that the reaction between oxalic acid and acetic anhydride is so rapid that the water does not have opportunity to react with the anhydride. The only considerable error that can be introduced was found to be a lowering of the results caused by the vaporization of the anhydride due to the heating when pyridine was added. This error varied from 0.2 to 0.5% but is avoided by cooling the container. The amount of pyridine added was varied from 1 to 5 cc. with no effect on the results. An error of 0.1 cc. in the potassium permanganate titration causes a deviation of only 0.05%.

## Summary

A method has been devised for the determination of the purity of acetic anhydride based on the decomposition of anhydrous oxalic acid by acetic anhydride using pyridine as a catalyst, and subsequently determining the excess oxalic acid with potassium permanganate. The method is simple, rapid and easily accurate to within 0.1%.

MADISON, WISCONSIN

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

# SYMMETRICAL DIALKYL-TETRA-TERTIARY-BUTYLETHINYLETHANES

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Recent work by Ziegler and Schnell[1] and by Conant and his students[2] has indicated that certain dialkyl-tetra-arylethanes have properties that resemble quite closely those of the hexa-arylethanes. In particular, it has been found that a tertiary butyl group or a cyclohexyl group can replace a phenyl group without greatly changing the amount of dissociation of the ethane. Work in this Laboratory on the acetylenic ethanes has shown that hexa-*tert.*-butylethinylethane[3] (I) is cleaved by 1% sodium amalgam and resembles in this respect the hexa-arylethanes. Rossander and Marvel[4] have observed that diphenyl-tetra-*tert.*-butylethinylethane (II) requires 40% sodium amalgam for cleavage and hence is more stable toward alkali metals than is the hexa-acetylenic compound. The series of tetra-acetylenic ethanes has now been extended to include di-*tert.*-butyl-tetra-*tert.*-butylethinylethane (III) and dicyclohexyl-tetra-*tert.*-butylethinylethane (IV).

$$[(CH_3)_3C{-}C{\equiv}C]_3{-}C{-}C[C{\equiv}C{-}C(CH_3)_3]_3$$

I

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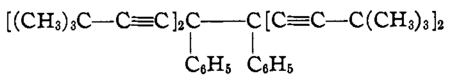
[1] Ziegler and Schnell, *Ann.*, **437**, 252 (1924).

[2] Conant and Small, THIS JOURNAL, **47**, 3068 (1925); Conant, Small and Sloan, *ibid.*, **48**, 1743 (1926); Conant and Bigelow, *ibid.*, **50**, 2041 (1928).

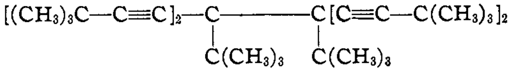
[3] Salzberg with Marvel, *ibid.*, **50**, 1737 (1928).

[4] Rossander and Marvel, *ibid.*, **51**, 932 (1929).



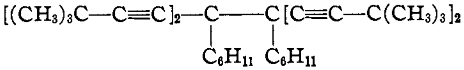
$[(CH_3)_3C{-}C{\equiv}C]_2\underset{C_6H_5}{C}{-}\underset{C_6H_5}{C}[C{\equiv}C{-}C(CH_3)_3]_2$

II



$[(CH_3)_3C{-}C{\equiv}C]_2{-}\underset{C(CH_3)_3}{C}{-}\underset{C(CH_3)_3}{C}[C{\equiv}C{-}C(CH_3)_3]_2$

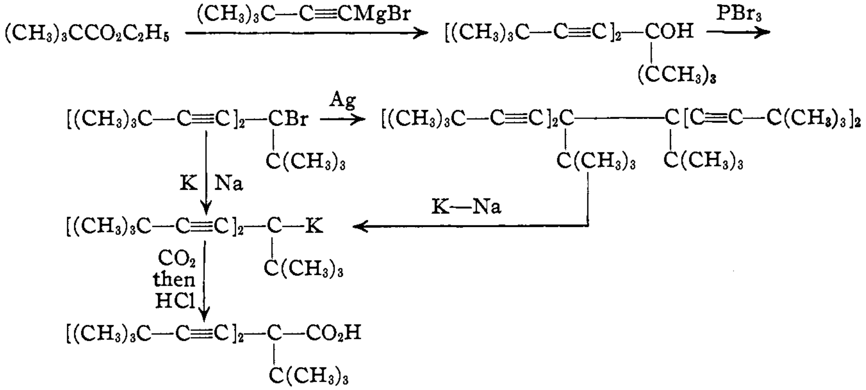
III



$[(CH_3)_3C{-}C{\equiv}C]_2{-}\underset{C_6H_{11}}{C}{-}\underset{C_6H_{11}}{C}[C{\equiv}C{-}C(CH_3)_3]_2$

