- 4. H. G. Giles, R. A. Marty, and P. de Mayo, Can. J. Chem., <u>54</u>, 537 (1976); Chem. Commun., 409 (1974).
- 5. R. D. Brown, P. D. Godfrey, R. Champion, and M. Woodruff, Austr. J. Chem., <u>35</u>, 1747 (1982).
- 6. R. H. Judge and D. C. Moule, J. Mol. Spectrosc., 104, 248 (1984).
- 7. G. Martin, N. Lugo, M. Ropero, and H. Martines, Phosphorus Sulfur, 17, 47 (1983).
- 8. T. A. Hase and H. Peräkyla, Synthetic Commun., 12, 947 (1982).
- 9. M. Jacox and D. E. Milligan, Chem. Phys., 4, 45 (1974).
- 10. G. W. King and D. Moule, Spectrochim. Acta, <u>17</u>, 287 (1961).
- 11. W. W. Sander and O. L. Chapman, J. Org. Chem., 50, 543 (1985).
- L. Bellamy, New Data on the IR Spectra of Complex Molecules, Halsted Press, New York (1975).

EFFECTS OF OXYGEN IN THE PHOTOLYSIS OF 2,6-DI-TERT-BUTYL-1,4-BENZOQUINONEDIAZIDE IN CC14

A. Z. Yankevich, S. V. Rykov, and G. A. Nikiforov UDC 543.422.25:541.141.7:547.567.5:546.21

The major reaction product in the thermolysis of 2,6-di-tert-butyl-l,4-benzoquinonediazide (I) in CCl₄, namely, halocyclohexadienone (II), is formed as the result of the insertion of the singlet cyclohexadiene carbene into the C-Cl bond and cross reactions of radicals escaping into the bulk. The second reaction pathway is extremely sensitive to the addition of radical traps. Molecular oxygen not only accepts escaped radicals but also facilitates the singlet-triplet transition of the excited molecules formed in the photolysis [2]. Thus, we may expect that the composition of the final mixture in the photolysis of quinonediazide (I) in CCl₄ will also be a function of the presence of O_2 in the reaction mixture.

The preparative photolysis of quinonediazide (I) in CC14 with the continuous introduction of CO₂ gives dienone (II) in yields up to 95%. Furthermore, the reaction mixture also contains traces of 2,6-di-tert-butyl-1,4-benzoquinone (III) and 3% 3,3',5,5'-tetra-tertbutyldiphenoquinone (IV). The behavior is significantly altered when oxygen is present in the mixture to be photolyzed. When the solution of (I) in CC14 is saturated by air or O₂,



the yield of (II) is markedly reduced, while the yield of (III) is enhanced. The content of (IV) is virtually independent of the nature of the gas introduced (Table 1).

The PMR spectra of the mixtures obtained upon the irradiation of oxygen-saturated solutions of (I) in CCl, shows a singlet at 6.75 ppm which disappears over time with the concurrent rise of a singlet for the ring protons of (III) at 6.49 ppm in addition to signals for the ring protons of (I) at 7.07 ppm and of (II) at 6.83 ppm. This process is accelerated upon heating the irradiated mixture. The intermediate formed is apparently converted to (III) in a thermal reaction. The half-life of this intermediate at about 20°C is approximately 4 h as indicated by PMR spectroscopy. Nevertheless, this compound could not be isolated. The chromatographic separation of the mixture on silica gel gives only (II), (III), and (IV).

The position of the PMR signal for the ring protons of this intermediate (6.75 ppm) indicates its quinoid structure. 4-Chloro-2,6-di-tert-butylphenoxyl and trichloromethyl radicals

Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2325-2327, October, 1987. Original article submitted December 26, 1986.

TABLE .

Gas	Yield, %			
duced	(II)	(III)	(IV)	
$\begin{array}{c} \mathrm{CO}_2 \\ \mathrm{Air} \\ \mathrm{O}_2 \end{array}$	94 76 49	Traces 14 40	3 3 5	

escape into the bulk from the primary radical pair formed upon the reaction of cyclohexadiene carbene with CCl_4 in the photolysis of (I) in CCl_4 . Therefore, we may assume that, in the presence of O_2 , the formation of (III) is preceded by thermally unstable quinoid peroxides (V).



Indeed, in the oxidation of 4-chloro-2,6-di-tert-butylphenol by PbO_2 in CCl₄ in the presence of O_2 , we obtained up to 30% (III) in addition to (IV). We should note that a signal at 6.75 ppm is observed in the PMR spectra of the reaction mixtures in this case, which disappears over time with the rise of the signal for the ring protons of (III).

