Photochemistry of 2,3,4,4-Tetrachloro-1-oxo-1,4-dihydronaphthalene and 2,2,3,4-Tetrachloro-1-oxo-1,2-dihydronaphthalene in Liquid Solutions

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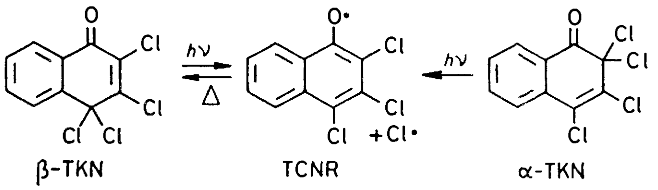
The stable products, which result from the u.v. photolysis of 2,3,4,4-tetrachloro-1-oxo-1,4-dihydronaphthalene (β-TKN) and 2,2,3,4-tetrachloro-1-oxo-1,2-dihydronaphthalene (α-TKN) in cyclohexane and in CCl_4 have been isolated and identified. From the hydrogen abstraction reactions of the two compounds in their lowest triplet state it is concluded that this is a $^3(n-\pi^*)$ state in both compounds. Heterolytic photodissociation proceeds from the first excited singlet state of α-TKN $^1(\pi-\pi^*)$ and of β-TKN $^1(n-\pi^*)$. Also homolytic photodissociation of β-TKN is observed, after excitation into the first absorption band. The branching ratio of triplet formation and homolytic and heterolytic photodissociation is found to differ for the two compounds. The carbenium ion formed in the heterolytic photodissociation has a lifetime which varies with the solvent used. The decay of the carbenium ion is determined by both ion recombination and reactions with other photoproducts in the solution. The carbenium ion is responsible for the photochromic effect of α- and β-TKN in CCl_4.

SINCE its discovery by Marckwald,[1] the photochromic behaviour of 2,3,4,4-tetrachloro-1-oxo-1,4-dihydronaphthalene (β-TKN) has been the subject of many investigations. In the crystalline state, the phenomenon is restricted to one particular crystal modification of the compound.[2] These colourless crystals become purple when exposed to u.v. light and regain their transparency by a slow thermal reaction.

Scheibe and Feichtmayr [3] discovered that the coloured photoproduct can also be observed after u.v. irradiation of solutions of α- (2,2,3,4-tetrachloro-1-oxo-1,2-dihydronaphthalene) or β-TKN. They proposed as the mechanism a homolytic photodissociation of the aliphatic C–Cl bond, yielding the 2,3,4-trichloro-1-naphthoxyl radical (TCNR), which they assumed to be coloured. In a recent publication [4] we showed that the explanation of the photochromism given by Scheibe and Feichtmayr is incorrect. We presented evidence for an alternative mechanism. This involves heterolytic photodissociation of an aliphatic C–Cl bond, leading to a coloured carbenium ion.

When generated by irradiation of solutions of α- or β-TKN in CCl_4, the coloured species has a rather long lifetime ($t_{\frac{1}{2}}$ 2 min at room temperature [5]). However, when the photolysis is carried out in cyclohexane or in benzene,[3] the lifetime is reduced by a factor of 10^5. No reaction occurs when these solvents are added to a coloured solution of the carbenium ion in CCl_4. Therefore the reduction in the lifetime must be caused by consecutive reactions with other, simultaneously formed photoproducts.

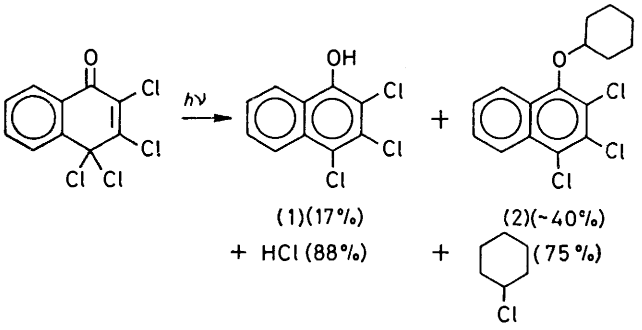
In this paper we report on the various photochemical reactions of α- and β-TKN in cyclohexane and in CCl_4.



SCHEME 1

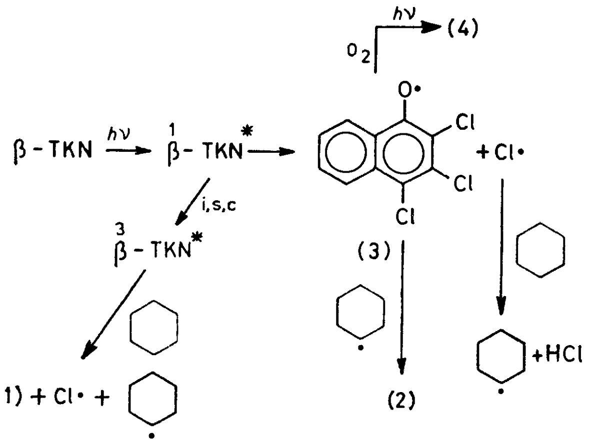
It will be shown that the carbenium ion plays a minor role in the formation of stable photoproducts.

