

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

**THE REARRANGEMENT OF CERTAIN POLY-INES. THE  
STRUCTURE OF THE PRODUCT OBTAINED BY THE  
REARRANGEMENT OF TETRAPHENYLDI-TERTIARY-  
BUTYLETHINYLETHANE**

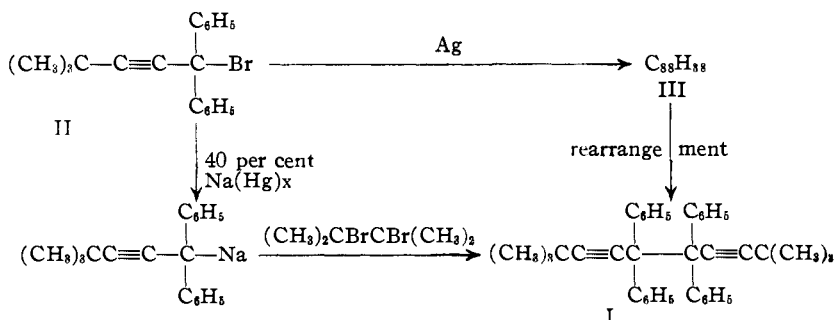
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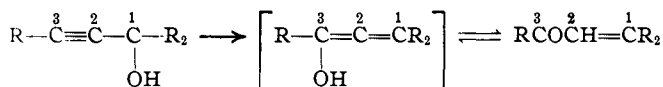
During the last few years a number of hexa-substituted ethanes containing acetylenic groups have been prepared and characterized in this Laboratory.<sup>1</sup> It has been observed that most of these compounds are unstable toward heat and under its influence they isomerize to give more stable hydrocarbons. Since this rearrangement seems to be characteristic of the type of poly-ine hydrocarbon which we have been studying, it has become important to investigate the structure of the rearranged compounds. The present communication describes some observations which have been made on the structure of the hydrocarbon which was formed by the rearrangement of symmetrical tetraphenyldi-*tert.*-butylethinylolethane (I).

The first attempt<sup>1c</sup> to prepare tetraphenyldi-*tert.*-butylethinylolethane (I) by the action of silver on diphenyl-*tert.*-butylethinylolethane (II) gave a hydrocarbon, C<sub>38</sub>H<sub>38</sub> (III). However, this compound did not have the reactions that would be expected of the hexa-substituted ethane which was sought. More recently the true ethane (I) was prepared by a different series of reactions.<sup>1h</sup> The ethane was quite unstable and very quickly rearranged to produce the same isomeric hydrocarbon, C<sub>38</sub>H<sub>38</sub>, which had been obtained in the earlier work.



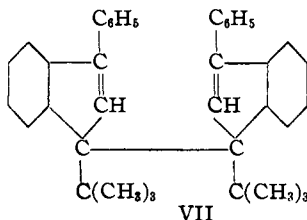
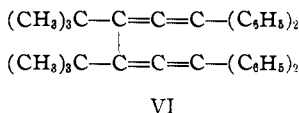
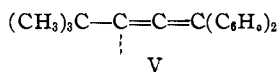
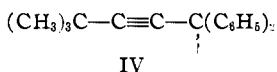
<sup>1</sup> The papers in this field are as follows: (a) Gray with Marvel, *THIS JOURNAL*, 47, 2796 (1925); (b) Salzberg with Marvel, *ibid.*, 50, 1737 (1928); (c) Salzberg and Marvel, *ibid.*, 50, 2840 (1928); (d) Rossander and Marvel, *ibid.*, 51, 932 (1929); (e) Gillespie and Marvel, *ibid.*, 52, 3368 (1930); (f) Ozanne and Marvel, *ibid.*, 52, 5267 (1930); (g) Davis and Marvel, *ibid.*, 53, 3840 (1931); (h) Stampfli and Marvel, *ibid.*, 53, 4057 (1931).

In searching for a plausible formula for the rearranged compound it occurred to us that the rearrangement of these ethanes might be related to the rearrangement of the acetylenic carbinols which has been studied by Meyer and Schuster.<sup>2</sup> This rearrangement is illustrated by the following formulas. The same type of rearrangement has also been observed in



many olefinic derivatives and the shift of a group from carbon atom 1 to carbon atom 3 in such a system is not unusual.

In order to have some basis for the investigation of the structure of the hydrocarbon  $\text{C}_{33}\text{H}_{38}$  (III) it was assumed that the rearrangement of the ethane (I) proceeded through the stage of the free radical diphenyl-*tert.*-butylethynylmethyl (IV). This free radical would also be the first product of the action of silver on the bromide (II). If this free radical (IV) undergoes a rearrangement similar to the Meyer and Schuster rearrangement, the allene free radical (V) should result.



