the previous acidic conditions (37%).[8]

(12) Reduction and other reactions of norbornen-7-one proceed similarly, although the reported stereospecificity is somewhat lower: R. S. Bly, C. M. Dubose, Jr., and G. B. Konizer, *J. Org. Chem.*, **33**, 2188 (1968), and references cited therein. From examination of models it would appear that the axial hydrogens at C(2) and C(4) provide effective additional hindrance to approach to the carbonyl group of **15** from that side of the molecule, and this may account for the greater stereoselectivity observed in the bicyclooctenone system.

(13) H. Krieger, *Suom. Kemistil. B*, **38**, 260 (1965).

(14) R. A. Appleton, J. C. Fairlee, R. McCrindle, and W. Parker, *J. Chem. Soc. C*, 1716 (1968).

(15) Assignment of this upfield signal to the anti proton at C(8) in **18** is required by the observed spectra of **16** and **17** taken with the fact that **12b** is known[8] to react under solvolysis conditions with retention of configuration. It is also in line with earlier assignments for the anti proton at C(7) in various norbornene epoxides: K. Tori, K. Kitahonoki, Y. Takano, H. Tanida, and T. Tsuji, *Tetrahedron Lett.*, 559 (1964); J. E. Franz, C. Osuch, and M. W. Dietrich, *J. Org. Chem.*, **29**, 2922 (1964); R. Huisgen, L. Moebius, G. Mueller, H. Stangl, G. Szeimies, and J. M. Vernon, *Chem. Ber.*, **98**, 3992 (1965). The only previous observations concerning bicyclo[3.2.1]oct-6-ene epoxides known to us are those of P. R. Jefferies, R. S. Rosich, and D. E. White [*Tetrahedron Lett.*, 1853 (1963)] on oxiranes derived from the diterpene alcohol beyerol and its esters. This was the original report that epoxides cause an upfield shift of suitably located nearby hydrogens, but in this work the unique upfield signal was attributed to the C(8) proton syn rather than anti to the epoxide ring. The subsequent results with norbornene epoxides cited above, along with our present findings with **16–18**, suggest that this original assignment by Jefferies et al. should be reversed.

(16) In contrast, reduction of **12b** with lithium aluminum deuteride in refluxing ether gave ~15% inversion and ~85% retention from similar analysis of the derived epoxide.

(17) H. C. Brown, "Organic Syntheses via Boranes", Wiley, New York, N.Y., 1975.

(18) A small amount (8%) of aldehyde **21** is also formed, but this is believed to arise from inverted conformer **2e**. See ref 3 for discussion.

(19) Such substitution also has an important effect in related ground state reactions: W. C. Agosta and S. Wolff, *J. Org. Chem.*, **40**, 1027 (1975).

(20) R. H. Shapiro, *Org. React.*, **23**, 405 (1976).

(21) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 1241 (1961).

(22) S. Wolff, W. L. Schreiber, A. B. Smith, III, and W. C. Agosta, *J. Am. Chem. Soc.*, **94**, 7797 (1972).

(23) H. O. House, "Modern Synthetic Reactions", 2nd ed, W. A. Benjamin, Menlo Park, Calif., 1972, pp 412–414, and references cited therein.

(24) Spectral assignments for these ketones are given by W. C. Agosta and S. Wolff, *J. Org. Chem.*, **40**, 1665 (1975).

(25) D. Y. Curtin and D. B. Kellom, *J. Am. Chem. Soc.*, **75**, 6011 (1953).

(26) P. J. Boddy and E. W. R. Steacie, *Can. J. Chem.*, **38**, 1576 (1976); J. H. Current and B. S. Rabinovitch, *J. Chem. Phys.*, **38**, 783 (1963).

(27) W. B. Hammond and T. S. Yeung, *Tetrahedron Lett.*, 1173 (1975), and references cited therein.

(28) Only a small steric effect is anticipated since $\Delta G°_{25}$, for *cis*- and *trans*-hydrindan is only ~0.3 kcal/mol and actually favors the trans isomer. For discussion and references see E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis", Wiley, New York, N.Y., 1965, pp 228–230.

(29) A. L. J. Beckwith and G. Phillipou, *Aust. J. Chem.*, **29**, 123 (1976); A. L. J. Beckwith, *Chem. Soc., Spec. Publ.*, **No. 24**, 239 (1970); J. W. Wilt in "Free Radicals", Vol. 1, J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, Chapter 8. These articles contain extensive references to earlier literature.

(30) P. Livant and R. G. Lawler, *J. Am. Chem. Soc.*, **98**, 6044 (1976).

(31) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis", Wiley, New York, N.Y., 1965, p 9, and references cited therein.

(32) C. H. Bushweller and W. G. Anderson, *Tetrahedron Lett.*, 1811 (1972).

