

out by heating for half an hour on a boiling water-bath the following mixture: 2.5 g. of unbleached cotton, 50 cc. of 0.1% dye solution (0.05 g. of dye), 62 cc. of water, 10 drops of 10% sodium carbonate solution and 37 cc. of 1% sodium chloride solution.

3. From the *p*-Amino Derivative.—This was prepared in the same way as the *m*-isomer. The dye was a purplish-red solid, soluble in water, but insoluble in alcohol or in concentrated sodium hydroxide solution. It dissolved slightly in concentrated sulfuric acid, to a reddish-brown solution. It dyed unmordanted cotton a burgundy shade, which was fast to light and also showed good fastness to laundering and to bleeding tests.

Summary

1. 2-*R*-*peri*-naphtho-*m*-thiazines have been synthesized from *peri*-aminonaphthyl mercaptans.

2. In methods of synthesis, structure and properties, these new products resemble closely the benzothiazoles.

3. A convenient process of acylation is described, in which complex tin derivatives of the amines are used as initial materials.

4. The new compounds described are the mono (*o*-nitrobenzoyl) and di (*o*-, *m*- and *p*-nitrobenzoyl) *peri*-aminonaphthyl mercaptans; the 2-methyl, 2-styryl, 2-(*o*-, *m*- and *p*-nitrophenyl), 2-(*o*-, *m*- and *p*-aminophenyl), 2-(*m*- and *p*-hydroxyphenyl) *peri*-naphthothiazines, and the phthalone of the 2-methyl compound.

5. The investigation is being continued.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

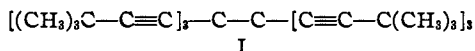
TETRAPHENYL-DI-TERTIARY-BUTYLETHINYLETHANE

BY J. GAIL STAMPFLI AND C. S. MARVEL

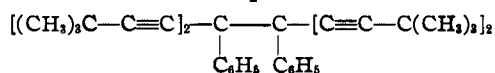
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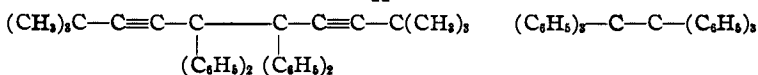
After the discovery that hexa-*tert.*-butylethinyne (I) could be readily cleaved with sodium-potassium alloy and the liquid sodium amalgams,¹ an attempt was made to synthesize two other compounds, symmetrical diphenyl-tetra-*tert.*-butylethinyne (II) and symmetrical tetraphenyl-di-*tert.*-butylethinyne (III), in order to compare the stability of the ethane linkages in these three acetylenic hydrocarbons with that in hexaphenylethane (IV).



