COMMUNICATIONS TO THE EDITOR

THE REACTION OF OLEFINS AND CHLORO-HYDROSILANES

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

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

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

$$\ce{>C=C< + HSiR_2Cl -> HC-C-SiR_2Cl}$$
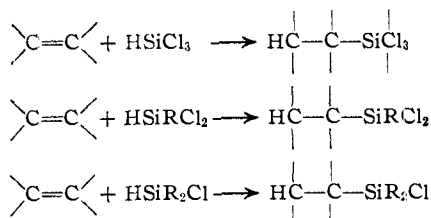
These reactions were accomplished without addition of catalyst or other reagent, by merely heating the reaction mixtures under pressure. The times and temperatures were chosen by a consideration of reaction kinetics determined at several temperatures. Temperatures employed varied from 160°, where the 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	109–116	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 re-

vealed some interesting and useful properties of the acyl radical.

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

$$RCHO + P\cdot \longrightarrow R\dot{C}O + PH$$

$$R\dot{C}O \longrightarrow R\cdot + CO$$

$$R\cdot + RCHO \longrightarrow RH + R\dot{C}O$$
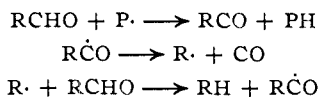
(P· representing a free radical generated in the peroxide decomposition) similar to that observed in the gas phase photolysis.[1] Thus a mixture of 0.265 mole of β-phenylisovaleraldehyde, b. p. 86.5–87.5° (3 mm.), n^{20}D 1.5107, and 0.030 mole of di-t-butyl peroxide evolved 90% of the theoretical amount 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:

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

$$Cl_3C\cdot + RCHO \longrightarrow HCCl_3 + R\dot{C}O$$
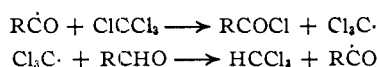
An attempt to reverse the reaction by refluxing

(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).

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.)

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

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RECEIVED OCTOBER 20, 1947

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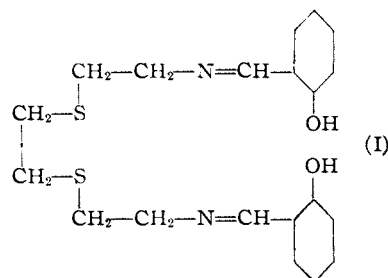
Aerial oxidation of the orange-red solution obtained by treating I with cobaltous acetate in hot methanol, followed by dilution with water, gives a deep green solution from which potassium iodide precipitates a very dark iodide $[CoS]^+I^-$ (II), readily obtained in well-formed dark brown crystals, m.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

(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).

Electrical conductivity measurements indicate that III behaves in aqueous solution as a binary strong electrolyte.

The d-α-bromocamphor-π-sulfonate of this cobaltic complex of I can be prepared from II and silver d-α-bromocamphor-π-sulfonate, and separated from a mixture of methanol and ether into a sparingly soluble crystalline brown solid (IV) and a very soluble gum (V). The aqueous solution of IV is strongly levorotatory, a 0.01% solution having a specific rotation of $-7,000°$ (Hg green line 5461). Iodides precipitate from this solution the levorotatory iodide 1-[CoS]$^+$I$^-$ (found: C, 41.5; H, 3.8; N, 4.9. I, 22.0%) m. p. 268° (dec.). After six recrystallizations from 20% methanol-water, the molecular rotation (Hg green line) was $-50,160°$. Solutions of this salt can be boiled for twenty minutes without appreciable racemization. The aqueous solution of V is strongly dextro-rotatory. From it, after considerable difficulty the pure d-iodide was obtained, with molecular rotation of $+50,160°$ (nine recrystallizations of the iodide were necessary).

Models show that I can function as a sexadentate chelate compound, occupying all six octahedrally disposed coördination positions about a six-covalent atom in one or other of two enantiomorphous strainless configurations provided that the nitrogen atoms are in *trans* positions and the sulfur atoms and oxygen atoms in *cis* positions to each other. The experimental evidence is wholly in favor of I being able to function as a sexadentate chelate compound.

