benzofuran (**17**),[19] a bluish green fluorescening compound, **17** is thought to be the precursor of **16** in the above reaction.

Reaction of Anhydrous HCl with *anti*-7-*t*-Butoxybenznorbornadiene (14).—Using the previously reported procedure of Story and Saunders,[17] a solution of 1.45 g (6.7 mmoles) of *anti*-7-*t*-butoxybenznorbornadiene (**14**) in 15 ml of acetyl chloride was treated in an inert atmosphere with dry hydrogen chloride gas for 10 min. The reaction mixture was then heated to boiling and refluxed for 1 hr. During reflux, dry hydrogen chloride gas was bubbled through the solution for two 5-min periods. After cooling to room temperature, the excess acetyl chloride was removed under partial vacuum and the remaining residue was chromatographed on standard alumina. Elution with hexane gave a liquid which after distillation through a micro Hickman still, bath temperature *ca.* 130° (0.20 mm), afforded 0.39 g (29%) of *anti*-7-benznorbornadienyl acetate (**18**),[2] $n^{21}\text{D}$ 1.5494.

Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 78.09; H, 6.14.

The infrared spectrum (neat) of **18** showed absorption at 5.78 (s), 6.41 (w), 6.92 (s), 7.30 (m), 8.10 (m), 13.40 (s), and 14.34 (s) μ; the nmr spectrum is listed in Table I.

Further elution with anhydrous ether gave 0.345 g (32.5%) of *anti*-7-benznorbornadienol (**2**), mp 102–105°, identical in all respects with an authentic sample.

In a similar reaction, a solution of 0.650 g (3.0 mmoles) of **14** in 10 ml of glacial acetic acid was treated with dry hydrogen chloride for a period of 10 min. The solution was then allowed to stir at room temperature for 23 hr, at which time ice and water was added and the whole was extracted several times with ether. The ether extracts were washed with 10% aqueous sodium carbonate solution and water, and then dried over anhydrous magnesium sulfate. Removal of the ether gave a crude yellow oil which was chromatographed on standard alumina using hexane to give 0.300 g (50%) of *anti*-7-benznorbornadienyl acetate (**18**). Elution with anhydrous ether gave 0.050 g (10%) of *anti*-7-benznorbornadienol (**2**).

None of the starting *t*-butyl ether **14** was recovered from either reaction, and in the reaction employing acetyl chloride as solvent, no *anti*-7-chlorobenznorbornadiene (**12**) was detected.

Acknowledgment.—The authors gratefully acknowledge the generous financial support of this research by the National Science Foundation, Grants No. GP-254 and GP-3352. Partial support of this work in its later stages by the Air Force Office of Scientific Research (AF-AFOSR-738-69) is also gratefully acknowledged.

Free-Radical Hydrogen Atom Abstractions from Substituted Cumenes

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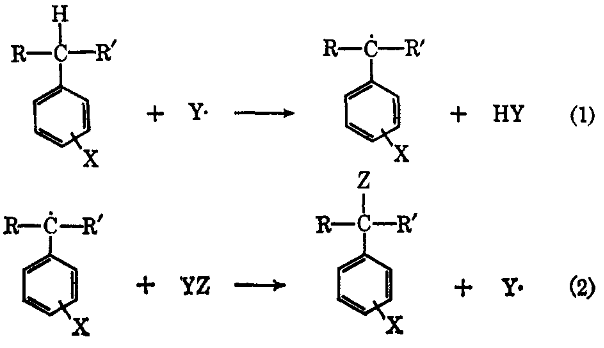
Making use of the Hammett equation, a study of the substituent effects operative in α-hydrogen abstraction from cumenes by bromine atoms and trichloromethyl radicals has been carried out. The study was conducted at 70.0°. It is felt that the ρ value of -0.38 obtained for the abstraction utilizing bromine atom represents a "normal" substituent effect. The corresponding value utilizing the trichloromethyl radical, -0.67, shows unexpected selectivity. Possible explanations for this in terms of the steric requirements of the system are offered.

