3. The properties of its triacetate, tri-*p*-toluenesulfonate, tri-*p*-nitrobenzoate, and trimethyl ether are described.

4. The glucosan contains a *trans*-glycol group which is not oxidized by periodic acid or lead tetraacetate under conditions used for the detection of adjacent hydroxyl groups.

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NOTES

Preparation of Triethylchlorosilane from Ethyl Orthosilicate[1]

BY P. A. DI GIORGIO, W. A. STRONG, L. H. SOMMER AND F. C. WHITMORE

For studies on organosilicon compounds, large quantities of pure triethylchlorosilane and other trialkylchlorosilanes were needed. The preparation from silicon tetrachloride and ethylmagnesium bromide required a time-consuming fractional distillation to separate the desired compound (b. p. 144°) from diethyldichlorosilane (b. p. 128°). Moreover, the yield of triethylchlorosilane by this method is only 30–35%. The present method gives a 60% yield of pure product, diethyldichlorosilane not being formed.

Reaction of ethyl orthosilicate with three equivalents of ethylmagnesium bromide gave triethylethoxysilane which was converted to hexaethyldisiloxane by acid hydrolysis. Addition of ammonium chloride to a concentrated sulfuric acid solution of the disiloxane gave pure triethylchlorosilane.[2]

$$(EtO)_4Si \xrightarrow{EtMgBr} Et_3SiOEt \xrightarrow{Acid}$$

$$(Et_3Si)_2O \xrightarrow[H_2SO_4]{NH_4Cl} Et_3SiCl$$

It is not necessary to isolate the disiloxane. The unpurified product from the reaction of ethyl orthosilicate and ethylmagnesium bromide can be dissolved directly in concentrated sulfuric acid and treated with ammonium chloride to give triethylchlorosilane. Diethyldichlorosilane and ethyltrichlorosilane are not formed in this step.

We have applied this method to the corresponding *n*-propyl and *n*-butyl compounds.

Experimental

Hexaethyldisiloxane from Ethyl Orthosilicate.—In a 12-liter three-necked flask, fitted with a mercury-sealed stirrer, reflux condenser and dropping funnel, there was prepared 22 equivalents of ethylmagnesium bromide in 10 liters of ether.[3] The flask was cooled with tap water and 1450 g. (7.0 moles) of ethyl orthosilicate was added during one hour. After stirring at room temperature for another hour, the ether was distilled and the product heated on the steam-bath for twelve hours. The ether was then returned to the flask followed by hydrolysis of its contents with ice water and acid. After separation of the ether layer, the ether was distilled from the product; a small amount of ethanol was also removed by distillation. The product was then dissolved, with cooling, in 1.5 liters of concentrated sulfuric acid. This was then added to 6 liters of cold water and the organic layer separated, dried with calcium chloride, and fractionated. There was obtained 573 g. (2.5 moles) of hexaethyldisiloxane,[4] b. p. 233° (734 mm.), $n^{20}D$ 1.4340, a yield of 66%.

Triethylchlorosilane from Hexaethyldisiloxane.—To 275 cc. of cold concentrated sulfuric acid there was added 265 g. (1.08 moles) of hexaethyldisiloxane. To this there was added, with stirring, 175 g. (3.1 moles)of ammonium chloride over a period of two hours. Stirring was continued for an additional hour, and the upper layer was then separated and fractionated in a column of 15 theoretical plates. All but 8 g. of this material proved to be triethylchlorosilane, 286 g. (1.9 moles), b. p. 144° (735 mm.), $n^{20}D$ 1.4314, d^{20} 0.8967, a yield of 86%. Triethylchlorosilane was analyzed for chlorine content as follows: Weighed samples, about 0.5 g., were added to a mixture of 30 cc. of methanol and excess standard alkali, followed by titration with acid.

Anal. Calcd. for $C_6H_{15}SiCl$: Cl, 23.5. Found: Cl, 23.5, 23.6.

Isolation of the hexaethyldisiloxane is unnecessary; in other preparations, the undistilled reaction product from ethyl orthosilicate and ethylmagnesium bromide was dissolved in concentrated sulfuric acid and ammonium chloride was added. The yield of pure triethylchlorosilane by this shorter method was 60–70%.

