Experimental[3]

Preparation of Triphenylgermyllithium.—To a nitrogen-flushed flask was added 7.12 g. (0.0187 mole)[4] of tetraphenylgermane, 2.0 g. (0.288 g. atom)[5] of lithium wire, cut into 2–3 mm. lengths, and about 5 ml. of sodium-dried, redistilled ethylene glycol dimethyl ether. After about 40 minutes the reaction had started as was evidenced by the development of a brown color.[6] After the color deepened to a very dark brown (usually 1–2 hours after reaction began) an additional 20 ml. of solvent was added and the mixture was stirred until there was no evidence of unreacted solid (usually 4–5 hours after the reaction has begun).[7] The dark-colored solution was pipetted into a dropping funnel and the residual lithium washed with solvent, with the washings being added to the main solution.

Yields of products from many reactions of triphenylgermyllithium indicate that the reagent is obtained in approximately 70% yield. In no reaction has there been isolated any product from the phenyllithium which should be present from the cleavage of tetraphenylgermane with lithium. Presumably it is destroyed by reaction with the solvent.

Reactions of Triphenylgermyllithium. **With Methyl Triphenylgermanecarboxylate.**—A triphenylgermyllithium solution as prepared above from 7.12 g. of tetraphenylgermane was added portionwise to 1.82 g. (0.005 mole) of methyl triphenylgermanecarboxylate[8] dissolved in 20 ml. of ethylene glycol dimethyl ether. Immediately upon this addition, a gas was evolved vigorously which blackened a piece of filter paper moistened with a dilute solution of palladium chloride[9]; thus indicating that the gas was carbon monoxide. In addition, heat was generated and a white solid precipitated. When the addition was complete the mixture was stirred 18 hours then hydrolyzed by pouring it into a mixture of ammonium chloride and crushed ice. When the ice melted the mixture was filtered and the precipitate was washed with ether. The remaining solid weighed 2.5 g. and melted over the range 328–340°. Recrystallization from benzene gave 2.3 g. (75% yield based on methyl triphenylgermanecarboxylate) of hexaphenyldigermane (mixed melting point) melting 340–342°. The aqueous solution was extracted three times with ether and the combined ether washings were dried over anhydrous sodium sulfate. The solvent was removed by distillation leaving a small amount of oil from which no products have been isolated.

With a Deficiency of Diethyl Carbonate.—A solution of triphenylgermyllithium as prepared above was added portionwise to a stirring solution of 0.59 g. (0.005 mole) of freshly distilled diethyl carbonate dissolved in 20 ml. of ethylene glycol dimethyl ether. Carbon monoxide was again evolved vigorously (palladium chloride test), heat was generated and a white solid precipitated. After the addition was complete the mixture was stirred 12 hours then worked up as previously to yield 2.7 g. (88% based on diethyl carbonate) of hexaphenyldigermane melting 340–342°.

With an Excess of Diethyl Carbonate.—A repeat of the previous experiment using 1.18 g. (0.01 mole) of diethyl carbonate and triphenylgermyllithium from the cleavage of 3.81 g. (0.01 mole) of tetraphenylgermane gave 1.4 g. (47% based on tetraphenylgermane) of hexaphenyldigermane melting 338–340°. Working up the ether portions gave 0.45 g. of a substance as yet unidentified melting 98–99°.

Reaction of Triphenylsilyllithium with Methyl Triphenylgermanecarboxylate.—Triphenylsilyllithium was prepared in ethylene glycol dimethyl ether from 5.19 g. (0.01 mole) of hexaphenyldisilane in accordance with recent directions,[10] and added portionwise to 1.82 g. (0.005 mole) of methyl triphenylgermanecarboxylate dissolved in 20 ml. of ethylene glycol dimethyl ether. Carbon monoxide was evolved, *heat was generated and a solid precipitated.* Working up the mixture as described previously gave 2.45 g. (84% based on methyl triphenylgermanecarboxylate) of triphenylsilyltriphenylgermane melting 357–359°. A mixed melting point with an authentic sample prepared from the reaction of triphenylsilylpotassium[11] with triphenylchlorogermane showed no depression.

Acknowledgment.—The authors wish to express their appreciation to the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio, for their financial support of this work.

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[3] All melting points are uncorrected. Reactions involving organometallic compounds were carried out in an atmosphere of dry, oxygen-free nitrogen.

[4] Runs made using amounts of tetraphenylgermane in excess of 40 g. gave poor results due to the fact that the two phase reaction requires such long reaction time that side reactions involving the soluble triphenylgermyllithium, the solvent and the lithium metal reduced the concentration of the triphenylgermyllithium.

