

averaging 93% of NBS reacted with the toluene experiments and 86% in the other systems. Considering that some polybromination and NBS decomposition to β -bromopropionyl isocyanate must be occurring, the agreement is very satisfactory.

Bromine Reactions.—The data of Table IV were obtained by direct competition reactions, essentially as in the case of NBS; relative reactivities (per molecule), ethylbenzene:toluene, 8.70, 8.27. The competitive bromination of ethylbenzene and toluene by NBS in the presence of 6 mole % added bromine was also carried out directly: relative reactivity per molecule, ethylbenzene:toluene 7.74, 7.79, 10.21, 8.24.

Detection of β -Bromopropionyl Isocyanate.—Decomposition of 0.1 mole of NBS in dry refluxing chloroform in the presence of 2 mole % benzoyl peroxide and 10 mole % allyl chloride gave a reaction mixture with an infrared spectra showing the peaks reported for β -bromopropionyl isocyanate.³⁰ Removal of solvent and treatment of the residue with methanol gave 11.3 g. of β -

bromopropionyl carbamate after recrystallization from methanol; m.p. 132–134.5 (lit.³¹ 137–138°). The isocyanate was also detected by infrared spectra (but not determined quantitatively) in decompositions run in methylene chloride with and without allyl chloride, and its characteristic odor noted in other systems containing relatively unreactive substrates.

NBS Reactions in Presence of Olefins.—Typically 380 mg. of NBS and 0.320 ml. each of toluene, *o*-xylene, and ethylbenzene were allowed to react in the presence of 0.4 mg. of AIBN, 0.320 ml. of olefin, 2.60 ml. of CCl₄, and 0.320 ml. of chlorobenzene as an internal standard. Reactions took 90 min. for complete reaction as compared with 45 min. in the absence of olefin. Products were analyzed as before. Little olefin (0–10%) was consumed, but *trans*-dichloroethylene underwent 70–74% isomerization to *cis*. Similar experiments in the presence of either 0.320 or 0.032 ml. of styrene showed no significant reaction in 6 hr. at 80° at which time the initiator was essentially exhausted.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NEW YORK 27, N. Y.]

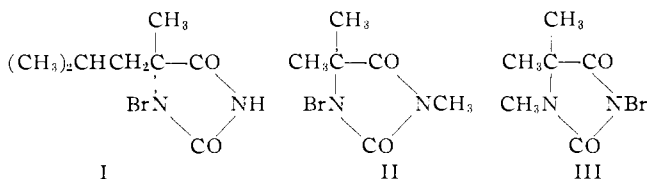
Positive Halogen Compounds. IX. Structure and Reactivity in Halogenation with Some Further N-Haloamides¹

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Relative reactivities of a series of hydrocarbons toward bromination with three N-bromohydantoins and N-bromoacetamide have been determined and compared with results from N-bromosuccinimide bromination. Relative reactivities for ethylbenzene:toluene are quite similar (6–15) and ρ -values for substituted toluenes appear within experimental error (–1.10 to –1.36). It is concluded that all reactions occur most probably through bromine atom chains. Relative reactivity of cyclohexane:toluene toward N-chlorosuccinimide is 3.9 ± 0.3 , indicating a chlorine atom chain in this case.

Although they have attracted much less attention and received less use than N-bromosuccinimide (NBS), a number of other N-haloamides are known to act as effective halogenating agents for the replacement of allylic and benzylic hydrogen by what are quite evidently free radical chain processes. In particular, the series of N-bromohydantoins have been studied in some detail by Orazi,³ and an allylic bromination by N-bromoacetamide (NBA) was reported as early as 1919 by Wohl.⁴ It accordingly seemed worthwhile to extend our studies with NBS⁵ to a series of other such N-haloamides, both to see whether differences in selectivity exist which would be of synthetic interest, and to identify if possible the chain carriers in the radical reactions involved. This paper reports an investigation of the reactions of 1-bromo-5-isobutyl-5-methylhydantoin (I), 1-bromo-3,5,5-trimethylhydantoin (II), 3-bromo-1,5,5-trimethylhydantoin (III), N-bromoacetamide (NBA), and N-chlorosuccinimide.



