

TABLE VII
RELATIVE REACTIVITIES OF ARAKYL HYDROCARBONS TOWARD
THE TRICHLOROMETHYL RADICAL^a

Hydrocarbon	CCl ₄ , 40° (this work)	From retardation of telomerization, 91.5° (ref. 10)
Toluene	1.00 ^b	1.00 ^b
Ethylbenzene	50	3.1
Cumene	260	4.2
Diphenylmethane	50	8.0
Triphenylmethane	160	16.7

^a Per α -hydrogen atom. ^b Assumed.

better except for bromotrchloromethane (Eastman practical grade) which was about 96 mole per cent pure. All reagents except for bromotrchloromethane and elemental bromine were dried by percolation through activated silica gel before use.

Procedure for Reactions with Elemental Bromine.—Approximately 25 mmoles of each of two hydrocarbons and 15 mmoles of bromobenzene were accurately weighed out and diluted to 50 ml. with carbon tetrachloride. This was the reaction mixture. Since the bromobenzene did not react under the bromination conditions it was used as the internal standard for the g.l.c. analysis. Experiments in which the internal standard was added after bromination gave the same results as those in which the bromobenzene was present during reaction. The reaction mixture was placed in a 100-ml. three-necked round-bottomed Pyrex flask equipped with a nitrogen inlet tube to remove hydrogen bromide from the solution, a cold finger condenser containing Dry Ice and carbon tetrachloride, a dropping funnel for bromine, and a magnetic stirrer. The flask was immersed in a $40 \pm 0.5^\circ$ water bath and illuminated with a 100-watt unfrosted tungsten

lamp. Enough bromine was added dropwise to react with approximately half of the hydrocarbons present. The rates of addition of bromine and nitrogen were varied in several reactions. After the reaction was completed, the reaction mixture was hydrolyzed to remove lachrymatory products and analyzed by g.l.c. In competitive brominations involving toluene no products of ring substitution could be detected by g.l.c. indicating that less than 1% of the toluene reacting in these reactions was converted to products of nuclear substitution.

Procedure with Bromotrchloromethane.—Approximately 25 mmoles of each of two hydrocarbons and 15 mmoles of bromobenzene were accurately weighed and diluted with carbon tetrachloride. About 5 ml. of the reaction mixture and an equal volume of bromotrchloromethane were placed in a Pyrex ampoule, degassed by freeze-thawings, and sealed. The tube was immersed in a $40 \pm 0.5^\circ$ water bath and illuminated with a 275-watt sun lamp. Under these conditions about half of the hydrocarbons was consumed in 24 hr. The tubes were opened and the contents analyzed by g.l.c. soon after the reaction was quenched.

The choice of column and gas chromatograph was dictated by the hydrocarbon mixture being analyzed. For mixtures which had widely separated boiling points, an F. and M. model 500 gas chromatograph was used and the temperature was hand programmed during the analysis. Another procedure for mixtures with widely separated boiling points was to add two internal standards and make two separate analyses at uniform temperatures. For analyses wherein no temperature change was required during the analysis a Perkin-Elmer Model 154D vapor fractometer with thermistor detector was used. The columns used, either separately or in series, were a 2-m. diisodecyl phthalate, a 1-m. methyl silicone grease, a 1-m. Apiezon N, a 2-m. *n*-propyl tetrachlorophthalate, a 1-m. β,β' -oxydipropionitrile, and a 1-m. column of silicon grease (G. E. XF1105) column in which 5% of the methyl groups have been replaced by cyano-methyl groups.

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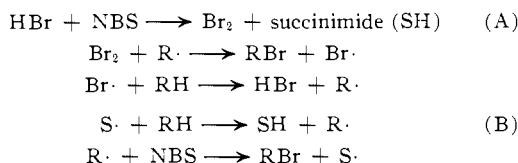
Directive Effects in Aliphatic Substitutions. XIX. Photobromination with N-Bromosuccinimide¹

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Competitive photobromination of aralkyl hydrocarbon in methylene chloride solution at 40° by N-bromosuccinimide yields a relative reactivity series so similar to that observed in photobromination by molecular bromine that it appears that under the reaction conditions both reactions involve the bromine atom as the hydrogen abstracting species.