IV

Di-*tert.*-butyl-tetra-*tert.*-butylethinylethane (III) was prepared by a series of reactions starting with ethyl trimethylacetate and *tert.*-butylethinylmagnesium bromide. The steps in the synthesis and structure proof are indicated



This ethane was found to be more stable than the corresponding diphenyl derivative (II) since cleavage could be accomplished only by use of liquid sodium–potassium alloy. The ethane was stable toward heat at 140°, since it could be recovered unchanged after boiling the xylene solution. It did not absorb oxygen when dissolved in *p*-dibromobenzene and heated to 140°.

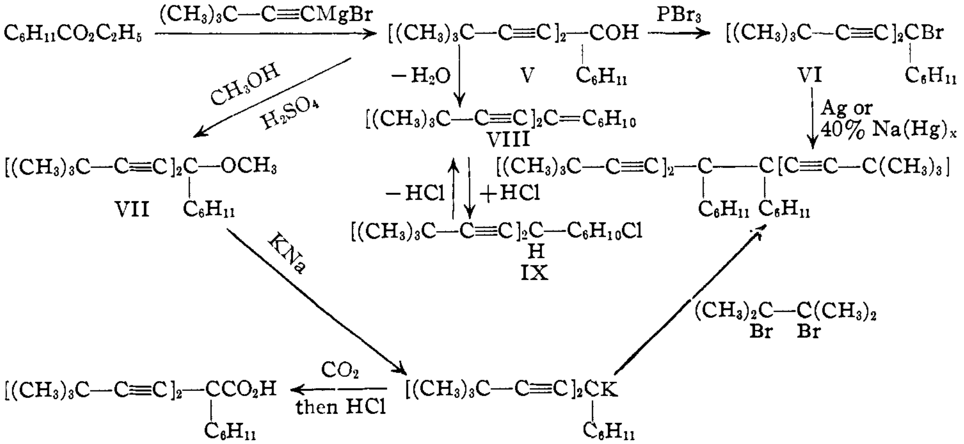
Dicyclohexyl-tetra-*tert.*-butylethinylethane was prepared from ethyl hexahydrobenzoate by much the same method that had been used for the tertiary butyl derivative. Cyclohexyl-di-*tert.*-butylethinylbromomethane (VI) did not react readily with silver although a low yield of a hydrocarbon was obtained. Then several other methods of preparation were studied. When the bromide was treated with 40% sodium amalgam, very little metal alkyl was obtained, but the same hydrocarbon was formed. This hydrocarbon was not cleaved by liquid sodium–potassium alloy. Some metal alkyl was obtained by the action of liquid sodium–potassium alloy[5] on the methyl ether of cyclohexyl-di-*tert.*-butylethinylcarbinol (VII).

[5] Ziegler and Schnell, *Ann.*, **437**, 227 (1927).

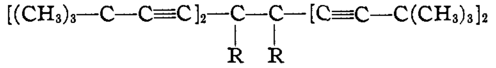
From this derivative the acid was obtained by the action of carbon dioxide. With tetramethylethylene dibromide the metal alkyl gave the same hydrocarbon that had been obtained previously by the action of silver on the bromide.

Since this hydrocarbon was not cleaved by alkali metals its structure has not been established beyond question. However, the fact that it has been obtained by so many different methods seemed to leave little doubt concerning its structure. An attempt was made to prepare the isomeric hydrocarbon which would have formed if the carbinol (V) had been dehydrated and then halogen acid had added to the double bond to give an isomeric halogen derivative of the structure represented in formula IX. The carbinol (V) was dehydrated to give di-*tert.*-butylethinylcyclohexylidenemethane (VIII) and hydrogen chloride was added to the olefin in alcohol solution. The chloride was oily and was never obtained in a pure condition. When this crude chloride was treated with 40% sodium amalgam, no evidence of metal alkyl formation was found. The only hydrocarbon that could be isolated from this reaction mixture was the original olefin. This behavior of the isomeric chloride furnished additional evidence that the hydrocarbon obtained from the true chloride of cyclohexyl-di-*tert.*-butylethinylcarbinol is the desired dicyclohexyltetra-*tert.*-butylethinylethane.

