

1,2-Diphenyl-3-chloro-3-(chlorodicyanomethyl)cyclopropene. Into a mixture of 0.1 g. (0.39 mmole) of 1,2-diphenyl-3-dicyanomethylencyclopropene in 10 ml. of acetonitrile was introduced a slow stream of chlorine gas. Immediate reaction occurred, and the starting material dissolved completely. After adding an excess of chlorine, the mixture was evaporated to dryness on a rotary evaporator leaving an essentially pure white crystalline solid (0.091 g.). Recrystallization from benzene-hexane gave crystals, m.p. 118–120°. The infrared spectrum (CCl₄) showed weak absorption at 2250, 1820, and 1600, and stronger bands at 1450, 1335, 1170, 1100, 1010, 918, and 877 cm.⁻¹. The yields varied from 89 to 92%.

Anal. Calcd. for C₁₈H₁₀Cl₂N₂: C, 66.48; H, 3.10; N, 8.61; Cl, 21.80. Found: C, 66.11; H, 3.14; N, 8.60; Cl, 21.25.

The ultraviolet spectrum in acetonitrile showed λ_{\max} 347 m μ (ϵ 1950), 314 (23,412), 299 (33,167), 287 (26,014 sh), 277 (19,835 sh), 228 (21,786), and 220 (23,087).

1,2-Dicyano-3-chloro-3-(carbethoxychlorocyanomethyl)cyclopropene. In the manner described above, 0.2 g. (0.655 mmole) of 1,2-dicyano-3-(cyanocarbethoxymethylene)cyclopropene in 10 ml. of acetonitrile was combined with chlorine to give 0.233 g. (94.3%) of the title compound, m.p. 118–123°. Recrystallization

from benzene-hexane gave product, m.p. 116–118.5°.

The infrared spectrum in chloroform showed strong carbonyl absorption at 1770 cm.⁻¹. The ultraviolet spectrum in acetonitrile showed λ_{\max} 350 m μ (ϵ 7080), 295 (22,650), 267 (15,800), 240 (13,400), 228 (12,850), and 220 (13,000).

Anal. Calcd. for C₂₀H₁₂Cl₂NO₂: C, 64.53; H, 4.06; N, 3.76; Cl, 19.05. Found: C, 64.88; H, 4.21; N, 3.48; Cl, 19.09.

Mass Spectrum of 1,2-Diphenyl-3-dicyanomethylene-cyclopropene. Since this spectrum was obtained by direct introduction of the sample into the isatron, the intensities throughout the duration of the scan were not reproducible. In addition to the most abundant parent ion, other intense peaks occurred at the following *m/e* values with the approximate relative abundances parenthesized: 256 (2.1%), 255 (20.3%), 254 (100%), 227 (24.9%), 226 (12.1%), 100 (15.8%), 77 (11.4%), 63 (12.8%), 51 (32.9%), 50 (12%), and 39 (19.3%).

Mass Spectrum of 1,2-Diphenyl-3-(cyanocarbethoxymethylene)cyclopropene. The *M* + 1 and *M* + 2 peaks with abundances relative to the parent peak (*m/e* 301) were 302 (22.0%) and 303 (2.2%). Calculated intensities based on natural isotopic abundances were 21.8 and 2.3%, respectively. Other prominent peaks were observed at these *m/e* values: 273, 256, 229, 228, 227, 178, and 77.

Homolytic Abstraction of Benzylic Hydrogen

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*The rates of abstraction of benzylic hydrogen from *m*- and *p*-methyl-, *m*- and *p*-chloro-, *p*-bromo-, *p*-phenoxy-, and *p*-cyano-substituted toluenes were measured relative to toluene. For the reaction with *t*-butoxy radicals generated from *t*-butyl hypochlorite a better correlation was obtained with σ -substituent constants (ρ , -0.75) than with σ^+ . The *p*-phenyl group was found to deviate from this correlation only slightly but gave considerable deviation for the reaction with bromine atom. These results are discussed in terms of resonance stabilization of the incipient benzylic radical.*

Introduction

The formation of substituted benzylic radicals by abstraction of hydrogen by bromine¹ and chlorine² atoms, *t*-butoxy radicals,³ trichloromethyl radicals,⁴ and peroxy radicals² has been found to obey the Hammett $\rho\sigma$ relationship. Better correlations in all cases except the *t*-butoxy radical have been obtained with σ^+ rather than σ ,⁵ but Russell and Williamson²

have pointed out that the proper substituents for a clear distinction have not been investigated for the *t*-butoxy radical. With at least one abstracting species, the phenyl radical,⁶ little or no polar effect is observed. We have re-examined the competitive abstraction of benzylic hydrogen using *t*-butyl hypochlorite as a source of *t*-butoxy radical including selected *para*-substituted toluenes having significantly different σ - and σ^+ -constants.

