3. The amount of 1,4 addition with *t*-butylmagnesium chloride, on the contrary, is large, and with *t*-amylmagnesium chloride, exceeds that of 1,2 addition.

4. Ethylidene acetone forms more 1,4 addition product with *t*-butylmagnesium chloride than with ethylmagnesium bromide.

5. Mesityl oxide forms no 1,4 addition product with *t*-butylmagnesium chloride.

CAMBRIDGE, MASS. RECEIVED APRIL 18, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ILLINOIS]

The Decomposition of Triphenylmethyl Hyponitrite

BY M. A. SPIELMAN[1]

Alkoxyl radicals have been postulated as fugitive intermediates in certain organic reactions,[2] but the study of their behavior is complicated by the fact that the temperatures at which they are formed are too high to permit distinction between primary reactions and secondary pyrolytic effects. The decomposition of alkyl hyponitrites offers an attractive method of forming such radicals at moderate temperatures, and this paper presents a preliminary investigation of the problem.

The few esters of hyponitrous acid in the literature, prepared from silver hyponitrite and alkyl halides, are said to decompose below 100° to give nitrogen, an aldehyde and an alcohol.[3] This may be viewed as a prefatory decomposition to nitrogen and two alkoxyl radicals, followed by disproportionation of the latter.

$$RCH_2—O—N{=}N—O—CH_2R \xrightarrow{-N_2} 2RCH_2—O— \longrightarrow RCHO + RCH_2OH$$

In the present study, the triphenylmethoxyl radical was selected for investigation because simple disproportionation is impossible, and because a previous preparation by an independent method allows a comparison of results to be made.

Triphenylchloromethane in benzene reacted readily with silver hyponitrite, but evolution of nitrogen began at once, and the triphenylmethyl hyponitrite proved to be too unstable for isolation. Its transitory existence was clearly shown, however, by measuring a significant escape of nitrogen after the reaction mixture had been filtered from inorganic matter. The products of the reaction were, in order of amounts isolated, benzopinacol diphenyl ether, benzophenone, triphenylmethyl peroxide, phenol, triphenylmethyl, triphenylcarbinol and *p*-hydroxytetraphenylmethane. Large amounts of nondescript oily and resinous material were also encountered. This series of products is seen to parallel that which Wieland[4] found to result from the dissociation of triphenylmethyl peroxide in boiling xylene. He isolated benzopinacol diphenyl ether, benzophenone, phenol and triphenylcarbinol.

The first step in the decomposition of the ester (I) undoubtedly incurs the formation of the triphenylmethoxyl radical (II), and the combination of two of these yields the triphenylmethyl peroxide (III) present in the end-products. Rearrangement antecedent to combination, as suggested by Wieland, explains the origin of the benzopinacol diphenyl ether (V). The source of benzophenone is obscure. An effort was made to show that it came directly from the triphenylmethoxyl radical with concomitant elimination of a phenyl radical, much as the ethoxyl radical may throw off a methyl radical to give formaldehyde.[5] No trace of the phenyl radical could be found, either by careful search for diphenyl or by carrying out the reaction in the presence of quinone and making examination for quinhydrone.[6] A possible precursor of benzophenone is the mixed benzophenone acetal (VI), some of which must certainly result from the combination of the triphenylmethoxyl radical with its rearrangement product (IV). Presupposing inherent instability in such a molecule, there is no difficulty in explaining the series of substances actually found. Thus, fission at a, followed by

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[1] National Research Council Fellow.

[2] Rice and Rice, "The Aliphatic Free Radicals," The Johns Hopkins Press, Baltimore, 1935, pp. 115, 139.

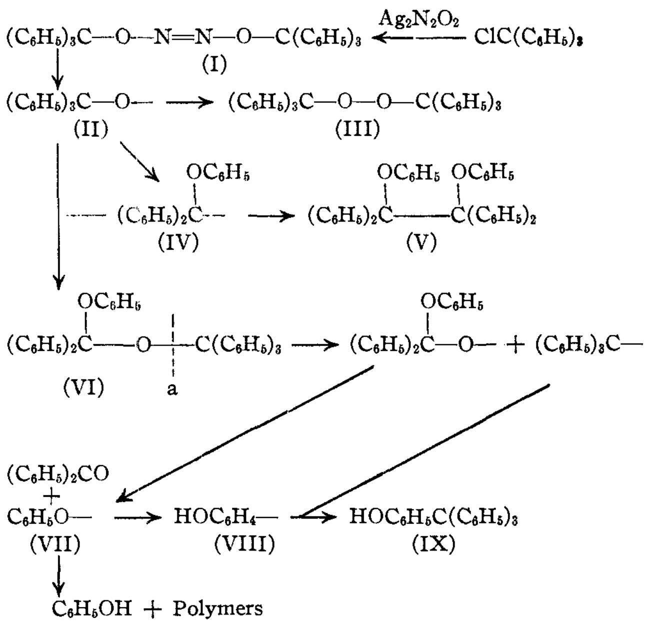
[3] Zorn, *Ber.*, **11**, 1630 (1878); Hantzsch and Kaufmann, *Ann.*, **292**, 329 (1896); Partington and Shah, *J. Chem. Soc.*, 2593 (1932).

