TABLE I

ADDITION OF TRICHLOROSILANE TO 2-METHYL-1-BUTENE

—Reactants, mmoles[a]—			
$HSiCl_3$	C_2H_5-(CH_3)-$C{=}CH_2$	Catalyst	Yield, %[b]
62	50	0.0664 g of 5% Pt–C	55.3
63	50	0.65 mmole of H_2PtCl_6	93.0
58	49	No catalyst	0.0

[a] Conditions: in sealed tube, 20 hr at 100°. [b] Product is racemic 2-methylbutyltrichlorosilane.

TABLE II

(+)-(*S*)-2-METHYLBUTYLSILANES IN THE PRESENCE OF HYDROSILYLATION CATALYSTS

Silane,[a] g	Catalyst, moles/mole of silane	Reacn conditions	$[\alpha]^{20}D$, deg Before	$[\alpha]^{20}D$, deg After[d]
$RSiH_3$, 2.98	Pt,[b] 1.5 × 10^{-5}	20°, 96 hr	+9.68	+9.45
$RSiH_3$, 3.10	Pt,[b] 3.3 × 10^{-5}	75° (reflux), 20 hr	+9.68	+9.58
$RSiH_3$, 3.00	Pt,[b] 1.0 × 10^{-4}	100° (sealed tube), 20 hr	+9.58	+9.56
$RSiH_3$, 2.77	Pt,[c] 0.056 g	100° (sealed tube), 20 hr	+9.56	+9.52
$RSiCl_3$, 4.11	Pt,[b] 1.5 × 10^{-4}	100° (sealed tube), 24 hr	+11.45	+11.32
$RSiCl_3$, 5.15	Pt,[c] 0.063 g	100° (sealed tube), 24 hr	+11.32	+11.54

[a] R = (*S*)-2-Methylbutyl. [b] Catalyst is *ca.* 10^{-2} *M* $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol. [c] Catalyst is 5% platinum on powdered charcoal. Value in grams is actual weight. [d] Rotation of product silane isolated after reaction.

uncertainty and imply absence of significant racemization.

To provide a more stringent test, two additional types of experiments were conducted. In the first, the attempted racemizations were performed in the presence of more than equivalent molar quantities of 2-methyl-1-butene with the goal of competing with any possibly stereospecifically oriented olefin in a tight complex with a hydrosilane as the right-hand side of equilibrium 1. No racemization occurred. In the second set of runs, the active trichlorosilane (Ib) was present in equimolar quantities with 2-methyl-1-butene undergoing hydrosilylation with a 33% excess of trichlorosilane. The reaction went well and the mixture of original active and *in situ* generated inactive product, when isolated, displayed a rotation value consistent with nonracemization, if one accepts the reasonable assumption that asymmetric induction is not significant in this system. If it were it would have to counterbalance rather closely the degradation in activity due to racemization since the observed rotation agrees with that predicted if the active material behaved solely as a labeling component in the total product.

It appears then that, under a variety of dynamic conditions, an asymmetric hydrogen-bearing carbon atom in the β position to silicon does not racemize under hydrosilylation conditions. Hence, this latter reaction does not, at least for the primary alkylsilane case (*i.e.*, terminal silicon), involve a kinetically significant equilibrium between hydrosilylation products and their precursors.

Experimental Section

All inorganic reagents and solvents were obtained from Matheson Coleman and Bell, Inc. Trichlorosilane (bp 31–33°), chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$), and 5% platinum on powdered charcoal were used without further purification. In the reactions, chloroplatinic acid was employed as a freshly prepared solution, approximately 10^{-2} *M*, in isopropyl alcohol. 2-Methyl-1-butene was distilled (bp 31–32°) prior to use. The optically active compounds, (+)-(*S*)-2-methylbutylsilane and (+)-(*S*)-2-methylbutyltrichlorosilane, were prepared as described elsewhere.[9]

The sealed tube experiments were performed in 18-mm-o.d. Pyrex glass tubing. A smaller bore tube, containing the catalyst was placed within the larger one charged with the other reactants. Under dry nitrogen purge, the system was chilled in liquid nitrogen and flame sealed, and the reactants were mixed by inversion. After the indicated reaction time, the tubes were again cooled in liquid nitrogen before being opened.

Optical rotation values were obtained on a Rudolph Model 80 polarimeter.