The *p*-phenyl substituent does not give a good fit with the Hammett equation using standard substituent constants.⁷ We have examined the effect of this group in the abstraction reaction using both bromine atom and *t*-butoxy radical as examples of abstracting species giving large and small ρ -values.

Experimental

Materials. Reagent grade commercial toluene, benzene, and cyclohexane were distilled from sodium as constant-boiling heart cuts. *p*-Bromotoluene, *m*-chlorotoluene, and *p*-chlorotoluene were commercial, reagent grade materials. They were distilled taking constant-

(1) R. E. Pearson and J. C. Martin, *J. Am. Chem. Soc.*, **85**, 354 (1963).

(2) G. A. Russell and R. C. Williamson, Jr., *ibid.*, **86**, 2357 (1964).

(3) C. Walling and B. B. Jacknow, *ibid.*, **82**, 6113 (1960).

(4) E. S. Huyser, *ibid.*, **82**, 394 (1960).

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

(6) R. F. Bridger and G. A. Russell, *J. Am. Chem. Soc.*, **85**, 3754 (1963).

(7) K. M. Johnston and G. H. Williams, *J. Chem. Soc.*, 1446 (1960).

boiling heart cuts. *m*-Xylene and *p*-xylene, Phillips 99.9%, were used as supplied. *p*-Tolunitrile and *p*-phenyltoluene were commercial materials used after recrystallization. Bromine was Baker Analyzed Reagent material used as supplied.

p-Phenoxytoluene was prepared in low yield by the method of Russell and Williamson.⁸ Distillation afforded material, b.p. 102° (1.3 mm.) (lit.⁸ b.p. 110–111° (2 mm.)). *t*-Butyl hypochlorite was prepared by treating 420 ml. of cooled, 1.0 *M* aqueous sodium hypochlorite (0.42 mole) with 36 g. of glacial acetic acid and 74.1 g. (0.42 mole) of *t*-butyl alcohol at 0° with stirring for 1 hr. in the dark. The organic layer was separated, extracted with 5% aqueous sodium bicarbonate, and dried over anhydrous sodium sulfate. Distillation afforded 22 g., 49%, of material, b.p. 78.5–80.0° (lit.⁹ b.p. 79.4–79.6°).

Procedure for Competitive Reactions. Reactions with *t*-butyl hypochlorite were run at 39.6° in a 50-ml., three-necked flask fitted with a nitrogen bubbling tube, a water condenser, and a stopper. Hydrocarbons to be studied were weighed into the flask along with an internal standard, chlorobenzene, when gas chromatographic analysis was employed. Enough benzene, usually 10–15 ml., was added to keep the ratio of total moles of aromatic hydrocarbon to moles of hypochlorite approximately the same in each run. After placing the solution in the constant temperature bath, it was degassed by bubbling nitrogen for 15 min. Neat hypochlorite was pipetted into the solution under reverse nitrogen flow. The solution was irradiated with a 275-w. Sylvania sunlamp, placed externally, until all hypochlorite was consumed as shown by the KI test. Slow nitrogen bubbling was used for agitation throughout each run. Gas chromatographic analysis was carried out by the method of Walling and Jacknow.⁹ In these runs *m*- and *p*-xylene, *m*- and *p*-chlorotoluene, and *p*-bromotoluene were each compared directly to toluene. The relative reactivity, *r*, was determined using the relation

$$r = (\log A/A_0)/(\log T/T_0)$$

A_0 and T_0 are the peak heights of the substituted toluene and of toluene relative to chlorobenzene prior to reaction, and A and T are the same quantities after reaction. The results are reported in Table I. The

Table I. Competitive *t*-Butyl Hypochlorite Reactions at 39.6° in C₆H₆. Gas Chromatographic Data

