Steric Effects in Hydrogen Atom Abstractions[1]

William D. Totherow[2a] **and Gerald Jay Gleicher**[2b]

Contribution from the Department of Chemistry, Oregon State University, Corvallis, Oregon 97331. *Received July 14, 1969*

Abstract: The reaction of a series of substituted neopentylbenzenes with trichloromethyl radicals and bromine atoms has been carried out at 70.0°. Utilizing the Hammett equation a ρ value of -0.74 is obtained for hydrogen abstraction by the bromine atom. This result is not unexpected and is in keeping with the normal substituent dependence for abstraction at a secondary benzylic position. However, the ρ value for the trichloromethyl radical (-0.94) is much larger than would be expected from electronic effects alone. An explanation in terms of specific nonbonded interactions associated with the trichloromethyl radical is offered.

The study of free-radical benzylic hydrogen abstractions from series of substituted alkylbenzenes has been pursued with much vigor. The use of rather selective abstracting agents has shown that the electron-donating substituents greatly favor the reaction. Correlation by various forms of linear free-energy relationships has been possible in most cases. It had also been observed that as alkyl substituents are introduced at the benzylic carbon of toluene the ρ value of the reaction decreases in absolute magnitude. Use of the trichloromethyl radical from bromotrichloromethane as the abstracting agent yields a ρ value of -1.46 for substituted toluenes,[3] but values of only -0.63 for substituted allylbenzenes[4] and -0.53 for substituted ethylbenzenes.[5] Similar results are found if bromine atoms generated from N-bromosuccinimide are the abstracting species. A ρ value of -1.39 is found for the toluenes[6] while the allylbenzenes and ethylbenzenes have respective values of -0.76[4] and -0.69.[7] These results are in keeping with the expectation that electron-donating groups at the reaction site should stabilize the transition state and decrease any substituent effect for the series. In order to extend this observation to tertiary benzylic positions, a series of substituted cumenes was treated with the aforementioned radicals.[8] The ρ value for hydrogen abstraction by bromine atom was -0.38. The corresponding value for the trichloromethyl radical, however, was a surprising -0.67. This is not only greater selectivity than is shown by the bromine atom, but, is greater than that found for examples of secondary benzylic hydrogen abstraction given above.

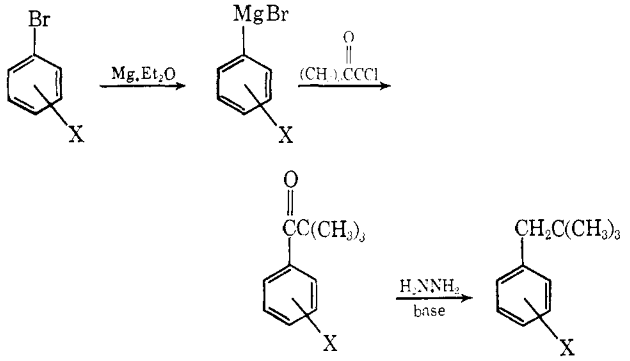
It was felt that the explanation for this result lay in possible unfavorable interactions in the transition state between the alkyl groups at the benzylic positions and the attacking radical. Such destabilization might easily increase the substituent dependence for the reaction. Other workers have also noted instances of radical selectivity increasing in reactions at hindered sites. Minisci and coworkers have found that the selectivity of dialkylamino abstraction increases as the size of the alkyl group becomes larger.[9] Radical bromination of 2,4,4-trimethyl-1-pentene involves hydrogen abstraction at the unhindered primary allylic position rather than at the hindered secondary allylic position despite the inherently greater reactivity of the latter site.[10]

In order to test this hypothesis, it was decided to study the hydrogen abstractions from a series of neopentylbenzenes. Should steric factors be of importance in hydrogen abstractions, the substitution of a *t*-butyl group for the α-methyl group of the ethylbenzenes will lead to a change in substituent dependence.

Results and Discussion

With the exception of *p*-nitroneopentylbenzene, all of the members of this series of compounds were prepared by the procedure in Scheme I. The *p*-nitroneopentylbenzene utilized was obtained by direct nitration of the parent compound.[11] The physical properties of all compounds are shown in Table I.

