Anal. Calcd. for $C_{16}H_{16}N_4$: C, 72.70; H, 6.10; N, 21.20. Found: C, 72.33; H, 6.42; N, 21.00.

Attempts to carry out this condensation with potassium *t*-butoxide in *t*-butyl alcohol, or with sodium ethoxide in ethanol, were ineffectual. Infrared inspection of aliquots of the reaction mixtures even after several weeks at the reflux temperature indicated the presence of *ca.* 90% unconsumed benzyl azide.

Gradual addition of a solution of a slight excess of potassium *t*-butoxide in tetrahydrofuran (freshly distilled over lithium aluminum hydride) to a cold equimolar mixture of hydrocinnamonitrile and benzyl azide in tetrahydrofuran according to the general procedure of Lieber, *et al.*,[42] led to the formation of a product (90%, if assumed to be the Thorpe condensation product of hydrocinnamonitrile), m.p. 88–90°; λ_{max} (CH_2Cl_2) 2.95, 3.01, 4.50, 6.25 (complex) μ.

5-Benzamido-1,4-dibenzyl-1,2,3-triazole (XLI).—Benzoyl chloride (0.3 ml., 2.2 mmoles) was added dropwise to a cooled solution of the aminotriazole XL (5.30 mg., 2.0 mmoles) in pyridine (*ca.* 5 ml.). The mixture was kept at room temperature for 30 min., poured into dilute hydrochloric acid, and the precipitated solid was collected. Recrystallization from benzene–hexane afforded colorless needles of XLI (500 mg., 68%), m.p. 177–178°. Several recrystallizations from benzene–hexane afforded an analytical sample, m.p. 178.5–179°; λ_{max} (CH_2Cl_2) 2.95, 5.91, 6.25, 6.69, 6.87 μ.

Anal. Calcd. for $C_{23}H_{20}N_4O$: C, 74.98; H, 5.47; N, 15.21. Found: C, 74.90; H, 5.25; N, 14.96.

5-Benzamido-4-benzoyl-1-benzyl-1,2,3-triazole (XLII).—A solution of chromium trioxide (140 mg., 1.4 mmoles) in a little water was added to a warm solution of the benzamidotriazole XLI (370 mg., 1.0 mmole) in acetic acid (*ca.* 5 ml.). The mixture was cooled, and concentrated sulfuric acid (10 drops) was added. A small sample of the mixture was withdrawn, heated strongly on the steam bath until a green precipitate was observed, then returned to the reaction mixture. After 6 hr. at room temperature, the mixture of white crystals and green precipitate was diluted with water, stirred to effect solution of inorganic salts, and the white needles of XLII (380 mg., 100%) were collected and washed well with water. Several recrystallizations from benzene afforded an analytical sample, m.p. 201.5–202°; λ_{max} (Nujol) 3.12, 6.05, 6.12, 10.82 μ.

Anal. Calcd. for $C_{23}H_{18}N_4O_2$: C, 72.23; H, 4.74; N, 14.65. Found: C, 72.11; H, 4.74; N, 14.43.

Attempted hydrogenolysis of this substance in ethanol in the presence of acid-washed 10% palladium–charcoal catalyst at room temperature and atmospheric pressure resulted in the uptake of more than one equivalent of hydrogen without a sharp break in the hydrogenation curve. The crude product obtained upon evaporation of the solvent, after removal of an insoluble hydroxyl-containing component (λ_{max} (Nujol) 2.88, 3.07, 5.95, 6.26, 9.60 μ) by crystallization from ethanol, exhibited an infrared spectrum identical with that of XLI. Chromic acid oxidation of the total crude product according to the procedure used above quantitatively regenerated XLII.

Addition of a large excess of metallic sodium, in small portions, to a stirred slurry of XLII in liquid ammonia resulted in the formation of a transient chocolate-brown coloration and a yellow precipitate. Isolation of the organic product from this reaction by the addition of excess solid ammonium chloride, evaporation of the solvent, and extraction with boiling ethanol afforded a 90% recovery of XLII.

A solution of XLII and excess potassium thiocyanate in hot 95% ethanol was boiled under reflux for 24 hr. Upon cooling of the solution, XLII was quantitatively recovered as a deposit of colorless needles.

A solution of XLII in hot, concentrated hydriodic acid was boiled under reflux for 1 hr. The fluorescent organic material isolated from this reaction mixture by dilution with water and extraction with ethyl acetate showed, in its infrared spectrum, all of the characteristic bands of XLII and only weak absorption characteristic of XXXV.

4-Benzamido-5-benzoyl-1,2,3-triazole (XXXV).—A solution of chromium trioxide (140 mg., 1.4 mmoles) in a little water was added to a slurry of the benzoyltriazole XLII (380 mg., 1.0 mmole) in acetic acid (*ca.* 5 ml.). Concentrated sulfuric acid (10 drops) was then added, and a small portion of the mixture was withdrawn, heated strongly on the steam bath, and returned to the main reaction mixture. After 1 week at room temperature, the resultant suspension containing white crystals and green solid was diluted with water, stirred to effect solution of the inorganic material, and allowed to stand overnight at room temperature. The faintly yellow, crystalline precipitate thus obtained was recrystallized from ethyl acetate to give faintly yellow needles (80 mg., 27%), m.p. 266–268°, exhibiting a bright yellow-green fluorescence under ultraviolet light. The melting point of this product was undepressed upon admixture with XXXV and the infrared spectra (Nujol) of the two products were identical.

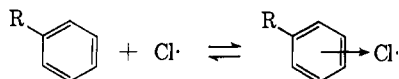[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA]

Solvent Effects in the Reactions of Free Radicals and Atoms. VIII. The Photochlorination of Aralkyl Hydrocarbons[1,2]

BY GLEN A. RUSSELL,[3] AKIHIKO ITO, AND DALE G. HENDRY

In the side-chain photochlorination of aralkyl hydrocarbons, high selectivity is often observed because of complex formation between the aromatic nucleus and the chlorine atom. This complexed chlorine atom displays considerably greater selectivity in hydrogen abstraction reactions than the free chlorine atom. Dilution of aralkyl hydrocarbons by inert noncomplexing solvents destroys the high selectivity often noted in photochlorination. Extrapolation of selectivity data to an infinite dilution of the aralkyl hydrocarbon yields reactivity data toward the free chlorine atom.

Previous communications have emphasized the importance of specific solvent effects, particularly of aromatic solvents, in the reactions of chlorine atoms.[4] This has prompted us to re-examine the photochlorination of aralkyl hydrocarbons since in these cases the substrate itself could also act as a specific complexing agent for the chlorine atom.[5] The results obtained have

been in complete agreement with those obtained in a study of solvent effects in the photochlorination of aliphatic substances. Thus, the addition of an aromatic solvent in the photochlorination of a branched-chain hydrocarbon, such as 2,3-dimethylbutane, makes the chlorine atom more selective in its attack on the 3°- and 1°-hydrogen atoms, the effect becoming more pronounced at the higher concentration of aromatic solvent.[4] In the chlorination of aralkyl hydrocarbons, such as ethylbenzene, cumene, indan, and tetralin, the present work has demonstrated the same effect. Dilution of the aralkyl substrate by an aliphatic solvent, such as carbon tetrachloride or cyclohexane, or by a weakly basic aromatic such as nitrobenzene, has a pronounced effect on the reactivity of the chlorine atom, dilution favoring a lower selectivity in the attack of the chlorine atom upon a system of 1°-, 2°-, and 3°-carbon–hydrogen bonds. By extrapolation to infinite dilution it is possible to obtain for the first time the relative reactivities of the hydrogen atoms in the side

(1) Directive Effects in Aliphatic Substitutions. Part XX.