I



II



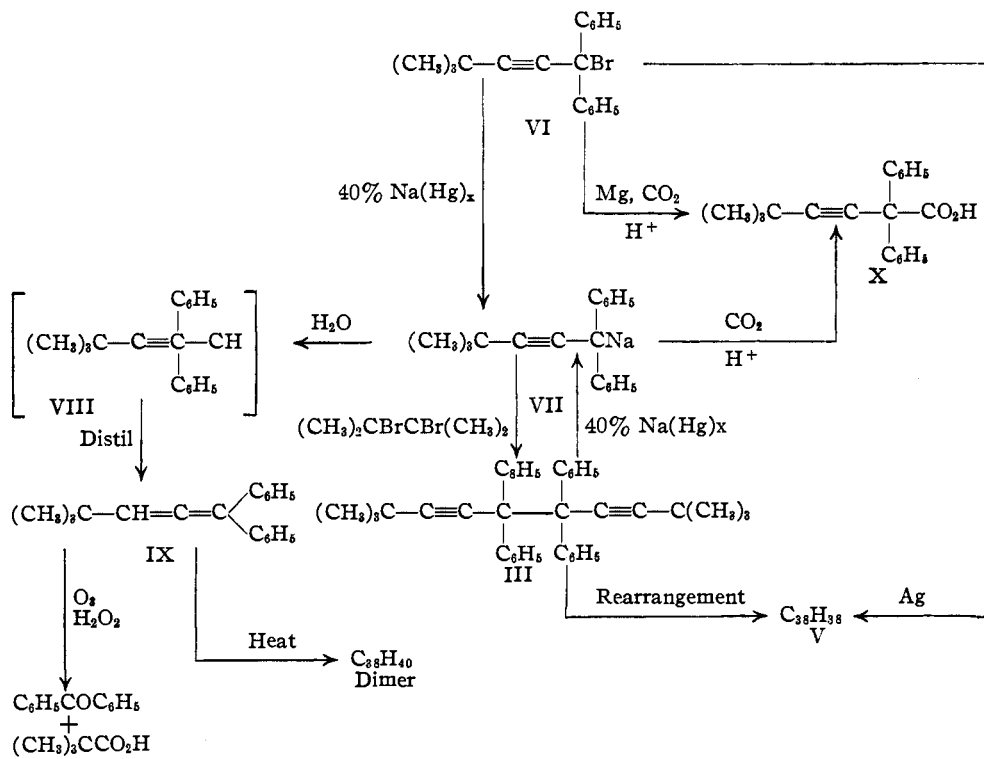
III

IV

¹ Salzberg and Marvel, THIS JOURNAL, 50, 1737 (1928).

No difficulty was experienced in the synthesis of diphenyl-tetra-*tert.*-butylethynylethane² (II) and its chemical and physical properties agreed with those expected for this structure. The attempt to prepare tetraphenyl-di-*tert.*-butylethynylethane (III) by the action of silver on diphenyl-*tert.*-butylethynylbromomethane³ gave a hydrocarbon of the correct theoretical composition, C₃₈H₃₈ (V), for the desired product. However, its reactions were not those which had been predicted for an ethane of the type which should have formed if a simple coupling had occurred.

The present communication describes the synthesis of tetraphenyl-di-*tert.*-butylethynylethane (III) by a series of reactions which are analogous to those successfully used for the synthesis of tetracyclohexyldiphenylethane.⁴ Diphenyl-*tert.*-butylethynylbromomethane (VI) on treatment with 40% sodium amalgam yielded the sodium alkyl (VII) and this in turn on treatment with tetramethylethylene bromide gave the desired hydrocarbon (III). The chart shows the method of synthesis and indicates the reactions used to establish the structure of the new hydrocarbon.



² Rossander and Marvel, *THIS JOURNAL*, 51, 932 (1929).

³ Salzberg and Marvel, *ibid.*, 50, 2840 (1928).

⁴ Rossander, Bock and Marvel, *ibid.*, 52, 2976 (1930).

The new hydrocarbon (III) was quite unstable. Its solution in hexane absorbed oxygen at a fairly rapid rate but no peroxide was isolated. Apparently the molecule was oxidized to much simpler products. When the hydrocarbon was dissolved in an organic solvent, such as ether, and this solution was allowed to stand at room temperature for a few hours or was heated to about 50° for a few minutes, a rearrangement occurred and the isomeric hydrocarbon, C₃₈H₃₈ (V), was obtained.

The differences between the true tetraphenyl-di-*tert.*-butylethynylethane (III) and the isomeric hydrocarbon, C₃₈H₃₈ (V), are best illustrated in their respective reactions with bromine and 40% sodium amalgam. The true ethane (III) in carbon tetrachloride solution added bromine readily. The isomeric hydrocarbon (V) did not add bromine under the same conditions.

When the true ethane (III) was treated with 40% sodium amalgam, a metal alkyl was obtained. This was identified as the cleavage product, diphenyl-*tert.*-butylethynylmethyl-sodium (VII), by converting it into diphenyl-*tert.*-butylethynylacetic acid (X) which had previously been obtained from diphenyl-*tert.*-butylethynylbromomethane (VI) by means of the Grignard reaction. The sodium alkyl was also decomposed with water to yield the acetylenic hydrocarbon (VIII) which rearranged during its isolation to produce the allene (IX), which was identified by the products of ozonization.