There is considerable evidence that photobromination by N-bromosuccinimide (NBS) proceeds through a free alkenyl or aralkyl radical. For example, the occurrence of allylic rearrangement³ and the essentially complete racemization observed in the bromination of (–)-ethylbenzene- α -d⁴ are consistent with such a radical mechanism. However, the question as to whether the free radical is formed by process A or B or by both A and B has never been completely resolved.



Competitive brominations of substituted toluenes has been interpreted as evidence in support of process B⁵ and process A.⁶ *cis-trans* Isomerization of unreacted olefins has also been interpreted in terms of mechanism

B⁴ as well as process A.⁷ The formation of dibromides in NBS reactions with certain olefins⁸ would seem to support process A or a competing ionic process whereas the formation of 1:1 adducts between NBS and other olefins⁹ can be interpreted in terms of process B.

Another complication rests in the fact that as usually performed the Wohl-Ziegler reaction utilizes refluxing carbon tetrachloride as a solvent. Both NBS and succinimide are rather insoluble in carbon tetrachloride and a third possible reaction mechanism involving succinimidyl radical propagation occurring on the surface of NBS crystals has been suggested.¹⁰ To avoid this problem we have studied the competitive bromination of a series of aralkyl hydrocarbons in methylene chloride solution at 40°, a solvent in which NBS is soluble to the extent of *ca.* 0.25 M.

Results

The competitive photochemical bromination of toluene and ethylbenzene by NBS in refluxing methylene chloride solution was carefully studied as a function of hydrocarbon and NBS concentrations. Sufficient NBS was employed so that upon completion of

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(2) Alfred P. Sloan Foundation Fellow 1959–1963.

(3) G. F. Bloomfield, *J. Chem. Soc.*, 114 (1944).

(4) H. J. Dauben, Jr., and L. L. McCoy, *J. Am. Chem. Soc.*, **81**, 5404 (1959).

(5) E. C. Kooyman, R. van Helden, and A. F. Bickel, *Koninkl. Ned. Akad. Wetenschap., Proc.*, **66B**, 75 (1953).

(6) F. L. J. Sixma and R. H. Riem, *ibid.*, **61B**, 183 (1958).

(7) B. P. McGrath and J. M. Tedder, *Proc. Chem. Soc.*, 80 (1961).

(8) P. L. Southwick, L. A. Pirsiglove, and P. Numerof, *J. Am. Chem. Soc.*, **72**, 1600 (1950); E. J. Corey, *ibid.*, **75**, 2251 (1953).

(9) P. Couvreur and A. Bruylants, *Bull. soc. chim. Belges*, **61**, 253 (1952); W. J. Bailey and J. Bello, *J. Org. Chem.*, **20**, 525 (1955).

(10) L. Horner and E. H. Winkelmann, *Angew. Chem.*, **71**, 349 (1959).

TABLE I
RELATIVE REACTIVITY OF TOLUENE AND ETHYLBENZENE IN NBS
BROMINATION IN METHYLENE CHLORIDE AT 40°

Toluene ^a		Ethylbenzene ^a		NBS ^a	$\frac{k_{\text{toluene}}}{k_{\text{ethylbenzene}}}$
Initial	Final	Initial	Final		
0.169	0.136	0.133	0.00635	0.16 ^b	13.4
.166	.147	.142	.0230	.14 ^b	14.9
.147	.134	.140	.0112	.15 ^b	14.2
.210	.191	.290	.0678	.24 ^b	15.5
.247	.213	.290	.0424	.22 ^{b,c}	13.0
.390	.191	.290	.0678	.38	15.0
.396	.308	.365	.0114	.44	13.7
.365	.313	.413	.0514	.40	13.4
.462	.390	.544	.0392	.34 ^d	15.5
.724	.620	.798	.108	.80	12.7
.798	.652	.772	.0904	.80	14.7
1.27 ^e	1.12 ^e	1.246	.188	.60	14.6
10.15 ^e	9.20 ^e	13.15 ^e	3.23 ^e	11 ^{b,e,f}	13.9

Av. 14.2 ± 0.9^g

^a Moles per liter. ^b Initially homogeneous. ^c 20 mole % (based on NBS) of molecular bromine added. ^d 45 mole % (based on NBS) of molecular bromine added. ^e Millimole in an initial volume of 85 ml. ^f NBS added over a 2-hr. period as a solution in methylene chloride. ^g Standard deviation.

sluggishly if at all with NBS and attempts to include these compounds in a reactivity scale failed owing to their inhibition of the Wohl-Ziegler reaction. Pertinent results are summarized in Table II.