These reactions are represented graphically as follows



It is interesting to note the variation in the ease of cleavage of the compounds of the general formula



$$[(CH_3)_3-C-C\equiv C]_2-\underset{R}{C}-\underset{R}{C}-[C\equiv C-C(CH_3)_3]_2$$

with alkali metals as R changes. When R is the cyclohexyl group the molecule is very stable; when R is the tertiary butyl group the molecule is cleaved by liquid sodium–potassium alloy; when R is the phenyl group the molecule is cleaved by 40% sodium amalgam; and when R is the *tert.*-butylethinyl group the molecule is cleaved by 1% sodium amalgam. The stability of the cyclohexyl derivative is particularly surprising in view of the ease with which tetracyclohexyldiphenylethane reacts with 1% sodium amalgam to give a metal alkyl.[6]

## Experimental Part

***Tert.*-butyl-di-*tert.*-butylethinylcarbinol.**—*Tert.*-butylethinylmagnesium bromide was prepared by adding 35 g. of *tert.*-butylacetylene from a dropping funnel to 108 cc. of a 3.945 *N* ether solution of ethylmagnesium bromide during four hours. The heat of reaction was sufficient to cause the ether to reflux and an efficient condenser filled with water at about 5° was needed to avoid loss of acetylene. Half of the theoretical amount (13.4 g.) of ethyl trimethylacetate was then added during three to four hours and the mixture was stirred overnight. The remainder of the ester (13.4 g.) was added during four hours. The mixture was stirred for about three hours longer and then decomposed by pouring it on cracked ice and 25 g. of ammonium chloride and then adding the theoretical quantity of dilute hydrochloric acid. The ether layer after being dried over anhydrous magnesium sulfate was heated on the steam-bath to remove the solvent. The residue was distilled under diminished pressure and the fraction boiling at 95–99° at 5 mm. or 103–107° at 7 mm. was collected. This distillate solidified on standing to give white rhombic crystals; m. p. 46–47°. The yield was 40–42 g. (78–82% of the theoretical amount).

*Anal.* Subs., 0.2429: $CO_2$, 0.7322; $H_2O$, 0.2487. Calcd. for $C_{17}H_{28}O$: C, 82.19; H, 11.37. Found: C, 82.20; H, 11.46.

***Tert.*-butyl-di-*tert.*-butylethinylbromomethane.**—Three grams of the carbinol was dissolved in 25 cc. of low-boiling petroleum ether and the solution was cooled to 0°. Then 1 g. of phosphorus tribromide was added and the solution stirred at 0° for one hour. To the mixture was slowly added 100 cc. of 10% sodium bicarbonate solution and stirring was continued for ten minutes. The ether layer, after being dried over anhydrous magnesium sulfate, was evaporated under reduced pressure. The bromide appeared as a viscous yellow oil. All attempts to crystallize it failed. The yield of crude product was 2.4–2.6 g. (63–69% of the theoretical amount). This crude bromide was sufficiently pure for the preparation of the ethane.

One run of the bromide was distilled under reduced pressure and the fraction boiling at 68–71° at 13 mm. was collected.

*Anal.* (Stepanow). Subs., 0.1482: 11.19 cc. of 0.4387 *N* $AgNO_3$. Calcd. for $C_{17}H_{27}Br$: Br, 25.69. Found: Br, 26.12.

***Sym.*-di-*tert.*-butyl-tetra-*tert.*-butylethinylethane.**—The crude *tert.*-butyl-di-*tert.*-butylethinylbromomethane obtained from 3 g. of carbinol was dissolved in 10 cc. of dry ether and shaken mechanically with 3 g. of molecular silver for twenty-four hours. The ether solution was evaporated under reduced pressure almost to dryness and 5 cc. of absolute alcohol was added. The evaporation was continued until crystallization began and then the mixture was cooled. The yield was 0.87 g. (31.6% of the theoretical amount); m. p. 120–120.5°.

