in 10 ml. of anhydrous toluene was refluxed under a nitrogen atmosphere for 7 hr. Solvent removal *in vacuo* left a crystalline residue of 5, which, after one washing and one recrystallization from a small volume of hexane, weighed 2.6 g. (44%), m.p. 63.5–66.5°. A sample for analysis was recrystallized from hexane: m.p. 65–66°; infrared absorptions (KBr), 6.20 and 6.30 μ; n.m.r. spectrum (CCl$_4$), doublet at 1.18 and septet at 2.85 (isopropyl group), broad peak at 1.44 (three methylene

groups of piperidine ring), broad peak at 2.85 (–CH$_2$NCH$_2$–),

doublet at 4.77 (J = 14.4 c.p.s., –CH=C–N<), and multiple peaks at 6.95 p.p.m. (other olefinic proton and aromatic protons).

Anal. Calcd. for C$_{17}$H$_{24}$N$_2$: C, 79.6; H, 9.4; N, 10.9. Found: C, 79.6; H, 9.4; N, 11.0.

2-Isopropylquinoline from 4.—A solution of 1 g. of 4 in 10 ml. of *o*-dichlorobenzene and a few milligrams of *p*-toluenesulfonic acid was refluxed for 21 hr. under an atmosphere of nitrogen. Distillation gave 0.55 g. (70%) of 2, b.p. 70–73° (0.07 mm.). The infrared spectrum of this material was identical with that of authentic 2-isopropylquinoline.

Reaction of Piperidine with 4.—A solution of 0.65 g. (0.003 mole) of 4 and 0.33 ml. (0.0033 mole) of piperidine in 3 ml. of toluene was refluxed 5 hr. under a nitrogen atmosphere. The volatile material was removed *in vacuo*. The residue (0.62 g.) had an infrared spectrum identical with that of 5 which was prepared by the action of piperidine on 3. The residue was treated with hexane to give crystals, m.p. 61.5–65°, m.m.p. with authentic 5 62–65°.

N,N'-(3-Isopropyl-1-propen-1-yl-3-ylidene)dianiline (7).—When 6.5 g. (0.03 mole) of 4 was added to a solution of 2.8 g. (0.03 mole) of aniline in 15 ml. of hexane, the solution became warm spontaneously. After 15 hr. the solvent was removed *in vacuo*, leaving a crystalline residue, which, after washing with hexane, gave 5.6 g. (70%) of 7: m.p. 65–67°; infrared absorptions (KBr), 6.15, 6.28, 6.45, 6.73, 7.75, 9.70, 13.25, 13.50, and 14.4 μ; n.m.r. spectrum (CCl$_4$), doublet at 1.04 and septet at 2.83 (isopropyl group), doublet at 4.98 (J = 8.4 c.p.s.,

–CH=C–N<), and multiple peaks at 7.1 p.p.m. (other olefinic proton, –NH–, and aromatic protons).

Anal. Calcd. for C$_{18}$H$_{20}$N$_2$: C, 81.8; H, 7.6; N, 10.6. Found: C, 81.7; H, 7.7; N, 10.8.

Reactions of 1 with *p*-Phenylenediamine.—A mixture of 112 g. (0.8 mole) of 1, 38 g. (0.35 mole) of *p*-phenylenediamine, 1.6 g. of *p*-phenylenediamine hydrochloride, and 640 ml. of toluene was refluxed at 50° at a reduced pressure of 70 mm. with the use of a Dean–Stark water collector. After 7 hr. 10.6 ml. (84%) of water had separated. The resulting solution was concentrated to a final pot temperature of 75° at 0.1 mm. The 115 g. of crude 8 that remained was added during 20 min. to 1250 ml. of stirred 96% sulfuric acid at 15–20°. The resulting black solution was left at 25° for 4 hr., and then drowned on 5 kg. of ice and made basic with sodium hydroxide. The mixture of products that separated was taken up in ethyl ether and dried over solid potassium hydroxide. Rapid distillation gave 60 g. of a fraction boiling at 140–175° (0.1 mm.). Refractionation through a 6-in. packed column gave 13 g. (19%) of 9, b.p. 135–143° (0.07 mm.). 9 readily formed a hydrate, m.p. 116° dec. An additional distillation fraction boiled at 143–160° (0.07 mm.). Treatment of this fraction with hexane gave 2 g. (2%) of 10 as an insoluble solid. Recrystallization from methanol gave pure 10, m.p. 166–168°. The hexane-soluble portion of the above fraction was redistilled through a 6-in. packed column to give 38 g. (42%) of 11, b.p. 158° (0.07 mm.), m.p. 34–39°.