(2) This research was supported by the Air Force Office of Scientific Research and by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of these funds.

(3) Alfred P. Sloan Foundation Fellow, 1959–1963.

(4) G. A. Russell, *J. Am. Chem. Soc.*, **79**, 2977 (1957); **80**, 4987, 4997, 5002 (1958).

(5) G. A. Russell and H. C. Brown, *ibid.*, **77**, 4031 (1955).

chains of these aralkyl hydrocarbons toward the chlorine atom without complications owing to complex formation between the aromatic ring of the substrate and the chlorine atom.

Results

The relative reactivities of the α- and β-hydrogen atoms of cumene, ethylbenzene, indan, and tetralin are summarized in Table I as a function of hydrocarbon concentration.

TABLE I

PHOTOCHLORINATION OF ARALKYL HYDROCARBONS AT 40°

| Hydrocarbon | mmoles | Concn.[a] | Solvent[b] | mmoles chloro derivatives | | $k\alpha/k\beta$ [c] |
				α	β	
Ethylbenzene	121	8.10	None	4.80	0.50	14.5
Ethylbenzene	128	5.14	NB	2.76	.65	6.15
Ethylbenzene	124	4.98	CY	3.52	.94	5.65
Ethylbenzene	60.0	3.07	NB	0.97	.40	3.63
Ethylbenzene	73.0	2.93	CY	.66	.295	3.36
Ethylbenzene	37.5	1.50	CY	.135	.084	2.42
Ethylbenzene	37.4	1.49	NB	.390	.217	2.70[d]
Ethylbenzene	...	0	NB or CY	Extrapolated		2.0[e]
Cumene	105	7.05	None	3.75	0.549	42.2[d]
Cumene	75.6	5.04	NB	2.70	.781	20.8
Cumene	45.0	3.00	NB	1.15	.654	10.6
Cumene	22.4	1.49	NB	0.706	.810	5.24
Cumene	...	0	NB	Extrapolated		3.5[e]
Indan	119	7.96	None	3.96	0.310	6.39
Indan	74.6	4.97	NB	1.87	.250	3.73
Indan	44.5	2.96	NB	0.846	.173	2.46
Indan	22.2	1.48	NB	0.379	.106	1.78
Indan	...	0	NB	Extrapolated		1.2
Tetralin	108	7.21	None	3.26	0.585	5.57
Tetralin	74.1	4.94	CY	1.32	.353	3.74
Tetralin	44.9	2.99	NB	1.84	.790	2.32
Tetralin	...	1.47	NB	0.560	.397	1.41
Tetralin	21.8	1.45	CY	1.26	.828	1.52
Tetralin	...	0	NB or CY	Extrapolated		1.15

[a] Mole l.$^{-1}$ at 40°   [b] NB = nitrobenzene, CY = cyclohexane.
[c] Per hydrogen atom.   [d] Average of four experiments.   [e] From Fig. 1.

The data of Table I were obtained by photochlorinating the aralkyl hydrocarbons in an appropriate solvent at 40° to an extent not greater than five mole per cent followed by analysis of the chlorination products by methods based on chemical reactivity or by gas liquid chromatography (g.l.c.). Extrapolated values of the relative reactivities at infinite dilution of the aralkyl hydrocarbon were obtained from plots similar to Fig. 1. Nitrobenzene was chosen as a diluent for these photochlorinations since it is quite inert to reaction with chlorine atoms and because previous work had indicated that it exerts but a small effect on the selectivity of chlorine atoms, presumably owing to its low basicity.[4] The extrapolated relative reactivities are thus those expected in pure nitrobenzene solution at infinite dilution of the substrate. In the case of ethylbenzene, data using cyclohexane as solvent indicate excellent agreement with the data using nitrobenzene as solvent in accord with the low complexing ability previously assigned to nitrobenzene and with the assumption that nitrobenzene is inert in the chlorination reaction and does not bring about side reactions, such as aromatic substitution.

The curves of Fig. 1 are quite similar in shape to those obtained previously in the chlorination of alkanes such as 2,3-dimethylbutane and n-pentane in the presence of various aromatic materials.[4] The greatest curvature was observed in the case of cumene, presumably owing to the fact that the reactivity between α- and β-positions of cumene toward "free" chlorine atoms is greater than for any other hydrocarbons examined. The fact that cumene itself is a more basic hydrocarbon than ethylbenzene is a second contributing factor to the shapes of the curves obtained. After
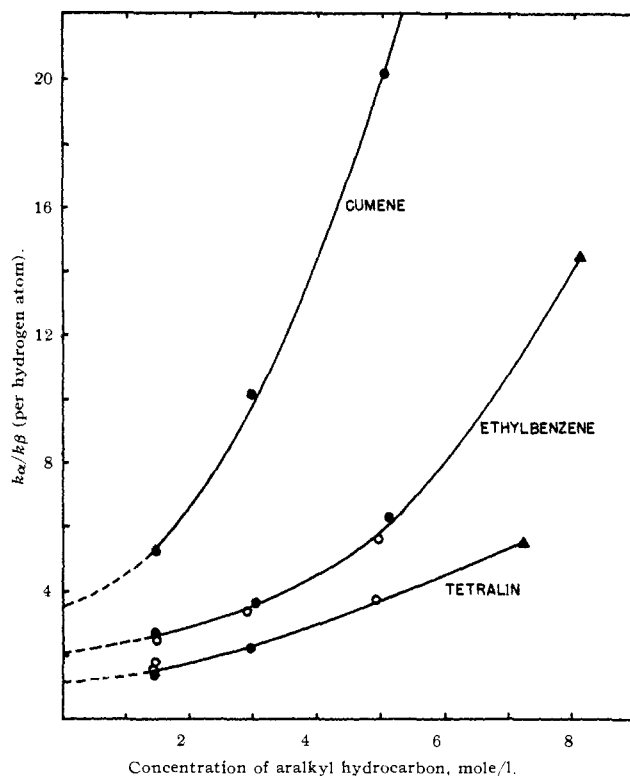

Fig. 1.—Photochlorination of aralkyl hydrocarbons at 40°: ●, nitrobenzene solvent; ○, cyclohexane solvent; ▲, no solvent.
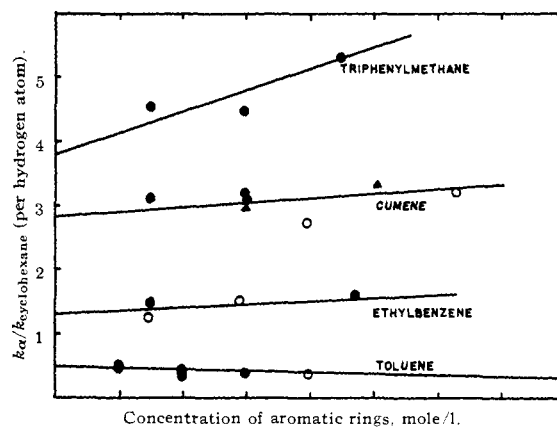

Fig. 2.—Competitive photochlorination of cyclohexane and aralkyl hydrocarbons at 40°: ●, nitrobenzene solvent; ▲, carbon tetrachloride solvent; ○, no solvent.