The recombination of two free radicals of structure V would produce the double allene molecule indicated in formula VI. For a considerable time it was believed that this formula represented the structure of the rearranged hydrocarbon under investigation. However, the final rearrangement to a di-indene derivative was indicated by the reactions of the product. This rearrangement of a phenylallene to an indene has been amply demonstrated by the work of Vorländer and his co-workers,<sup>3</sup> Kohler,<sup>4</sup> Hurd and Webb<sup>5</sup> and Ziegler and Sauermilch.<sup>6</sup>

The reactions of the hydrocarbon,  $\text{C}_{33}\text{H}_{38}$ , which must be explained are the following: (1) oxidation by ozone to yield trimethylacetic acid, oxalic acid and phthalic acid besides other products which are tars; (2)

<sup>2</sup> Meyer and Schuster, *Ber.*, **55**, 819 (1922).

<sup>3</sup> Vorländer and co-workers, *ibid.*, **39**, 1024 (1906); **56**, 1122 (1923).

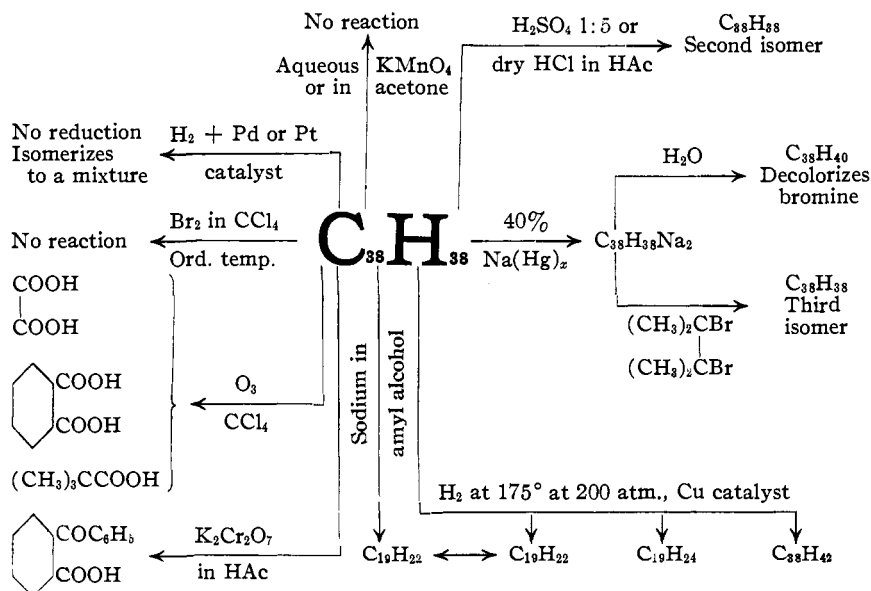
<sup>4</sup> Kohler, *Am. Chem. J.*, **40**, 217 (1908).

<sup>5</sup> Hurd and Webb, *THIS JOURNAL*, **49**, 546 (1927).

<sup>6</sup> Ziegler and Sauermilch, *Ber.*, **63**, 1851 (1930).

oxidation with potassium dichromate in acetic acid to yield *o*-benzoylbenzoic acid; (3) failure to oxidize with an aqueous alkaline potassium permanganate solution or an acetone solution of potassium permanganate; (4) failure to add bromine on treatment with bromine in carbon tetrachloride; (5) failure to reduce with hydrogen under slight pressure in the presence of platinum-oxide platinum black<sup>7</sup> or palladium-oxide palladium black;<sup>8</sup> (6) reduction with hydrogen over a copper chromite catalyst at 175° under a pressure of 200 atmospheres to give three hydrocarbons, C<sub>19</sub>H<sub>22</sub>, C<sub>19</sub>H<sub>24</sub> and C<sub>38</sub>H<sub>42</sub>;<sup>9</sup> (7) reduction with sodium and amyl alcohol to give a hydrocarbon, C<sub>19</sub>H<sub>22</sub>, which is identical with the product of this composition obtained in the high pressure reduction; (8) a reaction with 40% sodium amalgam to give a red metal alkyl which is not a cleavage product; (9) rearrangement to a more stable isomer by heating the solution in acetic acid with hydrogen chloride or sulfuric acid.

These facts are summarized in the chart.



The di-indene formula which has been proposed above will account for all of these reactions in a satisfactory fashion. The ozonization of the product is very difficult to control and the benzene rings seem to be attacked almost as readily as the indene double bonds. The trimethyl-

<sup>7</sup> Adams and Shriner, *THIS JOURNAL*, **45**, 2171 (1923).