Scheme I



Reaction of neopentylbenzene with N-bromosuccinimide has been shown to yield α-bromoneopentylbenzene.[12] This was the sole product obtained in this study, not only for this reaction, but also for the corresponding reaction with bromotrichloromethane. With the exception of the methyl derivatives, each of the ring-substituted neopentylbenzenes also produced but a single compound. In the case of *p*-chloroneopentylbenzene this compound was shown to be *p*-chloro-α-bromoneopentylbenzene.

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[2] (a) Taken in part from the M.S. Thesis of William D. Totherow; (b) Alfred P. Sloan Fellow (1969–1971). To whom inquiries should be addressed.

[3] E. S. Huyser, *J. Am. Chem. Soc.*, **82**, 394 (1960).

[4] M. M. Martin and G. J. Gleicher, *J. Org. Chem.*, 28, 3266 (1963).

[5] K. H. Lee, private communication.

[6] C. Walling, A. L. Rieger, and D. D. Tanner, *J. Am. Chem. Soc.*, **85**, 3129 (1963).

[7] R. L. Huang and K. H. Lee, *J. Chem. Soc., C*, 935 (1966).

[8] G. J. Gleicher, *J. Org. Chem.*, 33, 332 (1968).

[9] R. Bernardi, R. Galli and F. Minisci, *J. Chem. Soc., B*, 324 (1968).

[10] K. Ziegler, A. Speata, E. Schaaf, W. Schumann, and E. Winkelmann, *Ann.*, **551**, 80 (1942).

[11] D. F. Gurka and W. M. Schubert, *J. Org. Chem.*, **31**, 3146 (1966).

[12] H. Meislich, J. Costanza, and J. Streilitz, *ibid.*, 3221 (1968).

Table I. Physical Properties of *meta*- and *para*-Substituted Neopentylbenzenes

X	Bp, °C (mm)	$n^{23}D$	Formula	Calcd, % C	Calcd, % H	Calcd, % Other	Found, % C	Found, % H	Found, % Other
H	73–73.5 (22)[a]	1.4868[a]	$C_{11}H_{26}$						
p-CH_3	66–67 (3.3)	1.4879	$C_{12}H_{18}$	88.89	11.11		88.85	11.14	
m-CH_3	64–65 (3.2)	1.4878	$C_{12}H_{18}$	88.89	11.11		88.80	11.00	
p-*t*-C_4H_9	45–46 (0.14)	1.4888	$C_{15}H_{24}$	88.23	11.77		88.08	11.68	
p-CH_3O	49–50 (0.30)	1.4991	$C_{12}H_{18}O$	80.90	10.12		80.74	10.18	
p-Cl	87–89 (9.0)	1.5038[b]	$C_{11}H_{15}Cl$						
m-Cl	63.5–65 (1.7)	1.5042	$C_{11}H_{15}Cl$	72.33	8.22	19.45	72.16	8.23	19.29
m-CF_3	55–55.3 (3.0)	1.4391	$C_{12}H_{15}F_3$	66.67	6.94	26.39	66.51	6.84	26.24
p-NO_2	94–95 (0.43)[c]	1.5247	$C_{11}H_{15}NO_2$						

[a] Lit.[12] bp 185.0–185.5°, $n^{20}D$ 1.4888. [b] Lit.[11] $n^{26}D$ 1.5033. [c] Lit.[11] mp 29°.

Table II. Relative Rates of Reaction between Toluene and Neopentylbenzenes for Radicals at 70°

	Radical Br·	Radical ·CCl_3
$k[C_6H_5CH_2C(CH_3)_3]/k[C_6H_5CH_3]$	0.45 ± 0.02	0.27 ± 0.09
% reaction at $CH_2C(CH_3)_3$ position	31.4	21.3

