# THE EFFECT OF OXYGEN ON THE MATRIX
CHEMISTRY OF DIPHENYLCARBENE

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Summary: The effect of oxygen on the matrix chemistry of diphenylcarbene is
described.

The chemistry of carbenes in general and diphenylcarbene (DPC) in particular is com-
plicated by competing reactivity of two closely spaced spin states.[2,3,4] One can frequent-
ly obtain exclusive singlet carbene chemistry with a particular substrate by the addition
of a selective triplet carbene scavenger such as butadiene[5] or oxygen.[6] Oxygen reacts with
triplet DPC at a nearly diffusion controlled rate to give first carbonyloxide 1 and ulti-
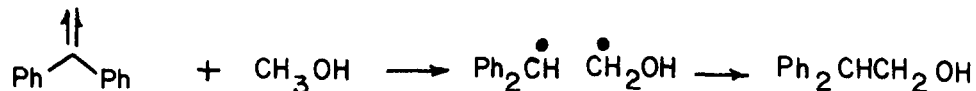mately benzophenone (BZ).
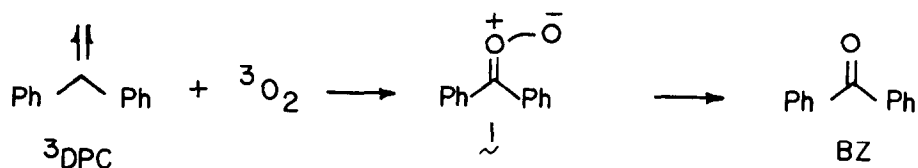
Ylid 1 has recently been observed by laser flash photolysis.[7] The ylid derived from cyclo-
pentadienylidene and oxygen has been observed by matrix isolation infrared spectroscopy.[8]
Wasserman had earlier discovered that upon thawing matrix isolated ^{3}DPC in the presence of
oxygen a chemiluminescent reaction ensues where the emission is due to triplet BZ.[9]

Molecular oxygen and nitrogen were bubbled into 0.1M solutions of diphenyldiazomethane
in methanol, 2-propanol, and d,ℓ-2-butanol at -78°. This temperature was utilized rather
than room temperature so as to maximize the solubility of the appropriate gas in the alco-
hol. After the solutions were saturated with the gas (10 minutes) the samples were stop-
pered and irradiated at -196° for 2-2.5 hrs. EPR signals due to ^{3}DPC were observed for
both the oxygen and nitrogen saturated samples and the signals decayed at the same rate in
both samples.[10] The rigid matrix greatly retards the rate of reaction of ^{3}DPC with oxygen.
Upon thawing the samples acrylonitrile was added to consume excess diphenyldiazomethane and
the samples were analyzed by gas chromatography (see Table).[11] As expected from the work
of Tomioka the matrix chemistry of DPC produces large amounts of both formal CH and OH in-
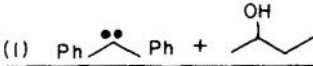sertion products.[12] The OH insertion process is thought to be a reaction of ^{1}DPC.[13]
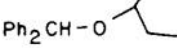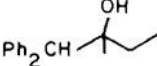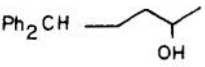
$$\text{Ph} \overset{\uparrow\downarrow}{\diagup\diagdown} \text{Ph} \quad + \quad CH_3OH \quad \longrightarrow \quad Ph_2CHOCH_3$$
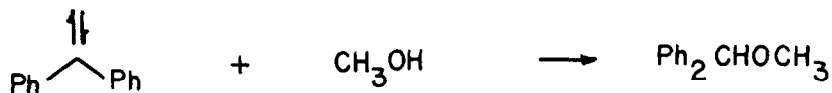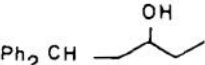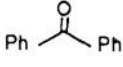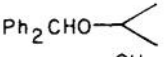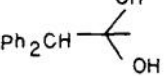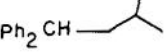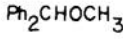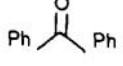
The formal CH insertion product is generally ascribed to ^{3}DPC reaction.[12]

$$\text{Ph} \overset{\uparrow\downarrow}{\diagup\diagdown} \text{Ph} \quad + \quad CH_3OH \quad \longrightarrow \quad Ph_2\overset{\bullet}{C}H \quad \overset{\bullet}{C}H_2OH \quad \longrightarrow \quad Ph_2CHCH_2OH$$

Direct photolysis of diphenyldiazomethane in methanol, 2-propanol, or d,ℓ-2-butanol over a wide temperature range produces only the OH insertion product. Triplet sensitized photolysis of diphenyldiazomethane in methanol[13] or d,ℓ-2-butanol[14] solutions also gives only the OH insertion product. This is consistent with rapid equilibration between singlet and triplet DPC.