correcting for the complexing ability of the aromatic ring it is seen that the relative reactivities of the 3°- and 1°-hydrogen atoms of cumene ($k_\alpha/k_\beta = 3.55$) are not significantly different from the ratio of $k_{3°}/k_{1°}$ obtained for 2,3-dimethylbutane (4.0 at 40°).[4] Similarly, k_α/k_β for ethylbenzene (2.0) is about the same as $k_{2°}/k_{1°}$ for n-pentane (2.6) while at infinite dilution the ratio of k_α/k_β for indan and tetralin are nearly unity. These results are in agreement with the previous conclusion that toward the very reactive and highly unselective chlorine atom the activation expected from benzyl radical formation is very small.[5] Thus the benzyl hydrogen of toluene has nearly the same reactivity toward chlorine atoms as the 1°-hydrogen atoms of 2,3-dimethylbutane, n-pentane, or tetramethylsilane.[4]

Competitive photochlorinations were performed between cyclohexane and the various aralkyl hydrocarbons. Again the percentage chlorination was never allowed to exceed five mole per cent. Analysis for chlorocyclohexane was performed by g.l.c. while the α-

TABLE II

Aralkyl hydrocarbon, mmoles	Cyclohexane, mmoles	Concn. aralkyl hydrocarbon[a]	Added solvent[b]	Chlorocyclohexane	α-Chloro aralkyl	k_α/k_{CY}[c]
Toluene						
..	..	0	NB or CY	Extrapolated		0.5[d]
15.0	7.34	1.00	NB	0.872	0.213	.45
15.0	1.88	1.00	NB	0.381	.407	.485
29.7	14.7	2.00	NB	1.077	.211	.35
29.9	3.60	1.99	NB	0.525	.446	.38
..	..	2.0	None	...	...	.40[e]
44.9	5.49	3.0	NB	0.782	0.613	.35
..	..	4.0	None	...	...	.375[e]
..	..	8.0	None	...	...	.35[e]
Ethylbenzene						
..	..	0	NB or CY	Extrapolated		1.3[d]
37.5	182	1.50	None	3.18	0.135	1.24
37.8	151	1.51	NB	1.38	.084	1.46
73.0	145	2.93	None	5.10	.660	1.50
118.0	46.7	4.72	NB	1.29	.860	1.58
Diphenylmethane						
..	..	0	NB or CY	Extrapolated		1.5
15.1	14.9	1.01	NB	1.40	0.283	1.15
14.9	14.9	0.99	NB	1.59	.332	1.20
14.9	112	0.99	None	2.57	.082	1.44
22.5	22.6	1.50	NB	1.09	.301	1.64
32.5	32.3	2.17	NB	1.12	.275	1.42
32.3	85.8	2.15	None	3.42	.326	1.50
54.7	51.4	3.64	None	2.08	.802	2.15
Cumene						
..	..	0	NB, CY, or CCl₄	Extrapolated		2.85[d]
22.9	3.79	1.53	NB	0.183	0.288	3.12
44.7	7.45	2.98	NB	.495	.786	3.18
45.5	7.59	3.03	NB	.297	.456	3.07
45.0	7.50	3.00	CCl₄	.135	.200	2.96
75.5	12.6	5.04	CCl₄	.149	.246	3.31
94.4	15.8	6.29	None	.516	.816	3.16

Aralkyl hydrocarbon, mmoles	Cyclohexane, mmoles	Concn. aralkyl hydrocarbon[a]	Added solvent[b]	Chlorocyclohexane	α-Chloro aralkyl	k_α/k_{CY}[c]
Triphenylmethane						
..	..	0	NB	Extrapolated		3.7[d]
7.50	7.50	0.50	NB	0.631	0.246	4.54
15.0	37.6	1.00	NB	2.619	.390	4.48
22.5	22.4	1.50	NB	0.927	.415	5.28
Indan						
..	..	0	NB or CY	Extrapolated		2.2
22.2	110	1.48	None	0.396	0.805	3.02
42.2	39.9	2.81	NB	0.985	1.290	3.71
44.3	85.7	2.95	None	2.45	1.44	3.41
74.0	51.8	4.93	None	0.429	0.952	4.63
Tetralin						
..	..	0	NB or CY	Extrapolated		2.1
221	107	1.47	None	4.53	0.845	2.72
44.5	44.5	2.97	NB	0.551	.579	3.16
44.5	79.5	2.97	None	.158	.102	3.46
74.1	42.9	4.94	None	.336	.795	4.11
Phenylcyclohexane						
..	..	0	NB	Extrapolated		3.6
17.7	18.5	1.18	NB	0.837	0.214	3.17
17.8	18.5	1.18	NB	0.596	.159	3.31
35.3	36.1	2.35	NB	1.409	.348	2.99
35.3	36.1	2.35	NB	1.135	.263	2.84
52.2	53.6	3.48	None	1.029	.211	2.50
Phenylcyclopentane						
..	..	0	NB	Extrapolated		4.7
15.0	15.2	1.00	NB	0.600	0.210	4.21
18.9	18.9	1.26	NB	.498	.160	3.81
37.9	37.5	2.52	NB	.635	.164	3.08
37.9	37.5	2.52	NB	.888	.227	3.03

[a] Mole liter⁻¹ at 40°. [b] NB = nitrobenzene, CY = cyclohexane. [c] Per hydrogen atom. [d] From Fig. 2. [e] Ref. 4.

TABLE III

PHOTOCHLORINATION OF BUTYLBENZENE AT 40°

Butylbenzene mmoles	Concn.[a]	Solvent	α	β	γ	ω	$\dfrac{k_\alpha^b}{k_\omega}$	$\dfrac{k_\beta}{k_\omega}$	$\dfrac{k_\gamma^b}{k_\omega}$	$\dfrac{k_\gamma^b}{k_\beta}$
94.2	6.28	None	2.56	1.35	1.69	0.28	13.9	7.3	9.2	1.25
44.9	2.99	CCl₄	2.25	1.26	1.60	.40	8.5	4.7	6.0	1.3
19.9	0.99	CCl₄	1.94	1.11	1.48	.44	6.6	3.8	5.0	1.3
19.8	0.99	C₆H₆[c]	2.84	1.42	1.76	.21	20	10	13	1.2
	0	Extrapolated	..	..	..	..	5.9	2.7	4.0	1.3

[a] Moles l.⁻¹ at 40°. [b] Per hydrogen atom. [c] 9.23 moles l.⁻¹.

aralkyl chlorides were analyzed by selective hydrolysis. In cases where the ratio of the hydrocarbons changed significantly during chlorination, relative reactivities were calculated from the expression

$$k_{R_1H}/k_{R_1H} = \frac{\log\left([R_1H]_f/[R_1H]_i\right)}{\log\left([R_2H]_f/[R_2H]_i\right)}$$

when the subscripts refer to initial and final concentrations. These results are summarized in Table II as a function of aralkyl hydrocarbon concentration. Plots of relative reactivity as a function of aralkyl hydrocarbon concentration yield a series of straight lines easily extrapolated to infinite dilution. A few representative examples are plotted in Fig. 2.

In general the data of Table II and Fig. 2 seem to have a consistent trend. As the reactivity of the hydrogen increases the slope of the plot of $k_\alpha/k_{cyclohexane}$ becomes more positive. Again this is in part due to the intrinsic reactivity differences of the hydrogen atoms and in part due to the differences in the basicity of the aralkyl hydrocarbon involved. Phenylcyclopentane and phenylcyclohexane have rather high reactivities of the α-hydrogens at infinite dilution with negative rather than positive slopes when $k_\alpha/k_{cyclohexane}$ is plotted as in Fig. 2.

