The Peroxide- and Light-Induced Reactions of Trichloromethanesulfonyl Chloride with Hydrocarbons[1]

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Trichloromethanesulfonyl chloride can be used to chlorinate alkanes and alkyl aromatics. Sulfur dioxide and chloroform are produced as by-products in these light- and benzoyl peroxide-induced reactions. The site of chlorination on hydrocarbons is more specific than observed in halogenations with chlorine and with sulfuryl chloride. Competitive reactions show that cyclohexane is more reactive than toluene toward chlorination with this reagent. The kinetic chain lengths of the reactions of trichloromethanesulfonyl chloride with cyclohexane, toluene, and cumene are in the order cyclohexane > toluene > cumene. These observations are discussed from the standpoint of a free radical chain reaction involving the following two steps: (1) abstraction of a hydrogen atom from the hydrocarbon by $Cl_3CSO_2\cdot$ yielding a hydrocarbon free radical and trichloromethanesulfinic acid which decomposes to chloroform and sulfur dioxide, and (2) abstraction of the sulfur-bonded chlorine atom from trichloromethanesulfonyl chloride by the hydrocarbon free radical yielding the chlorinated hydrocarbon and $Cl_3CSO_2\cdot$.

Trichloromethanesulfonyl chloride (I) has been found to be an effective chlorinating agent.[2] Equivalent amounts of the chlorinated product, chloroform and sulfur dioxide are formed in the benzoyl peroxide and photoinitiated reactions of I with various alkyl aromatics and alkanes (see Table I).

$$RH + \underset{I}{Cl_3CSO_2Cl} \xrightarrow[\text{or } Bz_2O_2]{h\nu} RCl + HCCl_3 + SO_2 \quad (1)$$

This reagent shows a very high degree of selectivity as to the site of chlorination on certain compounds compared to the more random chlorination observed when chlorine or sulfuryl chloride are used as the chlorinating agents. Chlorination of ethylbenzene with I gave a monochlorinated product, the infrared analysis of which showed only α-chloroethylbenzene and no detectable amounts of β-chloroethylbenzene. Under comparable conditions, chlorination of ethylbenzene with chlorine and sulfuryl chloride gave monochlorinated products containing 10 and 7%, respectively, of the β-isomer. Gas chromatographic analysis of the reaction mixture obtained from the chlorination of *n*-hexane with I showed that only secondary chlorides were formed as monochlorinated products, whereas chlorination of *n*-hexane with chlorine and sulfuryl chloride gave monochlorinated products containing 22 and 17% 1-chlorohexane, respectively. A photochemically induced reaction of 2,3-dimethylbutane with I yielded mainly 2-chloro-2,3-dimethylbutane. Gas chromatographic analysis of the reaction mixture before distillation showed that only a trace amount of 1-chloro-2,3-dimethylbutane was formed in the reaction. The primary halide is the major product obtained in the chlorination of 2,3-dimethylbutane with either chlorine or sulfuryl chloride.[3] The alkyl side chain of *p*-bromotoluene was chlorinated with I without any substitution of the aromatically bonded bromine by chlorine. This substitution is reported to occur in chlorinations of *p*-bromotoluene with both chlorine and sulfuryl chloride.[4]

Inasmuch as these chlorinations of hydrocarbons by I can be induced by peroxides or by light, the mechanism of the reaction very likely involves a free radical chain. Initiation of the chain reaction by benzoyl peroxide presumably consists of a thermal decomposition of the peroxide into benzoyloxy radicals which attack the hydrocarbon. This

$$Bz_2O_2 \longrightarrow 2BzO\cdot \quad (2)$$

$$BzO\cdot + RH \longrightarrow BzOH + R\cdot \quad (3)$$

is evidenced by the formation of benzoic acid in the benzoyl peroxide-induced reactions. In the photoinitiated reactions, the free radicals that initiate the chain reaction very likely result from the photochemical cleavage of I into free radicals which react with the hydrocarbon.

$$I \xrightarrow{h\nu} Cl_3C\cdot + SO_2 + Cl\cdot \quad (4)$$

$$Cl_3C\cdot \text{ (or } Cl\cdot) + RH \longrightarrow HCCl_3 \text{ (or } HCl) + R\cdot \quad (5)$$

Two plausible free radical chain sequences can be suggested to account for the products of these reactions:

