The dealcoholation of methyl orthophenylacetate by a variety of strong bases is reported. Of these bases mesitylmagnesium bromide was selected as the most efficient for the preparation of the ketene acetal.

Methyl orthopropionate and methyl orthoisobutyrate have been dealcoholated by mesitylmagnesium bromide to the respective ketene acetals: methylketene dimethylacetal and dimethylketene dimethylacetal. The latter compound is the first dialkylketene acetal to be prepared.

The aprotic acid, aluminum methoxide, at 210° promotes a smooth and rapid dealcoholation of methyl orthophenylacetate to produce phenylketene dimethylacetal in 92% yield.

Methyl orthopropionate is partially (15%) dealcoholated by aluminum methoxide at 240–245°. Methyl orthoisobutyrate requires a reaction temperature of 290–300° for dealcoholation over aluminum methoxide, but only 8.6% yield of the dimethylketene dimethylacetal is produced; the principal reaction products are the normal ester, methyl isobutyrate, and dimethyl ether.

MADISON, WISCONSIN RECEIVED NOVEMBER 7, 1949

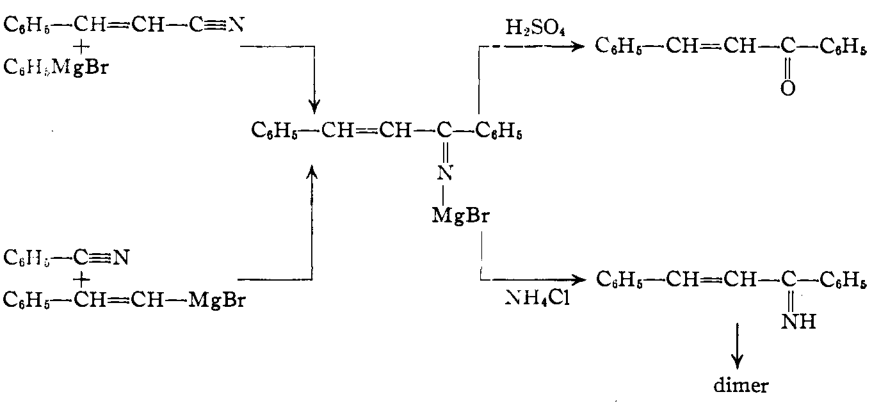
[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF TORONTO]

The Grignard Reaction of Styryl Cyanide[1]

BY D. E. PIPER[2] AND GEORGE F WRIGHT

When the reaction mixture obtained by adding phenylmagnesium bromide to styryl cyanide is hydrolyzed with an ice-cold aqueous sulfuric acid solution, there is obtained[3] a 68% yield of benzalacetophenone. However when the reaction mixture is hydrolyzed with an ice-cold aqueous ammonium chloride solution little or no benzalacetophenone is formed but, instead, a 40% yield of a white crystalline compound melting at 183° and having the empirical formula $C_{15}H_{13}N$.[4] The present paper deals with the structure of this compound and its reactions.

Molecular weight determinations showed that the compound had the formula $C_{30}H_{26}N_2$, that is, double the formula of styryl phenyl ketimine, the ketimine corresponding to benzalacetophenone.



The fact that the compound is a dimer of styryl phenyl ketimine was demonstrated by its synthesis from styrylmagnesium bromide and benzonitrile. The aqueous ammonium chloride hydrolysis of this reaction mixture should produce styryl phenyl ketimine as did the former reaction.

The reactions of this dimer are best explained by structure I, 2,4,6-triphenyl-2,5-endo-(2′-phenylethylene)-2,3,4,5-tetrahydropyrimidine. A proposed mechanism for the formation of this compound from styryl phenyl ketimine is outlined.

Active hydrogen determinations using a half-mole excess of methylmagnesium iodide showed the presence of one active hydrogen per molecule. With a large excess of the Grignard reagent a total of 1.7 active hydrogens per molecule was indicated and at the same time a clear orange solution was formed instead of the white precipitate as in the previous case. This behavior is believed due to formation of a polymolecular complex in the presence of a large concentration of Grignard reagent. Determinations using lithium aluminum hydride showed the presence of 1.0 active hydrogen per molecule even when a large excess of the hydride was used. There was no indication of a Grignard absorbing group. Since the compound formed a mononitroso derivative when treated with very dilute nitrous acid in methanol, the active hydrogen is logically accounted for by a secondary amino group.