(33) N. Ya. Buben, Yu. N. Molin, A. I. Pristupa, and V. N. Shamshev, *Dokl. Akad. Nauk SSSR*, **152**, 352 (1963); S. Ogawa and R. W. Fessenden, *J. Chem. Phys.*, **41**, 994 (1964).

(34) K. U. Ingold in "Free Radicals", Vol. 1, J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, Chapter 2.

(35) See, for example, P. D. Hobbs and P. D. Magnus, *J. Am. Chem. Soc.*, **98**, 4594 (1976).

(36) For a recent study of substituent effects that are interpreted as introducing barriers to conformational change in biradicals arising in a rather different kind of photochemical reaction see J. R. Scheffer, B. M. Jennings, and J. P. Louwerens, *J. Am. Chem. Soc.*, **98** (1976).

The Photochemistry of Chloroaromatic Compounds. Is "π-Chlorobenzene" an Intermediate?[1]

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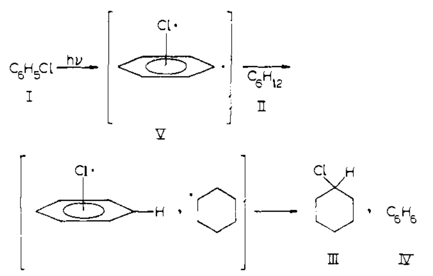
Abstract: In 1973 Lemal and co-workers[2a] reported that irradiation of dilute solutions of chlorobenzene in cyclohexane gave significant amounts of chlorocyclohexane (53%). To account for this unexpected observation they proposed a mechanism involving hydrogen abstraction from cyclohexane by a phenyl radical which is complexed with a chlorine atom ("π-chlorobenzene"). The cyclohexyl radical and the chlorine atom then couple in the solvent cage. We have reexamined this reaction and our results lead us to propose an alternative explanation. We present evidence that the chlorocyclohexane derives from the photosensitized addition of hydrogen chloride to cyclohexene and that the cyclohexene is formed by disproportionation of cyclohexyl radicals.

In 1973 Lemal and co-workers reported that irradiation of dilute solutions of chlorobenzene (I) in cyclohexane (II) gave chlorocyclohexane (III, 53%) as a major product.[2] They recognized that formation of this product could not simply be explained as the reaction of the phenyl and chlorine radical, which would result upon bond homolysis, since both the phenyl radical and the chlorine atom are relatively reactive radicals and would abstract hydrogen, predominantly from the solvent. Benzene was a major product but there was less than an equivalent amount of hydrogen chloride. To account for this unexpected result they proposed a mechanism, the key step of which was a hydrogen abstraction from cyclohexane by the phenyl radical moiety of a chlorine atom–phenyl radical complex (V, "π-chlorobenzene") giving a chlorine atom (complexed with benzene)-cyclohexyl radical pair in a solvent cage (Scheme I).

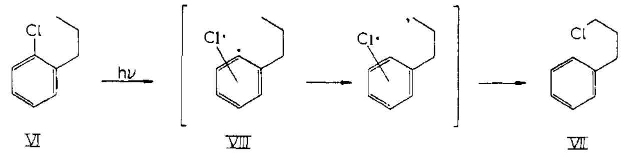
We were attracted to this area by the unusual nature of this suggested mechanism and particularly by the possibility that reactions involving this type of intermediate (V) might offer a synthetically useful procedure for functionalizing an unactivated, saturated, proximate alkyl position. For example, *o*-chloropropylbenzene (VI) would be expected to yield 3-chloropropylbenzene (VII) since the hydrogen abstraction from the terminal methyl group by the phenyl radical moiety is favored in a six-membered transition state as shown in Scheme II.

This type of intramolecular hydrogen abstraction has been observed by Beckwith and co-workers using electron spin resonance (ESR) techniques.[3] We recognized that this particular example puts a heavy demand upon the intramolecular reactivity of the intermediate VIII since the hydrogen being abstracted is attached to a terminal carbon (i.e., primary hy-

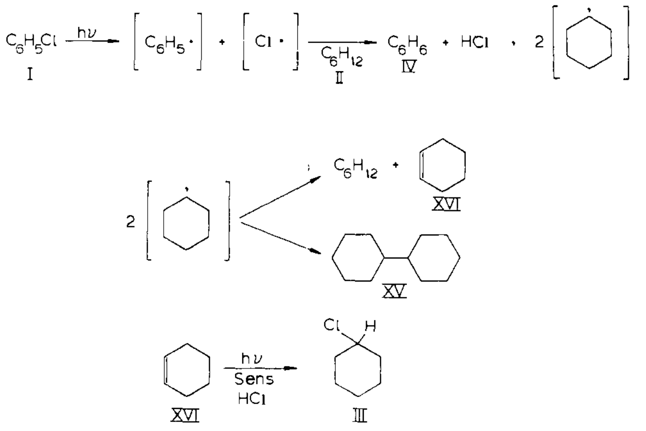
Scheme I



Scheme II



Scheme III



drogen), if the reaction were carried out in cyclohexane. Therefore, we use neopentane (IX) as solvent.

