iodine. It was probably phenylmercuric iodide and may have resulted from the action of metallic mercury on the iodobenzene which was present.

There was no evidence of reaction when ethyl benzoate and triphenylindium were refluxed in xylene solution for twenty-four hours. Of the ethyl benzoate used, 99% was recovered as benzoic acid.

Triphenylindium did not react with benzonitrile when a xylene solution of the two compounds was refluxed for twenty-four hours.

Acknowledgment.—The authors are grateful to Margaret M. Burkey for assistance.

Summary

An examination has been made of a series of reactions of triphenylindium. The order of decreasing activity of the triphenyl derivatives of gallium, indium and thallium is: R_3In, R_3Ga, R_3Tl. Attention is directed to correlations of ionization potentials of metals with the relative reactivities of corresponding organometallic compounds toward functional groups like carbonyl.

AMES, IOWA RECEIVED JULY 15, 1940

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Phenylthallium[1]

BY HENRY GILMAN AND R. G. JONES

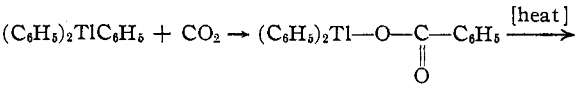
This paper presents, among other things, evidence for the transitory formation and the reactions of a new type of organometallic "radical" or compound, phenylthallium.

High Temperature Carbonation of Triphenylthallium.—As mentioned in the preceding paper,[2a] triphenylthallium is less reactive than triphenylgallium and triphenylindium. The passage of carbon dioxide through a benzene solution of triphenylthallium for a long period gave no benzoic acid.[2b] However, when carbon dioxide was added to a refluxing xylene solution of triphenylthallium there resulted a 70% yield of benzoic acid and a 73% yield of biphenyl. This suggests the following reactions:

$$(C_6H_5)_3Tl \xrightarrow{[heat]} C_6H_5Tl + C_6H_5{\cdot}C_6H_5 \qquad [I]$$

$$C_6H_5Tl + CO_2 \xrightarrow{[HOH]} C_6H_5CO_2H \qquad [II]$$

An alternative sequence of reactions makes unnecessary the postulate of the intermediate phenylthallium, and involves carbonation of one of the phenyl–thallium bonds in triphenylthallium



$$(C_6H_5)_2TlC_6H_5 + CO_2 \rightarrow (C_6H_5)_2Tl{-}O{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}C_6H_5 \xrightarrow{[heat]} C_6H_5{\cdot}C_6H_5 + C_6H_5COOTl \qquad [III]$$

$$C_6H_5COOTl \xrightarrow{[HOH]} C_6H_5CO_2H \qquad [IV]$$

Although reaction [III] has some plausibility because of the known distinctly higher reactivity of one of the phenyl groups in triphenylthallium, it was shown experimentally to be invalid. An authentic sample of the diphenylthallium benzoate postulated in reaction [III] was refluxed in xylene in an atmosphere of carbon dioxide, but no benzoic acid or biphenyl was formed, and the diphenylthallium benzoate was recovered practically quantitatively.

As supplementary support for reaction [I], pyrolysis of triphenylthallium in xylene gave metallic thallium and biphenyl. Indirect evidence is presented later for the thermal conversion of phenylthallium to thallium and biphenyl.

Reactions with Benzophenone and Benzonitrile.—There was no reaction between triphenylthallium and benzophenone in benzene.[2b] However, at the more elevated temperature provided by boiling xylene, reaction took place and triphenylcarbinol and biphenyl were formed. These products are consistent with the pyrolysis of triphenylthallium to biphenyl and phenylthallium, and the reaction of the latter *in situ* with benzophenone: $C_6H_5Tl + (C_6H_5)_2C{=}O \longrightarrow (C_6H_5)_3COH$. Under corresponding conditions, triphenylthallium and benzonitrile gave thallium, the trimer of benzonitrile, benzophenone and biphenyl: $C_6H_5Tl + C_6H_5CN \longrightarrow (C_6H_5)_2C{=}O$.