The effects of ring substitution on reactions involving free-radical hydrogen abstraction from toluenes have been evaluated for several systems. Among the more common radicals which have been employed are chlorine atoms,[1,2] bromine atoms,[3-5] and the trichloromethyl radical.[6] It should be of at least equal interest to examine the relative magnitudes of these same effects in other hydrocarbon systems which also contain readily abstractable hydrogen atoms. Some studies along these lines have already appeared in the literature. All of the hydrocarbons involved may be said to undergo the reaction sequence given by eq 1 and 2. The following represent some specific examples of hydrocarbon systems other than toluenes. Martin and Gleicher have examined the abstraction by both bromine atoms and trichloromethyl radicals of the very labile hydrogen atoms in allylbenzenes.[7] Russell and Williamson have studied the oxidation of substituted cumenes by peroxy radicals.[2] More recently Huang and Lee have carried out the free-radical α-bromination of substituted ethylbenzenes.[8]



This present investigation was prompted by the appearance of the last item mentioned above. It was expected that a corresponding study on the bromination of substituted cumenes would produce a ρ value which was less than that encountered for the ethylbenzenes which, in turn, was less than that found for the toluenes.

Experimental Section

Materials.—Bromotrichloromethane (Matheson Coleman and Bell) was distilled three times and collected over the range 103.0–103.2°. Gas–liquid partition chromatography showed the presence of a single impurity comprising no more than 0.3% of the mixture. The impurity had the same retention time as carbon tetrachloride. Chlorobenzene (Matheson Coleman and Bell) was washed with dilute sulfuric acid and water and then dried over magnesium sulfate. The material was then dis-

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[1] C. Walling and B. Miller, *J. Am. Chem. Soc.*, **79**, 4181 (1957).

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

[3] E. C. Kooyman, R. van Helden, and A. F. Bickel, *Koninkl. Ned. Akad, Wetenschap, Proc. Ser. B*, **56**, 75 (1953).

[4] R. E. Pearson and J. C. Martin, *J. Am. Chem. Soc.*, **85**, 365, 3142 (1963).

[5] C. Walling, A. L. Rieger, and D. D. Tanner, *ibid.*, **85**, 3129 (1963).

[6] E. S. Huyser, *ibid.*, **82**, 394 (1960).

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

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

tilled and the portion boiling at 130.0–131.0° collected. N-Bromosuccinimide (Matheson Coleman and Bell), mp 182–183, and carbon tetrachloride (Matheson Coleman and Bell, Spectroquality Grade) were used without further purification. Cumene (Matheson Coleman and Bell), *p*-cymene (Matheson Coleman and Bell), and *p*-fluorocumene (Aldrich) were obtained commercially.

p-Nitrocumene was prepared *via* the direct nitration of cumene according to the procedure of Brown and Bonner:[9] bp 120–122° (10 mm); $n^{22}{}_{\mathrm{D}}$ 1.5360 (lit.[9] $n^{20}{}_{\mathrm{D}}$ 1.5369).

p-Carboethoxycumene was obtained by refluxing *p*-isopropylbenzoic acid with excess ethanol and 2% concentrated sulfuric acid: bp 122–124.5° (10 mm); $n^{22}{}_{\mathrm{D}}$ 1.5049 (lit.[10] $n^{20}{}_{\mathrm{D}}$ 1.5083).

m-Methoxycumene was prepared by treating a solution of freshly distilled *m*-isopropylphenol (Columbia) in aqueous sodium hydroxide with a slight excess of dimethyl sulfate. The normal work-up procedure was employed:[11] bp 90–91° (12 mm); $n^{23}{}_{\mathrm{D}}$ 1.5050 (lit.[12] $n^{19}{}_{\mathrm{D}}$ 1.5042).

p-Methoxycumene was synthesized in analogous fashion utilizing *p*-isopropylphenol prepared from cumene *via* the method of Frank, *et al.*:[13] bp 82–84° (10 mm); $n^{21}{}_{\mathrm{D}}$ 1.5062 (lit.[14] $n^{20}{}_{\mathrm{D}}$ 1.5070).

p-Cyanocumene was obtained *via* conversion of the corresponding acid to the amide followed by dehydration of the amide with phosphorus pentoxide:[11] bp 122–124° (9 mm); $n^{22}{}_{\mathrm{D}}$ 1.5192 (lit.[15] $n^{25}{}_{\mathrm{D}}$ 1.5202).

p-Chlorocumene was synthesized using the method described by Yamamoto:[16] bp 71–72° (10 mm); $n^{22}{}_{\mathrm{D}}$ 1.5123 (lit.[16] $n^{20}{}_{\mathrm{D}}$ 1.5127).

m-Nitrocumene was prepared from *p*-nitrocumene according to the reaction sequence devised by Carpenter, *et al.*:[17] bp 110–112° (12 mm); $n^{22}{}_{\mathrm{D}}$ 1.5308 (lit.[17] $n^{20}{}_{\mathrm{D}}$ 1.5301).

