COMMUNICATIONS TO THE EDITOR

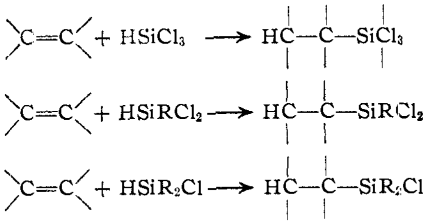
THE REACTION OF OLEFINS AND CHLOROHYDROSILANES

Sir:

The preparation of octyltrichlorosilane from octene and trichlorosilane using diacetyl peroxide or ultraviolet light as catalyst was reported by Sommer, *et al.*[1]

While a good yield of product was obtained, certain disadvantages are resident in the use of peroxides to facilitate this reaction.

In an extensive program considerably prior to the above publication, we synthesized many organosilicon derivatives by reactions of the following types, employing a wide variety of hydrocarbons containing olefinic double bonds



$$>C{=}C< + HSiCl_3 \longrightarrow HC{-}C{-}SiCl_3$$

$$>C{=}C< + HSiRCl_2 \longrightarrow HC{-}C{-}SiRCl_2$$

$$>C{=}C< + HSiR_2Cl \longrightarrow HC{-}C{-}SiR_2Cl$$

These reactions were accomplished without addition of catalyst or other reagent, by merely heating the reaction mixtures under pressure. The times and temperatures were chosen by a consideration of reaction kinetics determined at several temperatures. Temperatures employed varied from 160°, where the reactions are slow, to 400°, where the reactions are rapid but where some decomposition may occur. The method is illustrated by the following experiments.

Octadecyltrichlorosilane was prepared by heating in a 2.4-liter bomb a mixture of 406 g. of trichlorosilane and 756 g. of octadecene. The temperature was raised to 300° over a two and one-half-hour period. The pressure increased regularly to 276 p. s. i. maximum at 276°, then dropped to 180 p. s. i. when 300° was reached; when it leveled at 65 p. s. i. after eighteen hours at 300°, the run was discontinued. The yield was 94% of the theoretical.

n-Propylmethyldichlorosilane was prepared by similarly bombing 345 g. of methyldichlorosilane with 128 g. of propylene overnight at 300° (1120 p. s. i. max.) On distillation, propylmethyldichlorosilane was isolated at 123–124° (747 mm.). The yield was 72% of the theoretical; some hexylmethyldichlorosilane was formed.

A wide variety of compounds were similarly prepared by treating 1-alkenes from ethylene through octadecene, 2-butene, isobutene, cyclohexene, diisobutylene, 1,3-butadiene and 1,5-hexadiene with trichlorosilane, tribromosilane, methyldichlorosilane, ethyldichlorosilane, phenyldichlorosilane, diethylchlorosilane, diphenylchlorosilane and methylphenylchlorosilane.

The 1-alkenes yielded *n*-alkyl derivatives almost exclusively. With trichlorosilane, 2-butene yielded *s*-butyltrichlorosilane while isobutene gave only isobutyltrichlorosilane. Thus it is evident that the electron-rich carbon of the olefin becomes linked to the electron-accepting silicon in trichlorosilane, the HSi nucleus of which may be regarded as a pseudo-aluminum; a chlorine likely becomes bonded, at least in a transition state, to the adjacent electropositive carbon whereafter its exchange with the labile H on the silicon generates the normal alkyltrichlorosilane. Silicon tetrachloride does not react similarly.

Of the various compounds prepared by this method, the following are new to the literature:

Compound	Boiling point °C.	Mm.
s-Butyltrichlorosilane	145–146	736
2-Methylpentyltrichlorosilane	98	50
3-(2,2,4-Trimethylpentyl)-trichlorosilane	94–96	20
n-Hexadecyltrichlorosilane	194–196	7.5
n-Octadecyltrichlorosilane	185–199	2–3
n-Butenyltrichlorosilane	64	40
Trichlorosilyl-(trichlorosilylethyl)-cyclohexane	161	6
n-Hexenyltrichlorosilane	103–140	50
bis-(Trichlorosilyl)-hexane	148-153	10
n-Propyltribromosilane	183	756
Ethylmethyldichlorosilane	100	744
Methylpropyldichlorosilane	123–124	747
n-Butylmethyldichlorosilane	147.5–148	744
n-Hexylmethyldichlorosilane	192	743
Methyloctyldichlorosilane	100–116	20
Methyloctadecyldichlorosilane	200–210	6
Cyclohexylmethyldichlorosilane	204	745
Phenylpropyldichlorosilane	140–144	44–47
Diethylpropylchlorosilane	164–166	742
Methylphenylpropylchlorosilane	124–126	30
Diphenylpropylchlorosilane	174–176	10

A series of papers on this subject will be forthcoming.

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[1] L. H. Sommer, E. W. Pietrusza and F. C. Whitmore, This Journal, **69**, 188 (1947).

FREE RADICAL REACTIONS OF ALDEHYDES

Sir:

Some recent work of ours on free radical reactions of aldehydes in the liquid phase has revealed some interesting and useful properties of the acyl radical.

It is easy to produce a peroxide catalyzed chain decomposition (decarbonmonoxylation) of aldehydes

$$\mathrm{RCHO + P\cdot \longrightarrow RCO + PH}$$
$$\mathrm{R\dot{C}O \longrightarrow R\cdot + CO}$$
$$\mathrm{R\cdot + RCHO \longrightarrow RH + R\dot{C}O}$$

(P· representing a free radical generated in the peroxide decomposition) similar to that observed in the gas phase photolysis.[1] Thus a mixture of 0.265 mole of β-phenylisovaleraldehyde, b. p. 86.5–87.5° (3 mm.), $n^{20}\mathrm{D}$ 1.5107, and 0.030 mole of di-*t*-butyl peroxide evolved 90% of the theoretical amount of carbon monoxide in five hours at 130° under reflux. Fractionation yielded 70% of an approximately 1:1 mixture of *t*-butylbenzene (monoacetamido derivative, m. p. 168.5–169.0°; perbromo derivative, m. p. 318–320°) and isobutylbenzene (monoacetamido derivative, m. p. 127.0–127.5°; perbromo derivative, m. p. 75.0–75.5°). Thus the partial rearrangement of the neophyl radical (migration of phenyl) previously reported by Kharasch and Urry[2] is confirmed.