*Anal.* Subs., 0.1942: $CO_2$, 0.6267; $H_2O$, 0.2042. Calcd. for $C_{34}H_{54}$: C, 88.23; H, 11.76. Found: C, 88.00; H, 11.77. *Mol. wt.* (Cryoscopic in benzene). Subs., 0.0901, 0.2421; benzene, 13.1765; $\Delta t$, 0.086, 0.208°. Calcd. for $C_{34}H_{54}$: mol. wt., 462. Found: 452, 449.3.

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[6] Rossander, Bock and Marvel, THIS JOURNAL, 52, 2976 (1930).

**Cleavage of the Ethane with Alkali Metals.**—A solution of 0.1 g. of ethane in 10 cc. of dry ether was shaken with 2 cc. of liquid sodium–potassium alloy in an atmosphere of dry nitrogen. The solution instantly became yellow in color and a deep red color developed within one to two minutes. The isolation of the *tert.*-butyl-di-*tert.*-butylethinylacetic acid is described below.

When 0.1 g. of ethane was shaken for twenty-four hours with 4–5 cc. of 40% sodium amalgam under the conditions described above, no red coloration appeared and most of the ethane was recovered.

A solution of 0.5 g. of the bromide in dry ether was shaken for twenty-four hours with 4–5 cc. of 40% sodium amalgam in an atmosphere of nitrogen. No red color developed and no acid was formed upon treating the reaction mixture with carbon dioxide and mineral acid. From the ether of the reaction there was obtained 0.05 g. of the ethane melting at 119–120°.

***Tert.*-butyl-di-*tert.*-butylethinylacetic Acid. (A) From Di-*tert.*-butyl-tetra-*tert.*-butylethinylethane.**—One gram of ethane was shaken for twenty-four hours with 4–5 cc. of liquid sodium–potassium alloy in ether. Dry carbon dioxide was then passed into the reaction mixture until the red color disappeared. The ether and acid salt were decanted from the excess alloy and carefully treated with a little absolute alcohol to decompose any small particles of the alloy, then with water and finally with dilute hydrochloric acid. The ether layer was extracted with a solution of 2.5 g. of potassium hydroxide in 50 cc. of water. The alkaline layer was cooled to 0° and acidified. The brown oil which separated was extracted with ether and the ether solution was dried over anhydrous magnesium sulfate. The ether was then evaporated at room temperature. The oil was shaken up in a little hot glacial acetic acid and filtered. The crystals which separated on cooling the filtrate were again recrystallized from glacial acetic acid. The yield was 0.426 g. (35.7% of the theoretical amount); m. p. 151.5–152.5°. This acid caused no depression of the melting point when mixed with a sample of the acid prepared from the bromide.

**(B) From *Tert.*-butyl-di-*tert.*-butylethinylbromomethane.**—The crude bromide obtained from 6 g. of carbinol was dissolved in 20 cc. of dry ether and shaken with a large excess (8–10 cc.) of liquid sodium–potassium alloy for twenty-four hours in an atmosphere of dry nitrogen. Dry carbon dioxide was then passed into the reaction mixture until the red color disappeared. The ether and acid salt were then treated as described above with a little absolute alcohol and then with water. The ether layer was separated and thoroughly extracted with water. The extracts were added to the main aqueous layer, which was then cooled to 0° and acidified. The red gum which separated was extracted with ether and reprecipitated by extracting the ether solution with a solution of 5 g. of potassium hydroxide in 50 cc. of water and acidifying the alkaline extract. The gum was then isolated as described above and recrystallized several times from glacial acetic acid. The yield of pure acid was 0.75 g. (11.2% of the theoretical amount); m. p. 152.5–153.5°.

*Anal.* Subs., 0.2007: $CO_2$, 0.5781; $H_2O$, 0.1860. Calcd. for $C_{18}H_{28}O_2$: C, 78.21; H, 10.21. Found: C, 78.53; H, 10.37. *Neutral equivalent.* Subs., 0.1069: 3.35 cc. of 0.1153 *N* NaOH. Calcd. for $C_{18}H_{28}O_2$: 276.3. Found: 276.7.

