

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

Some Solvent and Structural Effects in Free Radical Chlorination¹

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The large effect of certain solvents (aromatics and CS₂) on the isomer distributions obtained in the free radical chlorination of hydrocarbons, first observed by Russell, has been confirmed and extended to a number of other systems. These solvents also greatly increase the temperature dependence of this distribution, and the whole phenomenon is discussed in terms of the formation of relatively stable π -complexes by Cl· which convert its reactions with primary, and perhaps secondary hydrogen to endothermic processes. Solvent effects in the chlorination of ethyl and *n*-butyl chlorides indicate that here the electron-accepting properties of Cl· are increased by complexing. Competitive chlorination of small ring compounds at 68° shows a continuous decrease in reactivity from cyclohexane to cyclopropane. Remarkably, the spread in reactivity decreases at 0°, and evidence is presented that cyclopropane acts as a complexing solvent for Cl·.

It has commonly been assumed that solvents, providing they are not actually attacked by free radicals, exert only negligible or second-order effects on the rates or course of free radical reactions between uncharged species. Thus, the first-order rates of decomposition of benzoyl peroxide and azobisisobutyronitrile change only slightly with medium,² and Leffler has noted small but largely compensatory changes in ΔH^\ddagger and ΔS^\ddagger in the decomposition of phenylazotriphenylmethane.³ Extensive studies of copolymerization again have shown no significant change in the relative reactivities of olefins in a wide variety of media.⁴

In contrast to this simple situation, recent results indicate that the reactive properties of chlorine atoms may be profoundly solvent dependent. In their survey of the field in 1935-1936, Hass, McBee and Weber⁵ noted that the selective tendency of chlorine atoms to attack aliphatic C-H bonds in the order primary < secondary < tertiary was somewhat greater in the gas than in the liquid phase, and, in 1955, Russell and Brown⁶ reported that this selectivity is very notably larger when SO₂Cl₂ is used as the chlorinating agent. Again, Miller⁷ has found that the relative reactivity of *p*-chlorotoluene *vs.* toluene toward chlorine atoms decreases from 0.69 to 0.46 when the predominantly aromatic medium of mixed toluenes is diluted with CCl₄. This importance of solvent effects in chlorine atom reactions was very dramatically emphasized, in 1957, by Russell⁸ who showed that the ratio of reactivities of tertiary to primary hydrogen in 2,3-dimethylbutane may be increased from approximately 3.5 to over 50 by carrying out the reaction in aromatic solvents. A parallel investigation was under way in this Laboratory at the time of Russell's striking communication, and this paper reports some of our results to date which give data on reactivities of primary, secondary and tertiary hydrogen in

various molecules, results of the halogenation of small rings, and some observations on solvent effects in the chlorination of molecules with polar substituents.

Results and Discussion

Relative Reactivities of Primary, Secondary and Tertiary Hydrogens.—Typical data comparing relative reactivities of neopentane, cyclohexane and 2,3-dimethylbutane toward chlorine atom attack in carbon tetrachloride and in benzene at 68° appear in Table I.

Experiments were run photochemically in sealed tubes using chlorine plus excess hydrocarbon and products analyzed by gas chromatography. Relative reactivities of the hydrocarbons were determined by analysis for unreacted hydrocarbon which eliminates any error due to polychlorination. The reported values were calculated by the usual relation for competitive chain-carrying steps in radical chain reactions involving the same attacking radicals

$$\frac{\log [R_1H]_0/[R_1H]}{\log [R_2H]_0/[R_2H]} = \frac{k_1}{k_2} \quad (1)$$

where [R₁H] and [R₂H]₀ are the initial concentrations of two hydrocarbons, [R₁H] and [R₂H] final concentrations and k_1/k_2 the ratio of rate constants for chlorine atom attack on the two species. For convenience all reactivities are referred to 2,3-dimethylbutane as standard. Partial rate factors were calculated from these relative reactivities together with gas chromatographic measurements of the relative amounts of primary and tertiary chlorides formed from the dimethylbutane.

Our data on the ratio of tertiary to primary substitution in 2,3-dimethylbutane show the same sort of striking solvent dependence reported by Russell, although our results in benzene indicate a slightly higher selectivity than would be predicted by extrapolation of Russell's data to 68°. They also show that the solvent effect extends to competitive reactions between different molecules, to the relative reactivities of primary and secondary hydrogens, and even different types of primary hydrogen.