All of the cumenes used in these studies were redistilled before use. All had purities in excess of 97% according to gas–liquid partition chromatography.

Products.—Free-radical bromination of cumene with either N-bromosuccinimide or bromotrichloromethane should yield α-bromocumene as a product. Unfortunately, cumyl halides are known to be highly reactive compounds which readily lose a molecule of hydrogen halide, on attempted work-up, to form an α-methylstyrene system.[18] The literature already contains a specific example concerning the inability to isolate cumyl bromide from the reaction of cumene with bromotrichloromethane.[19]

In selected kinetic determinations, however, a 1:1 material balance was noted between the number of moles of cumene and the number of moles of radical source consumed. It was also possible to gain spectroscopic evidence that cumyl bromide was produced. The mixture arising from the reaction of cumene with an equimolar amount of N-bromosuccinimide in carbon tetrachloride or with an excess of bromotrichloromethane were examined *via* nmr spectra. Virtually the same spectrum was obtained in both instances. Excluding peaks which could be correlated to small amounts of unreacted cumene, and with the single proton in chloroform for the reaction with the trichloromethyl reaction, a simple spectrum was noted. The expected absorption of the aryl protons occurred at 7.16 ppm. There was also a single sharp absorption at 2.12 ppm. Making use of Shoolery's rules,[20] one may predict a value of 2.06 ppm for absorption of the methyl protons in α-bromocumene. No absorption was observed in the region 5.0–5.4 ppm which would be associated with the two, nonequivalent, terminal, olefinic protons in α-methylstyrene. It may be assumed that little, if any, elimination of hydrogen bromide from the product occurred under the conditions employed.

Procedure for Kinetic Runs Using N-Bromosuccinimide.—Solutions of two cumenes, chlorobenzene, and carbon tetrachloride were prepared in the approximate molar ratio 1:1:0.5:10. Small portions of these solutions were reserved for analysis as starting material. The remainders were added to Pyrex ampoules containing 1 equiv of N-bromosuccinimide. The ampoules were sealed and placed horizontally just under the surface of mineral oil constant temperature bath maintained at 70.0 ± 0.5°. Energy was provided by a General Electric 275-w sun lamp placed 22 cm from the surface of the oil. Reaction times varied from 4 to 7 hr by which time 30–60% of the cumenes had reacted. The ampoules were then cooled and opened and the solutions decanted from the solid materials. Analyses of the mixtures, both before and after reaction, were carried out *via* gas–liquid partition chromatography utilizing a Varian Aerograph 202B equipped with linear temperature programming and a Sargent recorder with disk integration. A 10-ft column of S.E. 30 on Chromosorb G was used throughout this investigation. All determinations were run in replicate. The usual procedure was to have some substituted cumene compete directly with the parent compound for the attacking radical. In the case of the *p*-fluoro derivative, however, it proved impossible to effect chromatographic separation of this material from cumene under the conditions employed. The rate constant for the reaction of *p*-fluorocumene was determined relative to the *p*-methyl derivative and converted into the desired form through the expression

$$\frac{k_{p\text{-F}}}{k_{\mathrm{H}}} = \frac{k_{p\text{-F}}}{k_{p\text{-CH}_3}}\,\frac{k_{p\text{-CH}_3}}{k_{\mathrm{H}}}$$

Procedure for Kinetic Runs Using Bromotrichloromethane.—The techniques employed here were completely analogous to those given above. The reaction mixtures compounded consisted of two cumenes, chlorobenzene, and bromotrichloromethane in the approximate molar ratio 1:1:0.5:10. Reaction times were from 8 to 12 hr by which time 30–50% of the reaction had occurred.