Ethyl Benzoate.—In the Entemann–Johnson[3] series of relative reactivities of functional groups with phenylmagnesium bromide, ethyl benzoate is more reactive than benzonitrile. However, we have observed that under conditions where triphenylthallium reacted with benzonitrile, there

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[1] This is paper XXXIII in the series "Relative Reactivities of Organometallic Compounds." The preceding paper is in THIS JOURNAL, **62**, 2353 (1940).

[2] (a) Gilman and Jones, *ibid.*, **62**, 2353 (1940); (b) Gilman and Jones, *ibid.*, **61**, 1513 (1939).

[3] Entemann and Johnson, *ibid.*, **55**, 2900 (1933).

was an essentially quantitative recovery of ethyl benzoate. This somewhat anomalous result finds its counterpart with other RM compounds like those of lithium, zinc and cadmium. That is, the series of relative reactivities of functional groups with phenylmagnesium bromide is not rigorously applicable to other organometallic compounds which may be more or may be less reactive than Grignard reagents.

Thallous Chloride and Phenyllithium.—The preceding evidence having indicated that triphenylthallium is pyrolyzed to biphenyl and phenylthallium, and that phenylthallium is of a relatively high order of reactivity but also thermally unstable, experiments were carried out to prepare phenylthallium at low temperatures from thallous chloride and phenyllithium. Even at −70° there was an immediate deposition of metallic thallium, and this indicates that phenylthallium is formed first and then disproportionates to give thallium and triphenylthallium, in accordance with the reactions

$$C_6H_5Li + TlCl \longrightarrow C_6H_5Tl + LiCl \qquad \text{[V]}$$

$$3C_6H_5Tl \longrightarrow (C_6H_5)_3Tl + 2Tl \qquad \text{[VI]}$$

The isolation of some biphenyl indicates that a part of the thallium may owe its formation to the reaction

$$2C_6H_5Tl \longrightarrow C_6H_5{\cdot}C_6H_5 + 2Tl$$

although it is more probable that some of the biphenyl came from a Wurtz reaction incidental to the formation of phenyllithium from bromobenzene and lithium, and some of it from a coupling reaction like

$$2C_6H_5Li + 2TlCl \longrightarrow C_6H_5{\cdot}C_6H_5 + 2LiCl + 2Tl$$

The concept of RTl compounds has been used by earlier workers. Hein and Segitz[4] observed a rapid darkening of the electrolyte and a fall in electrical resistance in the electrolysis of a solution of ethylsodium in diethylzinc using a thallium electrode. They suggested that the first reaction was the formation of ethylthallium which then disproportionated to triethylthallium and the free metal

$$3C_2H_5Tl \longrightarrow (C_2H_5)_3Tl + 2Tl$$

the finely divided metal accounting for the darkening of the solution and the lowering of resistance. Menzies and Cope[5] examined the reaction of ethylmagnesium bromide with thallous chloride and thallous ethoxide. Ethylthallium may have been formed initially and their results can be formulated as follows

$$3C_2H_5MgBr + 3TlCl \longrightarrow (C_2H_5)_3Tl + 2Tl + 3MgBrCl$$

Birch[6] treated thallous chloride with phenyllithium and obtained thallium and triphenylthallium which he suggested were probably formed by way of the mono-aryl compound, in accordance with reactions [V] and [VI].

