While there are many examples of one-electron transfers from various donors to TCNQ, electron transfer from carboxylate ion is less common. In fact only the Kolbe synthesis unequivocally involves such a process. TCNQ appears to be a strong enough oxidant for carboxylate anion. Little or no decarboxylation is observed in agreement with the observation of others[7,8] on the fate of benzoyloxy radicals in solution. The isolation of dimer I suggests hydrogen abstraction from solvent, acetone.

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**Registry No.**—I, 57362-36-4; II, 57379-37-0; TCNQ, 1518-16-7; sodium benzoate, 532-32-1; acetone, 67-64-1; $Na^+TCNQ\cdot^-$, 12153-63-8; sodium acetate, 127-09-3; sodium salicylate, 54-21-7; sodium carbonate, 144-55-8; $\alpha,\alpha$-dicyano-$p$-toluoyl cyanide sodium salt, 57379-38-1.

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## Photochemistry of 2,2,4,4-Tetraphenyloxetan-3-one. Intermediates in the Photofragmentation of Aryl Substituted Oxiranes

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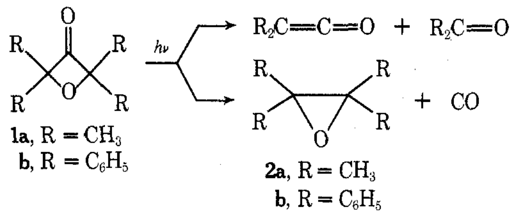
The photochromic behavior of vicinally substituted aryloxiranes has been investigated in rigid glasses[2] and the intervention of ionic and free-radical intermediates has been proposed for the fragmentation of these oxiranes to arylcarbenes and carbonyl compounds.[3] During these investigations the development of a blue-colored species ($\lambda_{max}$ 610 nm) was observed upon irradiating tetraphenyloxirane (**2b**) at 254 nm in hydrocarbon glasses (77K). That carbon–carbon bond cleavage is associated with this phenomenon was confirmed by low-temperature rigid matrix studies on 2,2,4,4-tetraphenyloxetan-3-one (**1b**).[4] The colored intermediate that forms from the oxetanone on decarbonylation at 350 nm, under conditions in which the oxirane is photostable, was shown to be spectroscopically identical with that obtained from **2b** at 254 nm. We now wish to report additional photochemical results obtained on **1b** in solution.

Hammond and co-workers[5a,b] studied the solution photolysis of a related compound, 2,2,4,4-tetramethyloxetan-3-one (**1a**). In polar solvents, the principal reaction path involved cycloelimination to give dimethylketene and acetone, rather than decarbonylation to tetramethyloxirane. In nonpolar solvents, both reactions were found to occur (Scheme I). An acyl–alkyl biradical intermediate which decomposes by two different solvent-dependent paths was proposed for these processes, although complete product identification was not achieved.

Scheme I

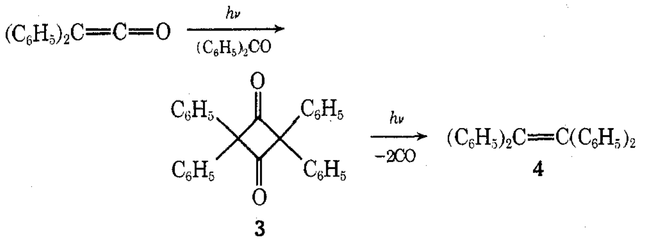


The results with **1a** suggested that the tetraphenyl analogue **1b** would photolyze in a similar manner upon irradiation above 300 nm to give tetraphenyloxirane (**2b**). Under these conditions the oxirane is known to be photostable and, if formed, should be isolable.

Irradiation of **1b** in benzene (350 nm, Pyrex, *c* 20 mmol/l.) for 17 hr resulted in the conversion of the starting material (76%) to a mixture of the expected oxirane **2b** (36%), carbon monoxide (detected by gas-phase infrared spectroscopy), benzophenone (55%), and diphenylketene (Scheme I), as well as tetraphenylethylene (10%). Diphenylketene was shown to be present among the primary photoproducts by infrared spectroscopy ($\nu_{C=C=O}$ 2080 cm$^{-1}$) and was trapped as methyl diphenylacetate (13%) by quenching the benzene solution with methanol after irradiation. The benzophenone and methyl diphenylacetate were separated from unreacted **1b** and other photoproducts by elution chromatography on silica gel. The relative amounts of the two components were established by NMR.