A notable feature of these solvent effects, and one which has an important bearing on our interpretation of their origin, is the pronounced temperature dependence of chlorine atom selectivity in solvents where this selectivity is high. Tables II and III illustrate this phenomenon in the cases of the chlorination of *n*-butane and 2,3-

(1) Supported in part by a grant from the National Science Foundation.

(2) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 478, 512.

(3) M. G. Alder and J. E. Leffler, *THIS JOURNAL*, **76**, 1425 (1954); J. E. Leffler and R. A. Hubbard, *J. Org. Chem.*, **19**, 1089 (1954).

(4) F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 191 (1950).

(5) H. B. Hass, E. T. McBee and P. Weber, *Ind. Eng. Chem.*, **27**, 1190 (1935); **28**, 333 (1936).

(6) G. A. Russell and H. C. Brown, *THIS JOURNAL*, **77**, 4031 (1955).

(7) B. Miller, Thesis, Columbia University, 1955; C. Walling and B. Miller, *THIS JOURNAL*, **79**, 4181 (1957).

(8) G. A. Russell, *ibid.*, **79**, 2977 (1957).

TABLE I
 COMPETITIVE CHLORINATIONS OF NEOPENTANE (N), CYCLOHEXANE (C) AND 2,3-DIMETHYLBUTANE (D) AT 68°

System and solvent ^a	Relative reactivities ^b			Partial rate factors ^c			
	N	C	D	N(1°H)	C(2°H)	D(1°H)	D(3°H)
N,D,CCl ₄ (4.1)	0.79	..	1.00	1.38	..	1.00	3.7
N,D,C ₆ H ₆ (5.6)	.34	..	1.00	1.70	..	1.00	24
C,D,CCl ₄ (5.2)	..	1.16	1.00	..	2.1	1.00	4.1
C,D,C ₆ H ₆ (5.6)	..	1.42	1.00	..	5.8	1.00	18
N,C,DCCl ₄ (4.5)	.87	1.14	1.00	1.48	1.94	1.00	4.2
N,C,D,C ₆ H ₆ (5.6)	.33	1.15	1.00	1.66	5.8	1.00	24

^a Solvent molarity in parentheses. ^b Relative to dimethylbutane. ^c Relative to a single primary hydrogen of dimethylbutane.

dimethylbutane in bulk and in carbon disulfide solution. Carbon disulfide was chosen as a solvent in which selectivities are particularly high,⁹ and, in fact, measurements on 2,3-dimethylbutane were not made at above 11.1 *M* CS₂ since selectivities become too high for very accurate measurement.

 TABLE II
 SOLVENT EFFECTS IN THE CHLORINATION OF *n*-BUTANE

Solvent	T, °C.	Rel. react. (s/p) ^a	$\frac{\Delta H_p^* - \Delta H_a^*}{\Delta H_a^*}$ (cal./mole)
None	68 ^b	2.69 ± 0.08	
	0	3.09 ± .03	400
	-75	4.00 ± .03	
C ₆ H ₆ (9 <i>M</i>)	68	5.11	..
	CS ₂ (11.1 <i>M</i>)	68	6.55
34		7.8	1800
CS ₂ (13.3 <i>M</i>)	0	13.2	
	68	8.00	
	34	39.6	5600
	0	62.5	

^a Per hydrogen. ^b Actually in nitromethane (a non-complexing solvent) to reduce vapor pressure.

 TABLE III
 SOLVENT EFFECTS IN THE CHLORINATION OF 2,3-DIMETHYLBUTANE

Solvent	T, °C.	Rel. react. (t/p) ^a	$\Delta H_p^* - \Delta H_a^*$
None	68	4.04	
	0	4.96	800
	-75	11.0	
CS ₂ (11.1 <i>M</i>)	68	34.0	
	34	51.4	2300
	0	93.2	

^a Per hydrogen.

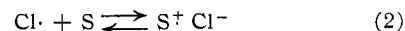
From the variation in ratios of secondary to primary and tertiary to primary halides in the products with temperature, differences in activation energy for chlorine atom attack on the different types of hydrogen may be calculated and are given in the tables. In bulk, differences are small and comparable to those calculated from gas-phase data.⁹ However, in carbon disulfide the differences amount to several kcal./mole, and are in fact significantly larger than the actual activation energy for chlorine atom attack on primary hydrogen (0.7–1 kcal.) determined by Pritchard, Pyke and Trotman-Dickenson¹⁰ for the reaction in the gas phase.