Organometallic radicals of mercury, germanium, tin, lead and chromium have been described.[7] The tendency of such radicals is to be converted thermally to organometallic compounds with the metal in a higher valence state. An interesting illustration is the stepwise transformation of organolead compounds

$$PbCl_2 + 2RMgX \longrightarrow R_2Pb + 2MgXCl$$

$$3R_2Pb \xrightarrow{[heat]} 2R_3Pb + Pb$$

$$4R_3Pb \xrightarrow{[heat]} 3R_4Pb + Pb$$

It is probable that phenylthallium may go stepwise to triphenylthallium *via* diphenylthallium. We have shown that when diphenylthallium bromide is treated in liquid ammonia with one equivalent of sodium, triphenylthallium and thallium metal are formed, perhaps in essential accordance with the following reactions:

$$(C_6H_5)_2TlBr + Na \longrightarrow (C_6H_5)_2Tl + NaBr$$

$$3(C_6H_5)_2Tl \longrightarrow 2(C_6H_5)_3Tl + Tl$$

The several known organometallic radicals are more thermally stable than phenylthallium, and also decidedly less reactive with an organic functional group like carbonyl. This general correlation between thermal instability and reactivity of the organometallic radicals finds a parallel in the greater tendency of the more reactive unsymmetrical organometallic compounds to disproportionate to the symmetrical compounds. That is, a compound like $RR'Zn$ rearranges to R_2Zn and R'_2Zn more rapidly than $RR'Hg$ disproportionates to R_2Hg and R'_2Hg.

Inasmuch as alkylmetallic radicals are less stable than arylmetallic radicals having the same metal, it is probable that a radical like ethylthallium will be found to be less stable than phenylthallium. Also, it is probable that the radicals phenylgallium and phenylindium will be found to be much less stable than the related phenylthallium because thallium has a greater tendency to

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(4) Hein and Segitz, *Z. anorg. allgem. Chem.*, **158**, 162 (1927).

(5) Menzies and Cope, *J. Chem. Soc.*, 2862 (1932).

(6) Birch, *ibid.*, 1132 (1934).

(7) Gilman, "Organic Chemistry," John Wiley and Sons, New York, N. Y., 1938, pp. 478–481.

form univalent compounds than do gallium and indium.

Relative Reactivities.—On the basis of the chemical behavior of triphenylgallium, triphenylindium, triphenylthallium and phenylthallium, the order of decreasing reactivity of these RM compounds is: RTl, R_3In, R_3Ga, R_3Tl. Although phenylthallium is most reactive in this series, it is less reactive than a Grignard reagent like phenylmagnesium bromide.

Metal–Metal Interconversion.—Triphenylthallium and *n*-butyllithium underwent a prompt metal–metal interconversion of the general kind described recently with triarylbismuth compounds[8]

$$(C_6H_5)_3Tl + 3n\text{-}C_4H_9Li \longrightarrow 3C_6H_5Li + (n\text{-}C_4H_9)_3Tl$$

Diphenylthallium Bromide and Benzoyl Chloride.—Apropos the relatively great inertness of the two R groups in an R_2TlX compound, we have shown that no appreciable quantity of benzophenone was formed after refluxing diphenylthallium bromide with benzoyl chloride in benzene or toluene. Triphenylthallium and all RM compounds of Group III metals react with benzoyl chloride. Actually, the reaction of organoaluminum compounds with acid halides and acid anhydrides is one of the better ways for the preparation of ketones.

Experimental Part

Triphenylthallium.—Triphenylthallium, prepared from diphenylthallium bromide and phenyllithium,[2b,6] was recrystallized by dissolving in warm benzene, filtered under nitrogen, precipitated by the addition of an equal volume of petroleum ether (b. p. 65–68°), and finally washed with petroleum ether and dried under nitrogen. The compound melted under nitrogen to a clear, colorless liquid at 169–170° (with softening at 167°), and then decomposed with blackening at 180–185°. After exposure to the air for a few minutes the material melted considerably higher (see preceding paper for a related phenomenon with triphenylindium).

Anal. Calcd. for $C_{18}H_{15}Tl$: Tl, 46.95. Found: Tl, 46.86.