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α-PELTATIN, A NEW COMPOUND ISOLATED FROM *PODOPHYLLUM PELTATUM*

Sir:

The drug podophyllin N. F., prepared from the dried rhizomes and roots of *Podophyllum peltatum* L., has been shown to produce severe damage to mouse tumor cells both *in vivo*[1,2a] and *in vitro*.[2b] Chemical fractionation involving solvent extraction and chromatographic adsorption on alumina,[2a] guided by bioassay,[3] yielded two tumor-necrotizing agents in pure form. One of these was identical with the well-known podophyllotoxin; the other was a new substance which was provisionally referred to as NCI-1074.

The new compound, for which the name α-peltatin is proposed, has now been conveniently isolated from podophyllin in a yield of about 9%

(1) M. Belkin, *Federation Proceedings*, **6**, 308 (March, 1947).

(2) (a) J. L. Hartwell and M. J. Shear; (b) R. A. Ormsbee and I. Cornman: both papers presented before the American Association for Cancer Research, annual meeting, May 16, 1947. Abstracts in *Cancer Research*, in press.

(3) The bioassay phase of the coöperative project was carried out by Dr. Virginia Downing, Mr. A. Perrault, and Dr. M. J. Shear

by chromatographic adsorption on alumina. α-Peltatin crystallizes from alcohol in colorless, transparent prisms, m. p. 230.5–232.5° (cor.) (shrinks at 222.5° and darkens at m. p.); $[\alpha]^{20}$D $-115°$ (c 1.0, absolute alcohol).[4] *Anal.*[5] Calcd. for $(C_{11}H_{11}O_4)_x$: C, 63.75; H, 5.35. Found: C, 63.4; H, 5.3. Calcd. for one methoxyl group per C_{11} unit: 15.0; found, 15.7. Discrepancies between the values for the molecular weight as determined by different methods make it impossible to report a true value at this time; other methods are being tried.

Solutions of the pure substance in alcohol and benzene exhibit a strong blue fluorescence under ultraviolet light, in distinction from solutions of podophyllotoxin which have only a weak blue fluorescence.

Structural, pharmacological and cytological studies with α-peltatin are in progress.

(4) Through the courtesy of Dr. N. K. Richtmyer, National Institute of Health.

(5) By Mr. C. A. Kinser and Mrs. M. M. Ledyard, National Institute of Health.

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　　　　RECEIVED OCTOBER 20, 1947

ELECTROPHORETIC RESOLUTION OF HEPARIN AND RELATED POLYSACCHARIDES

Sir:

Sodium heparinate has been found to give an electrophoretic pattern indicating the presence of two components. The apparatus described by Longsworth and MacInnes[1] was used. The schlieren method was employed in photographing the moving boundaries.[2]

One per cent. solutions of the sodium salt of heparin (prepared from the crystalline barium acid salt of 500–600 Roche anticoagulent units[3] per mg.) in acetate and phosphate buffers of ionic strength 0.2 separated into two fractions under a potential gradient of 3 to 5 volts/cm. The major component migrated as an anion with a mobility at 0° of 0.8 × 10^{-4} to 2.4 × 10^{-4} cm.^{2}/sec./volt over a pH range of 3 to 9. The higher values were obtained in the alkaline range.

The minor component was electrically neutral and sulfate-free. From the peak areas the two fractions were found to be present in approximately a 3:2 weight ratio.

A comparison between the schlieren patterns obtained when the boundaries moved through the buffer and when they moved through the solution indicated that there was an association between the two components.

(1) L. G. Longsworth and D. A. MacInnes, *Chem. Revs.*, **24**, 271 (1939).

(2) We are indebted to Professor W. G. France and Dr. Q. Van Winkle of this Laboratory for assistance in the electrophoretic techniques and to Hoffmann-La Roche, Inc., of Nutley, New Jersey. for the bioassays.

(3) R. H. K. Foster. *J. Lab. Clin. Med.*, **27**, 820 (1942).

The two components were separated in the electrophoretic cell and bioassays showed that the moving component contained all the anticoagulant activity. The biologically active substance was stable, as tested over a period of several months, in the salt solution employed in the electrophoretic separation. It showed an activity in solution of 900–1000 Roche anticoagulant units[3] per mg. (neutral sodium salt basis).

