Saponification.—In 25 ml. of ethanol was dissolved 20 g. (0.05 mole) of IX. The solution of 2.5 g. of potassium hydroxide in 5 ml. of water and 25 ml. of ethanol was added with agitation at room temperature. The clear solution was heated for 3 hr. at 50°. During this time two phases formed. The lower, oily phase was separated at room temperature, taken up in ether, washed with water, and dried over sodium sulfate. Ether was evaporated, and the remaining colorless oil was purified by high vacuum distillation. VII was obtained in 78% yield (14.2 g.).

A Hammett Study of Hydrogen Abstraction from Substituted Allylbenzenes

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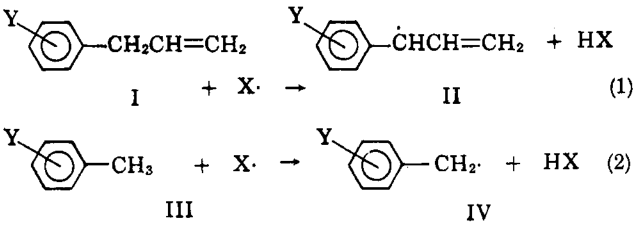
This study is a comparison of the polar effects operating in the abstraction of a hydrogen atom from a series of substituted allylbenzenes (reaction 1) and the more extensively investigated abstraction of a hydrogen atom from substituted toluenes (reaction 2).[2-7] The greater stability of the α-vinylbenzyl radical (II) compared to the benzyl radical (IV) would be expected to compress the activation energy scale for reaction 1 compared to reaction 2, and thereby decrease the effect of a polar substituent on reaction rate in the case of the allylbenzenes. In order to determine the extent to which this effect is reflected in the magnitude of the Hammett ρ-value for reaction 1 as compared to reaction 2, reaction constants have been determined for abstraction of a hydrogen atom from allylbenzenes by the trichloromethyl radical, generated from bromotrichloromethane, and by the bromine atom, generated from N-bromosuccinimide.[8]



Experimental

Materials.—The **substituted allylbenzenes** were all prepared by the coupling reaction of allyl bromide with an aryl Grignard reagent. The procedural details and properties of these compounds are reported elsewhere.[10] The **N-bromosuccinimide** was purified by recrystallization from petroleum ether (80°–100°), m.p. 179°. **Chlorobenzene** was purified by shaking with three portions of sulfuric acid, once with water, three times with 5% sodium bicarbonate, again with water, drying successively over calcium chloride, calcium sulfate, and phosphorus pentoxide, and distilling, b.p. 130–130.5°. Merck, Reagent **carbon tetrachloride** was used without further purification.

Products.—A mixture of 17.3 g. (0.147 mole) of allylbenzene, 26.1 g. (0.146 mole) of N-bromosuccinimide, and 100 ml. of carbon tetrachloride under nitrogen was refluxed for 24 hr. while being irradiated by a 275-w. General Electric sun lamp directed through the side of the reaction flask. At the end of this time the solution was cooled, whereupon 13.65 g. (94%) of succinimide, m.p. 124.5–126.5° (lit.[11a] 125–126°), separated. Solvent was removed from the liquid filtrate by distillation at reduced pressure, and the residue distilled through a Vigreux column, giving 25.8 g. (89%) of a liquid identified as cinnamyl bromide, b.p. 120–124° (30 mm.), m.p. 29° (lit.[11b] 31°). Vapor phase chromatography on a diethylene glycol succinate column indicated only one component, and the infrared spectrum was devoid of any absorption bands which would be characteristic of the possible isomeric product, phenylvinylcarbinyl bromide.

These results confirm the contention that the dominant reaction of an olefin with N-bromosuccinimide is allylic hydrogen abstraction and not addition to the double bond, and justifies the assumption in the kinetic studies that olefin disappears only by hydrogen abstraction without significant competition by addition.

Procedure for Kinetic Runs Using N-Bromosuccinimide.—Equimolar quantities of two allylbenzenes, N-bromosuccinimide and chlorobenzene (present as an inert internal standard for v.p.c. analysis) were sealed under a nitrogen in small Pyrex ampoules and placed in a horizontal position just beneath the surface of an oil bath maintained at 69.5 ± 0.2° and irradiated by a General Electric 275-w. sun lamp placed 19 cm. from the surfaces until anywhere from 45 to 70% of the total number of moles of allylbenzenes present had been consumed. An irradiation time of about 5 to 5.5 hr. was employed. After the ampoules had cooled, they were opened, the liquid portion decanted from undissolved solids, and analyses conducted by v.p.c. on a 6-ft. 10% diethylene glycol succinate column. *p*-Dimethylamino-, *p*-methoxy-, *p*-phenyl-, *m*-methoxy-, *p*-chloro-, and *m*-chloroallylbenzene were run in competition with the unsubstituted allylbenzene, whereas *p*-methyl-, *m*-methyl-, *p*-fluoro-, *p*-trifluoromethyl- and *m*-trifluoromethylallylbenzene were run against *m*-chloroallylbenzene to give better separation on v.p.c., and therefore better analytical results. The ratio of rate constants relative to the unsubstituted compound was then calculated from the expression