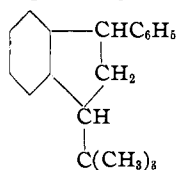
<sup>8</sup> Shriner and Adams, *ibid.*, **46**, 1683 (1924).

<sup>9</sup> The reduction of the hydrocarbon at higher pressures was carried out by Professor Homer Adkins and Mr. Ralph Connor at the University of Wisconsin. We take this opportunity to express our deep appreciation for their kindness in aiding us in this investigation.

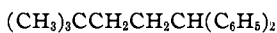
acetic acid and oxalic acid are formed from the ozonide in which the aromatic rings are attacked. The phthalic acid is formed by an opening of the indene ring and more extensive oxidation of the material. It is never present in the oxidation products in very large amounts. The oxidation with potassium dichromate in acetic acid to yield *o*-benzoylbenzoic acid is in good agreement with the results which Kohler<sup>4</sup> has obtained in the oxidation of 1,2,3-triphenylindene to *o*-dibenzoylbenzene. The stability of the di-indene toward potassium permanganate is in agreement with the observation of Kohler<sup>4</sup> that 1,2,3-triphenyl-1-ethylindene is stable toward potassium permanganate in acetone solution and that of Thiele<sup>10</sup> that compound (A) is not attacked by aqueous alkaline potassium permanganate.

The failure of the hydrocarbon to add bromine in cold carbon tetrachloride is not unusual. The phenylindenes<sup>4</sup> have to be heated with bromine in order to get a reaction to occur. The failure of the di-indene to reduce when treated with hydrogen in the presence of platinum and palladium catalysts is more surprising but Schlenk and Bergmann<sup>11</sup> have made similar observations on a compound which seems to be related in structure.

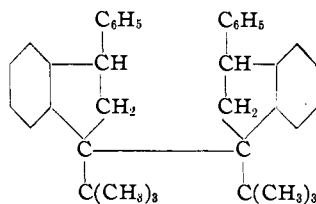
The three hydrocarbons,  $C_{19}H_{22}$ ,  $C_{19}H_{24}$  and  $C_{38}H_{42}$ , which have been obtained by the high pressure reduction over copper chromite catalyst, are probably the following compounds.

 $C_{19}H_{22}$ 

VIII

 $C_{19}H_{24}$ 

IX

 $C_{38}H_{42}$ 

X

The main product of the reduction is 1-phenyl-3-*tert.*-butyldihydroindene (VIII) which is formed by the cleavage of the bond between the two indene nuclei and then hydrogenation of the remaining indene molecules. The cleavage of the molecule at this point is not surprising. Kohler<sup>4</sup> has shown that silver reacts with 3-bromo-1,2,3-triphenylindene to give the free radical 1,2,3-triphenylindyl rather than the di-indene molecule. The linkage between the two indene nuclei in formula VII might be expected to be of the type which is easily broken. The hydrocarbon  $C_{38}H_{42}$  which was isolated in small amounts from the reduction products is undoubtedly represented by formula X and came from reduction of the two indene rings without cleavage. The hydrocarbon  $C_{19}H_{24}$  was also

<sup>10</sup> Thiele and Rugglis, *Ann.*, 393, 61 (1912).

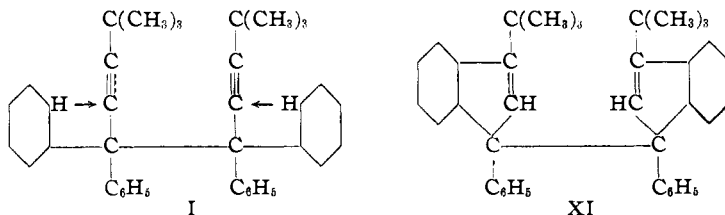
<sup>11</sup> W. Schlenk and Ernst Bergmann, *ibid.*, 463, 252 (1928)

isolated in small amounts. Oxidation of this hydrocarbon gave benzophenone. Since the same hydrocarbon was obtained by the catalytic reduction of diphenyl-*tert.*-butylethynylcarbinol with hydrogen and palladium-oxide palladium black,<sup>8</sup> it must have been 1,1-diphenyl-4,4-dimethylpentane produced by cleavage of the dihydro-indene derivative (VIII) under the conditions of the reduction. This reaction is unusual but there seems to be no other explanation of the formation of the open-chain derivative. Reduction of the original di-indene with sodium and amyl alcohol results in a cleavage of the molecule to produce 1-phenyl-3-*tert.*-butyldihydro-indene (VIII).