As was shown in the earlier work,³ the isomeric hydrocarbon, C₃₈H₃₈ (V), gave a colored alkali metal derivative when treated with sodium-potassium alloy or with 40% sodium amalgam. This metal alkyl was not identical with the one which has been obtained by cleavage of tetraphenyl-di-*tert.*-butylethynylethane for it did not give diphenyl-*tert.*-butylethynylacetic acid when treated with carbon dioxide. Moreover, with water the sodium derivative from C₃₈H₃₈ (V) gave a solid hydrocarbon which melted at 162.8–163.8° and in no way resembled the liquid allene obtained from diphenyl-*tert.*-butylethynylmethyl-sodium. It is significant that no solid hydrocarbon was obtained by the action of water on this latter metal alkyl.

Tetraphenyl-di-*tert.*-butylethynylethane was not cleaved by 1% amalgam. When a solution of the hydrocarbon was shaken for five days with the dilute amalgam no color was developed and on examining the reaction mixture only the rearranged hydrocarbon, C₃₈H₃₈ (V), was obtained. It is evident that the ease of cleavage by alkali metals cannot be taken as the only criterion for the stability of the central ethane linkage in the acetylenic ethanes. Oxygen absorption and ease of rearrangement must also be considered. If all of these factors are taken into account it becomes evident that in the series of compounds, hexa-*tert.*-butylethynylethane (I), diphenyl-tetra-*tert.*-butylethynylethane (II), tetraphenyl-di-*tert.*-butylethynylethane (III), and hexaphenylethane (IV) there is a fairly regular gradation in properties from the most stable hexa-acetylenic derivative to the least stable hexa-arylethynylethane derivative.

Experimental Part

Diphenyl-*tert.*-butylethynylmethyl-sodium.—A solution of 10 g. of diphenyl-*tert.*-butylethynylbromomethane in 200 cc. of anhydrous ether⁵ was placed in a 500-cc. round-bottomed flask and 25 cc. of 40% sodium amalgam was added. The flask was then stoppered and placed on a mechanical shaking machine. The reaction set in at once and the solution became warm. The color changed from light yellow to a deeper yellow with strong green fluorescence. After one hour of shaking, the mixture showed the deep red color characteristic of the metal alkyl. To complete the reaction shaking was continued overnight.

The stopper was then quickly removed from the flask and in its place was inserted a stopper bearing two glass tubes. Dry oxygen-free nitrogen was passed in one tube and out the other so that no air could enter the flask. The flask was then set in an ice-bath and the amalgam was frozen. The metal alkyl solution was then quickly poured through one of the glass tubes into another flask previously flushed out with dry nitrogen. This flask was fitted with a stopper carrying one glass tube fitted with a stopcock and another inside of which was sealed an alundum filter plate. The solution was then filtered into a second flask. The metal alkyl was not isolated but this ether solution was used in all subsequent reactions.

In the laboratory it was found convenient to use the apparatus shown in Fig. 1 for filtering the ether solution of the metal alkyl. The solution was drained from the frozen amalgam in the original reaction flask into flask A, which had a stopcock C sealed in its side to admit nitrogen gas or more ether if needed. The alundum filter is shown at D. The solution was filtered under atmospheric pressure by gravity into flask B in which an atmosphere of dry nitrogen was maintained by introducing nitrogen through stopcock E and out tube F.

Tetraphenyl-di-*tert.*-butylethynylethane.—The ether solution of diphenyl-*tert.*-butylethynylmethyl-sodium prepared from 9.5 g. of diphenyl-*tert.*-butylethynylbromomethane was cooled to 0° and to this cold solution was added dropwise a 10% solution of tetramethylethylene bromide in anhydrous ether. The reaction between the sodium derivative and the bromide proceeded rapidly and the reaction mixture changed from deep red to yellow and finally became practically colorless. At this stage the addition of the solution of tetramethylethylene bromide was discontinued. Usually about 30 cc. of the solution of tetramethylethylene bromide was required. The reaction mixture was evaporated under reduced pressure until the volume was about 25 cc. No air or nitrogen was admitted during this stage.