(9) G. A. Russell, private communication, July, 1957.

(10) H. O. Pritchard, J. B. Pyke and A. F. Trotman-Dickenson, *THIS JOURNAL*, **77**, 2629 (1955).

The foregoing certainly indicates that the properties of chlorine atoms are profoundly altered in aromatic solvents and in carbon disulfide, and the most plausible explanation^{7,8} appears to be that they associate with such solvents, presumably in the form of π -complexes. Since such complex formation should be accompanied by a loss of entropy, its occurrence indicates that it must be an exothermic process, and the resulting energetics are indicated in Fig. 1. The curves for uncomplexed chlorine atoms are drawn accurately from gas phase data and known bond dissociation energies.¹¹ Those for complexed atoms are more schematic, but they indicate both the origin of the greater selectivity, and its greater temperature dependence. If complex formation is exothermic to the extent of 10 kcal., chlorine atom attack on primary and secondary C–H bonds is transformed from an exothermic to an endothermic process with a corresponding increase in activation energy and also in selectivity between bonds of different strength. Here it may be noted that hydrocarbon chlorination is probably a particularly favorable system for observing a large solvent effect of this sort, first because the chlorine atom is strongly electronegative and accordingly shows a strong tendency to complex with electron-donating solvents and, second, because the energetics are so poised that a small amount of stabilization of the chlorine atom transforms its resulting reactions from exothermic to endothermic processes with a consequent great increase in selectivity.

Both Russell's results⁸ and our own indicate that the selective properties of chlorine atoms increase smoothly with increasing concentration of complexing solvents, as might be expected if an equilibrium is involved. However, plots of selec-



tivity (*i.e.*, k_1/k_2 ratios from eq. 1) vs. concentration of complexing solvent are in general concave upward, suggesting a series of complexes with one or more solvent molecules.⁸ Alternatively, since it is plausible that chlorine atoms are always to some extent associated with surrounding solvent,¹² the fraction "complexed" could depend as a first approximation upon the *ratio* of the solvents present and thus account for the relation observed in terms of a single complex. Sufficient data are not yet available to attempt to work out these relations in detail, but, from the energetics indicated in

(11) *Cf.* ref. 2, sec. 8.3.

(12) The strength of such association should be at least of the same order of magnitude as the heat of vaporization of simple non-polar molecules, 1–5 kcal./mole.

TABLE IV
 CHLORINATION OF SMALL RING COMPOUNDS (REACTIVITIES ALL RELATIVE TO CYCLOHEXANE)

Compound	Solvent	T, °C.	Total	Rel. react vs. C ₆ H ₁₂ Per C-H	ΔH* - ΔH*C ₆ H ₁₂ ^c
Cyclopentane	CCl ₄ (5 M)	68	0.75 ± 0.01	0.90 ± 0.01	
		0	.78 ± .02	.94 ± .03	- 140
Cyclobutane	CCl ₄ (5 M)	68	.67 ± .04	.81 ± .05	
		0	.57 ± .02	.85 ± .02	- 480
Cyclopropane	CCl ₄ (5 M)	68	.69 ± .03	1.03 ± .05	
		0	.57 ± .03	0.85 ± .04	
<i>n</i> -Butane	CCl ₄ (5 M)	68	.105 ± .014	.210 ± .027	
		0	.157 ± .011	.315 ± .023	-1700
Norcamphane	CCl ₄ (5 M)	68	.141	.283	
		0	.60 ± .01	1.17 ± .02 ^a	
Norcamphane	CCl ₄ (5 M)	68	.567 ± .01	1.12 ± .02 ^a	
		0	.43	1.28	
Norcamphane	CCl ₄ (5 M)	68	.75 ± .05	1.04 ± .05 ^b	
		0			

^a Per secondary H. ^b For 2,3,5,6-hydrogens, see text. ^c Cal./mole.

Fig. 1, we would anticipate that kinetic chain lengths and the rates of chlorinations carried out in complexing solvents should both be markedly reduced.

