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The Photochemical Approach to the Functionalization of Open-Chain and Cyclic Alkanes: 2. Hydrogen Abstraction.

Mariella Mella, Mauro Freccero and Angelo Albini
Dipartimento di Chimica Organica dell'Universita', v.Taramelli 10, 27100 Pavia, Italy

Abstract. Chloranil (Chl) has been irradiated in the presence of the alkanes 2,3-dimethylbutane, cyclohexane, norbornane, adamantane in acetonitrile. The primary step is hydrogen abstraction by triplet Chl, k_H 0.8 to $2x10^9$ $M^{-1}s^{-1}$, as confirmed by the detection of the $ChlH^·$ radical. Hydrogen abstraction from the alkanes is unselective. The thus formed alkyl radicals undergo different reaction, viz: coupling with $ChlH^·$ (both C-O coupling to give hydroquinonemonoethers and C-C coupling to give hydroxydihydrobenzofurans are observed); addition to ground state Chl to yield ultimately alkoxyphenoxyquinones; oxidation by groud state Chl (this process is fast only with tertiary radicals, and the cations formed in this case are trapped by the solvent MeCN to yield acetamides). Different methods for alkane funtionalization are compared. Copyright © 1996 Elsevier Science Ltd

Radical-initiated processes are largely used for the functionalization of alkanes and have industrial significance.[1,2] However, such processes involve a high energy barrier, since the first step is homolytic hydrogen abstraction (eq. 1,2), and the energy involved is in the range 92-105 kcal mol^{-1}. Thus highly reactive, and often poorly selective, reagents are usually employed.

$$R\text{-}H \rightarrow R^· + H^· \qquad (1)$$

$$R^· \rightarrow \text{Products} \qquad (2)$$

A better understanding of the single steps involved in the overall process would be obtained if the reactions were carried out under more easily controlled conditions. The photochemical approach may be useful for this aim, since the actual reagent, the excited state, is generated in situ at a low steady state concentration under mild conditions. Triplet state ketones are well known for their hydrogen abstracting properties (eq.3), and their reactivity is similar to that of alkoxy radicals. (eq.4).[3-5]

$$K^{3*} + R\text{-}H \rightarrow K\text{-}H^· + R^· \qquad (3)$$

$$R'O^· + R\text{-}H \rightarrow R'OH + R^· \qquad (4)$$

However, the synthetic utility of alkyl radicals produced in this way has been scarcely explored, while this has been done for other more stable species, e.g. α-hydroxy or α-amino radicals.[6] In an effort to compare the characteristics of different methods for hydrocarbon functionalization, we undertook a study of the photochemistry of various alkanes in the presence of 2,3,5,6-tetrachloro-1,4-benzoquinone (chloranil, Chl). The triplet state of this molecule is expected to abstract hydrogen efficiently from alkanes. Furthermore, the phenoxy and alkyl radicals thus produced are expected to couple and to give easily identified products. Thus, a product study might reveal important features of radicalic functionalization of alkanes.

RESULTS

Photochemical reactions were carried out in degassed acetonitrile solution 0.1 M in the alkane (or saturated when less soluble). In order to explore the possibility of a selective functionalization, both linear and cyclic alkanes were used. Preparative irradiations were supplemented by physico chemical experiments.

Preparative photochemical reactions. Irradiation of Chl in acetonitrile solutions of all the alkanes tested caused a fast reaction. Although the raw photolysate was in every case a complex mixture, chromatographic separation allowed separation of the main products, which included alkylated Chl derivatives from which the pattern of alkanes reactivity could be deduced (see Schemes 1, 2 and Table 1A).

The irradiation of a solution of Chl and 2,3-dimethylbutane (**1**) afforded, besides 2,3,5,6-tetrachlorohydroquinone ($ChlH_2$) and a small hydrocarbon fraction which was not investigated, two main products. One of these was a hydroquinone mono ether, namely the 2,3-dimethylbutyl ether (**2**) as shown i.a. by the characteristic signal of the *O*-linked methylene in the ^1H NMR. The latter also showed a phenolic group, and three chlorine atoms instead of four and an isolated methylene group; all other properties were in accord with a dihydrobenzofuran structure (**3**) for this compound. A further fraction contained a minor product which arose from two Chl units and the 2,3-dimethylbutyl radical. The structure of the alkoxyphenoxyquinone **4** was assigned in accordance with spectroscopic data (in particular mass and ^{13}C NMR spectra). Traces (below 10% of the main ones) of other products with phenyl ether or dihydrobenzofuran structure, but containing the 1,1,2-trimethylpropyl rather than the 2,3-dimethylbutyl radical were detected in the chromatographic fractions.

Table 1. Photochemical reaction of Chl in the presence of alkanes in acetonitrile.

A. Product distribution.[a]

Alkane	Irradiation time (h)	Chl consumed	Products (% Yield)
1	2	70	$ChlH_2$(48), **2**(18), **3**(16), **4**(2)
5	2	80	$ChlH_2$(40), **6**(21), **7**(18)[b]
8	2	80	$ChlH_2$(35), **9**(Trace), **10**(25), **11**(5), **12**(18)
13[c]	2	80	$ChlH_2$(41), **14**(43), **15**(2.5), **16**(10.4), **17**(12.5), **18**(8), **19**(10.8),