The irradiation of *o*-chloropropylbenzene (VI) in neopentane (IX) solution led to a complex mixture of products; the major products were *n*-propylbenzene (X) and hydrogen chloride. Most significant for the present discussion was the *absence* of a detectable amount of 3-chloropropylbenzene (VII), nor were the other side chain chlorinated propylbenzenes (i.e., 1-chloropropylbenzene (XI) or 2-chloropropylbenzene (XII)) significant products. Furthermore, neopentyl chloride (XIII) was only a minor (<5%) product. These results caused us to question Lemal's mechanism and in this paper we present evidence supporting a more traditional mechanism for chlorocyclohexane (III) formation; this is shown in Scheme III.

Results

The irradiation apparatus and procedure, described in detail in the Experimental Section, were similar to those used by previous workers.[2]

When a dilute solution of *o*-chloropropylbenzene (VI) in neopentane (IX) was irradiated, *n*-propylbenzene (X) was the major product; at least seven other products were also detected. From the known vapor phase chromatography (VPC) retention times of VII, XI, and XII, we concluded that little or none of these possible products were present. A small VPC peak in the region expected for neopentyl chloride (XIII) indicates that no more than 5% of this product was formed. A small amount of 2,2,5,5-tetramethylhexane (XIV) was also detected.

The reaction mixture was considerably less complex when cyclohexane (II) was the solvent. For example, in one run four major products were characterized: *n*-propylbenzene (X, 37%), chlorocyclohexane (III, 45%), bicyclohexyl (XV, 43%), and hydrogen chloride (34%). The VPC conditions used did not allow complete separation of cyclohexane (II) and cyclohexene (XVI); therefore, small amounts of this olefin may also have been present. No other volatile products were detected in significant amounts.

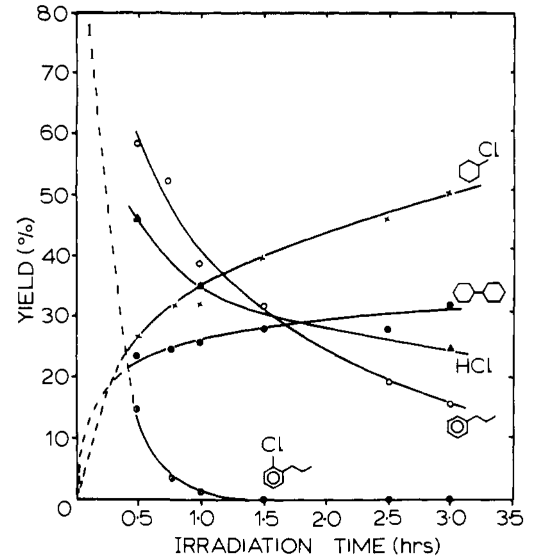


Figure 1. Product distribution of irradiated solution of *o*-chloropropylbenzene in cyclohexane vs. irradiation time.

We noticed that the product yields from the irradiation of VI in II varied considerably from run to run (see Experimental Section, Table I) and a series of experiments were carried out to determine the effect of extent of irradiation on the yields. The first analysis was on a sample after 0.5-h irradiation; 85% of the *o*-chloropropylbenzene (VI) was consumed, the yield of *n*-propylbenzene (X, 58%) was at a maximum value (73% of the aromatic moiety was accounted for at this point), chlorocyclohexane (III) was present to the extent of three-fifths of the ultimate yield (i.e., 50%), and the yield of hydrogen chloride was at a maximum value (46%) (90% of the initial chlorine content was accounted for). After 0.75-h irradiation, 97% of VI was consumed and III was two-thirds of the ultimate yield. After 1-h irradiation, consumption of VI was complete, III had attained three-quarters of the final yield, and hydrogen chloride had decreased to 35%. The yield of III continued to increase so that after 3-h irradiation the yield became 50%; however, the yield of X had decreased so that only 17% remained. The yield of bicyclohexyl (XV) remained constant after complete disappearance of VI (i.e., 30% after 1 h, 32% after 3-h irradiation). These results are summarized in Figure 1.

For reasons which will be discussed below, we also irradiated *o*-propylchlorobenzene (VI) in cyclohexane-d_{12}. The monodeuterated *n*-propylbenzene was isolated and nuclear magnetic resonance (NMR) and mass spectral evidence indicated that the deuterium was entirely in the phenyl position.

We next turned our attention to the system previously studied by Lemal and co-workers.[2] Irradiation of a dilute solution of chlorobenzene (I) in cyclohexane (II), until complete disappearance of I, gave four major products: benzene, chlorocyclohexane (III), hydrogen chloride, and bicyclohexyl (XV). This mixture of products is similar to that observed previously; however, the yield of bicyclohexyl (XV, 42%) was significantly higher than the published value.[4]

The product yields in this case also varied with irradiation time (Figure 2, Table II, and Experimental Section). If the irradiation was continued for 1 h after the complete disappearance of I, the hydrogen chloride yield decreased by one-third while the chlorocyclohexane (III) yield increased by one-quarter. The yield of benzene dropped with longer irradiation time. The yield of bicyclohexyl (XV), ca. 40%, remained essentially constant after complete disappearance of I.