Forty per cent. sodium amalgam might be expected to cleave a di-indene molecule of the type (VII) which has been postulated. However, molecular weights of the products which were obtained from the metal derivative showed that no cleavage had occurred. Treatment of the sodium derivative with water produced a hydrocarbon  $C_{38}H_{40}$  or a dihydro derivative of the original substance. This substance was unsaturated toward bromine in carbon tetrachloride but no definite bromination product was isolated. When the sodium derivative of the di-indene was treated with tetramethylethylene bromide another isomer of  $C_{38}H_{38}$  was produced. It is as yet impossible to assign definite structures to either of these new hydrocarbons.

The rearrangement of the original di-indene hydrocarbon  $C_{38}H_{38}$  (VII) to produce an isomer when its acetic acid solution is heated with either hydrochloric acid or sulfuric acid is not so readily accounted for. There are possible explanations. The new compound may be a geometric isomer of the original. Formula VII permits two geometrical forms. However, the rearranged product is much more stable to oxidation and reduction than is the original di-indene. The mere change in geometrical configuration might produce this stabilization. Another suggestion is that a truxane type of molecule is formed by the two indene residues combining through the double bonds. Steric considerations make this seem unlikely.

An alternate formula (XI) for the di-indene will explain the reactions of this hydrocarbon. In it the positions of two phenyls and the tertiary butyl groups are interchanged. Its formation could be accounted for by a simple shift of the hydrogen atoms and ring closure in the original tetraphenyl di-*tert.*-butylethynylethane.



This formula is not favored at the present time. The evidence that a free radical is formed when silver reacts with the bromide<sup>1c</sup> seems quite conclusive. If the free radical is an intermediate in the production of the di-indene, formula VI seems the more likely.

### Experimental

**Bis-(1-phenyl-3-*tert.*-butylindyl).**—Most of the hydrocarbon used in this work was prepared from diphenyl-*tert.*-butylethynylbromomethane by the action of silver<sup>1c</sup> although some material was prepared by the rearrangement of tetraphenyldi-*tert.*-butylethynylethane.<sup>1b</sup> It was found that the di-indene could be purified by recrystallization from glacial acetic acid or by dissolving it in the least amount of petroleum ether (b. p. 65–110°) and adding two volumes of ethyl alcohol. The hydrocarbon then melted sharply at 150–151°.

**Oxidation of the Di-indene with Ozone.**—Some thirty experiments on the ozonization of this hydrocarbon were performed. The principal conditions which were changed were amount of material, volume and nature of the solvent and the time of treatment. Some experiments were made with ozonized air but most of the important results were obtained using ozonized oxygen.

The general procedure used in the ozone oxidation may be briefly summarized. The hydrocarbon was dissolved in 200–300 cc. of solvent and ozonized oxygen was passed through the solution at the rate of 0.4 liter per minute. The ozonide thus formed was decomposed with water in the presence of either oxidizing or reducing agents. Some typical runs are listed in Table I. Many of these experiments were repeated several times in order to check the results with certainty.

TABLE I  
OZONIZATION OF THE DI-INDENE

Run	Hydrocarbon, g.	Solvent	Time of ozonization, hrs.	Reagents used to decompose ozonide	Products isolated
5	2.9	Carbon tetrachloride	3	H <sub>2</sub> O + H <sub>2</sub> O <sub>2</sub>	Unchanged hydrocarbon
9	2.2	Petroleum ether	6	H <sub>2</sub> O + H <sub>2</sub> O <sub>2</sub>	Unchanged hydrocarbon
10	1.4	Petroleum ether	8	H <sub>2</sub> O + H <sub>2</sub> O <sub>2</sub>	Unchanged hydrocarbon
2	3.0	Carbon tetrachloride	10	H <sub>2</sub> O + H <sub>2</sub> O <sub>2</sub>	Phthalic acid, oxalic acid
11	1.5	Petroleum ether	16	H <sub>2</sub> O, Zn + CH <sub>3</sub> CO <sub>2</sub> H	Yellow oil
4	2.9	Carbon tetrachloride	18	H <sub>2</sub> O + H <sub>2</sub> O <sub>2</sub>	Phthalic acid, oxalic acid
1	2	Carbon tetrachloride	18.5	H <sub>2</sub> O + H <sub>2</sub> O <sub>2</sub>	Phthalic acid, oxalic acid
3	8.5	Carbon tetrachloride	21.5	H <sub>2</sub> O + H <sub>2</sub> O <sub>2</sub>	Phthalic acid, trimethylacetic acid, oxalic acid
7	5	Petroleum ether	23.5	H <sub>2</sub> O + H <sub>2</sub> O <sub>2</sub>	Trimethylacetic acid, oxalic acid
8	2	Carbon tetrachloride	25	H <sub>2</sub> O + H <sub>2</sub> O <sub>2</sub>	Phthalic acid, oxalic acid
6	2.4	Carbon tetrachloride	30	H <sub>2</sub> O + H <sub>2</sub> O <sub>2</sub>	Completely burned

The carbon tetrachloride was always carefully dried over calcium chloride and redistilled before using in these experiments. The petroleum ether was treated with 10% potassium permanganate several times, washed with concentrated sulfuric acid, then with water, dried over fused calcium chloride and then sodium and redistilled. The portion boiling at 60–90° was used.