Although the compound could not be dehydrogenated by mild catalytic methods, there were obtained by heating with sulfur at 190° two fragments which were identified as styrene and 2,4,6-triphenylpyrimidine (II).[5] The compound when heated to about 300° in the absence of sulfur was found to decompose to three fragments which were

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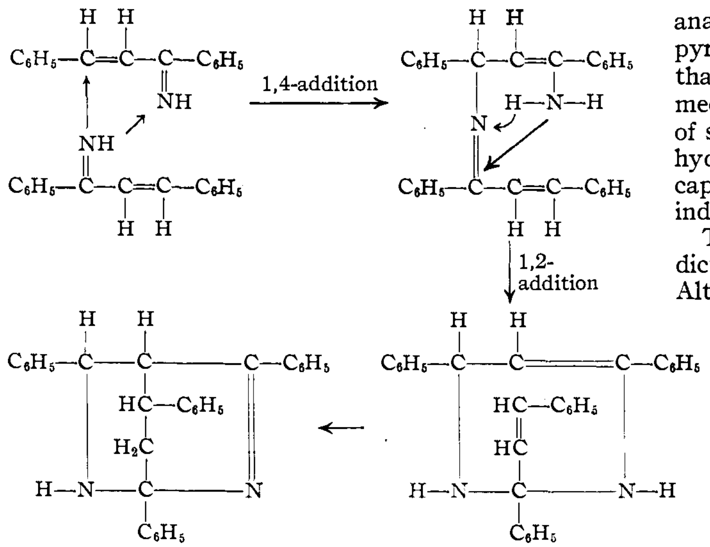
(1) Presented before the Division of Organic Chemistry at the Atlantic City meeting of the American Chemical Society, September 19, 1949.

(2) Holder of Imperial Oil Fellowship in Chemistry, 1946-1949.

(3) E. P. Kohler, *Am. Chem. J.*, **35**, 386 (1906).

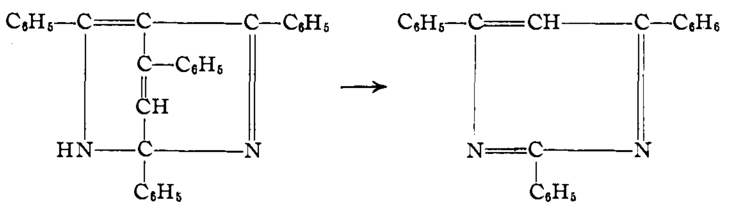
(4) J. C. Bond and George F Wright, THIS JOURNAL, **72**, 1023 (1950).

(5) Asahina and Kuroda, *Ber.*, **47**, 1815 (1914).



I

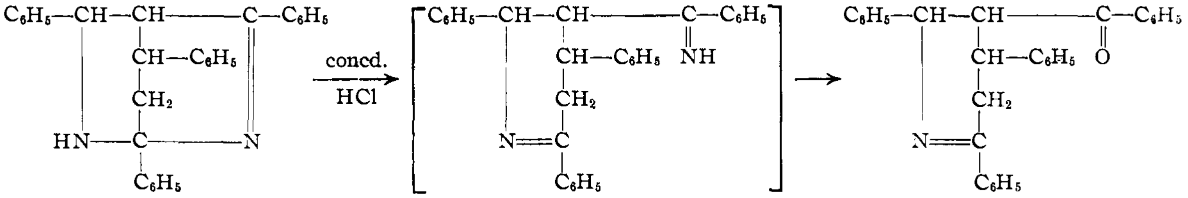
identified as toluene, ammonia and 2,4,6-triphenylpyridine (III).[6] Structure I which contains both the 2,4,6-triphenylpyrimidine and 2,4,6-triphenylpyridine nuclei accounts for these reactions.



IV II

+ C_6H_5—C≡CH

When the compound I was treated with bromine in ethanol, there was isolated a very inert compound the analysis of which corresponded to that of dibromotriphenylpyridine. This compound was reduced to 2,4,6-triphenylpyridine (III) by treatment with sodium in liquid ammonia.



I X V

It is of interest in connection with the dehydrogenation of I that the only isolable product from the reaction of phenylmagnesium bromide with phenylcyanoacetylene was 2,4,6-triphenylpyrimidine (II). That is to say the reaction of phenylmagnesium bromide with the dehydro-analog of styryl cyanide, instead of producing the dehydro-analog of I, gave the product formed by pyrolysis of I with sulfur. If it is assumed that this reaction has followed the same mechanism as that for the Grignard reaction of styryl cyanide, it is evident that the dehydro-analog of I, marked IV below, is not capable of existence but breaks down as indicated.

The failure to isolate IV might be predicted from consideration of the Bredt rule.[7] Alternately, if a 1,3-hydrogen shift in IV be postulated such that two ketimine linkages once removed from the phenylethylene bridge bonds are formed, the easy fission of the phenylethylene bridge may be thought of in terms of the Schmidt rule.[8]

Compound I was found to be unstable toward strong acids. It dissolved slowly in concentrated hydrochloric acid but after about one hour there was precipitated the hydrochloride of the hydrolysis product of I. This product is 2,4,6-triphenyl-3-benzoyl-2,3,4,5-tetrahydropyridine (V). The hydrolysis may be pictured as shown below.

Compound V was isolated in two polymorphic forms melting, respectively, at 145 and 158°. The 158° form was the stable one at room temperature.

