Intramolecular Transfer of Complexed Radicals as a Possible Explanation for Long-Range Substituent Effects Observed in a Hydrogen Abstraction Reaction

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Abstract: A series of 4-methyl-1-phenyl-4-(4-substituted phenyl)pentanes were reacted photolytically with bromotrichloromethane at 70°. Hydrogen abstraction occurred only at the benzylic position. Treatment of the data in a linear free-energy relationship produced a ρ value of -0.40. This is very large for a system in which the substituted phenyl group is insulated from the reaction site by three saturated carbon atoms. A complementary Taft study on a series of 1-phenyl-4-substituted butanes showed a reaction parameter of -0.32 indicative of some long-range inductive effect. Corresponding Taft treatments of the initial group of compounds, however, yielded ρ values of -1.34 and -1.54. A classical inductive effect, therefore, seems to account for only a small portion of the overall substituent dependence. It is felt that the present results illustrate a process where a complexed radical is intramolecularly transferred to the site of hydrogen abstraction.

Fifteen years ago Russell noted the important effect of variation of solvent on radical hydrogen abstraction reactions.[1] Since that time additional cases of specific solvent effects have also been noted for radical additional reactions[2] and the decomposition of radical precursors.[3] The wide scope of such effects has been reviewed both by Huyser[4] and by Martin.[5] Of particular interest within the framework of the present report are those species involving formation of a π or charge-transfer type complex between some reactive radical and an aromatic system. Formation of such complexes should increase the selectivity shown by the radical. Radical halogenation reactions have been extensively studied from this viewpoint. The rate-determining hydrogen-abstraction step is usually carried out by some "electrophilic radical." The presence of aromatic systems containing electron-donating groups uniformly increases the selectivity. Radical sources included molecular chlorine,[1,6] di-*tert*-butylperoxyoxalate,[7] and molecular bromine.[6]

An interesting problem can arise when the complexing agent is the substrate of the reaction rather than some solvent species. In a study of the radical addition of bromotrichloromethane to 3-aryl-1-propenes and 4-aryl-1-butenes, Martin and Gleicher concluded that the relatively large observed substituent effects were explicable by a sequence in which a trichloromethyl radical, complexed by the aromatic portion of the arylalkene, was intramolecularly transferred to the terminal position of the olefin.[8] A similarly large substituent effect was not noted for nonaromatic ω-substituted 1-alkenes.[9] A study of ω-phenyl-1-alkenes showed a rate

dependence on chain length which is supportive of the above reaction sequence.[10]

The question of whether an analogous hydrogen abstraction reaction exists had not as yet been fully defined. Russell, Ito, and Hendry have studied the photochlorination of n-butylbenzene.[11] They noted that the relative amounts of 2-chloro-1-phenylbutane and 3-chloro-1-phenylbutane formed remained essentially constant over a variation of solvent identity and irrespective of dilution. Although this might indicate the absence of intramolecular transfer of a complexed radical to the site of hydrogen abstraction, certain problems are apparent. These mainly concern the steric and electronic nonequivalence of the two reaction sites chosen for study and the utilization of an unselective abstracting agent. It has subsequently been noted that bromination of α,ω-diphenylalkanes using bromotrichloromethane shows a large dependence on chain length.[12] This result is analogous to that observed for intramolecular transfer in an addition process.[10] In the present paper the effect of substituents in hydrogen abstraction from 4-methyl-1-phenyl-4-(4-substituted phenyl)pentanes by the trichloromethyl radical (eq 1) will be discussed.[13]
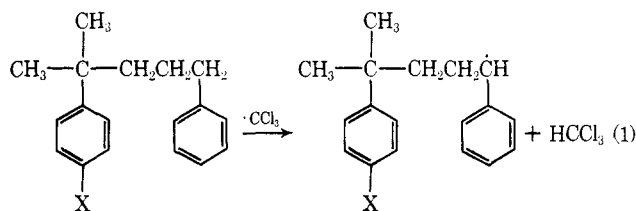

Certain problems encountered in previous studies are

(1) G. A. Russell, *J. Amer. Chem. Soc.*, **79**, 2977, (1957).

(2) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **42**, 1044 (1964).

(3) R. C. Lamb, J. G. Pacifici, and P. W. Ayers, *J. Amer. Chem. Soc.*, **87**, 3928 (1965).

(4) E. S. Huyser, *Advan. Free-Radical Chem.*, **1**, 77 (1965).

(5) J. C. Martin in "Free Radicals," Vol. II, J. Kochi, Ed., Wiley, New York, N. Y., 1973, p 493.

(6) J. Hradil and V. Chvalovsky, *Collect. Czech. Chem. Commun.*, **33**, 2029 (1968).

(7) H. Sakurai and A. Hosomi, *J. Amer. Chem. Soc.*, **89**, 458 (1967).

(8) M. M. Martin and G. J. Gleicher, *J. Amer. Chem. Soc.*, **86**, 233 (1964).

(9) M. M. Martin and G. J. Gleicher, *J. Amer. Chem. Soc.*, **86**, 242 (1964).

(10) M. M. Martin and G. J. Gleicher, *J. Amer. Chem. Soc.*, **86**, 238 (1964).