Then 50 cc. of absolute alcohol was added quickly and the mixture was placed in a solid carbon dioxide-acetone cooling mixture for about one hour. The ethane crystallized during this time.

The mixture of sodium bromide and hydrocarbon was filtered with suction and dried for a short time in a desiccator to remove the organic solvent. The mixture was then thoroughly washed with water to remove the sodium bromide and the remaining crystals were again thoroughly dried in a vacuum desiccator. The yield of solid hydrocarbon was about 2.4 g. (33% of the theoretical amount based on the diphenyl-*tert.*-butylethynylbromomethane).

⁵ All anhydrous ether used in this work was distilled from a solution of ethylmagnesium bromide.

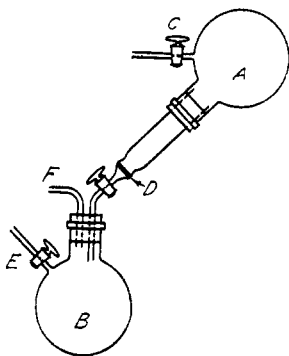


Fig. 1.

The new hydrocarbon melted at 141–142° on a Maquenne block. By the capillary tube method, the melting point varied from 120–125° if the sample was placed in a bath previously heated to about 115°. When the crystals were slowly heated in a capillary tube, the product rearranged and the melting point was about 147–149° which is approximately that of the isomeric hydrocarbon, C₃₈H₃₈, previously described.⁸

The hydrocarbon which was obtained in this way was necessarily too impure for an analysis to be significant. It has been characterized by the reactions which are described below. Any delay during the preparation always resulted in the rearrangement of the product.

Reactions of Tetraphenyl-di-*tert.*-butylethinyethane

Reaction with Gaseous Oxygen.—A solution of 1 g. of the ethane in 40 cc. of hexane was shaken in an atmosphere of oxygen in an apparatus which permitted measurement of the amount absorbed. The oxidation proceeded rapidly. A typical case is shown in Table I.

TABLE I

OXYGEN ABSORBED BY 1 G. OF TETRAPHENYL-DI-*tert.*-BUTYLETHINYLETHANE

Time in minutes,.....	3	15	60	250
Oxygen absorbed at 27.5°, cc.....	10.6	17.6	18.3	18.3

Some preliminary experiments on oxygen absorption by ether solutions of the crude ethane, which also contained the sodium bromide formed during the preparation, gave similar results. These solutions absorbed oxygen more readily than did those of the ethane which had been further purified. Some experiments were continued over several days but there was little evidence of further oxidation after a few hours.

Several attempts were made to isolate a crystalline peroxide from these reaction mixtures but none was ever obtained. In every case some of the rearranged hydrocarbon, C₃₈H₃₈, was isolated. Apparently oxidation and rearrangement had proceeded simultaneously and the products of oxidation were not stable crystalline substances. No oxidation products were isolated although in one or two cases the oxidized solution was acidic to moist litmus.

Rearrangement of the Ethane.—A solution of 0.25 g. of the ethane in 20 cc. of heptane was gently refluxed under an atmosphere of nitrogen for one hour. The solution was filtered, evaporated to a volume of about 5 cc. in a current of air and then poured into 20 cc. of absolute alcohol. On cooling overnight an isomeric hydrocarbon crystallized. The yield was 0.17 g. and the melting point was 153–153.8°. Mixtures of this rearrangement product with the isomeric hydrocarbon, C₃₈H₃₈, which had been prepared by the action of silver on diphenyl-*tert.*-butylethynylbromomethane melted at the same temperature.

A solution of 0.23 g. of the ethane in 30 cc. of acetone was refluxed in an atmosphere of nitrogen for about forty-five minutes. From this reaction mixture 0.18 g. of the isomeric hydrocarbon melting at 153–154.4° was obtained.