Hydrocarbon A	A_i^a	A_f^a	T_i^b	T_f^b	k_a/k_t
<i>p</i> -Xylene	1.61	1.16	1.88	1.68	3.04
<i>m</i> -Xylene	1.61	1.16	1.88	1.62	2.28
<i>p</i> -Bromotoluene	1.62	1.30	1.87	1.37	0.71
<i>p</i> -Chlorotoluene	1.66	1.42	1.88	1.49	0.67
<i>m</i> -Chlorotoluene	1.68	1.43	1.88	1.38	0.52

^a Initial and final moles of hydrocarbon A × 10². ^b Initial and final moles of toluene × 10².

relative reactivities of the less volatile *p*-phenyl- and *p*-phenoxytoluene and *p*-tolunitrile, as well as a check with *m*-xylene, were determined by selective solvolysis. Aliquots of the reaction solution were analyzed for

(8) G. A. Russell and R. C. Williamson, Jr., *J. Am. Chem. Soc.*, **86**, 2362 (1964).

(9) C. Walling and B. B. Jacknow, *ibid.*, **82**, 6108 (1960).

Table II. Competitive *t*-Butyl Hypochlorite Reactions at 39.6° in C₆H₆. Solvolytic Data

Hydrocarbon B	A_i^a	A_f^a	B_i^b	B_f^b	C^c	k_a/k_b
Toluene	5.253	5.108	5.398	5.261	8.19	5.17
	4.983	4.323	5.186	5.048	8.19	5.21
	4.763	4.099	4.878	4.741	8.19	5.20
<i>p</i> -Phenoxytoluene	3.224	2.591	2.806	2.652	8.19	3.92
	1.466	1.162	1.427	1.337	4.10	3.60
	1.401	1.140	1.416	1.408	3.46	3.45
<i>p</i> -Tolunitrile	2.175	1.413	2.104	2.058	8.19	17.73
<i>m</i> -Xylene	4.673	4.105	4.084	3.865	8.19	4.44
<i>p</i> -Phenyltoluene	1.142	0.960	0.982	0.466	2.50	3.18
	1.415	1.218	1.372	0.738	2.80	3.16

^a Initial and final moles of cyclohexane × 10². ^b Initial and final moles of hydrocarbon B × 10². ^c Moles of *t*-butyl hypochlorite × 10³.

benzylic halogen by solvolysis. Aliquots were also analyzed for total alkyl halogen. The difference was considered to be cyclohexyl chloride. Relative reactivities were determined using the relation

$$r = [\log (A_0 - X)/A_0]/[\log (B_0 - Y)/B_0]$$

A_0 and B_0 are initial moles of the two hydrocarbons and X and Y are the values for the corresponding halides after the reaction. Results of this method are given in Table II. The relative reactivity of *m*-xylene determined by the solvolytic method is in good agreement with that obtained by the gas chromatographic method. To reduce polychlorination, the total consumable hydrocarbon was always in at least fivefold mole excess and in most runs exceeded a tenfold excess. A large-scale competitive experiment with cyclohexane and toluene permitted isolation of cyclohexyl chloride and benzyl chloride by distillation. They were identified by boiling point, infrared spectroscopy, and gas chromatographic retention times.

Competitive brominations were carried out at 75.3°. Techniques employed were exactly like those used with hypochlorite except that an addition funnel was used to add a benzene solution of bromine. The rate of addition was adjusted so that the reacting solution remained nearly colorless. Evolved hydrogen bromide was entrained by bubbling nitrogen through the solution into a sodium hydroxide trap. It was determined in most reactions by subsequent titration of the remaining base. Agreement between hydrogen bromide evolved and bromine added was 90–98%. The solution was washed with aqueous sodium thiosulfate, sodium bicarbonate, and water, and dried over anhydrous sodium sulfate. The reaction mixture was analyzed by selective solvolysis. Results are reported in Table III. Bromination of a large sample of *p*-phenyltoluene in carbon tetrachloride afforded a high yield of *p*-phenylbenzyl bromide, m.p. 84.8–85.8° (lit.¹⁰ m.p. 85°), after recrystallization from petroleum ether (b.p. 60–90°).

Solvolytic Halide Analysis. Benzylic chloride analysis was achieved by refluxing aliquots of the product solution with 0.25 *N* ethanolic potassium hydroxide for 2 hr. Total alkyl chloride was determined by the method of Walling and Miller.¹¹ Duplicate analyses were obtained on all runs and agreed to within 1%. The reliability of these methods was checked on authentic mixtures of pure chlorides.