Active hydrogen tests using methylmagnesium iodide indicated that the compound contained no active hydrogen and one Grignard absorbing group per molecule. Because of the apparent lack of active hydrogen the compound was assigned the 2,3,4,5-tetrahydro structure shown. Despite this it formed the N-benzoyl derivative (VI) by the Schotten–Baumann reaction. This could be accounted for either by a 1,3-shift of hydrogen or by ring opening and reclosing during benzoylation. It was found that 2,4,6-triphenyltetrahydropyridine[9] also was capable of benzoylation despite an apparent lack of active hydrogen. The structure of tetrahydropyridines in general will bear further study.

Compound V, unlike compound I, was smoothly dehydrogenated without decomposition by heating with sulfur. The compound which was ob-

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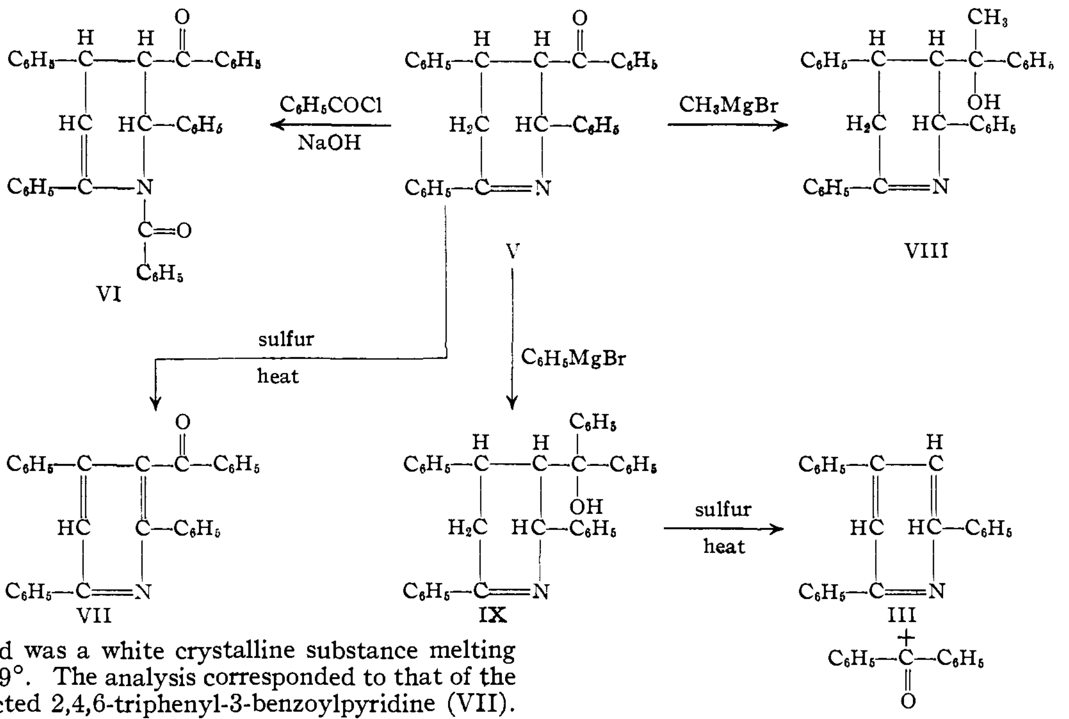
[6] Reddelien, *Ber.*, **53B**, 334 (1920).

[7] Bredt, *Ann.*, **437**, 1 (1924).

[8] Otto Schmidt, *Z. physik. Chem.*, **159A**, 337 (1932).

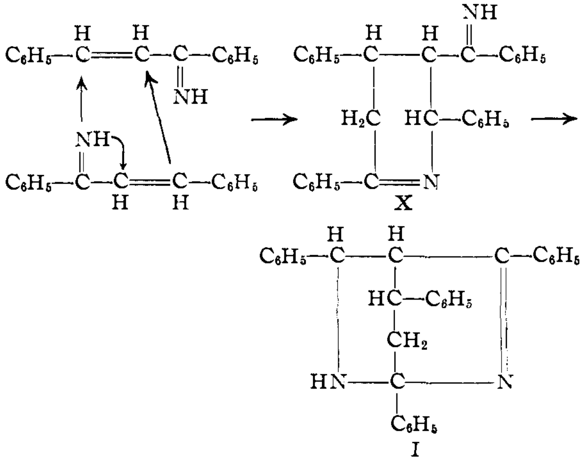
[9] Merz and Richter, *Arch. Pharm.*, 294 (1937).



tained was a white crystalline substance melting at 169°. The analysis corresponded to that of the expected 2,4,6-triphenyl-3-benzoylpyridine (VII). The compound was chemically very inert. This inert character was found in all the compounds of the triphenylpyridine type which were prepared.

The existence of the Grignard absorbing group was verified by treatment of compound V with methyl and phenyl Grignard reagents. The respective addition products, 2,4,6-triphenyl-2,3,4,5-tetrahydropyridyl-3-methylphenylcarbinol (VIII) and 2,4,6-triphenyl-2,3,4,5-tetrahydropyridyl-3 diphenylcarbinol (IX) as expected, showed the presence of one active hydrogen per molecule and no Grignard absorbing groups. The phenyl addition product (IX), like I, underwent decomposition when dehydrogenated with sulfur. The two fragments isolated from this reaction were 2,4,6-triphenylpyridine (III) and benzophenone.

