Summary

1. Various reactions of the hydrocarbon $C_{38}H_{38}$ which is obtained by the rearrangement of tetraphenyldi-*tert.*-butylethinylethane have been described.

2. All of these reactions can be explained by the postulation of a di-indene structure for the rearranged hydrocarbon.

3. The mechanism of the rearrangement of the hexasubstituted ethane to the di-indene has been discussed.

URBANA, ILLINOIS

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

THE REDUCTION OF ACETYLENIC CARBINOLS WITH TITANIUM TRICHLORIDE

BY R. S. SWEET AND C. S. MARVEL

RECEIVED OCTOBER 23, 1931 PUBLISHED MARCH 5, 1932

The classical method of Gomberg[1] for the preparation of hexa-arylethanes does not always lead to the expected product when it is applied to the corresponding acetylene derivatives. The general method which Ziegler and Schnell[2] have developed is more reliable for producing compounds of the normal type in the acetylene series. These facts have been well established in connection with the study of the preparation and rearrangement of tetraphenyldi-*tert.*-butylethinylethane.[3]

A third general method for the preparation of aryl substituted ethanes is the reduction of aryl carbinols with vanadous, chromous or titanous salts. This method was first described by Conant and Sloan.[4] Two attempts to apply this method to the preparation of acetylenic ethanes have been recorded. Tri-*tert.*-butylethinylcarbinol gave no products which could be isolated and characterized when it was treated with vanadous chloride.[5] Wieland and Kloss[6] have reduced diphenylphenylethinylcarbinol (I) with titanium trichloride and obtained the same hydrocarbon which Moureu, Dufraisse and Houghton[7] had previously prepared by the action of iron on diphenylphenylethinylchloromethane (II). This hydrocarbon has been assumed to be *sym.*-tetraphenyldiphenylethinylethane (III).

---

[1] Gomberg, THIS JOURNAL, **22**, 757 (1900).

[2] Ziegler and Schnell, *Ann.*, **437**, 244 (1924).

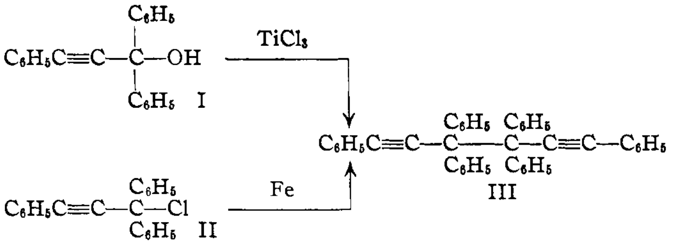
[3] (a) Salzberg and Marvel, THIS JOURNAL, **50**, 2840 (1928); (b) Stampfli and Marvel, *ibid.*, **53**, 4057 (1931); (c) Althausen and Marvel, *ibid.*, **54**, 1174 (1932).

[4] Conant and Sloan, *ibid.*, **45**, 2466 (1923).

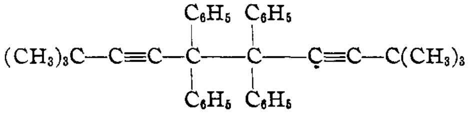
[5] Salzberg with Marvel, *ibid.*, **50**, 1737 (1928).

[6] Wieland and Kloss, *Ann.*, **470**, 217 (1929).

[7] Moureu, Dufraisse and Houghton, *Bull. soc. chim.*, [4] **41**, 56 (1927).