Gas–liquid partition chromatography (glpc) indicated that two products were produced from each of the methylneopentylbenzenes. It is obvious that hydrogen abstraction may occur at either of the nonequivalent benzylic positions. In order to estimate the relative lability of the two types of hydrogen, competitive experiments were run between neopentylbenzene and toluene for the abstracting species. The results are presented in Table II. These correction factors were used to determine that portion of methylneopentylbenzene which disappeared by reaction at the secondary benzylic position. This comparative technique has been frequently employed in studies on free-radical hydrogen abstractions.[13] It was felt that further corroboration of these factors might be obtained. Although the isomeric products arising from the bromination of *m*-methylneopentylbenzene could not be separated, the total product fraction could be collected by glpc. An nmr spectrum of this sample showed two upfield singlets attributable to the *t*-butyl groups in the products. The larger had a chemical shift of δ 0.88. As this was also the value for the *t*-butyl group in the starting material, this product must arise from bromination of the primary benzylic position. The smaller *t*-butyl peak had a chemical shift of δ 1.05. The downfield shift of δ 0.17 units appears reasonable for a compound which has undergone bromination in a position adjacent to the absorbing protons.[14] The areas of these two peaks correspond to 23.0% reaction at the secondary benzylic position if bromine atom is the abstracting species and 19.2% if the trichloromethyl group is the abstracting agent. It is felt that the agreement between the two sets of results is reasonable.

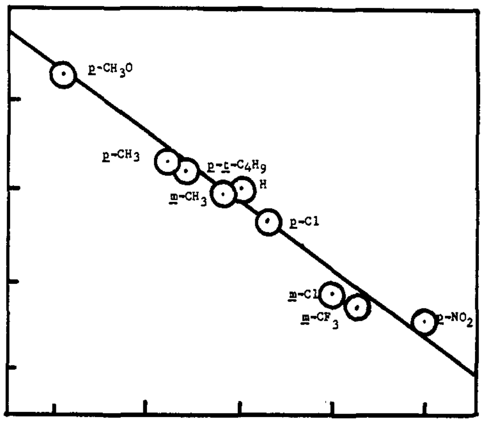

Figure 1. Relative rates of hydrogen abstraction by bromine atoms from substituted neopentylbenzenes *vs.* σ^+.

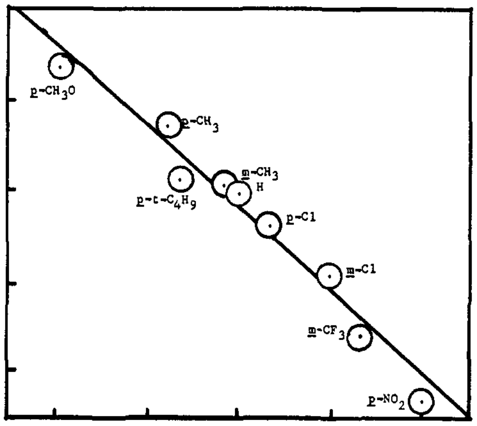

Figure 2. Relative rates of hydrogen abstraction by trichloromethyl radicals from substituted neopentylbenzenes *vs.* σ^+.

Competition experiments were carried out in replicate in which two neopentylbenzenes competed for limited amounts of either bromine atoms or trichloromethyl radicals. The results of these experiments are presented in Table III.

It is immediately apparent that electron-donating substituents greatly facilitate rate of reaction. Application of the Hammett equations using both σ and σ^+ constants yields the results shown in Table IV. The correlations obtained with σ^+ constants are more precise for both bromine atoms and trichloromethyl radicals. These are shown in Figures 1 and 2, respectively.

As was found in earlier work, the selectivity exhibited by the large trichloromethyl radical for abstraction from a sterically hindered benzylic position is greater than might be expected.[8] Not only is the selectivity greater

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[13] For example, M. Arai, *Bull. Chem. Soc. Jap.*, 35, 1272 (1962).

[14] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, London, 1959, p 53.

Table III. Relative Rates of Secondary Benzylic Hydrogen Abstraction from Substituted Neopentylbenzenes at 70°

Substituent	σ^a	σ^{+b}	$Cl_3C\cdot$	$k_X/k_{H}{}^d$	$Br\cdot$	d
p-CH_3O	−0.268	−0.778	3.52 ± 0.29[c]	7	3.16 ± 0.17	5
p-CH_3[e]	−0.170	−0.311	1.96 ± 0.18	4	1.29 ± 0.08	6
p-t-C_4H_9	−0.197	−0.256	1.12 ± 0.02	5	1.51 ± 0.05	5
m-CH_3[e]	−0.069	−0.066	1.04 ± 0.01	5	0.99 ± 0.10	4
H	0	0	1.00		1.00	
p-Cl	0.227	0.114	0.71 ± 0.03	5	0.75 ± 0.03	5
m-Cl	0.373	0.399	0.44 ± 0.03	5	0.34 ± 0.03	5
m-CF_3	0.430	0.520	0.33 ± 0.01	5	0.40 ± 0.01	4
p-NO_2	0.778	0.790	0.12 ± 0.01	5	0.25 ± 0.01	4

[a] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1963, p 173. [b] H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958). [c] Average deviation. [d] Number of kinetic runs. [e] Corrected for reaction at both benzylic positions.