Chain sequence A

$$R\cdot + I \longrightarrow RCl + SO_2 + Cl_3C\cdot \quad (6)$$

$$Cl_3C\cdot + RH \longrightarrow HCCl_3 + R\cdot \quad (7)$$

Chain sequence B

$$R\cdot + I \longrightarrow RCl + Cl_3CSO_2\cdot \quad (8)$$

$$Cl_3CSO_2\cdot + RH \longrightarrow Cl_3CSO_2H + R\cdot \quad (9)$$

$$Cl_3CSO_2H \longrightarrow HCCl_3 + SO_2 \quad (10)$$

The significant difference between these two chain sequences is the mode of hydrogen abstraction. In chain sequence A, hydrogen abstraction is

(1) Taken in part from the thesis of B. Giddings submitted in partial fulfillment of the requirements for the Master of Science degree at the University of Kansas, 1961.

(2) E. S. Huyser, *J. Am. Chem. Soc.*, **82**, 5246 (1960).

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

(4) B. Miller and C. Walling, *ibid.*, **79**, 4187 (1957).

TABLE I

REACTIONS OF Cl_3CSO_2Cl WITH VARIOUS COMPOUNDS

Compound (moles)	Cl_3CSO_2Cl, moles	Initiation	Time, hr., temp.	Products: $HCCl_3$, moles	Products: Chlorinated product (moles)	Per cent conversion
Toluene (2.00)	0.20	Bz_2O_2 (0.01)	21 79–80°	0.07	Benzyl chloride (0.10)	50
Toluene (1.00)	.10	$h\nu$	8 110–115°	(.08)[a]	Benzyl chloride (0.08)	80
Ethylbenzene (1.00)	.20	Bz_2O_2 (0.012)	72 78–80°	.11	α-Chloroethylbenzene (0.10)	50
Ethylbenzene (1.00)	.115	$h\nu$	6 130–133°	(.10)[a]	α-Chloroethylbenzene (0.10)	87
o-Xylene (1.00)	.20	Bz_2O_2 (0.01)	24 79–82°	.13	α-Chloro-*o*-xylene (0.13)	65
m-Xylene (1.00)	.20	Bz_2O_2 (0.01)	24 75–79°	.12	α-Chloro-*m*-xylene (0.12)	60
p-Xylene (1.00)	.20	Bz_2O_2 (0.01)	24 70–75°	.16	α-Chloro-*p*-xylene (0.16)	80
α-Chloro-*p*-xylene (1.00)	.18	$h\nu$	6 110–115°	.10	α,α′-Dichloro-*p*-xylene (0.05)	28
p-Bromotoluene (0.50)	.115	$h\nu$	10 110–115°	.10	*p*-Bromobenzyl chloride (0.11)	97
p-Bromotoluene (1.00)	.20	Bz_2O_2 (0.01)	24 80–85	.12	*p*-Bromobenzyl chloride (0.07)	35
Cyclopentane (1.00)	.20	$h\nu$	24 75–77°	.18	Cyclopentyl chloride (0.15)	75
n-Hexane (0.30)	.10	$h\nu$	15 70–72°	.028	*sec*-Hexyl chlorides (0.026)	28
Cyclohexane (1.25)	.25	$h\nu$	14 89–93	.23	Cyclohexyl chloride (0.21)	84
Cyclohexane (2.50)	.20	Bz_2O_2 (0.02)	4 80°	.20	Cyclohexyl chloride (0.20)	100
2,3-Dimethylbutane (1.00)	.20	$h\nu$	30 70°	...	2-Chloro-2,3-dimethylbutane (0.19)	96

[a] Moles of SO_2.

TABLE II

COMPETITION REACTIONS OF CYCLOHEXANE AND TOLUENE

Run	Toluene[a]: Initial amount	Toluene[a]: Amount reacted	Cyclohexane: Initial amount	Cyclohexane: Amount reacted	$HCCl_3$ produced	k_c/k_t[b]
			$BrCCl_3$, photoinitiated at 78°			
1	9.81	2.60	9.59	0.65	3.25	0.22
2	10.28	2.76	9.45	0.45	3.37	0.15
3	10.91	7.07	9.71	2.00	...	0.22
			Cl_3CSO_2Cl, Bz_2O_2 induced at 80°			
1	8.24	0.86	7.02	1.43	1.80	1.3–4.9
2	8.98	1.22	7.20	1.67	2.25	1.1–3.9
3	8.61	0.97	6.81	1.36	1.96	1.3–3.1