(11) G. A. Russell, A. Ito, and D. G. Hendry, *J. Amer. Chem. Soc.*, **85**, 2976 (1963).

(12) D. D. Newkirk, G. J. Gleicher, and V. R. Kock, *Tetrahedron*, **28**, 449 (1973).

(13) The identity of the radical involved in hydrogen abstraction by bromotrichloromethane has recently been questioned. Although long considered to be trichloromethyl radical, Tanner and his associates have suggested that bromine atom is the actual abstracting agent.[14] In either event a single such agent is operative and discussion of the structure-reactivity relationship appears valid.

(14) D. D. Tanner, R. J. Arhart, E. V. Blackburn, N. C. Das, and N. Wada, *J. Amer. Chem. Soc.*, **96**, 829 (1974).

not found in the present systems. Reaction is basically limited to the benzylic position. One can estimate that a secondary benzylic position is approximately four powers of ten more reactive than other secondary sites.[15] The reactive positions are sterically equivalent and in essentially the same electronic environment. The parent compound and methyl and methoxy derivatives were prepared *via* the sequence shown in Scheme I.

Scheme I. The Synthesis of 4-Methyl-1-phenyl-4-(4-substituted phenyl)pentanes Where the Substituent is Hydrogen, 4-Methyl, or 4-Methoxy
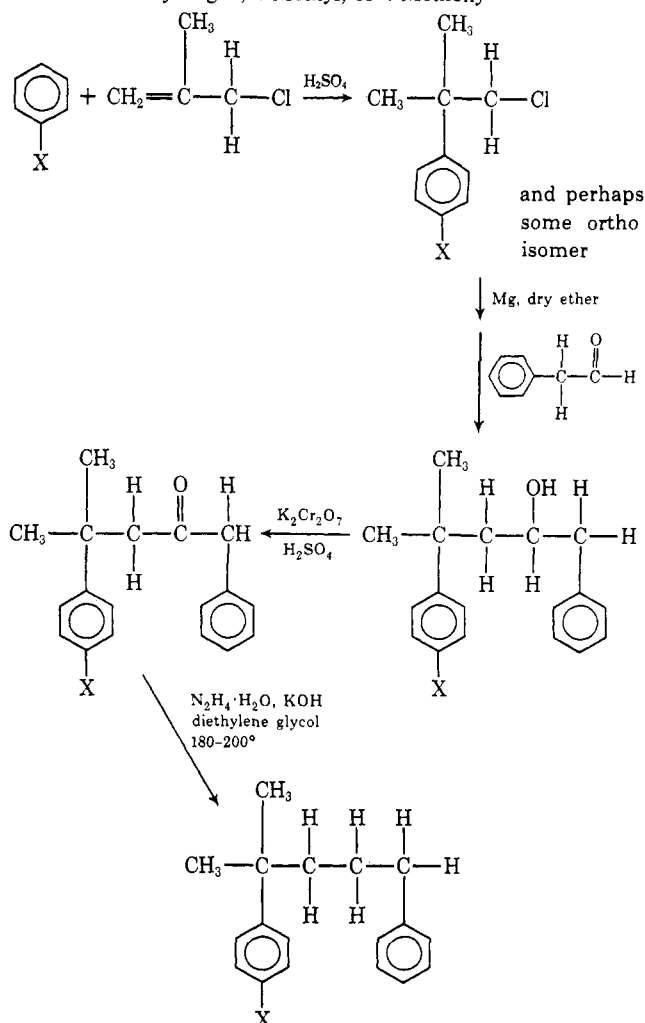
Scheme II outlines the preparation of the amino derivative. This could be converted to the chloro, bromo, and nitro derivatives. Complete details are given in the Experimental Section. In the case of the methyl and methoxy derivatives some ortho isomer may have also been formed. In the latter compound the two isomers could be separated and individually characterized. After repeated attempts, no such separation could be obtained for 4-methyl-1-phenyl-4-(4-methylphenyl)pentane. It is possible that only the para compound was formed; however, a shoulder on the aromatic methyl absorption in the nmr spectrum indicates that as much as 8% of the ortho isomer might be present. All other compounds exhibited purities in excess of 97%.

In Table I are found the results for the rates of reaction of this series of compounds with the trichloro-

(15) G. A. Russell and C. DeBoer, *J. Amer. Chem. Soc.*, **85**, 3136 (1963).

Table I. Relative Rates of Hydrogen Abstraction from a Series of 4-Methyl-1-phenyl-4-(4-substituted phenyl)pentanes by Trichloromethyl Radical at 70°[a]

Substituent	σ	σ^+	No. of kinetic runs	$(k_X/k_H)_{H-abst}$
p-CH$_3$O	−0.268	−0.778	5	1.25 ± 0.03
p-CH$_3$	−0.170	−0.311	5	1.06 ± 0.04
H	0.000	0.000	12	1.04 ± 0.04
p-Cl	+0.227	+0.114	7	0.66 ± 0.03
p-NO$_2$	+0.778	+0.790	6	0.48 ± 0.02
p-Br[b]	+0.232	+0.150	13	1.09 ± 0.10
o-CH$_3$O[b]	?	?	6	1.50 ± 0.03

[a] Diphenylmethane is the reference compound. [b] Not used in the calculation of ρ from the Hammett equation.

methyl radical. These results are all expressed relative to that of diphenylmethane. All results were obtained in replicate at 70°. The abstracting species was generated photolytically from bromotrichloromethane. The reactions were run competitively using nmr as the analytical tool. The reaction was monitored by following the decrease in benzylic hydrogen signal. The signals from the nonreacting alkyl protons were utilized as the internal standard. Signals from protons in the products were of course also observed. These indicated exclusive benzylic bromination (*ca.* 98% within the limits of the analytical method) and no dehydrobromination to form secondary olefinic products. It had originally been planned to follow the reaction by glc. Unfortunately, dehydrobromination took place during analysis to form olefins which eluted with unreacted starting materials.