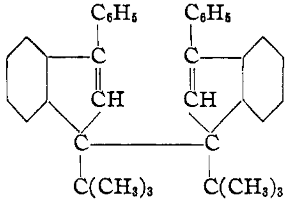


There is a considerable difference in the properties of this tetra-aryl diacetylenic ethane and the closely related tetraphenyldi-*tert.*-butylethinylethane (IV) which has recently been prepared and characterized.[3b] This latter compound undergoes rearrangement in solution at room temperature to give a more stable substance which has a di-indene (V) structure.[3c]



$(CH_3)_3C—C\equiv C—C(C_6H_5)_2—C(C_6H_5)_2—C\equiv C—C(CH_3)_3$

IV



V

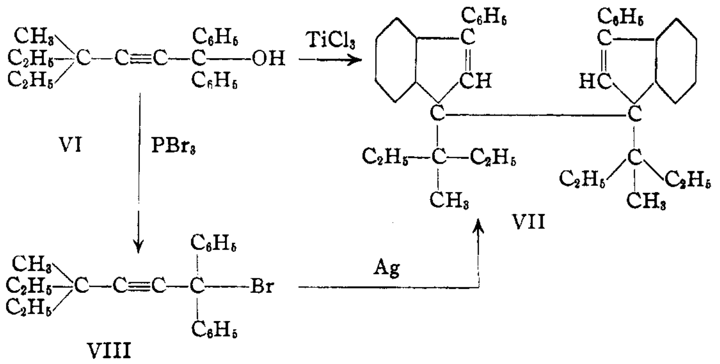
On the other hand the hydrocarbon which has been assumed to be tetraphenyldiphenylethinylethane has been found to be quite stable.

The differences in the properties of these two closely related hydrocarbons suggest that Moureu and his co-workers and Wieland and Kloss may have obtained some product other than the true ethane by their methods of preparation. It is as yet impossible to state definitely that such is the case. However, this paper will present data to show that titanium trichloride does not produce the expected hexasubstituted ethanes from some typical acetylenic carbinols.

The reaction between titanium trichloride in alcoholic hydrochloric acid solution and diphenyl-*tert*-.butylethinylcarbinol proceeded rather smoothly and yielded about 25% of the theoretical amount of a hydrocarbon, $C_{38}H_{38}$. At the same time about 50% of the carbinol was converted to the unsaturated ketone $(CH_3)_3CCOCH{=}C(C_6H_5)_2$. The hydrocarbon, $C_{38}H_{38}$, was found to be identical with the di-indene derivative (V) which results from the rearrangement of tetraphenyldi-*tert.*-butylethinylethane.

Similarly titanium trichloride reduced diphenyl-(3-methyl-3-ethylpentinyl-1)-carbinol (VI) to produce a hydrocarbon, $C_{42}H_{46}$.

The same hydrocarbon was obtained by converting the carbinol to the bromide (VIII) and treating this with silver. Since these reactions are exactly analogous to those used on the *tert.*-butyl derivative, it seems logical to assume here that the hydrocarbon has the di-indene structure.



When tri-*tert.*-butylethinylcarbinol (IX) was treated with titanium trichloride, a compound containing chlorine (X) was the main product of the reaction. This chloro compound was found to correspond in composition to a di-hydrochloride of the expected hydrocarbon. When the chlorine containing compound was treated with sodamide, two molecules of hydrogen chloride were removed and a hydrocarbon (XI) was obtained. This hydrocarbon was not hexa-*tert.*-butylethinylethane (XII) but the isomeric compound which is formed when this ethane is heated.[5]

$$\begin{tikzcd}
{[(CH_3)_3C{-}C{\equiv}C]_3\,COH} \arrow[r, "TiCl_3"] & C_{38}H_{56}Cl_2 \arrow[r, "NaNH_2"] & C_{38}H_{54} \\
\text{IX} & \text{X} & \text{XI} \\
{[(CH_3)_3C{-}C{\equiv}C]_3C{-}C[C{\equiv}C{-}C(CH_3)_3]_3} \arrow[rr, "Heat"] & & {} \arrow[u] \\
\text{XII} & &
\end{tikzcd}$$

The structure of this hydrocarbon (XI) is still uncertain. It has been found to be attacked slowly by bromine in carbon tetrachloride, and by aqueous potassium permanganate solution. Its solution in glacial acetic acid does not yield colored compounds with tetranitromethane. It is not easily reduced with hydrogen in the presence of a platinum-oxide platinum black catalyst.[8] It gives colored products on treatment with 40% sodium amalgam but these have not been characterized.