Some preliminary experiments were conducted on the rearrangement of the ethane in ether solution at ordinary temperatures. The ether solution of the ethane prepared from 6.2 g. of diphenyl-*tert.*-butylethynylbromomethane was allowed to stand for five days and by evaporation of the solvent and crystallization of the residue 2.1 g. of the rearranged hydrocarbon, C₃₈H₃₈, was obtained. Similarly in two days the rearrangement occurred and the ethane from 8 g. of the bromide gave 2.4 g. of rearranged hydrocarbon.

Four 1-g. samples of the crystalline ethane were dissolved in 100-cc. portions of ether and allowed to stand for 0, 4, 12 and 19 hours, respectively. These solutions were then treated with 40% sodium amalgam and later worked up as will be described under

the cleavage experiments in order to see what amounts of diphenyl-*tert.*-butylethynylacetic acid could be isolated. From the solution which was immediately treated with the amalgam, 0.45 g. of the acid was obtained. From the solution which stood for four hours, 0.12 g. of acid was obtained. No acid was isolated from the solutions which had stood for twelve and nineteen hours, thus indicating that the tetraphenyl-di-*tert.*-butylethynylethane had completely rearranged to the isomeric hydrocarbon in this time. These solutions did yield very small quantities of the yellow compound melting at 168–170° which Salzberg and Marvel³ had previously obtained by the action of 40% sodium amalgam and carbon dioxide on the isomeric hydrocarbon, C₃₈H₃₈.

Reaction with Bromine.—To a solution of 0.1 g. of the ethane in 5 cc. of dry carbon tetrachloride was added slowly a 5% solution of bromine in carbon tetrachloride. The color of the bromine disappeared quickly and several cc. of the bromine solution had to be added to give a permanent color to the mixture.

Cleavage of the Ethane with Alkali Metals. With Sodium-Potassium Alloy.—A solution of 1 g. of the crude ethane in 100 cc. of dry ether was shaken by hand in an atmosphere of nitrogen with 10 cc. of liquid sodium-potassium (4 to 10) alloy. In fifteen seconds a deep yellow color appeared, which changed to orange in thirty seconds and red in forty-five seconds. The solution was put on a mechanical shaker and shaken for two hours. Dry carbon dioxide was passed over the surface of the solution until the red color disappeared. The reaction mixture was worked up as described under diphenyl-*tert.*-butylethynylacetic acid. The reaction mixture yielded 0.45 g. of crude acid which on further purification gave 0.15 g. of acid melting at 165–171°.

With 40% Sodium Amalgam.—A solution of 1 g. of the crude ethane in 50 cc. of dry ether was shaken under nitrogen with 15 cc. of 40% sodium amalgam. The solution turned red in five minutes. The shaking was continued for twelve hours and then dry carbon dioxide was passed over the solution until the red color of the metal alkyl had disappeared. The reaction mixture was worked up as described for diphenyl-*tert.*-butylethynylacetic acid. The yield of crude acid was 0.63 g. (53% of the theoretical amount). This was dissolved in 10 cc. of a 10% solution of potassium hydroxide in 50% alcohol, filtered, precipitated with acid and recrystallized from petroleum ether (b. p. 65–110°). This treatment gave 0.32 g. of acid melting at 170–172°. A mixed melting point with the acid prepared from diphenyl-*tert.*-butylethynylbromomethane through the Grignard reagent showed no depression.

With 1% Sodium Amalgam.—A solution of 1 g. of the crude ethane in 100 cc. of dry ether was shaken with 13 cc. of 1% amalgam under an atmosphere of nitrogen for forty hours. No coloration appeared. The ether was poured off the amalgam and the latter washed twice with 30 cc. of dry ether. The ether was filtered, evaporated to a volume of 5 cc. in a current of dry air and 20 cc. of absolute alcohol was added. The solution was well cooled and 0.7 g. of impure rearranged hydrocarbon, C₃₈H₃₈, was obtained.

Two similar runs were made in which the solutions were shaken for five and eight days, respectively. No coloration developed and only the impure rearranged hydrocarbon, C₃₈H₃₈, could be isolated.