A general trend of reactivities can be observed with electron-donating groups favoring reaction. It was found that these results could be correlated by the Hammett equation. The reaction parameters which will be discussed are based on the parent compound and the para nitro, chloro, methyl, and methoxy derivatives. The ortho methoxy compound was not utilized in view of the plethora of substituent parameters available.[16] It was virtually impossible to single out one of these without *post hoc* reasoning. Values could be chosen, however, which very nicely correlate with the experimental results.[17–19] The para bromo compound gave poor agreement with all correlations attempted. This will be discussed later in this report. The actual correlations obtained are summarized in Table II. The

Table II. Summary of Attempted Linear Free-Energy Relationships

Parameter	ρ	Correlation coefficient
σ	−0.40	−0.971
σ^+	−0.28	−0.928
σ^*	−1.34	−0.960
$\sigma^{*\prime}$	−1.54	−0.975

optimum correlation was with σ parameters and showed a reaction parameter of −0.40. This is shown in Figure 1.
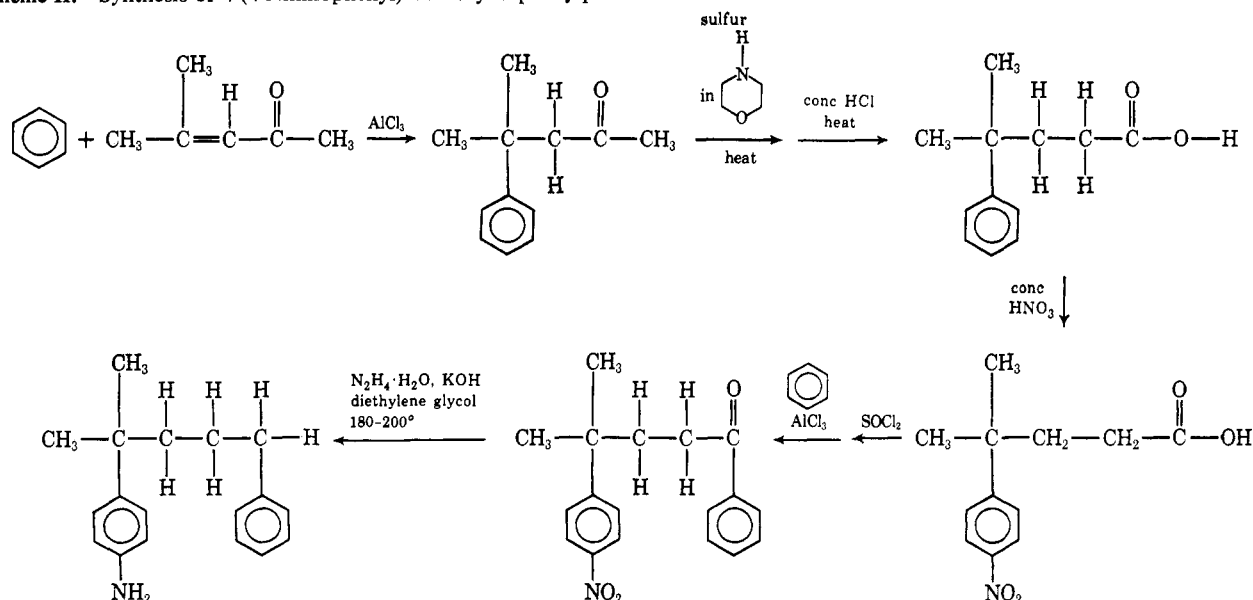
(16) M. Charton, *Progr. Phys. Org. Chem.*, **8**, 235 (1971).
(17) R. W. Taft, Jr., *J. Amer. Chem. Soc.*, **75**, 4231 (1953).
(18) W. F. Little, C. N. Reilly, J. D. Johnson, K. N. Lynn, and A. P. Sanders, *J. Amer. Chem. Soc.*, **86**, 1376 (1964).
(19) C. Eaborn, G. A. Skinner, and D. R. M. Walton, *J. Chem. Soc. B*, 922 (1966).

Scheme II. Synthesis of 4-(4-Aminophenyl)-4-methyl-1-phenylpentane

In his early studies on the effect of complexing, Russell observed correlation of chlorination selectivity with the σ parameters of the solvent substituents.[20] Similar correlations have been observed by Hradil and Chvalovsky for the rates of photochlorination of toluene[6] and by Martin and Gleicher for the addition of trichloromethyl radical to ω-aryl-1-alkenes.[8] Although a correlation with σ plus substituent parameters was observed by Hradil and Chvalovsky for the effect of aromatic solvents on the competitive bromination of toluene,[6] correlation with σ substituent parameters must be considered as the more general occurrence.