The peculiar behavior of phenylcyclohexane and phenylcyclopentane suggested the possibility that intramolecular reactions of complexed chlorine atoms with alkyl side chains might somehow be involved. We therefore studied the effect of solvents on the photochlorination of n-butylbenzene. The β, γ, and ω-chlorides of butylbenzene were analyzed by g.l.c. and the α-chloride was determined by hydrolysis. The results of the chlorinations are summarized in Table III.

TABLE IV

REACTIVITIES OF CARBON–HYDROGEN BONDS TOWARD CHLORINE ATOMS

Hydrocarbon	Solvent	Reference hydrocarbon	k, 1./mole sec. (40°)	Rel. react. (per hydrogen atom)	Ref.
Alkanes					
Methane	Vapor	Hydrogen	1.2×10^7	0.0044	6
Ethane	Vapor	Methane	2.8×10^9	1.05	7
Propane 1°	Vapor	Ethane	3.4×10^9	1.25	8
2°	Vapor	Ethane	1.2×10^{10}	4.42	8
n-Butane 1°	Vapor	Ethane	4.0×10^9	1.47	8
2°	Vapor	Ethane	1.4×10^{10}	5.15	8
i-Butane 1°	Vapor	Ethane	3.5×10^9	1.29	8
3°	Vapor	Ethane	1.7×10^{10}	6.25	8
Neopentane	Vapor	Propane	3.2×10^9	1.18	8
2,3-Dimethylbutane 1°	Reactants	Cyclopentane	2.7×10^9	1.0	4
3°	Reactants	Cyclopentane	1.1×10^{10}	3.9	4
Cycloalkanes					
Cyclobutane	Vapor	Propane	8.5×10^9	3.1	8
Cyclopentane	Vapor	Neopentane	7.6×10^9	2.8	9
Cyclopentane	Reactants	2,3-Dimethylbutane	7.6×10^9	2.8	4
Cyclohexane	Reactants	Cyclopentane	7.3×10^9	2.7	4
Cycloheptane	Reactants	Cyclohexane	8.1×10^9	3.0	4
Cyclooctane	Reactants	Cyclohexane	1.2×10^{10}	4.3	4
Aralkyl hydrocarbons					
Toluene	NB, CY	Cyclohexane	3.7×10^9	1.4	
Ethylbenzene, α	NB, CY	Cyclohexane	9.5×10^9	3.5	
β	NB	α-Position	4.8×10^9	1.8	
Cumene, α	NB, CCl$_4$, CY	Cyclohexane	2.1×10^{10}	7.8	
β	NB	α-Position	6.0×10^9	2.2	
Indan, α	NB, CY	Cyclohexane	1.6×10^{10}	6.1	
β	NB	α-Position	1.3×10^{10}	4.7	
Tetralin, α	NB, CY	Cyclohexane	1.6×10^{10}	5.8	
β	NB	α-Position	1.5×10^{10}	5.5	
Diphenylmethane	NB, CY	Cyclohexane	7.3×10^9	2.7	
Triphenylmethane	NB	Cyclohexane	2.8×10^{10}	10	
Phenylcyclopentane, α	NB	Cyclohexane	3.5×10^{10}	13	
Phenylcyclohexane, α	NB	Cyclohexane	2.7×10^{10}	9.9	
t-Butylbenzene, β	CCl$_4$	Cyclooctane	1.7×10^9	0.63	
n-Butylbenzene, α	CCl$_4$	. . .	. . .	5.9	
β	CCl$_4$	. . .	. . .	2.7	
γ	CCl$_4$	. . .	. . .	4.0	
ω	CCl$_4$	. . .	. . .	1.0[a]	
Substituted alkanes					
t-Butyl chloride	Reactants	Cyclopentane	3.3×10^3	0.12	4
Methyl chloride	Vapor	Cyclopentane	1.8×10^8	.066	9
Methylene chloride	Reactants	t-Butyl chloride	3.0×10^7	.011	4
Chloroform	Reactants	t-Butyl chloride	1.4×10^7	.0051	4
Acetonitrile	Reactants	t-Butyl chloride	1.1×10^7	.004	4

[a] Assumed to have the same reactivity as a 1°-hydrogen atom of n-pentane.[4]

The extrapolated values of the relative reactivities, obtained from Fig. 3, clearly indicate a greater reactivity for the α- and γ-hydrogen atoms of butylbenzene than for the β-hydrogen atoms toward the free chlorine atom. This difference persists even in benzene solution and in neat butylbenzene where the hydrogen abstracting species would be mainly the benzene–chlorine atom complex and the butylbenzene–chlorine atom complex I, respectively. The ratio k_γ/k_β is essentially constant

I
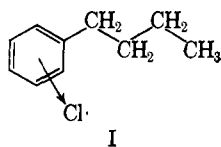
as the concentration of the butylbenzene is varied. These results appear to exclude the occurrence of intramolecular chlorine abstraction in I or at least an intramolecular reaction with any preference for a given position. If this intramolecular reaction had occurred a gradual change in relative reactivities would not have

been expected in going from very low butylbenzene concentrations (free chlorine atom) to moderate butylbenzene concentrations (intramolecular reaction favored) and finally to high butylbenzene concentrations (intermolecular reaction favored).

Discussion

The relative reactivities of Tables I and II can be combined to give the reactivity data summarized in Table IV. The reactivity of cyclohexane has been taken as 2.7 so that the data can be compared directly with our previous reactivity data.[4]

We have also included in Table IV our previous data based on competitive chlorinations together with the vapor phase results of Pritchard, Pyke, and Trotman-Dickinson[6] and of Knox.[7–9] Some comments about

(6) H. O. Pritchard, J. B. Pyke, and A. F. Trotman-Dickenson, J. Am. Chem. Soc., 77, 2629 (1955).

(7) J. H. Knox, Chem. Ind. (London), 1631 (1955).

(8) J. H. Knox and R. L. Nelson, Trans. Faraday Soc., 55, 937 (1959).

(9) J. H. Knox and A. F. Trotman-Dickenson, "Reactions of Free Radicals in the Gas Phase," Special Publication No. 9, The Chemical Society (London), 1957, p. 35.
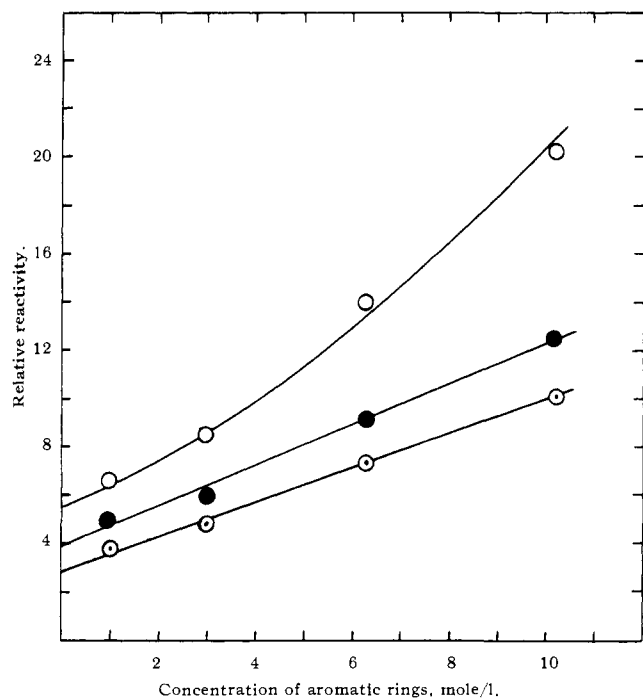
Fig. 3.—Relative reactivity (O, k_α/k_ω; ◐, k_β/k_ω; ●, k_γ/k_ω) of hydrogen atoms of butylbenzene in photochlorination at 40°.