[5] A large excess of lithium is desirable due to the fact that tetraphenylgermane is insoluble in the solvent and the large metal excess permits better contact of the reactants.

[6] In a large number of preparations it has been observed that the time required for the color to appear varies from 5 minutes to 2.5 hours. The reaction starts faster if the amount of solvent added initially is kept to a minimum. Reactions which failed to start when too much solvent was added initially developed a color when the excess solvent was removed by evaporation in a stream of nitrogen.

[7] It has been observed that the concentration of triphenylgermyllithium decreases with time, presumably by reaction with the solvent, so it is necessary to use the reagent as soon as it is prepared.

[8] A. G. Brook and H. Gilman, This Journal, **76**, 77 (1954).

[9] R. Nowicki, *Chem. Z.*, **35**, 1120 (1911).

[10] A. G. Brook and H. Gilman, This Journal, **76**, 278 (1954).

[11] H. Gilman and T. C. Wu, *J. Org. Chem.*, **18**, 753 (1953).

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Studies on the Reversal of the Mannich Reaction

BY KENNETH A. KUN[1] AND PAUL E. SPOERRI

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Taber,[2] while studying the addition of bases to polar hydrocarbons, attempted to cause the addition of piperidine to the exocyclic double bond of 2,3,4,5-tetraphenylfulvene. Instead of the desired product, 1-(N-piperidylmethyl)-2,3,4,5 tetraphenylcyclopenta - 2,4 - diene,2,3,4,5 - tetraphenylcyclopenta-2,4-diene was obtained. This reaction appeared to be a reversal of the formation of a Mannich base of a hydrocarbon. Taber went on to show that 2,5-diphenyl-3,4-(4′-methoxyphenyl)-fulvene reacted in the same manner. The discovery of this type of reversal of the Mannich reaction and its application to the synthesis of two tetraphenylcyclopentadienes with yields better than previously reported[3] gave hopes that this was a superior general method of synthesis for substituted tetraphenylcyclopentadienes through the usually available tetraphenylcyclones. The preparation of some *para* substituted tetraphenylfulvenes and their conversion to the corresponding dienes were studied in this work.

2,4,5-Triphenyl-3-(4′-tolyl)-fulvene (I) was prepared from 2,4,5-triphenyl-3-(4′-tolyl)-cyclopenta-2,4-diene-1-one[4,5] by the formation of the corresponding tertiary carbinol *via* the Grignard reaction using methylmagnesium iodide which in turn was dehydrated easily to the desired fulvene. Treating

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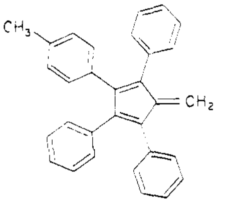
[1] The material reported here is a portion of the thesis for the degree of Master of Science in Chemistry presented by Kenneth A. Kun to the Graduate School of the Polytechnic Institute of Brooklyn, September, 1954.

[2] D. Taber, E. I. Becker and P. E. Spoerri, This Journal, **76**, 776 (1954).

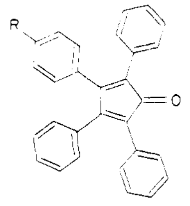
[3] L. Mehr, Dissertation, Polytechnic Institute of Brooklyn, June, 1953.

[4] D. Trucker, Dissertation, Polytechnic Institute of Brooklyn, June, 1951.

[5] W. Dilthey, O. Trösken, K. Plum and W. Schommer, *J. prakt. Chem.*, **141**, 331 (1934).



I



II

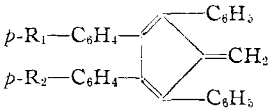
this fulvene with dry piperidine gave good yields of 2,4,5-triphenyl-3-(4′-tolyl)-cyclopenta-2,4-diene. In a similar manner 2,5-diphenyl-3,4-bis-(4′-tolyl)-fulvene was treated with dry piperidine to yield the corresponding diene. For an additional proof of structure of the dienes, 2,5-diphenyl-3,4-bis-(4′-tolyl)-fulvene was prepared both by the method described above[6] and by preparing 2,5-diphenyl-3,4-bis-(4′-tolyl)-cyclopenta-2,4-diene[3] which when refluxed with formaldehyde yielded the desired fulvene. In both cases the fulvene showed the reversal to give the diene. These fulvenes were characterized by their intense red color and their ultraviolet absorption spectra as shown in Table Ia. The dienes compared to those made by Mehr[3] and were easily converted back to the original tetraphenylcyclones through the anil.