[a] All amounts in mmoles. [b] Calculated in the usual manner by means of the kinetic expression

$$\frac{k_A}{k_B} = \frac{\log(A_{Init}/A_{Fin})}{\log(B_{Init}/B_{Fin})}$$

where the subscripts Init. and Fin. refer to the amounts of the reactants A and B before and after the reaction, respectively.

performed by a trichloromethyl radical (reaction 7) which results, along with sulfur dioxide, from the breakdown of the trichloromethanesulfinyl radical ($Cl_3CSO_2\cdot$). In chain sequence B, $Cl_3CSO_2\cdot$ is the hydrogen abstracting radical (reaction 9) producing trichloromethanesulfinic acid which is reported to be unstable, decomposing into chloroform and sulfur dioxide (reaction 10).[5]

Although both chain sequences could proceed concurrently, competition experiments involving halogenation of cyclohexane and toluene with bromotrichloromethane in one case and I in another show that hydrogen abstraction exclusively by $Cl_3C\cdot$ does not occur. The relative reactivity ratios k_c/k_t, shown in Table II, were determined from the amounts of cyclohexane and toluene that were removed from a mixture of the two hydrocarbons in reactions with the halogenating agents.

$$X\cdot + C_6H_{12} \xrightarrow{k_c} HX + C_6H_{11}\cdot$$

$$X\cdot + C_6H_5CH_3 \xrightarrow{k_t} HX + C_6H_5CH_2\cdot$$

($X\cdot$ is the hydrogen abstracting radical)

(5) M. Battegay and W. Kern, *Bull. soc. chim.*, **41**, 38 (1927).

TABLE III

EFFECT OF HYDROCARBON STRUCTURE ON CONVERSION AND KINETIC CHAIN LENGTH

	Temp., °C.	Time, hr.	Method of initiation	Per cent conversion	Kinetic chain length
Cyclohexane[a]	100	4	$h\nu$	100	...
Cyclohexane[b]	80	16	Bz_2O_2	83	6.4
Toluene[a]	100	4	$h\nu$	75	...
Toluene[b]	80	16	Bz_2O_2	51	3.9
Cumene[a]	100	4	$h\nu$	22	...
Cumene[b]	80	16	Bz_2O_2	10	0.83

[a] $[RH]:[Cl_3CSO_2Cl]:[C_6H_5H] = 5:1:1$. [b] $[RH]:[Cl_3CSO_2Cl]:[C_6H_5]:[Bz_2O_2] = 10:1:1:0.07$.

Photochemical bromination of hydrocarbons with bromotrichloromethane (reaction 11) clearly involves a chain sequence (reactions 12 and 13) in which $Cl_3C\cdot$ is the hydrogen abstracting radical.[6] Our data show that toluene is about five

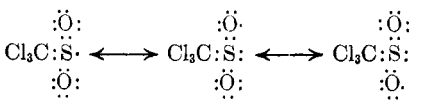
$$BrCCl_3 + RH \xrightarrow{h\nu} HCCl_3 + RBr \quad (11)$$

$$R\cdot + BrCCl_3 \longrightarrow RBr + Cl_3C\cdot \quad (12)$$

$$Cl_3C\cdot + RH \longrightarrow HCCl_3 + R\cdot \quad (13)$$

times more reactive than cyclohexane toward hydrogen abstraction by $Cl_3C\cdot$ (Table II). On the other hand, cyclohexane is more reactive than toluene toward chlorination with I (Table II).[7]

The higher reactivity of cyclohexane with respect to toluene toward hydrogen abstraction in reactions with I not only eliminates the possibility of hydrogen abstraction exclusively by $Cl_3C\cdot$ but also supports the suggestion that $Cl_3CSO_2\cdot$ may be the hydrogen abstractor. This radical very likely is a resonance hybrid of three canonical forms, two of which have the unpaired electron on oxygen.



