TABLE I

PRODUCTS AND YIELDS FROM REACTIONS OF ORGANOBORANES WITH N-CHLORODIALKYLAMINES

Reactants		Products					
Organoborane	Chloroamine	Neutral	B.p., °C.(mm.)	%[a] yield	Basic	B.p., °C.	% yield
Tricyclohexyl	N-Chlorodiethylamine	Cyclohexyl chloride	43–45 (36)	37.8	Diethylamine	54–55	20.3
Tricyclohexyl	N-Chlorodiethylamine	Cyclohexyl chloride Tar (1.1 g.)	40–41 (23)	31.4	Diethylamine	55	28.9
Tricyclohexyl[b]	N-Chloropiperidine[b]	Cyclohexyl chloride	85–87 (190)	31.6	Piperidine	88	38.8
Tricyclohexyl	N-Chloropiperidine	Cyclohexyl chloride Tar (0.7 g.)	47–48 (31)	52.9	Piperidine	95–96	65.5
Tricyclohexyl	N-Chloro-*n*-butylamine	Tar (2.6 g.)			*n*-Butylamine		Trace
Tri-*n*-octyl	N-Chlorodiethylamine	1- and 2-chlorooctane Tar (1.7 g.)	80–82 (80)	39.7	Diethylamine	55	48.9
Tri-*n*-octyl	N-Chloropiperidine	1- and 2-chlorooctane	62–63 (47)	37.6	Piperidine	92–94	31.4
Tri-*n*-octyl	N-Chloro-*n*-butylamine	Tar			None		

[a] Based on trialkylborane. [b] In this run the conversion of cyclohexene to tricyclohexylborane was poor and the concentration of organoborane was about one-half its usual value.

syringe into a 250-ml. flask and there was then similarly added 24.0 ml. of tetrahydrofuran. To this there was added 23.3 mmoles of a 1.0 M solution of diborane in tetrahydrofuran which was analyzed as was the reaction mixture to determine unreacted diborane and conversion to trialkylborane. When reaction was complete, excess diborane was destroyed with 3.0 ml. of water and there was added 33 ml. of 3 N NaOH and 8.0 ml. (7.5 g.) of N-chlorodiethylamine that had been prepared by the procedure of Coleman.[10] Completion of this reaction was determined with starch–iodide paper and the reaction mixture was made acidic with 6 M HCl and extracted twice with 50 ml. of ether. The aqueous phase was separated, made basic with 6 M NaOH, and also extracted twice with 50 ml. of ether. The ether extracts were dried over anhydrous Na_2SO_4, the ether was removed, and the residue was distilled under reduced pressure. The amines were determined by removing 5-ml. aliquots from the ether extract and titrating with standard 0.100 N HCl; they were identified by their boiling points and infrared spectra. The chlorooctanes were identified and analyzed by their infrared spectra and gas–liquid partition chromatography.

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Polar and Solvent Effects in Photochlorination Reactions

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In the photochlorination of normal paraffins a series of consecutive reactions quickly develops, yielding a mixture of products. The ratio of RH to RCl depends on the ratio of k_1 to k_2. It has been stated[1] from both theoretical considerations and experimental results that the introduction of a chlorine atom into a long-chain paraffin (C_8–C_{26}) has little effect on its reactivity, and that k_1/k_2 is nearly unity. However, many workers[2] have shown that in chlorination of 1-chloro paraffins in the carbon skeleton range of C_5–C_8 the presence of chlorine on the primary carbon atom in a molecule deactivates the carbon–hydrogen bonds of the carbon containing the chlorine atom and those of the next three carbon atoms. Other workers[3] have shown that in the chlorination of a series of carbonyl-containing paraffins, the reactivity of the α-carbon atom was less than that of the same carbon atom in an unsubstituted paraffin.

$$Cl_2 + h\nu \xrightarrow{k_i} 2Cl\cdot$$

$$RH + Cl\cdot \xrightarrow{k_1} R\cdot + HCl \xrightarrow[\text{fast}]{Cl_2} RCl + Cl\cdot$$

$$RCl + Cl\cdot \xrightarrow{k_2} RCl\cdot + HCl \xrightarrow[\text{fast}]{Cl_2} RCl_2 + Cl\cdot$$

$$RCl_n + Cl\cdot \xrightarrow{k_n} RCl_n\cdot + HCl \xrightarrow[\text{fast}]{Cl_2} RCl_{n+1} + Cl\cdot$$

$$2 \text{ radicals} \xrightarrow{k_t} \text{nonradical}$$

In general, these latter authors[2,3] have shown that the chlorine atom or carbonyl group reduces the reactivity of adjacent carbon–hydrogen bonds by reducing the electron density through an inductive effect. The effect of this deactivation should be that a paraffin undergoes chlorination faster than a chlorinated paraffin; *i.e.*, $k_1/k_2 > 1$.

