

The pyridines had identical ultraviolet spectra in acetonitrile exhibiting absorption maxima at 271 $m\mu$ ($\log \epsilon$ 4.2) and 315 $m\mu$ ($\log \epsilon$ 4.4).

Table I records the pertinent data for each pyridine prepared by this procedure.

B. General Procedure from the Potassium Salt of 1,1,3,3-Tetracyanopropene.—To a solution of the sodium alkoxide prepared by treating sodium metal (0.002 g.-atom) in about 20 ml. of the dry alcohol, the potassium salt of IV⁹ (0.0055 mole) was added. The solution was refluxed for the desired period and the solvent was then removed with a Rinco evaporator. Water was added, and the solid which separated was removed by filtration. The infrared spectra of these solids were identical to those of the pyridines previously prepared. The pertinent data for each run is presented in Table II.

In the case of the *t*-butoxypyridine the same procedure was followed except that potassium metal was substituted for sodium. The infrared spectra of this product was similar to those of the pyridine systems previously prepared; the ultraviolet spectra in acetonitrile were identical. The compound commenced to change color at about 215° and melted at about 320°.

C. Isolation of the Salt of IV. (a) **From Malononitrile-Chloroform-Sodium Isopropoxide.**—After the reaction components were combined as in procedure A, the mixture was stirred for 2 hr. at room temperature and then refluxed for 15 min. The precipitated solid was filtered from the hot solution. The filtrate was evaporated to dryness with a Rinco evaporator and yielded a solid whose infrared spectrum indicated the presence of the salt of IV along with the sodium salt of malononitrile. The ultraviolet spectrum exhibited a molar extinction coefficient of 14,000, which corresponds to 30% of the salt of IV (molar extinction coefficient of the potassium salt of IV in methanol is 35,000).

The crude sample was dissolved in 150 ml. of methanol, and 150 ml. of ether was added to this solution. The solid which separated was filtered off and the filtrate was concentrated to 25 ml. and placed in the freezer. On standing a solid separated. The infrared spectrum of this sample was identical to the spectrum of the pure potassium salt of IV, except for a weak band at 6.2 μ . An additional amount of solid which had the same infrared spectrum as the initial product was collected from the filtrate on standing. The combined weights of these solids represent a 27% yield.

(b) **From Malononitrile-Chloroform-Potassium *t*-Butoxide.**—The components were combined according to procedure A using potassium (0.063 g.-atom) and the corresponding amount of the other reactants. The mixture was stirred at room temperature overnight and then refluxed for 1 hr. The precipitated solid was removed by filtration, and a solid separated from the filtrate on standing. This solid was taken up in acetone and some insoluble material was removed by filtration. The filtrate was concentrated, and an oil separated. On addition of ether a solid formed. The ultraviolet spectrum indicated this to consist of 66% of the salt of IV (20% over-all yield).

D. Reaction of the Sodium Salt of Malononitrile with Sodium Trichloroacetate.—The sodium salt of malononitrile was prepared by treating a 50% dispersion of sodium hydride in mineral oil (0.01 mole) with malononitrile (0.01 mole) in about 75 ml. of the dry solvent. An equimolar amount of sodium trichloroacetate was added and the mixture was refluxed until the evolution of carbon dioxide ceased. Then the precipitated solid was filtered and analyzed by ultraviolet and infrared spectroscopy.

In the case of 1,2-dimethoxyethane as solvent the infrared spectrum of this solid was identical to the sodium salt of malononitrile, and the ultraviolet spectrum of the sample exhibited no absorption at 344 $m\mu$, indicating the absence of the sodium salt of IV.

In the case of tetrahydrofuran as solvent the ultraviolet absorption corresponded to about 1% of the salt of IV (ϵ of 420 at 344 $m\mu$).

An additional run was performed using 20 ml. of tetrahydrofuran in the aforementioned procedure and the reflux period was shortened to 20 min. The solid which separated from the solution in a 90% yield was identified as the sodium salt of malononitrile by infrared analysis.