$$\frac{k_X}{k_0} = \frac{k_X}{k_{m\text{-Cl}}} \times \frac{k_{m\text{-Cl}}}{k_0}$$

where k_X is the rate constant for the substituted allylbenzene in question, k_0 the rate constant for the unsubstituted allylbenzene and $k_{m\text{-Cl}}$ the rate constant for *m*-chloroallylbenzene.

Determination of k_x/k_0.—The rate of hydrogen abstraction from the substituted compound relative to the unsubstituted compound was calculated from the expression

$$\frac{k_X}{k_0} = \frac{\log X_0/X_f}{\log U_0/U_f}$$

where X_0 and U_0 are the number of moles initially present of substituted and unsubstituted allylbenzene, respectively, and X_f and U_f are the number of moles present at the end of the irradiation period. The ratios X_0/X_f and U_0/U_f were determined by v.p.c. analysis from the expression

$$\frac{X_0}{X_f} = \frac{(\text{area under X peak/area under } C_6H_5Cl \text{ peak})_{\text{initially}}}{(\text{area under X peak/area under } C_6H_5Cl \text{ peak})_{\text{finally}}}$$

and the analogous one for the unsubstituted olefin. Areas were determined with the aid of a disk integrator.

Procedure for Kinetic Runs Using Bromotrichloromethane.—The experiments from which reactivity ratios for hydrogen abstraction by the trichloromethyl radical were determined are described elsewhere.[10] The results are included in this note for

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[1] Petroleum Research Fund Predoctoral Fellow, 1961–1962 and 1962–1963.

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

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

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

[5] C. Walling and B. Jacknow, *ibid.*, **82**, 6113 (1960).

[6] G. A. Russell, *ibid.*, **78**, 1047 (1956).

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

[8] Recent studies[4,9] have demonstrated that the bromine atom is the hydrogen abstracting species in benzylic brominations involving N-bromosuccinimide, and not the N-succinimidyl radical as had been originally believed.[2]

[9] G. A. Russell, C. DeBoer, and K. M. Desmond, *J. Am. Chem. Soc.*, **85**, 365 (1963).

[10] M. M. Martin and G. J. Gleicher, *ibid.*, in press.

[11] (a) I. Heilbron, "Dictionary of Organic Compounds," Vol. 4, Oxford University Press, London, England, 1953, p. 384; (b) Vol. 1, p. 364.

the sake of completeness and comparison with the studies using N-bromosuccinimide.

Calculations.—The Hammett ρ-values were calculated from least squares slopes of the lines resulting from plots of log k_X/k_0 *vs.* σ^+ or *vs.* σ°. The expected errors in ρ and the correlation coefficients were calculated by standard statistical methods.[12]

Relative Reactivity of Allylbenzene and Toluene toward N-Bromosuccinimide.—The procedure and calculations were the same as those employed to study relative reactivities of the various allylbenzenes.

Results and Discussion

In Table I are presented the relative rates of hydrogen abstraction from allylbenzenes by bromine atoms and trichlormethyl radicals. From the data in this Table it is possible to calculate reaction constants, that is ρ-values, for these reactions. The ρ-values, obtained by calculating the slopes of the regression lines resulting from plots of log k_X/k_0 *vs.* σ^+ or σ^0 are presented in Tables II and III. In the reaction with N-bromosuccinimide, the allylbenzenes were studied at a lower temperature than the toluenes (69.5° compared with 80°), whereas in the reaction with bromotrichloromethane, the allylbenzenes were studied at a higher temperature than the toluenes (69.5° compared with 50°). Since the magnitude of a ρ-value varies inversely with temperature below the isokinetic temperature, the ρ-values for the two systems in their reactions with N-bromosuccinimide would be further apart if studied at the same temperature than they are at the temperatures indicated in Table II, whereas for the reaction with bromotrichloromethane, the ρ-values would be nearer to each other in magnitude when studies at the same temperature, then they are at the temperatures indicated in Table III. Making allowances for the differences in temperatures at which these studies have been conducted, it would appear that hydrogen abstraction reactions from allylbenzenes have Hammett ρ-values of the order of one half to one-third as great in magnitude as those for abstraction from toluenes by the same radical.