[4] Wieland, *Ber.*, **44**, 2551 (1911).

[5] Rice and Rodowskas, THIS JOURNAL, **57**, 350 (1935). In this connection compare also the decomposition of *t*-butyl hypochlorite to acetone and methyl chloride, Chattaway and Backeburg, *J. Chem. Soc.*, **123**, 2999 (1923).

[6] Wieland, *Ann.*, **514**, 145 (1934), has shown that the free phenyl radical combines instantly with benzene to form diphenyl with the liberation of atomic hydrogen which may be captured by quinone.

disproportionation, would give triphenylmethyl, benzophenone and the phenoxyl radical (VII). The last would, in turn, yield phenol and congeneric polymers, and any part which first underwent rearrangement to the hydroxyphenyl radical (VIII)



could, by union with triphenylmethyl, form the *p*-hydroxytetraphenylmethane (IX).

Experimental Part

In order to gage the speed of the reaction, 0.5 g. of triphenylchloromethane, 0.25 g. of silver hyponitrite[7] and 15 cc. of bromobenzene were placed in a nitrogen-filled flask and connected to a gas buret. At 25°, 18.1 cc. (corr.) or 90% of the theoretical amount of nitrogen was given off in twenty-four hours. To demonstrate the transitory existence of triphenylmethyl hyponitrite, 1.0 g. of triphenylchloromethane, 0.5 g. of silver hyponitrite and 25 cc. of bromobenzene were allowed to stand at 0° for twenty-four hours. The mixture was rapidly filtered and placed in connection with a gas buret. In ten hours 7.4 cc. of nitrogen was evolved. An appropriate blank experiment, using bromobenzene saturated with nitrogen at 0° gave a volume increment of only 0.9 cc. The filtered solution must therefore have contained a source of molecular nitrogen.

Preparation and decomposition of triphenylmethyl hyponitrite was carried out in a number of ways, and the following experiment is to be regarded as typical. In a dry nitrogen-filled bottle were placed 3.0 g. of triphenylchloromethane, 1.5 g. of silver hyponitrite and 40 cc. of dry benzene. A trap was arranged to permit escape of nitrogen without ingress of air. Evolution of nitrogen began at once, and the reaction mixture soon assumed a bright orange-yellow color. After three days it was filtered in an atmosphere of carbon dioxide and the precipitate of silver chloride was washed several times with benzene. An additional washing with warm chloroform gave a little gummy solid from which was isolated by washing with ether 25 mg. of triphenylmethyl peroxide; m. p. and mixed m. p. 183°.

The main filtrate was evaporated to a paste under diminished pressure of carbon dioxide, taken up in ether, and filtered to give precipitate A and filtrate B. The latter was bright orange in color, but exposed to air the color soon faded until the solution was almost water-white; 40 mg. of solid was filtered off leaving filtrate C. The solid was pure triphenylmethyl peroxide; m. p. and mixed m. p. 185°.

Precipitate A was creamy-white, crystalline, and weighed 1.18 g. It consisted of triphenylmethyl peroxide and benzopinacol diphenyl ether. The relative amounts were estimated by taking advantage of the fact that the peroxide dissolves in cold concd. sulfuric acid while the ether is practically unattacked.[4] A 0.1153-g. sample in a Gooch crucible was washed with three portions of sulfuric acid, followed by water and a little cold alcohol. The loss in weight was 0.0225 g., which indicated that not more than 20% of the mixture was triphenylmethyl peroxide. A synthetic mixture was similarly separated: ether calcd., 51%; found, 48%. The balance of precipitate A was separated by fractional crystallization from chloroform–ether and benzene–ether. Triphenylmethyl peroxide collected in the top fractions; m. p. and mixed m. p. 185°. Benzopinacol diphenyl ether in the bottom fractions was finally crystallized from alcohol–benzene. It came out in crusts of rhombs as described by Wieland, and on melting it exhibited the behavior he found so distinctive. It sintered at indefinite temperatures from 150–200° and melted at 215° to a garnet-red liquid whose color faded perceptibly on cooling. Mixed with an authentic specimen the melting point was unchanged.

Anal. Calcd. for $C_{38}H_{30}O_2$: C, 88.03; H, 5.79. Found: C, 87.88; H, 6.20.

Filtrate C was evaporated to dryness and washed several times with petroleum ether. The petroleum ether-insoluble part (0.31–0.58 g.) was an exceedingly thick oil, very soluble in all organic solvents save petroleum ether. Attempts at fractional precipitation gave only gummy substances of evident polymeric nature.

