proton shift to yield vinyl ether (**3**), and (c) reaction with a second acetone molecule leading to dioxolane (**4**). A sharp decrease in the yield of **4** in the solid phase reaction is then expected on the basis of the above scheme since mobility of a molecule in a matrix is limited and the intermolecular pathway becomes unfavorable.

Table 1. Product distribution as a function of temperature in photolysis of **1** in acetone-H_6 (D_6)

T/°C	Yield/%[a]			
	2	**3**	**4**	**5**
0[b]	4.6 (5.9)	10.8(5.7)	20.9(41.6)	0(0)
−78[b]	4.5 (2.2)	6.9(3.6)	16.2(33.5)	0(0)
−110[c]	10.5 (2.3)	8.2(4.7)	12.3(31.2)	<1(0)
−150[c]	6.0 (2.6)	9.8(3.8)	5.5 (0.7)	20.0(4.7)
−196[c]	1.9(11.4)	1.8(4.3)	1.3 (1.3)	21.1(0.7)

a) Determined by GC. Yields in parentheses are for irradiations in acetone-d_6. Other products detected in each experimental condition were toluene, bibenzyl, stilbenes and aldehyde azine. b) Liquid phase. c) Solid phase.



4-Phenyl-2-butanone on the other hand, should presumably arise from insertion of phenylcarbene into the C–H bonds of acetone. Since this compound is only formed in a matrix environment, we propose that the triplet state is responsible for its formation. Thus, triplet phenylcarbene (**8**) generated in the matrix abstracts hydrogen from the host acetone to give the radical pair (**9**), which recombines with high efficiency to afford **5** due to the limited diffusibility of the radical pair.

The reason why triplet reactivity appears at low temperature has been a key question. A reasonable explanation has been advanced recently by Senthilnathan and Platz.[3] Their kinetic analysis of the decay of triplet arylcarbenes in a rigid matrix has demonstrated that a predominant decay path of triplet carbene is by hydrogen atom tunneling. The availability of this tunneling pathway at low temperature leads to the hydrogen abstraction products. One of the characteristic phenomena of the tunneling reaction is a large kinetic isotope effect. For example, Wong and Williams[9] have observed that k_H/k_D is larger than 1.3×10^3 for intermolecular hydrogen atom abstraction by $CH_3\cdot$ from a CH_3NC matrix at −150 °C. Measured isotope effects with triplet arylcarbenes are much more modest. Thus, k_H/k_D is 23 for hydrogen atom abstraction by diphenylcarbene from toluene at −196 °C.[3a] The kinetic results are consistent with the isotope effects on the product distribution. For example, product analyses of the reaction of phenylcarbene in deuterated alcoholic matrices at −196 °C revealed that a substantial isotope effect was observed for C–H (D) insertion while the isotope effect on O–H (D) insertion was small.[1h,3c] With these precedents in mind we irradiated **1** in acetone-d_6 at various temperatures. The results summarized in the Table clearly indicate that there is a substantial isotope effect in the C–H insertion process at −196 °C; the yield of 4-phenyl-2-butanone is reduced by almost a factor of 20 in acetone-d_6. In the light of the lack of an isotope effect on the O–H (D) insertion process of singlet phenylcarbene compared with a substantial isotope effect in C–H insertion in deuterated alcoholic matrices at −196 °C, the considerable isotope effect on C-H insertion leading to **5** supports the view that **5** arises from a triplet carbene, presumably *via* hydrogen atom tunneling followed by recombination of the resulting radical pairs (**9**).

Experimental

Materials. Phenyldiazomethane **1** was prepared immediately before use as described in the literature. Acetone-d_6 was purchased from E. Merck and used without purification. Authentic samples of the phenylcarbene adducts with acetone (**2**—**5**) were prepared as follows. Oxirane **2** was obtained by the oxidation of 2-methyl-1-phenyl-1-propene with *m*-chloroperbenzoic acid. Vinyl ether **3** was prepared by the reaction of benzyl alcohol with propylene in the presence of iodine and mercuric oxide followed by treatment of the resulting 2-benzyloxypropyl iodide with ethanolic KOH. 1,3-Dioxolane **4** was isolated from the reaction mixture by column chromatography on silica-gel. Satisfactory spectroscopic and mass spectral data have been obtained on all compounds.

Product Analyses. All irradiations for product analyses were conducted with use of a water-cooled Halos 300-W high-pressure mercury lamp. In a typical procedure, 0.005 mmol of **1** was added to 2.0 cm^3 of acetone in Pyrex tubes. The sample was then degassed by three freeze-thaw cycles, and the sample tube sealed under vacuum. The tube was suspended in a transparent Pyrex Dewar flask filled with coolant and irradiated until all **1** was destroyed.[1c] The product identification and yields were conveniently determined by GC (Silicone OV-17 on Diasolid L) and GC-MS (Shimadzu GC-MS 1000 spectrometer) techniques.

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