At an ionic strength of 0.02, a 0.1% solution of the sodium salt of heparin, in acetate buffer at pH 6.9, migrated as a single component. This is in agreement with the results obtained by chargaff, Ziff and Moore.[4]

Previously described preparations[5] of chondroitinsulfuric acid and mucoitinsulfuric acid were examined in the electrophoretic apparatus. One per cent. solutions in phosphate buffers of ionic strength 0.2 and pH near neutrality were used. The chondroitinsulfuric acid was found to be composed of approximately equal amounts of stationary and moving components, while the mucoitinsulfuric acid was composed of a stationary component (40%) and two moving components (41% and 19%). The mobilities were less than that of heparin at the same pH.

Further work is in progress on the separation and characterization of these fractions.

(4) E. Chargaff, M. Ziff and D. H. Moore, J. Biol. Chem., **139**, 383 (1941); cf. also O. Wilander, Skand. Arch. Physiol., **81**, suppl. 15, 20 (1939).

(5) M. L. Wolfrom, D. I. Weisblat, J. V. Karabinos, W. H. McNeely and J. McLean, THIS JOURNAL, **65**, 2077 (1943).

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NOTICE

The Conversion Factor for kX Units to Ångström Units

X-Ray wave lengths have been expressed in X units. The X unit is defined in terms of the calcite spacing and is nearly 10^{-11} cm., but is now known to differ from 10^{-11} cm. by about 0.2%. During the last twenty-five years X-ray diffraction workers have expressed X-ray wave lengths and crystal dimensions in terms of a unit which was 1000 X units, but instead of calling it 1000 X units have erroneously called it an Ångström unit. In recent years, the X-ray diffraction groups have agreed to use the term kilo X unit (abbreviated kX) in place of the incorrectly used Ångström unit, until agreement was reached on the best conversion factor to use for converting from kX to Ångström units. Agreement on the factor has now been reached.

As secretary of the American Society for X-ray and Electron Diffraction, I have been instructed to call the attention of American X-ray workers to the following announcement which appeared in the January, 1947, issue of the Journal of Scientific Instruments. Because of its importance it is here reproduced in its entirety.

"At the annual conference of the X-ray Analysis Group of the Institute of Physics in July, 1946, it was announced that agreement had been reached concerning the factor for converting measurements in kX units to Ångström units. The factor agreed upon, after consultation with the American Society for X-ray and Electron Diffraction and Prof. Siegbahn was 1.00202. This factor is probably correct to 0.003%. Since wave lengths in X-units have been measured to an accuracy of 0.001%, the wave lengths in Ångström units can be taken as accurate to 0.004% in general.

"The following is a list of values of wave lengths in Ångström units of certain emission lines and absorption edges in common use. The column headed $K\alpha$ gives the mean value of $K\alpha_1$ and $K\alpha_2$, $K\alpha_1$ being allowed twice the weight of $K\alpha_2$.

"Current values of the physical constants, such as those quoted by Birge in the 1941 volume of the Physical Society's Reports on Progress in Physics, should be used in conjunction with these wave lengths. In particular density ρ is given by the equation

$$\rho = 1.66020 \, \Sigma A / V$$

where ΣA is the sum of the atomic weights of the atoms in the unit cell, and V is the volume of the unit cell in A^3.

	$K\alpha_1$	$K\alpha_1$	$K\alpha$	$K\beta_1$	Absorption edge
Cr	2.28962	2.29352	2.2909	2.08479	2.0701
Mn	2.10174	2.10570	2.1031	1.91016	1.8954
Fe	1.93597	1.93991	1.9373	1.75654	1.7429
Co	1.78890	1.79279	1.7902	1.62073	1.6072
Ni	1.65783	1.66168	1.6591	1.50008	1.4869
Cu	1.54050	1.54434	1.5418	1.39217	1.3802
Zn	1.43510	1.43894	1.4364	1.29520	1.2831
Mo	0.70926	0.71354	0.7107	0.63225	0.6197
Rh	.61326	.61762	.6147	.54559	.5341
Pd	.58545	.58982	.5869	.52052	.5090
Ag	.55941	.56381	.5609	.49701	.4855

"It is recommended that in any published work the values of the wave-lengths used should be explicitly stated."

W. L. BRAGG, Chairman
X-Ray Analysis Group of the
Institute of Physics (England)

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Bell Telephone Laboratories
Murray Hill, N. J.