Two runs were made in which the ethane from 7.4 g. of bromide and 10.5 g. of bromide was not isolated in the solid state. The solutions of the ethane were shaken as soon as they were formed with 80 cc. and 105 cc. of 1% amalgam, respectively. No coloration developed and only impure rearranged hydrocarbon, C₃₈H₃₈, could be isolated from these reaction mixtures.

Diphenyl-*tert.*-butylethynylacetic Acid. From the Grignard Reaction.—To a solution of 4.65 g. of diphenyl-*tert.*-butylethynylbromomethane in 20 cc. of dry ether was added 0.5 g. of dry magnesium turnings and 0.1 g. of iodine. The mixture was stirred

and a slow current of dry carbon dioxide passed over the surface of the solution. More ether was added from time to time as it evaporated. After seven hours the mixture was decomposed, first with water and then with 10% hydrochloric acid. The ether layer was separated from the water layer and the latter extracted with 50 cc. of ether. The combined ether extract was washed with water, then with sodium bisulfite solution, again with water, and then dried over sodium sulfate. The ether was evaporated completely under reduced pressure, a few cc. of petroleum ether was added, and the mixture was well cooled. A yield of 1.37 g. (34% of the theoretical) of crude acid was obtained. This was dissolved in 10 cc. of ether, the solution filtered, evaporated under reduced pressure to a volume of 3 cc. and cooled in a bath of solid carbon dioxide and acetone. The crystals which separated were filtered off. After three such recrystallizations, about 0.3 g. of pure acid melting at 171.2–172° was obtained.

From Diphenyl-*tert.*-butylethynylmethyl-sodium.—In a 200-cc. round-bottomed flask was placed 4 g. of diphenyl-*tert.*-butylethynylbromomethane, 100 cc. of dry ether and 10 cc. of 40% sodium amalgam and the air was swept out with nitrogen. The flask was tightly stoppered and placed on a mechanical shaker. After one hour the solution was deep red in color. The shaking was continued for forty-eight hours. The flask was removed and dry carbon dioxide passed over the surface of the solution until the characteristic red color of the metal alkyl had disappeared completely. The amalgam was frozen, the ether suspension poured off, and the amalgam washed twice with dry ether. The ether suspension (including the washings) was acidified with dilute hydrochloric acid. The ether layer was separated, washed twice with water, dried over sodium sulfate and evaporated to dryness under reduced pressure. A few cc. of petroleum ether was added and the mixture well cooled. The yield of crude acid was 2.15 g. (60% of the theoretical amount). After several recrystallizations from petroleum ether (b. p. 80–100°), the acid melted at 171–172° and showed no depression in melting point when mixed with the acid obtained from the same bromide by means of the Grignard reaction.

Anal. Subs., 0.2012, 0.1934: CO₂, 0.6041, 0.5810; H₂O, 0.1236, 0.1201. Calcd. for C₂₀H₂₀O₂: C, 82.21; H, 6.86. Found: C, 81.89, 81.93; H, 6.83, 6.86. *Neutral equivalent.* Subs., 0.1253: 3.49 cc. of 0.1228 *N* NaOH. Calcd. for C₂₀H₂₀O₂: Neut. eq., 292. Found: 292.4. *Mol. wt.* (Rast Method). Subs., 0.0499: camphor, 0.4439: Δ*t* (depression), 16.5°. Calcd. for C₂₀H₂₀O₂: 292. Found: 272.5.

1,1-Diphenyl-4,4-dimethylpentadiene-1,2 (IX).—An ether solution of diphenyl-*tert.*-butylethynylmethyl-sodium was prepared from 20 g. of diphenyl-*tert.*-butylethynylbromomethane according to the procedure described above. To this well-cooled solution, water which had been boiled previously was slowly added until the red color of the solution had disappeared. Then about 200 cc. of water was added. The ether layer was separated, washed twice with 200-cc. portions of water, dried over sodium sulfate, filtered and the solvent evaporated. The remaining liquid was distilled under reduced pressure. A yield of 5.2 g. (34% of the theoretical amount) of the allene boiling at 115–118° (0.55 mm.) was obtained; d_4^{20} 0.9661; n_D^{20} 1.569.