The monochloride produced in the chlorination of a paraffin is composed of the isomeric secondary chlorides and the primary chloride. The relative amounts of each are dependent on the difference in carbon–hydrogen bond strengths and the reactivity of the chlorine atoms, with the latter being a function of temperature[4] and solvent.[5] The composition of the

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(1) (a) C. Schuhler, *Z. Physik. Chem.* (Leipzig), **219**, 56 (1962); (b) C. Schuhler, Von E. Leibnitz, H. G. Könnecke, and E. Schmidt, *J. prakt. Chem.*, **15**, 155 (1962); (c) A. Hopfinger and J. Kruzel, *Monatsch. Chem.*, **92**, No. 6, 1279 (1961); (d) H. G. Könnecke, C. Schuhler, and P. Hahn, *J. prakt. Chem.*, **14**, 269 (1961).

(2) (a) C. Walling and M. F. Mayahi, *J. Am. Chem. Soc.*, **81**, 1485 (1959); (b) L. Horner and L. Schläfer, *Ann. Chem.*, **635**, 31 (1960); (c) H. C. Brown and A. B. Ash, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **9**, 81 (1948); (d) H. C. Brown and A. B. Ash, *J. Am. Chem. Soc.*, **77**, 4019 (1945); (e) A. L. Henne and F. B. Hinkamp, *ibid.*, **77**, 1194, 1197 (1945).

(3) (a) M. S. Kharasch and H. C. Brown, *ibid.*, **62**, 925 (1940); (b) A. Bruylants, M. Tits, and R. Danby, *Bull. soc. chim. France*, **58**, 210 (1949); (c) A. Bruylants, M. Tits, C. Dieu, and R. Gauther, *ibid.*, **61**, 266 (1952); (d) H. J. den Hertog and P. Smit, *Proc. Chem. Soc.*, 132 (1959).

(4) B. Blouri, C. Cerceau, and G. Lanchec, *Bull. soc. chim. France*, 394 (1963).

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

secondary chlorides is supposedly statistically distributed among the various secondary carbon atoms, but is actually a function of the chlorinating agents[6] and the solvent employed.[7]

At the outset of our work on the photochlorination of paraffinic hydrocarbons in the C_{10}–C_{16} range we questioned the work negating polar effects in these compounds. The purpose of the work reported in this paper was not only to show that these polar effects are important, but to give a quantitative interpretation to these effects, and to report and interpret in more detail some previous work using benzene as the solvent for these reactions.[7]

The model compound *n*-dodecane used in this study was chosen because it was both long enough to prove our point and short enough to be analyzed accurately in a reasonable period of time. Similar results were obtained with *n*-undecane or *n*-tridecane, although they were not so extensively studied.

From the earlier kinetic expressions it can readily be seen that

$$\frac{d[RCl]}{dt} = k_1[RH][Cl\cdot] - k_2[RCl][Cl\cdot]$$

At the maximum concentration of RCl, $d[RCl]/dt = 0$ and $k_1/k_2 = [RCl]/[RH]$. Thus, if the concentration of paraffin and monochloride are plotted against a suitable reaction coordinate such as the extent of chlorination, the relative rate constants can be determined. These results are plotted in Figure 1 and show that $k_1/k_2 = 1.23 \pm 0.02$. These limits are not determined by the analytical precision but by the shallowness of the curve at the point of inflection ($N_1 = 0.98$). A further check on the accuracy of this ratio is obtained when a comparison is made between the experimentally and theoretically derived curves. The theoretical curves were obtained from RH and RCl values obtained by assuming $k_1/k_2 = k_2/k_3 = 1.25$. These values were only calculated to the point of intersection ($N_1 = 0.833$). As seen in Figure 1, the curves and the points of intersection of RH and RCl for both the theoretically and experimentally derived curves agree well. The chlorination of RCl_3 to RCl_4 at the chlorination level of the intersection point was neither considered significant nor included in the calculations.

The carbon–hydrogen bonds near the carbon–chlorine bond of a chloro paraffin are weaker than the carbon–hydrogen bonds of a paraffin. For this reason one might argue that in the photochlorination of a paraffin–chloro paraffin mixture in a solvent which makes the chlorine radical more selective, the chloro paraffin might show some enhanced reactivity. This argument was advanced by den Hertog[3] in the analogous work with acyl paraffins. Russell,[8] however, has argued that when polar effects are important in a radical reaction, changes in solvent have little effect on the selectivity of the attacking radical. The latter concept appears to be correct since we obtained essentially the same distribution of mono- to di- to trichlorides when benzene was employed as the solvent as when the reaction was run in neat paraffin. It is readily seen from the nearly identical curves in Figure 1 that there is little difference in the product distribution.

