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STERIC AND COMPLEXATION FACTORS IN HYDROGEN ABSTRACTION FROM 1-PHENYLALKANES AND α, ω-DIPHENYLALKANES

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Abstract—As part of a systematic study of steric effects, 1-phenylalkanes and α, ω-diphenylalkanes were reacted at 70° with bromine atoms and trichloromethyl radicals. Exclusive benzylic bromination occurred in all cases. The 1-phenylalkanes reacted with both abstracting agents with rates which were largely independent of substrate. Intermolecular steric interactions must be negligible. In reaction with bromine atoms the α, ω-diphenylalkanes behaved in similar fashion. With trichloromethyl radicals, however, strong rate dependence with structure was observed. A maximum rate was found for 1,6-diphenylhexane. This is felt to be the result of intramolecular transfer of a complexed radical to the reaction site.

THE role of possible intermolecular steric interactions in the course of free-radical hydrogen abstraction has recently attracted some attention. Minisci *et al.* have commented on the preference for hydrogen abstraction to occur in the penultimate position of heptane.[1] Although the three possible secondary radicals formed from this hydrocarbon should be nearly electronically equivalent, the 2 position is most sterically accessible. These same workers showed an increased tendency for reaction to occur in this position as the size of the attacking species was increased. The observation that allylic bromination reactions often involve exclusive hydrogen abstraction from the least hindered among possible sites has also been documented.[2] Experiments conducted within this laboratory have been concerned with the use of substituent dependences as a measure of possible intermolecular interactions. Prior work has established that bromine atoms are slightly more selective than trichloromethyl radicals in abstracting hydrogens from relatively unhindered positions such as are encountered in substituted toluenes[3, 4] ethylbenzenes,[5, 6] allylbenzenes,[7] and adamantanes.[8, 19] It was shown, however, that the more bulky trichloromethyl radical had the greater selectivity for the abstraction of benzylic hydrogen atoms from certain tertiary positions[10] and hindered secondary positions.[11] The latter of these studies involved a series of neopentylbenzenes. Steric hindrance was provided by a large tertiary group attached to the benzylic position. While other workers have shown that introduction of moderately sized groups introduce no steric control in this reaction,[12] it was felt that a systematic study of the effect of increasing the chain length of alkyl substituents would be of value. With this view, relative rates of hydrogen abstraction from series of 1-phenylalkanes (**1**) and α,ω-diphenylalkanes (**2**) were obtained.

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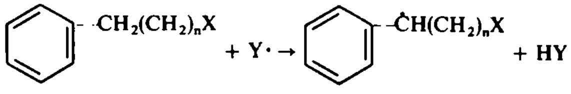
RESULTS AND DISCUSSION

The rate determining step of all these reactions is shown below.



1 : X = H
2 : X = Ph
n = 1 − 9

The abstracting agents were bromine atoms and trichloromethyl radicals generated photolytically from N-bromosuccinimide and bromotrichloromethane at 70° respectively. Results were obtained in replicate using GLC analyses of mixtures.

TABLE 1. BENZYLIC HYDROGEN ABSTRACTION FROM 1-PHENYLALKANES BY BROMINE ATOMS AND TRICHLOROMETHYL RADICALS AT 70°

 $CH_2(CH_2)_nH$	k_n/k_1	
n	Br·	·CCl_3
1	1·00	1·00
2	0·87 ± 0·04	0·85 ± 0·03
3	0·76 ± 0·02	0·73 ± 0·05
4	0·85 ± 0·05	0·67 ± 0·04
5	0·76 ± 0·05	0·70 ± 0·04
6	0·83 ± 0·04	0·64 ± 0·01
7	0·76 ± 0·04	0·73 ± 0·01
8	0·70 ± 0·03	0·67 ± 0·01
9	0·78 ± 0·05	0·70 ± 0·04

Table 1 presents the relative rate data for hydrogen abstraction from series 1. As an extra methylene unit is introduced into the side chain of ethylbenzene, the ease of hydrogen abstraction decreases. This may be regarded as a consequence of increased hindrance at the reaction site due to the presence of an alpha Et group rather than a Me group. A less likely explanation could involve a possible lessened radical stabilizing ability in the former case.* Addition of a second methylene unit causes a similar small decrease, however, further chain elongation does not seem to produce additional effects. Indeed, for compounds with n values of three to nine, nearly consistent average relative rate values of 0·78 ± 0·03 and 0·70 ± 0·3 are found for bromine atom and trichloromethyl radical respectively. This indicates a decreasing contribution from methylene moieties as the character of the side chain becomes constant. More importantly, however, is the lack of any large selectivity shown by the trichloromethyl radical. It must be concluded that simple n-alkyl groups have negligible steric hindrance associated with them in this particular reaction.

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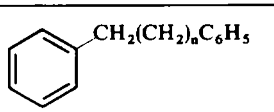
* While Et has usually been considered more electron donating than Me, conflicting views based on hyperconjugation, are possible.