In one run similar to the one described above, not enough of the alloy was used to provide a large excess. In this case a few white crystals were isolated from the ether of the reaction mixture after its separation from the aqueous solution. After recrystallization from ether and alcohol these melted at 170–173.5°. This was probably a rearranged hydrocarbon but not enough was isolated for further identification. Conant and Bigelow[2] observed a similar production of a rearranged hydrocarbon when diphenyl-*tert.*-butylchloromethane was shaken with an insufficient quantity of liquid sodium–potassium alloy.

**Effect of Heat on the Ethane.**—A solution of 0.1 g. of ethane in 4 cc. of absolute alcohol was heated in a sealed tube at 100° for one hour. No color was developed. Upon concentrating the alcoholic solution and cooling to 0°, 0.07 g. of ethane was recovered (m. p. 120.5°).

A solution of 0.1 g. of ethane in 3 cc. of dry xylene was heated in a sealed tube to 140° for one hour. No color developed and 0.05 g. of ethane was recovered (m. p. 120.5°).

**Oxygen Absorption.**—Seven hundredths of a gram of di-*tert.*-butyl-tetra-*tert.*-butylethinylethane was placed in a 50-cc. Florence flask and 5 g. of *p*-dibromobenzene was added. The flask was then placed in an oil-bath at 140° and connected to a eudiometer filled with oxygen. The same temperature was maintained for one and one-half hours but no absorption of oxygen was observed.

**Cyclohexyl-di-*tert.*-butylethinylcarbinol.**—The same procedure was followed in the preparation of this carbinol as described under *tert.*-butyl-di-*tert.*-butylethinylcarbinol. The *tert.*-butylethinylmagnesium bromide was made from 24 g. of *tert.*-butylacetylene and 93.5 cc. of a 3.12 *N* ether solution of ethylmagnesium bromide. To the acetylenic Grignard reagent was added 22.5 g. of ethyl hexahydrobenzoate. The carbinol was isolated and distilled under diminished pressure, collecting the material boiling at 123–128° at 3 mm. The yield was 28 g. (70% of the theoretical amount). It had the following constants: sp. gr. $^{20}_{20}$, 0.8991; $n^{20}_{\mathrm{D}}$ 1.4729. Calcd. for $C_{19}H_{30}O$: $M_{\mathrm{D}}$, 85.42. Found: $M_{\mathrm{D}}$, 85.47.

*Anal.* Subs., 0.2294: $CO_2$, 0.6984; $H_2O$, 0.2202. Calcd. for $C_{19}H_{30}O$: C, 83.21; H, 10.95. Found: C, 82.02; H, 10.74.

In a small side-arm test-tube (25 cc.) was placed 0.293 g. of pure carbinol dissolved in a few cc. of dry benzene. The side arm was connected to an outfit for drying and collecting ethane gas. An excess of ethylmagnesium bromide was added to the carbinol from a dropping funnel, and 25 cc. of ethane at S. T. P. was collected. The theoretical yield of ethane is 23.9 cc.

The carbinol was further characterized by converting it to a solid acetate.

**Cyclohexyl-di-*tert.*-butylethinylmethyl Acetate.**—One and one-half grams of the carbinol was added to a suspension of 1 g. of powdered potassium in petroleum ether (b. p. 40–60°) and stirred for about ten minutes. The supernatant liquid was decanted and treated with 2 cc. of acetic anhydride with stirring. The mixture was decomposed with water and neutralized with sodium bicarbonate solution. The ether layer was separated, dried with magnesium sulfate and concentrated to 3–4 cc. under diminished pressure. On cooling, the ester crystallized. The yield was 0.5 g.; m. p. 91–93° Recrystallization from acetone raised the melting point to 95–96°.

*Anal.* Subs., 0.1725: $CO_2$, 0.5018; $H_2O$, 0.1584. Calcd. for $C_{21}H_{32}O_2$: C, 79.69; H, 10.20. Found: C, 79.33; H, 10.28. *Mol. wt.* (cryoscopic in benzene). Subs., 0.1513; benzene, 13.1765; $\Delta^t$, 0.195°. Calcd. for $C_{21}H_{32}O_2$: mol. wt. 316.4. Found: 301.5.