The formation of tetraphenylethylene (**4**) was noted with great interest. 2,2,4,4-Tetraphenylcyclobutane-1,3-dione (**3**), the head-to-tail dimer of diphenylketene which is known to decarbonylate to **4**,[6] appeared to be a reasonable precursor[7a] (Scheme II). While benzene solutions of diphenylketene are stable to irradiation at 350 nm for prolonged periods (90 hr) in the absence of benzophenone (92% recovery), tetraphenylethylene (66%) and traces of biphenyl are formed when benzophenone is added to the solution. Since both benzophenone and diphenylketene are primary cycloelimination products obtained from **1b**, the proposed mechanism for the formation of **4** is clearly consistent with the experimental results. Benzophenone presumably behaves as a sensitizer for the dimerization of diphenylketene and experiments designed to test this proposal are in progress. An alternative route to **4** involving dimerization of diphenylcarbene, formed from diphenylketene in a sensitized process, is unlikely, at least in solution, at the wavelength employed.[7b,c]

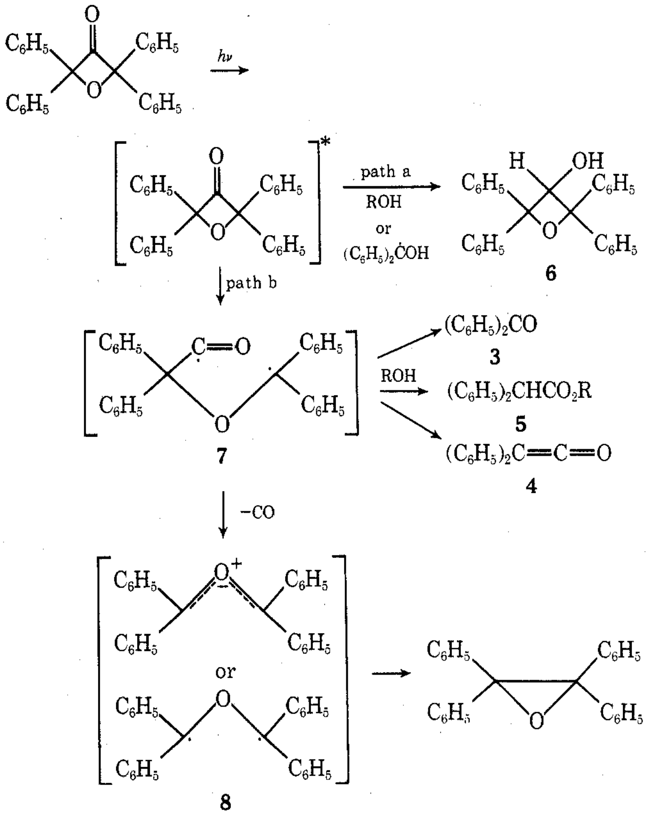
Scheme II



In an attempt to trap diphenylcarbene, a potential primary photoproduct of **1b**, irradiation of a solution of **1b** in methanol (*c* 3.3 mmol/l.) was undertaken.[8] After 18 hr exposure and 99% conversion of **1b**, the only photoproducts found were carbon monoxide, tetraphenyloxirane (**2b**, 30%), methyl diphenylacetate (51%), and benzophenone (35%). Benzhydryl methyl ether, the product formed by the reaction of the carbene with methanol, could not be detected by GLC analysis, demonstrating, within the capabilities of our analytical technique (~1%), that no diphenylcarbene was formed either directly from **1b** or in secondary photoreactions involving diphenylketene or tetraphenyloxirane, both of which are possible precursors.[7c,9] Similar results were obtained even when **1b** was irradiated in methanol with a more intense source, provided that a Pyrex filter ($\lambda > 320$ nm) was employed; i.e., no benzhydryl methyl ether was formed, although, as observed earlier, **1b** fragments to give diphenylketene (as evidenced by isolation of methyl diphenylacetate, 52.3%) and benzophenone (16.2%), and also undergoes decarbonylation to afford the oxirane **2b** (39.5%). Irradiation of **1b** in methanol using a Corex filter (*c* 2.5 mmol/l.) resulted in the formation of substantial amounts of benzhydryl methyl ether (31%) and a concomitant decrease in the amount of oxirane (5.5%) produced. While direct fragmentation of a decarbonylation intermediate cannot be excluded as a source of diphenylcarbene, the oxirane **2b** is photolabile under the cited conditions and most, if not all, of the diphenylcarbene probably arises from a secondary photoreaction of the oxirane. We therefore conclude that oxirane **2b**, carbon monoxide, benzophenone, and diphenylketene are the primary photoproducts arising from fragmentation of **1b** at wavelengths above 320 nm.