Determination of $k_{\mathrm{X}}/k_{\mathrm{H}}$.—The ratios of relative rate constants were obtained using the usual competitive procedure[5-7] in which the relative rates of disappearance for two materials are given by the expression

$$\frac{k_{\mathrm{X}}}{k_{\mathrm{H}}} = \frac{\log\,(X_{\mathrm{o}}/X_t)}{\log\,(H_{\mathrm{o}}/H_t)}$$

where X_{o} and H_{o} are the number of moles originally present of a substituted cumene and the parent compound, respectively, and X_t and H_t are the corresponding terms for the final number of moles present. The above ratios may be directly obtained from the chromatographic analyses utilizing the relationship

$$\frac{X_{\mathrm{o}}}{X_t} = \frac{(\text{area under X peak/area under chlorobenzene peak})_{\text{originally}}}{(\text{area under X peak/area under chlorobenzene peak})_{\text{finally}}}$$

Results and Discussion

The results of the relative rates of hydrogen abstraction from substituted cumenes by bromine atoms and trichloromethyl radicals are given in Table I. It is immediately observable that the presence of electron-donating groups in the aromatic ring facilitates the removal of the labile hydrogen atom in both cases. Table II presents the results of correlation of the kinetic data within the framework of the Hammett linear free-energy relationships. Correlations were made utilizing both the "normal" σ function and the σ^+ function originated by Brown and coworkers for carbonium ion reactions. Figure 1 shows a plot of the logs of the relative rate constants for reaction with bromine plotted against σ. Figure 2 shows the corresponding reaction with the trichloromethyl radical plotted against σ^+.

As regards these correlations, the situation in these reactions is quite unlike that encountered in the

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(9) H. C. Brown and W. H. Bonner, *J. Am. Chem. Soc.*, **76**, 605 (1954).

(10) R. L. Herbst and M. E. Jacox, *ibid.*, **74**, 3004 (1952).

(11) A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., London, 1959.

(12) W. J. Hickenbottom and N. W. Rogers, *J. Chem. Soc.*, 4124 (1957).

(13) R. L. Frank, R. E. Berry, and O. L. Shotwell, *J. Am. Chem. Soc.*, **71**, 3889 (1949).

(14) V. Tambovtseva and I. Tsukervanik, *J. Gen. Chem. USSR*, **15**, 820 (1945); *Chem. Abstr.*, **41**, 732e (1947).

(15) T. L. Brown, *J. Am. Chem. Soc.*, **81**, 3232 (1959).

(16) T. Yamamoto, *Bull. Chem. Soc. Japan*, **40**, 642 (1967).

(17) M. S. Carpenter, W. M. Foster, and T. F. Wood, *J. Org. Chem.*, **16**, 586 (1951).

(18) H. C. Brown, J. D. Brady, M. Grayson, and W. H. Bonner, *J. Am. Chem. Soc.*, **79**, 1897 (1957), and subsequent papers.

(19) E. S. Huyser, *ibid.*, **82**, 391 (1960).

(20) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Ltd., London, 1959, p 53.

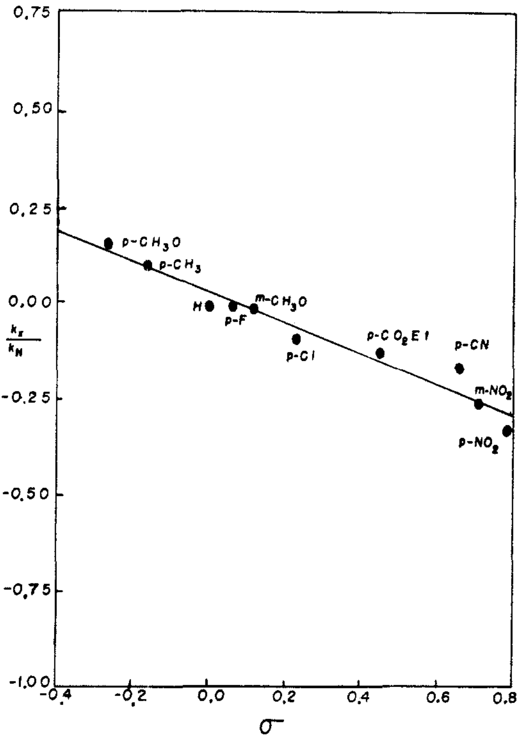


Figure 1.—Correlation of log k_X/k_H and σ for hydrogen abstraction from substituted cumenes by bromine atoms.