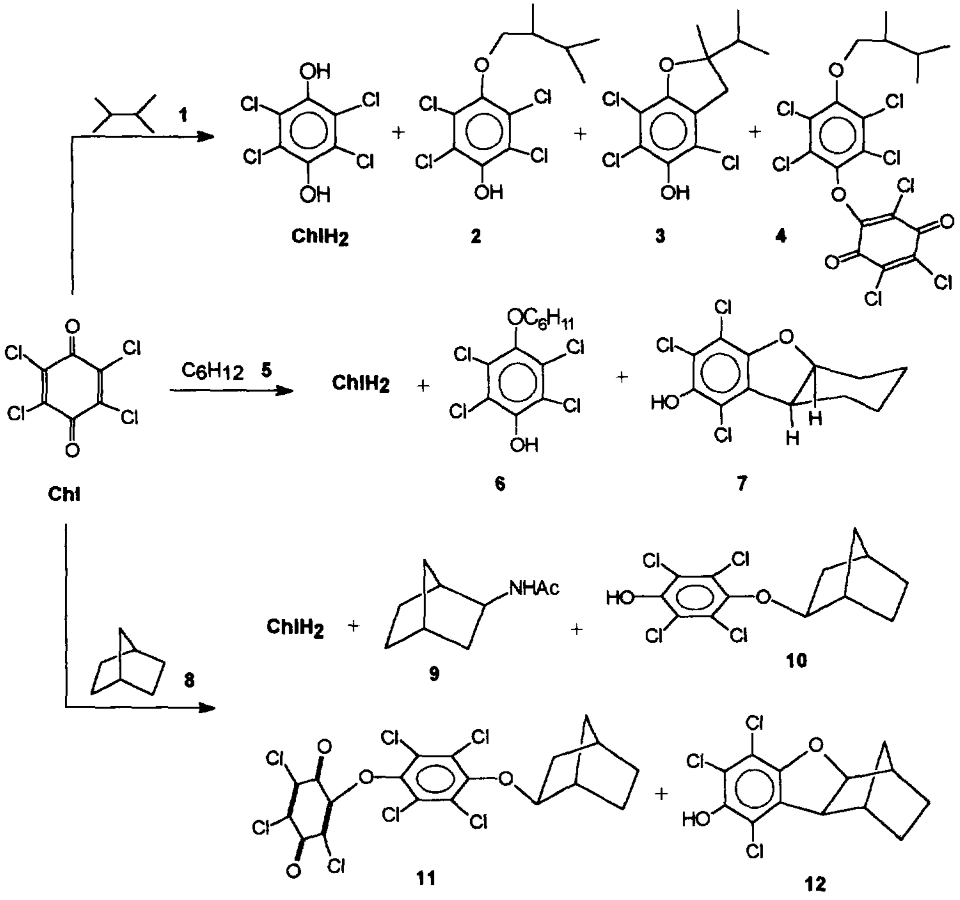
a. Yield calculated on the consumed acceptor. b. Traces of cyclohexanol and cyclohexanone also revealed by GC/MS. c. In this case the reported yields are deduced from the NMR spectrum of the raw photolysate and GC. Isolated yields are lower, since some of the products are partially hydrolised during chromatography. A small amount (ca 2%) of adamantyloxyphenoxyquinones also formed, see Experimental. Traces of 2-adamantanone, 1-and 2-adamantanol detected by GC/MS

B. Quenching constants and quantum yield data.

Substrate	$k_q(Chl^{3*})$ ($M^{-1}s^{-1}$)	Φ(Chl)
5	$0.8x10^6$	0.035[a]
13	2.2	0.013[b]

a. Substrate concentration 0.1 M. b. Substrate 0.02 M.

Scheme 1

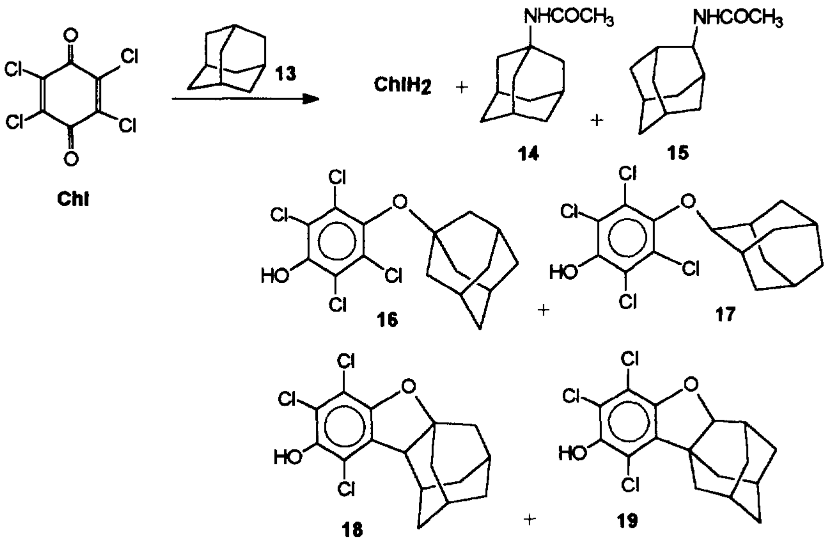


The reaction of Chl with cyclohexane (**5**) gave, besides $ChlH_2$, the cyclohexyl ether **6** and the hydroxytrichlorobenzofuran **7** (the latter compound had a *cis* fusion of the aliphatic rings, as shown by NMR spectra, see Experimental). GC/MS examination of the raw mixture showed the presence of traces of cyclohexanol and cyclohexanone.

With norbornane (**8**) several photoproducts were separated and identified. These included $ChlH_2$, *N*-(2-norbornyl)acetamide (**9**) as well as three compounds resulting form the Chl-alkane combination similar to the previous case: the aryl alkyl ether **10** (with the 2-norbornyl radical in the *exo* position), the alkoxyphenoxyquinone **11** (a crystalline orange material, see Experimental for details of structure attribution), the dihydrobenzofuran **12** (with *cis exo* fusion at the norbornane skeleton).

In the reaction with adamantane (**13**), $ChlH_2$ and *N*-(1-adamantyl)acetamide (**14**) were major products, and were accompanied by a small amount of the isomeric 2-adamantyl acetamide (**15**) and of 2-adamantanone, as well as by traces of 1- and 2-adamantanol. Furthermore in the raw mixture were present mainly four alkylated Chl derivatives formed by substitution at secondary and primary position of adamantane; these were obtained in two chromatographic fractions. The first one contained two isomers easily identified as the 1- and the 2-adamantyl aryl ethers **16** and **17**. The latter one showed NMR signals which allowed the identification of the main components as the two isomeric dihydrobenzofurans **18** and **19**, although a satisfactory elemental analysis was not obtained, since the fraction contained some $ChlH_2$, and attempted further chromatographic purification led to extensive hydrolysis (see Experimental). Finally, a small amount of an orange material shown by mass spectrometry to be a mixture of two adamantyloxyphenoxyquinones analogous to product **4** was also obtained, but not completely characterised.

Scheme 2



Mechanistic Studies. Quantum yields were measured in separate experiments and are reported in Table 1B. In order to ascertain the mode of the initial interaction between Chl and the alkane, flash photolysis experiments were carried out. As it appears in Fig. 1, the absorption of the Chl triplet was quenched (measured quenching constants were in the order of 10^6 M^{-1} s^{-1} and are reported in Table 1B), and was substituted by a further transient absorbing in the visible, with λ_{max} ca 440 nm. The latter absorption well corresponded to the reported spectrum for reduced chloranil radical,[7a,b] and differed from that of the Chl radical anion (which is at somewhat longer wavelength).[7b-c] It decayed through a first order process which was linearly dependent on the laser pulse energy (see Fig. 2), with k_{obs} ranging from 0.97 to 1.54 and 2.61×10^4 s^{-1} for 22, 45 and 90 mJoule power respectively.