Photochemical Reactions of β-TKN *in Cyclohexane.*—U.v. irradiation of a deoxygenated solution of β-TKN in cyclohexane through a Pyrex filter yields 2,3,4-trichloro-1-naphthol (1) and cyclohexyl 2,3,4-trichloronaphthyl ether (2). The formation of HCl indicates that release of a chlorine arom from β-TKN must be one of the primary steps in the photolysis. A similar observation has been reported for halogen-containing cyclohexa-2,5-dienones.[6] It has been shown that in such cases the chlorine atom does not survive more than one or two collisions with solvent molecules before it abstracts a hydrogen atom.[7] In the case of β-TKN the resulting cyclohexyl radical may escape from the cage surrounding the originally excited molecule, and it can then abstract a Cl atom from the starting compound to yield cyclohexyl chloride. When the cyclohexyl radical reacts within the cage with the 2,3,4-trichloro-1-naphthoxyl radical (TCNR) the cyclohexyl ether (2) is formed. However, an alternative route to (2) might be the reaction of the cyclohexyl radical with β-TKN and subsequent loss of Cl.



SCHEME 2

When the TCNR is generated by reaction of either α- or β-TKN with activated silver in cyclohexane, it is very stable.[4] Therefore the photochemically produced 2,3,4-trichloro-1-naphthol (1) cannot result from abstraction of hydrogen from the solvent by the naphthoxyl radical.



SCHEME 3

Very probably (1) is formed by photoreduction of β-TKN in its lowest triplet state, followed by release of a Cl atom from the ketyl radical. A justification for this point of view follows from the fact that formation of (1) is suppressed, when the reaction is carried out in the presence of 3,3′,4,4′-tetramethyldiazetine dioxide (TMDD) or oxygen. Both reagents are known to quench triplet states. Hydrogen abstraction reactions of excited cyclohexa-2,5-dienones, leading to the corresponding phenols, have been shown to involve the lowest triplet state of the dienone.[8] Since the primary photodissociation of β-TKN into TCNR (3) and atomic chlorine is not influenced by the presence of oxygen (see below), this reaction presumably takes place from an excited singlet state.

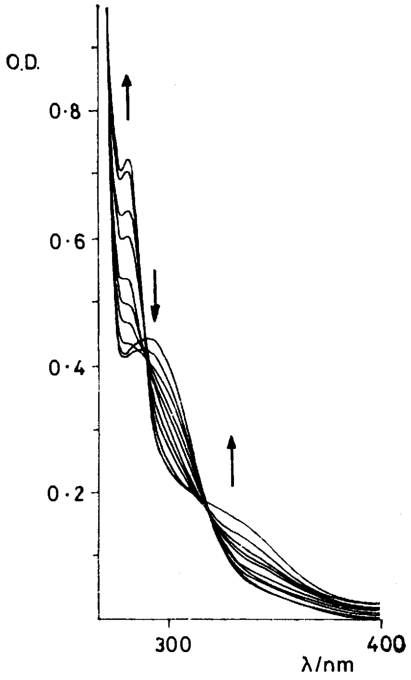
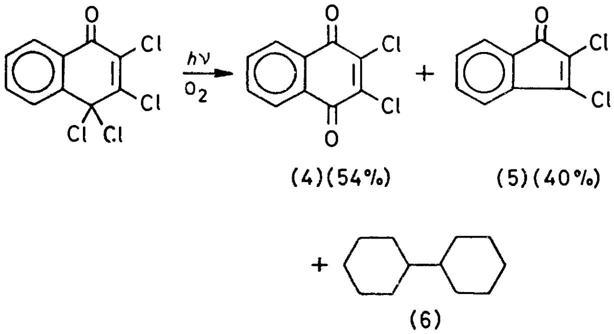


FIGURE 1 Change in the u.v. spectrum during irradiation ($320 < \lambda < 400$ nm) of a 10^{-3}M solution of β-TKN in aerated cyclohexane. While the absorption of the starting compound (295 nm) diminishes, new bands at 279 and 332 nm due to 2,3-dichloro-1,4-naphthoquinone (4) appear

When oxygen is present the photochemical reaction of β-TKN in cyclohexane takes a different course (Figure 1). As a consequence of triplet quenching by oxygen only traces of the naphthol (1) are formed. The major photoproducts are 2,3-dichloro-1,4-naphthoquinone (4) and 2,3-dichloroindenone (5).



