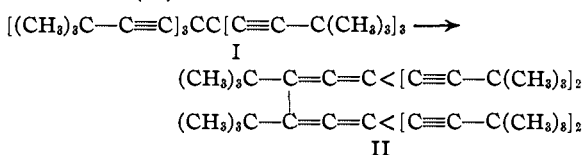


[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

## Rearrangements of Polyynes. X<sup>1</sup> Rearrangement Product of Hexa-*t*-butylethyne

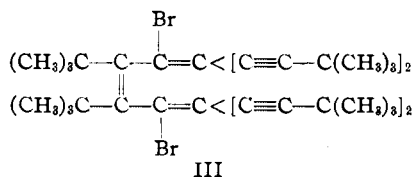
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Hexa-*t*-butylethyne (I) when heated in alcoholic solution rearranges to an isomeric hydrocarbon,<sup>2</sup> for which no structure has been suggested previously. In view of the work of Farley and Marvel,<sup>3</sup> which showed that related acetylenic ethanes rearranged to diallenes, it is now suggested that the rearrangement of hexa-*t*-butylethyne likewise gives a diallene derivative (II).



The following facts support this structure:

(1) The hydrocarbon combines with bromine or chlorine to give a crystalline dibromide or dichloride in practically theoretical yields. Further introduction of chlorine or bromine leads to amorphous products. The dibromide reacts with alkali to regenerate the hydrocarbon. If addition of bromine takes place at the ends of the conjugated system in the diallene (II) to give a molecule of structure III, the compound would be expected to react as this one does.



(2) Catalytic reduction of the hydrocarbon, using platinum oxide-platinum black<sup>4</sup> in acetic acid solution, adds sixteen hydrogen atoms very rapidly, and reduction then stops. Experiments with tri-*t*-butylethynylcarbinol show that the acetylenic bonds in this type of molecule are reduced readily by hydrogen in the presence of this platinum catalyst. The hydrogen absorbed in reducing the rearranged hydrocarbon is exactly the amount needed to reduce the four triple bonds which are shown in formula II.

(1) For the ninth communication on this subject, see Sparks and Marvel, *THIS JOURNAL*, **58**, 865 (1936).

(2) Salzberg and Marvel, *ibid.*, **50**, 1737 (1928).

(3) Farley and Marvel, *ibid.*, **58**, 29 (1936).

(4) Adams, Voorhees and Shriner, "Organic Syntheses," Coll. Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 452.

(3) The partially reduced hydrocarbon, on treatment with bromine according to the method of Rossmann,<sup>5</sup> absorbs eight atoms of bromine. This corresponds to the unsaturation due to the four double bonds of the diallene structure, which were not affected by catalytic reduction.

(4) Treatment of the rearranged hydrocarbon with ozone followed by hydrogen peroxide produced trimethylacetic acid. This shows that no stable four- or six-membered rings are produced in the rearrangement of the acetylenic ethane. Oxidation of the rearranged hydrocarbon with chromic oxide produces a non-crystalline product which seems to be identical with the polyketofuran reported as an oxidation product of the dimer of tri-*t*-butylethynylchloromethane.<sup>1</sup> This fact also indicates that no stable cyclic molecules are produced during the rearrangement of the hexa-*t*-butylethyne.

All of these facts support the view that the rearrangement of hexa-*t*-butylethyne yields the diallene derivative 2,2,13,13-tetramethyl-5,10-di-*t*-butylethynyl-7,8-di-*t*-butyltetradeca-5,6,8,9-tetraene-3,11-diyne (II).

### Experimental

**Catalytic Reduction of Tri-*t*-butylethynylcarbinol.**—To a solution of 1.0 g. of this carbinol in 25 g. of glacial acetic acid was added 0.2 g. of platinum oxide,<sup>4</sup> and the solution was shaken with hydrogen at about three atmospheres. Within forty minutes, the drop in pressure showed that reduction was complete. The saturated carbinol, after recrystallization from alcohol, melted at 44–45°.

*Anal.* Calcd. for C<sub>19</sub>H<sub>40</sub>O: C, 80.26; H, 14.10. Found: C, 80.18; H, 14.0.

**Preparation of the Diallenic Hydrocarbon (II).**—This hydrocarbon was prepared as described by Salzberg and Marvel.<sup>2</sup> As reported by Sweet and Marvel,<sup>6</sup> the hydrocarbon thus prepared cannot be reduced with hydrogen and a platinum oxide-platinum black catalyst<sup>4</sup> in acetic acid solution. However, by boiling the hydrocarbon, first with alcoholic silver nitrate solution, then with alcoholic potassium hydroxide solution, then washing with water and recrystallizing from ether and alcohol, it is pure enough for reduction experiments; m. p. 172–173°.