(10) L. Zervas and I. Dilaris, *ibid.*, **77**, 5354 (1955).

(11) C. Walling and B. Miller, *ibid.*, **79**, 4181 (1957).

Table III. Competitive Photobromination at 75.3° in C₆H₆

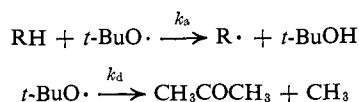
Hydrocarbon B	A _i ^a	A _f ^a	B _i ^b	B _f ^b	Moles of Br ₂ × 10 ³	k _a /k _b
Toluene	5.968	5.780	7.450	2.790	6.53	0.0331
	6.175	6.091	6.301	2.151	5.99	0.0282
	6.508	6.305	6.702	2.556	6.23	0.0326
	6.217	6.086	5.751	1.982	6.29	0.0352
	6.004	5.785	5.852	1.804	6.37	0.0315
	6.324	6.075	5.776	2.142	6.37	0.0386
	5.981	5.727	5.321	1.608	6.44	0.0356
	8.782	8.680	10.953	6.663	5.31	0.0241
	8.177	8.118	21.653	17.580	4.66	0.0345
	6.685	6.615	5.664	2.462	6.03	0.00427
<i>p</i> -Phenyltoluene	6.741	6.720	5.699	2.702	3.29	0.00432
	6.477	6.441	8.865	4.100	5.12	0.00715

^a Initial and final moles of cyclohexane × 10². ^b Initial and final moles of hydrocarbon B × 10³.

Benzyl bromide was analyzed by stirring an aliquot of the reaction mixture with 0.125 *N* sodium hydroxide in aqueous ethanol for 6 hr. at room temperature followed by Mohr titration. The method of Walling and Miller¹¹ was used to determine total alkyl halide. Duplicate analyses were obtained and were within 1% of each other. Prepared mixtures of pure bromides were employed to demonstrate that the reliability of these methods was accurate to less than 1%.

Results

t-Butyl Hypochlorite. Benzene was employed as solvent to keep medium changes to a minimum.⁵ Optimum concentrations of substrates were used to minimize competing decomposition reactions which give acetone and methyl radical. Walling and Wagner¹² have reported that k_a/k_b for a benzene solution of cyclohexane is 24.7 at 40°. From this value it can



be calculated that no more than 1% of the total *t*-butoxy radicals formed under our conditions undergo decomposition. We were unable to analyze for acetone quantitatively. Using synthetic mixtures and gas chromatographic techniques, the maximum amount of acetone in the product mixture was fixed at less than 2% of the *t*-butoxy radicals formed.

The results obtained by gas chromatographic analysis are combined with the solvolytic results and are tabulated in Table IV. The gas chromatographic method monitors disappearance of reactants, while the selective solvolysis technique measures the formation of products. Good agreement of the two methods was demonstrated for *m*-xylene. This agreement strongly argues against the occurrence of such side reactions as dimerization and disproportionation. Agreement with the values reported by Walling and Jacknow^{8,9} is excellent. The value (5.19) for cyclohexane relative to toluene obtained in this work and of that (6.00)⁹ of Walling and Jacknow are at variance. This disagreement may arise from differences in activation energies for the abstraction reaction resulting from solvent effects¹² (CCl₄ → C₆H₆). It should be largely self-compensating in our values of k_x/k_{toluene} derived

(12) C. Walling and P. J. Wagner, *J. Am. Chem. Soc.*, **86**, 3368 (1964).

Table IV. Reactivities of Substituted Toluenes toward *t*-Butoxy Radicals

Substituent	Relative reactivity ^a
<i>p</i> -Phenoxy	1.42 ± 0.10 ^b
<i>p</i> -Methyl	1.52 ± 0.16 (1.53) ^c
<i>m</i> -Methyl	1.14 ± 0.02 (1.17) ^c
Hydrogen	1.00 (assumed)
<i>p</i> -Bromo	0.71 ± 0.07
<i>p</i> -Chloro	0.67 ± 0.01 (0.71) ^c
<i>m</i> -Chloro	0.52 ± 0.02 (0.52) ^c
<i>p</i> -Cyano	0.29 ± 0.02
<i>p</i> -Phenyl	1.64 ± 0.01 ^b

^a Experimental error represents spread of multiple analysis unless otherwise stated. ^b Experimental error represents spread of multiple experiments. ^c Reference 3.

from the equation

$$k_x/k_{\text{toluene}} = (k_{\text{C}_6\text{H}_5}/k_{\text{toluene}})/(k_{\text{C}_6\text{H}_5}/k_x)$$

The excellent agreement of k_x/k_{toluene} for *m*-xylene derived in this manner with the value obtained directly by gas chromatography (*vide supra*) support this assumption.