The dimerization of styryl phenyl ketimine to form structure I was pictured as taking place in such a manner that the pyrimidine ring was first formed and the structure completed by internal addition of the phenylethylene group. As is indicated below, structure I might also be thought of as arising in such a manner that the pyridine ring was formed initially. It will be noted that it is necessary to postulate the existence of the pyridine compound X during the hydrolysis of I to V. It is thus necessary to consider structure X, itself, as an alternative to structure I. Structure X, 2,4,6-triphenyl-2,3,4,5-tetrahydropyridyl-3 phenyl ketimine would be expected to show the required one active hydrogen per molecule and while a structure must be devised for the nitroso derivative, there is some evidence in the literature for nitroso ketimines.[10] It also explains the derivatives containing the 2,4,6-triphenylpyridine nucleus but does not explain so satisfactorily the 2,4,6-triphenylpyrimidine obtained by sulfur dehydrogenation. As is evident from the Grignard reaction by phenylcyanoacetylene, the dehydro-analog of the compound must be unstable, breaking down to 2,4,6-triphenylpyrimidine. With this in mind, the dehydro-analog of X, 2,4,6-triphenylpyridyl-3 phenyl ketimine, was synthesized from 2,4,6-triphenyl-3-cyanopyridine[11] and phenylmagnesium bromide. It was found, like the other triphenylpyridine compounds, to be very stable and it did not rearrange to 2,4,6-triphenylpyrimidine.



A further argument favoring structure I over structure X is offered by a consideration of the

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[10] Lochte, Horeczy, Pickard and Barton, THIS JOURNAL, **70**, 2012 (1948).

[11] v. Meyer, *J. prakt. Chem.*, [2] **78**, 527 (1908).

ultraviolet absorption spectrum of the compound. If structure X were the correct one, it would be expected that the spectrum would be close to that of 2,4,6-triphenyl-3-benzoyl-2,3,4,5-tetrahydropyridine, (V) Fig. 1, since the spectrum of 2,4,6-triphenylpyridyl-3 phenyl ketimine is nearly identical with that of 2,4,6-triphenyl-3-benzoylpyridine (VII), Fig. 2. This is not the case.

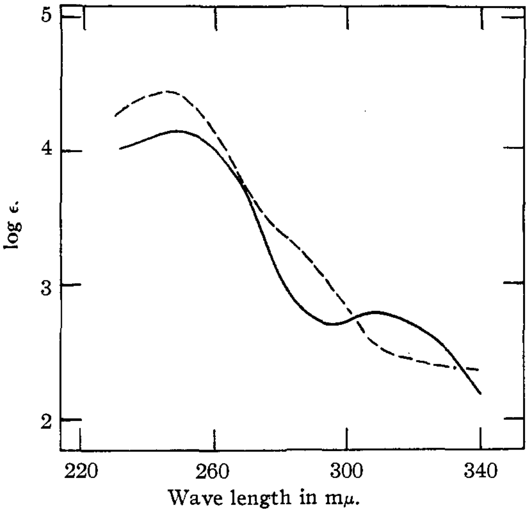

Fig. 1.—Ultraviolet absorption spectra in absolute ethanol: ——, the dimer of styryl phenyl ketimine; - - - -, 2,4,6-triphenyl-3-benzoyl-2,3,4,5-tetrahydropyridine.

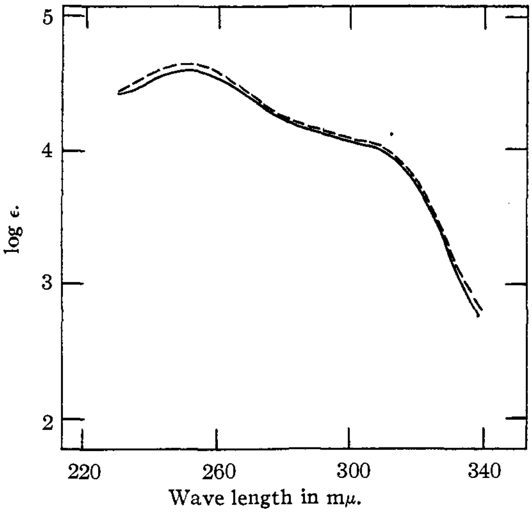

Fig. 2.—Ultraviolet absorption spectra in absolute ethanol: ——, 2,4,6-triphenylpyridyl-3 phenyl ketimine; - - - -, 2,4,6-triphenyl-3-benzoylpyridine.