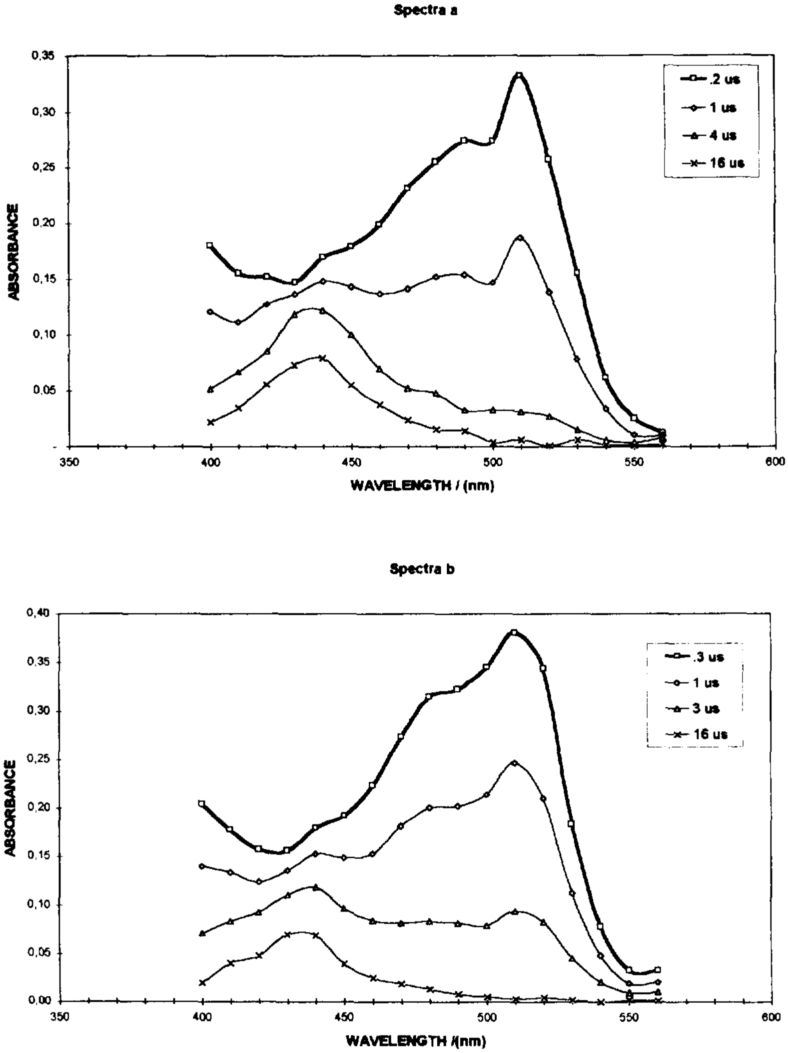


Fig. 1 Absorptions observed after flashing a Chl (0.0025 M) solution in MeCN in the presence of adamantane (0.02 M, spectra a) and of cyclohexane (1.5 M, spectra b). The end of pulse spectrum (λ_{max} 445, 485 and 510 nm) is attributed to the chloranil triplet, the spectrum at t>16μs to the ChlH· radical

DISCUSSION

The Hydrogen Abstraction Step. Product distribution and kinetic data clearly indicate that the reaction with chloranil involves hydrogen transfer. The photochemical reactivity of Chl with alkanes had not been previously explored, but studies of the reactions in the presence of other non-electron donating substrates showed that the lowest triplet of this molecule has $n\pi^*$ character, or at least that $n\pi^*$ and $\pi\pi^*$ states are close one to another.[8,9]

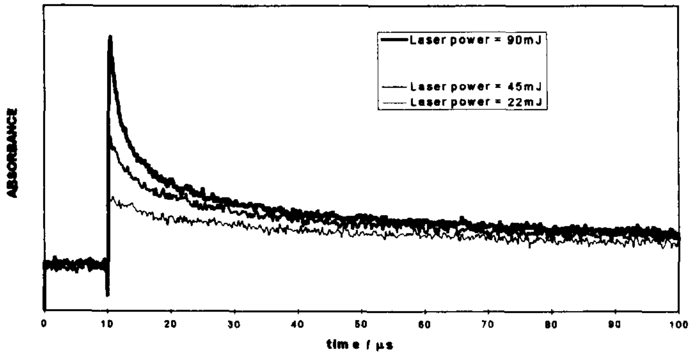


Fig.2 Decay of absorption at 440 (attributed to the Chl. radical) observed by flashing a Chl (0.0025 M) solution in MeCN in the presence of adamantane (0.01 M) with different laser powers.

Indeed, the present results show that quenching of Chl triplet occurs at a rate constant (ca 10^6) similar to that observed for intermolecular hydrogen transfer from alkanes by other $n\pi^{3*}$ ketones.[3-5] In turn this is similar to that measured for alkoxy radicals (e.g. the rate constant for H abstraction by the *tert*-butoxy radical from **8** is $5.8\mathrm{x}10^5$ $M^{-1}s^{-1}$).[10] Furthermore, the transient spectrum observed in flash photolysis well corresponds to that reported for the ChlH· radical[7] (see Fig.1). The reaction is somewhat affected by the substrate oxidation potential, and the rate constant (k_q) rises by a factor of 3 between adamantane and cyclohexane (see Table 1B). It has been previously observed that the rate of hydrogen abstraction by ketone triplets depends on the ionization potential of the radicals formed,[5] and these may parallel the oxidation potential of the substrates.