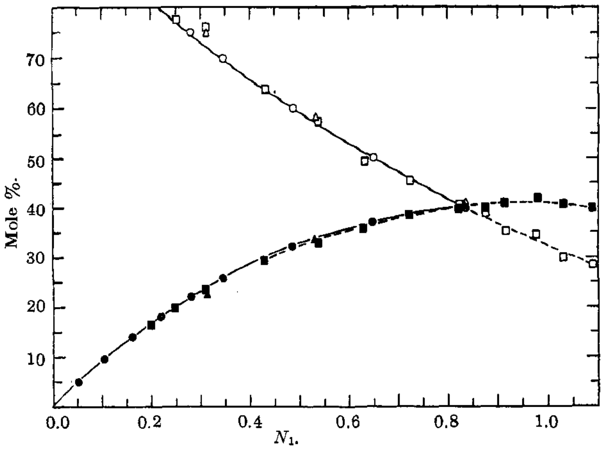

Figure 1.—Variation in product composition with the level of chlorination: solid symbols represent monochlorides; open symbols represent hydrocarbon; ○, calculated; □, chlorinations done neat; △, chlorinations done in 4 *M* benzene; N_1 = atom of bound chlorine/mole of RH_0; ———, calculated; and – – – –, observed.

An interesting effect of using benzene as a solvent was the nearly statistical distribution (60% internal–40% external) of the secondary monochlorides formed as compared to that in the neat chlorinations (Table I). Table I also shows that these distributions are essentially constant over a wide range of chlorination levels.

Asinger and Fell[6] have shown that the distribution of the secondary chlorides produced with a variety of chlorinating reagents is controlled by steric considerations. The results of their work (Table II) show that the external secondary chlorides increase with an increase in the size of the attacking radical.

The difference in secondary isomer distributions observed between neat chlorination and chlorination in benzene must be due to some hitherto unrealized effects of solvent changes in free-radical reactions. Since the chlorine atom is complexed with benzene as Russell[5] had depicted, it would certainly not be less bulky than a "free" chlorine atom. Thus, it would not seem as if this change in isomer distribution could be accounted for on steric grounds. However, the nonstatistical distribution obtained when the paraffins are chlorinated neat seems to be most likely explained by steric factors. If a coiled or helical conformation of a long-chain paraffin is used as the model for the chlorination reaction, the internal carbon–hydrogen bonds are hindered to the chlorine radical approach. This is not true for the extended conformation where all of the secondary carbon–hydrogen bonds are equivalent. Blouri, *et al.*,[4] used a similar concept, but in the opposite direction, to explain the decrease in the primary chloroheptane when the reaction temperature exceeds an arbitrary level.

It is our contention that a possible reason for the increase in internal isomer distributions is due to the uncoiling of the paraffin by a solvent such as benzene making the extended conformation the most probable, if not the only conformation available to the chlorine atom. In a poor solvent such as a fluorocarbon this trend might be reversed. This same phenomenon

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(6) F. Asinger and B. Fell, *Erdoel Kohle*, **17**, No. 2, 80 (1964).

(7) D. J. Hurley, R. W. Rosenthal, and R. C. Williamson, *Ind. Eng. Chem., Prod. Res. Develop.*, **4**, 22 (1965).

(8) G. A. Russell, *Tetrahedron*, **8**, 101 (1960).

TABLE I

MONOCHLORODODECANE ISOMER DISTRIBUTION IN CHLORINATED DODECANE[a]

		4,5,6 isomers		2,3 isomers		
Solvent[b]	N_1	% of secondary chlorides	% of total chlorides	% of secondary chlorides	% of total chlorides	1 isomer
Benzene	0.13	58.0	56.1	41.2	39.2	4.8
Benzene	0.31	58.9	55.8	41.1	39.1	5.1
Benzene	0.52	59.0	55.8	41.0	38.9	5.2
Benzene	0.84	60.0	57.1	40.0	37.9	5.0
None	0.56	56.9	51.0	43.1	38.4	10.6
None	0.76	56.3	50.1	43.7	39.1	10.8
None	0.86	55.5	49.2	44.5	40.0	10.8

[a] Chlorination carried out at 70–75°. [b] Four moles/mole of RH.