Such a free radical could abstract hydrogen atoms from the hydrocarbon in such a manner that an oxygen–hydrogen bond is formed. If this is the case, the higher reactivity of cyclohexane with respect to toluene is not surprising. Walling and Jacknow found that cyclohexane is about six times more reactive than toluene toward hydrogen abstraction by a *t*-butoxy radical at 40°.[8] This radical abstraction also involves the formation of an oxygen–hydrogen bond. The lower value of k_c/k_t that we observe in our work could result from the fact that our values were found at a higher temperature or it could be due to the resonance stabilization of the trichloromethanesulfinyl radical. It is also possible that some of the $Cl_3CSO_2\cdot$ radicals may have decomposed and some of the hydrogen abstraction is performed by $Cl_3C\cdot$.

The suggestion that $Cl_3CSO_2\cdot$ is the hydrogen abstracting radical in these halogenations with I suffers from the fact that most alkanesulfinyl radicals are unstable at the temperature used in our competitive reactions. They decompose into the alkyl free radical and sulfur dioxide.[9] However, the energy gained in the formation of the oxygen–hydrogen bond in the hydrogen abstraction reaction may be enough to allow this reaction to compete favorably with the decomposition reaction in our reactions.

Although the selectivity displayed by I as a chlorinating agent is determined by the nature of the hydrogen abstraction reaction in the chain sequence, the limiting factor in the usefulness of this reagent as a chlorinating agent appears to be the ability of the radical R· to abstract a chlorine atom from I (reaction 8). This conclusion is based on the data in Table III which show the per cent conversions and kinetic chain lengths of the reactions of cyclohexane, toluene, and cumene with I. Cumene, although more reactive than either toluene or cyclohexane toward hydrogen abstraction by most free radicals,[8] including *t*-butoxy radicals and chlorine atoms, both of which have k_c/k_t greater than one, is chlorinated less readily by I than either cyclohexane or toluene under comparable conditions. The comparatively high amount of resonance stabilization of the α-cumyl radical makes it less reactive than either the benzyl or cyclohexyl radicals in the chlorine abstraction reaction. The longer chain length of cyclohexane with respect to toluene may be due in part to the greater ease of abstraction of a hydrogen atom from the former but could also result partly from the higher reactivity of the cyclohexyl free radical compared to that of the resonance stabilized benzyl radical. Thus, the over-all reactivity of these hydrocarbons in reactions with I parallels the

(6) E. S. Huyser, *J. Am. Chem. Soc.*, **82**, 391 (1960); E. C. Kooyman and G. C. Vegter, *Tetrahedron*, **4**, 382 (1958); E. I. Heiba and L. C. Anderson, *J. Am. Chem. Soc.*, **79**, 494 (1957).

(7) A range of values for k_c/k_t in the case of reactions with trichloromethanesulfonyl chloride is given in Table II since the short kinetic chain length of the reactions involved (see Table III) present some difficulties in determining a reliable single value. Calculations based solely on the removal of the two hydrocarbons in these benzoyl peroxide-induced reactions would be subject to some doubt since some of the hydrocarbons might have reacted with benzoyloxy radicals (reaction 3). That this very likely did occur in our experiments is indicated by the fact that the total amount of hydrocarbon that reacted is greater than the amount of chloroform produced. The higher value for k_c/k_t results if it is assumed that the peroxide fragments attack only toluene while the lower value is found if the attack of the benzoyl radicals is assumed to be only on cyclohexane.

(8) C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108 (1960).

(9) For discussion of the stability of alkanesulfinyl radicals encountered in copolymerization of olefins with sulfur dioxide, see C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, pp. 223–228.

reactivity of the radicals participating in the chlorine abstraction [$C_6H_{11}\cdot > C_6H_5CH_2\cdot > C_6H_5\dot{C}(CH_3)_2$] rather than the reactivity of these hydrocarbons toward hydrogen abstraction [$C_6H_5CH(CH_3)_2 \geq C_6H_{12} > C_6H_5CH_3$].

Experimental

Reagents.—Trichloromethanesulfonyl chloride (Eastman Kodak) was used throughout without any further purification. All other reagents were commercial materials and, when necessary, distilled or recrystallized before using. All melting points and boiling points are uncorrected.