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The Reaction of Benzyne with Methyldiphenylphosphine. A New Route to Triphenylphosphinemethylene¹

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The electrophilic nature of benzyne is well documented.³ Of particular interest to this discussion is the reaction of benzyne with tertiary amines, which gave products which appear to have been obtained *via* the nitrogen ylids formed by primary coordination of the nitrogen lone pair with benzyne, followed by proton transfer to the ring from an alkyl group on the nitrogen atom.⁴ More recently Franzen, *et al.*,⁵ have shown that benzyne and dimethyl sulfide react to give a sulfur ylid, $C_6H_5(CH_3)S^{\oplus}-CH_2^{\ominus}$, which appears to be stabilized by the presence of an organolithium compound. The interactions of benzyne with triphenylphosphine⁴ and with phosphite esters⁶ have been described, but the obvious possibility of preparing a phosphinealkylidene by the reaction of benzyne with an alkyl-substituted phosphine has not yet been demonstrated.

It is the purpose of this note to show that phosphinealkylidenes in principle are accessible through a benzyne route. In practice, however, this route to triphenylphosphinemethylene itself is impractical because of complicating side reactions. Generation of benzyne by the *o*-bromofluorobenzene-magnesium reaction in tetrahydrofuran⁴ in the presence of an equimolar amount of methyldiphenylphosphine at 60° gave a red solution. Addition of cyclohexanone, followed by heating of the solution at reflux for 1.5 hr., resulted in a light tan precipitate, but the red color was not discharged. Distillation of volatiles at reduced pressure and gas chromatographic analysis of the distillate showed that methylenecyclohexane had been formed in 14% yield. Presumably the following sequence accounts for this product (see p. 2464, col. 1).

The low yield of methylenecyclohexane may be the result of several complicating factors. In particular, the following were considered as possibly important: (1) deactivation of I by reaction with magnesium halide (see ref. 4); or (2) competition of triphenylphosphinemethylene, itself a potent nucleophile, for the benzyne as it was being generated after the initial stages of the

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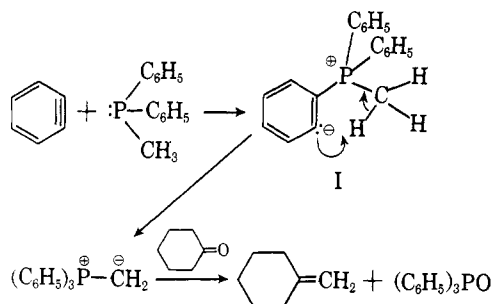
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reaction. In order to obtain more information concerning this question, benzyne was generated in the presence of an equimolar amount of methyltriphenylphosphine using the *o*-bromofluorobenzene-lithium amalgam procedure.⁷ Again, the yield of methylenecyclohexane obtained on treating the reaction mixture with cyclohexanone was low (21%). Since the deactivation of I by lithium bromide does not seem too likely, we tend toward the conclusion that it is a reaction between benzyne and triphenylphosphinemethylene which serves to complicate matters. Further evidence favoring this view was obtained in an experiment in which methyltriphenylphosphine was allowed to compete more effectively for the benzyne (generated by the lithium amalgam procedure) by having the phosphine present in large excess (methyltriphenylphosphine to *o*-bromofluorobenzene ratio = 11). In this case methylenecyclohexane was obtained in 52% yield.

The reaction of phosphinealkylidenes with benzyne is receiving further attention in these laboratories.

Experimental

Preparation of Methyltriphenylphosphine.—To a stirred solution of 75 g. (0.33 mole) of diphenylchlorophosphine in 100 ml. of ether at 0° (under nitrogen) was added 245 ml. (0.33 mole) of 1.35 *N* methylolithium in ether over a period of 2 hr. The ice bath was removed and the mixture stirred for an additional 30 min. The organic layer was decanted and fractionally distilled to give 52 g. (78%) of methyltriphenylphosphine, b.p. 108–110° (0.15 mm.); lit.⁸ b.p. 120–122° (0.15 mm.). The product was characterized by conversion to dimethyltriphenylphosphonium iodide, m.p. 253–255° (lit.⁸ m.p. 242–243°); a mixture melting point with an authentic sample was undepressed.