In view of the above findings, certain predictions might be ventured concerning series 2. In the reference compound, bibenzyl, the second Ph group is in closest proximity to the reaction site. This will not only introduce possible steric retardation, but, will also tend to decrease the ease of radical formation due to unfavorable electron withdrawing characteristics.[13] It would, therefore, be expected that the introduction of additional groups would lead to an increased lability of the benzylic hydrogens as the large electron withdrawing group is removed from the region of the reaction site. As in the former case some more or less constant value of relative rate might be expected. The experimental results are shown in Table 2.

TABLE 2. BENZYLIC HYDROGEN ABSTRACTION FROM α, ω-DIPHENYLALKANES BY BROMINE ATOMS AND TRICHLOROMETHYL RADICALS AT 70°

	k_n/k_1	
n	Br·	·CCl$_3$
1	1·00	1·00
2	1·48 ± 0·06	2·01 ± 0·11
3	1·64 ± 0·08	2·40 ± 0·14
4	1·35 ± 0·07	2·51 ± 0·25
5	1·55 ± 0·08	3·17 ± 0·16
6	1·46 ± 0·09	2·89 ± 0·10
7	1·35 ± 0·11	2·60 ± 0·14
8	1·37 ± 0·07	2·19 ± 0·11
9	1·61 ± 0·06	2·40 ± 0·12

It can be seen that the above "prediction" is essentially correct in the case of abstraction by the bromine atom. All of the compounds from 1,3-diphenylpropane to 1,10-diphenyldecane react some fifty per cent faster than bibenzyl. As in the case of hydrogen abstraction from 1-phenylalkanes a common relative rate term is soon achieved. Thus, it is found that an average value of 1·48 ± 0·09 exists for these eight compounds.

The situation which is encountered in the reaction of this same series of compounds with the trichloromethyl radical is markedly different from the above. Firstly, it is observed that the relative rate factors are all greater than found for bromine. This, of course, can be directly attributed to those steric factors previously discussed. Certainly, the steric environment in bibenzyl must be sufficiently crowded to cause slow reaction with the large trichloromethyl radical. Secondly, it is noted that no apparent common relative rate term is approached. Indeed, there is a steady rate increase through 1,6-diphenylhexane followed by an equally steady decrease through 1,9-diphenylnonane.

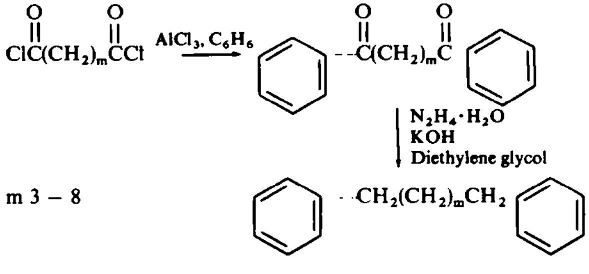
In light of the bromine results, it is inconceivable that this reflects a dampening of either electronic or steric factors. The rate maximum for 1,6-diphenylhexane also is not due to simple statistical uncertainty. The average relative rate for the compounds in which n is two to nine is 2·52 ± 0·27. Even allowing for the large experimental uncertainty, 1,6-diphenylhexane is not within this range.

It is felt that a possible example of the intramolecular transfer of a complexed radical is being observed. Russell originally showed that selectivity in hydrogen atom abstractions could be increased by carrying out the reaction in a complexing solvent.[14] These solvent effects are now known to be operative in other free-radical reactions as well.[15] The addition of the trichloromethyl radical to ω-phenyl-1-alkenes and ω-phenyl-2-methyl-2-alkenes has been investigated.[16] It was observed that the value for the relative rate of addition was strongly dependent on the number of intervening methylene groups between the olefin and aromatic moieties. Taken in conjunction with other experiments,[17] it was felt that the reaction involved an initial complexation of the trichloromethyl radical with the benzene ring followed by an *intramolecular* transfer of the radical to the olefinic side-chain. It is now proposed that the present hydrogen abstraction reaction proceeds analogously.

The possibility of this type of reaction has been invoked before.[18] In the photochlorination of n-butylbenzene Russell *et al.* tried to assess the importance of such a mechanism. By examining the relative amounts of 2-chloro-1-phenylbutane and 3-chloro-1-phenylbutane as a function of dilution, it was felt that evidence for this mechanism could be obtained. Their results were essentially negative. The ratio of these two products was constant, leading them to suggest that either no intramolecular transfer was occurring or that it occurred indiscriminately to all positions in the side-chain. The following reasons are offered as to why this was not the optimum system in which to observe this mechanism. Chlorine is a very reactive abstracting agent. The two reaction sites are in different electronic environment. Reaction is mostly taking place in neither of these positions, but, at the benzylic site. It is quite possible that a longer chain length between aromatic moiety and reaction site is necessary. The present trichloromethyl radical-α,ω-diphenylalkane system satisfies these criteria.

EXPERIMENTAL

Materials. All the compounds of series 1 were commercially available. Also purchased were N-bromosuccinimide, bromotrichloromethane, *o*-dichlorobenzene, CCl_4 and bibenzyl. The majority of the compounds in series 2 was prepared by the following sequence:



Acylations were based on standard techniques. The Huang–Minlon modification of the Wolf–Kishner reaction was used for reduction.[19]

1,3-Diphenylpropane was prepared by the Clemenson reduction of 1,3-diphenylacetone.