Table IV. ρ Values for Hydrogen Abstraction from Substituted Neopentylbenzenes at 70°

Radical	Substituent constant	ρ^b	r^a
$Br\cdot$	σ	−0.96 ± 0.04	−0.942
$Br\cdot$	σ^+	−0.75 ± 0.03	−0.986
$Cl_3C\cdot$	σ	−1.24 ± 0.05	−0.960
$Cl_3C\cdot$	σ^+	−0.94 ± 0.04	−0.980

[a] Correlation coefficient. [b] Average deviation.

than that found for the less reactive bromine atom, but the ρ value for this reaction is some 80% greater than the ρ value found in the reaction of the trichloromethyl radical with ethylbenzenes! It is felt that the difference in ρ values between the ethylbenzenes and the neopentylbenzenes in reaction with the trichloromethyl radical can be traced to the steric factors present in the latter system. In the absence of such steric effects the hydrogen abstraction from neopentylbenzenes might have been expected to show even less substituent dependence that the ethylbenzenes. This would be due to the greater electron-donating ability of a t-butyl group relative to a methyl group. The σ^* values for the two groups are, respectively, 0.0 and −0.30.[15] Such an electron-donating group should stabilize the radical formed and decrease the importance of ring substituents.[16]

In comparison to the above results, the reaction of ethylbenzenes and neopentylbenzenes with bromine atoms shows approximately the same substituent dependence when allowance is made for differences in temperature at which the two series were studied. This "normal" behavior again seems to rule out electronic factors as the sole cause of the enhanced selectivity shown by the trichloromethyl radical. In particular, any argument based on increased hyperconjugative stabilization of α-t-butylbenzyl appears invalid. Such stabilization should be largely independent of the nature of the abstracting species.

If unfavorable steric interactions are the cause of increased selectivity by large attacking species, there should be appreciable bond breaking in the transition state. For electrophilic radicals, such a situation leads to a preferred correlation with σ^+[17] even though other possibilities can be advanced.[18]

It will be noted that no direct relationship exists between the ρ values for different substituted aralkyl system and the relative rates of reaction of the parent compounds. The reaction of various α-substituted toluenes with NBS has been studied in some detail.[19,20] Ethylbenzene reacts 18 times faster than toluene while neopentylbenzene has a relative rate of one-half that of toluene. Despite this large difference in relative rates the substituent dependences of ethylbenzenes and neopentylbenzenes are approximately equal. It is felt that this latter result is a direct consequence of compensating steric and electronic factors.

Recently Friedrich, *et al.*, established a quantitative relationship for such a series of α-substituted toluenes.[21] They obtained a good correlation with σ^+ for the relative rates of hydrogen abstraction by bromine atom from a series of ten α-substituted toluenes under conditions very similar to those in the present study. It was concluded that steric effects played but a minimal role in this reaction. Their relationship would predict a relative rate of reaction of neopentylbenzene to toluene of 4.3. This differs from the experimental value by a factor of 10. It should be pointed out, however, that an expanded linear free energy relationship similar to that formulated by Taft can also be applied to this system.[22] Both reaction parameters, ρ and s, can be

$$\log \frac{k_X}{k_H} = \sigma^+\rho + sE_s$$

evaluated by an iterative method using only the data of Friedrich, *et al.*, to give the final expression shown below.[23] This expanded equation does not introduce

$$\log \frac{k_X}{k_H} = -2.47\sigma^+ + 0.53E_s$$

appreciable change in correlating the original data. In that case all substituents were of comparable size. When applied to neopentylbenzene with its large α-t-butyl group, however, a calculated relative rate of reaction between that compound and toluene of 0.51 is ob-

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(15) R. W. Taft, Jr., *J. Am. Chem. Soc.*, **74**, 2729 (1952).