TABLE II

MONOCHLORIDE DISTRIBUTION IN CHLORINATED HEPTANE

	Monochloride isomer distribution, %[a]			
Chlorination agent	1	2	3	4
Chlorine	15	35 (41)[b]	34 (40.0)	16 (19)
N-Chlorosuccinimide	15.4	38.4 (45.4)	31.9 (37.7)	14.2 (16.9)
t-Butylhypochlorite	9.4	44.7 (49.3)	31.5 (34.8)	14.4 (15.9)
Trichloromethanesulfonyl chloride	2	50 (51)	32 (32.6)	16 (16.4)
Carbon tetrachloride	2.0	49.0 (50.0)	35.0 (35.7)	14.0 (14.3)

[a] Determined by g.l.p.c. using 8% β,β'-iminodipropionitrile on 60–80-mesh Chromosorb R. [b] The numbers in parentheses are based on only the secondary chlorides as calculated by us.

is well recognized in the field of polymer chemistry where helical polymers are extended by a good solvent.[9]

Experimental Section

Chlorination Procedure.—The chlorinations were carried out at 70–75° in a 1-l. flask equipped with a mechanical stirrer, condenser with gas outlet, thermometer, and gas-inlet sparger. After the flask was charged with paraffin, the system was purged with nitrogen. Chlorine was then added from a lecture bottle while the system was illuminated by a GE 150-w. flood lamp placed 2–3 in. from the flask. Chlorine was added at about 0.5 g./min. until the reaction was terminated. Nitrogen was used to purge the mixture and the product was washed three times with water and dried over $MgSO_4$.

Analytical Procedures.—Analyses of the chlorination products were performed by g.l.p.c. using an F and M Model 500 programmed gas chromatograph containing 10% silicone gum nitrile (LP-125) on 70–80-mesh Diatoport S. For separation of the monochlorides into primary and secondary chlorides, a 6 ft. × 0.25 in. column was used with helium gas carrier at 30 p.s.i.g. and 40 cc./min. with temperature programming from 100 to 240° at 15°/min. For separation into the 1, combined 2 and 3, and remaining isomers, a 12 ft × $^1/_8$ in. column was used with helium carrier gas at 30 p.s.i.g. and 50 cc./min. with temperature programming from 75 to 240° at 5.6°/min. The decomposition to olefin was $<1.4\%$ and the reproducibilities were ± 1 and $\pm 3\%$ for the secondary and primary chlorides, respectively. The response factors for 1-chlorododecane and 2-chlorododecane were determined and the latter response factor was used for all secondary monochlorides.

Materials.—The dodecane used was between 96 and 98% pure by g.l.p.c. with the major impurity being the C_{12} isoparaffin. Benzene was washed with sulfuric acid, sodium hydroxide, water, and then dried. G.l.p.c. analysis showed no impurities.

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[9] This information can be found in any complete book in polymer chemistry.

Lithium Aluminum Hydride Reduction of 1-Methyl-*cis*- and -*trans*-4-*t*-Butylcyclohexene Oxide

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To facilitate the identification of several 1,2-substituted 4-*t*-butylcyclohexanes, we found it necessary to synthesize the isomeric 1-methyl-4-*t*-butylcyclohexene oxides and to study the products of their reaction with lithium aluminum hydride. The results provide further evidence that steric effects can modify the normal stereoelectronic preference for diaxial ring opening[2] in the hydride reductions of cyclohexene oxides.[3]

Epoxidation of 1-methyl-4-*t*-butylcyclohexene, as expected,[4] afforded a mixture of 1-methyl-*trans*- and -*cis*-4-*t*-butylcyclohexene oxide, **1** and **2**, respectively, in the approximate ratio of 45:55. Consequently, pure samples of each epoxide were obtained by the reaction sequences outlined in Schemes I and II. The intermediates were characterized by elemental analysis and infrared, and in some cases, n.m.r. spectroscopy. 2-Methyl-5-*t*-butylcyclohexanone was obtained by dehydration of the mixture of diols from the hydroxyla-

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[2] A. Furst and P. A. Plattner, Abstracts, 12th International Congress of Pure and Applied Chemistry, New York, N. Y., 1951, p. 409.

[3] A summary, discussion, and pertinent leading references are given by E. L. Eliel, "Steric Effects in Organic Chemistry," M. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y.. 1956, pp. 130–134; *cf.* also F. H. Newth, *Quart. Rev.* (London), **13**, 41 (1959).

[4] *Cf.* the epoxidation of 4-*t*-butylcyclohexene: (a) J. Sicher, F. Sipos, and M. Tichy, *Collection Czech. Chem. Commun.*, **26**, 847 (1961); (b) N. A. LeBel and R. F. Czaja, *J. Org. Chem.*, **26**, 4768 (1961); (c) B. Rickborn and J. Quartucci, *ibid.*, **29**, 2476 (1964).