Tetrahedron Letters No.36, pp. 3959-3962, 1968. Pergamon Press. Printed in Great Britain.

HALONIUM YLIDS II

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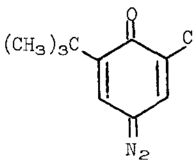
(Received in USA 25 April 1968; received in UK for publication 14 June 1968)

We find that while photolysis (λ>4800Å) of 3,5-di-t-butylbenzene-1,4-diazooxide, 1, in benzene (4.3×10^{-2} M) leads principally (89%) to the formation of 2,6-di-t-butyl-4-phenylphenol, 3, [m.p. 101-104°, lit. 101-102° (1)] with little formation (<1%) of diphenoquinone 4a, irradiation of 1 in i-propyl bromide or iodobenzene affords substantial amounts (38+% and 55+% respectively) of diphenoquinone 4a. We suggest that photolysis of diazooxide 1 in i-propyl bromide or iodobenzene gives rise to diphenoquinone 4a via intermediate halonium ylid 5a or 5b.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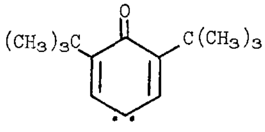
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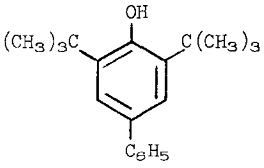
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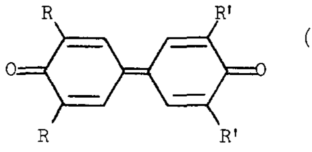
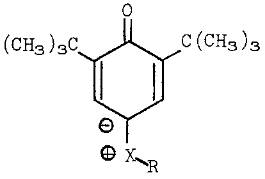

4a R=R'=t-butyl
4b R=t-butyl; R'=i-propyl
4c R=R'=i-propyl



	X	R
5a	Br	i-propyl
5b	I	C_6H_5
5c	Br	C_6H_5
5d	I	CH_3
5e	I	CF_3

An alternate mechanistic scheme which must be considered is that an initially formed singlet carbene, 2, which reacts with benzene to afford 3, is converted by heavy-atom solvents to its triplet ground state* which might then lead to diphenoquinone 4a. Heavy-atom (e.g., Br, I) induced multiplicity changes of aromatic hydrocarbon excited states are well documented (4,5),

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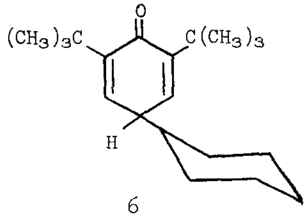
*Singlet carbene 2 has a triplet ground state which is observable by esr spectroscopy (Varian V4502 Spectrometer equipped with a variable temperature controller) upon photolysis (275 W G. E. sun lamp) of solid diazooxide 1 in a quartz tube at -180°. Resonances ascribed to the triplet were observed at 4688G; 4902G; 6755G; (very weak), and ca. 300G. D and E were determined to be 0.3141 cm^{-1} and 0.0051 cm^{-1} respectively. We wish to thank Mr. Dennis Chamot for his assistance in obtaining and interpreting the spectrum. Photolysis of other diazooxides likewise affords carbenes with triplet ground states (2,3).

although instances where such induced multiplicity changes affect chemical reactivity are rare (6,7). Instances of heavy-atom induced multiplicity changes of carbenes have been suggested (8) but not verified and a previous attempt to catalyze methylene singlet-triplet intersystem crossing with methyl iodide or ferric dipivaloylmethide was unsuccessful (9). However, cyanonitrene is reported to undergo a heavy-atom induced multiplicity change (10,11).

Singlet carbene 2 is implicated as an intermediate during the photolysis (>4800Å) of diazooxide 1 through the formation, in cyclohexane (4.5 x 10^{-2} M in 1), of carbon-hydrogen insertion product 6* (50+%) and by the stereoselective formation, in neat *cis* or *trans*-2-butene, of spirodienones 7 or 8 (85+%) (12). Dilution of *cis*-2-butene with an inert solvent such as hexafluorobenzene diminishes the stereoselectivity of the addition reaction (see Table I), presumably as a consequence of thermal deactivation of some singlet carbene to its less stereoselective triplet ground state. At the highest dilution studied, where at least one fourth of the carbene produced has reached the triplet state (*i.e.* 77% of $\frac{8}{7 + 8}$, assuming that 8 arises only via the triplet), diphenoquinone 4a could not be detected (nmr) in the crude product.