The data from Table IV were fitted by the method of least squares^{13,14} to the Hammett equation¹³ by standard methods.¹⁴ The correlations shown in Figure 1 are

$$\log k_x/k_{\text{toluene}} = -0.599\sigma^+ - 0.066; s, 0.092; r, 0.953$$

$$\log k_x/k_{\text{toluene}} = -0.750\sigma - 0.007; s, 0.047; r, 0.984$$

The *p*-phenyl substituent was omitted from all correlation (see Discussion).

Bromine. The results of competitive bromination reported in Table III do not agree with the value of 0.017 for k_{C₆H₅}/k_{toluene} obtained by Russell and Brown.¹⁵ The reason for this lack of agreement is uncertain. Solvent or any other effects may be self-compensating (*vide supra*). To test this possibility, *p*-xylene was competitively brominated. A derived value of 2.28, after correction for two methyl groups, was obtained. This is in good agreement with the value of 2.41

(13) The values of σ⁺ are those of Y. Okamoto and H. C. Brown, *ibid.*, **80**, 4979 (1958), with the exception of the value for *p*-phenoxy for which -0.57² was used. The values of σ are those of D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

(14) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

(15) G. A. Russell and H. C. Brown, *J. Am. Chem. Soc.*, **77**, 4578 (1955).

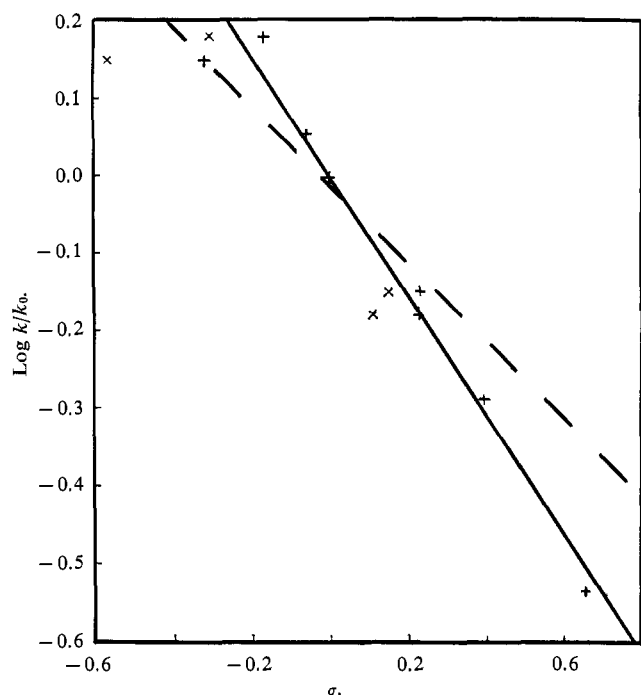
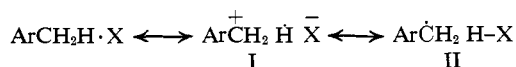


Figure 1. Benzylic hydrogen abstraction by *t*-butoxy radical, 39.6°: +, σ ; x, σ^+ ; —, correlation with σ ; ---, correlation with σ^+ .

obtained by Pearson and Martin¹ by direct measurement. The relative rate for *p*-phenyltoluene of 7.58 was derived from the results in Table III.

Discussion

From the data summarized in the previous section it is clear that the abstraction of benzylic hydrogen by *t*-butoxy radicals follows a σ rather than a σ^+ correlation as first reported by Walling and Jacknow.³ The results of similar reactions with other radicals have been collected recently by Howard and Ingold⁵ and by Russell and Williamson.² They find that many of the reactions are better correlated with σ^+ than with σ . They explain this behavior on the basis of stabilization of the transition state by a significant contribution of the polar structure I.