(16) M. M. Martin and G. J. Gleicher, *ibid.*, **86**, 233 (1964).

(17) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **41**, 1744 (1963).

(18) R. D. Gilliam and B. F. Ward, Jr., *J. Am. Chem. Soc.*, **87**, 3944 (1965).

(19) G. A. Russell, C. DeBoer, and K. M. Desmond, *ibid.*, **85**, 365 (1963).

(20) G. A. Russell and K. M. Desmond, *ibid.*, **85**, 3139 (1963).

(21) S. S. Friedrich, E. C. Friedrich, L. J. Andrews, and R. M. Keefer, *J. Org. Chem.*, **34**, 905 (1969).

(22) R. W. Taft in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., 1956, Chapter 13.

(23) In order to carry out this evaluation, E_s values were assigned to following three points: NO_2 = 0.33, CN = 0.05, $OC(=O)CH_3$ = 0.18. These estimates were based on steric factors for *ortho*-substituted benzenes and/or free energies for intraconversion of axial and equatorial substituents in cyclohexanes. The equation arrived at is essentially invariant to small changes in these values.

tained. This compares quite well with the experimental value of 0.45. It is felt that this provides further proof for the retarding effect of large substituents at the reaction site.

Experimental Section

Materials. Bromotrichloromethane, N-bromosuccinimide, carbon tetrachloride, and chlorobenzene were either purified by standard techniques or used as commercially obtained.[8]

Most of the neopentylbenzenes were prepared as follows. Grignard reagents were prepared from substituted bromobenzenes and a twofold excess of magnesium in ether. The reagents were decanted from the excess metal and slowly added to freshly prepared pivoyl chloride at a temperature of −10°.[24] The resulting substituted phenyl *t*-butyl ketones were distilled and reduced by the Huang–Minlon modification of the Wolff–Kishner procedure.[25] *p*-Nitroneopentylbenzene was prepared from the parent compound by reaction with nitric and sulfuric acids at 25° according to the method of Gurka and Schubert.[11] All starting materials showed purities in excess of 99.0% by glpc analysis. Nmr analysis showed absorption of a singlet at δ 0.88 for the *t*-butyl group at a singlet in the range δ 2.3–2.5 for the secondary benzylic position. The ratios of integrated areas was 9:2. Agreement with phenyl and other possible protons was also found.

α-Bromoneopentylbenzene was prepared by the method of Skell and Hauser.[26] Phenyl *t*-butyl ketone was reduced to the corresponding alcohol by lithium aluminum hydride and then converted to the bromide with phosphorus tribromide. Boiling point and refractive index agreed with literature values.

Product Studies. The Reaction of Neopentylbenzene with Bromotrichloromethane. A solution consisting of 2.99 g (20.22 mmoles) of neopentylbenzene and 25.0 g (126.0 mmoles) of bromotrichloromethane was placed in a Pyrex flask equipped with a condensor. The flask was then placed just below the surface of an oil bath maintained at 70.0 ± 0.5°. The solution was irradiated with a Sylvania 275-W sunlamp for a period of 9 hr. At this point, approximately 68% of the neopentylbenzene had reacted, as shown by glpc. The chloroform produced in the reaction, along with unreacted bromotrichloromethane, was removed under vacuum. The remaining products or the reaction were separated by fractional distillation. The amount of unreacted neopentylbenzene recovered was 0.96 g (6.52 mmoles). The only other product recovered weighed 2.93 g and was shown to be 99% pure by glpc. This material had a boiling point of 78–80° at 2.0 mm, which was identical with the literature value for α-bromoneopentylbenzene.[26] Infrared spectra and refractive indices also showed this compound to be identical with a known sample of α-bromoneopentylbenzene. The weight of the α-bromoneopentylbenzene produced in the product study corresponds to 12.90 mmoles. The total amount of material recovered from the reaction accounts for 96.0% of theoretical.

