an ether–acetone mixture, it gave white crystals melting at 58.8–59.0°. However, the crude II was found suitable for conversion to the tribromide (I), which was accomplished by melting the II, adding an excess of phosphorus tribromide, and heating to 140° for forty-eight hours. Purified by three crystallizations from 95% ethanol to remove a complex reddish phosphorus compound, the tribromide melted sharply at 94.3° and analyzed correctly for $C_6H_{11}Br_3$. In the ring closure, following a procedure which was essentially that of Murray and Stevenson,[2] use of the crude tribromide was found satisfactory.

The crude olefin mixture (yield 92% based on pure I) was separated into three fractions boiling at 65, 71 and 80.26° in an approximate ratio of 1:2:5, respectively. The highest boiling olefin (III) was proved to be a very pure individual compound by its time–temperature cooling curve, and its molecular refraction checked closely with that calculated for ethylidenecyclobutane.

Over Raney nickel at room temperature III absorbed one equivalent of hydrogen and gave ethylcyclobutane, b. p. 70.64°, f. p. −143.1°; Wibaut[3] found b. p. 70.7°, f. p. −142.9° for ethylcyclobutane prepared by a different method.

Ozonolysis of III gave acetaldehyde which was identified[4] through its 2,4-dinitrophenylhydrazone, m. p. 156–162° after five recrystallizations. An authentic sample of this derivative also melted at 156–162°, and the mixed melting point was identical; a mixed melting point with the corresponding derivative of formaldehyde showed a 20° depression. A second ozonolysis product, probably cyclobutanone, boiled at about 100° and gave a 2,4-dinitrophenylhydrazone which melted at 140–142°.

The other olefins are believed to be 2-ethyl-1-butene and a mixture of vinylcyclobutane with 3-methyl-2-pentene. An attempt is being made to identify these products, and other reactions of this type will be studied.

[3] Wibaut, *Rec. trav. chim.*, **58**, 329 (1939).

[4] R. C. Arnold, Master's Thesis, The Ohio State University 1945.

DEPARTMENT OF CHEMISTRY
THE OHIO STATE UNIVERSITY
COLUMBUS, OHIO, AND JOHN M. DERFER
AMERICAN PETROLEUM INSTITUTE
RESEARCH PROJECT 45
WAR RESEARCH BUILDING
OHIO STATE UNIVERSITY KENNETH W. GREENLEE
COLUMBUS, OHIO CECIL E. BOORD

RECEIVED AUGUST 31, 1945

THE ADDITION OF PHOSPHORUS TRICHLORIDE TO OLEFINS

Sir:

No satisfactory method is described in the literature for the preparation of phosphorus compounds of the type $RPCl_2$, where R is an aliphatic radical. The method considered most satisfactory is to heat for many hours a mixture of a mercury dialkyl and phosphorus trichloride in a sealed tube at 250°.[1] We have found that if an unsaturated compound is heated with an excess of phosphorus trichloride, in the presence of a small quantity of a diacyl peroxide (diacetyl or dibenzoyl peroxide), addition of the phosphorus trichloride to the double (or triple) bond takes place readily.[2]

$$RCH{=}CH_2 + PCl_3 \xrightarrow{\text{diacetyl peroxide}} RCHClCH_2PCl_2$$

A description of the experimental details of one example of the reaction is cited.

Octene-1 (0.16 mole) and phosphorus trichloride (1.0 mole) were mixed and placed in a two-necked dry flask equipped with a dropping funnel and a reflux condenser. The latter was connected to a tube immersed into mercury. The air in the flask was displaced by nitrogen, and the mixture heated to 85° under pressure (20 cm. of mercury extra pressure). Acetyl peroxide (0.025 mole) dissolved in octene-1 (0.17 mole) was added (in four equal portions) in the course of two hours. When all the peroxide had been added, the heating was continued for two hours longer.

The excess of phosphorus trichloride was removed from the reaction mixture at atmospheric pressure, and the octene-1, at reduced pressure. The residue was transferred to a small Claisen flask and twice distilled at reduced pressure. A colorless distillate, b. p. 85–88° (0.5 mm.), was collected (13 g.). The high boiling residue weighed about two grams.

Anal. Calcd. for $C_8H_{16}Cl_3P$: Cl, 42.6. Found: Cl, 41.1.

The reaction cited is assumed to proceed *via* a free-radical chain reaction initiated by the free radicals formed by the decomposition of the diacyl peroxide.

$$(CH_3COO{-})_2 \longrightarrow CH_3\cdot + CO_2 + CH_3COO\cdot \quad (1)$$

$$CH_3\cdot + PCl_3 \longrightarrow CH_3Cl + \cdot PCl_2 \quad (2)$$

$$RCH{=}CH_2 + \cdot PCl_2 \longrightarrow R\underset{\cdot}{C}HCH_2PCl_2 \quad (3)$$

$$R\underset{\cdot}{C}HCH_2PCl_2 + PCl_3 \longrightarrow RCHClCH_2PCl_2 + \cdot PCl_2 \quad (4)$$

$$R\underset{\cdot}{C}HCH_2PCl_2 + RCH{=}CH_2 \longrightarrow R\underset{\cdot}{C}HCH_2CHRCH_2PCl_2 \quad (5)$$

$$R\underset{\cdot}{C}HCH_2CHRCH_2PCl_2 + PCl_3 \longrightarrow RCHClCH_2CHRCH_2PCl_2 + \cdot PCl_2 \quad (6)$$

Whether reactions (5) and (6) are responsible for the formation of the high boiling residue, or the condensation of the compound $RCHClCH_2PCl_2$ in a manner similar to that indicated in (3) and (4) has not as yet been determined.[3]

For effective propagation of the chain reaction (3 and 4), the radical R must be aliphatic, and the carbon atom to which it is attached must

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[1] Guichard, *Ber.*, **32**, 1572 (1899); Michaelis, *ibid.*, **13**, 2174 (1880).