The success of this shorter method depends on: (1) no tetraethylsilane (b. p. 154°) is formed from ethyl orthosilicate even with four or more equivalents of ethylmagnesium bromide under the conditions used. (2) Diethyldichlorosilane is not formed on treatment of the corresponding diethoxy compound with sulfuric acid and ammonium chloride.

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[1] Paper VI on Organosilicon Compounds; for V see Sommer, Goldberg, Dorfman and Whitmore, THIS JOURNAL, **68**, 1083 (1946).

[2] *Cf.* Flood, *ibid.*, **55**, 1735 (1933).

[3] We now use copper lined reactors for all large Grignard reactions.

[4] Ladenburg, *Ann.*, **164**, 325 (1872), first prepared this compound.

The Purification of Thionyl Chloride

BY D. L. COTTLE

This substance is ordinarily purified by treatment with quinoline and linseed oil, a procedure that gives poor yields and difficult-to-handle residues. Pratt[1] modified the method by using a lower aliphatic ketone in place of quinoline and sulfur in place of the linseed oil. The latter procedure has been modified herein as follows: Nine hundred milliliters of crude technical thionyl

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[1] H. R. C. Pratt, British Patent 538,028, July 17, 1941.

chloride was refluxed for four and one-half hours with 25 g. of flowers of sulfur and distilled rapidly through a 30-bulb Snyder column attached to an all-glass setup. A 94% yield of colored product was taken overhead. The distillate was fractionated through the 30-bulb column, about twelve hours being needed to remove the colored forerun. The colorless portion was taken overhead in about two hours and distilled over no range with a thermometer that was graduated in degrees. The yield in the second step was 88% making an 82% over-all yield. The product was colorless when viewed crossways in a liter graduate and very slightly yellow when viewed from the top. The still went to dryness and the residue was yellow with some black material reminiscent of organic matter. No attempts to improve the above procedure were made.

The sulfur probably aids in changing the sulfuryl chloride to sulfur dioxide and sulfur chlorides. The sulfur monochloride, b. p. 135.6°, presumably is left behind in the first distillation and sulfur dichloride, b. p. 69°, is the forerun of the fractionation which gives the colorless thionyl chloride, b. p. 78.8°. It is probably impractical to try removing both sulfur chlorides in one distillation because of the equilibrium between sulfur monochloride on the one hand and sulfur dichloride and sulfur on the other.

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The Molecular Refractions of the Higher Acetylenic Hydrocarbons[1]

BY G. F. HENNION AND T. F. BANIGAN, JR.

It is well known that the calculated molecular refractivities of organic compounds usually do not agree exactly with the observed values given by the Lorenz–Lorentz equation. In the absence of structural complications, *e. g.*, conjugate unsaturation, the agreements are on the whole remarkably good for pure liquids. Notable exceptions to this fact are found among the higher acetylenic hydrocarbons. The treatises of organic chemistry uniformly cite the (D-line) value, 2.398, as the atomic correction factor for the triple bond, even though there is good evidence that this value is not entirely trustworthy. Auwers,[2] among others, called attention to this some years ago after examination of selected literature data. He suggested a triple bond correction of 2.325 for terminal acetylenes, $R—C\equiv CH$, and 2.573 for the non-terminal ones, $R—C\equiv C—R'$. Campbell and Eveslage[3] very recently showed that these values also are not fully reliable and recommended a new set of increments for 1-, 2-, 3-, 4-, and 5-acetylenes, respectively. Actually none of these approaches are accurate. This was brought to our attention recently during a study of di-*t*-butylacetylene.[4] Using the accepted value for the triple bond, 2.398, the calculated and observed refractions were 46.378 and 47.641, respectively, thus showing an apparent exaltation of 1.263 units. Campbell's increment for 3-acetylenes, 2.696, improves the agreement insufficiently. A study has therefore been made of the refractions of twenty purified acetylenes reported in the literature (Table I). In order to obtain exact agreement between the calculated and observed refractions of these compounds, twenty different triple bond increments are needed. They range from 2.219 for 1-pentyne to 3.661 for 2,2,5,5-tetramethyl-3-hexyne (di-*t*-butylacetylene). The required correction increases with alkyl chain lengthening on each side of the triple linkage and with chain branching nearby. The triple bond increment therefore depends upon the number of carbon (?) atoms which come under the influence of the triple linkage and it seems impossible to assign any satisfactory value or values to the triple bond, *per se*.

