

of neutral salts after saponification has proceeded for some time is not instantaneous.

In general, it is noted that the effect of the presence of neutral salts of the alkali metals in a reaction involving the saponification of cellulose acetate in colloidal dispersion in acetic acid, is opposite to that recorded by investigators of similar reactions involving crystalloids.

The subject matter of this paper is covered by a pending patent application of Eastman Kodak Company and the publication of this paper is not to be taken in any way as suggesting or permitting the commercial use of this development.

Summary

The effect of the presence of the nitrates, sulfates and chlorides of sodium and potassium on the rate of saponification of cellulose acetate dispersed in acetic acid has been studied.

It has been found that all of these salts appear to exert a retarding influence on the reaction rate. A greater effect was observed when nitrates and sulfates were used than when chloride was employed.

Addition of neutral salts after the reaction had proceeded for forty-two hours showed an effect similar to that noted when they were present at the beginning of the saponification.

ROCHESTER, NEW YORK

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

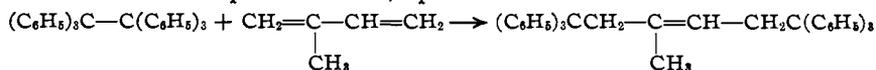
THE ADDITION OF FREE RADICALS TO UNSATURATED COMPOUNDS (PRELIMINARY PAPER)

BY J. B. CONANT AND H. W. SCHERP

RECEIVED MARCH 10, 1931

PUBLISHED MAY 6, 1931

Free radicals containing trivalent carbon such as triphenylmethyl are known to combine with quinones (forming a di-ether) and with free radicals containing divalent nitrogen. Aside from these reactions there seems to be no published account of the addition of a free radical to an unsaturated organic compound. We have now found that triphenylmethyl (hexaphenylethane) combines with isoprene and dimethylbutadiene; the addition takes place in the 1,4 position.



The structure of the product obtained from isoprene was established by ozonization. Triphenylpropionic acid and 1,1,1-triphenylbutanone-3 were obtained from the ozonide by decomposition and oxidation with silver oxide. The identity of these compounds was proved by mixed melting

point determinations with synthetic material. The ketone is new and was synthesized from triphenylpropionic acid by converting the latter into the acid chloride and treating with methyl zinc chloride in ether.

The nature of the product obtained with dimethylbutadiene was shown by the fact that on ozonization the same triphenylbutanone was obtained. The two new hydrocarbons obtained from isoprene and dimethylbutadiene, respectively, melted at 166 and 240°, respectively. Both combined with bromine in chloroform solution but considerable substitution takes place as evidenced by the copious evolution of hydrogen bromide.

It is a matter of considerable interest to see how far the type of addition reaction we have discovered can be extended. There seems no reason to believe that it is limited to dienes or to ethanes as highly dissociated as hexaphenylethane. Such reactive linkages as those in maleic anhydride or acrolein might well be expected to combine with free carbon radicals. Indeed, we have evidence that a reaction does take place between each of these compounds and triphenylmethyl but the nature of the product has not been as yet determined. We have been unable to bring about the addition of hexaphenylethane to 1,4-diphenylbutadiene, cinnamalacetophenone, or cinnamalmalonic acid. A study of the application of this reaction to the polyenes (including the carotinoid pigments) is now in progress.

Experimental Part

Reaction of Hexaphenylethane with Isoprene.—Three grams of hexaphenylethane (prepared from triphenylmethyl chloride and molecular silver) was treated with 40 cc. of isoprene in an atmosphere of nitrogen. After standing for two days, all the solid had dissolved and the orange-red color of the solution had changed to pale yellow. The excess isoprene was removed by distillation, the sirupy residue finally being heated on the steam-bath. On treatment with a mixture of ether and petroleum ether, 1.3 g. of slightly yellowish crystals was obtained which melted at 160–161°. On recrystallization from ether 0.6 g. of product melting at 164–165° was obtained. A more convenient method of obtaining crude hexaphenylethane in quantity is by the reduction of triphenylmethyl chloride. This crude material can be used directly in the addition reactions; an example of this procedure is as follows. The chloride (10 g.) was dissolved in 200 cc. of acetone in a 2-liter flask and 15 cc. of concentrated hydrochloric acid was added. A strong current of carbon dioxide was passed into the flask and 100 cc. of approximately 1 *N* vanadous chloride was run into the solution. On adding a liter of water, the product precipitated in granular form. It was filtered off, thoroughly washed with water and transferred without drying to a 200-cc. flask fitted with a two-holed stopper carrying a dropping funnel and connection to a nitrogen-vacuum pump apparatus. The flask was swept out three times with nitrogen, about 40 cc. of isoprene run in and finally the flask was left under a pressure of 1–2 cm. of mercury for three days with occasional shaking. The excess isoprene was then distilled off and the residue taken up in about 300 cc. of ether. The solution was filtered, evaporated to a small volume and on standing overnight at 0°, 6.3 g. of large glassy crystals formed, which melted at 162–163°. On recrystallization from ether, 4.5 g. melting at 164–164.5° was obtained; yield, 45% of the theoretical calculated from the triphenylmethyl chloride.