Hydrogen abstraction by Chl^{3*} shows a poor selectivity, and the alkylated derivatives obtained from the alkanes **1** (functionalization mainly at the methyl groups), **8** (mainly at the ethylene bridge) and **13** (overall, 1-adamantyl- and 2-adamantyl- derivatives are in the ratio 2.4 to 1, but the ratio changes if one considers chloranil adducts or acetamides, see below) are all in accordance with a limited selectivity in tertiary vs secondary hydrogen abstraction. With the polyclic hydrocarbons **8** and **13** it had previously observed that hydrogen abstraction by radicals shows little selectivity. Thus, chlorination of **8** both by chlorine[11] and by dialkylchloroamines under acidic conditions (in the latter case, the dialkylamino radical cation is the active species)[12] mainly gives the 2-chloro derivative, and bromination takes place similarly.[13] With adamantane (**13**) the results are more varied. When an alkoxy radical is the active species, the statistically corrected tertiary/secondary selectivity is ca 3,[14] but with electron poor species such as a dialkylamino radical cation[14,15] or the nitrate radical,[16,17] selectivity is much higher (30 to 100). A rationalization that has been proposed for the poor selectivity is that C-H bond energies are indeed similar;[14] e.g., PES measurements suggest that the bridgehead C-H bond in adamantane is stronger than a normal tertiary C-H bond, and as strong as a secondary one.[18]

With the open-chain alkane **1** a marked tertiary vs primary selectivity has been previously observed with alkoxy radicals[5,19a], iodosobenzene dichloride,[19b] as well as with aromatic ketone triplets.[3,5]. In the last method the selectivity increases with more easily reduced ketones. In the present case, only products arising from the primary radicals have been isolated. However, this can not be taken as a direct measurement of the initial selectivity in hydrogen abstraction, since the tertiary radicals formed probably undergo further oxidation and deprotonation to yield isobutene (see eq. 5, 6 and the discussion below), and thus may not be revealed by Chl trapping (oligomers are in fact formed, see the Result section).

$$Me_2CHCMe_2^{\cdot} + Chl \rightarrow Me_2CHCMe_2^{+} + Chl^{-\cdot} \qquad (5)$$

$$Me_2CHCMe_2^{+} \rightarrow Me_2C{=}CMe_2 \text{ and Oligomers} \qquad (6)$$

Nevertheless, the fact remains that abstraction from the primary position is certainly not a minor process.

Reactions of the Alkyl Radicals. The photochemical step generates a radical pair, and the final products arise from the recombination of these intermediates (or of further transients generated from them), as evidenced by the pulse energy dependent, single exponential decay observed for the ChlH· radical in flash photolysis. Indeed, as it appears in Schemes 1 and 2, the final products obtained do result from Chl-alkanes addition, but straightforward ChlH·-alkyl radical coupling to give phenyl alkyl ethers (compounds A in Scheme 3) accounts only for a part of the observed products, and compounds of different structure, viz dihydrobenzofurans (B), alkoxyphenoxyquinones (C) and acetamides (D) are also obtained. As for products B we first considered that these may arise through a secondary reaction from the ethers A, but separate experiments on a compound of this class (the ether **10**) showed that it did not reacted appreciably upon irradiation for several hours and was stable to the work up conditions. Futhermore, monitoring the product distribution showed no significant change during the progress of the reaction. We propose that compounds B arise through C-C coupling of the phenoxyl and alkyl radicals (path ***b***) alternative to C-O coupling (path ***a***) to yield, after hydrogen chloride elimination, the quinones E. These have an absorption spectrum similar to that of Chl, and are expected to cyclize via efficient intramolecular hydrogen abstraction, as shown in Scheme 3.

As for the other products, we consider that they arise via reaction of the alkyl radicals with *ground state* Chl. Indeed, it has been previously documented that phenyl and benzyl radicals add to the oxygen atom of chloranil.[20] This is shown in the present case as path ***c*** in Scheme 3, and leads to the phenoxyl radicals F. In turn, these exchange a hydrogen with the ChlH· radicals (thus affording an alternative way to products A, path ***e***) or add to them yielding, after hydrogen chloride elimination, products C (path ***f***).

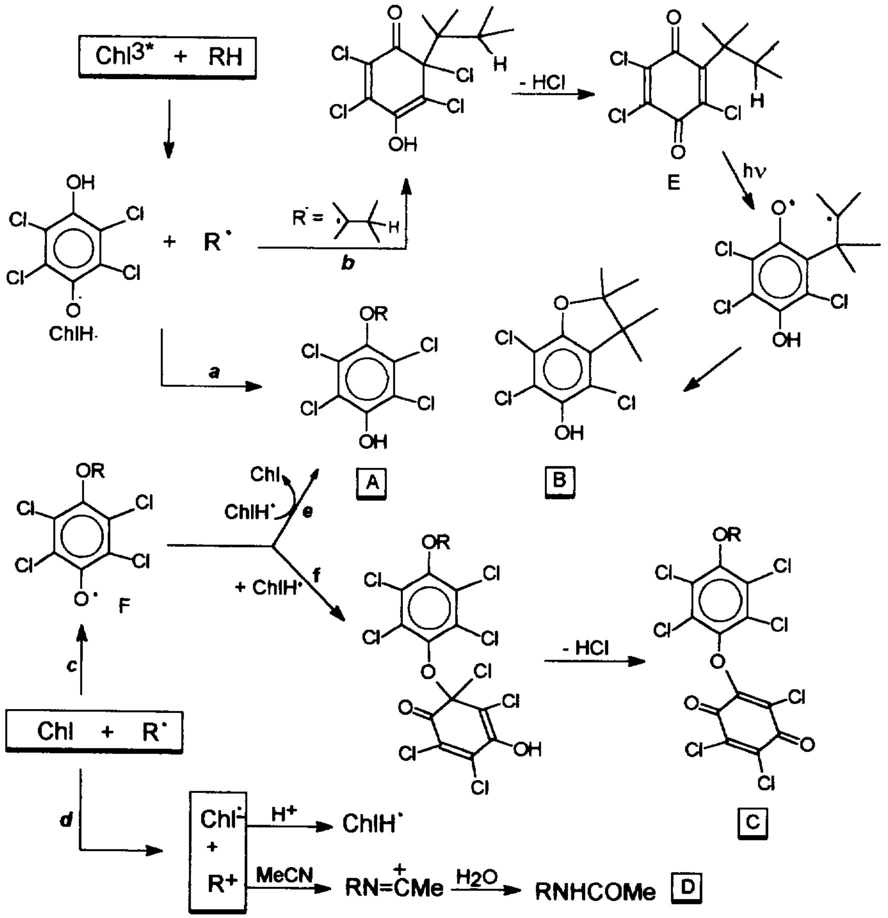
A final group involves *N*-alkylacetamides (D). Previous evidence in electrochemistry and metal- or photoinduced oxidation in acetonitrile shows that these arise from carbocation trapping by the solvent and water addition (MeCN contains ca 0.1% moisture).[17,21] Indeed, another relevant property of ground state Chl is its high-lying ground state reduction potential (0.02V vs SCE). This makes Chl a sufficiently good acceptor for the single electron oxidation (SET) of at least tertiary aliphatic radicals (for the *tert*-butyl radical the reported value is 0.09V vs SCE,[22] less substituted radicals are expected to oxidize at a more positive potential). Thus, oxidation of the adamantyl radical to the corresponding cation is a major path with **13**, and, to a lower degree a similar process is observed also with **8**, and formation of the cations is revealed by trapping by the solvent (path ***d*** in Scheme 3), a reaction for which there is some precedent. About this reaction one may notice that the amount of the *N*-(1-adamantyl) amide is 16 times as much as that of the 2-adamantyl isomer. On the other hand, the chloranil-adamantane adducts **16-19** show that there is no selectivity in the formation of the two adamantyl radicals. Therefore, the selectivity in the amide formation is reasonably due to the more positive E_{ox} of the 2-adamantyl radical, a secondary radical, in comparison with the isomeric radical in position 1, which makes