Table I
RELATIVE RATES OF BENZYLIC HYDROGEN ABSTRACTION FROM SUBSTITUTED CUMENES AT 70.0°

Substituent	σ[a]	σ^+ [b]	k_X/k_H $Cl_3C\cdot$	d	k_X/k_H $Br\cdot$	d
p-CH_3O	−0.268	−0.778	2.59 ± 0.04[c]	4	1.45 ± 0.06	6
p-CH_3	−0.170	−0.311	2.10 ± 0.05	4	1.27 ± 0.04	5
H	0	0	1.00		1.00	
p-F	0.062	−0.073	1.06 ± 0.01	5	1.00 ± 0.01	4
m-CH_3O	0.115	0.047	0.97 ± 0.04	4	1.00 ± 0.03	3
p-Cl	0.227	0.114	0.73 ± 0.04	4	0.83 ± 0.01	4
p-CO_2Et	0.450	0.482	0.53 ± 0.02	3	0.77 ± 0.02	4
p-CN	0.660	0.659	0.33 ± 0.03	4	0.70 ± 0.01	5
m-NO_2	0.710	0.674	0.31 ± 0.02	4	0.56 ± 0.02	4
p-NO_2	0.778	0.790	0.28 ± 0.04	4	0.48 ± 0.02	4

[a] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and 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.

Table II
ρ VALUES FOR HYDROGEN ABSTRACTION FROM SUBSTITUTED CUMENES AT 70.0°

Radical	Substituent constant	ρ	r[a]
$Br\cdot$	σ	−0.38 ± 0.02[b]	−0.974
$Br\cdot$	σ^+	−0.29 ± 0.04	−0.958
$Cl_3C\cdot$	σ	−0.89 ± 0.04	−0.988
$Cl_3C\cdot$	σ^+	−0.67 ± 0.04	−0.984

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

toluenes.[5,6] There, for both the bromine atom hydrogen abstraction and the abstraction by the trichloromethyl radical, a much better correlation was rendered by σ^+. For the cumenes this is not the case. As regards the reaction with the trichloromethyl radical, there is virtually nothing to choose between the two correlations given in Table II. It can also be seen that for the abstraction by bromine atoms an appreciably better correlation is found when the "normal" function is utilized. These findings in themselves should not be surprising. Those hydrogen abstraction reactions of electrophilic radicals which correlate better with the σ^+ function are those which proceed through a transition state in which there is already pronounced carbon–hydrogen bond breakage. Only in such cases should the transition state have the carbonium ion-like character which would require the use of σ^+.[21] It can be argued from Hammond's postulate[22] that in cases in which the transition state more closely resembles the starting material rather than the intermediate, there should be little carbonium ion-like character present and correlation with the "normal" σ function would be expected.

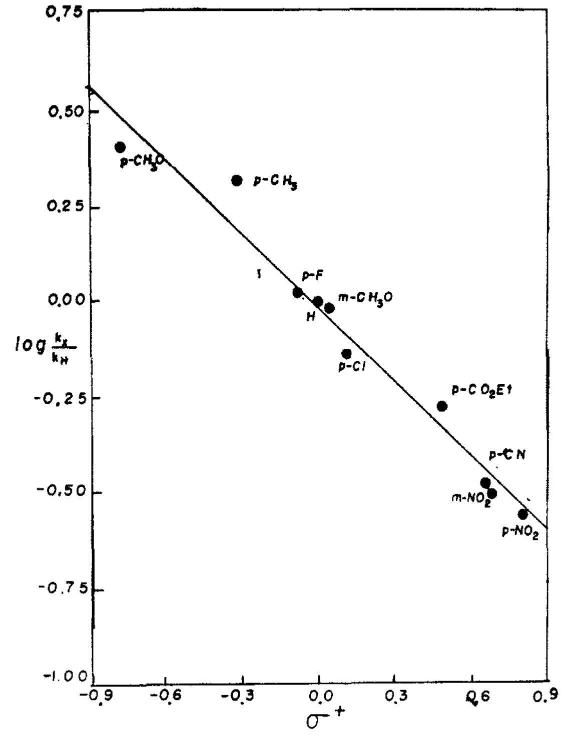


Figure 2.—Correlation of log k_X/k_H and σ^+ for hydrogen abstraction from substituted cumenes by trichloromethyl radicals.