Reactivities of Cyclic Compounds.—The relative reactivities of small ring compounds toward hydrogen abstraction by free radicals has been discussed by Brown¹³ in terms of the effect of "I-strain" on the stability of the resulting radicals. This approach predicts the order of reactivity cyclopentane > cyclohexane > cyclobutane > cyclopropane. The gas-phase reaction of methyl radicals with cycloparaffins has been investigated by Trotman-Dickenson and Steacie¹⁴ with results in agreement with this sequence. Our own data on chlorination in carbon tetrachloride and in benzene appear in Table IV. At 68° in carbon tetrachloride relative reactivities, both per molecule and per hydrogen, decrease continuously with ring size and there is no indication of any heightened reactivity of cyclopentane. Also, even in the case of cyclohexane, reactivity per hydrogen is less than that of the secondary hydrogens of *n*-butane.

The most striking feature of the table is the decrease in selectivity when reaction is carried out at 0°, implying that chlorine atom attack on the smaller rings actually involves a lower heat of activation coupled with a more negative ΔS‡. Since all experiments were run in duplicate with good reproducibility, we believe that this effect is real, and it is paralleled by the apparent decrease in selectivity observed in experiments run in 7.3 M benzene. While we have no comprehensive explanation to offer, it is conceivable that chlorine atoms can actually complex with small rings, and this then provides a lower energy path for their reaction. In support of this suggestion we find that when a mixture of 0.5 cc. of 2,3-dimethylbutane and 2 cc. of cyclopropane is chlorinated at 0° the *i/p* ratio of the resulting chlorohexanes increases to 34 ± 4, compared with 5 (Table II) without cyclopropane. We hope to investigate this interesting question further.

Table IV also reports results on bicyclo[2.2.1]-heptane (norcamphane). Here chlorine atom

(13) H. C. Brown, R. S. Fletcher and R. B. Johannesen, *THIS JOURNAL*, **73**, 212 (1951).

(14) A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 329 (1951).

attack yields almost exclusively *exo*-2-chloronorcamphane, 93%, plus small amounts of two other unidentified isomers in keeping with the observations of Roberts on the chlorination using sulfuryl chloride.¹⁵ In carbon tetrachloride at 68° the reactivity of the whole molecule is 0.75 that of cyclohexane, but there is little if any attack on either the endomethylene group or the bridgehead tertiary hydrogens. The reactivity per hydrogen of the C-H bonds which are attacked is essentially the same as in cyclohexane. This of course assumes that both *exo*- and *endo*-hydrogens react. The formation of predominantly *exo*-chloride probably has no bearing on this question due to the easy inversion (or planar structure) of carbon radicals.

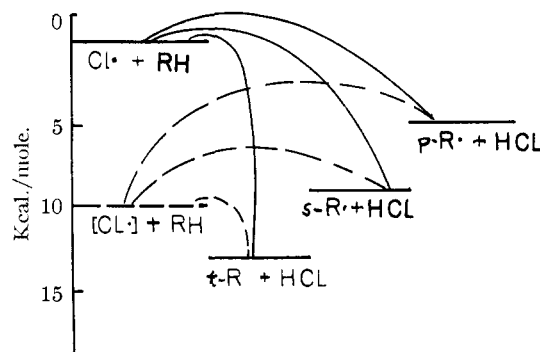


Fig. 1.—Energetics of reaction of complexed and uncomplexed chlorine atoms.

Molecules with Polar Substituents.—It is well recognized that electron-withdrawing substituents deactivate neighboring C-H bonds toward attack by chlorine atoms, the generally accepted explanation being that chlorine atoms are electron-accepting species.¹¹ Our investigations of the effect of complexing solvents on this deactivation were carried out on ethyl chloride and *n*-butyl chloride. Additional work on acid derivatives is currently in progress.

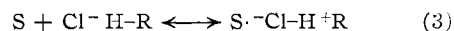
Results obtained with ethyl chloride, Table V, show that in CCl₄ the major product is 1,1-dichloride and that the molecule as a whole is less reactive than neopentane. Both results are in quali-

(15) J. D. Roberts, L. Urbanek and R. Armstrong, *THIS JOURNAL*, **71**, 3049 (1949).