When chlorobenzene (I) was irradiated in neopentane (IX) a complex mixture resulted. Among the products were benzene and a small amount of neopentyl chloride (XIII, ca. 5%).

To assess the importance of the hydrogen chloride for the formation of chlorocyclohexane (III) two tubes of dilute solution of I in II were irradiated simultaneously, one under constant argon bubbling and the other sealed in the usual way. The yield of bicyclohexyl (XV) obtained was approximately the same in both tubes; however, the yield of III dropped to one-half in the purged tube.

Lemal and co-workers considered the possibility that the chlorocyclohexane (III) arose from the addition of hydrogen chloride to cyclohexene (XVI). They rejected this possibility since, in their hands, triethylamine (XVII) failed to prevent its formation.[2a] We view the addition of XVII to the irradiation mixture as more than a minor perturbation, and consider that the mechanism may take a completely different course. In any event, contrary to Lemal's observation we found that from the irradiation of I and a slight excess of XVII in II, bicyclohexyl (XV) and triethylamine hydrochloride are formed, *but little or no III.*

To assess further the possibility that III can result from the addition of hydrogen chloride to cyclohexene (XVI) under the reaction conditions, we have irradiated both I and VI in II to which a tenfold excess of XVI was added. Both cases gave significantly higher yields of III and the hydrogen chloride assay dropped to zero.

Some experiments were carried out to obtain information about the mechanism for the addition of hydrogen chloride to XVI under these conditions. When a solution of XVI in II was kept in the dark and hydrogen chloride bubbled in, no reaction was observed; when this solution was irradiated, a trace of III was detected after 1 h. However, when benzene was added to the solution, a quantitative yield of III was obtained after 0.5 h of irradiation.

Discussion

Several of our results clearly negate Scheme I as the mechanism for the formation of chlorocyclohexane (III) upon irradiation of chlorobenzene (I) or *o*-chloropropylbenzene (VI) in cyclohexane (II). An alternative mechanism is outlined in Scheme III. Since our attention was initially attracted to this area by the synthetic possibilities implicit in Scheme I, and since a recent review[5] has called for "further amplification" of this mechanism, we will begin this section by summarizing these points of contradiction. We will then discuss the individual steps in Scheme III in more detail.

There is no apparent reason why Scheme I should be limited to the case in which cyclohexane (II) is the solvent; yet neopentyl chloride (XIII) is only a minor product upon irradiation of either I or VI in neopentane (IX) solution. Since the neopentyl radical cannot disproportionate, neopentyl chloride (XIII) cannot be formed by a mechanism analogous to Scheme III. The formation of the alkyl radical coupling product (2,2,5,5-tetramethylhexane, XIV) attests to the validity of the hydrogen abstraction step suggested in Scheme III. The small amount of XIII formed puts an upper limit on the involvement of Scheme I since this product can arise not only from Scheme I, but also by alkyl radical-chlorine atom coupling with and without cage effects. It is not yet possible to choose among these pathways for the formation of this minor product; however, it is clear that for the overall reaction, Scheme I is relatively unimportant.

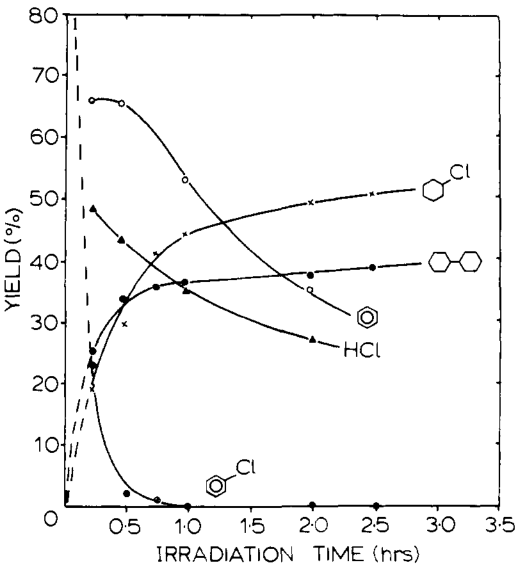


Figure 2. Product distribution of irradiated solution of chlorobenzene in cyclohexane vs. irradiation time.

The yield of III continues to increase, and the yield of hydrogen chloride decreases, after complete disappearance of I or VI. This is incompatible with Scheme I, where the yield of III should be directly related to the consumption of chloroaromatic. However, this result can easily be accommodated by Scheme III since the formation of III is a stepwise process.

The yield of III from the irradiation of I in II decreases when argon is bubbled through the solution to remove the hydrogen chloride. The concentration of hydrogen chloride should not affect the yield of III if Scheme I pertains.