There can be some exception taken to the above criterion that correlation with σ^+ rather than σ implies a greater degree of bond breakage in the transition state for a given reaction. Bridger and Russell have studied hydrogen atom abstraction *via* phenyl radicals and have shown that when substituted toluenes are used as the substrates almost no polar effect for the reaction is observed.[23] At the same time, however, primary isotope effect studies show a large degree of bond breaking in the transition state. It is still possible, however, to give some justification for utilizing the conceptualism given in the previous paragraph. The ρ value of −0.1 which Bridger and Russell reported for the reaction of substituted toluenes with phenyl radicals is based upon only six points and is small. The combination of these factors makes it very difficult to say whether σ or σ^+ will provide the better correlation. The phenyl radical is also very different in nature from the halogen atoms and trichloromethyl radical considered so far.

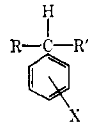
(21) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **41**, 1744 (1963).
(22) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).
(23) R. F. Bridger and G. A. Russell, *ibid.*, **85**, 3754 (1963).

The phenyl radical has a much greater degree of nucleophilic character associated with it. This may be shown by the results of various phenylations of substituted benzenes.[24] It is conceivable that the lack of a pronounced polar effect for the above reaction might be traceable to this. In any case the results obtained by Bridger and Russell for the phenyl radical, while best regarded as an exception to the formulation of Howard and Ingold,[21] have only tangential bearing on this study.

Table III presents a compilation of ρ values for benzylic hydrogen atom abstraction from hydrocarbons by bromine atom and trichloromethyl radical. Although these studies were carried out at different temperatures, these are sufficiently close to allow for direct comparison. The ρ values obtained in this study are appreciably smaller than those found in the reactions of toluenes with the same radicals. This can best be regarded as a consequence of the radical-stabilizing effects of increased alkyl substitution at the reaction site.[21,25] The findings presented here are particularly gratifying concerning the reaction with bromine atom. Huang and Lee[8] have examined the ρ values for hydrogen abstraction by bromine from systems containing α-alkoxy groups as well as hydrogen atoms and alkyl groups. A comparison was made between these values and the rates of abstraction from the unsubstituted systems relative to toluene.[5,7,26–28] The benzylic hydrogen in cumene is 50 times more labile toward abstraction than a hydrogen atom in toluene.[5] For α,α-dimethoxytoluene the corresponding value is 50.6 and the substituent dependence is −0.38.[8] Thus the ρ value reported here for the reaction of bromine atom with cumene is in more or less perfect agreement with expectation. Successive substitution of methyl groups for α-hydrogen atoms in toluene apparently decreases the substituent dependence by a factor of 0.5 per methyl group. Using the arguments previously advanced, this trend may be due to the degree of bond breaking in the transition state. Substantiation for this is found in the primary isotope effect for this reaction. The ratio k_H/k_D for the reaction of bromine atom with the series toluene, ethylbenzene, and cumene at a comparable temperatures is 4.86, 2.67, and 1.81, respectively.[29]

TABLE III

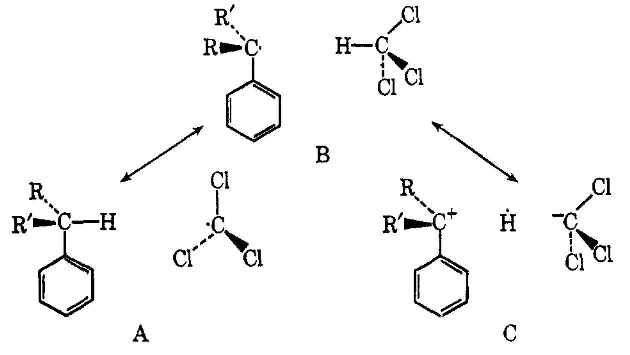
ρ VALUES FOR BENZYLIC HYDROGEN ABSTRACTION FROM



R	R′	Br· ρ		Cl$_3$C· ρ	
H	H	−1.39[a]	(80.0)[b]	−1.46[a]	(55.0)[c]
CH$_3$	H	−0.69[a]	(80.0)[d]	...	...
CH$_3$	CH$_3$	−0.38	(70.0)	−0.67[a]	(70.0)
CH$_2$=CH	H	−0.76[a]	(69.5)[e]	−0.63[f]	(69.5)

[a] Correlation with σ^+. [b] See ref 5. [c] See ref 6. [d] See ref 8. [e] See ref 7. [f] Recalculated from data in ref 7 using σ, r = −0.993.