The Reaction of Neopentylbenzene with N-Bromosuccinimide. A solution consisting of 3.20 g (21.60 mmoles) of neopentylbenzene and 1.38 g (7.76 mmoles) of N-bromosuccinimide in 25 ml of carbon tetrachloride was allowed to react for 4 hr in the manner described above. At this time, all of the N-bromosuccinimide had been converted to succinimide. The succinimide, which was filtered off and dried, weighed 0.75 g (7.56 mmoles) and accounted for 97.4% of the theoretical amount based on N-bromosuccinimide originally present. Fractional distillation of the liquid phase yielded 2.04 g (13.8 mmoles) of unreacted neopentylbenzene, and 2.61 g (7.10 mmoles) of α-bromoneopentylbenzene, which was identified as in the previous experiment. The over-all material balance accounted for 96.7% of the theoretical amount.

The Reaction of *p*-Chloroneopentylbenzene with N-Bromosuccinimide. A solution consisting of 3.70 g (20.22 mmoles) of *p*-chloroneopentylbenzene and 1.47 g (8.26 mmoles) of N-bromosuccinimide in 25 ml of CCl_4 was allowed to react for 6 hr in the manner described above. The succinimide produced, which was filtered off and dried, weighed 0.80 g (8.07 mmoles). This was 97.7% of the theoretical amount. A previous attempt at fractional distillation of the products of this reaction showed that the material which was presumed to be α-bromo-*p*-chloroneopentylbenzene decomposed at the temperature required for distillation. To avoid this, the compound was converted to the corresponding alcohol by stirring overnight in 200 ml of a 0.2 *M* solution of silver nitrate.[26] Silver bromide, formed in this procedure, was filtered off, dried, and weighed. The amount recovered was 1.33 g (7.10 mmoles). The alcohol which was formed, 1-(*p*-chlorophenyl)-2,2-dimethylpropanol, and unreacted *p*-chloroneopentylbenzene were then separated by fractional distillation. The alcohol recovered weighed 1.59 g (8.01 mmoles) and the unreacted starting material weighed 2.04 g (11.14 mmoles). The material balance showed that these products corresponded to 94.7% of the theoretical amount based on *p*-chloroneopentylbenzene originally present. The silver bromide recovered amounted to 88.6% of the theoretical amount.

1-(*p*-Chlorophenyl)-2,2-dimethylpropanol, a previously unreported compound, was identified. The nmr spectra in carbon tetrachloride showed peaks at δ 0.80, 2.58, 4.12, and 7.10 having areas of 9:1:1:4, respectively. The ir spectra showed a broad –OH stretch from 3200 to 3800 cm^{-1}, and a pattern indicating *para* disubstitution. The boiling point was 70–71.5° (0.27 mm) and n^{23}D 1.5250.

Anal. Calcd for $C_{11}H_{15}ClO$. C, 66.50; H, 7.56; Cl, 17.88. Found C, 66.50; H, 7.48; Cl, 17.88.

The Reaction of *p*-Chloroneopentylbenzene with Bromotrichloromethane. A solution consisting of 3.92 g (21.41 mmoles) of *p*-chloroneopentylbenzene in 25.0 g (126.0 mmoles) of bromotrichloromethane was allowed to react for 11 hr as described previously. The amount of unreacted *p*-chloroneopentylbenzene recovered was 1.69 g (9.21 mmoles). The amount of 1-(*p*-chlorophenyl)-2,2-dimethylpropanol recovered after conversion from the bromide, as described above, was 2.19 g (11.02 mmoles). The product accounted for 94.5% of the theoretical amount. The amount of silver bromide recovered from the conversion of *p*-chloro-α-bromoneopentylbenzene to the corresponding alcohol was 1.86 g (9.91 mmoles), 89.9% of the theoretical amount.

Procedure for Kinetic Runs Using Bromotichloromethane. Solution of two neopentylbenzenes, chlorobenzene, and bromotrichloromethane were prepared in the approximate molar ratios of 1:1:1:25. Approximately 0.75 ml of the solution was placed in each of several Pyrex ampoules which had been purged with nitrogen. The ampoules were cooled to Dry Ice–acetone temperature and sealed. One ampoule was reserved for analysis of starting materials; the others 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 sunlamp placed 20 cm above the surface of the oil. Reaction times varied from 2 hr to 7 hr, by which time 9–90% of the neopentylbenzenes 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.