The mechanism by which the diaryl monoacetylenic carbinols are converted to di-indene derivatives by the action of titanium trichloride is probably similar to that which has been suggested for the rearrangement of tetraphenyldi-*tert.*-butylethinylethane.[3c] The first step cannot be the conversion of the carbinol to the α,β-unsaturated ketone under the influence of the acid reagent, because this ketone is unaffected by the titanium trichloride.

Several other acetylenic carbinols were treated with this reagent but no definite products could be obtained. Since some of these carbinols are new, their synthesis has been included in the experimental part of this paper.

[8] Adams and Shriner, THIS JOURNAL, 45, 2171 (1923).

The three reduction experiments using diphenyl-*tert.*-butylethinylcarbinol, diphenyl-(3-methyl-3-ethylpentinyl-1)-carbinol and tri-*tert.*-butylethinylcarbinol are sufficient to show that titanium trichloride cannot always be relied upon to yield the expected hexasubstituted ethanes from the corresponding acetylenic carbinols. Further work is in progress on this reaction and on the structure of the hydrocarbon which has been described as tetraphenyldiphenylethinylethane in order to determine whether or not it has that structure or is of the di-indene type.

Experimental Part

(3-Methyl-3-ethylpentinyl-1)-diphenylcarbinol.—In a 200-cc. three-necked, round-bottomed flask, fitted with a mechanical stirrer, a separatory funnel and a reflux condenser was placed 56 cc. of a 4.03 *N* ethylmagnesium bromide solution in ether. During a period of about twelve hours, 25 g. of 3-methyl-3-ethylpentine-1[9] was added to the well-stirred solution from the separatory funnel. To this solution was then added 36.1 g. of benzophenone dissolved in 100 cc. of dry ether over a period of about thirty hours. The mixture was well stirred during the entire reaction.

The Grignard reaction mixture was decomposed by pouring it onto about 300 g. of cracked ice and ammonium chloride solution was added to dissolve the magnesium salts. The ether layer was separated, dried over anhydrous sodium sulfate and the solvent was evaporated under ordinary pressure. The residue was distilled under reduced pressure. The carbinol came over at 154–156° (0.5 mm.). The yield was 40 g. (71% of the theoretical amount); n_D^{20} 1.5626; sp. gr. $^{20}/_{20}$ 1.0256.

Anal. Subs., 0.2064: CO_2, 0.6543; H_2O, 0.1504. Calcd. for $C_{21}H_{24}O$: C, 86.30; H, 8.21. Found: C, 86.45; H, 8.15.

(3-Methyl-3-ethylpentinyl-1)-diphenylbromomethane.—A solution of 3.0466 g. of the above carbinol in 25 cc. of petroleum ether (b. p. 25–65°) was placed in a 200-cc. flask fitted with a stirrer and protected from the air with a calcium chloride tube and then cooled in an ice-bath. To the well-stirred cold solution was added over a period of one-half hour, 1 cc. of phosphorus tribromide dissolved in 10 cc. of petroleum ether. After the phosphorus tribromide has been added the mixture was stirred for a few minutes and then 100 cc. of 5% sodium bicarbonate solution was added and stirring was continued for about ten minutes. The petroleum ether solution was separated, dried over anhydrous sodium sulfate and filtered. Attempts to isolate a crystalline bromide were unsuccessful and this solution was used directly in the next preparation.

The Hydrocarbon $C_{42}H_{46}$ from (3-Methyl-3-ethylpentinyl-1)-diphenylbromomethane and Silver.—The petroleum ether solution of the bromide prepared as described above was transferred to a 50-cc. round-bottomed flask and the solvent was removed by evaporation under reduced pressure at ordinary temperatures. The remaining bromide was taken up in 25 cc. of anhydrous ether, the flask was flushed out with dry nitrogen, 3 g. of molecular silver was introduced and the flask was tightly stoppered. The mixture was shaken on a mechanical shaker for about forty-eight hours and then the solution was filtered, and concentrated to about 5 cc. under reduced pressure at ordinary temperatures. To the residue was added 10 cc. of absolute alcohol and dry air was drawn through the solution to further concentrate it until crystals began to appear. The solution was cooled, and the crystals were collected on a Büchner funnel. After a second crystallization from ether and alcohol there was obtained 1.4877 g. (51.5% of the theoretical amount) of a hydrocarbon, m. p. 105–106°.