Addition of methylmagnesium iodide to substituted tetraphenylcyclones II (where R = Cl, $(CH_3)_2N$ and CH_3O),[4,5] gave carbinols which differed slightly in chemical characteristics from the carbinols which were unsubstituted or methyl substituted. Analysis showed these Grignard reaction products to have the empirical formula of the desired products and ultraviolet, Table Ib, and infrared spectra compare favorably to known compounds of this type. Infrared spectra showed a band at 2.8–3.0 μ but none in the region 5.6–6.1 μ indicating the presence of a hydroxyl group and the absence of the carbonyl group. Numerous attempts to dehydrate these Grignard products have failed to give the desired fulvenes.

TABLE I

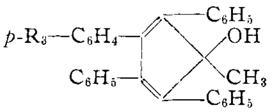
ULTRAVIOLET ABSORPTION SPECTRA

a. Fulvenes



R_1	R_2	λ_{max}	$\epsilon \times 10^3$
H	H	257	45.0
CH_3	CH_3	257	37.0
CH_3	CH_3	257	32.5

b. Carbinols



R_3	λ_{max}		$\epsilon \times 10^3$	
H[8]	247	348	24.5	6.5
CH_3	247	338	30.4	6.7
$(CH_3)_2N$	248–249	. . .	20.0	. .
CH_3O	247	338	30.3	6.9
Cl	247–248	335–337	26.3	5.9

Experimental[7]

A. **Addition of Methylmagnesium Iodide to 2,4,5-Triphenyl-3-(4′-tolyl)-cyclopenta-2,4-dien-1-one.**—Magnesium turnings (1.4 g., 0.059 mole) were suspended in 150 ml. of abs. ether with rapid stirring while methyl iodide (10 g., 0.07 mole) in 40 ml. of abs. ether slowly was added dropwise. 2,4,5-Triphenyl-3-(4′-tolyl)-cyclopenta-2,4-dien-1-one (2 g., 0.005 mole), in an ethereal slurry, was added to the Grignard reagent. The solution turned yellow in color forming an insoluble complex. When the addition was completed, the solution was refluxed for four hours. The Grignard complex was decomposed with a saturated ammonium chloride solution, the organic fraction was separated and dried over magnesium sulfate. The solvent was expelled from the solution *in vacuo* and the white solid residue was recrystallized from glacial acetic acid. The yield was 1.3 g. (64%), m.p. 185–186°.

Anal. Calcd. for $C_{31}H_{26}O$: C, 89.82; H, 6.32. Found: C, 89.95; H, 6.49.

B. **2,4,5-Triphenyl-3-(4′-tolyl)-fulvene.**—Dry hydrogen chloride was bubbled through a refluxing solution of 1-methyl-2,4,5-triphenyl-3-(4′-tolyl)-cyclopenta-2,4-dien-1-ol (4 g., 0.0098 mole) in 100 ml. of glacial acetic acid for one hour. The solution was allowed to stand overnight and the red crystals of fulvene were filtered off. This product was recrystallized from glacial acetic acid. The yield was 2.5 g. (60%), m.p. 202–203°.

Anal. Calcd. for $C_{31}H_{24}$: C, 93.90; H, 6.10. Found: C, 93.69; H, 6.03.

C. **2,4,5-Triphenyl-3-(4′-tolyl)-cyclopenta-2,4-diene.**—2,4,5-Triphenyl-3-(4′-tolyl)-fulvene (1 g., 0.0025 mole) in 35 ml. of piperidine, dried over potassium hydroxide, was refluxed for 1.5 hours. The solution was cooled, solvent was expelled from the solution *in vacuo* and the residue recrystallized twice from glacial acetic acid to 0.43 g. (45%), m.p. 161–162° (lit. m.p. 162–163°[4]).

D. **2,5-Diphenyl-3,4-(4′-tolyl)-fulvene.**—2,5-Diphenyl-3,4-(4′-tolyl)-cyclopenta-2,4-diene[4] (2 g., 0.005 mole) and a 37% solution of formaldehyde (2 g.) were refluxed together in 100 ml. of dry methanol while 200 ml. of a 4% sodium methoxide solution was added dropwise over a period of one-half hour. Refluxing was continued for two hours; the solution was then chilled overnight and the product was filtered off. The red fulvene was recrystallized from low boiling petroleum ether to yield 1.5 g. (73%) of product, m.p. 210–211°.

Anal. Calcd. for $C_{32}H_{26}$: C, 93.62; H, 6.38. Found: C, 93.41; H, 6.52.