Extrapolation of solution chemistry to the matrix would predict that oxygen would either increase the ratio of OH to CH insertion products (slow ^{1}DPC $\rightleftarrows$ ^{3}DPC) or leave the ratio unchanged (fast singlet triplet equilibration relative to carbene reaction with oxygen). Contrary to these expectations the OH/CH ratio is lower in oxygen than in nitrogen saturated samples. In 2-propanol and d,ℓ-2-butanol the yield of OH insertion and formal CH insertion prod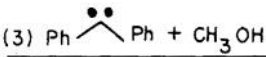ucts α to the hydroxyl are reduced by oxygen whereas the yield of formal CH insertion products remote from the hydroxyl group remains unchanged. It is not reasonable to conclude that only the OH and α CH insertion products are triplet derived in the matrix. A simpler explanation is that molecular oxygen is not homogeneously distributed in the matrix but is held tightly near the hydroxyl group, perhaps by hydrogen bonding in the solid state. Those diphenylcarbenes which are generated near the hydroxyl group consequently are scavenged by oxygen while those DPC's more remote from the hydroxyl are unaffected. In every matrix studied the yield of BZ in oxygen saturated matrices is virtually equal to the decline of OH and CH derived products relative to their yield in nitrogen saturated matrices. This is in further support of our interpretation of a non homogeneous distribution of molecular oxygen. Diffusion of DPC and oxygen must be exceedingly slow at -196°. The distribution of oxygen in frozen methanol containing diphenyldiazomethane must be particularly non homogeneous as only the yield of OH insertion product is effected. It is not clear why there is no formal CH insertion into the secondary position of d,l 2-

The distribution of products formed upon reaction of DPC with alcoholic matrices at 77K in the presence of oxygen and nitrogen.

(1) $Ph \overset{\bullet\bullet}{\wedge} Ph$ + (sec-butanol, OH)	O_2	N_2
Ph_2CH-O	6	11
Ph_2CH (OH)	15	26
Ph_2CH — (OH)	10	10
Ph_2CH — (OH)	32	32
$Ph \overset{O}{\underset{}{\wedge}} Ph$	16	—
OH/CH	0.10	0.16

(2) $Ph \overset{\bullet\bullet}{\wedge} Ph$ + (isopropanol, OH)		
Ph_2CHO—	5	13
Ph_2CH—(OH)	25	41
Ph_2CH—(OH)	13	13
$Ph \overset{O}{\underset{}{\wedge}} Ph$	27	—
OH/CH	0.13	0.24

(3) $Ph \overset{\bullet\bullet}{\wedge} Ph$ + CH_3OH		
Ph_2CHOCH_3	46	59
Ph_2CHCH_2OH	18	18
$Ph \overset{O}{\underset{}{\wedge}} Ph$	5	—
OH/CH	2.56	3.28

butanol at 77K. The results show that solution results and solution phase mechanistic rules can not be readily extrapolated to matrix conditions.

Finally, the OH/CH ratio reported herein for methanol is somewhat larger than we have found earlier.[15] We believe that the discrepancy is due to the different concentrations of diphenyldiazomethane employed in the two studies. The earlier study employed a ten times more dilute solution of the diazo compound than this work. We now believe that the higher dilution study was somewhat affected by carbene photochemistry in the matrix and will be described in a subsequent report.

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11. All sample tubes were irradiated at -196° with two rayonet RPR 3500 (3500Å bulbs). After photolysis the tubes were stored at -196° for 18 hours then thawed. Excess diphenyldiazomethane was consumed by the addition of acrylonitrile followed by immediate GC analysis (Hewlett Packard 5830, 6 ft 15% SE 30 column). The GC peaks were identified by GCMS and coinjection with authentic samples.

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14. 1.3×10^{-2} M xanthone (ε 3500Å = 2590), 0.4×10^{-2} M diphenyldiazomethane (ε 3500Å = 598) and 0.25×10^{-2} M naphthalene, internal standard (ε 3500Å $\simeq$ 0).

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