The Reaction of Benzyne (via the Magnesium Route) with Methyltriphenylphosphine.—Into a 200 ml., three-necked flask equipped with a mechanical stirrer, an addition funnel, and a reflux condenser, all maintained under an atmosphere of dry nitrogen, were placed 1.46 g. (0.06-g.-atom) of magnesium turnings and 50 ml. of tetrahydrofuran, freshly distilled from lithium aluminum hydride. The magnesium was activated with 3 drops of 1,2-dibromoethane, and then 12.0 g. (0.06 mole) of methyltriphenylphosphine was added with a syringe. The mixture was heated to 60°, and a solution of 8.95 g. (0.05 mole) of *o*-bromofluorobenzene in 30 ml. of anhydrous tetrahydrofuran was added, dropwise with stirring, over a period of 1 hr. The resulting burgundy red solution was stirred at reflux for 30 min.; it gave a negative Gilman Color Test I. The reaction mixture was cooled to room temperature, and 9.1 g. (0.1 mole) of cyclohexanone was added during 15 min. The mixture refluxed slightly and a tan precipitate formed, but the red color was not discharged. The reaction mixture was stirred while a gentle reflux was maintained for 3 hr., then was filtered under nitrogen. The tan residue was washed with tetrahydrofuran. All volatile material was removed from the combined filtrate and washings by trap-to-trap distillation at 85° (0.3 mm.). Analysis of the distillate by gas chromatography, using xylene as an internal standard, showed that 6.93 mmoles (13.8%) of methylenecyclohexane and 1.13 mmoles of cyclohexanone were

present. Methylenecyclohexane was identified by its retention time and infrared spectrum. Three similar reactions with reaction times of 1.5, 2.5, and 15 hr. gave methylenecyclohexane in yields of 13.8, 10.8, and 14.2%, respectively.

The Reaction of Benzyne (via the Lithium Amalgam Route) with Methyltriphenylphosphine.—Lithium amalgam, from 0.31 g. (0.045 g.-atom) of lithium and 125 g. of mercury, was prepared in a Schlenk tube under an argon atmosphere using the method of Wittig and Pohmer.⁷ To this was added a solution of 2.68 g. (0.015 mole) of *o*-bromofluorobenzene and 3.40 g. (0.017 mole) of methyltriphenylphosphine in 15 ml. of freshly distilled ether. The tube was sealed at atmospheric pressure (argon atmosphere) and shaken at room temperature for 24 hr. During this time the solution became dark red, and a very small amount of light-colored solid precipitated. The solution was decanted into a 100-ml. flask equipped with a reflux condenser and a side-arm inlet tube, maintained under an argon atmosphere. After the amalgam had been washed with 10 ml. of anhydrous ether and the washings combined with the solution, 2.94 g. (0.03 mole) of cyclohexanone in 5 ml. of ether was added and the mixture stirred at reflux under argon overnight. The resulting dark red solution was decanted from a cream-colored solid and separated into low [25–50°(0.3 mm.)] and high [50–85°(0.05 mm.)] boiling fractions by trap-to-trap distillation. Gas chromatographic analysis of the first fraction, using toluene as an internal standard, showed that 3.16 mmoles of methylenecyclohexane (21% based on the completely consumed *o*-bromofluorobenzene) had been formed. Analysis of the second fraction, 1.95 g., showed it to contain methyltriphenylphosphine, a minor amount of cyclohexanone, and another high boiling component which showed absorption in the infrared spectrum at 1725 cm.⁻¹; this suggests that it is a product of the base-catalyzed condensation of cyclohexanone itself.

Another experiment was carried out in the same manner in which the same quantities of lithium amalgam and *o*-bromofluorobenzene were allowed to react in the presence of 33.0 g. (0.165 mole) of methyltriphenylphosphine in 25 ml. of ether. Addition of 0.03 mole of cyclohexanone resulted in 7.85 mmoles (by gas chromatography) (52.4%) of methylenecyclohexane.

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A Novel Synthesis of 1,2,3-Triphenylisindole

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The synthesis of the remarkably stable *o*-quinoid compound 1,2,3-triphenylisindole (I) has been achieved only by the reaction of phenyllithium with 2,3-diphenylisindolone (II).¹ We have now prepared this isindole by a novel one-step process starting from the readily available 1,3-diphenylisobenzofuran (III).²

When furan III was mixed with an approximately equimolar amount of thionylaniline (IV) in benzene, a red color appeared immediately, indicative of a charge-transfer complex. After refluxing the mixture for thirty-six hours, none of the expected adduct (V) was obtained,³ and most of the furan was recovered

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