All determinations were run in replicate. The substituted neopentylbenzene competed directly with neopentylbenzene for the abstracting radical. In the case of the *m*-trifluoromethyl derivative, it was necessary to determine its relative reactivity to *p*-chloroneopentylbenzene. The rate constants thereby obtained were converted to the desired form through the expression

$$\left[\frac{k_{m\text{-CF}_3}}{k_{\text{H}}}\right]_{\text{dis}} = \left[\frac{k_{p\text{-Cl}}}{k_{\text{H}}}\right]_{\text{dis}}\left[\frac{k_{m\text{-CF}_3}}{k_{p\text{-Cl}}}\right]_{\text{dis}}$$

Procedure for Kinetic Runs Using N-Bromosuccinimide. The procedure was identical with that described above except that the solid N-bromosuccinimide was first introduced into the ampoule, followed by the solution of the two neopentylbenzenes and chlorobenzene dissolved in carbon tetrachloride. The two neopentylbenzenes, chlorobenzene and N-bromosuccinimide, were in the approximate molar ratio of 1:1:1:1. The reaction times varied from 25 min to 90 min and were from 5 to 80% complete when the reactions were terminated.

Determination of $(k_X/k_H)_{dis}$. The ratios of relative rate constants were obtained using the usual competitive procedures.[3,8,16] The following equation was employed, where $(k_X/k_H)_{dis}$ is the relative

$$\left[\frac{k_{\text{H}}}{k_{\text{X}}}\right]_{\text{dis}} = \frac{\log\left[\dfrac{X_0}{X_f}\right]}{\log\left[\dfrac{H_0}{H_f}\right]}$$

rate constant of disappearance of the X-substituted neopentylbenzene to the unsubstituted neopentylbenzene; X_0 and H_0 are

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(24) G. Vanan and J. De'combe, *Compt. Rend*, 214, 360 (1942).

(25) A. I. Vogel, "Textbook of Practical Organic Chemistry," Longnans, Green and Co., London, 1959, p 510.

(26) P. Skell and C. R. Hauser, *J. Am. Chem. Soc.*, **64**, 2633 (1942).

$$\frac{X_0}{X_f} = \frac{\left[\dfrac{\text{area under X peak}}{\text{area under chlorobenzene peak}}\right]_{\text{initial}}}{\left[\dfrac{\text{area under X peak}}{\text{area under chlorobenzene peak}}\right]_{\text{final}}}$$

the number of mmoles originally present of the X-substituted neopentylbenzene and neopentylbenzene, respectively; H_f and X_f are the corresponding terms for the final number of mmoles present. The above ratios may be directly obtained from the chromatographic analysis using the relationship shown.

Acknowledgments. We wish to thank Mr. Victor R. Koch for obtaining the nmr spectra needed for this investigation.

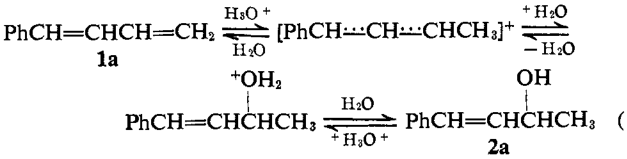
Deuterium Isotope Effects in the Acid-Catalyzed Hydration of 1-Phenyl-1,3-butadiene[1]

Y. Pocker[2] and Martin J. Hill

Contribution from the Department of Chemistry, University of Washington, Seattle, Washington 98105. Received June 16, 1969

Abstract: The kinetics of the acid-catalyzed hydration of 1-phenyl-1,3-butadiene and the acid-catalyzed dehydration of 1-methyl-3-phenylallyl alcohol have been studied in aqueous sulfuric acid and deuteriosulfuric acid starting with both deuterated and nondeuterated substrates. The rate constants obtained can be rationalized by a consideration of the component processes involved in the approach to equilibrium. From such a treatment the isotope effects were calculated as follows. In the forward reaction (hydration) the primary solvent isotope effect is 2.97 and the secondary isotope effect using 1-phenyl-4,4-dideuterio-1,3-butadiene is too small to be observed. In the reverse reaction the combined primary and secondary isotope effect arising from complete deuterium substitution in the terminal methyl group of 1-methyl-3-phenylallyl alcohol is 5.5. These results are shown to be consistent with the previously postulated mechanism for the hydration of 1-phenyl-1,3-butadiene and the dehydration of the adduct.

