

As Hemilian, Allen and Kölliker, and Herzig and Wengraf have all used acetyl chloride in the preparation of the substance described by them as triphenylmethyl acetate, and as the latter is decomposed by that reagent, it follows that the substance described by them as triphenylmethyl acetate, and as the latter it was, we believe, triphenylchloromethane. The latter would give, on treatment with water or with alcohol, the same products as the acetyl compound: the carbinol or the ethoxy compound. In fact, this is true of all the salts of triphenylmethyl: the halides, the sulphate, the picrate, etc., are readily hydrolyzed.

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ON THE POSSIBLE EXISTENCE OF A CLASS OF BODIES ANALOGOUS TO TRIPHENYLMETHYL.

[PRELIMINARY NOTICE.]

By M. GOMBERG.

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IN THE several papers which I have published on the subject of triphenylmethyl, some important features in regard to the behavior of that substance were brought out.

(1) The extreme unsaturation of the compound, as evidenced by the action of atmospheric oxygen and of iodine upon it.

(2) The unusual property possessed by that unsaturated hydrocarbon of entering into combination with different oxygen compounds, such as ethers, esters, etc. It appeared probable that these combinations represent compounds wherein the oxygen acts as being tetravalent. It might be added here that triphenylmethyl unites with equal readiness with nitriles.

(3) Triphenylmethyl may be considered as a distinctly basic radical. This furnishes an explanation why triphenylchloromethane, also the bromide and the iodide, are *salts*, as judged by their purely chemical behavior, as well as by the physico-chemical tests; these halides, dissolved in liquid sulphur dioxide, are true electrolytes.¹ The same is true of the sulphate, as was found by Mr. L. H. Cone² in this laboratory. Even triphenyl-

¹ Gomberg: *Ber. d. chem. Ges.*, **35**, 2403 (1902); Walden: *Ibid.*, **35**, 2018 (1902).

² Mr. L. H. Cone, holder of a research assistantship to the Carnegie Institution, will publish his results in full later.

methyl itself possesses. in that solvent, a decided electrical conductivity, as has been recently shown by Walden.¹

(4) Under the influence of catalyzing agents, such as dilute hydrochloric acid in benzene, ether, or some other solvent, triphenylmethyl is readily condensed to hexaphenylethane.²

It could hardly be expected that, whatever the constitution of triphenylmethyl, there should not be some other similar compounds capable of existence. The reaction which served for the preparation of triphenylmethyl was accordingly further studied, and an attempt has been made to apply it to compounds analogous to triphenylchloromethane. The following substances were subjected to this test:

Para-ditolyphenylchloromethane, $(\text{CH}_3\text{C}_6\text{H}_4)_2(\text{C}_6\text{H}_5)\text{C.Cl}$.

Tritolylchloromethane, $(\text{CH}_3\text{C}_6\text{H}_4)_3\text{C.Cl}$.

Paratrinotriphenylchloromethane, $(\text{NO}_2\text{C}_6\text{H}_4)_3\text{C.Cl}$.

Paratrimethoxytriphenylchloromethane, $(\text{CH}_3\text{O.C}_6\text{H}_4)_3\text{C.Cl}$.

In every case the initial stage of the reaction has been found to be the same as when triphenylchloromethane itself had been employed. A solution of the latter in benzene or in ether, when treated with zinc, silver, or mercury, assumes instantly a yellow color, which, as has been conclusively shown, is due to the formation of triphenylmethyl. Now, when any one of the four above-mentioned derivatives of triphenylchloromethane is treated in the same manner, the reaction is strikingly similar to the one with triphenylchloromethane itself. The introduction of the metal into a solution of those substances is followed in every case by the instantaneous formation of a substance which imparts color to the solution. Moreover, just as the exposure to air in the case of triphenylmethyl brings about rapid oxidation of the hydrocarbon and the consequent decolorization of the yellow solution, so also in the case of the other four instances; exposure of the solutions to air destroys their color at once—due, no doubt, also to oxidation.

But while in the case of triphenylmethyl the oxidation is comparatively simple, and the resulting product, the peroxide, can be readily isolated, the oxidation by the atmospheric oxygen in the other instances is more complex. So far, I have succeeded in isolating the oxidation product pure enough for analysis only in one

¹ *Ztschr. phys. Chem.*, **43**, 443 (1903).