Assuming that the consumption of the hydrocarbons involves only attack of an atom or radical on hydrogen atoms α to a double bond or the aromatic ring, the relative reactivity series of Table III can be constructed. No attempt has been made to estimate experimental uncertainties except for the first four hydrocarbons in the table.

Discussion

The similarity of the reactivity sequence observed for the bromination of aralkyl hydrocarbons with molecular bromine and with NBS appears to be strong evidence for the occurrence of mechanism A in NBS brominations, at least for aralkyl hydrocarbons under our reaction conditions. The uniqueness of this reactivity series has been discussed previously.¹¹

The greater reactivity observed for allylic hydrogen atoms than for similar types of benzylic hydrogen atoms is qualitatively in agreement with reactivity data toward the *t*-butoxy¹² and phenyl¹³ radicals.

TABLE II
COMPETITIVE BROMINATIONS WITH NBS IN METHYLENE CHLORIDE AT 40°

Hydrocarbon A	Hydrocarbon B	[A] ₀ ^a	[A] _f ^a	[B] ₀ ^a	[B] _f ^a	NBS ^a	Vol., cc.	k _A /k _B
Ethylbenzene	Toluene			Average value, Table I				14.2 ± 0.9
Cumene	Toluene	22.8	8.40	9.90	9.20	17	50	14
Cumene	Toluene	13.5	3.20	11.3	10.4	13	25	16
Cumene	Toluene	15.3	8.60	10.2	9.80	8.3 ^b	25	13
Cumene	Ethylbenzene	6.38	3.95	5.02	3.02	5.9	75	1.05
Cumene	Ethylbenzene	10.7	6.60	11.8	7.30	9.5	80	1.0
Cumene	Ethylbenzene	39.6	25.0	20.0	12.7	26	50	1.0
Ethylbenzene	Diphenylmethane	6.95	2.62	6.97	4.55	7.0	25	2.3
Ethylbenzene	Diphenylmethane	7.57	3.00	6.97	4.22	7.2	25	2.0
Ethylbenzene	Allylbenzene	8.38	5.52	5.58	3.10	6.5	25	0.71
Ethylbenzene	Allylbenzene	6.82	4.40	4.54	2.62	6.5	50	0.78
Indan	Ethylbenzene	21.9	12.4	21.0	18.0	11	60	3.6
Indan	Ethylbenzene	27.0	13.4	18.8	15.7	16	50	3.7
Indan	Tetralin	11.9	5.90	22.6	11.7	20	70	1.06
Indan	Tetralin	11.2	6.40	22.85	12.3	17	70	1.05
Cyclohexene	Ethylbenzene	11.6	4.40	14.2	13.0	11	50	11.1
Cyclohexene	Ethylbenzene	9.47	2.51	15.9	14.3	12	50	11.7
Cyclohexene	Cyclopentene	19.95	17.1	24.3	7.65	20	50	0.21
Cyclohexene	Cyclopentene	95.0	72.6	91.0	23.0	104	100	.20
Cyclohexene	Cycloheptene	64.5	49.7	72.6	13.6	67	100	.15
Cyclohexene	Cycloheptene	46.2	37.4	58.1	13.5	49	50	.14
Cyclopentene	Cycloheptene	10.9	6.90	10.5	5.70	8.0	25	.75
Cyclopentene	Cycloheptene	11.2	7.60	10.3	5.70	8.0	50	.67
Cyclooctene	Cycloheptene	8.83	7.25	9.90	6.45	9.5	50	.46
Cyclooctene	Cycloheptene	8.42	6.55	9.88	5.54	9.4	25	.44

^a Millimoles. ^b Containing 45% (based on NBS) of elemental bromine.

the reaction about 50% of the total toluene and ethylbenzene initially present was consumed. The concentrations of toluene and ethylbenzene after bromination were measured by gas-liquid chromatography (g.l.c.) and the relative reactivities of the hydrocarbons calculated by the equation

$$k_A/k_B = \frac{\log ([R_AH]_f/[R_AH]_0)}{\log ([R_BH]_f/[R_BH]_0)}$$

where the subscripts refer to final and initial concentrations. Pertinent data are summarized in Table I.