Stabilization of the transition state by structure I may be important in many cases. The fact, substantiated in this work, that the correlation is sometimes better with σ and other times with σ^+ suggests that a contribution by structure II may also be important. Significant contributions from structures like II have been demonstrated in other atom-transfer processes. Klopman¹⁶ studied the polarographic reduction of several substituted benzyl bromides. He found that all of the substituents studied facilitate reduction of benzyl bromide. Streitwieser and Perrin have reported a similar study using substituted benzyl chlorides.¹⁷ Their results are in qualitative agreement with the results of Klopman. Kochi and Davis¹⁸ investigated the chromous ion reduction of benzyl bromides, a

(16) G. Klopman, *Helv. Chim. Acta*, **44**, 1908 (1961).

(17) A. Streitwieser, Jr., and C. Perrin, *J. Am. Chem. Soc.*, **86**, 4938 (1964).

(18) J. K. Kochi and D. D. Davis, *Nature*, **202**, 690 (1964); *J. Am. Chem. Soc.*, **86**, 5264 (1964).

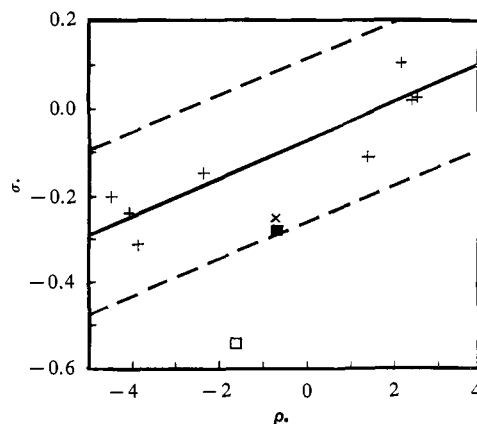


Figure 2. Correlation of σ for *p*-phenyl with ρ : ---, 1% confidence limit; +, values from ref. 20; x, Cl from ref. 2; ■, *t*-BuO; □, Br.

process forming benzylic radicals. They found that all substituents studied increased the rate of this reaction slightly. All of the above results may be interpreted by a significant contribution of structures like II to the transition state involved in each process.

If the stability of the incipient benzylic radical is important in chlorine and bromine atom transfer reactions, a contribution of structure II may also be significant in hydrogen atom transfer reactions. The polar effect, as measured by σ (or σ^+), operates on I but radical stabilization effects, which are not at all measured by σ (or σ^+), operate on II. That is, a substituent of modest polarity which can stabilize an odd electron can facilitate hydrogen transfer by stabilization of II. To test this point the *p*-phenyl group was chosen. The σ -value of *p*-phenyl is -0.01 , but the radical-stabilizing ability is well known.¹⁹ The polar-stabilization effect of *p*-phenyl is variable, σ^+ is -0.18 , and an enhanced reactivity of this substituent might also be due to this variability. To sort out any increased reactivity due to stabilization of II, the polar effect arising from stabilization of I must be predictable. To test the predictability of the polar effect, the σ -values reported by Van Bekkum, Verkade, and Wepster²⁰ were plotted against the corresponding ρ -values given by these workers (Figure 2). The method of least squares was used.²¹ Although the correlation is only fair, 1% confidence limits can be established and at least a qualitative evaluation of the polar effects can be made. Fitting the values obtained by the method of Van Bekkum, *et al.*,²¹ for abstraction reactions to Figure 2 should give an indication of the importance of the polar effect. A good fit implies that only a polar effect is operative and that structure I is a good model of the transition state. A negative deviation of σ (for negative values of ρ) may imply additional stabilization *via* structure II. The σ -values for both chlorine atom² and *t*-butoxy radical abstractions deviate from the correlation in the direction of enhanced rates. The deviation may not be large enough to be significant. The greatly enhanced

(19) The value of the C-H bond dissociation energy of methane is about 25 kcal./mole higher than it is for toluene.

(20) H. Van Bekkum, P. E. Verkade, and B. M. Wepster, *Rec. trav. chim.*, **78**, 815 (1959).

(21) The data reported²⁰ for the reaction of substituted anilines with 2,4-dinitrochlorobenzene was omitted from the correlation. This reaction is abnormal because resonance stabilization of the reactant is lost in the transition state.

reactivity of *p*-phenyltoluene in the bromination reaction is not predicted on a purely polar basis. We believe that the large reactivity is due to a contribution of structure II to the transition state.