Contrasted with what was felt to be the predictable behavior of bromine atoms in the reaction with cumenes, the results obtained using the trichloromethyl radical appear anomalous. Although it has been claimed that the trichloromethyl radical is inherently slightly more selective than bromine atom,[26,30] there is some doubt as to whether this is indeed the case. When allowance is made as to the different temperatures at which results have been obtained, studies on the toluenes[5,6] and allylbenzenes[7] indicate that this radical is slightly less selective than bromine atom. The ρ value of −0.67 obtained in this study for the reaction of cumenes with trichloromethyl radicals appears, therefore, unusually large. It is possible to explain this enhanced selectivity in terms of possible steric interactions present. Assuming a planar structure for the trichloromethyl radical, its effective diameter, based upon generally accepted values for atomic covalent radii,[31] is twice as great as that of the bromine atom. Nonbonded interactions between this radical and the α-methyl groups in cumene may be severe. This concept may be utilized in the framework of either the transition state theory or the collision theory. In the latter the attacking radical may be constrained to approach the cumene molecule only along the axis of the carbon–hydrogen bond. Any such constraint should increase the selectivity of the system. Alternatively, making use of the usual representation for the transition state of the hydrogen atom abstraction shown below,[32] it follows that the nonbonded interactions would tend to keep the radical and the cumene further apart in space and therefore lead to a greater than expected degree of bond breaking in the transition state. This would also explain the ability to correlate the kinetic data for trichloromethyl radical abstraction with σ^+ while bromine atom correlates only with σ.



It should be pointed out that a second explanation for correlation with σ^+ exists.[33] The correlation may *not* indicate appreciable carbonium ion character as shown by canonical structure C above. Instead, an enhanced ability of certain substituents to favor electron transfer by allowing for a large contribution of canonical form B to the hybrid structure may be

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(24) G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, Inc., New York, N. Y., 1960, p 57.

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

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

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

(28) R. L. Huang and K. H. Lee, *J. Chem. Soc.*, *Sect. C*, 932 (1966).

(29) K. B. Wiberg and L. H. Slaugh, *J. Am. Chem. Soc.*, **80**, 3033 (1958).

(30) G. A. Russell, C. DeBoer, and K. M. Desmond, *ibid.*, **85**, 3136 (1963).

(31) E. S. Gould, "Inorganic Reactions and Structure," Henry Holt and Co., New York, N. Y., 1955, p 442.

(32) W. A. Prior, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, p 172 ff.

(33) Thanks are given to a referee for pointing this out.

operative.[34] Support for this view is to be found in the studies of polarographic reduction of certain benzylic compounds.[35,36] If the idea that steric hindrance is a key factor in the reaction of cumenes with the trichloromethyl radical is correct, it would appear, however, that correlation with σ^+ does, at least partially, indicate a greater degree of bond breaking in the transition state than "expected."

One experimental finding may be offered in support of the steric explanation advanced above. Despite the fact that trichloromethyl radicals and bromine atoms usually show similar selectivity in benzylic hydrogen abstraction, methyl α-methoxyphenylacetate undergoes no reaction with the trichloromethyl radical while the reaction with the bromine atom is comparable to ethylbenzene on a mole-to-mole basis.[28] This may be directly attributable to the steric requirements of the radical–substrate system. Against the steric interpretation offered here there stands the fact that selectivity ratios among aliphatic primary, secondary, and tertiary hydrogen atoms are nearly identical for reaction with bromine atom[37,38] and trichloromethyl radical.[39] It should be pointed out, however, that these determinations were conducted at higher temperatures. They also refer to gas-phase reactions while the attacking radicals in the reactions described in this report may be effectively larger due to solvation. Future experiments are planned in which the steric bulk at the reaction sites of both the hydrocarbon and the attacking radical will be systematically varied to test this hypothesis.

