SOME TRI-*p*-TOLYLMETHANE DERIVATIVES.

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Received August 6, 1904.

Two tritolylmethanes are mentioned in the literature. Rosenstiehl and Gerber[1] obtained, by the reduction of a rosaniline dye of the composition $C_{22}H_{25}N_3O$, a crystalline compound melting at 73° C., which they describe as tri-*m*-tolylmethane. Later Elbs and Wittich[2] found that the condensation of chloropicrin, CCl_3NO_2, with toluene, by means of aluminium chloride, does not proceed as smoothly as that with benzene. They have, however, obtained, by the fractional distillation of the resulting mixture, a body which boiled above 360° and remained viscous at —10°, and which they consider as tritolylmethane, or a mixture of such isomers. The position of the three methyl groups has not been determined by them. Gomberg and Vödisch[3] showed that carbontetrachloride, analogously to chloroform, does not condense with toluene as readily as it does with benzene. While the yield of triphenylchlormethane is 90 to 95 per cent. of the theoretical amount, in the case of the tritolyl compound it is at best 20 to 30 per cent. We have now definitely established the constitution of this body as a *p*-tritolyl derivative and, with the chloride as a starting-point, we have also studied some other derivatives of tri-*p*-tolylmethane.

Tri-p-tolylchlormethane.—To a mixture of 350 cc. carbontetrachloride, 700 cc. toluene and 1000 cc. carbon disulphide, 350 grams of aluminium chloride were added in small amounts, the addition extending over two or three days. When the reaction, which proceeded at room temperature, had ceased the mixture was poured into ice-water to break up the compound with aluminium chloride. The carbon disulphide solution was then saturated with dry hydrochloric acid gas in order to convert any tritolylcarbinol formed back into the chloride, and dried over calcium chloride. On distilling off the carbon disulphide, tritolylchlormethane separated in yellow crystals. The crystals were filtered off by means of suction and washed with petroleum ether. One hundred and fifty grams of the recrystallized product were obtained, which represents a yield of 32.8 per cent. of the calculated amount. The condensation of carbontetrachloride with toluene at higher

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[1] *Ann. chim. phys.* [6], **2**, 353, 368 (1884).

[2] *Ber. d. chem. Ges.*, **18**, 347 (1885).

[3] This Journal, **23**, 177 (1901).

than ordinary room temperature gives much smaller yields of the tritolylchlormethane. Attempts to substitute ferric chloride in place of aluminium chloride gave unsatisfactory results. The chloride dissolves readily in benzene, ether and carbon disulphide, and may be recrystallized from cold acetic ether or petroleum ether, in which it is but slightly soluble. It melts usually at 165° to 168°, but when perfectly pure it shows a melting-point of 173°. An estimation gave 10.99 per cent. of chlorine; calculated, 11.06 per cent.

The molecular weight was determined by the freezing-point method in benzene. 0.5601 gram substance in 18.461 grams benzene gave a depression $\Delta = 0.500°$. This corresponds to a molecular weight of 303.5; calculated, 320.5.

Synthesis by Means of Grignard's Reaction.—The constitution of the above chloride as a *p*-tritolyl-compound, follows from the synthesis of the identical compound from *p*-tolyliodide and *p*-toluic ethylester, by means of Grignard's reaction. *p*-Tolyliodide and *p*-toluic acid were both prepared from pure *p*-toluidine. The *p*-toluic acid was converted into *p*-toluic ethylester by heating with alcohol and sulphuric acid.[1] Fifty grams of the *p*-tolyliodide, 4.8 grams magnesium and 60 grams absolute ether were heated on the water-bath until the magnesium had gone into solution. To this solution of the *p*-tolylmagnesiumiodide compound 18 grams *p*-toluic ethylester, in an equal amount of absolute ether, were then gradually added through a dropping funnel and the mixture heated two hours on the water-bath. Ice-water was then added to decompose the magnesium compound, and the ether and excess of *p*-tolyliodide were driven off by distillation with steam. The carbinol remained in the distillation flask as a dark viscous mass which refused to crystallize. It was dissolved in ether, the solution dried over calcium chloride and saturated with dry hydrochloric acid gas, in order to change the carbinol into *p*-tritolylchlormethane. On concentrating the solution the chloride separated in almost colorless crystals, melting at 164°. To estimate the chlorine, the substance was dissolved in warm, concentrated sulphuric acid, and the escaping hydrochloric acid fumes were led into a solution of silver nitrate and weighed as silver chloride.[2] This gave 11.4 per cent. chlorine; calculated, 11.06 per cent.

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[1] *Ann. Chem.* (Liebig), **63**, 295.

[2] *Ber. d. chem. Ges.*, **35**, 2400 (1902).