The steps involved in Scheme III are (1) homolytic cleavage of the phenyl-chlorine bond upon irradiation; (2) hydrogen abstraction from the solvent by both the phenyl radical and the chlorine atom; (3) disproportionation and coupling of the cyclohexyl radical to give cyclohexene and cyclohexane, and bicyclohexyl; and, (4) photosensitized addition of hydrogen chloride to cyclohexene.

The first step is a well-established process for I and other aryl halides in nonnucleophilic solvents and in the gas phase. Flash photolysis studies allow direct evidence for formation of phenyl radicals upon gas phase irradiation of chlorobenzene (I).[6] The quantum yield for photodecomposition of I is fairly high ($\Phi = 0.4$ upon 253.7 nm excitation) under these conditions.[7] Irradiation of chloro-, bromo-, and iodobenzene in 2-propanol gives the halogen acid and benzene (70–80%).[8] A significant yield (>50%) of pinacol attests to the free-radical nature of this reaction.[9] The formation of biphenyl upon irradiation of I in IV is another indication of phenyl radical formation.[10]

The nature of the excited state involved in the homolytic cleavage has been the subject of some debate; the π,π^* singlet and triplet and the σ,σ^* triplet have all been considered.[7,10] An argument against the triplet, based on energetic considerations, has been advanced.[10] The lowest triplet may not have enough energy to overcome the carbon–chlorine bond strength (85.6 kcal mol^{-1}). The σ,σ^* triplet, however, is not the phosphorescent state and may in fact have sufficient energy. This state is repulsive between the phenyl moiety and the chlorine atom.[7]

From the yield of bicyclohexyl (XV) we know that enough cyclohexene (XVI) must have been produced to account for the yield of chlorocyclohexane (III). Since hydrogen chloride is produced in excess it is the cyclohexene (XVI), resulting from disproportionation of the cyclohexyl radical, which limits the yield of III.

Hydrogen atom abstraction from cyclohexane by the phenyl radical and the chlorine atom are well known, highly energetically favorable processes. The photolysis of diphenylmercury in cyclohexane gives phenyl radicals which abstract hydrogen from the solvent. The cyclohexyl radicals then disproportionate and couple. The ratio of disproportionation to coupling (k_d/k_c) was found to be 1.1 under these conditions.[11] The ratio of the yield of chlorocyclohexane (III) vs. bicyclohexyl (XV) (i.e., III/XV = ca. 1) is in good agreement with the observed value for disporportionation vs. coupling.

The last step in Scheme III is the photosensitized addition of hydrogen chloride to XVI. If XVI is added to the initial irradiation mixture the yield of III increases and the yield of hydrogen chloride drops to zero. We believe this to be a photosensitized reaction. No reaction took place when hydrogen chloride was bubbled through a solution of XVI and IV in II kept in the dark. When this mixture was irradiated, however, a quantitative yield of chlorocyclohexane (III) was rapidly formed. Furthermore, if benzene (IV) was omitted from this mixture a very much slower formation of III resulted. Presumably I and VI can also photosensitize this reaction. The photosensitized addition of alcohols to cyclohexene is a related reaction which has been studied in some detail.[12] The mechanism is believed to involve protonation of the strained *trans*-cyclohexene which is formed by photosensitized isomerization. It should also be noted that the cyclodimerization of cyclohexene, which occurs upon photosensitization in cyclohexane solution, is suppressed when hydrogen chloride is present. Similar behavior was observed when methanol and acidic methanol were the solvents.[12a]

An original objective of this work was to exploit the intramolecular hydrogen abstraction process possible with "π-chloro-*o*-propylbenzene" (VIII). Obviously, if Scheme II does not pertain, the lack of primary chloride from this irradiation is not unexpected. However, even with Scheme III, intramolecular hydrogen abstraction might occur; the resulting primary radical could abstract hydrogen from the solvent; this sequence might then go unnoticed.

Monodeuteriopropylbenzene was obtained when VI was irradiated in cyclohexane-d_{12}. Analysis of the NMR and mass spectra of this product indicated that the deuterium was entirely on the phenyl ring. Thus, intramolecular hydrogen abstraction from the primary position via a six-membered transition state is unable to compete with deuterium abstraction from cyclohexane-d_{12} solvent. The possibility of intramolecular hydrogen abstraction still exists for the case where neopentane (IX) was the solvent.

Beckwith and Gara have observed this intramolecular hydrogen abstraction.[3a] Reduction, with titanium(III) ion, of *o*-propylbenzenediazonium fluoroborate *in aqueous solution* gives the rearranged primary radical detected by ESR spectroscopy. These workers estimate the rate for the intramolecular hydrogen transfer to be greater than 10^2 s^{-1}, and also noted that this is not sufficiently rapid to compete effectively with some intermolecular reactions (e.g., reaction with ethanol and maleate ion).[3a] Our results support this view.