the assumptions involved in constructing Table IV are in order. The absolute rate constant for the attack of chlorine atoms in the vapor phase upon cyclopentane and other alkanes has been determined by Trotman-Dickinson and Knox by competitive methods based on the known rate constant for attack upon molecular hydrogen. In the liquid phase relative reactivities of numerous materials, including cyclopentane, are available as a result of competitive measurements. The two sets of data have been combined by the assumption that the rate constant for attack of chlorine atoms upon cyclopentane is the same in vapor and liquid phases. Evidence in support of this assumption is available in the similar selectivities displayed by chlorine atoms in vapor and liquid phase reactions. For example in the chlorination of n-butane, vapor phase experiments indicate $E_a(1°)$ — $E_a(2°)$ = 480 cal./mole[10] while in the liquid phase $E_a(1°)$ — $E_a(2°)$ = 400 cal./mole.[11] For n-butane the reactivity ratio $k_{2°}/k_{1°}$ is found to be 2.7 at 68° in the liquid phase[11] and 3.7 at 68° in the vapor phase.[11] At 0° the relative reactivities are 3.1 (liquid) and 4.2 (vapor). A slightly greater selectivity of vapor phase reactions is also shown in the chlorination of isobutane, $k_{3°}/k_{1°}$ being 4.5 at −15° in the liquid phase[4] and 6.0–6.2 in the vapor phase at −15° (extrapolated).[8,10] In the chlorination of 1-chlorobutane the liquid phase reaction appears to be somewhat more selective. Fredricks and Tedder report the relative reactivities of the 1-, 2-, 3-, and 4-positions to be 0.7:2.2:4.2:1.00 at 35° in the vapor phase,[12] whereas Walling and Mayahi report relative reactivities of 0.36:1.3:2.8:1.00 at 34° in the liquid phase.[11] In the gas phase, competitive experiments indicate that the 2°-hydrogen atoms of cyclopentane and n-butane have relative reactivities of 0.55:1 at 68°, while in the liquid phase relative reactivities are 0.77:1.[8,10,11] The vapor phase competitive chlorination of toluene and cyclohexane indicates a relative reactivity (per hydrogen atom) of

(10) P. C. Anson, P. S. Fredricks, and J. M. Tedder, *J. Chem. Soc.*, 918 (1959).

(11) C. Walling and M. F. Mayahi, *J. Am. Chem. Soc.*, **81**, 1485 (1959).

(12) P. S. Fredricks and J. M. Tedder, *J. Chem. Soc.*, 144 (1960).

0.47:1.00 at 70°,[13] whereas in the liquid phase a relative reactivity of 0.54:1.00 at 40° is observed. On the basis of the similar reactivities observed in vapor and liquid phase reactions of chlorine atoms the assumption that the rate constant for reactions of chlorine atoms in vapor liquid phase are identical is not an unreasonable one.

In regard to the reactivity of the aralkyl hydrocarbons toward chlorine atoms it is seen that substitution of a phenyl group for a hydrogen atom activates the remaining α-hydrogen atoms, but the magnitude of this activation is fairly small except for the change in the reactivity between methane and toluene. The relative reactivities of the hydrogen atoms of methane, toluene, diphenylmethane, and triphenylmethane are 1:320:615:2300. Substitution of phenyl for hydrogen in ethane results in an activation of only 3-fold, the relative reactivities of the hydrogen of ethane and ethylbenzene (α-position) being 1:3.3. Similarly, substitution of a phenyl group for a secondary hydrogen in propane produces only a small activation, the relative reactivities of the 2°-hydrogen of propane and the α-hydrogen of cumene being 1:1.4. Substitution of phenyl for hydrogen in cyclopentane and cyclohexane produces an activation of 5-fold and 3.5-fold, respectively, for the hydrogen atom attached to the point of substitution (according to the data of Table IV the hydrogen atoms of cyclopentane and cyclohexane are less reactive toward chlorine atoms than the secondary hydrogen atoms of propane). In general, the amount of activation resulting from the substitution of phenyl for hydrogen is inversely proportional to the reactivity of the hydrogen atom in the alkane before substitution. Thus the carbon–hydrogen bonds in methane are quite unreactive toward chlorine atoms and substitution of phenyl produces a large increase in reactivity (>300-fold). The secondary hydrogens of propane are about one thousand times as reactive as the hydrogens of methane and substitution of phenyl produces only a small (<2-fold) activation. The nearly 4-fold difference in reactivity between the hydrogens of diphenylmethane and triphenylmethane is somewhat inconsistent with this general trend.

Another explanation can be advanced for the trend in reactivities observed when phenyl groups are substituted for hydrogen atoms. Instead of phenyl-group activation being inversely proportional to the reactivity of the hydrogen atom for which the phenyl group is substituted, it can be argued that the activating influence of a phenyl group depends upon its environment and factors such as steric inhibition of resonance are important. Evidence against this explanation can be found when the effects of substituting phenyl groups for methyl groups are considered. Thus, when the hydrogens of methane are substituted by methyl groups the relative reactivities (per hydrogen atom) toward chlorine atoms are methane:ethane:propane (2°-hydrogen):isobutane (3°-hydrogen) = 1:240:1000:1400 at 40°. Substitution of phenyl groups for the hydrogens of methane gives the relative reactivities of methane: toluene:diphenylmethane:triphenylmethane as 1:320: 615:2300. Thus, phenyl and methyl groups activate carbon–hydrogen bonds toward attack by chlorine atoms to practically the same degree. These data emphasize a point made previously—that in chlorination the phenyl group fails to produce an activation consistent with its effect in many other free radical processes or with the resonance stabilization expected for the benzyl radical.[5] The present findings are in complete agreement with the conclusion that in chlorin-

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

ation the transition state involves little breaking of the carbon–hydrogen bond and therefore is rather insensitive to resonance stabilization. Moreover, the conclusion that there is little difference in the activating influence of a phenyl or methyl group on an α-carbon–hydrogen bond suggests that the activating ability of phenyl, albeit low, is either independent of steric considerations or affected by steric considerations to the same degree as the methyl group.

This conclusion is further substantiated when the effect of substitution of a phenyl group for a methyl group in ethane, propane, and isobutane is considered. Again there is little change in relative reactivity of the hydrogen atoms: toluene:ethane = 1:0.75, ethylbenzene (α-hydrogen):propane (2°-hydrogen) = 1:1.5, cumene (α-hydrogen):isobutane (3°-hydrogen) = 1: 0.81, ethylbenzene (α-hydrogen):diphenylmethane = 1:0.8. The variation in these ratios is small, and shows no consistent trend.