**Cyclohexyl-di-*tert.*-butylethinylbromomethane.**—Five grams of the carbinol was dissolved in 25 cc. of petroleum ether (b. p. 20–40°) and treated with 2 g. of phosphorus tribromide as described under *tert.*-butyl-di-*tert.*-butylethinylbromomethane. The crude bromide was isolated and used in subsequent experiments without purification as it was feared that distillation would cause the elimination of hydrogen bromide from the molecule.

**Cyclohexyl-di-*tert.*-butylethinylchloromethane.**—Five grams of the carbinol was dissolved in 15 cc. of dry benzene and 1.8 g. (10% excess) of acetyl chloride was added. The mixture was allowed to stand for twenty-four hours with occasional shaking. The benzene was then evaporated under reduced pressure and 5 cc. of absolute methyl alcohol was added to destroy the excess acetyl chloride. The methyl acetate was then evaporated under reduced pressure. The crude chloride was used for subsequent experiments.

**Cyclohexyl-di-*tert.*-butylethinylmethyl Methyl Ether.**—Ten grams of carbinol was dissolved in 10 cc. of absolute methyl alcohol (5 times the theoretical amount) and 0.4 cc. of concentrated sulfuric acid (sp. gr. 1.84) was slowly added with shaking and cooling. The amount of acid added did not exceed 3% of the total weight. The mixture separated into two layers within a few hours. The reaction was complete in twenty-four hours. Water was then added and the organic material was extracted with ether. The ether layer was dried over magnesium sulfate and the solvent evaporated. The residue was distilled under diminished pressure and the fraction boiling at 116–121° at 3.5 mm. was collected. The yield was 5 g. (52.6% of the theoretical amount). The constants found were: sp. gr. $^{20}_{20}$, 0.8680; $n^{20}_{D}$ 1.4640. Calcd. for $C_{20}H_{32}O$: $M_D$, 90.04. Found: $M_D$, 91.55.

*Anal.* Subs., 0.1865: $CO_2$, 0.5683; $H_2O$, 0.1887. Calcd. for $C_{20}H_{32}O$: C, 83.33; H, 11.11. Found: C, 83.10; H, 11.32.

***Sym.*-di-cyclohexyl-tetra-*tert.*-butylethinylethane. (A) From the Bromide and Molecular Silver.**—The crude bromide from 2 g. of carbinol was dissolved in 10 cc. of dry ether and was shaken mechanically for twenty-four hours with 2 g. of molecular silver in an atmosphere of dry nitrogen. The ether solution was then filtered, concentrated to about 2 cc. under reduced pressure and 5 cc. of absolute alcohol was added. The concentration was continued until crystals appeared and the mixture was then cooled. The solid material was filtered and recrystallized from an ether–alcohol mixture. It melted at 149–150°.

**(B) From the Bromide and Liquid Sodium–Potassium Alloy.**—The alcoholic filtrate from the above hydrocarbon was evaporated to dryness under diminished pressure. The residue contained bromine. It was dissolved in 10 cc. of dry ether and shaken for twenty-four hours with 3–4 cc. of sodium–potassium alloy in an atmosphere of dry nitrogen. The solution had a reddish-brown tint. It was treated with dry carbon dioxide and worked up as described under *tert.*-butyl-di-*tert.*-butylethinylacetic acid. The ether contained more of the hydrocarbon obtained above, m. p. 149–150°. A small amount of acid was isolated as a yellow powder (m. p. 114–117°). Further treatment of this will be described later. Several runs of the bromide were then treated directly with liquid sodium–potassium alloy. The results were exactly the same.

**(C) From the Bromide and 40% Sodium Amalgam.**—The bromide from 5 g. of carbinol was dissolved in 50 cc. of dry ether and placed in a 250-cc. flask. Forty grams of 40% sodium amalgam was added, the flask was filled with nitrogen and the mixture was shaken mechanically for twenty-four hours. The amalgam was frozen and the ether decanted into a 3-liter nitrogen-filled flask. The amalgam was washed once with 50 cc. of petroleum ether (b. p. 40–60°), freshly dried over ethylmagnesium bromide. The petroleum ether washing was also poured into the 3-liter flask and 100 cc. of dry petroleum ether was added to insure precipitation of all metal alkyl. A cloth filter reinforced by copper gauze was then fitted to the flask which was inverted and the petroleum ether filtered out while maintaining a nitrogen atmosphere.