Lemal and co-workers reported that triethylamine (XVII) added to the irradiation mixture of I in II did not prevent chlorocyclohexane (III) formation. This is contrary to our experience. Triethylamine (XVII) suppressed formation of III; however, XV and triethylamine hydrochloride were formed. We are unable to provide an explanation for this inconsistency; in any event, it seems likely that in the presence of an amine the reaction becomes more complicated and may in fact involve a different mechanism.

The irradiation of I in triethylamine (XVII) solution has been reported.[13] The product is described as polymeric and no triethylanilinium chloride (XVIII) was found; however, it was noted that the quaternary salt was rapidly converted to tar upon irradiation and thus formation of triethylanilinium chloride could not be excluded. When irradiation was carried out in the presence of piperidine a large amount of polymer was formed but *N*-phenylpiperidine was isolated as a minor product. This example was one of many of a class of reactions the authors refer to as photonucleophilic substitution. Several mechanisms were considered for these reactions and, while the arguments against the homolytic cleavage were not compelling, the favored mechanism involves addition of the nucleophile to the carbon bearing the chlorine of the aromatic substrate in the σ,σ^* singlet excited state. The intermediate cyclohexadiene anion then aromatizes with loss of chloride ion. We saw no evidence for formation of XVIII upon irradiation of I and XVII in II.

Very different behavior is observed when this reaction is "photosensitized" by aromatic amines.[14] Irradiation of a methanolic, triethylamine solution of dimethylaniline and I gave triethylamine hydrochloride in quantitative yield, along with products indicative of phenyl radical formation: benzene, diphenyl, *o*- and *p*-dimethylaminodiphenyls. From photophysical and kinetic studies these authors conclude that the phenyl radical results from a cleavage of the chlorobenzene anion radical formed by electron transfer from the excited state of dimethylaniline to chlorobenzene (I).

Experimental Section

General. Irradiations were carried out using a GE 1-kW medium-pressure mercury arc lamp with a quartz jacket which was immersed in a constant temperature bath at 10 °C. Quartz ampules with a Teflon seal were usually placed ca. 3 cm from the jacket of the lamp. Degassing was carried out by either three cycles of freeze–thaw (residual pressure 2×10^{-3} mmHg) or by flushing with argon gas for 5 min. Both methods gave the same ratio of products. NMR spectra were obtained from a Varian T-60 spectrometer. Quantitative VPC analyses were done on a Pye Unicam series 104 chromatograph with a 10% SE-30 column or a 5% diisodecyl phthalate plus 10% Bentone column (specially for separating benzene from cyclohexane) by calibrating the flame ionization detector with standard solutions. Infrared spectra were obtained from a Beckman IR5A infrared spectrometer.

Materials. Cyclohexane (II), obtained from Anachemic, was treated with concentrated sulfuric acid and distilled over phosphorus pentoxide. Cyclohexene (XVI) obtained from BDH was passed through a column of alumina before use. Bicyclohexyl (XV) was obtained from Chemical Sample and chlorocyclohexane from Eastman Kodak Co. Chlorobenzene (I) from BDH was fractionated twice before use.

The three side-chain chloropropylbenzene isomers (VII, XI, XII) were synthesized by standard methods. Their spectral data are given below: 3-chloropropylbenzene (VII), NMR ($CDCl_3$) δ 2.2 (2 H, m), 2.8 (2 H, t), 3.5 (2 H, t), 7.2 ppm (5 H, s); 1-chloropropylbenzene (XI), NMR ($CDCl_3$) δ 1.0 (3 H, t), 2.1 (2 H, m), 4.8 (1 H, t), 7.3 ppm (5 H, s); 2-chloropropylbenzene (XII), NMR ($CDCl_3$) δ 1.5 (3 H, d), 3.0 (2 H, d), 4.2 (1 H, m), 7.2 ppm (5 H, s).

***o*-Chloropropylbenzene.** A nonspecific industrial synthesis of *o*-chloropropylbenzene (VI) has been described.[15] This compound was incorrectly cited from early literature in the "Dictionary of Organic Compounds".[16] A specific method of making *o*-chloropropylbenzene is described below. The Grignard reagent was prepared by slow addition of a solution of ethyl iodide (24.7 g, 0.16 mol) in 40 mL of dry ether to magnesium turnings (3.3 g, 0.14 mol) under a nitrogen atmosphere. After all the halide solution had been added, the reaction mixture was brought to reflux for about 15 min and then was cooled to 0 °C. The *o*-chlorobenzaldehyde solution (2.1 g, 0.15 mol) in 30 mL of dry ether was added slowly at reflux temperature. Reflux was continued for an additional 0.5 h after all the aldehyde had been added. The mixture was then quenched by 20% ammonim chloride solution and the product extracted with ether. The combined ether extracts were dried over anhydrous magnesium sulfate. The crude oil, after the solvent was removed, was purified by distillation (bp 68 °C at 0.9 mmHg) to yield 19 g (74%) of colorless liquid corresponding