Another equally convenient procedure for preparing the addition product of iso-

prene and hexaphenylethane is to employ benzene as a solvent and form the free radical from the chloride and metallic mercury in the presence of the unsaturated compound. The following is a typical procedure: 15 g. of triphenylmethyl chloride, 3.6 g. of isoprene, 50 cc. of thiophene-free benzene and 50 g. of mercury were sealed in a nitrogen filled capsule and shaken for seventeen hours. After ten days' standing, the reaction mixture was worked up in the same fashion as the previous preparation; yield, after one recrystallization from benzene and ether, 10.8 g. or 72%; melting point, 163–164°.

1,4-(Triphenylmethyl)-2-methylbutene-2.—A portion of this substance was carefully crystallized from ether for analysis; melting point, 166°.

Anal. Calcd. for $C_{48}H_{38}$: C, 93.1; H, 6.9. Found: C, 92.7, 92.8, 92.6, 92.6, 93.0; H, 7.07, 7.04, 6.91, 6.98, 7.0.

Molecular weight (neglecting the first increment) in benzene, cryoscopic. Benzene, 25.47, 25.47 g.; substance, 0.1799, 0.1928 g.; Δt , 0.076, 0.079°. *Molecular weight*, 475, 490. Calcd. for $C_{48}H_{38}$: 554.

Ozonization.—Two grams of the hydrocarbon was dissolved in about 200 cc. of carbon tetrachloride and ozonized oxygen prepared by means of an electric discharge apparatus was bubbled through for three hours, when the solution was very turbid. The solution was cooled with ice during the reaction. On shaking with water and zinc dust, and filtering, a clear solution was obtained. The carbon tetrachloride was evaporated off under reduced pressure and the yellow gummy residue was taken up in ether. This solution was shaken for one-half hour with saturated sodium bisulfite solution, and the aqueous layer was acidified with hydrochloric acid. A small amount of oily material separated, but not enough to indicate that any appreciable extraction had occurred.

The ether was then boiled off and the residue dissolved in methyl alcohol. About one gram of sodium hydroxide and the freshly precipitated silver oxide from 3 g. of silver nitrate were added. After three hours' boiling, during which a characteristic "silver mirror" appeared, the hot solution was filtered, acidified with hydrochloric acid and evaporated to a small volume under reduced pressure. There was no precipitate of silver chloride. The mixture was dissolved in ether and extracted with sodium carbonate solution. The aqueous layer was acidified with hydrochloric acid, extracted with ether, and the acid removed once more with sodium carbonate solution. The acid was then reprecipitated by hydrochloric acid, extracted with ether, and crystallized from ether and petroleum ether; yield, 0.6 g. melting at 177.5–178.5°. Calculated as β -triphenylpropionic acid, the yield was 55%.

A duplicate experiment was carried out, but no sodium hydroxide was used in the silver oxide oxidation. At the end of the oxidation, 10 cc. of concentrated hydrochloric acid was added and boiling continued for one-half hour to liberate the acid from the silver salt; yield, 0.4 g. (37%) melting at 179°. The combined acids were recrystallized from 50% alcohol, the product being in the form of fine needles and melting at 180.5°. A mixed melting point with synthetic β -triphenylpropionic acid showed no depression.¹

The non-acid fractions from the ozonizations were concentrated and treated with petroleum ether to the point of cloudiness. On standing overnight at 0°, a total of 0.85 g. of crystalline material melting at 135–137° was obtained; yield calculated as 1,1,1-triphenylbutanone-3, 39%. After two recrystallizations from ether, the substance melted at 140.5–141°. A mixed melting point with the synthetic material (see below) gave no depression.