[2] The addition of phosphorus trichloride to acetylene compounds will be reported shortly.

[3] The diacyl peroxide catalyzed condensation of compounds of the type $RPCl_3$ with olefins is under way.

have as the second substituent a hydrogen atom. The basis for this statement, as well as the basis for the structure assigned to the free radical formed in step 3, will be presented in our next publication dealing with this interesting reaction.

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M. S. KHARASCH
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RECEIVED SEPTEMBER 14, 1945

CHROMATOGRAPHY OF CARBOHYDRATES AND SOME RELATED COMPOUNDS

Sir:

We wish to report that we have developed a method for the chromatography of the carbohydrates and related polyhydroxy compounds. Columns of adsorptive clays were used as adsorbents; an example is a Florida clay sold by the Floridin Co. of Warren, Pennsylvania, under the name Florex XXX. As developer we have used various low molecular weight hydrophilic solvents such as the alcohols, hydroxylic ethers, ether, dioxane, ketones, acids, pyridine, and water, either singly or in admixture.

Streak reagents that have been used on the extruded columns to detect the zones are alkaline permanganate, 2,6-dichlorophenolindophenol and acid-base indicators. Water was the eluting agent.

By the use of this method we have arranged a large number of the members of this class of compounds in an adsorption series. This chromatographic sequence shows the position each compound occupies on the adsorption column in relation to the other members. We have included in this series three pentoses, nine hexoses, two heptoses, six disaccharides, two trisaccharides, one tetrasaccharide, two other oligosaccharides, four glycosides, twenty polyhydric alcohols, seven polyhydric alcohol inner ethers, and ten acids, lactones or salts. Several positions in the sequence are occupied by more than one compound with the degree of resolution currently in use.

As examples of the applicability of this method the following are given. On chromatographing a mixture containing equal amounts of sorbitol and D-glucose, the separated D-glucose zone showed the presence of 100% of the added sugar by a reducing sugar determination, and the sorbitol zone showed 99.7% of the sorbitol by periodic acid oxidation. The sorbitol zone gave a negative reaction toward Fehling solution. A mixture containing 98% sorbitol and 2% D-mannitol was chromatographed to exhibit the presence of two zones. A mixture of equal amounts of D-mannitol and dulcitol was chromatographed and each component eluted and crystallized. The first crop of D-mannitol gave a recovery of 90% with m. p. 166–167°; a second crop gave a further 6% with the same melting point. The accepted value for the m. p. of D-mannitol is 166°. The first crop of dulcitol gave 95% recovery with m. p. 187–188° (accepted value 188°). A mixture, in disproportionate amounts, of 1,4:3,6-dianhydrosorbitol, 1,4:3,6-dianhydro-D-mannitol, and 1,4:3,6-dianhydro-L-iditol was chromatographed to show three zones. The rate of lactonization and delactonization of D-gluconic acid was followed qualitatively since the acid and the lactones occupied different positions on the column. Lemon juice was chromatographed and the ascorbic acid content was concentrated into a zone detectable by 2,6-dichlorophenolindophenol.

Work is being continued on this method and details will be communicated at a later date.

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RECEIVED SEPTEMBER 19, 1945

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THE CONFIGURATION OF THE PYRANOSE RINGS IN POLYSACCHARIDES

Sir:

If one accepts the assumption that the C–C and C–O bond angles and distances occurring in polysaccharides are those found in simple molecules, then two *trans* configurations are possible for a pyranose ring. The important difference between these two *trans* configurations is the angle which the C_1- and C_4-to-glycosidic-oxygen bond makes with the "plane" of the pyranose ring.

In the present discussion we are concerned only with those polysaccharides in which the glycosidic oxygens are *trans* to one another. This includes polymers of β-glucose (cellulose), β-mannuronic acid (alginic acid) and α-galacturonic acid (pectic acid). With this restriction it follows, then, that in one *trans* configuration of the pyranose ring (I) the two carbon-glycosidic bonds make an angle of about 20° with the "plane" of the pyranose ring. In the other *trans* configuration (II) this angle is about 90°. This difference in angle results in a difference in the fiber identity period when units of the same configuration are joined together to make a long chain. A chain made with I has a projection per pyranose unit in the direction of the fiber axis equal to 5.15 Å., while the projection for a chain made from II is 4.37 Å.

It is now generally accepted that the pyranose rings in cellulose are I.[1] Recent X-ray studies on fibers of sodium pectate[2] and alginic acid[3]

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[1] Astbury and Davies, *Nature*, **154**, 84 (1944); Cox, *ibid.*, **154**, 84 (1944).

[2] Palmer and Lotzkar, THIS JOURNAL, **67**, 883 (1945); Palmer and Hartzog, *ibid.*, in press.

[3] Astbury, *Nature*, **155**, 667 (1945). We wish to express our thanks to Dr. Astbury for kindly sending us a copy of this paper before publication.