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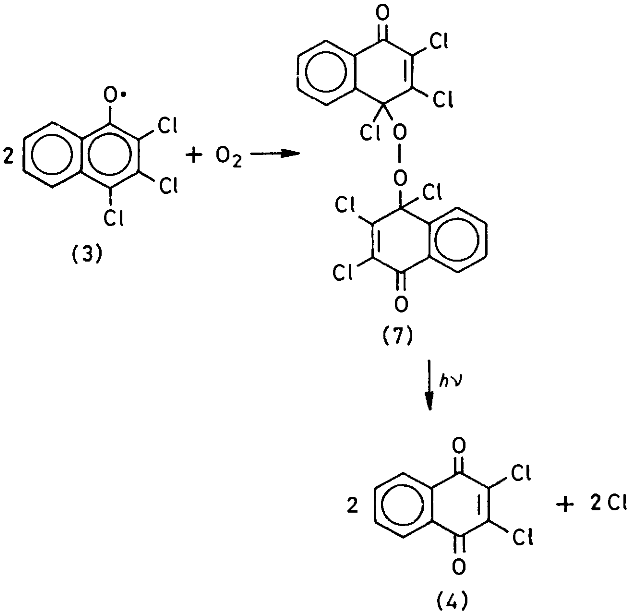


SCHEME 5

Very likely the quinone (4) results from consecutive reactions of the primary photoproduct (3). Most aroxyl radicals react rapidly with oxygen and form peroxides.[9] Even the very stable 2,4,6-tri-t-butylphenoxyl radical is readily converted into the corresponding peroxide when oxygen is available.[10] As has been reported, this peroxide is photochemically cleaved and then converted to 2,5-di-t-butyl-1,4-benzoquinone in large yield.[11] A similar mechanism may account for the formation of the naphthoquinone (4) from the photo-oxidation of TCNR (3). The Cl atoms generated by the photodissociation of the peroxide (7) will react with cyclohexane to form two cyclohexyl radicals, possibly forming a cage pair. A cage reaction of this pair gives bicyclohexyl (6). Neither (6) nor 2,3-dichloroindenone (5) could be detected when oxygen is excluded in the photolysis of β-TKN. Probably product (5) is formed photochemically from (4) by loss of CO.

Photolysis of α- and β-TKN in CCl_4.—Whereas β-TKN is destroyed very inefficiently by irradiation in deoxygenated CCl_4, α-TKN is readily converted to valence isomers in this solvent upon irradiation. The change in the u.v. spectrum during irradiation of a solution of α-TKN in CCl_4 is indicated in Figure 2. The long wavelength absorption band of α-TKN at 353 nm disappears and a new band at 295 nm appears. The quantum yield for destruction of α-TKN at 366 nm has been determined to be 0.36. Although an isosbestic point at 325 nm is observed, it may not be concluded that only one photoproduct is formed. The benzobicycloketone (8) and β-TKN, which appear as the stable photoproducts, both have an absorption band at 295 nm with practically the same extinction coefficient (Table). Many mechanistic studies on the photochemical transformations of cyclohexadienones are available.[12] It has been established that the rearrangement of heavily substituted cyclohexa-2,4-dienones to bicyclo[3.1.0]-hexenones proceeds *via* an intermediate ketene.[13,14] Hexamethylcyclohexa-2,4-dienone (9) reacts in this way to give the bicycloketone (11).[14] The photorearrangements of 2,2,3,4-tetramethylnaphthalen-1(2*H*)-one have been investigated by Hart.[15] This compound, which is the tetramethyl analogue of α-TKN gives similar photoproducts as depicted above for α-TKN. It has been argued [15] that the photoisomerization of 2,2,3,4-tetramethylnaphthalen-1(2*H*)-one does not involve an intermediate keten, but proceeds *via* bond crossing in the excited triplet state of the ketone. If the same mechanism applies to the photoisomerization of α-TKN, Scheme 8 is obtained. Product (8) has been isolated and its photolysis has been studied in a separate experiment. Irradiating a 2×10^{-3}M solution of (8) in CCl_4 through a Pyrex filter and analysing the reaction mixture by t.l.c. shows that it is largely converted into β-TKN. This proves that (8) may act as an intermediate in the photorearrangement of α- to β-TKN. Irradiation of α-TKN in CCl_4 with u.v. light which is only absorbed by the starting compound and not by the photoproducts (λ >340 nm) also produces (8) and β-TKN (mainly β-TKN). In principle β-TKN might be formed from (8) under these conditions, when (8) borrows electronic excitation energy from excited α-TKN. However, this is unlikely because no quenching of the photoreaction by oxygen is observed. Therefore another mechanism for the photoisomerization of α- and β-TKN must be involved (see later).