1,1,1-Triphenylbutanone-3 was prepared by the reaction of β -triphenylpropionyl chloride and zinc methyl chloride.² Methylmagnesium iodide was prepared in the usual

¹ Fosse, *Compt. rend.*, **145**, 197 (1907); Hellerman, *THIS JOURNAL*, **49**, 1737 (1927).

² This method was developed by W. D. Peterson in this Laboratory.

fashion from 0.45 g. of magnesium turnings, 2.7 g. of methyl iodide and 40 cc. of absolute ether. Four grams of stick zinc chloride was fused under reduced pressure until bubbling ceased. It was then taken up in 25 cc. of absolute ether and added to the Grignard reagent, cooling the latter meanwhile with an ice-salt mixture. The solution was then warmed to room temperature and stirred for fifteen minutes. β -Triphenylpropionyl chloride was prepared by treating β -triphenylpropionic acid with three times the calculated amount of thionyl chloride. The excess thionyl chloride was boiled off and the product heated under reduced pressure until odorless. A solution of 4 g. of this material in absolute ether was added to the zinc methyl chloride. After one hour's stirring with gentle boiling, the mixture was allowed to stand overnight. It was then decomposed with water and hydrochloric acid. The ether solution was washed with sodium hydroxide to remove any β -triphenylpropionic acid, dried with calcium chloride and evaporated to a small volume. On standing for some time, a crystalline product formed, which had a low indefinite melting point and was obviously impure. A portion was recrystallized twice from ether, and 0.33 g. of material melting sharply at 140.5–141° was obtained. In addition, 1.0 g. of another substance melting at 120–124° was obtained. (This was not further investigated.) The substance yielded iodoform on treatment with iodine and sodium hydroxide in methyl alcohol solution.

Anal. Calcd. for $C_{22}H_{20}O$: C, 88.0; H, 6.7. Found: C, 88.2, 88.0; H, 6.9, 6.7.

Reaction of Hexaphenylethane with Dimethylbutadiene.—2,3-Dimethylbutadiene was prepared by the catalytic dehydration of pinacol with iodine, following the directions of Hibbert.³ Five grams of triphenylmethyl chloride, 1.5 g. of dimethylbutadiene, 10 cc. of thiophene-free benzene and 15 g. of mercury were sealed in a nitrogen filled capsule and shaken on a machine for twelve hours. After one week's standing the contents of the capsule were shaken for some time with air to oxidize any hexaphenylethane, filtered, and concentrated. A slightly yellow crystalline material was precipitated by petroleum ether. This was recrystallized from benzene and petroleum ether, 1 g. melting at 227–231° being obtained. This was recrystallized twice from benzene and ether for analysis. It then melted at 240° under nitrogen with some decomposition.

*Anal.*⁴ Calcd. for $C_{44}H_{40}$: C, 92.9; H, 7.1. Found: C, 92.6, 92.6; H, 7.36, 7.38.

Ozonization.—Ozonized oxygen was bubbled for five hours through a solution of 0.8 g. of the hydrocarbon in 50 cc. of carbon tetrachloride chilled with ice. After shaking with water and zinc dust and filtering, the solution was evaporated to dryness under reduced pressure. The gummy residue was dissolved in 5 cc. of ether, and a sandy precipitate formed weighing about 0.025 g. and melting above 150°. The mother liquor was allowed to evaporate slowly at room temperature and the crystals which formed were washed with ether and recrystallized from the same solvent. The yield was 0.16 g. or 19%. The melting point was 140.5–141°. A mixed melting point with synthetic $(C_6H_5)_3CCH_2COCH_3$ showed no depression.

Summary

Triphenylmethyl combines with isoprene and dimethylbutadiene, addition taking place in the 1,4-position.

CAMBRIDGE, MASSACHUSETTS

³ Hibbert, *THIS JOURNAL*, 37, 1747 (1915).

⁴ We are indebted to Miss H. F. Hawes for these microanalyses.