tative agreement with gas-phase data in the literature,¹¹ although extrapolation of Pritchard's¹⁰ results to 0° gives a reactivity relative to neopentane of only 0.09. In complexing solvents the relative reactivity increases, as does the fraction of 1,1-dichloride formed. The values of $D(\text{CH}_3\text{-CHCl-H})$ have not been directly measured, but, since $D(\text{CCl}_3\text{-H})$ and $D(t\text{-C}_4\text{H}_9\text{-H})$ are both approximately 90 kcal.,¹⁶ it is probably comparable to that of a secondary C-H bond. Both results are thus qualitatively in agreement with the energy arguments given previously and may be explained as arising from a decrease in the ease of reaction of complexed Cl⁻ with neopentane and the primary hydrogens of ethyl chloride. More quantitatively, there is a 2.55-fold change in the relative reactivities of the 1- and 2-positions of ethyl chloride in going from CCl_4 to 11.1 M CS_2 , compared with a 4.3-fold change in the relative reactivities of the primary and secondary positions of *n*-butane at 0° on going from no solvent to 11.1 M CS_2 (Table II). Although the difference between these numbers may not be very significant, if complexing both

They report 7% 1,1-, 23% 1,2-, 46% 1,3- and 24% 1,4-dichlorides. On the same basis we obtain 7.8, 23.5, 49.2 and 19.5%, respectively. At lower temperatures the distribution widens. Activation energy differences thus appear to be the chief source of differences in reactivity of the various C-H bonds in *n*-butyl chloride, and these quantities appear at the bottom of Table VI. In Table VI attack on the hydrogens of carbon 3 has been taken as the standard of comparison, but apparently even they are somewhat less reactive than normal secondary C-H's. A competitive experiment with cyclohexane gives an over-all reactivity of only 0.192. This result combined with the isomer distribution data of Table VI indicates that reactivity per 3 (C-H) is only 0.28 that per C-H of cyclohexane.¹⁵

In complexing solvents the 1,4-/1,3-dichloride ratio decreases as would be anticipated from our hydrocarbon results. However the 1,2-/1,3- and 1,1-/1,3- ratios (all of which involve attack on C-H bonds of similar strength) also decrease while activation energy differences increase. These results seem the strongest evidence that, contrary to the former conclusion, in these systems complexing increases rather than decreases the electron-accepting properties of the chlorine atom. This conclusion, in terms of contributions of polar structures to the transition state, would suggest resonance structures such as



which would be particularly unlikely when R possesses strongly electron-withdrawing groups. If so, some portion in the increase of selectivity in the order $p < s < t$ observed in hydrocarbon chlorination in complexing solvents may arise from this change in electron-accepting properties of the chlorine atom, as well as from the (probably larger) effect due to change in over-all energetics. To put the matter another way, complexing may contribute something to the stabilization of the transition-state as well as to the chlorine atom reactant.

Finally we may ask ourselves whether results in complexing solvents shed any light on the question of the relative importance of polar effects and resonance stabilization of the resulting radical (*i.e.*, over-all energetics) in determining the $p < s < t$ sequence observed in hydrocarbon chlorination in their absence. We feel that they do not, although when the chlorine atom is sufficiently stabilized by complexing to produce the changes in energetics indicated in Fig. 1 resonance stabilization certainly becomes a controlling factor.

Experimental

Materials.—Except as indicated below all reagents and solvents were commercial materials. Their purity was checked by measurement of physical constants and by gas chromatographic analysis. Cyclobutane was prepared from 1,4-dibromobutane by treatment with sodium¹⁹ and purified by gas chromatography. This reaction gives a mixture of hydrocarbons, but they were well resolved in the chromatography and the cyclobutane had an infrared spec-

TABLE V
SOLVENT EFFECTS IN THE CHLORINATION OF ETHYL CHLORIDE (0°)

Solvent	1,1-Cl/1,2-Cl	Rel. react. vs. neopentane
CCl_4^a (6.9 M)	3.22 ± 0.1	0.13 ± 0.02
C_6H_6 (5.8 M)	..	0.23
C_6H_6 (7.6 M)	7.20	..
$\text{C}_6\text{H}_5\text{Cl}$ (6.6 M)	5.56	..
CS_2 (11.1 M)	8.20	..

^a Average of duplicate experiments.

decreases the reactivity of chlorine atoms and decreases their tendency to accept electrons as was suggested to interpret data on the chlorination of substituted toluenes,⁷ the change in case of ethyl chloride would be expected to be the larger of the two.