It is felt that the observed ρ value is quite large. Hydrogen abstraction from ethylbenzene by the trichloromethyl radical at 80° yields a ρ value of -0.53.[21] In that case the substituted phenyl group is directly attached to the radical site. If the Taft "fall-off" factor of 2.8 is utilized,[22] a series of substituted phenyl groups which are insulated from the reaction site by three saturated carbon atoms should cause an insignificant ρ value of only -0.02. This probably, however, exaggerates what might be expected.

In order to be more exact in determining the true magnitude of long-range inductive effects the following studies were undertaken. A series of 1-phenyl-4-substituted butanes were prepared and reacted with bromotrichloromethane under the same conditions. Reactions again occurred exclusively in the benzylic position. Table III summarizes the kinetic results. Application of a Taft type correlation yielded a reaction parameter of -0.32 with correlation coefficient of -0.94. Although the overall correlation can be defined as no better than fair, it does illustrate some long-range inductive effect to be operative.

The dependence of the relative rates of hydrogen abstraction upon substituent observed in the 4-methyl-1-phenyl-4-(4-substituted phenyl)pentane series might also, thus, seem to arise from a long-range inductive effect. If this is so, then the logarithms of the relative
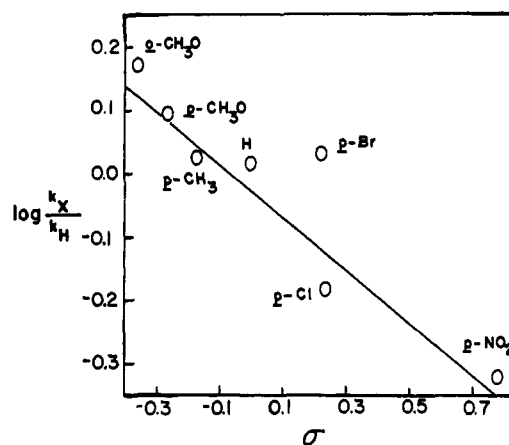
(20) G. A. Russell, *J. Amer. Chem. Soc.*, **80**, 4987 (1958).

(21) E. P. Chang, R. L. Huang, and K. H. Lee, *J. Chem. Soc. B*, 878 (1969).

(22) R. W. Taft in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, Chapter 13.

Figure 1. The relative rates of hydrogen atom abstraction by ·CCl₃ from 4-methyl-1-phenyl-4-(substituted phenyl)pentanes *vs.* σ: $\rho = -0.40$ (excluding *o*-OCH₃ and *p*-Br); correlation coefficient = -0.971.

Table III. Relative Rates of Hydrogen Abstraction from a Series of 1-Phenyl-4-substituted Butanes by Trichloromethyl Radical at 70° [a]

Substituent	σ^*	No. of kinetic runs	$(k_X/k_H)_{\text{B-abst}}$
CH₂CH₃	-0.10	6	1.11 ± 0.04
CH₂H	0.00	5	1.07 ± 0.04
CH₂OCH₃	$+0.64$	6	0.87 ± 0.03
CH₂C(=O)OEt	$+0.71$	7	0.55 ± 0.02
CH₂Cl	$+1.05$	6	0.57 ± 0.03
CH₂CN	$+1.30$	6	0.37 ± 0.04

[a] Diphenylmethane is the reference compound.

rates of hydrogen abstraction from these compounds should correlate with the respective σ^* constants for the substituted phenyl ring. This correlation should give a ρ value identical with that obtained above with the 1-phenyl-4-substituted butanes.

In order to maintain consistency with the 1-phenyl-4-substituted butane results, the substituents in the 4-methyl-1-phenyl-4-(4-substituted phenyl)pentane series

must be taken to be the substituted benzyl group consisting of carbon 4 and the substituted phenyl ring. The σ* values of substituted benzyl groups can be estimated in at least two different ways. They have been determined from ionization constant data from the corresponding arylacetic acids.[23] The Taft polar substituent constants have also been calculated from ^{29}Si–H coupling constants for a series of substituted phenylsilanes, phenylmethylsilanes, and phenyldimethylsilanes. This method gives the σ* values for substituted phenyl groups.[24] Division by 2.8, the fall-off factor per methylene group suggested by Taft,[22] should give the corresponding substituted benzyl σ* constants. Both sets of σ* values defined above were able to correlate the pK_a values of substituted β-arylisovaleric acids[25] with high precision.

The logarithms of the relative rates of hydrogen abstraction by trichloromethyl radicals from the 4-methyl-1-phenyl-4-(4-substituted phenyl)pentane can be correlated with σ* constants obtained by either method discussed above. The relative rates and the corresponding σ* values for each compound are shown in Table II. A ρ of −1.34 with a correlation coefficient of −0.960 is obtained with the σ* constants calculated from the ionization constants of arylacetic acids. Correlation with σ* constants obtained from ^{29}Si–H coupling constants gave a ρ value of −1.54 with a correlation coefficient of −0.975.