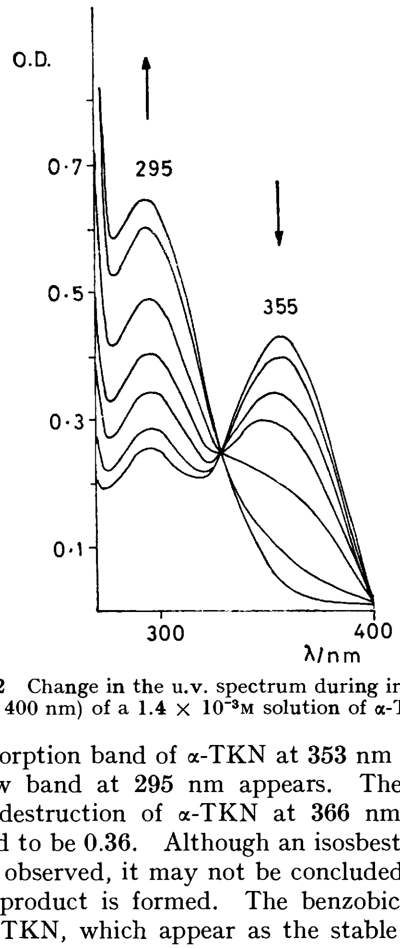
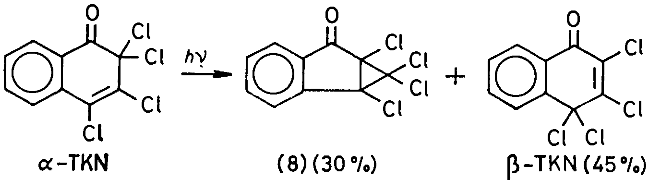
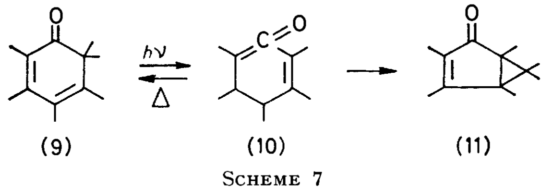


FIGURE 2 Change in the u.v. spectrum during irradiation ($340 < \lambda < 400$ nm) of a 1.4×10^{-3}M solution of α-TKN in CCl_4

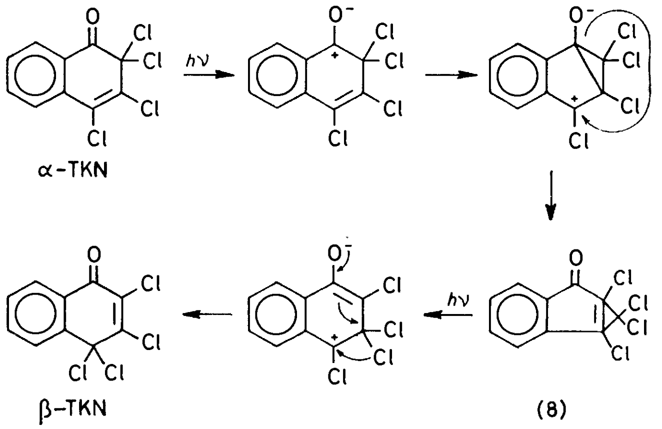


SCHEME 6



SCHEME 7

A small amount of (8) is also obtained upon exposure of a solution of β-TKN in CCl_4 to u.v. light, when oxygen is excluded. This type of reaction has been observed for a number of substituted cyclohexa-2,5-dienones, but the quantum yields are usually much higher than in the case of β-TKN.[16-18]



SCHEME 8

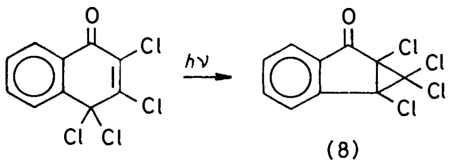
The photolysis of β-TKN in an air-saturated solution of CCl_4 gives predominantly 2,3-dichloro-1,4-naphthoquinone (4). This follows from the change in the u.v. spectrum during irradiation, which is essentially

Spectroscopic properties of starting compounds and photoproducts

Compound	ν_{max}/cm^{-1} [a]	λ_{max}/nm (log ε) [b]	*m*/*e* [c]
α-TKN, m.p. 104—105 °C	662, 703s, 720s, 770m, 803s, 882s, 858m, 1 022, 1 153s, 1 232s, 1 240m, 1 254s, 1 285m, 1 449, 1 559, 1 586s, 1 702s	353 (3.38) 296 (3.09) 250 (4.49) 242 (4.44)	280 (4)
β-TKN	663, 698, 707s, 719s, 806m, 818s, 875m, 885, 931, 1 092, 1 107, 1 145s, 1 168m, 1 301s, 1 570m, 1 595m, 1 680s	400 (0.52) 293 (3.65) 262 (4.16) 363 (1.30) 255 (4.17)	280 (4)
(1), m.p. 168 °C	740s, 759s, 813, 889s, 980, 1 085m, 1 165, 1 217m, 1 246s, 1 280, 1 345s, 1 357s, 1 382s, 1 447, 1 500m, 1 580s, 1 622, 3 535s	334 (3.42) 318 (3.59) 302 (3.77) 290 (3.71)	246 (3)
(2), impure	755s, 782s, 1 260m, 1 336s, 1 449s, 1 565s, 2 860m, 2 940s	333 290 318 236	
(4), m.p. 193—195 °C	710s, 820s, 880, 1 140s, 1 240m, 1 278s, 1 651s, 1 692s, 1 685s	332 (3.42) 252 (4.12) 279 (4.25) 245 (4.12)	226 (2)
(5)	757s, 1 470m, 1 620m, 1 740s	400 (2.84) 237 (4.63)	198 (2)
(8), m.p. 131—132 °C	747s, 759s, 796s, 818s, 891s, 1 081s, 1 240s, 1 332s, 1 556m, 1 600m, 1 722s	310 (3.52) 241 (4.50) 298 (3.65) 290 (3.62)	280 (4)

[a] Spectra taken in KBr, s = strong, m = medium, all others are weak. [b] Spectra taken in n-hexane. [c] Parent peaks; the number of Cl atoms derived from the mass spectrum, is in parentheses.

that observed for the photoreaction in aerated cyclohexane (Figure 1). Obviously the photodissociation of β-TKN also occurs in CCl_4, but in the absence of oxygen this is not followed by further reactions and the starting compound will be restored.