Registry No.—Bromine atom, 10097-32-2; trichloromethyl radical, 3170-80-7.

Acknowledgments.—Thanks are extended to the Office of the Dean of Research of Oregon State University for supplying the necessary funds for this project. Appreciation is also expressed to Mr. Jerry D. Unruh for obtaining the nmr spectra needed and to Professor John L. Kice for a helpful discussion of these results.

[34] R. D. Gilliom and B. F. Ward, Jr., *J. Am. Chem. Soc.*, **87**, 3944 (1965).

[35] G. Klopman, *Helv. Chim. Acta*, **44**, 1908 (1961).

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

[37] G. C. Fettis, J. H. Knox, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 4177 (1960).

[38] P. C. Anson, P. S. Fredricks, and J. M. Tedder, *ibid.*, 918 (1959).

[39] B. P. McGrath and J. M. Tedder, *Bull. Soc. Chim. Belges*, **71**, 772, (1962).

Reactions of Phosphorus Compounds. XIII. Preparations and Reactions of Cyclopropyltriphenylphosphonium Bromide

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Cyclopropyltriphenylphosphonium bromide (I) was prepared by a variety of methods. The corresponding cyclopropylidene compounds were prepared from benzaldehyde, cyclohexanone, and cyclopentanone. Reaction of salt I with the sodium salt of salicylaldehyde gave 2,3-dihydro-1-benzoxepin (XIII) and 2-methyl-3-chromene (XIV).

In an earlier communication,[1] we reported preparations of cyclopropyltriphenylphosphonium bromide (I) and its reactions with cyclohexanone and benzaldehyde to give cyclopropylidenecyclohexane (VI) (47%) and benzylidenecyclopropane (V) (60% yield), respectively.

In view of the considerable interest shown[2–4] recently in the preparation and reactions of salt I, we wish to report completely our experimental data on the above-mentioned reactions and other related work including a rather unique preparation of 2,3-dihydro-1-benzoxepin (XIII) and 2-methyl-3-chromene (XIV).

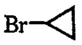
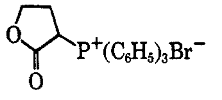
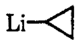
The reported preparations of salt I are listed in Table I and in the Experimental Section.

Lithium aluminum hydride reduction of the salt I gave cyclopropyldiphenylphosphine (II) which had previously been prepared by Bestmann and coworkers[2a] by the electrolytic reduction of I.

I II

Table I

Preparations of Cyclopropyltriphenylphosphonium Bromide (I)

Reactants	Reaction conditions	Yield of I, %
$(C_6H_5)_3P$ + 	*a*	<1
$C_6H_5O(CH_2)_3P^+(C_6H_5)_3Br^-$ + *n*-BuLi	*b*	19
	*c*	99+
$Br(CH_2)_3P^+(C_6H_5)_3Br^-$ + NaH	*d*	78
$(C_6H_5)_4PBr$ + 	*e*	35

[a] No solvent; sealed tube at 150°, 1 week. [b] In tetrahydrofuran (THF). [c] Thermal decomposition *in seco*, according to the method of Bestmann.[2a] [d] In dimethylformamide (DMF)–THF; 10/90; stirred 3 days at room temperature. [e] Method reported recently by Longone;[4] not attempted by us in the course of our investigation.

The cyclopropyldiphenylphosphine oxide (IV) was readily prepared in 96% yield in our laboratory[5] by treating the cyclopropylphosphonium salt, I, with

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[1] E. E. Schweizer and J. G. Thompson, *Chem. Commun.* (London), 666 (1966); previous paper in this series.

[2] (a) H. J. Bestmann, H. Hartung, and I. Pils, *Angew. Chem. Intern. Ed. Engl.*, **4**, 957 (1965); (b) H. J. Bestmann and T. Denzel, *Tetrahedron Letters*, 3591 (1966).

[3] K. Sisido and K. Utimoto, *ibid.*, 3267 (1966).

[4] D. T. Longone and R. R. Doyle, *Chem. Commun.* (London), 300 (1967).

[5] This is in contrast to Bestmann's results where a *n*-butyl for phenyl exchange occurred[2b] (conditions not specified).