The absolute values of ρ obtained by these correlations are approximately four to five times larger than the value of −0.32 obtained in the corresponding reaction of 1-phenyl-4-substituted butanes. The cause of the present large long-range substituent effect cannot, therefore, be completely attributed to inductive factors. It is felt that the substituent dependence can be explained if it is assumed that it reflects effects of complexation on the rate of hydrogen abstraction. The compounds with electron-donating substrates complex the most radicals. If the rate of intramolecular transfer and the rate of hydrogen abstraction by transferred trichloromethyl radicals are nearly constant for the whole series of compounds, then the differences in relative rates observed mirror the difference in the number of trichloromethyl radicals complexed. The compounds that complex the most radicals should react the fastest.

The reaction of the 1-phenyl-4-substituted butanes must also be considered as involving radical attack by a pathway other than intramolecular transfer. Attack by an uncomplexed radical is unlikely. Russell has estimated that a solution of chlorine atoms in benzene consists principally (>91%) of complexed species.[20] The radicals herein described should be complexed to a comparable extent. If the intermolecular transfer of a complexed radical is thus inferred, it is obvious that only limited selectivity is associated with that process. Extension of this conclusion to the reaction of 4-methyl-1-phenyl-4-(4-substituted phenyl)pentanes would not allow for the large substituent effect observed. It is felt, therefore, that a mechanism involving such an inter-molecular transfer is incompatible with the experimental results.

The results for 4-(4-bromophenyl)-4-methyl-1-phenylpentane do not correlate well with any parameter utilized. This compound is much more reactive than would be expected and its reactivity does in some degree parallel its ionization potential. Perhaps the trichloromethyl radical can complex with the bromine substituent itself and then be intramolecularly transferred to the site of hydrogen abstraction. This type of halogen-radical complex was suggested to explain the high tertiary to primary product ratio of 31 observed for the chlorination of 2,3-dimethylbutane in iodobenzene.[20]

Prior work indicated that hydrogen abstraction by trichloromethyl radical from α,ω-diphenylalkanes was dependent upon the distance between the two phenyl groups.[12] Results of hydrogen abstraction by trichloromethyl radical from 1-phenylalkanes and results from hydrogen abstraction by bromine atoms from both α,ω-diphenylalkanes and 1-phenylalkanes suggested that this effect did not arise from simple steric or electronic factors.[12] Present findings on hydrogen abstraction from 4-methyl-1-phenyl-4-(4-substituted phenyl)pentanes suggest that long-range substituent effects strongly influence the rate of reaction. Relative rates of hydrogen abstraction from the 1-phenyl-4-substituted butanes rule out that this influence is a purely inductive one. All these data can be explained by assuming that trichloromethyl radical can be complexed to an electron rich site in the substrate molecule. If the proper conformations are present, this complexed free radical can then be intramolecularly transferred to the site of hydrogen abstraction.

Experimental Section

Materials. Bromotrichloromethane and diphenylmethane were commercially obtained. The 1-phenyl-4-substituted butanes were all prepared by standard reactions. Their physical properties agreed with those found in the literature. All compounds were purified before use and showed purity in excess of 97% by glc.

Preparation of 4-Methyl-1,4-diphenylpentane. Neophyl chloride, (2-chloro-1,1-dimethylethyl)benzene, was prepared by the addition over 7 hr of 2.2 mol of distilled methallyl chloride to 10 mol of dry benzene containing about 0.4 mol of concentrated sulfuric acid.[26]

Addition of an ether solution containing 0.4 mol of neophyl chloride to 1.5-fold excess of magnesium turnings in ether, followed by 2.5 hr of refluxing, produced neophyl magnesium chloride. A solution of 0.4 mol of phenylacetaldehyde was slowly added over 5 hr to the ethereal solution of neophyl magnesium chloride. After stirring overnight and standard Grignard reaction work-up, 0.35 mol of crude 4-methyl-1,4-diphenyl-2-pentanol was obtained. This product was contaminated with about 10% of a compound believed to be 2,5-dimethyl-2,5-diphenylhexane. This compound probably formed from coupling of the Grignard reagent.

A solution of 0.2 mol of the crude alcohol from above, dissolved in benzene, was slowly added to a solution containing 0.35 mol of potassium dichromate, 76 ml of acetic acid, 136 ml of concentrated sulfuric acid, and 450 ml of water.[27] The whole mixture was stirred overnight After work-up 0.134 mol of crude 4-methyl-1,4-diphenyl-2-pentanone was obtained. Distillation on a spinning band column gave the product in 96% purity by gas–liquid chromatography. The 2,5-dimethyl-2,5-diphenylhexane impurity was completely removed at this point.

Reduction by the Huang-Minlon modification of the Wolff–Kishner reaction gave 4-methyl-1,4-diphenylpentane. A solution containing 0.05 mol of the above ketone and 0.20 mol of hydrazine

(23) C. J. Lancelot, J. J. Harper, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 4294 (1969).

(24) Y. Nagai, H. Matsumoto, T. NaKano, and H. Watanabe, *Bull. Chem. Soc. Jap.*, **45**, 2560 (1972).