TABLE VI
SOLVENT EFFECTS IN THE CHLORINATION OF *n*-BUTYL CHLORIDE

Solvent	$T, ^\circ\text{C.}$	1,1-Cl/1,3-Cl			1,2-Cl/1,3-Cl			1,4-Cl/1,3-Cl		
None ^a	68	0.158 ± 0.003	0.478 ± 0.05	0.397 ± 0.01						
	34	$.128 \pm .003$	$.458 \pm .05$	$.358 \pm .01$						
	0	$.099 \pm .002$	$.436 \pm .05$	$.323 \pm .01$						
CS_2 (11.1 M)	68	.122	.397	.208						
	34	.0875	.335	.163						
	0	.0608	.298	.124						
CS_2 (7.9 M)	68	.138	.430	.265						
C_6H_6 (5.7 M)	68	.114	.443	.317						
C_6H_6 (7.5 M)	68	.120	.441	.267						
		$\frac{\Delta H_{1,1}^*}{\Delta H_{1,3}^*}$	$\frac{\Delta H_{1,2}^*}{\Delta H_{1,3}^*}$	$\frac{\Delta H_{1,4}^*}{\Delta H_{1,3}^*}$						
None		1290	270	600						
CS_2 (11.1 M)		2040	810	1470						

^a Average of duplicate experiments. ^b In cal./mole.

Our most extensive experiments in this series were carried out with *n*-butyl chloride, Table VI, where measurements were made in several solvent systems and over a range of temperatures. At 68° bulk isomer distributions are similar to those reported by Brown and Ash using SO_2Cl_2 at 70°.¹⁷

(16) Reference 2, p. 50.

(17) H. C. Brown and A. B. Ash, *THIS JOURNAL*, **77**, 4019 (1955).

(18) Actually, this experiment was carried out in 3.3 M benzene. However, this low concentration of complexing solvent does not significantly disturb the isomer distribution.

(19) J. Cason and R. L. Way, *J. Org. Chem.*, **14**, 31 (1949).

trum indicating pure material. Norcamphane was prepared by hydrogenating a sample of bicyclo[2.2.1]heptadiene kindly supplied by the Shell Chemical Co.

Chlorinations were carried out in small sealed tubes using a 5-10-fold excess of hydrocarbon. This excess is important in isomer distribution studies to eliminate complications due to polychlorination. Measured amounts of hydrocarbon and solvent were placed in the tubes, which were then attached to a vacuum line and measured quantities of chlorine condensed in from a calibrated receiver. The tubes were finally degassed with liquid nitrogen cooling and sealed. Reactions were accomplished by placing the tubes in a thermostat and irradiating with a 100-watt incandescent light at approximately 25 cm. until the chlorine color had disappeared. When benzene was used as solvent, some hexachlorocyclohexane sometimes was formed. While this required separation before analysis, its formation does not interfere with our relative reactivity measurements. The molar concentration of solvents employed was determined by the ratio of solvent to substrate being chlorinated the balance of the system being substrate; see Table VI below for actual examples.

Analyses were carried out by gas chromatography, using either a Perkin-Elmer Vapor Fractometer or a Wilkens Instrument and Research Inc. Aerograph and whichever of several column substrates gave the most satisfactory resolution. Each reaction mixture was analyzed in duplicate or triplicate, and ratios of peak heights or areas usually agreed to within 2-3%. Experimental errors given in Tables I-V represent the spread of independent experiments.

In competitive halogenation of different molecules relative reactivities were determined by change in peak height or area relative to an internal standard (usually the solvent), and Table VI presents representative experimental results on pairs of cycloparaffins, chlorinated at 68° in CCl₄. Cyclohexane and cyclopropane differ too much in reactivity for accurate direct comparison. Accordingly cyclopropane was chlorinated with neopentane, relative reactivity *vs.* cyclohexane (determined independently) 0.555. Relative reactivities were calculated from original data *via* equation 1, assuming only that ratios of peak heights relative to internal standards before and after reaction were proportional to the amounts of substrate present. Thus in the first experiment of Table VII

$$\frac{\text{react. of cyclopentane}}{\text{react. of cyclohexane}} = \frac{\log(1.385/1.151)}{\log(1.909/0.712)} = 0.76$$

In experiments involving chlorine atom attack at different points on the same molecule to yield isomeric products, relative reactivities were determined by the relative amounts of chlorides produced (using a large hydrocarbon/chlorine

ratio to suppress further chlorination). The chlorination of *n*-butyl chloride represents the most complicated case, but clean separation was obtained using the "A" column in the Perkin-Elmer instrument at 115° and 25 p.s.i. helium pressure. Retention times observed were 1,1-dichlorobutane, 5.4 min.; 1,2-, 6.9 min.; 1,3-, 8.8 min.; 1,4-, 16.2 min. Experiments on known mixtures showed that peak areas were proportional to concentrations of each component. The "A" column was used also for the separation of isomers in the chlorination of ethyl chloride (at 50°), 2,3-dimethylbutane (at 114°) and for the analysis of the hydrocarbon mixtures in Table I (at 114°). Resolution of 1- and 2-chlorobutane in the presence of benzene (Table II) required "A" and "C" columns in series at 80°.