1,4-Diphenylbutane was prepared by the Wolf-Kishner reduction of the product obtained from the reaction of 3-phenylpropyl magnesium bromide with benzonitrile.

All compounds were purified before use. GLC showed in excess of 99% purity for all materials. M.ps, b.ps and RI's compared with literature values. In the case of a not fully characterized reported compound, 1,7-diphenylheptane, the following properties were found, b.p. 133–135 at 0·01 mm, n_D^{21} 1·5351.(Calc. for $C_{19}H_{24}$: C, 90·42: H, 9·58. Found: C, 90·42: H, 9·48%).

Product studies. Several product studies were carried out for all four possible reaction types. NMR spectra of mixtures showed only benzylic bromination to have occurred. Independent measurements indicate that as little as five mole-per cent of non-benzylic bromide could be detected in our reaction mixtures by nmr. Material balances were satisfactory as illustrated by the following example. A mixture of 4·731 g of 1-phenylhexane (29·152 mmoles) and 35·42 g of bromotrichloromethane (178·61 mmoles) were reacted under nitrogen for four hr at 70° with irradiation by our standard source. The excess bromotrichloromethane was removed by distillation. Further distillation yielded 1·946 g of the original starting material (11·993 mmoles) and 3·896 g of a second component, which was identified as 1-bromo-1-phenylhexane, (16·152 mmoles). The bromination product showed the expected NMR spectrum. The following properties were also noted: b.p. 59–60°/0·04 mm, n_D^{22} 1·5280. (Calc. for $C_{12}H_{17}Br$: C, 59·75; H, 7·12; Br, 33·13. Found: C, 59·90; H, 7·20; Br, 32·85%). Material balance was 96·55%. The product of this reaction was independently prepared by reaction of PhMgBr with hexanal followed with treatment of the alcohol formed by PBr_3. The compound formed by this process showed identical spectroscopic and chromatographic properties to that obtained from the reaction mixture, b.p. 75–76°/0·18 mm, n_D^{22} 1·5293. No evidence for the formation of dibrominated products was found.

Procedure for kinetic runs using bromotrichloromethane. Solutions of two hydrocarbons, *o*-dichlorobenzene, and bromotrichloromethane were prepared in the approximate molar ratios 1:1:1:25. Approximately 0·75 ml. of the solution was placed in each of several pyrex ampoules. The ampoules were cooled to dry ice-acetone temperature, evacuated, filled with N_2 at a reduced pressure and sealed. One ampoule was reserved for analysis of starting materials; the remainder were placed horizontally just below the surface of a mineral oil constant temperature bath maintained at 70·0 ± 0·5°. The samples were irradiated with ultraviolet light provided by a Sylvania 275-W sun lamp placed 20 cm. above the surface of the oil. Reaction times varied from two to six hr, by which time 30% to 70% of the total hydrocarbons had reacted. The ampoules were then cooled and opened. Analysis of the mixtures, both before and after reaction, was carried out *via* gas-liquid partition chromatography on a ten foot, 5%, S.E. 30 on chromosorb G, column.

All determinations were run in replicate. Most compounds were competed directly against the lowest member of the same series. In certain cases, however, to insure maximum separation, reference compounds other than bibenzyl or ethylbenzene were used. Thus, in series 1 it was necessary to compete 1-phenylpropane against 1-phenylnonane due to the similarity of its retention time with that of ethylbenzene. It was also necessary to compete 1-phenylpentane and 1-phenylhexane against 1-phenylnonane to avoid the peaks for these compounds eluting with that of the product of ethylbenzene 1-bromo-1-phenylethane. In series 2,1,4-diphenylbutane was run against 1,10-diphenyldecane to avoid possible contamination with 1-bromo-1,2-diphenylethane. The relative rate constants obtained in these experiments could easily be converted into the data reported in Tables 1 and 2.

The brominated hydrocarbons formed in these reactions were only moderately stable under the analytical conditions employed. Extensive tailing was observed and very small amounts of decomposition products noted. In certain cases these decomposition products (most likely olefins) had retention times which did not interfere with the analysis of the starting hydrocarbon. At other times, however, the decomposition products eluted with starting material. Consideration of the per cent of bromide decomposition under chromatographic conditions leads to the conclusion that no more than five per cent error was thus introduced.

Procedure for kinetic runs using N*-bromosuccinimide.* The procedure was identical to that described above except that the solid N-bromosuccinimide was first introduced into the ampoule, followed by a solution of the two hydrocarbons and *o*-dichlorobenzene in CCl_4. The two hydrocarbons, *o*-di-chlorobenzene and N-bromosuccinimide were in the approximate molar ratio of 1:1:1:1. CCl_4 was present in ten-fold excess of any other reagent. Reaction times, extent of reaction, and all analytical details were analogous to those using bromotrichloromethane as the radical source.

Determination of k_n/k_1. The kinetic expressions for determination of these relative rates constants have been previously reported.[10] No changes in those expressions were made.

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