Having established the reproducibility of the method, a variety of other aralkyl hydrocarbons and cycloalkenes were competitively brominated. The reactions involving aralkyl hydrocarbons were complete in 10 to 40 min. while those involving cycloalkenes or allylbenzene required 7–21 hr. for complete consumption of the NBS. Conjugated and 1,4-dienes react very

However, the magnitude of the difference is somewhat surprising¹⁴ as is the fact that the α -hydrogen atoms of the C₅–C₈ cycloalkenes are considerably more reactive than the α -hydrogen atoms of allylbenzene (see Table III). Admittedly the reactivities of the cycloalkenes, as determined by the disappearance of the hydrocarbons, involves a side reaction leading to the dibromocycloalkenes. Yields of 1,2-dibromocyclohexane in the range of 6–10% have been reported in this reaction.¹

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

(12) C. Walling and W. Thaler, *ibid.*, **83**, 3877 (1961).

(13) Unpublished work with Dr. Robert F. Bridger.

(14) Toward the *t*-butoxy radical at 40° an α -hydrogen atom of cyclohexene is about 11.5 times as reactive as an α -hydrogen atom of ethylbenzene (ref. 12) while toward the phenyl radical at 60° the relative reactivities are 2.64:1 (ref. 13).

(15) K. Ziegler, A. Spath, E. Schaaf, W. Schumann, and E. Winkelmann, *Ann.*, **551**, 80 (1942); W. J. Bailey and J. Bello, *J. Org. Chem.*, **20**, 689

TABLE III

RELATIVE REACTIVITIES IN BROMINATION REACTIONS AT 40°

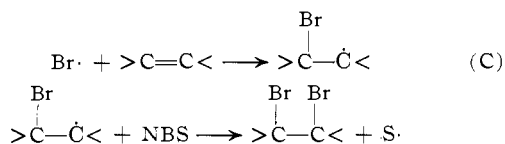
Hydrocarbon	NBS (CH ₂ Cl ₂)	Molecular bromine ^a (CCl ₄)	NBS (per α-hydrogen atom)
Toluene	1.0 ^b	1.0 ^b	1.0 ^b
Ethylbenzene	14 ± 1	11 ± 1	21 ± 2
Cumene	15 ± 1	12 ± 1	45 ± 3
Diphenylmethane	6.5 ± 1	6.5 ± 1	10 ± 1.5
Indan	49		36
Tetralin	47		36
Allylbenzene	19		28
Cyclopentene	780		600
Cyclohexene	160		160
Cycloheptene	1100		825
Cyclooctene	590		440

^a Ref. 16. ^b Assumed.

However, correction for this reaction would not appreciably effect the reactivity series of Table III.

The effect of all the alkenes studied, including allylbenzene, upon the rate of the brominations is surprising in view of the high reactivity of the alkenes observed in competition with aralkyl hydrocarbons. The competitive reactions involving only aralkyl hydrocarbons proceeded about 20–50 times as fast as those involving the olefins. Moreover, the competitive reaction between ethylbenzene and cyclohexene required about 20 times as long for complete consumption of the NBS as the competitive reaction between ethylbenzene and toluene. Possibly olefins inhibit reaction A and the slow reaction observed proceeds *via* mechanism B. Sixma and Riem have, however, argued that, since at low concentrations of molecular bromine cyclohexene yields 80% of the allylic bromide, NBS bromination of alkenes involves process A and the high yields of allylic bromides formed in NBS reaction result from the low bromine concentrations demanded by process A.

If the Wohl-Ziegler bromination is a process involving long kinetic chains, consumption of an occasional molecule of bromine by addition to the olefin would result in chain termination if no alternate chain propagation reaction is available for the alkenyl radical. Consumption of bromine in this way could force the alkenyl radical to react with NBS rather than molecular bromine and thus inhibit process A and force the reaction to proceed (slowly) by process B. The occurrence of process C would also force the reaction to proceed *via* a succinimidyl radical instead of a bromine atom.