² *Ber d. chem. Ges.*, **35**, 3914 (1902); **36**, 376 (1903).

other instance, namely, in the case of the unsaturated hydrocarbon from tritolychloromethane. Indeed, although there can be but little doubt that the action of metals upon the different triphenylchloromethane derivatives is probably the same in all instances, yet, in my experience, each case requires, for the successful course of the reaction, different experimental conditions. The nature of the metal, as well as the nature of the solvent, is of considerable influence upon the progress of the reaction. The subject becomes more difficult still because some of the chlor-compounds, as, for instance, the trinitrotriphenylchloromethane, are only slightly soluble in the usual organic solvents, which necessitates the use of large volumes of liquids.

The halides of triphenylchloromethane—the chloride, bromide, and iodide—are colorless in the solid state and also when dissolved in solvents which possess no ionizing power. But when dissolved in liquid sulphur dioxide, which does possess this power to a large extent, these halides dissociate into ions, $(C_6H_5)_3C\cdot$ and Cl' , as was proved by the electrical conductivity of the solutions. Moreover, such dissociation is invariably accompanied by the formation of a yellow color in the solvent. It was suggested¹ that the color was due to the ion $(C_6H_5)_3C\cdot$. Since the free hydrocarbon, triphenylmethyl itself, while colorless in the solid state, on dissolving gives yellow solutions, it was inferred that the hydrocarbon exists in solution as ions $(C_6H_5)_3\cdot$ and $(C_6H_5)_3C'$. The fact that triphenylmethyl, dissolved in liquid sulphur dioxide, shows very considerable electrical conductivity, argues, it seems to me, in favor of this view. There remains yet to account for the relation which exists between the two states of triphenylmethyl, the colorless solid and the yellow when in solution. If, however, it be true that the color of the solution of triphenylmethyl is really due to the latter existing in solution in the ionic state, then it must follow that a variation in complexity of the radical should also cause a variation in the color of the radical when the latter is in solution and hence in the ionic state. This is actually the case. Solutions of triphenylchloromethane acquire, on the addition of metals, a distinctly yellow color. The ditolyphenyl- and especially the tritolychloromethane, when subjected to the similar treatment, give orange solutions with quite a perceptible tinge of red. Trinitro-

¹ Gomberg: *Ber. d. chem. Ges.*, **35**, 2406 (1902).

triphenylchloromethane, even in minute quantities, gives, on the addition of metals (silver), a beautiful greenish-blue solution which changes, on warming, first to a violet-red and finally to a genuine fuchsine-red. On cooling, the blue color is restored; on exposure to air the solution is at once decolorized.

I shall continue the study of this reaction and shall extend it to other derivatives of triphenylhalogenmethane.

ANN ARBOR, MICH.,
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE NORTH CAROLINA DEPARTMENT OF AGRICULTURE.]

AN EFFICIENT ASBESTOS OR GRAPHITE MUFFLE.

BY J. M. PICKEL AND C. B. WILLIAMS.

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AT THAT point in the determination of potash in fertilizers, where ammonium salts and the excess of sulphuric acid are driven off, it was formerly the practice in this laboratory to accomplish the volatilization by placing the platinum dish on the top of the glass chimney of an Argand gas-burner, such as is commonly used for illuminating purposes. To afford air-vent and gas escape, the dish rested on small wires (of iron) bent over the edge of the chimney. A battery of ten or twelve of these burners was aligned on the same gas-pipe.

After excess of acid was evaporated and the ammonium salts more or less volatilized, the dishes were removed from the Argand burners to the blast-lamp, and there, at a red heat, the volatilization completed and the organic matter destroyed. In hope of obviating the necessity of transferring the dishes to the blast, one of us (Pickel) introduced, during the winter of 1900, the following modification:

The chimneys were cut down to a length of about 4 cm., and the dishes brought into close proximity with the flame. The dishes were, moreover, enclosed in asbestos cups, in the bottom of which were cut round holes of such diameter as to fit snugly over the chimneys which were thus made to support the cups. An asbestos lid, having a vent hole of about 2 cm. diameter, covers each cup. Each platinum dish rested on a pipe-stem triangle, or