(8)

SCHEME 9

Oxygen has no detectable influence on the type of photoproducts arising from α-TKN in CCl_4, when long wavelength u.v. light (λ >340 nm) is used for the excitation. Therefore it must be concluded that the homolytic dissociation of a tetrahedral C–Cl bond in α-TKN does not occur. This should lead to the formation of the 2,3,4-trichloro-1-naphthoxyl radical which reacts with oxygen to give 2,3-dichloro-1,4-naphthoquinone. This product is not found after photolysis of α-TKN in the presence of oxygen.

Flash Spectroscopic Investigations.—Figure 3 shows the absorption spectrum of a solution of α-TKN in CCl_4, taken 20 ns after excitation with a laser flash (353 nm). This spectrum remains unchanged for a few minutes after excitation and is the same as the one observed after steady irradiation of α- or β-TKN in CCl_4. In a previous paper,[5] we showed that this spectrum originates from the carbenium ion (12), formed by heterolytic cleavage of an aliphatic C–Cl bond in either α- or β-TKN. In a series of experiments with microsecond flash excitation, the possibilities of quenching this photoreaction have been investigated. A ten-fold excess of various triplet quenchers has been added to a solution of β-TKN in CCl_4, containing 10% $CHCl_3$. No quenching occurs with oxygen, TMDD, 1,4-benzoquinone, naphthalene, benzophenone, and acetophenone, which have triplet energies of 23, 35—42, 50, 60, and 75 kcal mol^{-1} respectively.[19] Triplet sensitization of the formation of (12) using thioxanthone (E_T 65.5 kcal mol^{-1} [19]) failed. Therefore heterolytic photodissociation probably takes place from an excited singlet state.

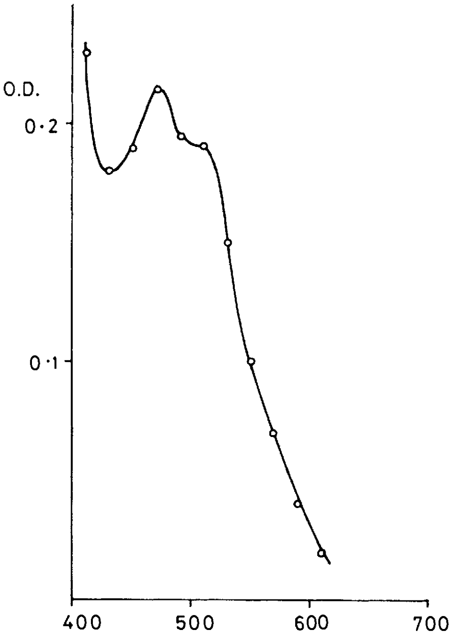
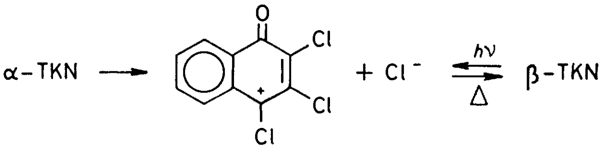


FIGURE 3 Absorption spectrum of a 3×10^{-4} molar solution of α-TKN in CCl_4, taken 20 ns after excitation with a 353 nm laser pulse

Previously reported experiments on the photochromism of β-TKN in CCl_4 [20] indicate that β-TKN is restored during the decay of the coloured photoproduct. Thus an alternative pathway for the photochemical isomerization of α- to β-TKN, involving migration of Cl^-, is feasible. This possibility has been investigated by observing the absorption at 490 nm for (12) and at 295 nm for β-TKN immediately after irradiating a solution of α-TKN in CCl_4 with u.v. light (λ >340 nm) for 10 s. After termination of the irradiation at time $t = 0$, the uncompleted



(12)

SCHEME 10

thermal reactions of the primary photoproducts can be monitored without disturbance by photoreactions (Figure 4). The thermal reactions cause the optical density to increase at 295 nm and to decrease at 490 nm. The final change of the initial optical density at $t = 0$ is much smaller at 295 than at 490 nm. Taking into account the extinction coefficient of β-TKN at 295 nm (ε 4 500) and of (12) at 490 nm (ε *ca.* 3 000 [3]), it can be concluded that *ca.* 20% of (12) is thermally converted to β-TKN. Nevertheless, as will be shown below, this reaction is not involved in the major route of isomerization of α-TKN.

Immediately after the 10 s period of irradiation the concentrations of β-TKN and of (12) give a ratio [β-TKN] : [(12)] of *ca.* 4.5 (Figure 4). This can be compared with the value calculated on the basis of equations (1)—(6).