Results and Discussion

Substituted Toluenes.—Relative reactivities of substituted toluenes toward the four N-bromoamides mentioned above were determined in CCl₄ solution at 80°, using azobisisobutyronitrile as initiator, essentially as in our work with NBS, employing stepwise comparisons when compounds differed markedly in

reactivity. Results are summarized in Table I together with our NBS results.⁵ Experimental errors are average deviation of the mean for duplicate experiments unless a larger number is indicated in parentheses. The Hammett ρ - σ relation was investigated for each N-bromoamide, and it was found in every case (as with NBS) that σ^+ -constants⁶ gave a better correlation with the data than did σ -constants. Values of ρ and r (the correlation coefficient) and s (standard deviation from the regression line) are included in the table. The close similarity of ρ 's for the different brominating agents strongly suggest a common radical chain carrier. In fact, treating all of the data as applying to a single reaction yields $\rho = -1.27$ with $r = 0.945$, $s = 0.15$. A similar comparison has recently been carried out for several substituted N-bromosuccinimides by Martin,⁷ and, since NBS and Br₂ also show parallel reactivities,^{5,7,8} he concludes that a bromine atom chain is involved in all his systems. The good fit of all of our data (including that on NBS) to a single ρ -value points to a similar conclusion here, further supported by the results described in the next section.

Other Hydrocarbons.—Relative reactivities of some other hydrocarbons are listed in Table II. The most critical reactivity is that of ethylbenzene, and values are again seen to be very close in all systems. Data for saturated hydrocarbons are subject to considerable uncertainty and may represent merely orders of magnitude. In any case, the results again support the hypothesis of a common bromine atom chain as the major reaction path, and suggest that as far as selectivity is concerned, all of the N-haloamides are equivalent for synthetic purposes.

N-Chlorosuccinimide.—The participation of chlorine atom chains in chlorinations involving N-chlorosuccinimide was first proposed by Goldfinger⁹ and has been supported by deuterium isotope effect measurements by

(1) Taken from the Ph.D. Dissertation of Anne L. Rieger, Columbia University, 1962. Support of this work by a grant from the National Science Foundation is gratefully acknowledged.

(2) Socony Mobil Oil Co. Fellow 1960–1961.

(3) O. O. Orazi and J. Meseri, *Anales asoc. quim. argentina*, **37**, 142 (1949), and subsequent papers.

(4) A. Wohl, *Ber.*, **52B**, 51 (1919).

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

(6) H. C. Brown and Y. Okamoto, *ibid.*, **80**, 4979 (1958).

(7) R. E. Pearson and J. C. Martin, *ibid.*, **85**, 354 (1963).

(8) G. A. Russell, C. De Boer, and K. M. Desmond, *ibid.*, **85**, 365 (1963).

(9) J. Adam, P. A. Gosselain, and P. Goldfinger, *Nature*, **171**, 704 (1953).

TABLE I
RELATIVE REACTIVITIES OF SUBSTITUTED TOLUENES TOWARD N-BROMOAMIDES IN CCl₄ AT 80°, PER BENZYL HYDROGEN

Toluene	Relative reactivities—				
	NBS ^a	I	II	III	NBA
<i>p</i> -OCH ₃	11.7	12.6 ± 0.5	6.75	5.7 ± 0.2	8.2 ± 0.4
<i>p</i> -CH ₃	2.56	2.33 ± .03	1.59	1.34 ± .02	1.21 ± 0.01
<i>m</i> -CH ₃	1.52	1.80 ± .08	1.18	1.06 ± .02	...
H (std.)	1.00	1.00	1.00	1.00	1.00
<i>m</i> -OCH ₃	0.75	...	0.88 ± 0.05(4)
<i>p</i> -Cl	.80	0.77 ± 0.01	.68 ± .1	0.46 ± 0.01	0.72 ± 0.01
<i>p</i> -Br	.58	.69 ± .01	.46 ± .1	.38 ± .02	.49 ± .02
<i>p</i> -F	.54	.55 ± .02	.77 ± .01	.62 ± .01	.64 ± .01
<i>m</i> -Cl28 ± .01	.24 ± .01	.22 ± .01	...
<i>m</i> -Br	0.2415 ± .002	.19 ± .01	0.38 ± 0.01
<i>ρ</i>	-1.35	-1.36	-1.28	-1.21	-1.10
<i>r</i>	0.955	0.955	0.967	0.980	0.967
<i>s</i>	0.15	0.16	0.12	0.10	0.12

^a From preceding paper⁵; *ρ*, *r*, and *s* here calculated for only points listed for better comparison with the other data (*ρ* for all points = -1.38).