The product was found to be identical in every respect with that obtained by the Friedel-Crafts reaction from carbontetrachloride and toluene.

Tri-p-tolylcarbinol, $(CH_3C_6H_4)_3COH$.—The carbinol was prepared from the chloride by dissolving the latter in a mixture of equal parts of sulphuric and acetic acids, and gently heating the mixture on the water-bath in order to drive off the hydrochloric acid. On the addition of ice-water the tri-*p*-tolylcarbinol was precipitated in coarse crystals. They were purified by recrystallization from petroleum ether. The carbinol is soluble in ether, alcohol, benzene and carbon disulphide, but only slightly soluble in petroleum ether, from which it crystallized in large, colorless crystals, melting at 94°. The analysis gave: C, 87.22; H, 7.44. Calculated for $(CH_3C_6H_4)_3COH$: C, 87.36; H, 7.34.

A molecular weight determination by the freezing-point method in benzene gave the following results: 0.8994 gram substance in 16.012 grams benzene gave a depression $\Delta = 0.952°$. This corresponds to a molecular weight of 291.9; calculated, 302.2.

Attempts to prepare tri-*p*-tolylphenolmethane, according to the method of Baeyer and Villiger,[1] were without results. Five grams of the carbinol and 15 grams of phenol were dissolved in a mixture of 100 grams acetic and 25 grams sulphuric acid. The solution was allowed to stand two weeks, but no condensation took place between the carbinol and the phenol. The experiment was repeated, using 25 grams acetic and 100 grams sulphuric acid. After standing five weeks the solution was poured into water and gave only unchanged carbinol.

Ethoxy Derivative, $(CH_3C_6H_4)_3COC_2H_5$.—Five grams of the tritolylchlormethane and slightly more than the theoretical amount of sodium ethylate, in absolute alcohol, were heated one hour under a reflux condenser. The solution was then cooled, filtered from the precipitated sodium chloride and concentrated. On standing a short time the pure ethyl ether of tri-*p*-tolylcarbinol crystallized out in fine, white, needle-shaped crystals. When recrystallized from petroleum ether the pure substance melted at 111° C. The yield was 4 grams. The analysis gave: C, 87.20; H, 7.80. Calculated for $(CH_3C_6H_4)_3COC_2H_5$: C, 87.20; H, 7.95.

Action of Acetyl Chloride.—It has been shown, in a previous paper,[2] that when the corresponding triphenylcarbinolether is

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[1] *Ber. d. chem. Ges.*, **35**, 3018 (1902).

[2] This Journal, **24**, 618 (1902); **25**, 1271 (1903).

treated with acetylchloride triphenylchlormethane is formed, and not the acetyl derivative, as has been reported by others.[1] With tritolylcarbinolether the result is analogous. The ethoxy compound dissolved readily in acetyl chloride with a slight evolution of heat and, on cooling, precipitated in small white crystals, which were washed with petroleum ether and carefully dried. The substance melted at 173°, showing it to be the pure chloride. Tritolylcarbinol was also treated with acetyl chloride. It dissolved quickly with a strong evolution of heat, and precipitated at once as the chloride, melting at 167°. On recrystallizing from petroleum ether the melting-point rose to 170°.

Tri-p-tolylbrommethane, $(CH_3C_6H_4)_3CBr$.—The action of hydrobromic acid on a solution of tritolylcarbinol is exactly analogous to that of hydrochloric acid. On conducting a stream of the dry gas into a solution of 10 grams of the carbinol in petroleum ether the yellow crystals of the tritolylbrommethane formed at once. The bromide was recrystallized from carbon disulphide by the addition of hot ligroin, in which it is but slightly soluble. Nine grams of the pure compound were obtained. The melting-point of the bromide is 165°. The analysis gave 22.3 per cent. bromine; calculated, 21.9 per cent.

Perhalides of the Tritolylhalogenmethanes.—A perbromide of the above compound was obtained by adding bromine to a solution of tritolylbrommethane in chloroform. A dark red oil separated from the solution and, on cooling, gave orange-red crystals of a perbromide, probably tritolylbrommethane pentabromide, as it contained 58 per cent. of "perbromine" (calculated 52.3 per cent.), as found by titration with sodium thiosulphate in presence of potassium iodide. The perbromide melted at a low temperature and it was found difficult to obtain it sufficiently pure for analysis. The tritolylcarbinolbromide, like the corresponding triphenyl compound, forms periodides. A solution of iodine in carbon disulphide was carefully added to a solution of tritolylbrommethane in the same solvent. The periodide crystallized at once in dark blue metallic-looking crystals, melting at 118° to 120°. Several analyses of the "periodine," by titration with sodium thiosulphate, showed that either the tetra- or the penta-iodide were formed, according to the conditions of the experiment.