E. **2,5-Diphenyl-3,4-(4′-tolyl)-cyclopenta-2,4-diene.**[3]—2,5-Diphenyl-3,4-(4′-tolyl)-fulvene was treated in the same manner as in B to yield 68% of the desired product, m.p 165–167° (lit. m.p. 165.5–166.5°).

F. **Addition of Methylmagnesium Iodide to 2,4,5-Triphenyl-3-(4′-dimethylaminophenyl)-cyclopenta-2,4-dien-1-one.**—Magnesium turnings (10 g., 0.45 mole) were suspended in 150 ml. of abs. ether with rapid stirring while methyl iodide (100 g., 0.7 mole) in 75 ml. of abs. ether slowly was added dropwise. The *p*-dimethylaminotetracyclone in an ethereal slurry was added to the Grignard reagent. When the addition was completed, the solution was of deep red in color forming a soluble complex. After refluxing two hours, the Grignard complex was decomposed and worked up as in A. The dried ether solution yielded a red-brown gum on evaporation of the solvent. This gum was recrystallized from aqueous ethanol to yield 8.5 g. (69%) of golden yellow product, m.p. 189–190°.

Anal. Calcd. for $C_{32}H_{29}NO$: C, 86.64; H, 6.59; N, 3.16. Found: C, 86.86; H, 6.37; N, 3.05.

G. **Addition of Methylmagnesium Iodide to 2,4,5-Triphenyl-3-(4′-methoxyphenyl)-cyclopenta-2,4-dien-1-one.**—The product was prepared in the same manner as in F using 2,4,5-triphenyl-3-(4′-methoxyphenyl)-cyclopenta-2,4-dien-1-one (37 g., 0.089 mole), magnesium turnings (20 g., 0.89 mole) and methyl iodide (115 g., 0.9 mole) to yield 30 g. (78%) of light yellow product, m.p. 171–172°.

Anal. Calcd. for $C_{31}H_{28}O_2$: C, 86.48; H, 6.09. Found: C, 86.28; H, 6.35.

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(6) H. Kuhefuss, B. S. thesis, Polytechnic Institute of Brooklyn.

(7) Melting points are uncorrected. The analyses were performed by Miss Linda Einstein of the Warner-Chilcott Research Laboratories.

H. Addition of Methylmagnesium Iodide to 2,4,5-Triphenyl-3-(4′-chlorophenyl)-cyclopenta-2,4-dien-1-one.—The product was prepared in the same manner as in F and G, using 2,4,5-triphenyl-3-(4′-chlorophenyl)-cyclopenta-2,4-dien-1-one (1 g., 0.0024 mole), magnesium turnings (2.4 g., 0.1 mole) and methyl iodide (14.0 g., 0.1 mole) to yield 0.9 g. (86%) of off-white product, m.p. 161–163°.

Anal. Calcd. for $C_{30}H_{23}OCl$: C, 82.84; H, 5.33; Cl, 8.17. Found: C, 83.27; H, 5.47; Cl, 8.36.

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An Improved Synthesis for 3-Chloropyridine

BY HAROLD L. RICE AND THOMAS E. LONDERGAN

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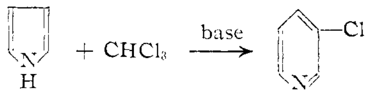
One of the more unusual reactions of pyrrole is its conversion to 3-chloropyridine through reaction with chloroform in the presence of bases.



This ring expansion reaction, carried out in ether with sodium ethoxide as catalyst, was reported first by Ciamician[1] and was extended by Dennstedt[2] to the sodium methoxide catalyzed reaction of pyrrole with methylene iodide to give pyridine. Extension of this reaction to the indole series has been reported by several workers.[3] Substituted quinolines were the reported products in yields as high as 50%. Recently Alexander and co-workers[4] made a study of catalysts for the pyrrole–chloroform reaction. Their best yield of 3-chloropyridine (12.8%) was obtained using pyrryllithium as a reactant. Reactions described in these references were carried out in the liquid phase, mostly in anhydrous media.

The chloroform–pyrrole reaction has been reexamined in our laboratory according to the directions given in the literature. Sodium hydroxide, sodium ethoxide and sodium methoxide were used as catalysts in liquid phase experiments. Results were erratic with low yields and the 3-chloropyridine was difficult to isolate from the mass of polymeric by-products. In attempts to improve yields and inhibit side reactions, a study of the vapor phase reactions of pyrrole and chloroform was initiated. Using alumina or molybdena on alumina as catalysts at 440–510°, only tars were formed. However, when chloroform and pyrrole vapors were passed through an empty glass reaction tube at 550°, 3-chloropyridine was formed in yields up to 33% of theory. In runs at 500°, yields of 20–25% were obtained. Increasing amounts of starting materials were recovered as temperatures were reduced below 500°, while increasing amounts of tars were produced above 600°. The best results were obtained when the chloroform to pyrrole ratio was about five to one. About one-third volume of nitrogen per volume of reactant mixture was passed into the reaction zone with the reactants. The contact time in the hot zone was about three seconds.