Table 2. Functionalization of Adamantane under Different Conditions

Reagent	Active Species	Rate Constant $M^{-1}s^{-1}$ a	Selectivity tert/sec	Fate of the Radicals	Ref.
t-BuOCl, hν	*t*-BuO·	1x10^{6} b	2.7	Ad· + RCl → AdCl	14
i-Pr_2NCl, H_2SO_4	*i*-$Pr_2N^{+\cdot}$		32	Ad· + RCl → AdCl	14
CAN,c hν	$NO_3^{\cdot}$	5.6x10^{7}	45	Ad· + Ce^{IV} → Ad^+ + Ce^{III}	16
Chl, hν	Chl^{3*}	2.2x10^{6}	7	1-Ad· + Chl → 1-Ad^+ and Adducts	this
				2-Ad· + Chl → Adducts	work
TCB,d hν	TCB^{1*}	1.1x10^{10}	100	Ad· + $TCB^{\cdot-}$ → Adduct	23

a. In MeCN at 20°C. b. Estimated from the measured rate with **8**, 5.8x10^{5} $M^{-1}s^{-1}$, ref. 10 c. CAN = $Ce(NH_4)_2(NO_3)_6$. d. TCB = 1,2,4,5-benzenetetracarbonitrile

Scheme 3



oxidation of the former species an exothermic process, too slow to compete with addition. The same reasoning explain why the 2-norbornyl radical formed from **8** is only slowly oxidized, and thus the carbocation trapping product (the amide **9**) is only a trace, the interaction of the radical with Chl involving predominantly addition rather than oxidation (path *c* rather than path *d*). Traces of 1-adamantanol are also formed from **13**, and similarly arise via trapping of the cation by traces of moisture present. Acetamides are not formed with monocyclic or open chain alkanes. This is due to the fact that even when tertiary radicals are formed, as with **1**, deprotonation to alkenes is the main path from the cation in that case (see above, eqs.5,6)

Thus, analysis of the end products from the photochemical reaction with Chl does allow to recognize the aliphatic radicals formed in the primary step, even if the chemistry observed is more complex than straightforward C-O recombination of the primarily formed radical pair

Comparison between Different Alkane Radicalic Reactions. Adamantane can be taken as a convenient probe (see Table 2) to compare the main features of some alkane functionalizations, all involving alkyl radicals as the key intermediate. When the alkyl radical is generated through a hydrogen abstraction process, the rate depends only slightly from the active species.[3-5] Chl^{3*} behaves similarly to an alkoxy radical, as it is general expected from $n\pi^*$ triplet state. However, the rate increases significantly with the electron affinity of the radical [$k_H(NO_3\cdot) >> k_H(t\text{-BuO}\cdot)$]. When the mechanism changes to single electron transfer (SET) - proton transfer, as in the reaction photosensitized by TCB,[23] the rate constant increases by several orders of magnitude to diffusion controlled. Selectivity is poor both with alkoxy radicals and triplet states, and is high both with strongly electron deficient radicals and via the SET mechanism.

The method chosen for the generation of radicals also determine the following reactions of such species. When the precursor of the initiator is not itself reactive with alkyl radicals, these can be trapped e.g. via atom transfer reactions.On the other hand, the nitrato radical is conveniently produced by photolysis of cerium (IV) amonium nitrate (CAN), and the strong oxidizing properties of this salt (E_{red} 1.37 V vs SCE) ensure that all radicals are oxidized to the cations. Chloranil is an intermediate case, a strong enough oxidant to affect tertiary, but not secondary, radicals, and at the same time is an excellent trap for addition of these nucleophilic radicals. Aromatic nitriles such as TCB are neither oxidants nor a trap via addition, but the corresponding radical anions do couple efficiently with the radicals.

As stated above, adamantane is a peculiar case, and adapting these conclusions to other alkanes requires some care. At any rate, Table 2 gives an idea of the different possibilities one should take into account when planning a synthesis. Obviously, several variations can be made. As an example, in the place of Chl, one may use a $n\pi^*$ triplet which is neither an oxidant or a radical trap, such as would be an aromatic ketone, or one which has only one of the two properties.

In conclusion, the present work evidences the convenience of the photochemical method for the generation of aliphatic radicals under mild conditions. This may be useful for selectivity studies. Furthermore, the efficiency of radicals generation makes this reaction well suited for using such radicals for preparative applications. Indeed, trapping by ground state molecules of such radicals is effective; in the present work the reaction occurring is addition to chloranil itself; but an alternative trapping can certainly be devised. We are confident that these data and the comparison established between different methods for the functionalization of alkanes may give useful suggestions for new synthetic methods.

EXPERIMENTAL

General ^{1}H, ^{13}C and ^{13}C-DEPT NMR spectra were recorded on a Bruker AC 300 spectrometer, and chemical shifts are reported in ppm downfield from TMS. Elemental analyses were made using a Carlo Erba Model 1106 instrument. Chl and alkanes **1**, **5**, **8**, and **13** were commercial products.