Table I. Irradiation of *o*-Chloropropylbenzene Solution in Cyclohexane under Various Conditions[a]

Concn of the reaction mixtures[b]	Irradiation time, h	Unphotolyzed *o*-chloropropylbenzene	% yield of propylbenzene	% yield of chlorocyclohexane	% yield of bicyclohexyl	% yield of HCl
0.025 M	2.5	0	37	45	43	34
		0	23	43	40	34
0.025 M	0.5	15	58	27	23	46
	0.75	3	52	32	24	
	1	1		33	25	35
	1.5	0	32	40	27	
	2.5	0	19	47	29	
	3	0	17	50	32	25
0.025 M without cyclohexene	3	0	14	39	33	22
with 0.25 M[c] cyclohexene	3	0	77	72	20	4

[a] All yields are referred to the starting *o*-chloropropylbenzene. [b] All solutions were *o*-chloropropylbenzene in cyclohexane. [c] Some dimers of cyclohexene were found with VPC retention time close to that of bicyclohexyl.

Table II. Irradiation of Chlorobenzene Solution in Cyclohexane under Various Conditions[a]

Concn of the reaction mixtures[b]	Irradiation time, h	% of unphotolyzed chlorobenzene	% yield of benzene	% yield of chlorocyclohexane	% yield of bicyclohexyl	% yield of HCl
0.025 M PhCl	1	0	70	43	42	35
		0	71	36	34	26
		0	67	36	35	36
		0	67	32	34	34
		0	76	38	37	41
0.025 M PhCl	0.25	23	66	19	26	48
	0.5	2	66	30	33	43
	0.75	1		42	36	
	1	0	53	44	37	35
	2	0	37	50	38	27
	2.5	0		51	39	
0.025 M PhCl no argon bubbling	1	0		42	55	
0.025 M PhCl with argon bubbling	1	0		21	54	
0.025 M PhCl no cyclohexene	2	0		31	40	23
0.025 M PhCl and 0.25 M cyclohexene[c]	2	5		48	20	0
0.025 M with 0.038 M triethylamine[d]	3	40		<1	21	

[a] All yields are referred to the starting chlorobenzene. [b] All reactions were done in cyclohexane solution. [c] Rate of destruction of PhCl was slower and dimers of cyclohexene were found with VPC retention times close to that of bicyclohexyl. [d] Triethylamine hydrochloride precipitated.

to 1-(*o*-chlorophenyl)-1-propanol. Dry ether (30 mL) was added slowly stirring to 16.4 g (0.12 mol) of aluminum chloride to give a greenish solution. Lithium aluminum hydride (2.7 g, 0.07 mol) was then added in small portions. The 1-(*o*-chlorophenyl)-1-propanol solution (6 g, 0.035 mol in 20 mL of dry ether) was added slowly to this mixture and the reaction mixture was refluxed for 24 h. Methyl acetate (10%) in ether was added to decompose the excess hydride complex. A saturated solution (25 mL) of sodium potassium tartrate was added. The mixture was then extracted with ether and dried over anhydrous magnesium sulfate and the solvent evaporated to give a pale yellow liquid (2.7 g, 47%). The crude product was purified by distillation under reduced pressure. Further purification by distillation, using a small spinning-band column, gave VI (bp 58 °C at 10 mmHg) (VPC pure): NMR ($CDCl_3$) δ 0.97 (3 H, t), 1.7 (2 H, m), 2.7 (2 H, t), 7.1 ppm (4 H, m); IR (neat) ν_{max} 2690, 1430, 1400, 1060, 1040, 1020, 743, 675 cm^{-1}.

Anal. Calcd for $C_9H_{11}Cl$: C, 69.90; H, 7.17; Cl, 22.92. Found: C, 69.90; H, 7.15; Cl, 22.79.

Irradiation of *o*-Chloropropylbenzene in Neopentane. *o*-Chloropropylbenzene (VI, 22 mg) in 2.0 g of neopentane (IX) was degassed and irradiated for 2 h so that almost all *o*-chloropropylbenzene (VI) had disappeared. The total reaction mixture was then dissolved in toluene and quantitative analysis of the products was carried out by VPC. The same conditions were used for irradiation of chlorobenzene solution. In both cases, products with long retention times were formed, but no product with retention time close to any one of the chloropropylbenzene isomers (VII, XI, XII).

Irradiation of *o*-Chloropropylbenzene in Cyclohexane. Several irradiations were carried out under various conditions. These are summarized in Table I.

o-Chloropropylbenzene (VI) in cyclohexane (II) (5 mL of 0.025 M) was degassed and irradiated for 2.5 h. Sodium acetate–acetic acid buffer (10 mL of 0.6 M 1:1) was used to extract hydrogen chloride for potentiometric titration. The organic products were separated by VPC and characterized by IR and NMR spectra.