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[1] *Ann. Chem.* (Liebig), **227**, 116 (1885).

When a solution of tritolylcarbinol is treated with dry hydrochloric or hydrobromic acids the corresponding chloride or bromide is formed. With hydriodic acid, however, a periodide of tritolyliodomethane, melting at 138°, was formed. The action of the hydriodic acid consists in changing some of the carbinol into the iodide, while another part of the carbinol is reduced to the tritolylmethane, whereby an equivalent of free iodine is liberated from the hydriodic acid. The iodine so formed combines with the tritolylcarbinol iodide to give rise to a periodide of variable composition. The pentaiodide was obtained by dissolving 2 grams of tritolylcarbinol and 5 grams of iodine in carbon disulphide, and saturating the solution with dry hydriodic acid. The dark, iridescent crystals were washed with benzene and dried in a vacuum desiccator. The melting-point was 77°. The analysis gave 60.99 per cent. iodine; calculated, 60.66 per cent.

Tri-p-tolylmethane, $(CH_3C_6H_4)_3CH$.—This compound was obobtained by the reduction of the chloride with zinc and acetic acid.[1] Ten grams of tritolylchlormethane were dissolved in 40 cc. acetic acid, and the solution was warmed gently. After displacing the air in the flask with carbon dioxide (to avoid the formation of the tritolylperoxide) 10 grams of zinc dust were added. The solution was kept at 50°, adding more zinc from time to time. A large excess of water was then added, the precipitated hydrocarbon extracted with ether and the solution dried. On distilling off the ether the tritolylmethane was obtained as a thick yellow oil. It distilled almost colorless at 260° to 262° under 28 mm. pressure. The analysis gave: C, 92.43; H, 7.90. Calculated for $(CH_3C_6H_4)_3CH$: C, 92.23; H, 7.76.

The molecular weight was determined by the freezing-point method in benzene. 0.4669 gram substance in 20.0708 grams of benzene gave a depression $\Delta = 422°$. This corresponds to a molecular weight of 267.1; calculated, 286.2.

Oxidation of the Tri-p-tolylcarbinol.—To a solution of 48 grams chromic acid in 72 grams acetic acid were added 12 grams tritolylcarbinol. The solution was heated three hours on the water-bath. A solid green mass separated in the bottom of the flask. This was filtered out and dissolved in a hot, 5 per cent. solution of sodium hydroxide. On filtering this solution and acidifying the clear filtrate with hydrochlorc acid a white, flocculent precip-

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[1] *Ber. d. chem. Ges.*, **36**, 283 (1903).

itate of the acid was obtained. When filtered, well washed and dried, it was found to be soluble in alcohol, benzene and acetic acid; insoluble in petroleum ether. But from none of these solvents could it be obtained in crystalline form. By dissolving in sodium hydroxide and carefully neutralizing with acetic or nitric acids the acid could be precipitated either as the lead salt, by addition of lead acetate, or as its silver salt, by adding silver nitrate. Neither of these salts were crystalline. The sodium salt, however, was obtained by the addition of sodium hydroxide to the alcohol solution of the acid. It precipitated in very fine, yellow crystals. An analysis of the sodium salt gave the following results: 14.59 per cent. Na; calculated, 14.53 per cent.

2.5 grams of the acid were then dissolved in potassium hydroxide, precipitated with hydrochloric acid, and carefully washed and dried. The low per cent. of carbon is occasioned by a small amount of potassium retained by the acid. The analysis gave: C, 66.51; H, 4.09. Calculated for $(C_6H_4CO_2H)_3COH$: C, 67.32; H, 4.12.

The acid volatilized slowly, without melting.

Tri-p-tolylaminomethane, $(CH_3C_6H_4)_3C.NH_2$.—It was shown by Nauen[1] that triphenylchlormethane reacts with ammonia to form triphenylaminomethane. In like manner, tritolylchlormethane reacts with ammonia to give tritolylaminomethane. Five grams of the chloride were dissolved in dry, thiophene-free benzene, and the solution was then saturated with dry ammonia gas. Ammonium chloride was formd at once, and after filtering and concentrating the solution the tritolylaminomethane separated in almost white crystals. The pure substance, recrystallized from ether and petroleum ether, melted at 112°. The analysis gave 4.73 per cent. N; calculated, 4.65 per cent.

Tri-p-tolylmethylaniline, $(CH_3.C_6H_4)_3C.HNC_6H_5$.—Tritolylchlormethane reacts also with amines, in like manner to triphenylchlormethane,[2] giving the corresponding substituted tritolylaminomethanes. Five grams of the chloride were dissolved in dry benzene, and to the warm solution 4 grams of aniline were slowly added. Aniline hydrochloride separated at once. After heating gently one hour the solution was filtered and the benzene distilled off. The tritolylmethylaniline compound re-

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[1] *Ber. d. chem. Ges.*, 17, 442.