Addition of Trichlorosilane to 2-Methyl-1-butene.—Neat mixtures of trichlorosilane and 2-methyl-1-butene with 5% platinum–charcoal, chloroplatinic acid (in isopropyl alcohol), and no catalyst, respectively, were heated in sealed tubes at 100° for 20 hr. Specific experimental parameters and yields of product, isolated by distillation (bp 162–169°) are presented in Table I. In all cases, the product was optically inactive. It is evident that, for these conditions, silylation requires a catalyst, and that the homogeneous platinum catalyst used is better, in terms of yield, than is the heterogeneous one.

Attempted Racemization of (+)-(*S*)-2-Methylbutylsilane and (+)-(*S*)-2-Methylbutyltrichlorosilane.—Subject silanes were treated with chloroplatinic acid and platinum–charcoal under the conditions given in Table II. Post-reaction work-up involved isolation of the silanes by distillation and comparison of optical rotation values ($[\alpha]^{20}D$) with those of the initial reactants.

Attempted Racemization in the Presence of Excess Olefin.—(+)-(*S*)-2-Methylbutyltrichlorosilane (7.12 g, 35 mmoles), 2-methyl-1-butene (3.00 g, 43 mmoles), and chloroplatinic acid (0.06 ml of 1.05 × 10^{-2} *M* solution in isopropyl alcohol, corresponding to 2.1 × 10^{-5} mole/mole of butene) were heated in a sealed tube for 20 hr at 100°. The silane isolated by distillation had $[\alpha]^{20}D$ 11.46° compared to an initial value of 11.45°.

Attempted Racemization in the Presence of a Dynamic Hydrosilylation Reaction.—(+)-(*S*)-2-Methylbutyltrichlorosilane (6.13 g, 30 mmoles), trichlorosilane (5.50 g, 41 mmoles), 2-methyl-1-butene (2.15 g, 31 mmoles), and chloroplatinic acid (0.06 ml of 1.05 × 10^{-2} *M* solution, corresponding to 2.1 × 10^{-5} mole/mole of butene) were heated in a sealed tube for 20 hr at 100°. The silane isolated by distillation, 12.09 g (59 mmoles), represented 93.5% yield in the hydrosilylation reaction. The observed $[\alpha]^{20}D$ value for the mixture of active and inactive silane product isolated by distillation was 5.76°. That calculated, by assuming that the added active silane took no part in the reaction (was not racemized) and that the hydrosilylation addition gave 100% yield of inactive silane, was 5.61°.

The Use of Benzophenone N-Chlorimine and N-Bromimine as Halogenating Agents[1]

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In the course of a study of the *syn–anti* isomerization of substituted benzophenone N-chorimines and N-bromimines[3] it was found that halogenation of cyclohexane used as a solvent was occurring under certain

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[1] Taken from the Ph.D. Thesis of C. G. M., University of Illinois, 1963.

[2] Roger Adams Fellow, 1959–1960. National Science Foundation Fellow, 1960–1961. Standard Oil of California Fellow, 1961–1962. Public Health Service Fellow, 1962–1963.

[3] D. Y. Curtin, E. J. Grubbs, and C. G. McCarty, *J. Am. Chem. Soc.*, **88**, 2775 (1966).

TABLE I

HALOGENATIONS WITH BENZOPHENONE N-BROMIMINE (I) AND N-CHLORIMINE (II)

Time, min, and temp, °C	Substrate (RH)	Catalyst or inhibitor	Halogen-substituted product (RX)	Starting material (I or II) recovered	Benzophenone imine (IV) Base (IV)	Benzophenone imine (IV) Hydrobromide (IV·HBr)	Benzophenone benzylimine (V)	Benzophenone azine (VI)
			Benzophenone N-Bromimine (I)					
720, 80	Cyclohexane[a]	Ultraviolet[b]	47	36	..	7	...	...
720, 80	Cyclohexene[c]	Ultraviolet[b]	43	0[d]	..	16	...	...
120, 40	Toluene[e]	None	0	101	..	...	...	...
120, 40		Ultraviolet[b]	14	67	13	17	0	0.6
120, 110		None	45	52	41	0.4	...	0.2
120, 110		AIBN[f]	60	24	52	4	...	2
300, 110		None[g]	74	0	66	13	10	1
120, 110		Ultraviolet[b]	78	0	72	13	4	3
120, 110	Toluene[h]	Benzophenone imine	81	10	70	5	0	...
120, 110	Toluene[i]	Hydrobromide	91	0	87	2	2	...
120, 150	Toluene[e]	None[g]	53	0	22	34	33	7
			Benzophenone N-Chlorimine (II)					
3000, reflux	Cyclohexane	None[j]	3	...	..	...	...	...
3000, reflux	Cyclohexane	$(C_6H_5COO)_2$[k]	18	...	..	...	...	...
3000, reflux		Hydroquinone[l,m]	0.2	...	..	...	...	...
3000, reflux	Toluene	None[j]	31	...	..	...	...	...
3000, reflux		$(C_6H_5COO)_2$[j,k]	31	...	..	...	...	...
3000, reflux		Hydroquinone[j,l]	4	...	..	...	...	...