Experimental Part[12]

2,4,6-Triphenyl-2,5-endo-(2′-phenylethylene)-2,3,4,5-tetrahydropyrimidine (I) from Phenylmagnesium Bromide and Styryl Cyanide.—To 147 g. (1.14 moles) of styryl cyanide[13] (distilled 100–160° (10 mm.)) in 125 cc. of absolute ether, was added under nitrogen 570 cc. (1.29 moles) of 2.25 molar phenylmagnesium bromide in ether at the rate of one drop per second so that the mixture refluxed gently. A deep red solution was immediately formed. After five hours a dense precipitate was thrown down. The entire mixture was hydrolyzed with an ice-cold aqueous solution of ammonium chloride. The mixture separated into a red ether solution, a cream-colored solid and an aqueous solution. The solid weighed 61 g., was very sparingly soluble in cold ethanol and melted at 180–182°. The ether layer together with an ether extract of the aqueous layer was evaporated to a red gum. This gum was dissolved in absolute ethanol. After standing for several days, 35 g. more of the above product was obtained as a white crystalline deposit. No benzalacetophenone was obtained from the residual solution. The total yield of compound I was 96 g., 0.23 mole (40%).

Anal. Calcd. for $C_{30}H_{26}N_2$: C, 86.92; H, 6.32; N, 6.75; mol. wt., 414. Found: C, 86.97; H, 6.47; N, 6.80; mol. wt., 410 ± 20.

2,4,6-Triphenyl-2,5-endo-(2′-phenylethylene)-2,3,4,5-tetrahydropyrimidine (I) from Styrylmagnesium Bromide and Benzonitrile.—To 115 cc. (0.072 mole) of 0.62 molar styrylmagnesium bromide in ether was added under nitrogen 5.15 g. (0.050 mole) of benzonitrile (distilled 88–90° (15 mm.)) in 50 cc. of absolute ether. Two layers were formed: a deep red layer amounting to about 10 cc. at the bottom and above it the rest of the mixture as a pale red solution. The mixture was stirred ten hours and then hydrolyzed with an ice-cold aqueous solution of ammonium chloride. There were formed two layers; a red ether solution and a yellowish aqueous solution. The ether solution combined with an ether extract of the aqueous layer was evaporated at 100° first at atmospheric pressure and then at 15 mm. The residual oil was dissolved in 200 cc. of absolute ethanol. After the solution had been kept at room temperature for several days, there was obtained a yield of fine crystals weighing 2.72 g. and melting at 179–181°. A mixed melting point showed this material to be identical with compound I obtained from the styryl cyanide–phenylmagnesium bromide reaction. The yield was 0.0066 mole (26%). Isolation of the compound in this case was complicated by the presence of *trans–trans*-diphenylbutadiene which was formed in 20% yield from the styrylmagnesium bromide.

Nitrosation of I.—A solution of 10.00 g. (0.145 mole) of sodium nitrite in 300 cc. of methanol plus 10 cc. of water was added to a solution of 1.00 g. (0.0024 mole) of I in 300 cc. of methanol. The mixture was acidified with 8.7 g. (0.145 mole) of acetic acid and stirred for twenty hours. The solvent was evaporated and the residue washed with water and ethanol. There was obtained 1.03 g., 0.0023 mole (96%) of the mononitroso derivative melting at 186–188°. The compound gave a positive Liebermann test. It was very difficult to purify.

Anal. Calcd. for $C_{30}H_{25}N_3O$: C, 81.24; H, 5.68; N, 9.47. Found: C, 82.00; H, 5.86; N, 9.54.

By treatment with concentrated sulfuric acid, the compound was converted in 60% yield to V.

2,4,6-Triphenylpyrimidine from the Sulfur Dehydrogenation of I.—A mixture of 5.00 g. (0.0120 mole) of I with 0.80 g. (0.025 g. atom) of sulfur was heated at 180–190° at 8 mm. pressure for eight hours. The vacuum train led through a trap immersed in Dry Ice. At the end of the experiment there was obtained from the trap 0.60 g. of a liquid which distilled at 130–140°. This liquid was fractionated and 0.42 g., 0.0040 mole (33%) of pure styrene was obtained and identified as the dibromo derivative. The crude yield was 47%. The residue from the reaction flask was dissolved in acetone, leaving most of the excess sulfur behind. This solution was stirred with mercury to get rid of the sulfur compounds in solution, filtered, evaporated to a gum and crystallized from ethanol. There was obtained 3.24 g., 0.0106 mole (88%) of 2,4,6-triphenylpyrimidine which was identified by mixed melting point with that synthesized according to the method of Asahina and Kuroda.

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[12] All melting points are corrected against reliable standards.

[13] Ghosez, *Bull. soc. chim. Belg.*, **41**, 477 (1932).

Anal. Calcd. for $C_{22}H_{16}N_2$: C, 85.79; H, 5.24; N, 9.09. Found: C, 85.65; H, 5.25; N, 9.11.

2,4,6-Triphenylpyridine from the Pyrolysis of I.—In a test-tube whose side arm led into a condensing system containing a trap with an ice-bath followed by a trap with a Dry Ice-bath, was placed 1.50 g. (0.0036 mole) of I. The compound was refluxed gently at about 300° for one-half hour. At the end of this time there was a distillate in each trap and a red gum in the distilling tube. The gum was dissolved in ethanol and on cooling there was obtained 0.65 g., 0.0021 mole (59%) of 2,4,6-triphenylpyridine identical with that synthesized according to the method of Reddelien. The liquid in the trap at zero degrees weighed 0.134 g., and most of it distilled between 100 and 115°. This distillate was nitrated and the product shown to be identical with 2,4,6-trinitrotoluene. The slight residue in the zero degree trap was treated with 2,4-dinitrophenylhydrazine. The product was identical with benzaldehyde-2,4-dinitrophenylhydrazone. The total yield of toluene and benzaldehyde was 45%. The condensate in the Dry Ice-trap smelled strongly of ammonia. It was distilled at −25° into standard acid and titrated. The yield calculated as ammonia was 67%.