Procedure for Chlorination with Trichloromethanesulfonyl Chloride.—The data in Table I were accumulated in experiments performed in essentially the following manner. The trichloromethanesulfonyl chloride was dissolved in the material to be chlorinated in a round-bottom Pyrex flask of suitable size fitted with a 12- or 18-in. spiral condenser. In the photoinitiated reactions, a 275-watt General Electric sunlamp was placed about 4–6 in. from the bottom of the flask. This light furnished both the necessary radiation to initiate the reactions and heat to bring the reaction mixtures to the indicated temperatures. In the case of the benzoyl peroxide-induced reactions, the indicated temperatures were attained either by a heating mantle or by placing the flask containing the reactants in an oil bath. In all cases, the evolution of sulfur dioxide was observed. The determination of the amount of sulfur dioxide (see Table I) was accomplished by passing a stream of nitrogen gas through the reaction mixture and carrying the sulfur dioxide into a solution of standard sodium hydroxide. The amount of sulfite was ascertained by titrating an aliquot of this solution with a standard hydrochloric acid solution.

Distillation of the reaction mixtures yielded a fraction containing chloroform, the amount of which was determined by gas chromatographic analysis. In each case, the product was isolated by distillation and identified by comparison of its infrared spectrum with that of a known sample of the compound as well as, where applicable, by its melting point and retention time in a gas chromatographic column. The physical constants for the chlorinated products are as follows: benzyl chloride, b.p. 79–81° at 25 mm., m.p. of thiouronium picrate, 188–189°, reported m.p., 188°[10]; α-chloroethylbenzene, b.p. 77–78° at 17 mm., $n^{25}D$ 1.5230; α-chloro-*o*-xylene, b.p. 70–75° at 18 mm., $n^{25}D$ 1.5400; α-chloro-*m*-xylene, b.p. 40–45° at 5 mm., $n^{25}D$ 1.5319; α-chloro-*p*-xylene, b.p. 80–82° at 30 mm., m.p. from petroleum ether, 41–42°; reported m.p. 41°[11]; α,α′-dichloro-*p*-xylene, m.p. from petroleum ether, 98–99°; reported m.p., 100.5°[12]; cyclopentyl chloride, b.p. 108–115°, $n^{25}D$ 1.4500; cyclohexyl chloride, b.p. 140–142°, $n^{25}D$ 1.4610; 2-chloro-2,3-dimethylbutane, b.p. 110°, $n^{25}D$ 1.4160.

Comparative Selectivity of Chlorinating Agents (Ethylbenzene).—The infrared spectrum of the monochlorinated product (b.p. 87–91° at 24 mm.) obtained from the photochlorination gf ethylbenzene with chlorine at 80° showed an absorption at 718 cm.$^{-1}$. The infrared spectrum of the monochlorinated product (b.p. 81° at 19 mm.) obtained from the benzoyl peroxide-induced reaction of ethylbenzene and sulfuryl chloride at 80° showed a similar absorption. This absorption band is present in the infrared spectrum of an authentic sample of β-chloroethylbenzene prepared from β-phenylethanol and thionyl chloride. No absorption band at this frequency was found in the infrared spectrum of the chlorinated product obtained from the reaction of ethyl benzene and trichloromethanesulfonyl chloride. Calculations made from the infrared spectra of the chlorinated products obtained from the reactions with chlorine and sulfuryl chloride indicate the presence of 10 and 7% of β-chloroethylbenzene, respectively.

(*n*-**Hexane**).—Gas chromatographic analysis of the reaction mixtures obtained from the light induced reaction of chlorine and *n*-hexane on a seven foot by 1/4-in. column packed with 15% *sec*-octyl sebacate on Chromasorb W (column temp. 78°; helium used as carrier gas) showed two monochlorinated products. The larger peak corresponded in retention time to an authentic sample of 2-chlorohexane prepared from 2-hexanol and thionyl chloride. 3-Chlorohexane did not separate from the 2-chlorohexane under these conditions. The smaller peak which followed had a retention time identical with that of 1-chlorohexane prepared from 1-hexanol and thionyl chloride. These same two peaks were observed in the chromatogram of the mixture obtained from the benzoyl peroxide-induced reaction of *n*-hexane and sulfuryl chloride. Comparison of the peak areas showed that 22% of the monohalide was 1-chlorohexane in the reaction with chlorine and 17% 1-chlorohexane in the reaction with sulfuryl chloride. Only a trace (~1%) of 1-chlorohexane was found in the chlorination of *n*-hexane with trichloromethanesulfonyl chloride.