After ozonization the reaction mixture was poured into the media used for decomposition and stirred. Then the aqueous layer was made alkaline by the addition of 10% sodium hydroxide solution. This always produced a red color in the water

layer. After separating the two layers the aqueous portion was evaporated to about 50 cc., filtered, cooled in ice and carefully acidified. A very small precipitate was usually obtained. This amounted to only 0.16 to 0.24 g. in various runs. It was identified as phthalic acid by recrystallization from 50% alcohol until it melted at 190–196°. The neutral equivalent confirmed the identification.

*Neutral equivalent.* Subs., 0.0140: 14.3 cc. of 0.01153 *N* NaOH. Calcd. for  $C_6H_4(COOH)_2$ : 83. Found: 85.

The solution after the removal of the water-insoluble portion was extracted with ether. The aqueous layer was tested for oxalic acid by precipitation of the calcium salt. The calcium salt was identified by drying it and titrating it with standard potassium permanganate solution. Oxalic acid was identified in all runs which were exposed to ozone for more than ten hours.

The ether extract was shaken with water to which just enough 5% sodium hydroxide was added to keep the solution alkaline to phenolphthalein. The ether layer was then discarded and the aqueous layer was evaporated to dryness. The remaining salt was washed with ether a few times and dissolved in 50 cc. of 95% alcohol and filtered. The filtrate was evaporated to dryness and the weight of the salt noted. This salt was then treated with *p*-bromophenacyl bromide according to the directions of Judefind and Reid.<sup>12</sup> After three crystallizations from alcohol the ester thus obtained melted at 76–77° and was shown to be identical with an authentic specimen of the ester prepared from trimethylacetic acid as described by Powell.<sup>13</sup> A sample of our ester was analyzed to make sure of its composition.

*Anal.* (Parr bomb). Subs., 0.1960: 6.71 cc. of 0.09688 *N* AgNO<sub>3</sub>. Calcd. for  $C_{12}H_{16}O_2Br$ : Br, 26.75. Found: Br, 26.53.

The identification of trimethylacetic acid was carried out only in runs 3 and 7 (Table I). Its odor was noticeable in the other experiments.

When the ozonization experiments were first undertaken, it was thought that the hydrocarbon might be the di-allene (VI) which should yield dipivaloyl, carbon dioxide and benzophenone on ozonization. Experiments showed that dipivaloyl<sup>14</sup> was converted to trimethylacetic acid under the conditions used in the ozonization and decomposition of the ozonide. Benzophenone could be partially recovered when treated with ozone and then with hydrogen peroxide. No benzophenone was detected in the products of ozonization of the hydrocarbon in spite of every effort to find it.

**Oxidation with Potassium Dichromate in Acetic Acid.**—To a solution of 5.23 g. of the hydrocarbon in 100 cc. of glacial acetic acid was added 25 g. of potassium dichromate. The solution was boiled under a reflux condenser for about ten hours, then poured into 200 cc. of water, cooled and filtered. The precipitate and the aqueous layer were separately extracted with ether. The ether extracts were combined and extracted with sodium carbonate solution. The ether solution was evaporated and gave oily material which did not contain benzophenone. The aqueous alkaline solution was acidified with hydrochloric acid and gave 1.12 g. of water-insoluble acid. Four recrystallizations from 50% alcohol gave a product which melted at 90°. After thorough drying this material melted at 127–128°. These melting points agreed with those of hydrated and anhydrous *o*-benzoylbenzoic acid. A mixed melting point with known *o*-benzoylbenzoic acid showed no depression in melting point. The neutral equivalent furnished further evidence of this structure.

<sup>12</sup> Judefind and Reid, *THIS JOURNAL*, **42**, 1043 (1920).

<sup>13</sup> Powell, *ibid.*, **53**, 1172 (1931).

<sup>14</sup> This material used was furnished by Dr. S. M. McElvain of the University of Wisconsin.

*Neutral equivalent.* Subs., 0.2413: 24.85 cc. of 0.04315 *N* NaOH. Calcd. for  $C_{13}H_{10}O_2$ : neut. equiv., 226. Found: 225.

**Other Experiments on Oxidation.**—The hydrocarbon was oxidized with hot nitric acid in glacial acetic acid but no definite products could be isolated from the yellow resinous mass obtained by diluting the reaction mixture with water.