2,4,6-Triphenyldibromopyridine.—To a solution of 0.10 g. (0.0024 mole) of I in 10 cc. of carbon tetrachloride was added a large excess of bromine in carbon tetrachloride. A red gum was thrown out of solution and redissolved by the addition of 1 cc. of absolute ethanol. After allowing the mixture to stand for one day, the solvent and excess bromine were evaporated. The residual gum was dissolved in 2 cc. of absolute ethanol. After several days there was precipitated 0.07 g., 0.00015 mole (63%) of triphenyldibromopyridine which melted at 205–206°.

Anal. Calcd. for $C_{23}H_{15}NBr_2$: C, 59.38; H, 3.25; N, 3.01. Found: C, 58.76, 60.76; H, 3.25, 3.59; N, 3.15, 2.99.

A small yield of benzaldehyde-2,4-dinitrophenylhydrazone was obtained from the mother liquor, by treatment with 2,4-dinitrophenylhydrazine. The triphenyldibromopyridine was reduced quantitatively to 2,4,6-triphenylpyridine by treatment with a 5% solution of sodium in liquid ammonia. Otherwise it was a very resistant compound—even to boiling with zinc dust.

2,4,6-Triphenylpyrimidine from Phenylmagnesium Bromide and Phenylcyanoacetylene.—To 2.8 g. (0.022 mole) of phenylcyanoacetylene[14] in 75 cc. of absolute ether was added all at once 0.39 mole of phenylmagnesium bromide in ether. The mixture was stirred and refluxed for twenty-four hours and then hydrolyzed with an ice-cold aqueous solution of ammonium chloride. An ether layer and an aqueous layer were formed. The ether layer combined with an ether extract of the aqueous layer was evaporated and the residual gum dissolved in absolute ethanol. There was obtained 0.39 g., 0.0013 mole (6%) of 2,4,6-triphenylpyrimidine which melted at 181–182° and which was identical with that synthesized by the method of Asahina and Kuroda.

2,4,6-Triphenylpyridyl-3 Phenyl Ketimine.—To a solution of 11.6 g. (0.035 mole) of 2,4,6-triphenyl-3-cyanopyridine[11] in 500 cc. of absolute benzene was added 100 cc. (0.25 mole) of an ether solution of phenylmagnesium bromide. The ether was distilled off and the reaction mixture refluxed at 80° since no reaction took place at the reflux temperature of ether. After the mixture had refluxed for twenty hours it was hydrolyzed with an ice-cold aqueous solution of ammonium chloride. The benzene was distilled off and the residual oil dissolved in 500 cc. of 95% ethanol. From this solution was obtained 10.1 g., 0.025 mole (72%) of 2,4,6-triphenylpyridyl-3 phenyl ketimine. A small quantity of this material was crystallized from methanol to a constant melting point of 169.9–170.3°.

Anal. Calcd. for $C_{30}H_{22}N_2$: C, 87.88; H, 5.41; N, 6.83. Found: C, 86.03; H, 5.45; N, 6.86.

The compound is insoluble in 5% hydrochloric acid but soluble in 15% hydrochloric acid. It was not changed by heating at 100° for three hours in concentrated hydrochloric acid. The compound released one mole equivalent of hydrogen when treated with lithium aluminum hydride. Its ultraviolet absorption spectrum was nearly identical with that of 2,4,6-triphenylpyridyl-3 phenyl ketone. The compound was also produced from the reaction of 2,4,6-triphenyl-3-cyanopyridine with phenyllithium in 76% yield by stirring in an ether–benzene solution at room temperature for seventeen hours.

2,4,6-Triphenyl-3-benzoyl-2,3,4,5-tetrahydropyridine (V).—To 125 cc. of 37% hydrochloric acid was added 15.00 g. (0.0362 mole) of I. The compound slowly dissolved. After stirring for one hour a dense white precipitate formed. The mixture was poured into 2 l. of distilled water and the white precipitate centrifuged until a gummy cake was formed. This was dissolved in 50 cc. of 95% ethanol, and upon the addition of 1800 cc. of ether there was obtained as a crystalline deposit 13.20 g., 0.0292 mole (81%) of the hydrochloride of V. The free base was obtained quantitatively by treating this compound in methanol solution with the calculated quantity of sodium methoxide.

Anal. Calcd. for $C_{30}H_{25}NO$: C, 86.71; H, 6.06; N, 3.37. Found: C, 87.13; H, 5.86; N, 3.43.