In a previous paper[3] it was shown that the mechanism of the acid-catalyzed hydration of 1-phenyl-1,3-butadiene (**1a**) to yield 1-methyl-3-phenylallyl alcohol (**2a**) involves the following steps, of which the slowest (rate-determining) step is the protonation of **1a**.



$$\underset{\textbf{1a}}{\mathrm{PhCH{=}CHCH{=}CH_2}} \underset{\mathrm{H_2O}}{\overset{\mathrm{H_3O^+}}{\rightleftharpoons}} [\mathrm{PhCH{\cdots}CH{\cdots}CHCH_3}]^+ \underset{-\mathrm{H_2O}}{\overset{+\mathrm{H_2O}}{\rightleftharpoons}} \mathrm{PhCH{=}CH\overset{\overset{+}{O}H_2}{C}HCH_3} \underset{+\mathrm{H_3O^+}}{\overset{\mathrm{H_2O}}{\rightleftharpoons}} \underset{\textbf{2a}}{\mathrm{PhCH{=}CH\overset{OH}{C}HCH_3}} \qquad (1)$$

Whether or not a π complex is involved in the protonation, as Taft[4a] has suggested, has not been indisputably proven, but it is probably not necessary for the interpretation of the experimental data in the present case.[4b] Similar conclusions have been reached in studies of analogous reactions, namely the dehydration of 1,2-diphenylethanol[5] and the hydration of styrene[6,7] and variously substituted styrenes.[8]

As a continuation of the study of the reactions of **1a** and **2a** we have followed the kinetics of the hydration of **1a** and the dehydration of **2a** using deuteriosulfuric acid as solvent and also using 1-phenyl-4,4-dideuterio-1,3-butadiene (**1b**) and 1-trideuteriomethyl-3-phenylallyl alcohol (**2b**) as substrates. This has enabled us to study the effect of deuterium on both forward and reverse reaction rates directly. Since the systems studied earlier[5-7] reach equilibria which are essentially completely on one side or the other, it has not been possible until now to study the deuterium isotope effects on alkene–alcohol equilibration from both directions.

Experimental Section

Preparation of Materials. 1-Phenyl-1,3-butadiene and 1-methyl-3-phenylallyl alcohol were prepared as previously described.[3]

1-Trideuteriomethyl-3-phenylallyl Alcohol. To 5 g of *trans*-4-phenyl-3-buten-2-one (Eastman) was added 20 ml of 2 *M* sodium deuterioxide in deuterium oxide, and the mixture was stirred for 8 hr at room temperature, extracted with ether, the ether layer dried over calcium sulfate, filtered, and the ether evaporated. This procedure was repeated 3 times, each time using fresh sodium deuterioxide solution, until the nmr spectrum of the product showed that the terminal methyl group was 97% deuterated (yield 4.5 g). This deuterated ketone was dissolved in 25 g of methanol, cooled to −10°, 1.5 g of sodium borohydride was added neat, and the mixture was allowed to stand for 30 min. The mixture was added to 100 ml of water, extracted with ether, the ether layer dried over sodium sulfate, filtered, and the ether evaporated. The resulting 1-trideuteriomethyl-3-phenylallyl alcohol was distilled, bp 82–84° (0.6 mm), yield 2.9 g. The nmr spectrum of the product showed 97% deuterium in the terminal methyl group.

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(2) To whom inquiries should be directed.

(3) Y. Pocker and M. J. Hill, *J. Amer. Chem. Soc.*, **91**, 3243 (1969).

(4) (a) R. H. Boyd, R. W. Taft, Jr., A. P. Wolf, and D. R. Christman, *ibid.*, **82**, 4729 (1960), and references therein. (b) However, it should be noted that the vapor pressure of hydrogen chloride solutions in nitromethane is decreased by the addition of alkenes even before hydrogen exchange and/or addition take place. Such interactions could be due to π-complex formation between molecular HCl and alkene although for addition proper, fully developed carbonium ions were shown to be the crucial intermediates (Y. Pocker and K. D. Stevens, *ibid.*, **91**, 4205 (1969); Y. Pocker, K. D. Stevens, and (the late) J. McKee, unpublished observations).

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