---

[9] Davis and Marvel, THIS JOURNAL, **53**, 3840 (1931).

Anal. Subs., 0.1941, CO_2, 0.6535; H_2O, 0.1453. Calcd. for $C_{42}H_{46}$: C, 91.63; H, 8.36. Found: C, 91.82; H, 8.37. *Mol. wt.* (Cryoscopic in benzene). Subs., 0.1032; benzene, 21.679; Δt (depression), 0.048°. Calcd. for $C_{42}H_{46}$: mol. wt. 550. Found: 508.

This hydrocarbon did not absorb oxygen in the air. It did not rearrange further on heating alone or on heating it in acetic acid solution containing dry hydrogen chloride. It gave a colored sodium derivative when treated with 40% sodium amalgam but no evidence of cleavage could be obtained since this sodium derivative did not produce water-insoluble acids on treatment with carbon dioxide.

The hydrocarbon was oxidized in an attempt to obtain evidence to confirm its structure as a di-indene derivative. A solution of 2.227 g. of the hydrocarbon and 12.5 g. of potassium dichromate in 50 cc. of glacial acetic acid was refluxed for about ten hours. The solution was poured into 50 cc. of water. The mixture was thoroughly extracted with ether. The ether extract was in turn extracted with 10% aqueous sodium hydroxide solution but no water-insoluble acids were removed. On evaporation the ether solution yielded a solid which was recrystallized from alcohol. There was thus obtained about 0.15 g. of solid; m. p. 135–136°.

Anal. (Micro) Subs., 2.390, 2.142: CO_2, 7.626, 6.821; H_2O, 1.423, 1.216. Found: C, 87.02, 86.85; H, 6.66, 6.35.[10]

The nature of this oxidation product is uncertain.

Tri-isopropylethinylcarbinol.—Isopropyl methyl ketone was prepared in yields of 45% of the theoretical amount from isopropylmagnesium bromide and acetic anhydride following the directions of Adams and Roll for cyclohexyl methyl ketone.[11] This ketone was converted to isopropylacetylene in yields of about 18% following essentially the method previously described for the preparation of *tert.*-butylacetylene.[12] Tri-isopropylethinylcarbinol was prepared according to the procedure described for tri-(3-ethyl-3-methylpentinyl-1)-carbinol.[13] Using 34 g. of the acetylene, 146 cc. of 3.14 *N* ethylmagnesium bromide solution in ether and 48.5 cc. of diethyl carbonate, the yield of carbinol was 17.7 g. (45% of the theoretical amount); b. p. 118–121° (2 mm.); n^{20}_{D} 1.475; sp. gr. $^{20}/_{20}$ 0.8848.

Anal. Subs., 0.1530: CO_2, 0.4691; H_2O, 0.1322. Calcd. for $C_{16}H_{22}O$: C, 83.5; H, 9.56. Found: C, 83.62; H, 9.66.

Attempts to convert this carbinol to the bromide and the corresponding ethane by the usual methods gave unsatisfactory results.

Tricyclohexylethinylcarbinol.—Cyclohexyl methyl ketone was prepared in 56% yields from cyclohexylmagnesium bromide and acetic anhydride.[10] This in turn gave 70–80% of the theoretical amount of hexahydro-ω-chlorostyrene on treatment with phosphorus pentachloride. Cyclohexylacetylene was obtained in 46% yields from the chloro compound with powdered potassium hydroxide according to the method of Darzens and Rost.[14] The acetylene was converted to tricyclohexylethinylcarbinol by the usual process. However, this carbinol did not crystallize and decomposed on attempted distillation. Therefore, it could not be definitely characterized.