Attempts to oxidize the hydrocarbon with potassium permanganate in water and in acetone solutions were unsuccessful and the original material was recovered. In one typical experiment 2 g. of hydrocarbon in 150 cc. of acetone was treated with 20 g. of potassium permanganate and the mixture was refluxed for twelve hours. A 90% recovery of this hydrocarbon was obtained.

The hydrocarbon was not attacked by hydrogen peroxide in acid or alkaline solution at ordinary temperatures. No acidic compounds were obtained by fusion of the hydrocarbon with dry sodium hydroxide.

**Attempt to Brominate the Di-indene Derivative.**—To a solution of 0.1 g. of the hydrocarbon in 10 cc. of carbon tetrachloride was added 10 drops of a 5% solution of bromine in carbon tetrachloride. The color of the bromine had not disappeared after ten hours and no brominated derivative was obtained.

**Attempted Reduction with Hydrogen and Platinum or Palladium Catalysts.**—Several attempts were made to hydrogenate the hydrocarbon using hydrogen and platinum<sup>7</sup> and palladium<sup>8</sup> catalysts. At ordinary temperature and at 60–70° in either ethyl acetate or acetic acid solution, no hydrogenation occurred with these catalysts with hydrogen at 40 to 50 pounds' pressure in a Burgess–Parr hydrogenation apparatus.

**Hydrogenation of the Di-indene Derivative at High Pressures.**<sup>9</sup>—Ten grams of the hydrocarbon in methylcyclohexane solution was treated with hydrogen at 175° and 3000 pounds' pressure in the presence of a copper chromite catalyst. When no further hydrogen was absorbed, the catalyst was removed from the solution and the solvent was evaporated. A salve-like mixture of hydrocarbons remained. This residue weighed 8.5 g.

This sample was placed in a distilling bulb and heated under a pressure of 1 mm. to 185–195°. A small amount of distillate, 0.76 g., was obtained. This product boiled at 122–127° at 1 mm.,  $d_4^{20}$  0.9520;  $n_D^{20}$  1.5411;  $M_D$  calcd. for  $C_{19}H_{24}$  (1,1-diphenyl-4,4-dimethylpentane), 82.76. Found: 83.18.

*Anal.* Subs., 0.1262:  $CO_2$ , 0.4180;  $H_2O$ , 0.1074. Calcd. for  $C_{19}H_{24}$ : C, 90.40; H, 9.60. Found: C, 90.33; H, 9.52.

This liquid hydrocarbon did not absorb bromine in carbon tetrachloride. It is identical in properties with the hydrocarbon which was obtained by the reduction of diphenyl-*tert.*-butylethinylcarbinol with hydrogen over a palladium catalyst.

The solid which remained in the distilling flask was a mixture of hydrocarbons. After twenty-four recrystallizations from acetone a pure sample was isolated. This product weighed 0.09 g. and melted at 181–182°.

*Anal.* Subs., 2.627, 2.612 mg.:  $CO_2$ , 8.771, 8.746 mg.;  $H_2O$ , 1.903, 1.916 mg. Calcd. for  $C_{19}H_{22}$ : C, 91.13; H, 8.87. Found: C, 91.06, 91.32; H, 8.11, 8.21.<sup>15</sup> *Mol. wt.* (Rast). Subs., 0.00425; camphor, 0.01685;  $\Delta t$ , 39.7°. Calcd. for  $C_{19}H_{22}$ : mol. wt., 250. Found: mol. wt., 254.

The residue from the mother liquor of the recrystallizations was crystallized from methyl alcohol and yielded 0.0875 g. of a second hydrocarbon, m. p. 132–133°.

*Anal.* Subs., 2.880, 2.359 mg.:  $CO_2$ , 9.651, 7.912 mg.;  $H_2O$ , 2.067, 1.702 mg.

<sup>15</sup> We are indebted to Dr. W. H. Carothers and Mr. S. B. Kuykendall of the du Pont Experimental Station for the microanalyses reported in this paper.



Calcd. for  $C_{38}H_{42}$ : C, 91.50; H, 8.50. Found: C, 91.39, 91.47; H, 8.03, 8.02. *Mol. wt.* (Rast) Subs., 0.0058 g.; camphor, 0.0160;  $\Delta t$ , 29.87°. Calcd. for  $C_{38}H_{42}$ : *mol. wt.*, 498. Found: *mol. wt.*, 480.

This compound did not add bromine in carbon tetrachloride solution and was waxy in appearance.

An analysis on the crude mixture of hydrocarbons before the separation of these two compounds showed that the mixture had essentially the composition  $C_{15}H_{21-22}$ .