Photochemical reaction between Chl and 2,3-dimethylbutane 1. A solution containing 150 mg (0.6 mmol) of Chl and 345 mg (4 mmol) of 2,3-dimethylbutane **1** in 80 ml of MeCN purged with argon, was irradiated for two hours with an immersion well reactor fitted with a Philps HPK 125W medium pressure arc filtered through Pyrex. GC examination (using a HP-5 column, 0.5 mm) of the photolized solution showed two minor products, which had the GC/MS characteristics compatible with C_{12} alkanes. The solvent was evaporated and the raw mixture was separated on silica gel column using cyclohexane-EtOAc mixtures of increasing polarity. Two main products were isolated, both alkylated Chl derivatives. The first one was a hydroquinone mono ether (the isotopic pattern was that expected for a tetrachlorinated compound),[24] with a methylene group bonded to the oxygen (see ABX system at 3.75-3.9 ppm in the proton spectrum). The spectroscopic data and molecular mass allowed to attribute the structure of the 2,3,5,6 tetrachloro-4-hydroxyphenyl 2,3-dimethylbutyl ether (**2**) (25 mg, 18%) to this compound. The latter compound was likewise a hydroquinone mono ether containing again a phenolic group, but only three chlorine atoms; that it was a cyclic ether with bonding between carbons 1 and 2 of Chl and 1 and 2 of the alkane as shown by the AB system bonded to aromatic ring and the quaternary carbon at 77.53 ppm on oxygen. The proposed structure of 2,3-dihydro-3,5,6-trichloro-4-hydroxy-2-methyl-2-isopropylbenzofuran (**3**) (20 mg, 16 %) was in accordance with spectroscopic data. Furthermore, the initial chromatographic fraction (8 mg) besides contained a compound with the same proton signals observed for **2**, except for the hydroxylic proton. Also the ^{13}C spectrum had the same aliphatic carbons distribution but showed that it incorporated two Chl molecule: one as hydroquinonediether derivative and the second with quinone structure (see two different carbonilic groups). The molecular mass and the isotopic pattern confirmed the presence of seven chlorine atoms. The structures of 4-[4-(2,3-dimethylbutoxy)-2,3,5,6-tetrachlorophenoxy]-2,3,5-trichloro-1,4-benzoquinone (**4**) (5 mg, 2.2 %) was reasonably attributed, although the product was not sufficiently pure for elemental analysis. Finally, 50 mg (48%) of 2,3,5,6-tetrachlorohydroquinone (ChlH$_2$) was obtained. Minor amounts (< 10% of the previously described ones) of further compounds with phenyl ether or dihydrobenzofuran structure, were present in some of the chromatographic fractions, admixed with the main ones.

2: ^{1}H NMR (in CDCl$_3$) δ 0.92 (*d*, J = 7 Hz, 3H, Me), 0.97 (*d*, J = 7 Hz, 3H, Me), 1.04 (*d*, J = 7 Hz, 3H, Me), 1.9 (*m*, 2H, H-2 and H-3), 3.75 and 3.9 (ABX system, J = 6.5 and 5.5 Hz, 2H, H-1), 5.9 (*exch*, OH). ^{13}C NMR δ 12.77 (CH$_3$), 18.07 (CH$_3$), 20.40 (CH$_3$), 28.98 (CH), 39.49 (CH), 77.53 (CH$_2$-O), 118.75, 127.33, 145.78, 149.48. Anal. Calcd for $C_{12}H_{14}Cl_4O_2$: C, 43.41; H, 4.25. Found C, 43.2; H, 4.3. M^+ 330 m/e.

3: ^{1}H NMR (in CD$_3$COCD$_3$) δ 0.98 (*d*, J = 7 Hz, 3H, Me), 1.03 (*d*, J = 7 Hz, 3H, Me), 1.4 (*s*, 3H, Me), 2.05 (*sett*, J = 7 Hz, 1H, H-2), 3.0 and 3.3 (AB system, 2H, H-1), 8.5 (*exch*, OH). ^{13}C NMR *d* 17.76 (CH$_3$), 17.81 (CH$_3$), 23.89 (CH$_3$), 36.10 (CH), 40.61 (CH$_2$), 95.04 (C-O), 112.85, 116.69, 127.47, 141.48, 144.68, 150.57. Anal.Calcd for $C_{12}H_{13}Cl_3O_2$: C, 48.76; H, 4.43. Found C, 48.3; H, 4.3. M^+ 294 m/e.

4: ^{1}H NMR (in $CDCl_3$) δ 0.94 (*d*, J =7 Hz, 3H, Me), 0.99 (*d*, J = 7 Hz, 3H, Me), 1.07 (*d*, J = 7 Hz, 3H, Me), 1.92 (*m*, 2H, H-2 and H-3), 4.0 and 3.85 (AB part of ABX system, 2H, H-1). ^{13}C NMR δ 12.76 (CH_3), 18.10 (CH_3), 20.39 (CH_3), 28.96 (CH), 39.52 (CH), 77.53 (CH_2-O-), 125.85, 126.88, 129.52, 142.11, 143.22, 146.73, 148.49, 151.05, 172.98, 173,32. M^+ 538 m/e.

Photochemical Reaction between Chl and cyclohexane 5. A solution of Chl in 80 mL of MeCN and cyclohexane (330 mg, 4 mmol) was irradiated as above for 2h. The GC/MS analysis of the raw photolizate showed the presence of traces of cyclohexanol and cyclohexanone, while the *N*-methylcyclohexylacetamide was no detected. After general work-up and silica gel cromathography (cyclohexane/EtOAc 9:1 as eluant), two main alkylated Chl derivatives analogous to the previous case were isolated. In fact, besides 47 mg $ChlH_2$ (40%), 33 mg of 4-hydroxy-2,3,5,6-tetrachlorophenyl cyclohexyl ether **6** (21%, oil) and 25 mg of 2,3-dihydro-4-hydroxy-2,3,5-trichlorocyclohexa[*a*]benzofuran 7 (18%, oil) were obtained. The attributed structures were in accordance with spectroscopic data and in particular the coupling between H-1 and H-2 (J = 6 Hz) identified a *cis* fusion of the aliphatic ring in compound 7.

6: ^{1}H NMR (in $CDCl_3$) δ 1.25 (*m*, 2H), 1.55-1.65 (*m*, 4H), 1.8 (*m*, 2H), 2.0 (*m*, 2H, H-2 and H-6 equatorial), 4.15 (*tt*, J = 10 Hz, J = 4 Hz, H-1 axial), 5.85 (exch, OH). ^{13}C NMR (in $CDCl_3$) δ 24.29 ($2CH_2$); 25.20 (CH_2); 32.43 ($2CH_2$); 83.62 (CH); 118.73; 127.56; 145.61; 145.38. Anal.Calcd for $C_{12}H_{12}Cl_4O_2$: C, 43.67; H, 3.66. Found C, 43.7; H, 3.7. M^+ 328 m/e.