[a] Molar ratio of cyclohexane to bromimine, 1.5. Doubling the amount of cyclohexane gave 15% of benzophenone imine hydrobromide but left the other products unchanged. Addition of 3 mg of azoisobutyronitrile gave 2–6% of bromocyclohexane and 93–99% recovered bromimine I. [b] G.E. sunlamp at 6 in. [c] Ratio of cyclohexene/bromine, 1.5 in benzene solvent (3.8 ml of benzene/mmole of bromimine I. Doubling the amount of cyclohexene left the amounts of products essentially unchanged. Addition of 3 mg of azoisobutyronitrile/mmole of bromimine lowered the amount of bromocyclohexene formed to 27–35% and the imine hydrobromide to 1–9%. [d] Shown by a negative starch–iodide test. [e] Ratio of bromimine/toluene, 0.78–0.81 mmole/3 ml. [f] Ratio of azoisobutyronitrile/bromimine, 3 mg/0.8 mmole. [g] A duplicate run with the addition of 3 mg of azoisobutyronitrile per 0.8 mmole of bromimine I gave similar results. [h] Ratio of bromimine/benzophenone imine hydrobromide/toluene, 0.80 mmole/2 mg/3.0 ml. [i] Ratio of bromimine/benzophenone imine hydrobromide/toluene, 0.39 mmole/102 mg/3.0 ml. [j] Chlorimine (500 ± 13 mg) in 4 ml of hydrocarbon. [k] Benzoyl peroxide (25 mg) added. [l] Hydroquinone (15 mg) added. [m] Imine (442 mg) in 4.0 ml of cyclohexane.

conditions. There is presented here the resulting brief study of the reactions of benzophenone N-bromimine (I) and N-chlorimine (II) as halogenating agents.

$$(C_6H_5)_2C{=}NX$$
$$\text{I, X = Br}$$
$$\text{II, X = Cl}$$

As is shown in Table I the N-bromimine I reacts at temperatures above 80° with cyclohexane, cyclohexene, or toluene to give cyclohexyl bromide, 3-bromocyclohexene, or benzyl bromide, respectively. The reaction is assisted by illumination with a G.E. sunlamp. The products from toluene of a reaction carried out at 110° for 120 min with illumination are shown below. In parenthesis are mole per cents of product related to bromimine I.

$$\mathrm{I} + C_6H_5CH_3 \longrightarrow \underset{\text{III, 78\%}}{C_6H_5CH_2Br} + \underset{\text{IV, 72\%}}{(C_6H_5)_2C{=}NH} + \underset{13\%}{\mathrm{IV}\cdot HBr} + \underset{\text{V, 4\%}}{(C_6H_5)_2C{=}NCH_2C_6H_5} + \underset{\text{VI, 3\%}}{(C_6H_5)_2C{=}NN{=}C(C_6H_5)_2}$$

Lower yields were obtained when the chlorimine II was allowed to react with cyclohexane or toluene under reflux owing at least in part to incomplete reaction. As shown by the data in Table I the chlorination is assisted by the free-radical initiator, benzoyl peroxide, and inhibited by hydroquinone. No bromination of the aromatic ring of toluene by the N-bromimine I was observed; our experimental method could have detected as little as 1% of ring-brominated toluenes. Illumination of the bromimine I in benzene at the reflux temperature gave a 30% yield of benzophenone azine but other products were not investigated.