TABLE VII
REPRESENTATIVE RESULTS IN CHLORINATION OF CYCLOPARAFFINS AT 68° IN CCl₄^d

Compound	Ml.	Retention time	R ₀ ^b	R ^c
C ₅ H ₁₀	1.1	2.5 ^a	1.385 ± 0.035	1.151 ± 0.031
C ₆ H ₁₂	1.1	5.3 ^a	.909 ± .051	.712 ± .027
CCl ₄	2.0	6.5 ^a		
C ₄ H ₈	0.2	1.4	.0965 ± .007	0.368 ± .002
C ₅ H ₁₀	1.9	3.2	.715 ± .038	.208 ± .003
CCl ₄	2.0	8.8		
C ₃ H ₆	1.1	0.9	.477 ± .009	.303 ± .012
Neo-C ₅ H ₁₂	1.1	1.01	.752 ± .012	.0915 ± .003
CCl ₄	2.0	8.8		
<i>n</i> -C ₄ H ₁₀	1.1	0.9	1.42 ± .013	.886 ± .003
C ₅ H ₁₀	1.1	3.2	.734 ± .013	.421 ± .004
CCl ₄	2.0	8.8		

^a At 68°. ^b Ratio of peak height to CCl₄ before reaction. ^c Ratio of peak height to CCl₄ after reaction. Experimental errors here and in R₀ are the spread of 3 analyses on the same reaction mixture. ^d Using 0.3 cc. of Cl₂, analysis with Perkin-Elmer Fractometer, 2 meter "A" column, 25 p.s.i. helium Pressure at 50° unless noted.

The major product from the chlorination of norcamphane was separated and purified on an "A" column at 142°, *n*²⁵D 1.4837, lit. 1.4824¹⁵ (other reported values range up to 1.4849). It rapidly liberated chloride ion on treatment with alcoholic AgNO₃.

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[CONTRIBUTION NO. 499 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

Syntheses by Free-radical Reactions. VIII. Reactions of Amino Radicals with Olefins

BY C. J. ALBISETTI, D. D. COFFMAN, F. W. HOOVER, E. L. JENNER AND W. E. MOCHEL

RECEIVED JULY 28, 1958

A new synthesis of diamines has been found in the additive dimerization of dienes with amino radicals generated from hydroxylamine by reducing ions. Thus, 1,8-diamino-2,6-octadiene was obtained from butadiene, hydroxylamine and a titanium(III) salt. In a similar reaction, 2-butene has given 3,4-dimethyl-2,5-hexanediamine. Use of ethylene has given products containing from one to several ethylene units per molecule. With titanium(III) as reducing agent these products are monoamines and diamines, whereas with vanadium(III) the chief products are aminoalcohols.

Amino radicals have been shown to be intermediates in the reaction of hydroxylamine with a titanous salt,¹ and radicals produced in this way

$$\text{NH}_2\text{OH}^+ + \text{Ti}^{3+} \longrightarrow \text{NH}_2\cdot + \text{H}_2\text{O} + \text{Ti}^{4+}$$

have been used to initiate vinyl polymerization.²

(1) P. Davis, M. G. Evans and W. C. E. Higginson, *J. Chem. Soc.*, 2563 (1951).

(2) E. Howard, U. S. Patents 2,683,140, July 6, 1954, and 2,567,109, Sept. 4, 1951.

The reaction of amino radicals with benzene has been reported to yield an unstable intermediate which decomposed to ammonia, aniline and biphenyl.³ Toluene gave similar results, and cyclohexene formed cyclohexylamine.

It has now been found that amino radicals generated from hydroxylamine undergo additive dimer-

(3) H. Seaman, P. J. Taylor and W. A. Waters, *ibid.*, 4690 (1954).