TABLE II
RELATIVE REACTIVITIES OF OTHER HYDROCARBONS TOWARD NBS
PER MOLECULE IN CCl₄ AT 80°

Substrate	NBS	I	II	III	NBA
1-Octene	26.4	25 ± 10
Ethylbenzene	15.8	11 ± 4.5	6.2 ± 0.3	8.44	10 ± 1.4
<i>o</i> -Xylene	4.28	3.87 ± 0.8
Toluene (std.)	1.00	1.00	1.00	1.00	1.00
2,3-Dimethylbutane	0.07	0.10
Methylcyclohexane	.027	.06
<i>n</i> -Octane	.022	.017
Cyclohexane	.012	.017

Wiberg and Slaugh.¹⁰ We find further confirmation in competitive measurements on toluene-cyclohexane. Relative reactivity measurements (per H) gave cyclohexane: toluene 3.9 ± 0.3 per molecule, very close to the

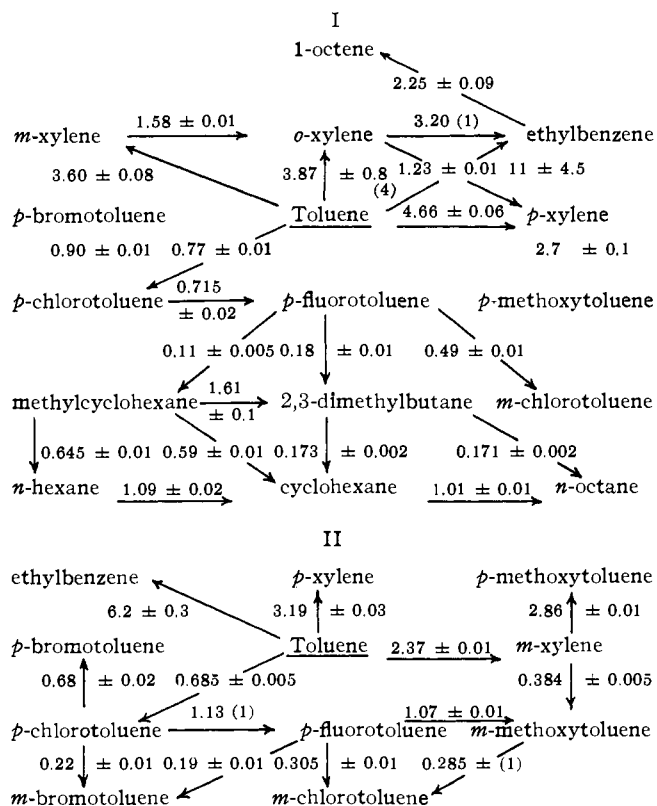


Fig. 1.—Competitive experiments using hydantoin I and II. Numbers are relative reactivities of compound at head of arrow to that at tail. All experiments in duplicate unless another number is shown in parentheses.

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

Cl· value (2.9)¹¹ and entirely different from that obtained with NBS (0.012).⁵ Furthermore, reactions of N-chlorosuccinimide carried out in the presence of bromobenzene (intended as an inert internal standard) yielded detectable quantities of chlorobenzene. Such a displacement is also a known reaction of chlorine atoms.¹²

Experimental

Materials.—The 1-bromo-5-isobutyl-5-methylhydantoin (I)¹³ was a gift from the Arapahoe Chemical Co.; purity (2 lots) 96.6 and 102.8% by titration. Attempts to purify it further by crystallization gave product with too high titration values, so it was used as received. The 1-bromo-3,5,5-trimethylhydantoin (II) was prepared as described by Orazi,¹⁴ m.p. 161-164°,