The above conclusion does not hold when the less reactive and more selective complexed chlorine atom is considered, presumably because the transition state involves more bond breaking and resonance stabilization is more important. The appropriate data for comparing the effect of structure upon reactivity toward the complexed chlorine atom should involve only a single complexing agent. Unfortunately data of this type are not available. Previously reported data in 4 M benzene and 4 M t-butylbenzene solution are available for the reactivity of 1°-, 2°-, and 3°-hydrogen atoms in branched-chain saturated compounds relative to cyclohexane.[4] Averaging these reactivities yields the reactivity series, 1°-hydrogen:2°-hydrogen:3°-hydrogen: cyclohexane hydrogen = 1:5.4:27:6. From Fig. 2 the reactivities of toluene, ethylbenzene, and cumene relative to cyclohexane can be obtained (the aralkyl hydrocarbon itself). These data yield the reactivity series (cyclohexane hydrogen = 6.0) of toluene:ethylbenzene(α-hydrogen):cumene (α-position):cyclohexane of 2.4:9: 20:6. Thus, toward the complexed chlorine atom in the presence of 4 M alkylbenzene the substitution of a phenyl group for an alkyl group in an alkane does not produce a constant activation. When comparing RCH_3 and $C_6H_5CH_3$ (R = alkyl) the phenyl group activates 2.4-fold over the alkyl group; comparing R_2CH_2 and $C_6H_5CH_2R$ the phenyl group activates 1.6-fold over the alkyl group; comparing R_3CH and $C_6H_5CH(R)_2$ the phenyl group fails to activate significantly and a deactivation of 0.7-fold is indicated. Here we see a consistent trend, possibly supporting the conclusion that in ethylbenzene, and to a larger degree in cumene, that the phenyl group does not make as large a contribution to activation as in toluene, possibly because of steric inhibition of resonance in the transition state for hydrogen abstraction.[14]

If steric inhibition of resonance in the transition state for attack of "free" chlorine atoms upon the α-hydrogens of ethylbenzene and cumene is unimportant, the conclusion seems inescapable that α-positions of indan, tetralin, and butylbenzene are intrinsically more reactive than the 2°-benzylic hydrogens of ethylbenzene. Possible steric effects in the reactions of indan and tetralin have been discussed previously.[15a,b] Excluding the previously reported data for the trichloromethyl radical[16] because of uncertainties in regard to the technique involved,[17] the available reactivity data for these compounds are given in Table V.

(14) E. C. Kooyman and A. Strang, *Rec. trav. chim.*, **72**, 329 (1953).

(15) (a) G. A. Russell, *J. Am. Chem. Soc.*, **78**, 1047 (1956); (b) J. A. Meyer, V. Stennett, and M. Szwarc, *ibid.*, **83**, 25 (1961).

(16) E. C. Kooyman, *Discussions Faraday Soc.*, **10**, 163 (1951).

From the data of Table V we see little support for Szwarc's suggestion[15b] that only two α-hydrogen atoms of tetralin (axial) are susceptible to attack or that the higher reactivity observed for indan and tetralin relative to ethylbenzene is due to steric inhibition of resonance in the incipient α-phenethyl free radical. The reactivity of the methylene group in indan and tetralin toward chlorine atoms is about in the range of what might be expected for an o- or p-substituted ethylbenzene. Thus, in dilute carbon tetrachloride solution a methyl group of p-xylene is 1.6 times as reactive as the methyl group of toluene toward a chlorine atom.[18]

The high reactivities noted for the 3°-hydrogen atoms of phenylcyclopentane and phenylcyclohexane remain somewhat puzzling. Phenylcyclopentane is more active than phenylcyclohexane, as has been previously observed in reactions with the peroxy radical, presumably because of steric considerations.[15a] However, toward the selective peroxy radical the α-hydrogen atom of phenylcyclohexane is considerably less reactive than the α-hydrogen atom of cumene, whereas toward the chlorine atom the 3°-hydrogens of both phenylcyclopentane and phenylcyclohexane are considerably more reactive than the 3°-hydrogen of cumene.

The effect of phenyl or methyl substitution for hydrogen in an alkane upon the reactivity of hydrogens on the carbon adjacent to the point of substitution is not clear. The reactivities of 1°-hydrogen atoms in alkanes (methane excluded) in Table III vary between 1 and 1.5 and are presumably determined by the bond dissociation energy involved and the polar factor; i.e., the electron density of the carbon–hydrogen bond is determined by inductive effects or the ability of the alkane to stabilize the transition state by a contribution of the form $R^+ \cdot H\ Cl:^-$,[19] as well as by the usual hyperconjugation structures.

In t-butylbenzene the reactivity of the β-hydrogens has been decreased to 0.63 vs. 1.2 for neopentane and 1.29 for isobutane. In n-butylbenzene the γ-hydrogen atoms are about 1.3 times as active as the β-hydrogen atoms but unfortunately no direct comparison can be made with the reactivity of 2°-hydrogen atoms of butane. On the other hand, in cumene and ethylbenzene the β-hydrogens seem to be activated by nearly 100% relative to the alkane analogs, while the β-hydrogens of indan and tetralin are 1.7 and 2.1 times as reactive as the hydrogens of cyclopentane and cyclohexane.

Experimental

Chlorination Procedure.—The apparatus used was similar to that described previously.[5] Liquid chlorine was stored in a small graduated tube in the apparatus and allowed to vaporize into a stream of nitrogen when needed. The chlorine was diluted with nitrogen (Matheson, prepurified, dried over phosphorus pentoxide beads) in a 500-ml. bulb before passing into the reaction flask. The reaction flask was a tube of approximately 30-ml. volume immersed in a thermostated water bath. The reaction flask was illuminated with a 200-watt unfrosted tungsten light bulb

(17) G. A. Russell and C. DeBoer, *J. Am. Chem. Soc.*, in press.

(18) Unpublished work with Mr. Roger C. Williamson.

(19) G. A. Russell, *J. Org. Chem.*, **23**, 1407 (1958).

immersed in the bath approximately 3 cm. from the reaction flask. The stream of nitrogen served both to remove traces of oxygen and to stir the reaction mixture. The exit gases were passed through an ice reflux condenser and an aqueous solution of sodium hydroxide.

The mixtures to be chlorinated were prepared by dilution of the appropriate amount of reagent with the desired solvent at 40°. The mixture was placed in the reaction flask and degassed with nitrogen before chlorination. The length of time for the addition of chlorine varied, depending on the amount of chlorine being added. After the chlorine had been added the reaction mixture was degassed for approximately an additional hour. The amount of the chlorine added was never allowed to exceed 5 mole % of the hydrocarbons being chlorinated.

Analytical Procedure.—Analyses of α-chlorides were obtained by selective hydrolysis of the reaction mixture in 80% alcohol. The progress of the hydrolysis was followed by titrating the hydrogen chloride formed with standard base. Upon the completion of the hydrolysis of the α-chloride, the mixture was acidified and titrated potentiometrically with standard silver nitrate. Analyses of β-chlorides were obtained by subtracting the amount of α-chloride from the amount of total chloride. Two methods were employed for determining the total chloride: the Rauscher[20] method which will detect all chloride, even aromatic chlorine, and a modification of this method which will determine only alkyl chlorides.[21] The first method was employed for ethylbenzene and cumene. Although both methods gave identical results in the analysis of chlorination products of ethylbenzene, the analysis of the chlorination products of tetralin and indan revealed a discrepancy between the two methods. The lower values obtained by the second method were used for the sum of α- and β-chlorides. It is surmised that both tetralin and indan underwent nuclear substitution.