[2] *Ibid.*, 17, 703.

mained as a brown viscous mass, soluble in ether, petroleum ether, toluene, etc.; less soluble in acetone, from which it crystallized in fine, white crystals, melting at 64°. The analysis gave 3.55 per cent. N; calculated, 3.71 per cent.

On boiling wth hydrochloric acid tritolylcarbinol is formed. When the aniline compound is heated for some time with alcohol a white crystalline substance was formed, containing no nitrogen, and melting at 111°. This proved to be the ethoxy derivative of tritolylmethane.

Tri-p-tolylmethylparatoluidine, $(CH_3.C_6H_4)_3C.HNC_6H_4.CH_3$.—This compound was made in exactly the same manner in which the aniline derivative was prepared. The yield was small, about half of the theoretical. On recrystallizing from petroleum ether several times the substance was obtained pure, in white crystalline form, and melted at 151°. The analysis gave 3.51 per cent. N; calculated, 3.58 per cent.

Conductivity of the Chlor- and Brom-derivatives.—It has been shown[1] that triphenylchlormethane, when dissolved in benzonitrile, possesses considerable electrical conductivity. The same has been found true in the case of tritolylchlormethane and tritolylbrommethane. Benzonitrile, which has been shown[2] to be a good ionizing solvent for many salts, was carefully dried and fractionated. It showed a specific conductivity of 4×10^{-5} at 20°. On addition of the electrolyte the solution at once assumed a greenish yellow color. The following results were obtained, the temperature being in all cases 20°.

TRITOLYLCHLORMETHANE.

v	1184	375.8	226.7	131.9	88.7	54.4	20.6
μ	1.713	1.023	0.8405	0.6413	0.5126	0.3621	0.2029

TRITOLYLBROMMETHANE.

v	1161	571.9	281.8	107.5	85.59	54.95	21.75
μ	4.515	3.969	2.621	1.611	1.464	1.196	0.7504

The volume in liters containing a gram-molecule is represented by v and the molecular conductivity by μ. It will be observed that the conductivity of the bromide is almost three times that of the chloride. Both compounds show a very measurable conductivity and may be classed, like the corresponding triphenyl derivatives,

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[1] *Ber. d. chem. Ges.*, **35**, 2404.

[2] *Ztschr. anorg. Chem.*, **15**, 31; *J. Phys. Chem.*, **3**, 22.

as compounds in the nature of salts. Qualitative tests with liquid sulphur dioxide as a solvent showed a much higher degree of molecular conductivity.

From the experimental results presented in this paper it is seen that tritolylmethane is, in all respects, analogous to triphenylmethane. The presence of so many methyl groups lowers greatly the melting-point of the hydrocarbon, so that even in a freezing-mixture it remains viscous. The two carbinols, those of tritolylmethane and of triphenylmethane, behave similarly toward halogen acids, acetylchloride, reducing agents, etc. The tritolylcarbinolhalides, like the corresponding triphenyl compounds, react readily with water, alcohol, halogens, ammonia and amines. With halide salts, such as mercuric chloride, ferrous chloride and zinc chloride, double salts are formed.[1] Also, as has been shown,[2] they react with zinc and silver in neutral solvents, giving rise to an extremely unsaturated substance, which, on exposure to air, forms tritolylmethyl peroxide, $(CH_3C_6H_4)_3COOC(C_6H_4CH_3)_3$, the reaction being strictly analogous to that of the triphenylhalogenmethanes.

ANN ARBOR, MICHIGAN,
July, 1904.

THE CHEMICAL COMPOSITION OF MAPLE-SYRUP AND MAPLE-SUGAR, METHODS OF ANALYSIS, AND DETECTION OF ADULTERATION.

BY JULIUS HORTVET.

Received August 26, 1904.

BY A rough classification, accountable by the fact that sucrose constitutes their chief ingredient, so-called maple-syrup and maple-sugar have long been classed with products obtained from sugar-cane, sugar-beet and sorghum. The statement that the sugar of the maple sap is identical in composition with that of the sugar-cane has been currently accepted, hence it has been concluded that chemical methods are helpless as a means of distinguishing the syrup or sugar prepared from the sugar-maple from like products prepared from the sugar-cane. Commercial interests have taken advantage of the unsatisfactory state of chemical knowledge regarding maple products, and have been active in

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[1] This Journal, **24**, 624 (1902).

[2] *Ber. d. chem. Ges.*, **37**, 1628 (1904).