At lower temperatures the acyl radical is considerably more stable. When the same reaction was carried out at 80° with benzoyl peroxide as catalyst, little, if any, carbon monoxide or butylbenzene was formed and 67% of the input aldehyde was recovered.

The use of carbon tetrachloride as solvent for the preceding reaction gives rise to reaction of the acyl radical with the solvent: 6.6 g. (0.04 mole) of β-phenylisovaleraldehyde and 1.0 g. (0.004 mole) of benzoyl peroxide were refluxed for twelve hours with 6.7 g. (0.05 mole) of redistilled carbon tetrachloride. No carbon monoxide was evolved. Fractionation yielded 1.6 g. (0.0135 mole) of chloroform, b. p. 60–63°, and 4.3 g. (0.0224 mole) of β-phenylisovaleryl chloride, b. p. 84.0–86.5° (3 mm.), neutral equivalent 99.0, the hydrolysis of which yielded β-phenylisovaleric acid, m. p. 58–59° (undepressed on admixture with authentic material.)

Similarly, from isovaleraldehyde was obtained isovaleryl chloride in 60% yield, b. p. 113–115°, neutral equivalent 61.1, m. p. of anilide 108.5–109.0° (undepressed on admixture with authentic isovaleranilide).

Since the yields of chloroform and acid chloride are considerably in excess of the amount of catalyst used it is evident that a chain reaction involving the aldehyde and carbon tetrachloride has been set up as follows:

$$\mathrm{R\dot{C}O + ClCCl_3 \longrightarrow RCOCl + Cl_3C\cdot}$$
$$\mathrm{Cl_3C\cdot + RCHO \longrightarrow HCCl_3 + R\dot{C}O}$$

An attempt to reverse the reaction by refluxing isovaleryl chloride with benzoyl peroxide and chloroform was unsuccessful.

Most of the previous interest in liquid phase radical reactions of carbon tetrachloride has been in connection with addition to the olefinic linkage.[3] The chlorination of the aldehydes represents a radical type exchange reaction, specifically the Cl–H exchange between carbon tetrachloride and a material with a uniquely active hydrogen atom (the carbonyl hydrogen atom in the aldehydes used.)

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[1] E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1946, p. 184 ff.

[2] Urry and Kharasch, THIS JOURNAL, **66**, 1438 (1944).

[3] Kharasch, Jensen and Urry, THIS JOURNAL, **69**, 1100 (1947).

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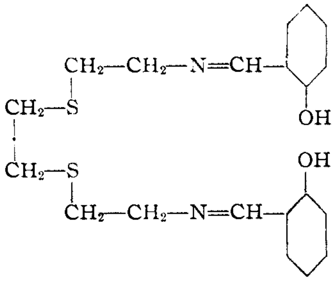
A SEXADENTATE CHELATE COMPOUND

Sir:

The dihydrochloride of 3,6-dithia-1,8-diaminooctane,[1] m. p. 186–188°, can be prepared by treating β-bromoethylphthalimide (2 moles) with ethylene dithiol in alcoholic alkali, followed by hydrolysis of the product with hydrazine and then hydrochloric acid[2] (calcd. for $C_6H_{18}N_2S_2Cl_2$: N, 11.0. Found: N, 11.2). Its hot aqueous alcoholic solution reacts with salicylaldehyde in the presence of sodium acetate to produce 3,6-dithia-1,8-bis-(salicylideneamino)-octane (I, hereafter designated SH_2), yellow leaflets, m. p. 115° (calcd. for $C_{20}H_{24}N_2O_2S_2$: C, 61.9, H, 6.2; N, 7.5. Found: C, 61.7; H, 6.3; N, 7.7).



(I)

Aerial oxidation of the orange-red solution obtained by treating I with cobaltous acetate in hot methanol, followed by dilution with water, gives a deep green solution from which potassium iodide precipitates a very dark iodide $[\mathrm{CoS}]^+\mathrm{I}^-$ (II), readily obtained in well-formed dark brown crystals, m. p. 245° (dec.) (calcd. for $[\mathrm{Co}(C_{20}H_{22}N_2O_2S_2)]^+\ \mathrm{I}^-$: Co, 10.3; C, 42.0; H, 3.8; N, 4.9; I, 22.2. Found: Co, 10.3; C, 41.4; H, 3.8; N, 4.9; I, 22.2). The sparingly soluble perchlorate and the very soluble nitrate and chloride (III, $[\mathrm{CoS}]^+\mathrm{Cl}^-$) are also easily prepared. III forms beautifully crystalline almost black needles, m. p. 210° (dec.) (calcd. for $[\mathrm{Co}(C_{20}H_{22}N_2O_2S_2)]^+\ \mathrm{Cl}^-\cdot H_2O$: Co, 11.7; Cl, 7.2. Found: Co, 11.7; Cl, 7.1; mol. wt. 251, cryoscopically in water).

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[1] For nomenclature *cf.* J. van Alphen, *Rec. trav. chim.*, **56**, 343 (1937), note 3.

[2] *Cf.* Ing and Manske, *J. Chem. Soc.*, 2348 (1926).