The petroleum ether was evaporated to dryness under reduced pressure and the residue was recrystallized from ether–alcohol mixture. Three-fourths of a gram of the same hydrocarbon described above was obtained, m. p. 149–150°. There was no depression of the melting point when it was mixed with the hydrocarbon from the reaction of silver with the bromide.

*Anal.* Subs., 0.1404, 0.1815: $CO_2$, 0.4542, 0.5898; $H_2O$, 0.1436, 0.1753. Calcd. for $C_{38}H_{58}$: C, 88.62; H, 11.38. Found: C, 88.42, 88.62; H, 11.45, 10.81. *Mol. wt.*

(cryoscopic in benzene). Subs., 0.3138; benzene, 13.1765; $\Delta^t$, 0.253°. Calcd. for $C_{38}H_{58}$: mol. wt., 514. Found: 482.

About 100 cc. of diethyl ether, freshly dried over ethylmagnesium bromide, was added to the residue of metal alkyl in the 3-liter flask. To this was added 0.5 g. of tetramethylethylene dibromide dissolved in 25 cc. of dry ether. The ether solution was then filtered and concentrated to dryness under reduced pressure. The residue was kept under reduced pressure for some time in order to volatilize the excess tetramethylethylene dibromide. It was then recrystallized from an ether–alcohol mixture. The yield was 0.1 g. of the same hydrocarbon. Apparently very little metal alkyl had formed in the reaction.

(D) **From the Chloride and 40% Sodium Amalgam.**—The chloride prepared from 5 g. of carbinol as previously described was treated with 40 g. of 40% sodium amalgam for a twenty-four hour period. Dry carbon dioxide was then passed into the reaction mixture. The amalgam was frozen and the ethereal suspension of the acid salt was decanted. This was worked up as described under *tert.*-butyl-di-*tert.*-butylethinylacetic acid. About 0.2–0.3 g. of a yellow powder was isolated which melted between 114–117° as did the acid from the reaction of sodium–potassium alloy on the bromide.

From the ether solution a small amount of hydrocarbon, m. p. 146–148°, was isolated with difficulty as it tended to form a paste.

(E) **From the Methyl Ether of the Carbinol.**—Three and one-half grams of cyclohexyl-di-*tert.*-butylethinylmethyl methyl ether was dissolved in 50 cc. of dry ether, placed in a nitrogen filled flask, and 10 cc. of liquid sodium–potassium alloy was added. This was shaken for twenty-four hours. The reaction mixture became yellowish-brown in color. Then 2 g. of powdered potassium was introduced into the flask and shaking was continued for another twenty-four hours. The ether suspension was then decanted from the excess alloy into another nitrogen-filled flask fitted with a dropping funnel. From the dropping funnel was added 1.4–1.8 g. of tetramethylethylene dibromide dissolved in 25 cc. of dry ether. The yellowish brown tint of the reaction mixture slowly changed to light greenish-blue. A small amount of alcohol was added to decompose any particles of the alloy, and then the ether solution was washed with water. The ether layer was dried over magnesium sulfate and the ether evaporated under reduced pressure. The residue was kept under diminished pressure for some time to remove all traces of tetramethylethylene dibromide. It was then recrystallized from an ether–alcohol mixture and melted at 149–150°. The yield of hydrocarbon was 0.8 g. (27% of the theoretical amount).

The hydrocarbon isolated in all five of the reactions as just described was undoubtedly the desired *sym.*-dicyclohexyl tetra-*tert.*-butylethinylethane.

**Cyclohexyl-di-*tert.*-butylethinylacetic Acid. (A) From the Bromide and Chloride.**—The isolation of an acid from the action of sodium–potassium alloy on the bromide, and also from the action of 40% sodium amalgam on the chloride, has already been mentioned. The acids from both sources melted in a similar fashion so they were combined and recrystallized from glacial acetic acid. The product was then pure white and melted at 125–126°.

*Neutral equivalent.* Subs., 0.1170: 3.30 cc. of 0.1163 *N* NaOH. Calcd. for $C_{20}H_{30}O_2$: 302. Found: 304.6.