The compound was isolated in two forms, apparently polymorphic, melting, respectively, at 145 and 158°. The 145° form was converted in solution to the 158° form by seeding with the latter. Indeed, after the laboratory had become contaminated with seeds of the 158° form, it was found impossible to isolate the 145° form. Both forms could be converted to the same picrate which melted at 188–189°. The compound formed an oxime which melted with decomposition at 156°.

N-Benzoyl-2,4,6-triphenyl-3-benzoyl-1,2,3,4-tetrahydropyridine.—To 1.49 g. (0.010 mole) of benzoyl chloride was added 0.10 g. (0.0024 mole) of V. The compound dissolved quickly and to this solution were added 10 cc., 0.025 mole of 10% sodium hydroxide solution and 50 cc. of water. When the benzoyl chloride was hydrolyzed, the mixture was extracted with ether. The ether extract, on evaporation, yielded 0.09 g., 0.007 mole (70%) of the benzoyl derivative melting at 210–215°. The compound was very difficult to purify. After several crystallizations from ethanol, 0.02 g. was obtained which melted at 226–227°.

Anal. Calcd. for $C_{37}H_{29}NO_2$: C, 85.63; H, 5.58; N, 2.67. Found: C, 84.24; H, 5.26; N, 2.79.

The compound was quantitatively hydrolyzed by hot acid to V. A small yield of benzoic acid was also isolated from the hydrolysis mixture.

2,4,6-Triphenyl-2,3,4,5-tetrahydropyridyl-3-methylphenylcarbinol.—To 0.16 g. (0.00145 mole) of V in 100 cc. of absolute ether was added an excess of methylmagnesium chloride in ether. The mixture was allowed to stir for twenty hours and was then hydrolyzed with an aqueous solution of ammonium chloride. The ether solution combined with an ether extract of the water layer was evaporated. There was obtained 0.60 g., 0.140 mole (97%) of the methyl Grignard addition product melting at 155–163°. After crystallization from isopropyl ether, dioxane plus water, isoamyl ether and 90–100° petroleum ether there was obtained 0.27 g. melting at 163.5–165.5°.

Anal. Calcd. for $C_{31}H_{29}NO$: C, 86.38; H, 6.78; N, 3.25. Found: C, 86.37; H, 6.58; N, 3.39.

2,4,6-Triphenyl-2,3,4,5-tetrahydropyridyl-3-diphenylcarbinol.—To a solution of 2.00 g. (0.0048 mole) of V in 250 cc. of absolute ether was added 0.012 mole of phenylmagnesium bromide in ether. After stirring for ten hours, the mixture was hydrolyzed with an ice-cold aqueous ammonium chloride solution. The ether layer combined with an ether extract of the aqueous layer was evaporated to an orange oil. This oil was dissolved in 20 cc. of acetone and water added until crystallization began. There were obtained 1.69 g., 0.0034 mole (71%) of the phenyl addition product melting at 230–235°. After crystalliza-

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[14] Grignard and Courtot, *Bull. soc. chim. France*, [4] **17**, 230 (1915).

tion from isoamyl ether and diethyl ether there was obtained 1.16 g. melting at 235–236°.

Anal. Calcd. for $C_{36}H_{31}NO$: C, 87.59; H, 6.33; N, 2.83. Found: C, 88.37; H, 6.15; N, 2.83.

Decomposition of 2,4,6-Triphenyl-2,3,4,5-tetrahydropyridyl-3-diphenylcarbinol.—A mixture of 1.50 g. (0.0030 mole) of 2,4,6-triphenyl-2,3,4,5-tetrahydropyridyl-3-diphenylcarbinol with 1.00 g. (0.031 g. atom) of sulfur was heated at about 300° for one hour. From the reaction mixture was obtained by vacuum distillation 0.33 g., 0.0018 mole (60%) of benzophenone which was identified by mixed melting point and by preparation of the 2,4-dinitrophenylhydrazone. From the distillation residue was obtained 1.01 g. of 2,4,6-triphenylpyridine contaminated with benzophenone. After two crystallizations from ethanol there was obtained 0.69 g., 0.0024 mole (75%) of 2,4,6-triphenylpyridine which was identified by mixed melting point and by preparation of the picrate.

2,4,6-Triphenyl-3-benzoylpyridine.—A mixture of 1.00 g. (0.0024 mole) of V and 2.00 g. (0.062 g. atom) of sulfur was heated for two hours until no more hydrogen sulfide was evolved. The product in the flask was extracted with six portions, each 50 cc., of boiling methanol. The extract was distilled to a volume of 30 cc. and after having stood for twenty-four hours deposited 0.92 g., 0.0022 mole (92%) of 2,4,6-triphenyl-3-benzoylpyridine melting at 157–160°. This material was freed from sulfur by stirring it in acetone solution with mercury. After several crystallizations from ethanol it melted at 169.0–169.5°.

Anal. Calcd. for $C_{30}H_{21}NO$: C, 87.56; H, 5.14; N, 3.40. Found: C, 87.53; H, 5.20; N, 3.34.