Pyrolysis.—A solution of 1.46 g. (0.0033 mole) of triphenylthallium in 25 cc. of xylene was refluxed under nitrogen for twenty-four hours. The black coating of metallic thallium which appeared on the walls of the flask was removed by amalgamation with mercury. The amalgam was treated with dilute sulfuric acid and the aqueous solution yielded 0.46 g. or 41% of thallous iodide subsequent to treatment with potassium iodide solution. The xylene solution was distilled, and from the residue was obtained 0.12 g. or 15.8% of biphenyl calculated on the basis of the following reaction: $2(C_6H_5)_3Tl \longrightarrow 3C_6H_5{\cdot}C_6H_5 + 2Tl$. All solid products were identified by the method of mixed melting points.

Carbonation.—A solution of 2.68 g. (0.0061 mole) of triphenylthallium in 25 cc. of xylene was refluxed for twenty-four hours during which time a slow stream of dry carbon dioxide was admitted over the surface of the boiling solution. Subsequent to cooling and hydrolysis by hydrochloric acid and extraction with sodium hydroxide solution, there was isolated from the aqueous layer 0.52 g. or 70% of benzoic acid, and 0.70 g. or 73% of biphenyl from the xylene layer. There was no evidence of the formation of metallic thallium. In a check experiment, the yield of benzoic acid was 74% and the yield of biphenyl 86%.

Reaction with Benzophenone.—A solution of 2.54 g. (0.0139 mole) of benzophenone and 2.03 g. (0.0046 mole) of triphenylthallium in 25 cc. of xylene was refluxed for twenty-four hours. The mixture was hydrolyzed by shaking with 20 cc. of 2 *N* hydrochloric acid, and the precipitate was filtered and washed with ether. The non-aqueous layer was distilled until a small quantity of brown oil remained, and the last of the xylene was removed in a current of air. Treatment of the residue with hydroxylamine yielded benzophenone oxime equivalent to 76% of the initial benzophenone. From the water-insoluble residue not reacted on by hydroxylamine was isolated (subsequent to drying and sublimation), 0.08 g. or 7.6% of biphenyl. The non-volatile portion yielded 0.05 g. of triphenylcarbinol or a 4.2% yield subsequent to purification from ethanol.

Reaction with Benzonitrile.—A solution of 2.0 g. (0.0192 mole) of freshly distilled benzonitrile and 2.80 g. (0.00643 mole) of triphenylthallium in 25 cc. of xylene was refluxed under nitrogen for twenty-four hours. A heavy black mirror of metallic thallium appeared on the walls of the flask.

After removing the xylene by distillation, and the unreacted benzonitrile by heating with alcoholic sodium hydroxide, the alcoholic solution was diluted with a large volume of water and the resulting solution extracted with ether. From the ether extract was obtained 0.025 g. of the trimer of benzonitrile (melting and mixed melting point, 229–230°). The residue of the ether extraction yielded, subsequent to treatment with hydroxylamine, 0.10 g. or 7.8% of benzophenone oxime, and then 0.14 g. or 9.6% of biphenyl by sublimation.

Reaction with Ethyl Benzoate.—A solution of 1.71 g. (0.0114 mole) of ethyl benzoate and 1.66 g. (0.0038 mole) of triphenylthallium in 25 cc. of xylene was refluxed for twenty-four hours. The black precipitate of metallic thallium dissolved incidental to hydrolysis by 20 cc. of 3 *N* sulfuric acid. A sodium alcoholate treatment of the xylene solution yielded 1.37 g. of benzoic acid which is equivalent to 98.5% of the initial ethyl benzoate. Essentially the same results were obtained in a duplicate experiment which also yielded 38% of biphenyl.

Diphenylthallium Benzoate.—A mixture of 1.90 g. (0.0043 mole) of triphenylthallium and 1.00 g. (0.0095 mole) of benzoic acid in 65 cc. of benzene was heated to boiling for five minutes and then filtered. Upon cooling the filtrate there deposited 2.02 g. or a 98% yield of

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[8] Gilman, Yablunky and Svigoon, This Journal, **61**, 1170 (1939).

crystalline diphenylthallium benzoate which melted, after crystallization from benzene, at 259–260° with decomposition.