(1955); H. J. Dauben and L. L. McCoy, *J. Am. Chem. Soc.*, **81**, 4863 (1959).

(16) G. A. Russell and C. DeBoer, *ibid.*, **85**, 3136 (1963).

Experimental

Reagents.—N-Bromosuccinimide was purified by recrystallization from ten times its weight of hot water, followed by rapid filtration. It was then allowed to dry in air for three days. Cyclopentene (99.89 mole % purity) and cyclohexene (99.83 mole % purity) were Phillips Petroleum research grade. Cycloheptene was prepared by lithium aluminum hydride reduction of cycloheptanone, followed by dehydration with α-naphthalene-sulfonic acid. Cyclooctene was a gift from City Service Research and Development Co. Cumene (99 mole % purity) was from Phillips Petroleum Co. Commercially available indan and tetralin were shaken with sulfuric acid, washed, and dried for further purification. All of the hydrocarbons, except those of research grade, were fractionally distilled. Constant boiling fractions were passed through activated silica gel before use and purity checked by gas-liquid chromatography (g.l.c.). Methylene chloride was washed with water and sodium carbonate, dried over calcium chloride, and fractionally distilled. The fraction used had a boiling range of 39.5–40°.

Bromination Procedure.—Weighed mixtures of two hydrocarbons were diluted to the desired volume with methylene chloride and placed in an erlenmeyer flask containing a known weight of NBS sufficient to react with about 50% of the total amount of hydrocarbon present. Hydrocarbon ratios (molar) were usually one to one, except where large reactivity differences were observed. The flask was attached to a water condenser and maintained under a positive nitrogen pressure. The reaction mixture was stirred with a glass-covered magnetic stirrer bar and illuminated with a 150-watt tungsten bulb a few inches from the flask. The illumination not only initiated the reaction but also maintained the reflux temperature (40°). Reaction was considered complete when the solution gave a negative test with starch-iodide paper.

Analytical Procedure.—Analyses for final concentrations of the hydrocarbons were made on a Perkin-Elmer Model 154D vapor fractometer employing a thermistor detector. Areas of the chromatography peaks were measured with a planimeter or by a recording automatic integrator. Accuracy of the two methods was comparable as shown by duplicate calculations on the same reaction mixture. Peak areas were converted to moles using the known number of moles of an internal standard and correction factors calculated from the analysis of standard solutions. Analyses were performed in triplicate. When bromobenzene was used as the internal standard for g.l.c. analysis, weighed amounts were added before the reaction. All other standards were added after reaction. In the reaction of ethylbenzene *vs.* diphenylmethane, owing to the great difference in boiling points, two standards were added and each compound was analyzed separately using different g.l.c. conditions.

Columns used for g.l.c. analysis utilized 80/100 mesh firebrick in 0.25-in. columns with the following substrates: (1) 2 m., 20% diisodecyl phthalate; (2) 2 m., 20% poly-(propylene glycol); (3) 1 m., 20% GE-XF1105 silicon oil (5% of methyl groups replaced by cyanoethyl groups); (4) 2 m., 20% GE-XF1150 silicone oil (50% cyanoethyl groups); (5) 1 m., 10% di-*n*-propyl tetrachlorophthalate. Table IV lists the analytical conditions employed.

TABLE IV
GAS-LIQUID CHROMATOGRAPHY ANALYSES

Hydrocarbon mixture	Internal standard	Temp., °C.	Column no.
Cyclopentene-cyclohexene	Trichloroethylene	70	2
Cyclopentene-cycloheptene	Trichloroethylene	75	2
Cycloheptene-cyclooctene	Trichloroethylene	90	3
Cyclohexene-ethylbenzene	Trichloroethylene	70	3
Toluene-ethylbenzene	Bromobenzene	125	1
Ethylbenzene-cumene	Bromobenzene	85	5
Indan-tetralin	Bromobenzene	115	5
Ethylbenzene-diphenylmethane	Bromobenzene	120	1
	Nitrobenzene	200	4
Allylbenzene-diphenylmethane	Nitrobenzene	175	3