7: ^{1}H NMR (in $CDCl_3$) δ 1.2 (*m*, 1H, H-3 axial), 1.25 (*m*, 1H, H-4 axial), 1.3 (*m*, 1H, H-5 axial), 1.65 (*m*, 1H, H-4 equatorial), 1.7 (*m*, 1H, H-5 equatorial), 1.75 (*m*, 1H, H-6 axial), 2.1 (*m*, 1H, H-3 equatorial), 2.35 (*m*, 1H, H-6 equatorial), 3.25 (*dt*, J = 10 Hz, J = 6 Hz, 1H, H-2), 4.7 (*ddd*, J = 6 Hz, J = 3 Hz, J = 4 Hz, H-1), 5.95 (exch, OH). ^{13}C NMR δ 19.83 (CH_2); 22.11 (CH_2); 26.80 (CH_2); 27.07 (CH_2); 41.65 (CH); 83.77 (CH); 113.07; 115.17; 117.89; 142.68; 149.65, 151.23. Anal.Calcd for $C_{12}H_{11}Cl_3O_2$: C, 49.10; H, 3.78. Found C, 48.9; H, 3.7. M^+ 292 m/e.

Photochemical reaction between Chl and norbornane 8. A MeCN solution of Chl and norbornane (384 mg, 4 mmol) was irradiated as above for 2h with a 80% Chl consumption (determined by GC). GC/MS analysis showed the presence of a small amount of *N*-norbornylacetamide (**9**, M^+ 153). After silica gel chromatography (cyclohexane/EtOAc) of the raw mixture, the following products were isolated sufficiently pure: 13 mg of 4-[4-(2-norbornyloxy)-2,3,5,6-tetrachlorophenoxy]-2,3,5,trichloro-1,4-benzoquinone **10** (5 %, mp 115-116 °C, Cy-Bz), ; 40 mg (25 %) of 4-hydroxy-2,3,5,6-tetrachlorophenyl *exo*-2-norbornyl-ether **11** (mp 98°C, cyclohexane-benzene); 26 mg (18%) (mp 87-91°C, cyclohexane-benzene) of the dihydrobenzofuran **12** and 41 mg (35%) of $ChlH_2$. All the norbornyl derivatives were obtained as a single regioisomer. Compound **11** was the *exo*-isomer, as shown by the fact the irradiation of H-2 at 4.25 ppm gave 4.9% NOE enhancement on H-6 at 1.05 and 1.4% on H-5 at 0.91. This NOE effect could have been observed only if H-2 was endo. Moreover it was apparent in the ^{1}H spectrum a ^{4}J (1.5 Hz) between H-2 and H-7. The cyclic structure of product **12** with *cis-exo* fusion at the norbornane skeleton was confirmed by the fact that the two vicinal hydrogen atoms, H-2 (4.83 ppm) and H-3 (3.45) had a long range coupling (1,5 Hz) with the same H-7 (1.25 ppm). As regard the alkoxyphenoxyquinone **10**, this time it was obtained pure as crystalline orange material and a complete characterization, including also elemental analysis was possible. It was the *exo* isomer as confirmed by the usual long range coupling between H-2 and H-7.

10: ^{1}H NMR (in $CDCl_3$) δ 0.95 (*m*, 1H, H-6 endo), 1.1 (*m*, 1H, H-5 endo), 1.3 (*dq*, ^2J = 9 Hz, ^3J = ^4J = 1.5 Hz, 1H, H-7), 1.45-1.55 (*m*, 2H, H-6 and H-5 exo), 1.82 (*m*, 2H, H-3), 1.92 (*dq*, ^2J = 9 Hz, ^3J = ^4J = 1.5 Hz, 1H, H-7), 2.35 (*m*, 1H, H-4), 2.48 (*m*, 1H, H-1), 4.3 (*m*, 1H, H-2 endo). ^{13}C NMR (in $CDCl_3$) δ 25.86 (CH_2-6), 29.97 (CH_2-5), 37.02 (CH-4), 37.07 (CH_2-7), 41.47 (CH_2-3), 43.62 (CH-1), 90.66 (CH-2), 126.57, 127.08, 129.62, 140.07, 142.58, 146.73, 152.25, 152.55, 172.16 (C=O), 172.86 (C=O). Anal.Calcd for $C_{19}H_{11}Cl_7O_4$: C, 41.38; H, 2.01. Found C, 41.5; H, 2.1. M^+548 m/e.

11: ^{1}H NMR (in CD_3COCD_3) δ 0.91 (*m*, 1H, H-5 endo), 1.05 (*m*, 1H, H-6 endo), 1.25 (*dqui*, ^2J = 9 Hz, ^3J = 1.5, ^4J con H-2 e H-3 = 1.5 Hz, 1H, H-7'), 1.45 (*m*, 1H, H-5 exo), 1.5 (*m*, 1H, H-6 exo), 1.78 (*m*, 2H, H-3 endo e H-3 exo), 1.91 (*dqui*, ^2J = 9 Hz, ^4J = 1.5 Hz, 1H, H-7), 2.33 (*m*, 1H, H-4), 2.45 (*m*, 1H, H-1), 4.25 (*m*, 1H, H-2), 9.1 (exch, OH). ^{13}C NMR (in $CDCl_3$) δ 24.00 (CH_2-6), 28.13 (CH_2-5), 35.11 (CH_2-7), 35.16 (CH-4), 39.40 (CH_2-3), 41.43 (CH-1), 88.24 (CH-2), 118.69, 127.14, 145.28, 146.29. Anal.Calcd for $C_{13}H_{12}Cl_4O_2$: C, 46.65; H, 3.78. Found C, 46.8; H, 3.7. M^+ 340 m/e.

12: ^{1}H NMR (in $CDCl_3$) δ 1.2 (*ddq*, 1H, H-7), 1.25 (*m*, 1H, H-6 endo), 1.35 (*m*, 1H, H-5 endo), 1.4 (*m*, 1H, H-7), 1.58 (*m*, 1H, H-6 exo), 1.6 (*m*, 1H, H-5 exo), 2.59 (*m*, 1H, H-1), 2.61 (*m*, 1H, H-4), 3.45 ('*dd*', ^3J = 7 Hz, ^4J =2 Hz, 1H, H-3 endo), 4.83 (*d't'*, ^3J = 7 Hz, ^4J = 1.5, 1H, H-2 endo), 8.3 (exch, OH). ^{13}C NMR (in $CDCl_3$) δ 22.80 (CH_2-6), 28.13 (CH_2-5), 29.48 (CH_2), 32.17 (CH_2), 39.65 (CH-4), 41.95 (CH-1), 52.76 (CH-3), 90.56 (CH-2), 111.36, 115.69, 118.25, 127.36, 142.27, 151.56. Anal.Calcd for $C_{13}H_{11}Cl_3O_2$: C, 51.10; H, 3.63. Found C, 51.4; H, 3.8. M^+ 304 m/e.