(25) A. J. Hoefnagel, J. C. Monshouwer, E. C. G. Snorn, and B. M. Wepster, *J. Amer. Chem. Soc.*, **95**, 5350 (1973).

(26) W. T. Smith, Jr., and J. T. Sellas, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 702.

(27) W. F. Bruce, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 139.

Table IV. Physical Properties of the 4-Methyl-1-phenyl-4-(4-substituted phenyl)pentanes

Substituent	Bp, °C	n^{20}D	Formula	% carbon		% hydrogen		% other	
				Calcd	Found	Calcd	Found	Calcd	Found
H	105° (0.2 mm)	1.5481	$C_{18}H_{22}$	90.69	90.57	9.31	9.27		
p-NO₂	150° (0.1 mm)	1.5690	$C_{18}H_{21}NO_2$	76.29	76.10	7.47	7.59	4.94	4.85
p-Cl	105° (0.1 mm)	1.5568	$C_{18}H_{21}Cl$	79.24	79.15	7.76	7.78	12.99	13.05
p-Br	120° (0.1 mm)	1.5690	$C_{18}H_{21}Br$	68.14	68.20	6.67	6.72	25.19	25.09
p-CH₃O	110° (0.05 mm)	1.5498	$C_{19}H_{24}O$	85.02	84.85	9.01	8.95		
p-CH₃	103° (0.1 mm)	1.5442	$C_{19}H_{24}$	90.42	90.36	9.58	9.66		

hydrate dissolved in diethylene glycol was refluxed for 45 min. Then, to this solution was added a solution of 0.20 mol of potassium hydroxide dissolved in 100 ml of diethylene glycol. This new solution was refluxed 1 hr. The apparatus was rearranged for distillation and 6 ml of liquid removed. At this point the pot temperature was 200°. The distillation head was removed and refluxing was continued for 3 hr. After standard work-up, 0.028 mol of 4-methyl-1,4-diphenylpentane was obtained. The product was 99% pure by gas–liquid chromatographic analysis. The nmr spectrum consisted of a multiplet centered at about δ 7.1 for the aromatic protons, a triplet centered at about δ 2.4 for the benzylic protons, a multiplet spread from about δ 1.7 to 1.2 for the other methylene protons, and a singlet at δ 1.2 for the methyl protons. The relative peak areas are approximately 10:2:4:6. The 4-methyl and 4-methoxy derivatives were prepared by the same overall approach. See Table IV for a summary of the physical properties of these compounds.

Preparation of 4-(4-Aminophenyl)-4-methyl-1-phenylpentane. Addition of 4-methyl-3-penten-2-one to a cold mixture of anhydrous aluminum chloride and benzene gave 4-methyl-4-phenyl-2-pentanone in 63% yield.[28]

The Kindler modification of the Willgerodt reaction was used to obtain 4-methyl-4-phenylpentanoic acid from the above ketone.[29,30] This material could be nitrated,[31] converted to its acid chloride, and reacted with benzene and aluminum chloride. After purification, 4-methyl-4-(4-nitrophenyl)-1-phenyl-1-pentanone was obtained as a waxy solid in 77% yield. The nmr spectrum of this compound consisted of a doublet centered at δ 8.05 for the two aromatic protons ortho to the nitro group, a multiplet of peaks centered at δ 7.48 for the rest of the aromatic protons, a triplet centered at δ 2.6 for the protons on the carbon α to the ketone, a triplet centered at δ 2.1 for the protons on the carbon β to the ketone, and a singlet δ 1.4 for the protons in the two methyl groups. The relative peak areas were 2:7:2:2:6.

Reduction by the Huang–Minlon modification of the Wolff–Kishner reaction reduces ketones to hydrocarbons and aromatic nitro substituents to amines.[32]

Preparation of 4-Methyl-4-(4-nitrophenyl)-1-phenylpentane. This compound was obtained from 4-(4-aminophenyl)-4-methyl-1-phenylpentane by oxidation of the amino substituent to a nitro substituent. Oxidation with peracetic acid, carefully following the procedure of Emmons,[33] gave the desired compound in 10% yield (97% pure by gas–liquid chromatography), See Table IV for physical constants and elemental analysis. The nmr spectrum consisted of a doublet centered at δ 8.0 for the aromatic protons ortho to the nitro substituent, a doublet centered at δ 7.3 for the protons meta to the nitro substituent, a multiplet centered at δ 7.05 for the rest of the aromatic protons, a triplet centered at δ 2.5 for the benzylic protons, a multiplet spread from δ 1.7 to 1.2 for the methylene protons, and a singlet at δ 1.1 for the methyl protons. The relative peak areas were approximately 2:2:5:2:4:6.