**Reduction of the Di-indene Derivative with Sodium and Amyl Alcohol.**—To a solution of 1.8 g. of the di-indene derivative in 100 cc. of hot amyl alcohol was added 15 g. of sodium in small pieces. When the sodium had dissolved, the mixture was cooled and treated with water. The alcohol layer was separated and washed several times with water. The alcohol was then removed under reduced pressure and the residue was crystallized from acetone. The product melted at 180–181° and by means of a mixed melting point determination was shown to be identical with the hydrocarbon  $C_{15}H_{22}$  obtained from the high pressure reduction of the di-indene.

A solution of 0.89 g. of this hydrocarbon in 25 cc. of glacial acetic acid was boiled with 5 g. of potassium dichromate for about ten hours. The material (0.69 g.) was recovered unchanged.

**Reaction of the Di-indene Derivative with Sodium Amalgam.**<sup>1a</sup>—A solution of 4 g. of the hydrocarbon in 100 cc. of dry ether was shaken with 5 cc. of 40% sodium amalgam in an atmosphere of nitrogen. A deep red color soon developed. After about thirty-six hours, the amalgam was frozen and the ether solution of the sodium derivative was transferred in an atmosphere of nitrogen to another flask. Then a 10% solution of tetramethylethylene dibromide was added gradually until the red color of the solution disappeared and a few cc. excess was then added. The ether solution was filtered and evaporated under reduced pressure. A little petroleum ether (b. p. 65–110°) was added to the residue and the mixture was cooled with solid carbon dioxide. Crystals separated and were collected on a Büchner funnel and washed with cold petroleum ether. There was thus obtained 1.34 g. of a white solid, m. p. 178.5–180°. Recrystallization from petroleum ether gave 1.02 g. of product, m. p. 179.3–180.3°.

*Anal.* Subs., 0.1706, 0.1725;  $CO_2$ , 0.5761, 0.5838;  $H_2O$ , 0.1188, 0.1202. Calcd. for  $C_{38}H_{38}$ : C, 92.31; H, 7.69. Found: C, 92.10, 92.30; H, 7.74, 7.74. *Mol. wt.*, (Rast) Subs., 0.0074; camphor, 0.0172;  $\Delta t$ , 36.9°. Calcd. for  $C_{38}H_{38}$ : *mol. wt.*, 494. Found: *mol. wt.*, 465.

When the sodium derivative was prepared in a similar fashion and then treated with dry carbon dioxide, no acid could be obtained from the reaction mixture. The sodium derivative with water gave a hydrocarbon  $C_{38}H_{40}$ .<sup>1b</sup>

**Reactions of the Hydrocarbon  $C_{38}H_{40}$ .**—The hydrocarbon  $C_{38}H_{40}$  was prepared as previously described.<sup>1b</sup> It decolorized bromine in carbon tetrachloride rather rapidly but no pure sample of brominated product could be obtained from the reaction mixture. When ozonized the molecule suffered rather complete cleavage and no products of significance could be isolated. It did not hydrogenate when treated with hydrogen in the presence of platinum-oxide platinum black. It did reduce when treated with sodium and alcohol.

To a solution of one gram of the hydrocarbon,  $C_{38}H_{40}$ , in 50 cc. of absolute alcohol, was added 7 g. of sodium cut in small pieces. When the sodium had dissolved, the reaction mixture was flooded with water and extracted with ether. On concentration of the ether a hydrocarbon crystallized and was collected on a filter. After recrystallization from ether it melted at 181–182°. It was not identical with the hydrocarbon

<sup>1a</sup> The reactions of this sodium derivative were studied by Dr. J. Gail Stampfli.

$C_{19}H_{22}$  previously described in this paper which melted at the same temperature. This was established by mixed melting point determinations as well as by the analysis and molecular weight determinations.

*Anal.* Subs., 0.1366;  $CO_2$ , 0.4576;  $H_2O$ , 0.1034. Calcd. for  $C_{19}H_{22}$ : C, 91.50, H, 8.50. Found: C, 91.36; H, 8.49. *Mol. wt.* (Rast). Subs., 0.00375; camphor; 0.01885;  $\Delta t$ , 15.84°. Calcd. for  $C_{19}H_{22}$ : mol. wt., 498. Found: mol. wt., 498.

**Rearrangement of the Di-indene Derivative by Heating an Acetic Acid Solution Containing Dry Hydrogen Chloride.**—Heating the solution of the di-indene derivative in acetic acid for as long as thirty-three hours did not cause it to isomerize. However, heating a solution of 2.4 g. of the hydrocarbon with 1 cc. of concentrated sulfuric acid in 50 cc. of glacial acetic acid for one hour gave evidence of some change, as the product melted over a wide range when isolated from the mixture. By continuing the heating for several hours an isomeric hydrocarbon melting at 166–168° was obtained. A pure sample was obtained by the use of hydrogen chloride in place of the sulfuric acid.