Table I

Relative Rates of Abstraction of a Hydrogen Atom from Substituted Allylbenzenes by a Bromine Atom and a Trichloromethyl Radical at 69.5°

Substituent	σ^{0a}	σ^{+b}	k_X/k_0 (Br·)	k_X/k_0 (Cl$_3$C·)^c
p-$(CH_3)_2N$	−0.44	−1.700	20.9 ± 0.07^d	
p-CH_3O	−0.16	−0.778	3.23 ± 0.20	1.46 ± 0.07^d
p-CH_3	−0.15	−0.311	1.89 ± 0.04	1.42 ± 0.03
p-C_6H_5	0.00	−0.179	1.70 ± 0.03	1.02 ± 0.08
p-F	+0.17	−0.073	1.08 ± 0.02	0.94 ± 0.03
m-CH_3	−0.07	−0.060	1.29 ± 0.13	1.15 ± 0.04
H	0.00	0.000	1.000	1.000
m-CH_3O	+0.13	+0.047	1.02 ± 0.01	0.82 ± 0.01
p-Cl	+0.27	+0.114	0.78 ± 0.05	0.78 ± 0.05
m-Cl	+0.37	+0.339	0.50 ± 0.06	0.60 ± 0.01
m-CF_3	+0.42^e	+0.562	0.40 ± 0.01	0.54 ± 0.02
p-CF_3	+0.55^e	+0.612	0.36 ± 0.01	0.47 ± 0.01

^{a} R. W. Taft, *J. Phys. Chem.*, **64,** 1805 (1960). ^{b} H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80,** 4979 (1958). ^{c} See ref. 10. ^{d} Average deviation. ^{e} σ^0 values are not available for *m*- and *p*-CF_3, but for strongly electron-withdrawing groups, $\sigma \approx \sigma^0$. The values indicated are σ values; J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 72.

Table II

ρ-Values for the Reactions, $Br\cdot + C_6H_5CH_2R \longrightarrow HBr + C_6H_5\dot{C}HR$

R	Temp., °C.	$\rho^a(r^b)$
CH=CH$_2$	69.5	−0.76 ± 0.03 (−0.99)
H^c	80.0	−1.39 ± 0.03 (−0.99)

^{a} Calculated using σ^+. ^{b} Correlation coefficient. ^{c} ref. 4.

Table III

ρ-Values for the Reactions, $Cl_3C\cdot + C_6H_5CH_2R \longrightarrow HCCl_3 + C_6H_5\dot{C}HR$

R	Temp., °C.	$\rho^a(r^b)$	$\rho^c(r^b)$
CH=CH$_2$	69.5	−0.39 ± 0.03 (−0.94)	−0.58 ± 0.03 (−0.99)
H^d	50.0	−1.46	−1.72 (−0.99)

^{a} Calculated using σ^+. ^{b} Correlation coefficient. ^{c} Calculated using σ^0. ^{d} See ref. 7.

It was also found that allylbenzenes is 17.5 ± 1.1 times as reactive toward hydrogen abstraction by the bromine atom as toluene at 69.5°, reflecting the stabilizing effect of the α-vinyl group. Comparing this figure with data recently published by Russell, Deboer, and Desmond,[9] it would appear that a hydrogen atom is more easily abstracted by a bromine atom from allylbenzene than from diphenylmethane. This is probably a consequence of the greater difficulty with which coplanarity is approached by the two phenyl groups of the diphenylmethyl radical compared to the phenyl group and vinyl group of the α-vinylbenzyl radical.

Acknowledgment.—It is a pleasure to thank the Donors of the Petroleum Research Fund for a grant (PRF-603A) which financed the greater part of this work.

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[12] W. J. Gore, "Statistical Methods for Chemical Experimentation," Interscience Publishers, Inc., New York, N. Y., 1952, Chap. 6.

Derivatives of 2-Benzyl-1-indanone. Competing Alicyclic and Aromatic Monobromination

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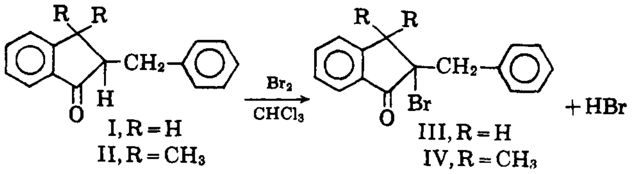
It has been shown previously that treatment of 2-benzyl-1-indanone (I) or 2-benzyl-3,3-dimethyl-1-indanone (II) with an equimolar quantity of bromine in chloroform leads to an excellent yield of the corresponding 2-bromo-2-benzyl-1-indanone.[2,3] The product controlling factor is the activating influence of the carbonyl group.



I, R = H
II, R = CH$_3$

III, R = H
IV, R = CH$_3$

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[1] To whom communications concerning this paper should be addressed.

[2] N. H. Cromwell and R. P. Ayer, *J. Am. Chem. Soc.*, **82**, 133 (1960).

[3] B. D. Pearson, R. P. Ayer, and N. H. Cromwell, *J. Org. Chem.*, **27**, 3038 (1962).