Anal. Subs., 0.1818: CO₂, 0.6120; H₂O, 0.1338. Calcd. for C₁₉H₂₀: C, 91.88; H, 8.12. Found: C, 91.81; H, 8.23. *Mol. wt.* (cryoscopic in benzene). Subs., 0.2307, 0.3204; benzene, 21.95: Δ*t* (depression), 0.22°, 0.303°. Calcd. for C₁₉H₂₀: mol. wt., 248. Found: 245, 247.

When the allene was distilled there remained in the distilling flask a brownish colored residue which would not distil below 200° at 0.55 mm. This was crystallized from petroleum ether (b. p. 25–65°) and yielded 4.2 g. of light yellow crystals, m. p. 177–180°. After repeated crystallization from petroleum ether, acetone and absolute alcohol the compound melted at 178.8–179.8°. This proved to be a dimer of the allene.

Anal. Subs., 0.1834: CO₂, 0.6174; H₂O, 0.1335. Calcd. for C₃₈H₄₀: C, 91.88; H, 8.12. Found: C, 91.81; H, 8.15. *Mol. wt.* (cryoscopic in benzene) Subs., 0.4330, 0.6566; benzene, 21.95: Δt (depression), 0.236°, 0.357°. Calcd. for C₃₈H₄₀: mol. wt., 496. Found: 428, 429.

This dimer was also obtained on redistillation of the purified allene or when the allene stood at room temperature for a few weeks.

Ozonization of 1,1-Diphenyl-4,4-dimethylpentadiene-1,2.—A stream of ozonized oxygen was passed through a solution of 2.5 g. of the allene in 75 cc. of dry carbon tetrachloride. The rate of flow of the gas was approximately 4 liters per minute and about two hours were required for complete ozonization as indicated by disappearance of the unsaturation of the solution toward bromine. The reaction mixture was poured into an equal volume of 30% hydrogen peroxide and allowed to stand overnight. Enough 10% sodium hydroxide was added to give an alkaline reaction toward phenolphthalein, the mixture was shaken and the carbon tetrachloride layer separated. On evaporation of this solvent, 1.28 g. of oil remained. This oil was shown to be benzophenone by conversion to a phenylhydrazone which melted at 135–137° and which when mixed with an authentic specimen of benzophenone phenylhydrazone showed no depression in melting point.

The aqueous alkaline solution was made acid to Congo red and extracted with two 50-cc. portions of ether. This ether solution contained a volatile acid which was converted to the sodium salt by treating the ether solution with just enough 2% sodium hydroxide solution to make the mixture alkaline to phenolphthalein after thorough shaking. The aqueous solution of the salt was separated and evaporated to dryness and the *p*-bromophenacyl ester was prepared according to the directions of Judefind and Reid.⁶ This ester melted at 73–75°. A portion was mixed with a sample of *p*-bromophenacyl ester of trimethylacetic acid,⁷ and the melting point of the mixture was 75–77°.

Action of Water on the Sodium Compound Prepared from the Rearranged Hydrocarbon, C₃₈H₃₈.—A solution of 10 g. of the rearranged hydrocarbon, C₃₈H₃₈, in 300 cc. of dry ether was shaken overnight with 75 cc. of 40% sodium amalgam under an atmosphere of dry nitrogen. The amalgam was frozen by cooling the mixture in an ice-salt bath and the solution of the sodium derivative was transferred to another flask filled with nitrogen. Water which had been boiled previously to remove oxygen was added slowly to the well-cooled solution until the red color disappeared. Then the reaction mixture was diluted with about 150 cc. of water and the ether layer was separated, washed with two 100-cc. portions of water, dried over sodium sulfate, filtered and evaporated to a volume of about 50 cc. An equal volume of absolute alcohol was added and the solution cooled overnight in an ice box. Crystals separated and were filtered with suction. The yield was 6.57 g. of a white crystalline product which melted at 162.8–163.8°. This compound decolorized bromine in carbon tetrachloride quite rapidly. There is some question concerning the number of hydrogens which have been added to the molecule but the best agreement between the analytical figure and the theoretical value is for a formula of C₃₈H₄₀ which should be produced by the addition of two atoms of hydrogen. This compound is to receive further study.