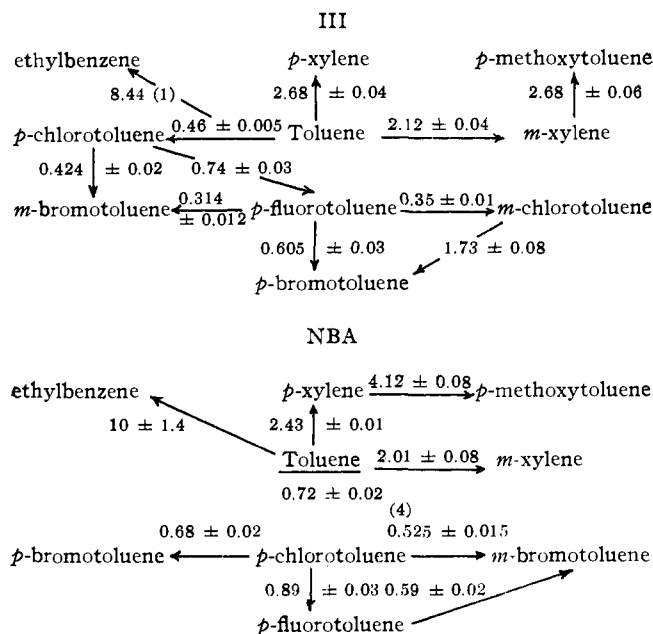


Fig. 2.—Competitive experiments with hydantoin III and N-bromoacetamide. Numbers have the same meaning as in Fig. 1.

purity 100.2% by titration after recrystallization from water and CCl₄. The 3-bromo-1,5,5-trimethylhydantoin (III) was prepared by variations of the method of Biltz and Slotta¹⁵ and Orazi.¹⁴ It was obtained from the hydantoin in 32% yield,

(11) G. A. Russell, *ibid.*, **80**, 4997 (1958). Relative reactivities for the chlorine reaction vary somewhat with reaction media.

(12) B. Miller and C. Walling, *ibid.*, **79**, 4187 (1957).

(13) Actually the position of the bromine in this molecule is not unequivocally established. Our hope that relative reactivity data might help to establish its position was thwarted by the similarity in reactivity of all the hydantoin studied.

(14) O. O. Orazi, R. A. Corral, and J. D. Bonafede, *Anales asoc. quim. argentina*, **46**, 139 (1957).

(15) H. Biltz and K. Slotta, *J. prakt. Chem.*, **113**, 233 (1926).

m.p. 169–170° dec., purity 100.1% by titration. **N-Bromoacetamide** was prepared by the method of Oliveto and Gerald¹⁶; m.p. 104–107°, purity 99.8%. **N-Chlorosuccinimide** was commercial material rapidly recrystallized from benzene; m.p. 149–150°, purity 98.6%.

Competitive experiments were carried out and products analyzed by gas chromatography essentially as in our NBS work.⁵ Relative reactivities were calculated from direct competitive experiments whenever possible, although a number of

(16) E. P. Oliveto and C. Gerold, *Org. Syn.*, **31**, 17 (1951).

cross checks were carried out as well. The actual competitions carried out are shown in Fig. 1 and 2.¹⁷ Reactions with *N*-chlorosuccinimide were very slow and required 24 hr. heating at 80° in the presence of benzoyl peroxide for complete reaction. Three experiments yielded relative reactivities for cyclohexane: toluene of 3.0, 3.3, and 5.7, and (using bromobenzene as an internal standard) chlorobenzene was detected among the products.

(17) Direct comparisons for toluene with *o*-xylene, *p*-xylene, and ethylbenzene using hydantoin (1) were carried out by Dr. D. D. Tanner.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA]

Substitutions at Saturated Carbon-Hydrogen Bonds Utilizing Molecular Bromine or Bromotrichloromethane^{1,2}

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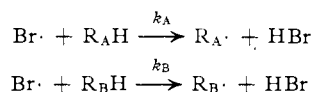
Competitive photobrominations of aralkyl hydrocarbons utilizing molecular bromine or bromotrichloromethane have been performed. The results establish reactivity scales of benzyl-type hydrogen atoms toward the bromine atom and the trichloromethyl radical.

Results

Table I summarizes a number of competitive brominations using molecular bromine in carbon tetrachloride at 40°. The last column of this table lists the relative reactivities calculated by the equation

$$\frac{k_A}{k_B} = \frac{\log ([R_A H]_i / [R_A H]_f)}{\log ([R_B H]_i / [R_B H]_f)}$$

where k_A and k_B are defined as



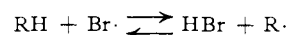
and the subscripts refer to initial and final concentrations.