Diphenyl-*tert.*-butylethinylcarbinol and Titanium Trichloride.—In a 200-cc. three-necked round-bottomed flask fitted with a short reflux condenser, a mechanical stirrer

---

[10] The authors are indebted to Dr. W. H. Carothers and Mr. S. B. Kuykendall of the du Pont Experimental Station for this analysis.

[11] Adams and Roll, private communication.

[12] Ivitzky, *Bull. soc. chim.*, [4] **35**, 357 (1924).

[13] Davis and Marvel, THIS JOURNAL, **53**, 3846 (1931).

[14] Darzens and Rost, *Compt. rend.*, **149**, 681 (1909).

and a separatory funnel was placed a solution of 4 g. of diphenyl-*tert.*-butylethinylcarbinol in 400 cc. of absolute alcohol. The mixture was warmed in a water-bath to 60–65°, a stirrer was started and 20 cc. of a 20% solution of titanium trichloride was added from the separatory funnel during one-half hour. The mixture was stirred about one-half hour longer, cooled, and extracted with ether. The ether layer was thoroughly washed with water and then dried over anhydrous sodium sulfate. The solution was filtered, the solvent evaporated, and the residue was crystallized from alcohol and ether. The yield was 0.9263 g. (24.7% of the theoretical amount) of a hydrocarbon melting at 150–151°. A mixture of this hydrocarbon with a sample of the di-indene obtained by the rearrangement of tetraphenyldi-*tert.*-butylethinylethane melted at the same temperature.

In another experiment 10 g. of the carbinol was treated with titanium trichloride. This gave 1.5 g. of the di-indene and 8 g. of a yellow oil which after distillation (b. p. 140° at 4 mm.) slowly crystallized. This product after recrystallization from alcohol melted at 65–66°. It gave no depression in melting point when mixed with an authentic specimen of 1,1-diphenyl-4,4-dimethylpentene-1-one-3 which had been prepared by the rearrangement of the same carbinol by treatment with acids.

1,1-Diphenyl-4,4-dimethylpentene-1-one-3 and Titanium Trichloride.—A solution of 5 g. of the ketone in 50 cc. of 95% alcohol was treated with 25 cc. of 20% titanium trichloride at 60° for two hours. On examining the reaction mixture 4 g. of unchanged ketone was recovered and no hydrocarbon could be detected.

(3-Methyl-3-ethylpentinyl-1)-diphenylcarbinol and Titanium Trichloride.—Three grams of this carbinol was treated with titanium trichloride as described above. After four recrystallizations from alcohol, the yield was 1.29 g. (44% of the theoretical amount). The product melted at 105–106° and was identical with the hydrocarbon, $C_{42}H_{46}$, previously prepared by treating (3-methyl-3-ethylpentinyl-1)-diphenylbromomethane with silver.

Tri-*tert.*-butylethinylcarbinol and Titanium Trichloride.—Three grams of this carbinol was treated with titanium trichloride and yielded 1.686 g. of a white crystalline compound, m. p. 175–176°, which contained chlorine.

Anal. (Micro) Subs., 4.513: AgCl, 2.36. Calcd. for $C_{38}H_{56}Cl_2$: Cl, 12.18. Found: Cl, 12.93.[15] *Mol. wt.* (cryoscopic in benzene). Subs., 0.3024, 0.6026; benzene, 21.679; Δt (depression), 0.129°, 0.262°. Calcd. for $C_{38}H_{56}Cl_2$: mol. wt. 583. Found: 553, 543.

This chloro compound was boiled with 10% alcoholic potassium hydroxide solution and recovered unchanged. Sodamide removed hydrogen chloride.