A further reaction, probably closely related to those above, is that of the N-bromimine I with benzaldehyde which was completed in 10 min at 80° in benzene solution with illumination and gave the products shown below.

$$\mathrm{I} + C_6H_5CHO \longrightarrow \underset{\text{VII, 50\%}}{(C_6H_5)_2C{=}NCOC_6H_5} + \underset{48\%}{(C_6H_5)_2C{=}NH_2{}^+Br}$$

There are evident points of similarity between the behavior of the halimines I and II and N-bromosuccinimide[4] and it is reasonable to suppose that they, like N-bromosuccinimide, react by a free-radical chain mechanism. Although a mechanism with the diphenylimine radical $[(C_6H_5)_2C{=}N\cdot]$ as a key intermediate should be considered, the possibility cannot be ruled out that, as in at least certain reactions of N-bromosuccinimide,[4b,5] the halimine is simply a source of molecular halogen which is supplied throughout the reaction in low concentrations.

This possibility is supported by the observation that reaction of the bromimine I with hydrogen bromide is instantaneous at −78° or in benzene solution at room temperature. Benzophenone imine was found to react rapidly with bromine in benzene at room temperature to form bromimine I and benzophenone imine hydrobromide. Thus the propagation steps of the free-radical chain mechanism could be the following.

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(4) See H. J. Dauben and L. L. McCoy [*J. Am. Chem Soc.*, **81**, 4863 (1959)] for a survey of that reaction; also G. A. Russell and Y. R. Vinson, *J. Org. Chem.*, **31**, 1994 (1966).

(5) R. E. Pearson and J. C. Martin, *J. Am. Chem. Soc.*, **85**, 354 (1963); G. A. Russell, C. DeBoer, and K. M. Desmond, *ibid.*, **85**, 365 (1963).

$$\mathrm{Br\cdot + RH \longrightarrow BrH + R\cdot}$$

$$\mathrm{BrH + Ar_2C{=}NBr \longrightarrow Ar_2C{=}NH + Br_2}$$

$$\mathrm{R\cdot + Br_2 \longrightarrow RBr + Br\cdot}$$

The competing reactions

$$\mathrm{Br_2 + 2Ar_2C{=}NH \rightleftharpoons Ar_2C{=}NBr + Ar_2{=}NH_2{}^+Br^-}$$

provide an additional complication. Benzyl bromide was shown to react with benzophenone imine in boiling toluene to give after 5 hr 17% of benzophenone N-benzylimine V and 18% of benzophenone imine hydrobromide, a reaction which may explain the small amounts of V found in the bromination reactions.

Experimental Section[6]

Benzophenone N-bromimine (I), mp 37–38° (petroleum ether bp 30–60°; lit.[7] mp 38.5°), was prepared from benzophenone imine and bromine in aqueous sodium carbonate solution.

Benzophenone N-chlorimine (II), mp 35–36° (petroleum ether bp 30–60°; lit.[8] mp 37°), was obtained by chlorination of benzophenone imine with chlorine in aqueous sodium bicarbonate.

Reactions of Bromimine I with Cyclohexane, Cyclohexene, and Toluene.—Cyclohexane and cyclohexene were heated with calcium hydride under reflux for several hours, fractionally distilled, and then stored over calcium hydride. Toluene (reagent grade) was treated for several hours with calcium hydride but not distilled. The bromimine I was recrystallized shortly before being used. Its purity was checked by a melting point determination and iodometric titration. Glassware was washed in chromic acid cleaning solution, rinsed with dilute, aqueous ammonia and distilled water, and dried in an oven at 130°. Reactions were carried out in a nitrogen atmosphere.

Characterization of the products was achieved by filtration of the imine hydrobromide salt IV · HBr (identified by comparison with an authentic sample) and separation of the other components by gas phase chromatography in sufficient quantity to permit determination of their infrared, nmr, and ultraviolet spectra. The quantitative determination of benzyl bromide was made by nmr with phthalide as an internal standard and working from an experimentally determined plot of ratio of areas of the CH_2 absorptions against composition. Average values of six to ten integrations were used. Benzophenone imine was determined by precipitation as the hydrochloride with dry hydrogen chloride and corrected for hydrochloride formed by the reaction of hydrogen chloride with unreacted N-bromimine. The unreacted N-bromimine was determined by iodometric titration. Benzophenone benzylimine was determined by an nmr method analogous to that used with benzyl bromide. Benzophenone azine was determined by ultraviolet spectroscopy by diluting an aliquot of the reaction mixture with ethanol and determination of the absorption at 350 mμ where none of the other known products absorbed.