Anal. Subs., 0.1476: CO₂, 0.4974; H₂O, 0.1076. Calcd. for C₃₈H₄₀: C, 91.88; H, 8.12. Found: C, 91.90; H, 8.16. *Mol. wt.* (cryoscopic in benzene). Subs., 0.2120; benzene, 21.95: Δt (depression), 0.108°. Calcd. for C₃₈H₄₀: mol. wt., 496. Found: 458.

⁶ Judefind and Reid, *THIS JOURNAL*, **42**, 1043 (1920).

⁷ This ester has been described by Powell, *ibid.*, **53**, 1172 (1931). It also has been characterized in this Laboratory by Mr. D. Althausen.

Summary

Tetraphenyl-di-*tert.*-butylethynylethane has been prepared and characterized. It has been found to be easily oxidized by gaseous oxygen, easily rearranged to an isomeric hydrocarbon on standing and easily cleaved by alkali metals.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF STANFORD UNIVERSITY]

SALTS OF THE AMMONO ENOLIC MODIFICATION OF PYRIDINES AND QUINOLINES ALKYLATED IN THE 2- AND 4-POSITIONS¹

BY F. W. BERGSTROM

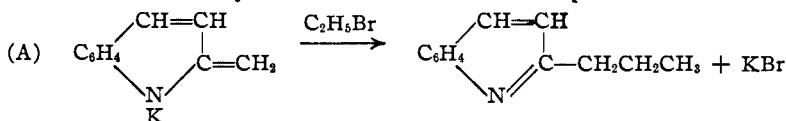
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Introduction

In previous articles it has been shown that 2-methylquinoline (quinaldine) and 2,3-dimethylquinoxaline are cyclic ketone-acetals of the ammonia system² because of the $\begin{matrix} \text{CH}_3 \\ \diagdown \\ \text{C}=\text{N}- \end{matrix}$ group which is a part of their structure. In conformity with this view both of these compounds have been shown to react with potassium amide, a base of the ammonia system, to form highly colored (red or reddish-brown) salts of the corresponding ammono enolic modification,³ that is to say, salts which contain the grouping $\begin{matrix} \text{CH}_2 \\ \diagdown \\ \text{C}=\text{N}- \\ \diagup \\ \text{R} \end{matrix}$.

In chemical reactivity these salts have been found to resemble in many respects the salts of the enolic modification of acetoacetic ester and related ketones of the water system. Thus, 2-methylquinoline and 2,3-dimethylquinoxaline may be alkylated by treating the potassium salt of the ammono enolic form with an alkyl halide in the sense of the equation



The resemblance of this reaction to the alkylation of acetoacetic ester has been pointed out by Ziegler and Zeiser.^{3b,2b,2c}

¹ Presented at the Pasadena Meeting of the A. A. A. S., June, 1931.

² (a) Ogg and Bergstrom, *THIS JOURNAL*, **53**, 1846 (1931); (b) Bergstrom, *ibid.*, **53**, 3027 (1931); (c) *Science*, **72**, 402 (1930).

³ (a) Ref. 2(a-c); (b) Ziegler and Zeiser, *Ann.*, **485**, 178 (1931), have made an examination of reactions of this type in connection with their very interesting work on the chemical reactivity of the lithium alkyls and aryls. Thus, lithium phenyl reacts with quinaldine to form benzene and the lithium salt of the ammono enol of quinaldine. 2-Picoline (2-methylpyridine) is likewise converted without difficulty to the lithium salt of the corresponding ammono enol.