There is no doubt that there is a polar effect operative in hydrogen abstraction reactions. In view of the present findings it seems highly doubtful that σ^+ is the appropriate measure of this effect. There must also be radical-stabilizing effects operating in these reactions. The suggestion of Streitwieser and Perrin¹⁷ that a modified form of the Hammett equation, $\rho(\sigma + \lambda\sigma^+)$, be used seems appropriate. Unfortunately,

no suitable values for the radical-stabilizing term, σ^+ , are available. Quantitative information on radical stabilization would be extremely valuable. The source of the radical-stabilizing effect is also unknown. It may arise from a changed Coulomb integral for the *para* carbon carrying a substituent or by extension of the π system. This problem is currently under investigation.

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Mechanisms of Substitution Reactions at Phosphorus. XII. A Kinetic Study of the Decomposition of Quaternary Phosphonium Hydroxides

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Contribution from the Chemistry Departments of the University of Kansas, Lawrence, Kansas, and the University of Massachusetts, Amherst, Massachusetts. Received January 21, 1965

A series of p-Y-benzyltribenzylphosphonium halides (where Y = p-NO₂, m-NO₂, m-Br, m-Cl, m-F, p-Cl, p-F, H, m-CH₃, p-CH₃, p-t-butyl, and p-CH₃O) has been subjected to reaction with sodium hydroxide in 50% (by volume) aqueous 1,2-dimethoxyethane. The determination of accurate rate and product ratio data revealed several facts: (1) all of the reactions were third order, with a first-order dependence on the concentration of phosphonium cation and a second-order dependence on the concentration of hydroxide ion; (2) the relative ease of elimination of the various benzyl groups paralleled their stability as anions; (3) the relative ease of departure of a given group was definitely influenced by the nature of the nondeparting groups; and (4) the rate data could be correlated with σ -values in a suitable adaptation of the Hammett equation.

The decomposition of a quaternary phosphonium hydroxide to give a phosphine oxide and a hydrocarbon is one of the best known nucleophilic displacement reactions at phosphorus. Although recent kinetic³⁻⁵ and stereochemical^{5,6} studies have clarified many of the details of the mechanism of this type of reaction, there are still a number of questions to be answered. Some of these questions arise from the early work of Fenton and Ingold⁷ and of Hey and Ingold.⁸ These workers, in an extension of earlier studies carried out by Mi-

chaelis^{9,10} and by Meisenheimer and Lichtenstadt,¹¹ subjected a series of mixed quaternary phosphonium hydroxides to the decomposition reaction, and, by determining the product ratios of the hydrocarbons produced, they proposed the following sequence for the ease of elimination of various groups: benzyl > phenyl > methyl > β -phenethyl > ethyl > higher alkyl groups.

The English workers also investigated the decomposition of quaternary phosphonium alkoxides¹² and compared the ratios of saturated hydrocarbon to olefin produced. They found that, in favorable structural situations, the stronger base, ethoxide ion, produces a greater proportion of olefin than the weaker base, hydroxide ion. From the results of the various competition reactions they came to the following conclusions. (1) Since olefin formation is dependent on base strength, paraffin formation must be similarly dependent. (2) The rate-determining step is therefore the initial formation of the pentacovalent intermediate. (3) The rate of the reaction is probably second order, showing a first-order dependence on the concentration of each of the phosphonium cation and the hydroxide (or alkoxide) ion. (4) An intermediate in which phosphorus is pentacovalent must be postulated, but the loss of a proton from this intermediate before it collapses to give products may not be an essential step in the reaction sequence. (5) The relative ease of elimination of the various groups parallels their anionic stability. (6) The relative ease of elimination of the various groups is independent of the other groups attached to the phosphorus.

(1) University of Massachusetts, Amherst, Mass.
(2) President, Hope College, Holland, Mich.
(3) M. Zanger, C. A. VanderWerf, and W. E. McEwen, *J. Am. Chem. Soc.*, **81**, 3805 (1959).
(4) H. Hoffmann, *Ann.*, **634**, 1 (1960).
(5) W. E. McEwen, K. F. Kumli, A. Blade-Font, M. Zanger, and C. A. VanderWerf, *J. Am. Chem. Soc.*, **86**, 2378 (1964).
(6) K. F. Kumli, W. E. McEwen, and C. A. VanderWerf, *ibid.*, **81**, 3805 (1959).
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