Photochemical reaction between Chl and adamantane 13. A solution containing 150 mg of Chl (0.61mmol) and 250 mg of adamantane was irradiated as above for two hours. As regard the low molecular weight products present in the raw photolized mixture, the GC/MS examination showed the presence of *N*-1-adamantyl-acetamide (**14**) as a major product, accompanied by a small amount of *N*-2-adamantyl-acetamide (**15**, in the ratio 15:1) and of 2-adamantanone and traces of 1- and 2-adamantanol. As for the products derived from Chl, besides $ChlH_2$, the mixture contained four main products formed by substitution at secondary and primary position of adamantane. In fact, the ^{13}C NMR of the raw photolizate, (recorded using Gate NOE technique with a long relaxation delay) showed the presence of four carbons (two methyne and two quaternary) bonded to an oxygen atom and of two carbons (methyne and quaternary) bonded to the aromatic ring. Comparison with the products previously obtained (in particular **11** and **12**), made it reasonable to suppose the existence of two ethers containing the 1- and the 2-adamantyl group respectively and of two dihydrobenzofurans (formed by the substitution of a chlorine atom followed by cyclization). The distribution between attack on the primary vs secondary position was 50 : 42. Others products were present in a lower amount. A first separation on a silica gel column (cyclohexane-EtOAc mixtures of increasing polarity as eluant), gave three main fractions thus subdivided: 80 of a mixture of alkylated Chl products (43%) containing some unreacted Chl, 48 mg of $ChlH_2$ (41%), 40 mg of 1-*N*-adamantylacetamide (43%). A further chromatographic separation (cyclohexane-EtOAc 9:1 as eluant) of the first fraction, gave with a sufficient purity 45 mg of a mixture of two isomers having the same molecular mass and identified as 2,3,5,6-tetrachloro-4-hydroxyphenyl 1-adamantyl ether (**16**) (10.4%) and 2,3,5,6-tetrachloro-4-hydroxyphenyl 2-adamantyl ether (**17**) (12.5%) as shown by the ^{13}C NMR signals positions and relative intensities. Two further fractions (total 31 mg) both containing two main products with the same molecular mass but in different proportion, were obtained.

The comparison between ^{1}H and ^{13}C NMR spectra of the separated fractions evidenced signals in good accordance with the structure of two isomeric dihydrobenzofurans. In particular the first fraction contained as the main product the dihydroadamantanobenzofuran (**18**)(8%), characterised by a methyne carbon at 92.66 ppm and a quaternary carbon at 46.16 ppm, and the latter one contained mainly the isomeric dihydroadamantanobenzofuran (**19**)(10.8%) identified by a methyne carbon at 56.58 ppm and a quaternary carbon at 89.90 ppm. Moreover the two ^{13}C spectra presented a similar aromatic carbons distribution and the aliphatic part was as expected for a 1,2-disubstituted adamantane derivatives (for isomer **19** a complete attribution of the aliphatic carbons was possible owing to its higher purity). All these compounds underwent partially hydrolisis on silica gel, so that they were partially lost during separation. Traces of two 4-(4-adamantyloxy-2,3,5,6-tetracholorophenoxy)-2,3,5-trichloroquinones were also present in the initial fraction, as revealed by mass spectroscopy(M$^+$ 588 m/e), even if their tiny amount excluded an unambiguous attribution of NMR signals.

16: ^{1}H NMR (in $CDCl_3$) δ 1.5-1.9 (*m*, 12H), 2.15 (*bs*, 3H), 5.9 (exch, OH). ^{13}C NMR (in $CDCl_3$) δ 31.47 (3CH), 35.78 (3CH_2), 42.99 (3CH_2), 88.60 (C-O-), 118.63, 127.20, 145.18 147.54. **17**: ^{1}H NMR (in $CDCl_3$) δ 1.55-1.7 (*m*, 6H), 1.8-1.9 (*m*, 4H), 2.25 (*m*, 2H), 2.42 (*m*, 2H), 4.15 ('*t*, J = 2 Hz, H-1), 5.9 (exch, OH). ^{13}C NMR (in $CDCl_3$) δ 26.93 (CH), 27.14 (CH), 31.59 (2CH_2), 32.93 (2CH), 36.75 (2CH_2), 37.23 (CH_2), 89.93 (CH-O-), 118.63, 127.20, 145.18, 147.54. Anal.Calcd for $C_{16}H_{16}Cl_4O_2$: C, 50.29; H, 4.22. Found C, 50.4; H,4.2. M$^+$380 m/e.

18: (in $CDCl_3$) In the proton spectrum the signal at 4.2 ppm corresponded to H-1, while all others signals were between 1.5 and 2.5 ppm. In the ^{13}C spectrum the signals at 92.66 ppm (CH-O-) and at 46.16 ppm certainly belonged to this dihydrobenzofuran, while an attribution of the others signal was impossible owing the complexity of the spectrum. **19**: In the proton spectrum the signal at 3.3 ppm corresponded to H-2 and the other protons laid between 1.5 and 2.5 ppm. ^{13}C NMR (in $CDCl_3$) δ 29.87 (CH), 30.25 (CH), 32.58 (CH_2), 33.27 (CH_2), 34.67 (CH_2), 35.95 (CH), 36.65 (CH_2), 41.20 (CH_2), 56.58 (CH), 89.90. The aromatic carbons were not unambiguously identified. M$^+$344 m/e.

Quantum Yield Determination. Quantum yields were determined on 3 mL of a MeCN solution of acceptor (0.002 M) in spectrophotometric cuvettes. After deaeration, these were irradiated by means of a focalized Osram 150-W high-pressure mercury arc fitted with an interference filter centered at 366 nm. The Chl consumption was determined through the UV absorption at 372 nm. A benzophenone-benzhydrol solution was used as an actinometer.

Flash Photolysis Measurements. The laser flash photolysis studies were carried out by using the third (355 nm) harmonic of a Q-switched Nd-YAG laser (Model HY 200 Laser Ltd Lumonics). The duration of the pulse was approximately 8 ns and its energy 30 to 90 mJ. The detection system consisted of a Laser kinetic spectrometer (Model K347 Applied Photophysics) and an oscilloscope(Tectronix Model 2467).

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