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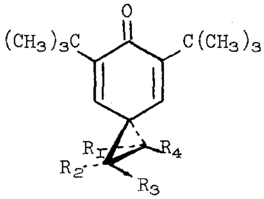
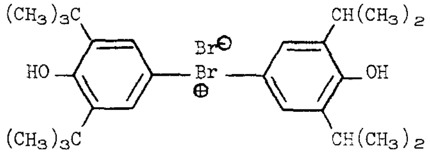


7 R_1,R_2=H; R_3,R_4=CH_3

8 R_1,R_3=H; R_2,R_4=CH_3



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On the other hand, dilution of *cis*-2-butene with heavy-atom solvents such as *i*-propyl bromide, methyl iodide, trifluoromethyl iodide, bromobenzene, or iodobenzene profoundly alters the reaction course, reducing the extent of olefin addition and leading to significant quantities of diphenoquinone 4a (see Table II).

Since examination of the data indicates that the triplet ground state of 2 adds to *cis*-2-butene with low stereoselectivity and leads to little diphenoquinone 4a, while iodinated solvents

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*Cyclohexadienone 6, identified in the crude photolysate by ir and nmr, readily tautomerizes to the corresponding phenol, m.p. 98 -99.5° [lit. 98 -99° (1)].

TABLE I

Photolysis[a] of *ca* 4 x 10^{-2} *M* Solutions of 3,5-Di-*t*-butylbenzene-1,4-diazooxide in *cis*-2-Butene Diluted with Hexafluorobenzene

Mole % C_6F_6[b]	Total % Yield[c] of	Product Ratio[c]
	7 + 8	7:8
0	*ca.* 100	18.0
74	85	4.5
90	77	2.0

[a] Conducted as described in (12) in sealed, degassed 17x22x615 mm Pyrex tubes.

[b] These values are approximate owing to difficulties in accurately measuring quantities of condensed *cis*-2-butene.

[c] Determined by nmr analysis of expanded high amplitude 100 MHz spectra of the vinyl proton region with durene as an internal standard. The olefin does not isomerize under reaction conditions.

TABLE II

Photolysis of *ca* 4 x 10^{-2} *M* Solutions of 3,5-Di-*t*-butylbenzene-1,4-diazooxide in *cis*-2-Butene Diluted with Heavy-atom Solvents

	Mole %	Product Ratio[a]		Olefin
Diluent	Diluent	7:8	4a:7 + 8	Isomerization[b]
$(CH_3)_2CHBr$	47	3.4	0.8	yes *cis*:*trans* 1.9
CH_3I	57	*ca.* all 7	2.3	no
C_6H_5I	44	*ca.* all 7	1.4	no
C_6H_5Br	42	5.4	0.2	yes *cis*:*trans* 4.1
CF_3I	47	*ca.* all 7	1.2	not analyzed

[a] Determined by nmr. Although absolute yields were not measured, nmr analyses of the crude products indicate that 4a, 7 and 8 are the principle products.

[b] Determined by glpc analysis of recovered olefin; 22' x 1/4" column of 18% SE-30 on Chromsorb P at 0°.

produce appreciable quantities of 4a but allow stereoselective addition, it is clear that singlet-triplet conversion is not a satisfactory explanation for the altered reaction course of carbene 2 in those iodinated solvents examined. Because brominated solvents lead to olefin isomerization, the degree of stereoselective addition is indeterminant, although the extent of addition is clearly reduced. These results are consistent with the formation, by electrophilic attack of carbene 2 on halogen, of iodonium and bromonium ylids 5a-5e which ultimately lead to diphenoquinone 4a. This ylid hypothesis is strengthened by the recent isolation of bromonium bromide 9 from the photolysis of 1 in the presence of 2,6-di-*i*-propyl-4-bromophenol and by the isolation of diphenoquinones 4a, 4b and 4c from the decomposition of the ylids generated by treating 9 with triethylamine (13).

It is interesting to note that while the ability of a heavy-atom solvent to cause excited state multiplicity changes parallels the ability of the halide to act as an electron acceptor (5), halonium ylid formation requires the halogenated solvent to function as an electron donor. Moreover, isolation of salt 9 demonstrates the strongly electrophilic nature of singlet 2 whose ground state may receive appreciable contribution from the zwitterionic resonance form.

Acknowledgement. This work has been partially supported by the Du Pont and the Rohm and Haas Companies and stimulated by discussions with Professor J. C. Martin.

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