Upon photolysis of **1b** in benzene–2-propanol solution (19:1), three reaction pathways were observed: decarbonylation to give tetraphenyloxirane (**2b**), cycloelimination to form benzophenone and diphenylketene [isolated as isopropyl diphenylacetate (**5**)], and reduction to 2,2,4,4-tetraphenyloxetan-3-ol (**6**). Although the photochemical ring expansion of cyclic ketones to cyclic acetals in hydroxylic solvents has been reported by several authors[10a–d] and is considered a general reaction for cyclobutanones,[10c] the photolysis of **1b** produced no detectable ring expanded products. Possible mechanisms consistent with these results are shown in Scheme III.

Scheme III



It is evident that the nonbonding orbital on oxygen in the n,π* excited state of ketones is a highly localized site of photochemical activity with radical characteristics[11] and, as a consequence, photoreduction of **2a** to give **6** (path a) may proceed by simple hydrogen abstraction from 2-propanol. Alternatively, however, some, if not all, of ketone **1b** may be reduced in a dark reaction by benzophenone ketyl generated, in turn, from triplet benzophenone and 2-propanol.[12] Path b involves a Norrish type I cleavage to give an acyl–alkyl diradical **7**[13] which, upon decarbonylation, produces **2b** via a diradical or zwitterion **8**. The fragmentation of **7** yields diphenylketene and benzophenone. In the presence of alcohol, the diphenylketene is converted to an ester of diphenylacetic acid. It is noteworthy that no diphenylcarbene is formed by collapse of **8**. Recently, Huisgen and co-workers reported that related oxo ylides produced by thermal cleavage of the oxirane carbon–carbon bond undergo typical dipolar additions without the elimination of carbenes.[14] These observations provide additional evidence that the mechanism for oxirane cycloelimination reactions leading to carbenes either requires initial carbon–oxygen bond cleavage or proceeds in a concerted fashion. All attempts to date to trap the oxo ylide **8** derived from **1b** or **2b** with electron-deficient dipolarophiles such as dimethyl fumarate, fumaronitrile, or their cis counterparts, which are effective in intercepting the corresponding ylides derived from stilbene oxides,[15] have proved unrewarding. We attribute this lack of reactivity to adverse steric factors in the addition complex.

## Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 521 double-beam spectrophotometer. NMR spectra were obtained on a Varian A-60A spectrometer. Chemical shifts are expressed in δ (parts per million) downfield from $Me_4Si$. The purity of liquid samples was verified by gas chromatography. If purification was required, the samples were distilled with a Nester-Faust NF-190 spinning band column (6 × 450 nm, 23 theoretical plates). Solid samples were purified by repeated recrystallizations from appropriate solvents until a constant melting point was obtained. Elemental analyses were carried out by Dr. A. Bernhardt Mikronalytische Laboratorium, West Germany, and Galbraith Laboratories, Knoxville, Tenn. Gas chromatographic analyses were conducted isothermally (180°) on a coated open-tubular capillary column available from Perkin-Elmer Corp., Norwalk, Conn., using a 900 Series Perkin-Elmer gas chromatograph. Yields are reported in terms of the weight of materials isolated assuming that only 1 mol of reactant is required for each mol of product formed regardless of the actual mechanism. Preparative VPC was achieved on a 20 ft × 0.25 in. column of 10% silicone rubber on 45-60 Chromosorb W at 100–110° (injection port, 180°) with a helium flow rate of 120 ml/min; retention times are reported relative to air coinjected as reference. The interpretation of VPC results was accomplished by standard calibration techniques.