In a 200-cc. three-necked round-bottomed flask fitted with a mechanical stirrer, a reflux condenser and a separatory funnel, was placed 4 g. of finely powdered sodamide suspended in 100 cc. of dry xylene. The xylene was heated to boiling, the stirrer was started and a solution of 1.3649 g. of the above chloro compound in 25 cc. of xylene was added from the separatory funnel during one-half hour. The reaction mixture was heated and stirred for one hour after the addition of the chloro compound was complete. The dark colored reaction mixture was poured on cracked ice, the xylene layer was separated, washed with 50 cc. of 10% sulfuric acid solution and then water. The solution was dried over anhydrous sodium sulfate, filtered and the solvent was evaporated under reduced pressure at ordinary temperatures. The residue was crystallized from alcohol and ether. The yield was 0.3140 g. (26.4% of the theoretical amount) of the hydrocarbon, $C_{38}H_{54}$, m. p. 171–172°. A mixture of this product with a sample of the hydrocarbon prepared by the action of heat on hexa-*tert.*-butylethinylethane[5] melted at 171–172°.

---

[15] This micro-analysis was made by Mr. K. Eder.

Reactions of the Hydrocarbon, $C_{38}H_{54}$ Prepared by the Rearrangement of Hexa-*tert.*-butylethinylethane.—A solution of 0.1 g. of the hydrocarbon in 3 cc. of carbon tetrachloride was treated with a few drops of a 5% solution of bromine in carbon tetrachloride. Only a very small amount of the bromine solution was decolorized.

To a solution of 0.1 g. of the hydrocarbon in 10 cc. of glacial acetic acid was added 3 to 4 drops of tetranitromethane. No color was developed in one hour. At the end of two hours a faint yellow color was noticeable.

Two grams of the hydrocarbon was refluxed with 100 cc. of 5% aqueous potassium permanganate solution for about forty hours. Extraction of this reaction mixture with ether yielded the original substance. After two recrystallizations the recovered product weighed 1.2 g. and melted at 171–172°.

Two grams of the hydrocarbon was dissolved in 30 cc. of dry ether and this solution was shaken with 5 cc. of 40% sodium amalgam in an atmosphere of nitrogen for about twenty-four hours. The solution became deep red in color in about fifteen minutes and was dark brown at the end of the treatment. The amalgam was frozen and the ether solution was decanted off and treated with dry carbon dioxide. The solution was not decolorized and no acid was obtained from the reaction mixture when it was worked up in the usual fashion.

Attempted Catalytic Reduction of Hexa-*tert.*-butylethinylethane.—Two grams of hexa-*tert.*-butylethinylethane was dissolved in 100 cc. of absolute alcohol and after the addition of 0.1 g. of platinum-oxide platinum black catalyst,[8] was treated with hydrogen under pressure in a Burgess–Parr reduction apparatus at 70–80°. Apparently no hydrogen was taken up by the solution. On working up the reaction mixture the isomeric hydrocarbon, $C_{38}H_{54}$, was obtained. This was undoubtedly produced by the rearrangement of the true ethane at the elevated temperature.

Action of Titanium Trichloride on Other Acetylenic Carbinols.—The action of titanium trichloride on tri-(3-methyl-3-ethylpentinyl-1)-carbinol, *tert.*-butyldi-*tert.*-butylethinylcarbinol, triphenylethinylcarbinol, tri-*iso*propylethinylcarbinol, tricyclohexylethinylcarbinol and ω-*tert.*-butylpropinyldiphenylcarbinol did not yield products which could be separated and characterized.

Summary

1. Some new acetylenic carbinols have been synthesized and characterized.

2. The reaction of titanium trichloride with three acetylenic carbinols has been studied and found to produce hydrocarbons which are not the expected hexa-substituted ethanes. Two diaryl-monoacetylenic carbinols gave di-indene derivatives. Tri-*tert.*-butylethinylcarbinol gave a dichloro compound which could be converted to an isomer of hexa-*tert.*-butylethinylethane.

3. Some reactions of this isomer of hexa-*tert.*-butylethinylethane have been described.

URBANA, ILLINOIS