The petroleum ether extract from above was washed with dilute sodium hydroxide, and the washings, after the customary bromination treatment, gave 0.26 g. of tribromophenol; m. p. 89°. The balance was freed of petroleum ether and steam distilled. The distillate weighed 0.40 g.; it solidified when seeded with benzophenone and was further identified as the oxime; m. p. 140°. The aqueous liquors in the distillation flask gave no test for phenol or chlorine, indicating that the benzophenone did not come from hydrolysis of its diphenyl acetal and that the triphenylcarbinol (below) was not traceable to unchanged triphenylchloromethane. The nonvolatile part weighed 0.30–0.95 g. It was a resinous solid interspersed with crystals. After much difficulty there was isolated 50 mg. of triphenylcarbinol; m. p. and mixed m. p. 158°. In one experiment in which the alkali extraction was omitted, this fraction also yielded 13 mg. of

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[7] Partington and Shah, *J. Chem. Soc.*, 2595 (1932).

p-hydroxytetraphenylmethane; m. p. and mixed m. p. 278°.

Anal. Calcd. for $C_{25}H_{20}O$: C, 89.28; H, 6.66. Found: C, 88.63; H, 6.83.

Summary

Triphenylchloromethane reacts with silver hyponitrite to give benzopinacol diphenyl ether, benzophenone, triphenylmethyl peroxide, phenol, triphenylmethyl, triphenylcarbinol and *p*-hydroxytetraphenylmethane. The interpretation rests upon the assumption that triphenylmethyl hyponitrite is first formed and then decomposes with the liberation of the triphenylmethoxyl radical.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA]

Disaccharides in "Hydrol"

BY GEORGE H. COLEMAN, MARION A. BUCHANAN AND PHILIP T. PAUL

In the commercial production of crystalline *d*-glucose by the hydrolysis of corn starch with dilute hydrochloric acid there is obtained a mother liquor known as "hydrol."

The concentrated hydrol contains about 75% of dissolved solids of which one-third is not fermentable by yeast. Berlin[1] has identified gentiobiose as one of the constituents of the non-fermentable portion. By acetylation he obtained a yield of β-octaacetylgentiobiose corresponding to 18.3% of the non-fermentable material.

Fischer[2] obtained a non-fermentable product which he called "isomaltose" by allowing *d*-glucose to stand in concentrated hydrochloric acid for about fifteen hours at 10–15°. Berlin[3] observed that the properties of the crude non-fermentable material from hydrol closely resembled those of isomaltose. He prepared isomaltose from *d*-glucose according to Fischer's method and from this by acetylation obtained β-octaacetylgentiobiose.

Pictet and Georg[4] by acetylation of Fischer's product also obtained gentiobiose octaacetate but pointed out that gentiobiose represented only a small percentage of the crude material. By fractional precipitation of the acetylated material they were able to obtain in addition to gentiobiose octaacetate the octaacetate of another disaccharide which they called "isomaltose."

Zemplén and Bruckner[5] synthesized 1-β-methyl heptamethyl-6-α-glucosidoglucose and thinking that Pictet's isomaltose might be 6-α-glucosidoglucose they repeated Pictet's work and methylated the isomaltose fraction. As a result of their work they concluded that Pictet's isomaltose was not a pure compound but was a mixture which contained 6-α-glucosidoglucose.

The present work was undertaken for the purpose of identifying if possible other material than gentiobiose in the non-fermentable portion of hydrol. Commercial hydrol[6] was fermented by yeast and non-fermentable material isolated by the method used by Berlin. This product was methylated using a combination of the dimethyl sulfate–sodium hydroxide method of Haworth[7] and the methyl iodide silver oxide method of Purdie and Irvine.[8] After several methylations there was obtained a fraction which distilled at about 200° under 1-mm. pressure. The methoxyl and molecular weight values of this product corresponded to an octamethyl disaccharide. After standing for some time partial crystallization occurred. When this partial crystallization was apparently complete the viscous sirup was separated from the crystals by centrifuge filtration. The crystalline material represented about 20% of this product and was identified as heptamethyl β-methylgentiobioside having a specific rotation of −24°. It was identified by its physical properties and by hydrolysis and isolation of the products of hydrolysis. The sirup representing about 80% of the product had a specific rotation of +80°. Zemplén and Bruckner record a specific rotation of +95° for 1-β-methylheptamethyl-6-α-glucosidoglucose.

The methoxyl content and the molecular weight of this sirup agreed with the calculated values

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[1] Berlin, THIS JOURNAL, **48**, 2627 (1926).

[2] Fischer, *Ber.*, **23**, 3687 (1890).

[3] Berlin, THIS JOURNAL, **48**, 1107 (1926).

[4] Pictet and Georg, *Helv. Chim. Acta*, **9**, 612 (1926).

[5] Zemplén and Bruckner, *Ber.*, **64**, 1852 (1931).

[6] The authors wish to express their appreciation to William B. Newkirk and Arthur Pulfry of the Corn Products Refining Company for their kindness in supplying the hydrol used and for suggestions made in connection with this work.

[7] Haworth, *J. Chem. Soc.*, **107**, 8 (1915); Haworth and Leitch, *ibid.*, **113**, 188 (1918).

[8] Purdie and Irvine, *ibid.*, **83**, 1021 (1903).