**Catalytic Reduction of the Diallene (II).**—The highly purified hydrocarbon (about 0.5 g.) was dissolved in about 100 cc. of glacial acetic acid and 0.2 g. of platinum black

(5) Rossmann, *Ber.*, **65**, 1847 (1932).

(6) Sweet and Marvel, *THIS JOURNAL*, **54**, 1184 (1932).

(the usual platinum oxide catalyst<sup>4</sup> previously reduced with hydrogen) was added. The solution was shaken with hydrogen in a machine carefully calibrated, so that a small drop in pressure was significant. Hydrogen was absorbed rapidly at first, but after about two hours no further hydrogenation occurred. Some typical runs are tabulated.

Sample, g.	Pressure drop, cm.	Calcd. pressure drop in cm. for addition of 16 atoms of H
0.5101	21.5	21.7
.5435	22.2	22.9
.5293	22.2	22.8
.85	27.5	26.6

The catalyst was filtered, and the acetic acid evaporated. The reduced hydrocarbon was thrown out of solution with water and collected in ether. Evaporation of the ether left a viscous product which could not be purified by crystallization.

*Anal.* Calcd. for  $C_{38}H_{70}$ : C, 86.7; H, 13.3; mol. wt., 526. Found: C, 86.5; H, 13.1; mol. wt. (Rast), sample, 0.0392 g.; camphor, 0.3177;  $\Delta T$ , 9°; mol. wt., 544.

**Addition of Bromine to the Reduced Hydrocarbon.**—A weighed sample of the viscous liquid, obtained by evaporating the solvent from the above catalytic reduction, was spread in a thin film on a watch glass and exposed to diluted bromine vapor in the dark for six to eight hours.<sup>5</sup> The film of brominated hydrocarbon was warmed to 50–60° to remove the excess bromine and weighed again. The following are typical runs.

Sample, g.	Br absorbed, g.	% Br in final product	Calcd. % Br $C_{38}H_{70}Br_2$
0.0022	0.0039	57.0	56.00
.0134	.0165	55.3	
.0107	.0137	56.1	
.0098	.0130	57.0	

**Bromination of the Diallene.**—A solution of 1 g. of the hydrocarbon in carbon tetrachloride was treated with 0.32 g. of bromine. On evaporating the solvent and crystallizing the residue from alcohol, the yield was 1.22 g. (93%) of a product melting at 169–170°.

*Anal.* Calcd. for  $C_{38}H_{74}Br_2$ : Br, 23.8. Found: Br, 23.75.

Treatment of this dibromo derivative with potassium hydroxide removed the halogen to regenerate the hydro-

carbon. Moist silver oxide in benzene also regenerated the hydrocarbon. Further bromination led to red-colored, non-crystalline products. The dibromo compound did not add maleic anhydride.

**Chlorination of the Diallene.**—A solution of 0.5 g. of the hydrocarbon in 10 cc. of carbon tetrachloride was treated with 27 cc. of chlorine gas at 25°. The solvent was distilled and the residue was crystallized from alcohol and ether. The product weighed 0.5 g. and melted at 161°.

*Anal.* Calcd. for  $C_{38}H_{74}Cl_2$ : Cl, 12.4. Found: Cl, 12.2.

**Ozonization of the Diallene.**—Ozonized air was passed through a solution of 4.5 g. of the hydrocarbon in 50 cc. of carbon tetrachloride for twenty hours, while the temperature was kept at 0°. The solution was then treated with 25 cc. of hydrogen peroxide. An alkaline extraction was concentrated, and from the sodium salt of the organic acid a *p*-bromophenacyl ester was prepared. The ester melted at 78°, and showed no depression in melting point when mixed with an authentic specimen of the *p*-bromophenacyl ester of trimethylacetic acid.<sup>7</sup>

There was no definite alkali insoluble oxidation product which could be isolated.

**Oxidation of the Rearranged Hydrocarbon with Chromic Oxide.**—One gram of the hydrocarbon was heated in 500 cc. of glacial acetic acid with 2–3 g. of chromic oxide for two to three hours. The reaction mixture was poured into water, and a yellow solid separated. It could not be recrystallized from common solvents, and was purified by solution in acetic acid and reprecipitation with water. It melted at 55–65°.

*Anal.* Calcd. for  $C_{38}H_{74}O_{11}$ : C, 66.4; H, 7.8. Found: C, 65.8, 67.0; H, 7.1, 7.2.

This compound appears to be identical with the substance obtained by the action of the same oxidizing agent on the dimer of tri-*t*-butylethynylchloromethane.

### Summary

Evidence has been presented to show that hexa-*t*-butylethynylethane rearranges under the influence of heat to give a hydrocarbon which contains two allenic groups.

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RECEIVED MAY 21, 1937

(7) Powell, THIS JOURNAL, 53, 1172 (1931).