9 had infrared absorptions (KBr) at 2.95, 3.05, 3.14, 6.12, 6.20, 6.65, 7.25, 7.31, 8.87, 9.60, 11.59, 11.65, and 12.08 μ; n.m.r. spectrum (C$_2$H$_2$Cl$_4$), doublet at 1.37 and septet at 3.32 (isopropyl group), singlet at 4.74 (amino group), close doublet at 6.98 (J = 2.3 c.p.s., 5-proton), pair of doublets at 7.97 and 8.06 (4- and 8-protons), doublet at 7.27 (J = 8.8 c.p.s., 3-proton), and a pair of doublets at 8.18 p.p.m. (J = 9.1 and 2.3 c.p.s., 7-proton).

Anal. Calcd. for C$_{12}$H$_{14}$N$_2$·0.5H$_2$O: C, 73.8; H, 7.7; N, 14.4. Found: C, 73.9; H, 7.7; N, 14.1.

10 had infrared absorptions (KBr) at 6.22, 11.23, and 12.18 μ; n.m.r. spectrum (CCl$_4$), doublet at 1.40 and septet at 3.21 (isopropyl group), doublet at 7.16 (3- and 8-protons), doublet at 8.12 (4- and 9-protons), and singlet at 8.43 p.p.m. (5- and 10-protons).

Anal. Calcd. for C$_{18}$H$_{20}$N$_2$: C, 81.8; H, 7.6; N, 10.6. Found: C, 81.9; H, 7.6; N, 10.8.

11 had infrared absorptions (KBr) at 6.26, 11.8, and 12.15 μ; n.m.r. spectrum (CCl$_4$), doublet at 1.38 and septet at 3.21 (isopropyl group), doublet at 7.18 (2- and 9-protons), singlet at 8.08 (5- and 6-protons), and doublet at 8.40 p.p.m. (1- and 10-protons).

Anal. Calcd. for C$_{18}$H$_{20}$N$_2$: C, 81.8; H, 7.6; N, 10.6. Found: C, 81.4; H, 7.3; N, 10.5.

The Reaction of Organoboranes with N-Chlorodialkylamines. A New Synthesis of Primary Alkyl Chlorides from Olefins by Hydroboration

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N-Chlorodialkylamines have recently been shown to react with olefins to form tertiary amines by free-radical[1] as well as ion-radical[2–4] mechanisms. Amination has also been reported by Kavacic[5,6] for toluene with trichloramine and a Lewis acid catalyst and by Brown[7] from the reaction of organoboranes with chloramine or hydroxylamine-O-sulfonic acid.

We wish to report that the only basic products from the reaction of N-chlorodialkylamines with trioctyl- and tricyclohexylboranes were the parent secondary amines. The data in Table I show that the neutral products obtained with N-chlorodiethylamine and N-chloropiperidine were cyclohexyl chloride from tricyclohexylborane and a mixture of 93% 1-chloro- and 7% 2-chlorooctane from the mixture of organoboranes prepared from 1-octene; these products were identified and analyzed by vapor phase chromatography and infrared spectroscopy. N-Chloro-*n*-butylamine and tri-*n*-octylborane gave only tars and no isolable products.

This "anti-Markovnikov" addition of the elements of HCl is a new method for preparing primary alkyl chlorides from terminal olefin bonds and should be applicable to the preparation of primary chlorides from olefins with central double bonds which Brown[8] has isomerized through their organoboranes. The 93 and 7% yields of 1-chloro- and 2-chloroct ane, respectively, are similar to the 93–94% to 6–7% ratio of 1- to 2-alkanols.

Experimental Section

Reactions were carried out under dry nitrogen and in a typical run 11.0 ml. (70 mmoles) of 1-octene, dried and distilled over sodium and under dry nitrogen, was injected with a hypodermic

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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 Na₂SO₄, 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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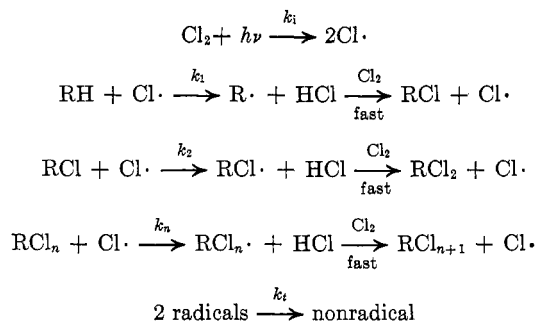
Polar and Solvent Effects in Photochlorination Reactions

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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

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

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

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

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

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

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.

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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