(**2,3-Dimethylbutane**).—Gas chromatographic analysis of the reaction mixtures of 2,3-dimethylbutane with both chlorine in a light-induced reaction and sulfuryl chloride in a benzoyl peroxide-induced reaction under conditions outlined above showed two monochlorinated products. The second chromatographic peak was the larger in both cases. An authentic sample of 2-chloro-2,3-dimethylbutane, prepared from thionyl chloride and dimethylisopropylcarbinol which was obtained from the reaction of methylmagnesium iodide and ethyl isobutyrate, had a retention time the same as that of the first peak. The second peak presumably is that of 1-chloro-2,3-dimethylbutane. Chlorination of 2,3-dimethylbutane with trichloromethanesulfonyl chloride yielded predominantly 2-chloro-2,3-dimethylbutane and only a trace of 1-chloro-2,3-dimethylbutane.

Determination of Relative Reactivity of Cyclohexane and Toluene toward Bromotrichloromethane.—Reaction mixtures consisting of about equivalent quantities of cyclohexane, toluene, and chlorobenzene and about one-half equivalent amount of bromotrichloromethane were chromatographed on a 10 ft. × 1/4 in. gas chromatographic column packed with 10% Kel-F Grease on Chromasorb W using helium as the carrier gas. The reaction mixtures were sealed in a Pyrex tube, placed in an ethanol vapor bath, and illuminated with a 275-watt G.E. sunlamp for about 1–2 hr. during which time about half of the bromotrichloromethane reacted. The mixtures were again chromatographed under the same conditions. Chlorobenzene, which does not react under these conditions, served as an internal standard allowing corrections to be made for any difference in the quantity of the sample chromatographed before and after the reaction. The amount of each hydrocarbon remaining was determined by comparison of its peak height after reaction with its peak height found in the chromatograms taken before reaction.

Chloroform was determined from the relation of its peak height to that of the internal standard. The peak height ratio and mole ratio of chloroform to chlorobenzene was previously determined. In one case (run 3) an equivalent amount of bromotrichloromethane was added and the reaction mixture illuminated for about 5 hr. to allow almost complete reaction of the polyhalomethane. The data obtained by this procedure are shown in Table II and treated as indicated in footnote *b* of this table.

Determination of Relative Reactivity of Cyclohexane and Toluene toward Trichloromethanesulfonyl Chloride.—Reaction mixtures consisting of about equivalent quantities of cyclohexane, toluene, chlorobenzene, and trichloromethanesulfonyl chloride were chromatographed in the manner described in the previous section. About 5 mole % benzoyl peroxide (based on the amount of trichloromethanesulfonyl

(10) E. L. Brown and H. Campbell, *J. Chem. Soc.*, 1699 (1937).

(11) M. J. Boeseken, *Rec. trav. chim.*, **23**, 99 (1904).

(12) H. Stephen, W. F. Short, and G. Gladding, *J. Chem. Soc.*, **117**, 519 (1920).

chloride) was then added. The reaction mixtures were sealed in Pyrex tubes and heated in an oil bath at 80° for about 8 hr. The amounts of the hydrocarbons that had reacted and the amount of chloroform produced were determined in the manner described in the previous experiment. The data obtained and the values of k_o/k_t are shown in Table II.

Comparative Reactions of Cyclohexane, Toluene, and Cumene (Photoinitiated Reactions).—Equivalent amounts of benzene and trichloromethanesulfonyl chloride were added to 5 equivalents of the hydrocarbon. The resulting mixtures were sealed in Pyrex tubes, supported in a large beaker of boiling water, and illuminated for 4 hr. by means of a sunlamp. In each case, the distance of the sunlamp from the reaction tube was the same (6 in.). The reaction mixtures were chromatographed on a 10 ft. × 1/4 column packed with "Craig Polyester" on Chromasorb W using helium as the carrier gas. The amount of chloroform produced was determined from its peak area using benzene as the internal standard. The relation that existed between the amounts of chloroform and benzene and their gas chromatographic peak areas had been previously determined.

(Peroxide-Induced Reactions).—These reactions were performed in the same manner except that twice as much hydrocarbon was employed and 7 mole % benzoyl peroxide based on the trichloromethanesulfonyl chloride was added to initiate the reactions. The reaction mixtures were heated in a constant temperature oil bath for 16 hr. (about four half-lives of the initiator). The amount of chloroform produced in each case was determined from the gas chromatogram of the reaction mixture in the manner described above.