2,2,4,4-Tetraphenyloxetan-3-one (**1b**) was prepared either by the method of Harper and Lester[5b] or Hoey, Dean, and Lester:[16] yield 50%; mp 198–199.5° (lit.[16] mp 199–201°); $\nu_{max}$ ($CHCl_3$) 1813 $cm^{-1}$ (C=O); NMR ($CDCl_3$) δ 7.26 (m).

All irradiations were conducted in serum-capped quartz or Pyrex test tubes. In each case, fluid solutions were degassed by sparging with nitrogen or argon prior to irradiation. A Rayonet Chamber Reactor (The Southern New England Ultraviolet Co., Middletown, Conn.) equipped with 16 G8T5 8-W low-pressure mercury lamps (254 nm) was used in some cases. The irradiation of **1b** in benzene in a Pyrex vessel for 17 hr was carried out with a source similar to that described above but fitted with F8T5 8-W lamps (350 nm) at 35°. The same source was used for the irradiation of **1b** in methanol. A quartz Hanovia probe, employing a 450-W high-pressure mercury lamp (Type 79A36), at 10° was also employed to irradiate **1b** in methanol. When a Pyrex filter ($\lambda >320$

nm) was employed, the results were the same as in the previous irradiation of **1b** in methanol; however, with a Corex filter (λ <300 nm), substantial amounts of benzhydryl methyl ether and less oxirane were produced.

The irradiation of **1b** in benzene–2-propanol was carried out as follows. A solution of **1b** (0.74 g, 0.002 mol) in 190 ml of dry benzene and 10 ml of 2-propanol was irradiated for 45 min with a 450-W Hanovia (Type L, Model 679A-36) high-pressure quartz mercury-vapor lamp. After the removal of solvent, crystals of tetraphenylethylene oxide formed, mp 194–195.5°.

Anal. Calcd for $C_{26}H_{20}O$: C, 89.62; H, 5.79. Found: C, 89.37; H, 5.70.

The physical properties of this product were identical in every respect with those of an authentic sample prepared by the method of Mosher, Steffgen, and Lansbury.[17] Benzophenone (**3**), isopropyl diphenylacetate (**5**), and 2,2,4,4-tetraphenyloxetan-3-ol (**6**) were identified by comparing their NMR and ir spectra and their VPC retention times with those of authentic samples.

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**Registry No.**—**1b**, 40112-59-2; **2b**, 470-35-9.

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# Deoxygenation of α,β-Unsaturated Aldehydes and Ketones via the Catecholborane Reduction of the Corresponding Tosylhydrazones

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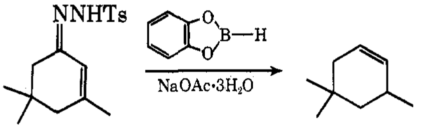
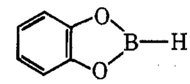
The reduction of tosylhydrazones with boron hydrides offers a mild and convenient alternative to the Wolff–Kishner and Clemmensen reductions.[2–4] In the initial reports, it was observed that α,β-unsaturated systems were reduced with migration of the double bond.[2,5]



This migration offers exciting synthetic possibilities such as the formation of less stable positional isomers (exocyclic double bonds vs. endocyclic double bonds) and deconjugation of conjugated double bonds. Indeed these synthetic manipulations have been recently reported to occur (except in cyclohexenone derivatives) using sodium cyanoborohydride as the reducing agent.[6] This report[6] has prompted us to report our studies utilizing catecholborane (I) for the reductions of α,β-unsaturated tosylhydrazones.



I

We find that catecholborane (I) cleanly reduces the tosylhydrazones of α,β-unsaturated carbonyl compounds, including the cyclohexenone derivatives, in high yields. The catecholborane procedure offers a number of advantages over the current procedures in that (1) the reaction requires only 1 equiv of hydride (as opposed to 12 equiv in the $NaBH_3CN$ procedure); (2) it is carried out under mild conditions (temperature below 62°, pH near neutral); (3) common organic solvents are employed such as chloroform (as opposed to the DMF–sulfolane system utilized in the $NaBH_3CN$ procedure); and (4) clean isomerizations are obtained with no alkane formation. The reductions are practical for sensitive systems since the necessary tosylhydrazones are prepared at neutral pH in ethanol.

Our results are summarized in Table I.

The reaction most likely proceeds via the formation of an unstable diazene intermediate.[7] A reasonable mechanism is outlined in Scheme I which is based on analogy to known

Scheme I