A solution of 7 g. of the di-indene derivative in 100 cc. of glacial acetic acid was boiled for forty-eight hours. A continuous stream of dry hydrogen chloride was passed through the solution during this time. On evaporating the solution and recrystallizing the residue from alcohol there was obtained 4.2 g. of a hydrocarbon which melted at 173–174°.

*Anal.* Subs., 0.1528;  $CO_2$ , 0.5109;  $H_2O$ , 0.1073. Calcd. for  $C_{18}H_{20}$ : C, 92.31; H, 7.69. Found: C, 91.20; H, 7.86. *Mol. wt.* (Rast) Subs., 0.0037; camphor. 0.0180;  $\Delta t$ , 18.45°. Calcd. for  $C_{18}H_{20}$ : mol. wt., 494. Found: mol. wt., 441.

This isomer of  $C_{18}H_{20}$  was recovered unchanged when a sample was boiled with an acetic acid solution of potassium dichromate. It could not be further reduced with sodium and hot amyl alcohol.

**1,1-Diphenyl-4,4-dimethylpentane.**—This hydrocarbon, which has previously been described as a reduction product of the di-indene derivative when hydrogen and copper chromite catalyst was used, was also obtained by the reduction of diphenyl-*tert.*-butylethynylcarbinol.

To a solution of 26.4 g. of the carbinol in 100 cc. of glacial acetic acid was added 0.5 g. of palladous oxide catalyst.<sup>8</sup> The solution was reduced with hydrogen in a Burgess–Parr hydrogenation apparatus. Reduction was complete in one hour. The solution was poured into water and extracted with ether. The ether layer was washed with sodium carbonate solution, dried and distilled. After the ether was removed at ordinary temperatures, the remaining oil boiled at 114–116° (0.65–0.70 mm.). The yield was 19 g. (75% of the theoretical amount);  $n_D^{20}$  1.5148;  $d_4^{20}$  0.9522.

*Anal.* Subs., 0.2304,  $CO_2$ , 0.7650;  $H_2O$ , 0.1968. Calcd. for  $C_{19}H_{24}$ : C, 90.40; H, 9.60. Found: C, 90.55; H, 9.56.

The structure of this hydrocarbon was confirmed by oxidation with chromic oxide in acetic acid solution. To a solution of 10 cc. of the hydrocarbon in 50 cc. of glacial acetic acid was added 10 g. of chromium oxide. The mixture was boiled under a reflux condenser for about five hours. Water was added and an oily substance separated. This material was dissolved in ether and extracted with aqueous alkali. No acidic substance insoluble in water was obtained by acidification of this alkaline extract. The ether was evaporated and the oil was dissolved in 2 to 3 cc. of ethyl alcohol. A few drops of phenylhydrazine were added and the mixture was heated for about one hour. The solution was cooled and after three days some crystals separated. These were filtered and recrystallized from alcohol. In this manner 0.165 g. of the phenylhydrazine of benzophenone melting at 137–138° was obtained. It was further identified by taking a mixed melting point with a known specimen of this phenylhydrazone.

### Summary

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

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

## THE REDUCTION OF ACETYLENIC CARBINOLS WITH TITANIUM TRICHLORIDE

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The classical method of Gomberg<sup>1</sup> for the preparation of hexa-aryl-ethanes does not always lead to the expected product when it is applied to the corresponding acetylene derivatives. The general method which Ziegler and Schnell<sup>2</sup> 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.*-butylethynylethane.<sup>3</sup>

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.<sup>4</sup> Two attempts to apply this method to the preparation of acetylenic ethanes have been recorded. Tri-*tert.*-butylethynylcarbinol gave no products which could be isolated and characterized when it was treated with vanadous chloride.<sup>5</sup> Wieland and Kloss<sup>6</sup> have reduced diphenylphenylethynylcarbinol (I) with titanium trichloride and obtained the same hydrocarbon which Moureu, Dufraisse and Houghton<sup>7</sup> had previously prepared by the action of iron on diphenylphenylethynylchloromethane (II). This hydrocarbon has been assumed to be *sym.*-tetraphenyldiphenylethynylethane (III).

<sup>1</sup> Gomberg, *THIS JOURNAL*, **22**, 757 (1900).

<sup>2</sup> Ziegler and Schnell, *Ann.*, **437**, 244 (1924).

<sup>3</sup> (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).

<sup>4</sup> Conant and Sloan, *ibid.*, **45**, 2466 (1923).

<sup>5</sup> Salzberg with Marvel, *ibid.*, **50**, 1737 (1928).

<sup>6</sup> Wieland and Kloss, *Ann.*, **470**, 217 (1929).

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