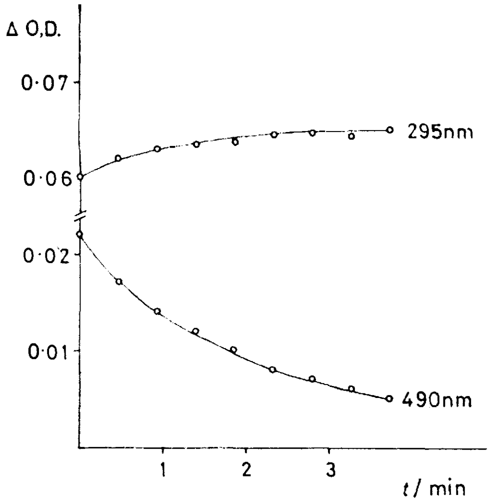


FIGURE 4 Thermally induced change at 22 °C in the absorptions at 295 and 490 nm of a solution of α-TKN in CCl_4 (2×10^{-4}M) exposed to u.v. light ($340 < \lambda < 400$ nm) for 10 s. At $t = 0$ illumination has ended

$$\alpha\text{-TKN} \xrightarrow{h\nu} (12) \xrightarrow{k} \beta\text{-TKN} \qquad (1)$$

Denoting the rate of formation of (12) by n mol l^{-1} s^{-1}, the rate of change of (12) is given by equation (2).

$$d\,[(12)]/dt = n - k\,[(12)] \qquad (2)$$

Considering that during the photolysis only a small fraction of the original amount of α-TKN is converted, *i.e.* n is constant, this equation integrates to (3). The

$$[(12)] = nk^{-1}\,[1 - \exp(-kt)] \qquad (3)$$

formation of β-TKN from (12) is governed by equation (4) which integrates to (5). Using the expressions for

$$d[\beta\text{-TKN}]/dt = k\,[(12)] \qquad (4)$$

$$[\beta\text{-TKN}] = nt - nk^{-1}\{1 - \exp(-kt)\} \qquad (5)$$

$$[\beta\text{-TKN}] : [(12)] = -1 + kt\,\{1 - \exp(-kt)\}^{-1} \qquad (6)$$

[β-TKN] and [(12)] one obtains equation (6). Taking $t = 10$ s and the value of k in CCl_4 at 295 K, *i.e.* $k = 7.4 \times 10^{-3}\,s^{-1}$,[4] the ratio is found to be [β-TKN] : [(12)] = 0.04. This is two orders of magnitude smaller than the experimental value quoted above. The thermal reaction of (12) should therefore be disregarded as a major mechanism in the formation of β-TKN.

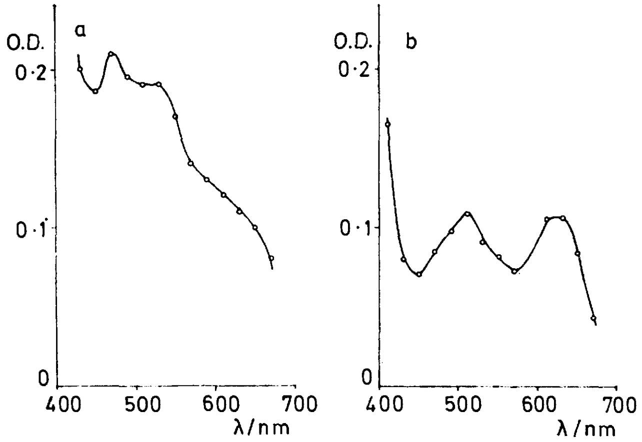
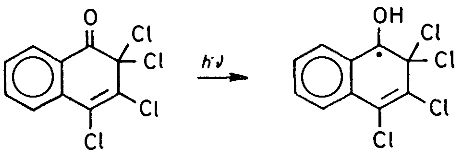


FIGURE 5 Transient absorption spectra taken 20 ns after laser excitation (353 nm) of a 3×10^{-4}M solution of α-TKN in benzene (a) and in cyclohexane (b)

Photochemical conversion of (12) to β-TKN is not involved because the growth rate of the optical density at 295 nm depends linearly on the excitation light intensity (366 nm). Therefore it must be concluded that yet another mechanism is operative in the isomerization. As a possibility we suggest a [1,3] sigmatropic shift of an aliphatic C–C bond.

Figure 5 presents the transient absorption spectra taken 20 ns after laser excitation of a solution of α-TKN in benzene (Figure 5a) and in cyclohexane (Figure 5b). The curves in Figure 5 are composed of the spectra of two different species. One is the carbenium ion (12), absorbing at 490 nm, the other has an absorption band in the same wavelength region and an additional band at 620 nm. The lifetimes of the two species are *ca.* 1 ms and 2 μs respectively. The shorter living absorption must probably be attributed to the ketyl radical (13), which is formed when α-TKN in the excited triplet state abstracts hydrogen from the solvent. This assignment is supported by the observation that the transient species absorbing at 620 nm is produced in lower yield in benzene than in cyclohexane with weaker C–H bonds. Ketyl radicals formed by photoreduction of cyclohexa-2,5-dienones exhibit absorptions in the visible region.[21] Steady irradiation of α-TKN in cyclohexane gives a complicated mixture of photoproducts. The presence of β-TKN and 2,3,4-trichloro-1-naphthol in this mixture has been established by t.l.c. The latter product may result from (13) by loss of a Cl atom.