Preparation of the 4-(4-Chlorophenyl)-4-methyl-1-phenylpentane. Glacial acetic acid was used to dissolve 4-(4-aminophenyl)-4-

methyl-1-phenylpentane. This solution was slowly added to a solution of sodium nitrite dissolved in concentrated sulfuric acid. During addition the system was cooled in an ice bath. To this solution of diazonium ions was rapidly added a solution of cuprous chloride dissolved in hydrochloric acid. The ice bath was then removed and the system stirred for 2.5 hr. The solution was then heated for 35 min. After cooling, the mixture was extracted with a solution of benzene and hexane. This solution was washed with water, 20% potassium hydroxide, and finally again with water. Removal of the solvent left an oil that was shown to be a mixture by gas–liquid chromatographic analysis. Repeated distillation at last gave 4-(4-chlorophenyl)-4-methyl-1-phenylpentane in 7% yield (97% pure by gas–liquid chromatography). See Table IV for a summary of the physical properties of this molecule. The nmr spectrum of this compound consisted of a multiplet centered at δ 7.1 for the aromatic protons, a triplet at δ 2.4 for the benzylic protons, a multiplet from δ 1.7 to 1.2 for the methylene protons, and a singlet at δ 1.2 for the methyl protons. The relative peak areas were approximately 9:2:4:6.

Preparation of the 4-(4-Bromophenyl)-4-methyl-1-phenylpentane. A mixture of 0.1 mol of 4-(4-aminophenyl)-4-methyl-1-phenylpentane and 250 ml of 48% hydrobromic acid was stirred and cooled in an ice bath. To this mixture a solution of 0.3 mol of sodium nitrite, dissolved in 25 ml of water, was added. Upon mixture of these two solutions, a blackish brown tar was formed. After 20 min of stirring this tarry mixture, a solution of 0.13 mol of cuprous bromide dissolved in 50 ml of 48% hydrobromic acid was added. The mixture was stirred in an ice bath for 1 hr and then allowed to warm to room temperature. The mixture was then heated for 2 hr. It was then cooled and extracted with benzene. This solution of the product in benzene was treated with base, washed until neutral, and then dried over anhydrous magnesium sulfate. Removal of the solvent left a reddish black oil. The nmr of this oil suggested that the mixture contained at least some of the desired compound. A crude separation was accomplished by adding the mixture to an alumina column and then eluting with hexane and benzene. The mixture was next distilled several times until after the last distillation it was 98% pure by gas–liquid chromatography. However, the nmr spectrum of this material clearly indicated the presence of at least 15% of the starting material. The mixture was added to a column of 80–200 mesh activated alumina (Matheson Coleman and Bell) and eluted with hexane. The 4-(4-bromophenyl)-4-methyl-1-phenylpentane was obtained in 5% overall yield (97% pure as indicated by analysis by both nmr and gas–liquid chromatograph). See Table IV for a summary of the physical properties of this compound. The nmr spectrum consisted of a doublet centered at δ 7.3 for the aromatic protons ortho to the bromo atom, a multiplet centered at δ 7.1 for the rest of the aromatic protons, a triplet centered at δ 2.4 for the benzylic protons, a multiplet from δ 1.8 to 1.2 for the methylene protons, and a singlet at δ 1.2 for the methyl protons. The relative peak areas were approximately 2:7:2:4:6.

Product Studies. Several 4-methyl-1-phenyl-4-(4-substituted phenyl)pentanes and 1-phenyl-4-substituted butanes were monitored by nmr over the course of reaction. No diminution of signal was noted for any aliphatic protons other than those in the benzylic position. The only new signal observed was found at δ 4.8 as would be expected for an α proton in a secondary benzylic bromide. No new signals in the region δ 3.2–3.4 were observed. Material balance based upon the area of signals for unreacted benzylic positions and product benzylic positions uniformly accounted for

(28) A. Hoffman, *J. Amer. Chem. Soc.*, **51**, 2444 (1929).
(29) R. D. Campbell and N. H. Cromwell, *J. Amer. Chem. Soc.*, **77**, 5169 (1955).
(30) V. L. Bell and N. H. Cromwell, *J. Org. Chem.*, **23**, 789 (1958).
(31) J. van der Scheer, *J. Amer. Chem. Soc.*, **56**, 744 (1934).
(32) Huang-Minlon, *J. Amer. Chem. Soc.*, **70**, 2802 (1948).
(33) W. D. Emmons, *J. Amer. Chem. Soc.*, **79**, 5528 (1957).

over 95% of the material. Attempts to isolate the product bromide were frustrated by rapid dehydrohalogenation.

Procedure for Kinetic Runs for the Reaction of Bromotrichloromethane with the 4-Methyl-1-phenyl-4-(substituted phenyl)pentanes. Attempted analyses by gas–liquid chromatography were unsuccessful. The brominated hydrocarbons formed as products decomposed under analytical conditions and the decomposition products eluted with the starting material. The error thus introduced made such analyses useless.

Analysis of the mixtures, both before and after reaction, was carried out *via* nmr spectroscopy. Some part of the spectra that did not change during the reaction, usually the methyl singlet at approximately δ 1.15, was used as an internal standard. The disappearance of the benzylic proton triplet of the 4-methyl-1-phenyl-4-(substituted phenyl)pentane and the benzylic proton singlet of diphenylmethane was used to determine the relative rates.

Solutions of a 4-methyl-1-phenyl-4-(4-substituted phenyl)pentane, diphenylmethane, and bromotrichloromethane were prepared in the approximate molar ratios of 1:2:30. Approximately 0.75 ml of the solution was put in each of several Pyrex ampoules. The ampoules were cooled to Dry Ice–acetone temperature, evacuated, filled with nitrogen gas, and then warmed to room temperature. This process was repeated three times. After cooling and evacuation, the tubes were 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 Ken-Rad 275-W sunlamp placed 20 cm above the surface of the oil. Reaction times varied from 3 to 5 hr, by which time 30 to 60% of the total hydrocarbons had reacted. The ampoules were then cooled and opened. All determinations were run in replicate.