Anal. Calcd. for $C_{19}H_{15}O_2Tl$: Tl, 42.63. Found: Tl, 42.33.

A partial suspension of 1.78 g. (0.0037 mole) of diphenylthallium benzoate in 25 cc. of xylene was refluxed for twenty-four hours in an atmosphere of carbon dioxide. The yield of recovered diphenylthallium benzoate was 1.73 g. or 96%. No trace of biphenyl was found in the xylene solution. The experiment was repeated with the same results.

Thallous Chloride and Phenyllithium.—To a rapidly stirred suspension of 15.2 g. (0.063 mole) of thallous chloride in 50 cc. of ether, cooled to −14 to −17°, was added slowly over a twenty-minute period an ether solution of phenyllithium prepared from 8.0 g. (0.051 mole) of bromobenzene and one gram of lithium. The reaction was carried out in an atmosphere of nitrogen. A finely divided black precipitate formed immediately, and the white thallous chloride disappeared as the phenyllithium solution was added. The mixture was stirred rapidly for an additional thirty minutes at −15° and then allowed to warm up to room temperature. The black precipitate was filtered and then washed with 25 cc. of warm benzene. From the combined ether and benzene solutions was obtained 1.41 g. or 17% of diphenylthallium chloride subsequent to hydrolysis. The source of the diphenylthallium chloride must have been triphenylthallium, which on hydrolysis in the presence of chloride ion gave diphenylthallium chloride. The latter was identified by conversion to the acetate. The ether–benzene solution was dried and distilled to yield 2.95 g. or 75% of pure biphenyl. The black solid from the reaction was shown to be metallic thallium, and the thallous iodide obtained from it weighed 14.00 g. or 67%.

The experiment was repeated but at a temperature of −70° (acetone and solid carbon dioxide bath). Here again black metallic thallium appeared immediately. The yield of diphenylthallium chloride was 1.85 g. or 22%.

Diphenylthallium Bromide and Benzoyl Chloride.—A suspension of 2.20 g. (0.005 mole) of diphenylthallium bromide in 20 cc. of dry benzene was treated with 1.40 g. (0.010 mole) of benzoyl chloride. The mixture was refluxed for thirteen hours and then allowed to stand at room temperature for four days. Concentrated ammonium hydroxide containing ammonium chloride was added, and the mixture (after standing several days) was filtered. From the dried benzene layer was obtained a trace of a brown oil from which could be obtained no benzophenone oxime subsequent to treatment with hydroxylamine.

In another experiment the reactants in 25 cc. of toluene were refluxed for sixteen hours. The quantity of benzoic acid recovered was equivalent to 87% of the initial benzoyl chloride.

Diphenylthallium Bromide and Sodium in Liquid Ammonia.—To the clear solution of 4.38 g. (0.01 mole) of diphenylthallium bromide in 200 cc. of liquid ammonia was added, with stirring, 0.23 g. (0.010 g. atom) of sodium in very small pieces. A finely divided black precipitate appeared as each piece of sodium was added. The ammonia was allowed to evaporate, and the residue was extracted with 50 cc. of warm benzene. From the filtered solution, subsequent to treatment with a benzene solution of benzoic acid, was isolated 1.0 g. or 31.5% of diphenylthallium benzoate. One of the better ways of characterizing triphenylthallium is to convert it by benzoic acid to the more stable and well crystallized diphenylthallium benzoate. No biphenyl was obtained.