In order to estimate the expected refractions more closely, an entirely different method of cal-

TABLE I

PHYSICAL CONSTANTS AND MOLECULAR REFRACTIONS OF HIGHER ACETYLENES

Compound	Formula	d^{20}	n^{20}D	*MR*D obsd.	—*MR*D calcd.— Present method	Old method
2-Butyne[a]	C_4H_6	0.6913	1.3921	18.637	18.638	18.670
1-Pentyne[a]	C_5H_8	.6908	1.3852	23.118	23.100	23.288
2-Pentyne[a]	C_5H_8	.7104	1.4039	23.444	23.443	23.288
1-Hexyne[a]	C_6H_{10}	.7156	1.3990	27.766	27.736	27.906
3-Hexyne[b]	C_6H_{10}	.7231	1.4110	28.204	28.248	27.906
3,3-Di-Me-1-butyne[c]	C_6H_{10}	.6686	1.3744	28.083	28.074	27.906
1-Heptyne[a]	C_7H_{12}	.7325	1.4088	32.444	32.336	32.524
5-Me-1-hexyne[a]	C_7H_{12}	.7274	1.4059	32.467	32.336	32.524
1-Octyne[a]	C_8H_{14}	.7460	1.4159	37.060	36.954	37.142
2-Octyne[a]	C_8H_{14}	.7596	1.4278	37.308	37.315	37.142
3-Octyne[a]	C_8H_{14}	.7522	1.4250	37.458	37.502	37.142
4-Octyne[a]	C_8H_{14}	.7509	1.4248	37.508	37.520	37.142
3-Nonyne[d]	C_9H_{16}	.7616	1.4295	42.090	42.120	41.760
3,3-Di-Me-4-heptyne[e]	C_9H_{16}	.7610	1.4360	42.679	42.494	41.760
5-Decyne[b]	$C_{10}H_{18}$	.7688	1.4332	46.746	46.756	46.378
3-Me-3-Et-4-heptyne[e]	$C_{10}H_{18}$	.7714	1.4386	47.104	47.130	46.378
2,2-Di-Me-3-octyne[e]	$C_{10}H_{18}$	.7491	1.4270	47.382	47.112	46.378
2,2,5,5-Tetra-Me-3-hexyne[f]	$C_{10}H_{18}$	.7120	1.4055	47.641	47.468	46.378
5-Undecyne[d]	$C_{11}H_{20}$	.7760	1.4360	51.306	51.374	50.996
3,3-Di-Me-4-nonyne[g]	$C_{11}H_{20}$	.7667	1.4317	51.480	51.748	50.996

[a] Henne and Greenlee, THIS JOURNAL, **67**, 484 (1945). [b] Campbell and Eby, *ibid.*, **63**, 2684 (1941). [c] Egloff, "Physical Constants of Hydrocarbons," Reinhold Publishing Co., New York, N. Y., 1939, Vol. I, p. 367. [d] Campbell and O'Connor, THIS JOURNAL, **61**, 2898 (1939). [e] Campbell and Eby, *ibid.*, **62**, 1800 (1940). [f] Hennion and Banigan, *ibid.*, **68**, 1202 (1946). [g] Eveslage, M.S. Dissertation, University of Notre Dame, 1945.

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[1] Paper I, on the chemistry of the substituted acetylenes; previous paper, THIS JOURNAL, **68**, 1202 (1946).

[2] Auwers, *Ber.*, **68**, 1635 (1935).

[3] Campbell and Eveslage, THIS JOURNAL, **67**, 1851 (1945).

[4] Hennion and Banigan, previous paper, ref. 1.