Reactions of (12) with various solvents have been

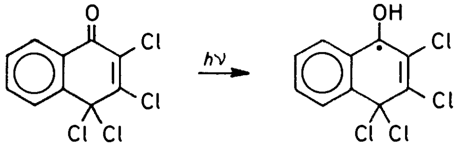


(13)

SCHEME 11

studied by adding them to a coloured solution of (12) in CCl_4. No reaction occurs with benzene or cyclohexane, but addition of a small amount of CH_3OH or any other nucleophilic compound immediately destroys the colour.

The transient absorption spectrum, observed after laser flash photolysis (λ_{exc} 353 nm) of α-TKN in methanol, shows the presence of (12) and (13). In this solvent the lifetime of (12) is reduced to 100 μs, whereas the lifetime of (13) remains unaffected. Presumably the lifetime of (12) is entirely determined in this case by reaction with the solvent. Hydrogen abstraction is also observed for



(14)

SCHEME 12

excited β-TKN. The appearance of the ketyl radical upon irradiation of β-TKN in cyclohexane is deduced from the production of the naphthol (1), which has been isolated after continous illumination of the solution. Very likely the naphthol (1) is formed from (14) by loss of Cl. The assumption of (14) as a precursor of (1) is consistent with the observation that oxygen quenches both the formation of (1) and the transient spectrum due to quenching of the triplet molecule, which has to abstract hydrogen from the solvent. When the solvent does not contain hydrogen, *e.g.* CCl_4, the compound (1) is not formed at all.

Figure 6 presents the transient absorption spectrum, obtained by exciting a 2×10^{-4}M solution of β-TKN in cyclohexane with a laser pulse ($\lambda_{exc.}$ 265 nm). The transient spectrum differs from Figure 5b mainly in the relative heights of the maxima. This suggests a branching ratio between triplet formation and homolytic and heterolytic photodissociation, which is different from the case of α-TKN. From the hydrogen abstraction reactions it follows that for both α- and β-TKN the lowest triplet is a $^3(n-\pi^*)$ state. The first absorption band involves a transition to a $^1(\pi-\pi^*)$ state in α-TKN ($\varepsilon_{max.}$ 2 375) and to a $^1(n-\pi^*)$ state in β-TKN ($\varepsilon_{max.}$ 20).[22] Taking these dissimilarities and the difference in structure of the two compounds into account, the branching ratios are anticipated to be unequal. Of course, the matter has to be settled by a determination of the primary yield of triplet, TCNR, and (12).

Although the final solvation of the ions, formed in the heterolytic photodissociation, will have no influence on the primary yield of the ions, it will control their reactions. Among the nonpolar solvents no large differences will be encountered in the ion–solvent interactions, arising from bulk dielectric polarization. However, complex formation of one of the ions with solvent molecules may introduce large differences in the total stabilization of the ion. These specific interactions may retard the recombination of ions considerably. It is conceivable that the Cl^- ion forms a stable charge transfer complex with CCl_4 and thus cause the carbenium ion (12) to survive for a few minutes in CCl_4. A charge-transfer complex between the carbenium ion as an electron acceptor and benzene as a donor also seems very realistic. In Figure 5a, referring to a solution of α-TKN in benzene there is a larger optical density around 490 nm due to the carbenium ion (12) than around 620 nm due to the ketyl radical (13). The optical densities in the wavelength region just mentioned are equal in the transient spectrum of α-TKN in cyclohexane (Figure 5b). Within the time period of observation of the two spectra the amount of products, formed upon encounter of initially remote primary photoproducts, may be neglected. Therefore it follows from Figures 5a and b, that ion recombination is much faster in cyclohexane than in benzene. However, the lifetime of the carbenium ion (12) is not solely determined by the recombination reaction. Reactions of (12) with other simultaneously formed photoproducts are definitely taking place and contributing to the decay of (12). When (12) is formed photochemically from α-TKN in CCl_4, the lifetime amounts to 120 s in non-degassed solutions, but is reduced to 0.5 s if the solutions are completely deoxygenated prior to irradiation. This indicates that oxygen scavenges the photoproducts, which are fatal to (12). At present it cannot be stated which of the various photoproducts arising from α-TKN in CCl_4 do react with (12). When (12) is generated photochemically from β-TKN in benzene or cyclohexane, products (1) and (2) probably react with (12).