Flushing of Argon Gas through Solution Being Irradiated. Chlorobenzene (I) in cyclohexane (II) (5 mL, 0.025 M) was irradiated while argon gas bubbled constantly through the solution. Yields of products analysed by VPC are summarized in Table I.

Trapping of Hydrogen Chloride from Photolysis with Cyclohexene. Both 0.025 M solutions of chlorobenzene and *o*-chloropropylbenzene (VI) in the presence of 0.25 M cyclohexene (XVI) in cyclohexane (II) were irradiated for 3 h. Products were analyzed as before and are listed in Tables I and II.

Photoaddition of Hydrogen Chloride to Cyclohexene. A dark reaction was carried out on a solution of cyclohexene (XVI) in cyclohexane (II) (0.12 M) degassed by flushing of argon gas and then hydrogen chloride gas was bubbled through the solution for 5 min. This solution was sealed with a rubber serum cap and kept in the dark at room temperature for 4 h. Analysis by VPC indicated that no reaction had occurred. Irradiation for 1 h of a 0.06 M solution of cyclohexene (XVI) in cyclohexane (II) after degassing and bubbling hydrogen chloride gave a very small amount of chlorocyclohexane (III) detected by VPC. The above solution after 0.5-h irradiation in the presence of 0.08 M benzene (IV) gave almost quantitative yield of chlorocyclohexane.

Irradiation of Chlorobenzene in Cyclohexane in the Presence of Triethylamine. A solution (5 mL, 0.025 M) of chlorobenzene (**I**) and 0.038 M triethylamine (**XVII**) in cyclohexane (**II**) was irradiated for 3 h after degassing. The reaction mixture consisted of a colorless liquid and a white precipitate. This precipitate was found to be the hydrochloride of triethylamine (NMR, D_2O). The solution analyzed by VPC showed consumption of chlorobenzene (60%), little or no chlorocyclohexane (**III**), but a significant amount of bicyclohexyl (**XV**, 21%).

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Flow Nuclear Magnetic Resonance Investigation of the Intermediates Formed during the Bromination of Phenols in Acetic Acid[1]

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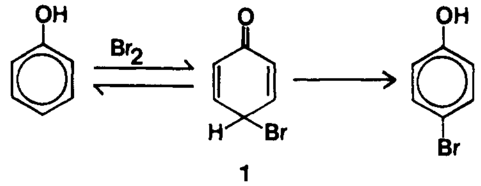
Abstract: High-resolution flow nuclear magnetic resonance spectroscopy has been used to detect and to characterize the 2,5-cyclohexadienone intermediates formed from the reaction of 2,6-disubstituted phenols ($R_1 = R_2 = t$-Bu; $R_1 = R_2 = sec$-Bu; $R_1 = R_2 = i$-Pr; $R_1 = CH_3$, $R_2 = t$-Bu; $R_1 = R_2 = CH_3$; $R_1 = H$, $R_2 = t$-Bu) with bromine in aqueous acetic acid solution. The lifetimes of these intermediates have been measured as a function of both temperature and acetic acid concentration and the results are compared with literature data on the reaction.

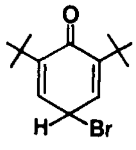
Originally, the characterization of intermediates depended on their isolation from the reaction mixture. The advent of spectroscopic techniques has since made possible the investigation of such species "in situ" and the development of flow and stopped-flow techniques employing UV-visible spectroscopy has made possible the investigation of very short-lived species. Although high-resolution nuclear magnetic resonance spectroscopy has become one of the most successful methods for the determination of organic structures, until very recently it has not been used in flow or stopped-flow methods. We have developed in our laboratory equipment and techniques for the measurement of high-resolution NMR spectra of flowing chemically reacting systems. The apparatus[2,3] and its application to the investigation of transient species[2,4-6] and effects[7] have been described. The main disadvantage of the flowing system compared to stopped-flow methods[8-11] is the relatively large quantity of material required, but it makes possible the measurement of spectra whose peak intensities are reliable, of transient species with half-lives which can be as short as 100 ms, and thus makes possible their identification. The purpose of the present work was to apply these techniques to the investigation of the transient intermediate species that are postulated to be formed during the electrophilic bromination of phenols with bromine in aqueous acetic acid solution.

The proposed mechanism[12] for this reaction involves the formation of a dienone intermediate **1** (eq 1).



1

Considerable support for the intermediacy of species of this general type in the reaction comes from the work of Ershov and Vold'kin[13] and subsequently De la Mare and co-workers,[14] who were able to isolate the corresponding species (4-bromo-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one, **2**) from the action of



2

bromine on 2,6-di-*tert*-butylphenol in acetic acid solution. Similar species have been detected during the reaction of bromine with 3,5-dibromo-4-hydroxybenzenesulfonate,[15] 3,5-dibromo-4-hydroxybenzoic acid,[16] and 4-R-2,6-di-*tert*-butylphenols.[17]