For the analyses of chlorobutylbenzenes a Perkin–Elmer Model 154D vapor fractometer with a 300-ft., $^1/_8$-in. internal diameter Golay column treated with polypropylene glycol was used at 128°. Nitrobenzene was used as the internal standard. Relative retention times were (nitrobenzene = 1.0); β-chloro, 1.31; γ-chloro, 1.36; ω-chloro, 1.81. The isomeric β-, γ-, and ω-chlorobutylbenzenes were synthesized and the peaks due to the separate isomers identified. The thermoconductivity of these isomers was assumed to be identical. In the injector of the chromatograph, a glass covered heating element was installed in order to prevent decomposition of the chlorides. However, α-chlorobutylbenzene still decomposed to give an extra peak, presumably due to β-ethylstyrene, and the extent of decomposition was not reproducible. For the analysis of α-chlorobutylbenzene, selective hydrolysis of aliquots of the chlorination product in 80% ethanol solution with stirring (heterogeneous) at 60° was employed. The hydrolysis was followed by directly titrating with 0.1 N sodium hydroxide the hydrogen chloride liberated. The hydrolysis was complete in 24 hr. as evidenced by the constancy of the sodium hydroxide titer. Under the same conditions the other isomeric chlorobutylbenzenes were not hydrolyzed. The hydrolyzed product was titrated potentiometrically with 0.05 N silver nitrate after the sodium hydroxide titer became constant. Blank corrections were applied.

In the competitive chlorination of the aralkyl hydrocarbons with cyclohexane the α-chloride was determined as above, and the chlorocyclohexane was determined by gas–liquid chromatography (g.l.c.). In the latter case toluene was used as an internal standard except in the chlorination of toluene where both chlorocyclohexane and benzyl chloride were analyzed by g.l.c. For all analyses by g.l.c. standard samples were prepared and experimentally determined correction factors were used to convert relative peak areas to relative molar concentrations. Excellent agreement was found when the above method of analysis for the chlorination products of cyclohexane–diphenylmethane was compared with the analysis based on the assumptions that the difference between total chlorine and easily hydrolyzed chlorine could be taken as chlorocyclohexane.

Reagents.—Phillips toluene, ethylbenzene, and cumene (99 mole % minimum purity) were used. Indan was prepared by the reduction of indene (Chemical Intermediates and Research Laboratories) over 5% palladium-on-charcoal catalyst. After the reaction mixture had been washed several times with neutral potassium permanganate and water, it was dried and distilled; b.p. 78–79° (30 mm.), n^{20}D 1.5390. Tetralin (Matheson Practical grade) was purified by repeated washing with both 90% sulfuric acid and water, dried, and distilled; n^{20}D 1.5416. Eastman Kodak Co. diphenylmethane, triphenylmethane, and phenylcyclohexane were used. Phenylcyclopentane was prepared from bromocyclopentane and benzene by the action of aluminum bromide; b.p. 216.0–216.5°, n^{20}D 1.5288. Eastman Kodak Co. cyclohexane (Spectro grade) and Phillips cyclohexane (99 mole %

minimum purity) were both used. The butylbenzene employed was Purist grade obtained from Aldrich Chem. Co. Nitrobenzene was distilled through a Vigreux column before use. All liquids were further purified by passage over activated silica gel in a nitrogen atmosphere and stored under nitrogen prior to chlorination.

α-Chlorobutylbenzene.—The synthesis of this compound from the reaction of α-propylbenzyl alcohol with thionyl chloride is reported.[22] α-Propylbenzyl alcohol (45 g., b.p. 110–113° at 10 mm., n^{20}D 1.5137) obtained from the reaction of benzaldehyde and propylmagnesium bromide was placed in a 100-ml. three-necked flask fitted with a filtered glass gas inlet tube and a calcium chloride drying tube. As anhydrous hydrogen chloride was passed into the alcohol, heat was evolved and a water layer separated in the bottom of the flask. Cooling by an ice–water bath was applied when necessary. The addition of anhydrous hydrogen chloride was continued until the amount of the water layer became constant. After the water layer was removed the organic layer was dried with anhydrous magnesium sulfate overnight. Hydrogen chloride was removed by evaluation of the flask containing the chloride. After distillation through a simple Claisen head at a pressure of 1 mm., 41 g. (81% yield) of the product was obtained, b.p. 60–61° (1 mm.), n^{20}D 1.5164. An analysis of this product by hydrolysis in 80% ethanol indicated that the chloride was 97% pure.

β-Chlorobutylbenzene has not been reported in the literature. A mixture of 1-phenyl-2-butanol (22 g.) and pyridine (238 ml.) was added dropwise to thionyl chloride (22.4 ml.) placed in a 250-ml. three-necked flask fitted with a dropping funnel, stirrer, and thermometer. During the addition the temperature was kept at 0–5°. Stirring was continued for 24 hr. after addition was complete. The mixture was poured over ice, transferred to a separatory funnel, ether (20 ml.) added, and the organic layer separated, washed with water six times and dried over anhydrous magnesium sulfate. This material was distilled at a pressure of 1 mm. by using a 30-cm. Daufton column; a fraction 63.2–64° (4.5 g., 18% yield) was collected. By g.l.c. analysis this product was shown to be composed of 91% of the desired chloride and 9% of unreacted 1-phenyl-2-butanol.

1-Phenyl-2-butanol.—An attempted synthesis was made by following the method described for 1-phenyl-2-propanol.[23] The reaction gave a very poor yield probably owing to the self-condensation of phenylacetaldehyde and purification by recrystallization of the half-ester of phthalic acid was required. The alcohol was prepared from 1-phenyl-2-butanone (100 g., K and K Laboratories) by reduction with lithium aluminum hydride (7.7 g.). After distillation through a Todd column packed with Monel helices, a fraction, b.p. 74–75° (1 mm.), n^{20}D 1.5161, was obtained in 74% yield.

γ-Chlorobutylbenzene.—Braun and Neumann synthesized this compound by decomposition of the benzamide of γ-aminobutylbenzene.[24] Later Schlenk and Bergman attempted to synthesize this compound by the reaction of 4-phenyl-2-butanol with thionyl chloride. They reported that the chloride was decomposed during distillation at a pressure of 16 mm.[25]

4-Phenyl-2-butanol (40 g.) was treated with thionyl chloride (40.4 ml.) in the pressure of pyridine (43 g.) in a similar manner to the procedure described for β-chlorobutylbenzene. The fraction, b.p. 61–64° (1 mm.), was found to be composed of 96% of the chloride and 4% of 4-phenyl-2-butanol by g.l.c. analysis. The yield was 10.1 g. (23%).

4-Phenyl-2-butanol was prepared from benzalacetone (250 g., Matheson Coleman and Bell) by hydrogenation in the presence of copper–chromium oxide catalyst under 2,000 p.s.i. at 150–175°.[26] The crude product gave a positive test with 2,4-dinitrophenylhydrazine. By the distillation through a Todd column packed with Monel helices, a fraction (100 g.), which was negative to 2,4-dinitrophenylhydrazine, b.p. 124° (14 mm.), n^{20}D 1.5172, was obtained.

ω-Chlorobutylbenzene was synthesized by the method described by Braun.[27] N-Benzoyl-4-phenyl-1-butylamine was prepared from 4-phenyl-1-butylamine (50 g., Aldrich Chem. Co.) and benzoyl chloride (54 g.) by the Schotten–Baumann reaction. After recrystallization from 95% ethanol the amide, m.p. 83–83.5°, was obtained in 70% yield. The benzamide (60 g.) and phosphorus pentachloride (50 g.) were placed in a 250-ml. distilling flask and were heated to 150° to distil phosphoryl chloride. Then the temperature was raised from 180 to 250° to distil the mixture of benzonitrile and ω-chlorobutylbenzene. For the separation of the benzonitrile, vacuum distillation through a 30-cm. Daufton column was employed, instead of the hydrolysis

(20) W. H. Rauscher, *Ind. Eng. Chem., Anal. Ed.*, **9**, 296 (1937).