(B) **From the Methyl Ether of the Carbinol.**—One and eight-tenths grams of the methyl ether of cyclohexyl-di-*tert.*-butyl-ethinylcarbinol was dissolved in 15 cc. of dry ether and shaken with 4–5 cc. of sodium–potassium alloy in an atmosphere of dry nitrogen for twenty-four hours. Dry carbon dioxide was then passed into the reaction mixture and the red color of the metal alkyl disappeared immediately. The ethereal suspension of the sodium salt of the acid was decanted from the excess alloy and water was added cautiously to the ether. The ether layer was extracted several times with water. The aqueous extracts were combined, cooled to 5° and acidified with dilute hydrochloric acid. The organic acid separated in white flocculent crystals, which were filtered. It was recrystallized from glacial acetic acid and melted at 125–126°. The yield was 0.5 g. (27% of the theoretical amount). When a sample of this acid was mixed with that obtained from the bromide and chloride, there was no depression of the melting point.

*Anal.* Subs., 0.1757: $CO_2$, 0.5090; $H_2O$, 0.1589. Calcd. for $C_{20}H_{30}O_2$: C, 79.41; H, 10.00. Found: C, 78.87; H, 10.10.

**Di-*tert.*-butylethinyl-cyclohexylidenemethane.**—Twenty-eight grams of cyclohexyl-di-*tert.*-butylethinylcarbinol was heated to 125–130° for twelve hours with 28 g. of potassium acid sulfate. The water was removed as formed by means of a current of dry air. The reaction mixture was extracted with ether and dried over magnesium sulfate. The solvent was evaporated and the residue distilled under diminished pressure. The portion boiling at 105–110° at 3 mm. was collected. The yield was only 5 g. The product gave an intense coloration when treated with tetranitromethane, whereas the carbinol gave no coloration with that reagent; sp. gr. $^{20}_{20}$, 0.8578; $n^{20}_{D}$ 1.4838.

*Anal.* Subs., 0.1676: $CO_2$, 0.5485; $H_2O$, 0.1635. Calcd. for $C_{19}H_{28}$: C, 89.06; H, 10.94. Found: C, 89.25; H, 10.92.

**Chlorocyclohexyl-di-*tert.*-butylethinylmethane.**—Five grams of di-*tert.*-butylethinyl-cyclohexylidenemethane was dissolved in 25 cc. of absolute alcohol. Dry hydrogen chloride was passed into the ice-cooled solution until it was saturated. The solution was then warmed to 40° for one-half hour and again saturated with dry hydrogen chloride. The alcohol was removed under reduced pressure. The residue was dissolved in dry ether and anhydrous sodium carbonate was added. The ether was evaporated under reduced pressure. There was left a brown oil which contained chlorine.

*Anal.* (Stepanow). Subs., 0.2263: 7.91 cc. of 0.1005 *N* $AgNO_3$. Calcd. for $C_{19}H_{29}Cl$: Cl, 12.14. Found: Cl, 12.43.

This oil was dissolved in 50 cc. of dry ether and shaken with 30 g. of 40% sodium amalgam for twenty-four hours in an atmosphere of dry nitrogen. Dry carbon dioxide was passed into the reaction mixture and it was worked up as described in the preparation of dicyclohexyl-tetra-*tert.*-butylethinylethane from the bromide and 40% sodium amalgam. No acid was isolated. From the ether there was isolated a light yellow oil, b. p. 105–110° at 3 mm.; $n^{20}_{D}$ 1.4843. This oil gave an intense coloration with tetranitromethane. It was di-*tert.*-butylethinyl-cyclohexylidenemethane.

## Summary

1. *Sym.*-di-*tert.*-butyl-tetra-*tert.*-butylethinylethane has been prepared by the action of silver on *tert.*-butyl-di-*tert.*-butylethinylbromomethane.

2. This hydrocarbon reacted with liquid sodium–potassium alloy to form the alkali metal derivative of *tert.*-butyl-di-*tert.*-butylethinylmethyl. It did not react with 40% sodium amalgam. It was not affected by heat and was more stable than *sym.*-di-phenyl-tetra-*tert.*-butylethinylethane.

3. *Sym.*-dicyclohexyl-tetra-*tert.*-butylethinylethane has been prepared by several methods. This hydrocarbon was not cleaved by liquid sodium–potassium alloy.

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