The preparation of 3-chloropyridine to the exclusion of the other isomeric monochloropyridines under such extreme conditions would seem unusual. In fact, 2-chloropyridine was produced in yields of 2 to 5%. Evidence that rearrangement of the 3-chloropyridine was not taking place was found in our unsuccessful attempts to interconvert 3-chloropyridine and 2-chloropyridine under the conditions of the reaction. The third isomer, 4-chloropyridine probably would not be recovered, even if formed, because it would not be stable at such high temperatures.[5]

The consideration of a mechanism for this high-temperature synthesis leads to the suggestion that it may be in part base-catalyzed by the glass of the tube. A recent report by Parham and Reiff[6] may indicate the reaction path. In their work, the synthesis of chloronaphthalene from chloroform and indenylsodium is described. These authors isolated the intermediate dichlorocyclopropane resulting from the attack on indene by the dichlorocarbene anion. The 3-chloropyridine synthesis may well proceed by such a mechanism.

Experimental

The vapor phase reactions were carried out in a 1.5 in. × 48 in. Pyrex glass tube. The tube was made up in two sections; the upper section was packed with Berl Saddles and used as a preheater, while the lower unpacked section served as the reactor. The sections of the tube were heated separately using a 12-in. (preheater) combustion furnace and an 18-in. (reactor) combustion furnace. Above the preheater was mounted a water-cooled dropping funnel. A mixture of 30 g. (0.45 mole) of pyrrole and 270 g. (2.25 moles) of chloroform was added to the preheater through the dropping funnel at the rate of 2–3 drops per second. A continuous flow of nitrogen through the preheater and reactor (600 ml./min.) was maintained. Products from the reaction were collected in a 2-liter flask which was cooled in an ice-bath. Hydrogen chloride was removed in a second trap by passing through a caustic solution, and any further condensable vapors were collected in a series of two Dry Ice-cooled traps. Temperatures during the reaction were measured with thermocouples inserted into a thermowell in the reactor. After the addition of reactants was complete the receivers were removed and the chloroform layers from the receiver and traps were combined and extracted with 6% hydrochloric acid. The acid extract was made alkaline with 30% sodium hydroxide solution and steam distilled. The distillate was extracted with four 30-ml. portions of methylene chloride and the product was recovered by distilling off the methylene chloride. The residue, 17.9 g., consisted of from 13 to 16.5 g. (25 to 33%) of 3-chloropyridine and from 1.0 to 2.5 g. (2 to 5%) of 2-chloropyridine.

The products from several such reactions were combined and fractionally distilled to separate the two products. The 3-chloropyridine distilled at 77–78° (62 mm.), while the 2-chloropyridine distilled at 81–85° (62 mm.). Redistillation of the 3-chloropyridine was carried out for analysis.

Anal. Calcd. for C_5H_4NCl: N, 12.34. Found: N, 12.22.

The picrate, recrystallized from ethanol, melted at 146–147°.[4]

A sample of 2-chloropyridine was added to a solution of picric acid in ethanol and the resulting picrate was recrystallized from ethanol; m.p. 92–93.5°. A mixed melting

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(1) G. L. Ciamician and M. Dennstedt, *Ber.*, **14**, 1153 (1881); G. L. Ciamician and P. Silber, *ibid.*, **18**, 721 (1885); **20**, 191 (1887).

(2) M. Dennstedt and J. Zimmerman, *ibid.*, **18**, 3316 (1885).

(3) P. C. Madnanini, *ibid.*, **20**, 2608 (1887); A. Ellinger, *ibid.*, **39**, 2515 (1906); A. Ellinger and C. Flamand, *ibid.*, **39**, 4388 (1906).

(4) E. R. Alexander, A. B. Herrick and T. M. Roder, THIS JOURNAL, **72**, 2760 (1950).

(5) J. P. Wibaut and F. W. Brookman, *Rec. trav. chim.*, **58**, 885 (1939).

(6) Parham and Reiff, Abstracts of Papers, Cincinnati Meeting of the A.C.S., March 29 to April 7, 1955, p. 20N.