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Synthetic Applications of the Titanium-Catalyzed Exchange of Olefins with Grignard Reagents[1a]

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The addition of a small amount of titanium tetrachloride to an ether solution of *n*-propylmagnesium bromide and certain olefins brings about a displacement reaction, forming propylene and a new Grignard reagent derived from the added olefin:

$$C_3H_7MgBr + RCH{=}CH_2 \xrightarrow{TiCl_4} C_3H_6 + RCH_2CH_2MgBr$$

A large number of olefins having terminal vinyl groups were exchanged in this way with *n*-propylmagnesium bromide and the reaction mixture was then treated with typical Grignard substrates (CO_2, HCHO, etc.). Products corresponding to the Grignard reagent derived from the olefin were isolated in 20–60% yields. Only the terminal Grignard reagent was obtained from 1-alkenes, but styrenes yielded both alpha- and beta-arylethylmagnesium bromides, with the former predominating. Only the terminal vinyl groups undergo the reaction; internal double bonds and vinylidene groups are unaffected, making it possible to prepare unsaturated Grignard reagents from suitable dienes (for example, β-cyclohexenylethylmagnesium bromide from 4-vinylcyclohexene). The olefin exchange reaction is a useful process for preparation of Grignard reagents in cases where the olefin is available and the corresponding halide is not.

In the previous paper[2] of this series it was shown that a small amount of titanium tetrachloride brings about an exchange between alkylmagnesium bromides and terminal olefins, forming a new Grignard reagent derived from the added olefin; for example, reaction between isopropylmagnesium bromide and 1-pentene yielded propylene and *n*-amylmagnesium bromide:

$$C_3H_7MgBr + CH_3CH_2CH_2CH{=}CH_2 \xrightarrow{TiCl_4} C_3H_6 + CH_3CH_2CH_2CH_2CH_2MgBr \quad (1)$$

The suggested reaction sequence involved the formation of an alkyltitanium compound by reaction of the Grignard reagent with titanium tetrachloride,[3] followed by elimination of the elements of TiH,[4] and addition terminally of the titanium hydride to the olefin. For the reaction to proceed with only catalytic[5] amounts of titanium tetrachloride a rapid and reversible exchange of alkyl groups between Grignard reagent and alkyltitanium compound must also be postulated.[6]

$$C_3H_7MgBr + TiCl_4 \longrightarrow C_3H_7TiCl_3 + MgBrCl \quad (2)$$

$$C_3H_7TiCl_3 \rightleftharpoons CH_3CH{=}CH_2 + TiHCl_3 \quad (3)$$

$$CH_3CH_2CH_2CH{=}CH_2 + TiHCl_3 \longrightarrow CH_3CH_2CH_2CH_2CH_2TiCl_3 \quad (4)$$

$$CH_3CH_2CH_2CH_2CH_2TiCl_3 + C_3H_7MgBr \rightleftharpoons CH_3CH_2CH_2CH_2CH_2MgBr + C_3H_7TiCl_3 \quad (5)$$

(1) (a) Presented in part at the 140th Meeting of the American Chemical Society, Chicago, Illinois, September, 1961; (b) present address, New Mexico State University, Box 756, University Park, New Mexico.

(2) G. D. Cooper and H. L. Finkbeiner, *J. Org. Chem.*, **27**, 1493 (1962).

(3) D. F. Herman and W. K. Nelson, *J. Am. Chem. Soc.*, **75**, 3877, 3882 (1953).

(4) Presumably the titanium hydride would make up part of the solid Ziegler-type complex which forms immediately upon the addition of the titanium tetrachloride but for the sake of simplicity it is shown as $TiHCl_3$. The Grignard reagent similarly is shown throughout as RMgBr, although such a structure is no longer considered probable. R. E. Dessy and G. S. Handler, *ibid.*, **80**, 5824 (1958).

(5) Titanium tetrachloride cannot properly be called a "catalyst," as it is converted to other products during the reaction, but no more suitable term appears to be available.

(6) Although this type of exchange has not been reported in the case of alkylmagnesium compounds a similar rapid exchange of alkyl groups between aluminum and titanium has been demonstrated: G. L. Karapinka and W. L. Carrick, *J. Polymer Sci.*, **55**, 141 (1961), and references cited therein.