The benzene-insoluble part of the reaction product was washed with water, filtered, and the filtrate treated with silver nitrate to yield 1.20 g. or 64% of silver bromide. The remaining solid was treated with dilute sulfuric acid, and the resulting solution yielded 1.06 g. or 96% of thallous iodide after adding potassium iodide solution. About one gram of product remained unidentified. The yields are based on the reactions

$$3(C_6H_5)_2TlBr + 3Na \longrightarrow 2(C_6H_5)_3Tl + Tl + 3NaBr$$

$$(C_6H_5)_3Tl + C_6H_5CO_2H \longrightarrow (C_6H_5)_2TlOCOC_6H_5 + C_6H_6$$

Triphenylthallium and *n*-Butyllithium.—A solution of *n*-butyllithium prepared from 8.25 g. (0.060 mole) of *n*-butyl bromide and one g. of lithium in 50 cc. of ether was added rapidly to a solution of 3.30 g. (0.0075 mole) of triphenylthallium in 25 cc. of ether. The mixture was stirred rapidly for ten minutes at room temperature, and then carbonated by pouring upon a mixture of solid carbon dioxide and ether. The yield of pure benzoic acid was 1.80 g. or 66%.

Ethylmagnesium Bromide and Silver Bromide.—The ease with which R_3Tl compounds undergo thermolysis suggests their use as a convenient, low temperature source of free radicals. There is, however, some question as to the mechanism of thermal decomposition of triphenylthallium in xylene solution. It is not known whether phenyl groups are liberated as radicals here, for in numerous cases where free radicals are formed in solution it has been well established that the radicals react immediately with the solvent and do not react with each other to give coupling products.[9] In this manner free phenyl radicals in xylene might be expected to give dimethylbiphenyl rather than biphenyl, and in a non-aromatic solvent like ether to give benzene and not biphenyl. It may be significant that in all reactions examined by us in the triphenylthallium–xylene studies, with the exception of the carbonation reaction, small quantities of unidentified tarry materials in addition to biphenyl were obtained. No search was made for benzene.

The thermal decomposition of RAg compounds in the presence of ether or other solvents gives almost exclusively coupling products with no indication of the solvent participating.[10] This and other evidence has led Bickley and Gardner[11] to postulate a bimolecular reaction in the thermolysis of organosilver compounds. Incidental to the study of some new types of RM compounds we have observed that the action of phenyllithium or phenylmagnesium bromide on zirconium tetrachloride etherate in ether gave significant yields (50%) of biphenyl. On the

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(9) Hey and Waters, *Chem. Rev.*, **21**, 169 (1937).

(10) Gilman and Kirby, *Rec. trav. chim.*, **48**, 155 (1929); Gardner and Borgstrom, THIS JOURNAL, **51**, 3375 (1929); Gardner, Joseph and Gollub, *ibid.*, **59**, 2583 (1937); Gardner and Joseph, *ibid.*, **61**, 2551 (1939); Joseph and Gardner, *J. Org. Chem.*, **5**, 61 (1940).

(11) Bickley and Gardner, *ibid.*, **5**, 126 (1940).

other hand, methyllithium gave a product with zirconium tetrachloride in ether at low temperature which decomposed at room temperature to give not ethane, but exclusively methane. In like manner, the product from the reaction of ethylmagnesium bromide on zirconium tetrachloride underwent thermal decomposition to give ethane exclusively, and no butane. In short, the aryl compound gave, in the zirconium tetrachloride studies, an RR product whereas the alkyl compounds gave RH products. This suggested an examination of the thermolysis of ethylsilver prepared from ethylmagnesium bromide and silver bromide in ether. The chief hydrocarbon obtained was butane.

A suspension of 20.0 g. (0.106 mole) of dry silver bromide (freshly prepared from silver nitrate and sodium bromide) in 25 cc. of dry ether was cooled in an ice-bath and stirred rapidly while 65 cc. of a 1.54 *M* solution of ethylmagnesium bromide in ether was added dropwise over a twenty-five minute period. After all the Grignard solution had been added the ice-bath was removed but stirring was continued. Within several minutes a vigorous evolution of gas took place and sufficient heat was evolved to boil the ether. The gas was collected over water and analyzed by absorption and combustion methods. The yield of butane was 42% and the yield of ethylene was 4.7%. From a duplicate experiment the yield of butane was 48% and the yield of ethylene 3.5%. The formation of olefins from reactions of silver halides and alkylmagnesium halides has apparently not been reported hitherto. The weight of metallic silver was 11.0 g. or 95% of the silver in the original silver bromide.