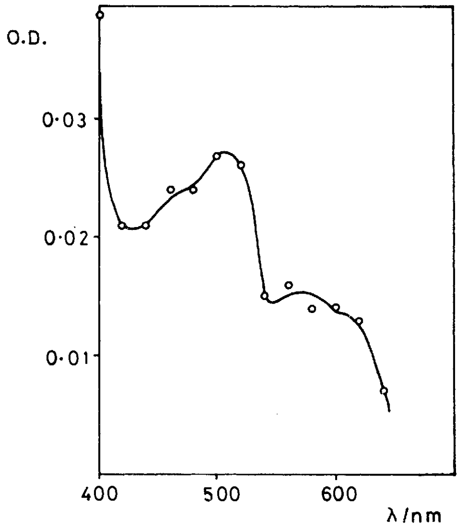


FIGURE 6 Transient absorption in a solution of β-TKN in cyclohexane (2×10^{-4}M) after laser pulse excitation at 265 nm

EXPERIMENTAL

Unless otherwise mentioned, a TQ 81 Hanau high pressure mercury lamp, surrounded by a Pyrex filter, was immersed in the solutions for preparative irradiations. Dry nitrogen gas was passed through the solution kept at room temperature by a water-bath. After irradiation the solvent was evaporated and the residue chromatographed on a silica gel column. Carbon tetrachloride and cyclohexane were distilled after drying over anhydrous $CaCl_2$.

The quantum yield for the photoconversion of α-TKN in CCl_4 at 366 nm has been determined using a ferrioxalate actinometer.[23] Growth rates of the optical absorption at 295 nm were determined for three different excitation light intensities at 366 nm (I_0, $0.4I_0$, $0.2I_0$).

Irradiation of β*-TKN in Cyclohexane.*—β-TKN (284 mg) was dissolved in cyclohexane (100 ml). Every 30 min during the irradiation portions were analysed by t.l.c. After 120 min, no β-TKN was present and virtually no further change in the composition of the reaction mixture occurred. The solvent was then removed and the remaining oil was chromatographed, using CCl_4–2% CH_3OH as eluant. This yielded a pale yellow solid (40 mg), which has been identified by i.r., u.v., and mass spectra as the naphthol (1). Furthermore a yellow oil (130 mg) was obtained which could not be purified chromatographically or by recrystallization. Its u.v. spectrum was practically identical with that of (1). N.m.r. and i.r. indicated the presence of aliphatic and aromatic protons (10 : 4). The impure oil must therefore largely contain the cyclohexyl ether (2). The nitrogen gas, passing through the solution, took HCl along during the photolysis. The amount of acid produced was determined by trapping it in NaOH solution prior to titration. The formation of cyclohexyl chloride was established by g.l.c. (SE 30 column; 180 °C). The amount was estimated by comparing the $C_6H_{11}Cl$ peak intensities of the reaction mixture to that of a standard solution of cyclohexyl chloride in cyclohexane. The presence of bicyclohexyl (6) could not be detected by g.l.c.

Irradiation of β*-TKN in Aerated Cyclohexane.*—β-TKN (230 mg) dissolved in cyclohexane (1 l) was irradiated for 50 min. The solvent was removed and the photolysis mixture was chromatographed using CCl_4 as eluant. The resulting products were identified by i.r. u.v., and mass spectra. Quinone (4) (100 mg) was a green-yellow solid, m.p. 193 °C, indenone (5) (64 mg) a yellow solid, and bicyclohexyl (50 mg) an oil.

Irradiation of α*- and* β*-TKN in* CCl_4.—α-TKN (295 mg) in CCl_4 (100 ml) was irradiated for 50 min. After removal of the solvent the mixture was chromatographed with CCl_4–2% CH_3OH as eluant. The first fraction contained a yellow solid (118 mg) which was purified by recrystallization from cyclohexane, giving crystals (90 mg), m.p. 130—132 °C. According to the i.r., u.v., n.m.r., and mass spectra this compound was the benzobicycloketone (8). The second fraction contained β-TKN (131 mg) (i.r.). Photolysis of α-TKN in CCl_4 with light of wavelength >340 nm has been performed by using a $CuSO_4$ filter solution. The reaction yields the products mentioned above.

Irradiation of β-TKN (300 mg) in CCl_4 (100 ml) for 120 min yields a small amount of (8) (identified by u.v. and i.r.). About 70% of the starting compound was regained.

Flash Photolysis.—Experiments were performed with either 353 or 265 nm laser pulses obtained from a Nd^{3+} glass laser. The pulse had a duration of 15 ns full width at half maximum and an energy of *ca.* 20 mJ for the 353 nm pulse and of *ca.* 1 mJ for the 265 nm pulse. Transient absorptions were monitored by a monochromatic light flash, obtained from a pulsed Xe lamp.[24] The pulse shape of the lamp flash exhibits a flat top with a section where the intensity remains constant within 0.2% during 100 μs. Within the time window of 100 μs the flash lamp signal is transmitted through a high pass wide band filter to a 500 MHz oscilloscope, without introducing a base line shift.[25] Within the period mentioned the sample is excited by the laser. The method enables detection of transient absorptions with lifetimes between 3×10^{-8} and 10^{-6} s. The lower limit is determined by the frequency response of the filter. In certain cases (*e.g.* high concentration of transients from α-TKN) lifetimes longer than 10^{-6} s have been determined by abandoning the filter and running the Xe lamp continuously.

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