The data summarized in Table I do not reflect a study of solvent effects in this reaction. The total concentration of aromatic hydrocarbon has been held at about 1 *M* in all of the experiments performed. The consistency of the experiments as summarized in Table II, which summarizes all the experiments of Table I, suggests that solvent effects are not important. It is difficult to estimate the experimental uncertainties involved in the averaged reactivity series given in Table II because of the number of "cross check" experiments. It is felt that the reactivity series has an uncertainty of about $\pm 5\%$.

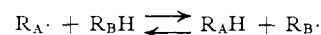
Table III gives data obtained using bromotrichloromethane in carbon tetrachloride solution at 40° as the bromination reagent.⁴ Variation in total aromatic hydrocarbon concentration between 2.5 and 1 *M* did not indicate any solvent effect on the reactivity of the trichloromethyl radical although the reproducibility of duplicate experiments was poor in several cases. Table IV summarizes the experiments of Table III and lists an averaged reactivity scale thought to involve experimental uncertainties not much greater than $\pm 10\%$.

Discussion

Photobrominations utilizing molecular bromine possess the experimental difficulty that the hydrogen abstraction reaction is reversible. In the case of meth-



ane the reaction between the methyl radical and hydrogen bromide occurs more readily than the reaction between methane and the bromine atom.⁵ For the aralkyl hydrocarbons investigated in this study reversal of the hydrogen-abstraction reactions would not be expected to be too important owing to the resonance stabilization of $R\cdot$. Nevertheless high bromine concentrations and a rapid removal of hydrogen bromide were employed to ensure the absence of this complication as well as the absence of exchange reactions of the type



The experimental variations listed in Table I, as well as the agreement between "cross checks" listed in this table, substantiate the assumption that we have measured the relative reactivities of these benzylic carbon-hydrogen bonds without complicating side reactions.

Table V summarizes the effect of structure upon the reactivities of benzylic carbon-hydrogen toward bromine atoms. Available data for the chlorine atom⁶ are given for comparison. Table V was constructed by combining the data for liquid phase competitive brominations of benzylic hydrogen atoms with vapor phase data for alkanes.⁷ The data used for alkanes (per hydrogen atom) were: methane, $\log PZ = 13.4$, $E_a = 18.3$; ethane, $\log PZ = 13.11$, $E_a = 13.4$; propane (2° H), $\log PZ = 13.41$, $E_a = 10.15$; isobutane (3° H), $\log PZ = 13.3$, $E_a = 7.5$.⁸ The 3°-hydrogen atoms of isobutane and 2,3-dimethylbutane have been assumed to have equal reactivity toward the bromine atom in order that the benzylic hydrogen atoms and the alkanes could be compared.⁹

As far as the bromine atom is concerned, Table V gives a very consistent picture. Comparisons in a horizontal direction from left to right represent acti-

(5) H. C. Andersen and G. B. Kistiakowsky, *J. Chem. Phys.*, **11**, 6 (1943); G. B. Kistiakowsky and E. R. Van Artsdalen, *ibid.*, **12**, 469 (1944).

(6) G. A. Russell, A. Ito, and D. G. Hendry, *J. Am. Chem. Soc.*, **84**, 2976 (1963).

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

(8) *PZ* in cc. mole⁻¹ sec.⁻¹; E_a in kcal. mole⁻¹.

(9) Rate data for the vapor phase photobromination of toluene (H. R. Anderson, H. A. Scheraga, and E. R. Van Artsdalen, *J. Chem. Phys.*, **21**, 1258 (1953)), $E_a = 7.2 \log PZ$ (per α -hydrogen atom) = 13.05, would give a relative reactivity for toluene of 17,000. However, these data have been criticized (S. W. Benson and J. H. Buss, *ibid.*, **28**, 301 (1958)).

(1) Directive Effects in Aliphatic Substitutions. XVIII.

(2) This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is made to the donors of this fund.

(3) (a) Alfred P. Sloan Foundation Fellow, 1959–1963; (b) National Science Foundation Undergraduate Research Participant, 1960–1962.

(4) E. S. Huyser, *J. Am. Chem. Soc.*, **82**, 391, 394 (1960).