These results indicate that the thermal decomposition of organometallic compounds in the presence of a solvent is not a simple reaction, and may or may not involve free radicals.

Summary

Evidence is presented for the formation of phenylthallium by pyrolysis of triphenylthallium in xylene. This thermally unstable organometallic "radical" is readily converted to triphenylthallium and metallic thallium, probably by way of diphenylthallium

$$C_6H_5Tl \longrightarrow Tl + (C_6H_5)_2Tl \longrightarrow Tl + (C_6H_5)_3Tl$$

When triphenylthallium is pyrolyzed in the presence of organic functional groups, the phenylthallium formed shows reactions of a typical moderately reactive organometallic compound.

The order of decreasing reactivity of some phenyl-metallic compounds is: RMgX, RTl, R_3In, R_3Ga, R_3Tl.

AMES, IOWA RECEIVED JULY 15, 1940

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE NEW YORK STATE COLLEGE OF FORESTRY AND SYRACUSE UNIVERSITY]

The Chemistry of Wood. VII. The Esters and Ethers of the Water Soluble Polysaccharides of Larch Wood[1]

BY F. C. PETERSON, A. J. BARRY, H. UNKAUF AND L. E. WISE[1]

The so-called ϵ-galactan isolated by means of water extraction from western larch wood[2] was later shown to be an arabo-galactan.[3] Very similar polysaccharides were also obtained from Eastern, European[4,5] and Siberian larches.[6] Investigators at Syracuse[3,4,5,7] noted that on hydrolysis these substances gave arabinose and galactose in an approximate ratio of 1 mole to 6 moles. It was assumed, with reservations, that these substances were homogeneous polysaccharides with the empirical formula $[(C_5H_8O_4)(C_6H_{10}O_5)_6]_n$. Although Wise and Unkauf found that the fractions obtained by the gradual addition of alcohol to a water solution of the polysaccharide appeared to be identical, the possibility remained that at the instant of precipitation the concentration of alcohol in the localized region of addition might be high. An aliquot of the polysaccharide might thus be precipitated instead of a less soluble fraction. Derivatives of the water-soluble polysaccharide fraction from three species of larch wood (Western, Eastern, and European) have now been prepared and studied by methods of fractionation in an effort to establish their homogeneity or non-homogeneity and thus that of the original polysaccharide preparations.

Preparation of Arabo-galactan.—The cold water extract prepared as formerly[3] was concentrated at 65° (40 mm.) to a sirup, containing about 9.3% solids, corresponding to a refractive index of about 1.3470. After an electrodialysis[5] to remove inorganic matter, the concentrate was poured into 10 volumes of 95% ethyl alcohol and the resulting precipitate was washed twice by decantation with alcohol. As the preparations reacted poorly with

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(1) Presented before the Division of Sugar Chemistry at the Baltimore meeting of the American Chemical Society, April 3–7, 1939. Paper VI, ref. 5.

(2) Schorger and Smith, *Ind. Eng. Chem.*, **8**, 494 (1916).

(3) Wise and Peterson, *ibid.*, **22**, 362 (1930).

(4) Wise, Hamer and Peterson, *ibid.*, **25**, 184 (1933).

(5) Peterson, Maughan and Wise, *Cellulosechem.*, **15**, 109 (1934).

(6) Nikitin and Soloviev, *J. Applied Chem.* (U. S. S. R.), **8**, 1016 (1935).

(7) Wise and Unkauf, *Cellulosechem.*, **14**, 20 (1933).