Reagent grade bromobenzene was used as an internal standard in the gas phase chromatographic analyses of 3-bromocyclohexene and bromocyclohexane which were carried out on a 4-ft SE-30 silicone column under conditions such that the internal standard and sample had similar retention times but were completely resolved. Standard curves were employed and ratios of average areas from three injections were used. Results are presented in Table I.

Irradiation of 122 mg of bromimine I in 3.0 ml of dry benzene under reflux with a G.E. sunlamp gave a deep yellow color after 2 min and after 4.0 hr the ultraviolet spectrum of an aliquot diluted with ethanol showed an absorbance at 350 mμ corresponding to 26 mg (30%) of azine VI.

Reactions of Benzophenone N-Chlorimine (II).—Reactions were carried out with equipment open to the atmosphere and exposed to ordinary laboratory lighting. Starch–iodide tests showed that none of the reactions were complete after 50 hr. Analyses were carried out by concentration of the solution and analysis by gas phase chromatography with a 10-ft Dow-11 silicone column. Standard solutions of cyclohexyl chloride in cyclohexane and benzyl chloride in toluene were prepared and injected alternately with the sample. The results, based on averages of three to five sets of areas, are presented in Table I.

Reaction of Benzophenone N-Bromimine (I) with Hydrogen Bromide. Benzophenone Imine Hydrobromide (IV · HBr).—A solution shown by titration with 0.10 *N* sodium hydroxide to contain 0.75 mmole of hydrogen bromide in dry benzene was added dropwise with stirring to 215 mg (0.83 mmole) of bromimine in dry benzene. The color of bromine was apparent with the addition of the first drop and a fine, white precipitate was visible after the addition of 2 or 3 drops. After the addition was complete the precipitate was collected, washed with benzene, and dried at 130°. The imine hydrobromide (IV · HBr) so collected amounted to 0.36 mmole or 48% based on the hydrogen bromide employed. The reaction was also observed to be instantaneous at −78°.

Anal. Calcd for $C_{13}H_{12}BrN$: C, 59.6; H, 4.6; N, 5.4. Found: C, 59.9; H, 4.6; N, 5.3.

Reaction of Benzophenone Imine (IV) with Benzyl Bromide.—A solution of 179 mg of benzophenone imine and 184 mg of benzyl bromide in 3.0 ml of toluene was heated under reflux for 5 hr under nitrogen in the dark with stirring. Determination of the amount of the hydrobromide salt IV · HBr and N-benzylimine V by the methods described previously for the bromination reactions gave values of 18 and 17% based on the imine IV.

Reaction of Bromimine I with Benzaldehyde.—A solution of 160 mg of freshly distilled benzaldehyde and 262 mg of bromimine I in 3.0 ml of benzene was stirred, heated under reflux in a nitrogen atmosphere, and illuminated with a G.E. sunlamp 6 in. from the flask. Within 1 min the solution had turned deep orange, a precipitate had appeared within 2 min, and the starting material had been totally consumed (starch–iodide) after 10 min. Filtration gave 116 mg (44%) of hydrobromide IV · HBr. Removal of a portion of the solvent gave a residue of which the infrared spectrum agreed with that of benzophenone N-benzoylimine,[9] but with a few extra bands of minor intensity. Analysis by gas phase chromatography with a 4-ft SE-30 silicone column (with a standard solution) indicated the presence of 143 mg (50%) of N-benzoylimine (VII).

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[6] Melting points are corrected. Infrared spectra were obtained in part by Mr. Dick Johnson and his associates with a Perkin-Elmer Model 21 spectrophotometer. Ultraviolet spectra were obtained with a Bausch and Lomb Spectronic 505 or, in part, by Mr. P. Hon with a Cary Model 14M spectrophotometer. Vapor phase chromatography was carried out with an Aerograph A-300 dual-column instrument equipped with a Brown recorder and Disc integrator. Important spectra and other detailed data may be found in the Ph.D. thesis of C. G. McCarty[1] available on microfilm from University Microfilms, Ann Arbor, Mich.

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A Convenient Preparation of Pyrrolizidine by Reductive Cyclization

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Pyrrolizidine compounds are of interest chiefly because of the occurrence of this bicyclic ring system in a number of alkaloids.[2] Although many syntheses of the simpler derivatives are known,[3,4] with one recent exception[5] they are uniformly inefficient in terms of the

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