(21) W. H. Rauscher, *ibid.*, **9**, 503 (1937). This method is ineffective for sterically hindered chlorides such as chlorocyclohexane and 2-phenyl-1-chloropropane.

(22) P. A. Levene and R. E. Marker, *J. Biol. Chem.*, **97**, 379 (1932); M. Protiva, J. Pliml, M. Borovicka, and V. Rericha, *Chem. Listy*, **46**, 346 (1952).

(23) M. M. G. Austerwell and G. Cochin, *Compt. rend.*, **150**, 1693 (1910); K. V. Auwers and O. Jordan, *Biochem. Z.*, **144**, 31 (1924).

(24) J. v. Braun and L. Neumann, *Ber.*, **50**, 50 (1917).

(25) W. Schlenk and E. Bergmann, *Ann.*, **479**, 58 (1930).

(26) H. Adkins and R. Connor, *J. Am. Chem. Soc.*, **53**, 1091 (1931).

(27) J. v. Braun, *Ber.*, **43**, 2837 (1910).

in concentrated hydrochloric acid at 160° used by Braun.[24] A fraction (12 g.), b.p. 118.5° (14 mm.), $n^{25}D$ 1.5167, was obtained. It was found to be 100% pure by g.l.c. analysis.

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

Photochlorination of Bromocyclopentane and Chlorocyclopentane[1]

BY GLEN A. RUSSELL[2] AND AKIHIKO ITO

The compounds mentioned in the title have been photochlorinated utilizing molecular chlorine, *t*-butyl hypochlorite, sulfuryl chloride, and trichloromethanesulfonyl chloride at 40 and −30°. A pronounced directive effect of the halogen substituent was observed in the hydrogen abstraction reaction as well as considerable stereoselectivity in the reaction of the resulting halocycloalkyl radical with the chlorinating agent. The *trans* products are always preferred. The unusually high reactivity noted for the hydrogen atoms at the 2-position in bromocyclopentane suggests that the bromine atom is participating as a neighboring group when a radical or atom attacks these hydrogen atoms. Competitive halogenations of the halocyclopentanes and halocyclohexanes with the parent hydrocarbons have also been performed.

The effects of polar substituents on the position of attack of chlorine atoms on acyclic molecules have been studied.[3] Similar effects in cyclic compounds have been less thoroughly studied, although Nevill has reported that the major products of chlorination of cyclobutanecarboxylic acid and 1,1-cyclobutanedicarboxylic acid are the *trans*-3-chlorides.[4] We have investigated the chlorination of bromo- and chlorocyclopentanes and cyclohexanes[5] to determine the effect of the substituent in directing the attack of a chlorine atom and the stereochemical effect of the substituent in the following reaction between molecular chlorine and the halocycloalkyl radical. Closely connected with this work is the question of conformational stability of radicals derived from the cyclohexane ring system.[5]

Results

Proof of Structure of Dihalocyclopentanes.—The photochlorination of chlorocyclopentane produced the expected 5 isomeric dichlorocyclopentanes which could be separated by gas–liquid chromatography (g.l.c.). The photochlorination of bromocyclopentane at 40° produced *trans*-1,2-dichlorocyclopentane in addition to the 5 bromochlorocyclopentanes (see Fig. 1). All of the isomeric dihalides except the 1,3-dihalides could be obtained by standard preparative methods. Assigning the *cis*-1,3-dichlorocyclopentane structure to peak B, Fig. 1, defined the chlorination products of chlorocyclopentane and bromocyclopentane since from the g.l.c. curves of Fig. 1 it immediately follows that A must be *trans*-1,3-dichlorocyclopentane, A′ must be *trans*-1,3-bromochlorocyclopentane, and B′ must be *cis*-1,3-bromochlorocyclopentane. For all 5 pairs of structurally similar dichlorocyclopentanes and bromochlorocyclopentanes a constant ratio of retention times of 1:1.55 was observed.

Additional proof for the structure assignments was provided by the observation that the dichlorides corresponding to peaks A and B (Fig. 1) were the only dichlorides formed from the reaction of 4-chlorocyclo-

pentane with hydrogen chloride, although again the yields of the dichlorides were very poor.
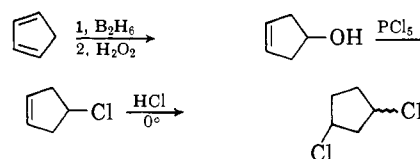
In addition, the dichlorides corresponding to peaks A, A′, B, and B′ were isolated by rectifications of large scale chlorinations of chlorocyclopentane and bromocyclopentane. Analysis of the proton nuclear resonance spectra completely confirmed the assignment of structures. The spectra of each pair of isomers (A and A′, B and B′) were nearly identical. The spectra for the dichlorides are given in Fig. 2 and 3. The spin–spin splitting of the methylene protons attached to carbon atom 2 is particularly instructive. In the *trans* dichloride these protons are equivalent and are split by the equivalent protons on carbon atoms 1 and 3 to give the well defined triplet at $\tau = 7.57$, $J = 5.3$ c.p.s. (Fig. 2). For the *cis* isomer (Fig. 3) the protons at carbon atoms 2 are not equivalent and a complex and broad pattern is found because of the strong coupling between these two protons. Moreover, in the *cis* compound coupling between H_C and H_D should be weaker (because of the dihedral angle) than coupling between H_A and H_B in the *trans*-dichloride. Consistent with
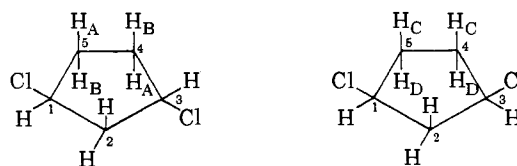
this prediction, the separation between lines for the high field methylene protons of the *trans* isomers are greater than the corresponding separations for the *cis* isomers.[6]

The n.m.r. spectra of all the dichlorocyclopentanes and bromochlorocyclopentanes have been recorded.[7]

(1) (a) Directive Effects in Aliphatic Substitution. Part XXI. (b) This work was supported by a grant from the Petroleum Research Fund, administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

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

(3) H. C. Brown and A. B. Ash, *J. Am. Chem. Soc.*, **77**, 4019 (1955); P. S. Fredricks and J. M. Tedder, *J. Chem. Soc.*, 918 (1959), 3520 (1961); L. Horner and L. Schläfer, *Ann.*, **635**, 31 (1960).

(4) W. A. Nevill, D. S. Frank, and R. D. Trepka, *J. Org. Chem.*, **27**, 422 (1962).

(5) G. A. Russell, A. Ito, and R. Konaka, *J. Am. Chem. Soc.*, **85**, 2988 (1963).

(6) These arguments apply strictly when eclipsed methylene groups are considered (F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961)). In cyclopentane the methylene groups are not completely eclipsed (K. S. Pitzer and W. E. Donath, *J. Am. Chem. Soc.*, **81**, 3213 (1959); F. V. Brutcher, T. Roberts, S. J. Barr, and N. Pearson, *ibid.*, **81**, 4915 (1959)) and in very flexible 5-membered rings, particularly those containing a hetero atom, the coupling constants of *trans*-hydrogen atoms can actually exceed those of *cis*-hydrogen atoms (F. A. L. Anet, *ibid.*, **84**, 747 (1962)).

(7) A. Ito, Ph.D. Thesis, Iowa State University Library, Ames, Iowa.