Summary

The dimer of styryl phenyl ketimine produced by neutral hydrolysis of the Grignard addition product from phenylmagnesium bromide and styryl cyanide has been found by degradation methods to be 2,4,6-triphenyl-2,5-endo-(2′-phenylethylene)-2,3,4,5-tetrahydropyrimidine.

The product from the pyrolysis of this compound with sulfur is 2,4,6-triphenylpyrimidine. When phenylcyanoacetylene is treated with phenylmagnesium bromide, 2,4,6-triphenylpyrimidine is obtained rather than 2,4,6-triphenyl-2,5-endo-(2′-phenylacetylene)-2,3-dihydropyrimidine. Since the latter would be expected to be unstable, this indicates that the reaction series may be typical for α,β-unsaturated ketimines.

The acid hydrolysis of 2,4,6-triphenyl-2,5-endo-(2′-phenylethylene)-2,3,4,5-tetrahydropyrimidine leads to 2,4,6-triphenyl-3-benzoyl-2,3,4,5-tetrahydropyridine. The reactions of this compound with Grignard reagents are normal and substantiate the original proof of structure, but the reaction with benzoyl chloride involves an abnormality which may be typical of tetrahydropyridines.

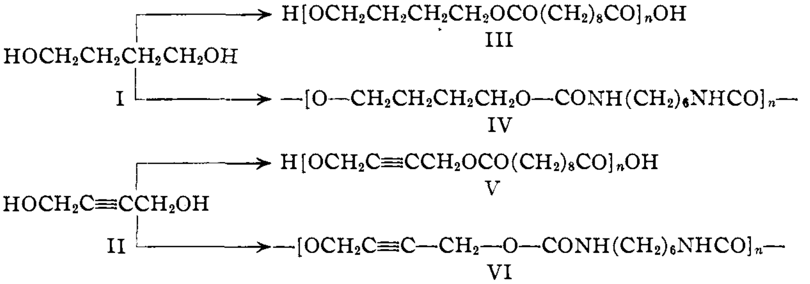
Toronto, Ontario Received September 22, 1949

[Contribution from the Noyes Chemical Laboratory, University of Illinois]

The Effect of an Acetylenic Unit on the Physical Properties of Polyesters and Polyurethans

By C. S. Marvel and John H. Johnson[1]

In order to learn what change in the physical properties of a polymer is produced when a regularly recurring $-CH_2CH_2-$ unit is replaced by a $-C{\equiv}C-$ unit, we have synthesized the polysebacates and the polyurethans from hexamethylene diisocyanate with butane-1,4-diol (I) and with 2-butyne-1,4-diol (II).



$$HOCH_2CH_2CH_2CH_2OH\ (I) \longrightarrow H[OCH_2CH_2CH_2CH_2OCO(CH_2)_8CO]_nOH\ (III)$$

$$HOCH_2CH_2CH_2CH_2OH\ (I) \longrightarrow -[O-CH_2CH_2CH_2CH_2O-CONH(CH_2)_6NHCO]_n-\ (IV)$$

$$HOCH_2C{\equiv}CCH_2OH\ (II) \longrightarrow H[OCH_2C{\equiv}CCH_2OCO(CH_2)_8CO]_nOH\ (V)$$

$$HOCH_2C{\equiv}CCH_2OH\ (II) \longrightarrow -[OCH_2C{\equiv}C-CH_2-O-CONH(CH_2)_6NHCO]_n-\ (VI)$$

The polytetramethylene sebacate (III) was prepared readily by standard ester interchange technique[2] from the glycol and dimethyl sebacate with litharge as the catalyst.[3] When the same procedure was tried with 2-butyne-1,4-diol, an insoluble polyester was obtained due to some secondary reactions which appeared to involve the triple bond. A low molecular weight soluble polyester was obtained from the acetylenic glycol in the ester interchange reaction when barium oxide was used as a catalyst. Direct esterification of the glycol by heating with sebacic acid appeared to be better than ester interchange as a method of preparing the acetylenic polyester. The intrinsic viscosity of the highest molecular weight acetylenic polyester which was obtained was 0.19, so the saturated ester was prepared with approximately the same intrinsic viscosity (0.26) in order that polymers of nearly equal size could be compared.

The polyurethans (IV and VI) were prepared from the glycols (I and II) and hexamethylene diisocyanate in chlorobenzene solution by the method used by Baeyer[4] for this type of polymer. Baeyer has described the polyurethans from tetramethylene glycol, but since his paper is not

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[1] Allied Chemical and Dye Corporation Fellow, 1948–1949.

[2] (a) Carothers and Arvin, This Journal, **51**, 2560 (1929); (b) Hardy, *J. Soc. Chem. Ind.*, **67**, 426 (1948).

[3] Harber and Yoran, *Ind. Eng. Chem.*, **37**, 953 (1945).

[4] Otto Baeyer, private communication, 1947; B. I. O. S. Final Reports 1947 and 1948; C. I. O. S. Report File No. XXIX-12 (Appendix); U. S. Patent 2,343,808 (1944); *C. A.*, **38**, 3393 (1944).