The chemically-induced dynamic nuclear polarization (CIDNP) data are also in accord with the proposed scheme for the photodecomposition of (I) in the presence of O_2 . The ring protons of (II) are negatively polarized in the photolysis of (I) in the absence of O_2 within a spectrometer probe. In the presence of O_2 , the polarization of these protons is initially positive, decreases to zero with the consumption of O_2 , and then becomes negative. A similar result was observed upon the irradiation of a deoxygenated solution of (I) in CCl₄ in the presence of $C_{10}H_{21}SH$ as a radical trap. Positive polarization of the ring protons of (II) is observed as long as the trap is present in the mixture. The ring protons of the peroxide intermediate are negatively polarized.

The ¹³C NMR spectra of the mixtures obtained upon the photolysis of (I) in CCl₄ in the absence of O₂ also shows polarization of the carbon nuclei of (II). As in the case of protons,

Ca	rbon	δ, ppm	Polarization	sign
O R 11 R	C1	183.6	-!-	
$-\sqrt{2}$	C^2 . C^6	150.2	_	
	C ³ , C ⁵	133.9	Nonpolarized	
5 /3 (C^4	72.6		
CI CCI (C7	103.7	+	

the sign of the polarization of the ¹³C nuclei in (II) shifts in the presence of O_2 or C_{10} -H₂₁SH. The following mechanism for the photolysis of (I) in CCl₄ on the basis of the data obtained.



If we assume that the fraction of triplet carbene $(\bar{Q}^T:)$ in the overall balance is low, then the presence of a radical trap (O_2) in the photolysis system should eliminate the formation of F-radical pairs. In such a case, we should expect positive polarization on the ring protons of (II) and negative polarization on the protons of (V) (the case product). This was observed experimentally. It was indicated above (see Table 1) that bubbling O_2 through the photolysis system leads to the formation of (III) in yields up to 40%. On first glance, this is not in accord with a low contribution of the triplet reaction pathway in the overall reaction balance. However, the contradiction is eliminated if we recall that O_2 facilitates the singlet-triplet conversion of the excited molecules [2]. In addition, we note that upon the saturation of a solution of (I) in CCl₄ by O_2 , there is broadening and an upfield shift of the signal for the ring protons by about 0.1 ppm. We may assume that this is a result of the formation of [(I)... O_2] complexes, which are in equilibrium with free O_2 and (I). If this is true, the radical cage in the photolysis of the complex would include an oxygen molecule in addition to the radicals indicated above (Cl^{*} and °CCl₃), which inevitably leads to an increase in the yield of (V) and, thus, of (III).

EXPERIMENTAL

In this work, we used CCl₄ for UV spectroscopy and quinonediazide (I) after reprecipitation from chloroform by the addition of hexane. The purity was checked by thin-layer chromatography on Silufol-254 plates.

The NMR and CIDNP spectra were taken on an NX-90EP NMR spectrometer with HMDS as the standard. The modified probe of the spectrometer permits the introduction of a light beam using a quartz light guide directly into the region of the reception coil. A DRSh-1000 lamp equipped with a heat filter and BS-8 light filter was used for irradiation in the spectral and preparative studies.

<u>Photolysis of quinonediazide (I)</u>. A solution of 0.7 g (3 mmoles) (I) in 35 ml CCl₄ was first flushed for 10 min with dry CO₂, air, or O₂ and then irradiated for 2.5-3 h with light (λ > 350 nm) at about 20°C with the continuous introduction of CO₂, air, or O₂, and strong stirring. The reaction was monitored by thin-layer chromatography relative to the disappearance of the starting compound. The solution was evaporated in vacuum and the residue was submitted to chromatography on silica gel 40/100 μ with 2:1 hexane-benzene as the eluent. The experimental results are given in Table 1.

Oxidation of 4-chloro-2,6-di-tert-butylphenol. A mixture of 1 g chlorophenol, 5 g PbO₂, and 30 ml CCl₄ was stirred for 2 h at 20°C. The precipitate was separated. The mother liquor was evaporated in vacuum. Then, 30 ml acetone was added to the residue and the mixture was heated at reflux for 10 min and cooled. The crystalline precipitate of (IV) was separated, washed on the filter with acetone, and dried to give 0.4 g (47%) (IV). The mother liquor was evaporated in vacuum. The residue was subjected to chromatography on a column packed with silica gel 40/100 μ to give 0.25 g (27%) (III).

CONCLUSIONS

The photolysis of 2,6-di-tert-butyl-1,4-benzoquinonediazide in CCl₄ gives 2,6-di-tertbutyl-1,4-benzoquinone in the presence of O_2 in addition to the cage product, 4-chloro-4-trichloromethyl-2,6-di-tert-butylcyclohexadienone. A mechanism has been proposed for the photolysis of the quinonediazide in the presence and absence of oxygen.

LITERATURE CITED

- G. A. Nikiforov, Sh. A. Markaryan, L. G. Plekhanova, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 93 (1974).
- Kh. S. Bagdasar'yan, Two-Quantum Photochemistry [in Russian], Izd. Nauka, Moscow (1976), p. 30.