Procedure for Kinetic Runs for the Reaction of Bromotrichloromethane with the 4-Phenyl-1-substituted Butanes. Solutions of 4-phenyl-1-substituted butanes, diphenylmethane, and bromotrichloromethane were prepared in the approximate molar ratio of 1:1:10. Analysis of the mixture both before and after reaction was carried out *via* nmr spectroscopy. Some part of the spectrum that did not change in integration during the reaction, usually all or part of the nonbenzylic aliphatic part of the spectrum, was used as an internal standard. The disappearances of the benzylic triplet of the 4-phenyl-1-substituted butane and the benzylic singlet of the diphenylmethane were used to determine the relative rates of reaction. In all other ways the procedure was the same as outlined above.

Determination of Relative Rates of Hydrogen Abstraction. The ratios of the relative rate constants were obtained using the usual competitive procedures.[34]

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(34) G. J. Gleicher, *J. Org. Chem.*, **33**, 332 (1968).

Stable Carbocations. CLXIV.[1] The Relative Ability of Charge Delocalization by Phenyl, Cyclopropyl, and Methyl Groups in Carbenium Ions

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Abstract: The relative order of charge delocalization by neighboring phenyl, cyclopropyl, and methyl groups in related series of stable, long-lived carbocations was studied by ^{13}C nmr spectroscopy. The decreasing order of charge delocalization was generally found to be Ph > c-Pr > CH₃. The results are interpreted in terms of differentiating *delocalization* in the intermediate ions (as measured by cmr spectroscopy) from *participation* of the same groups, showing the decreasing order c-Pr > Ph > CH₃, in solvolytic reactions. The latter is obviously affected by the energy differences in the case of the more strained ground state of the precursor esters as compared to the less strained carbenium ion like transition states. Some electrophilic addition reactions to phenylcyclopropyl-substituted ethenes proceeding *via* carbenium ion like transition states show comparable results to the solvolysis studies. A number of carbocations have also been studied in which phenyl, methyl, and cyclopropyl groups are potentially capable of competing with each other to stabilize an adjacent carbenium ion center.

The ability of a cyclopropyl group to stabilize an adjacent carbocation center is well documented.[3] It has been stated[4] from measurements of tricyclopropylcarbenium ion–tricyclopropylmethyl alcohol and triphenylcarbenium ion–triphenylmethyl alcohol equilibria that the cyclopropyl group is capable of stabilizing an adjacent carbocation center to a greater degree than a phenyl group. From a consideration of the relative rates of solvolysis of *p*-phenyl- and -cyclopropyl-*tert*-

cumyl chlorides, and the esters RMe₂COPNB (R = Ph, c-C₃H₅), Brown and Peters[5] also concluded that the cyclopropyl group is more electron releasing than the phenyl group.

In contrast to the above, on the basis of the ^{13}C chemial shifts of the carbenium ion centers in the phenyldimethylcarbenium ion,[6a,b] the cyclopropyldimethylcarbenium ion,[6c,d] and the trimethylcarbenium ion,[6e] in our preceding studies we concluded[6f] that the relative

(1) (a) Part CLXIII: G. A. Olah, P. Schilling, J. M. Bollinger, and J. Nishimura, *J. Amer. Chem. Soc.*, **96**, 2221 (1974); (b) Preliminary communication: G. A. Olah and P. W. Westerman, *ibid.*, **95**, 7530 (1973).

(2) Postdoctoral Research Associates 1971–1973.

(3) For recent reviews, see (a) K. B. Wiberg, B. A. Hess, Jr., and A. J. Ashe III in "Carbonium Ions," Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1972, pp 1295–1345; (b) H. G. Richey, Jr., ref 3a, pp 1201–1294.

(4) N. C. Deno, H. G. Richey, Jr., J. S. Liu, D. N. Lincoln, and J. O. Turner, *J. Amer. Chem. Soc.*, **87**, 4533 (1965).

(5) H. C. Brown and E. N. Peters, *J. Amer. Chem. Soc.*, **95**, 2400 (1973).

(6) (a) G. A. Olah, C. L. Jeuell, and A. M. White, *J. Amer. Chem. Soc.*, **91**, 3961 (1969); (b) G. A. Olah, R. D. Porter, C. L. Jeuell, and A. M. White, *ibid.*, **94**, 2044 (1972); (c) G. A. Olah, D. P. Kelly, C. L. Jeuell, and A. D. Porter, *ibid.*, **92**, 2544 (1970); (d) G. A. Olah, C. L. Jeuell, D. P. Kelly, and R. D. Porter, *ibid.*, **94**, 146 (1972); (e) G. A. Olah and A. M. White, *ibid.*, **91**, 5801 (1969); (f) G. A. Olah, R. D. Porter, and D. P. Kelly, *ibid.*, **93**, 464 (1971). (g) In subsequent studies with Dr. D. A. Forsyth this spectrum was, however, obtained and will be reported.