[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Di-*t*-butylacetylene[1]

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Introduction

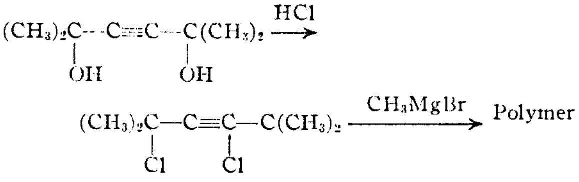
Di-*t*-butylacetylene, previously unknown, has been prepared to determine its physical properties and to study the behavior of the hindered triple bond in typical addition reactions. Since the alkylation of sodium acetylide fails with secondary and tertiary halides,[3] it was necessary to introduce the *t*-butyl groups by another method. Of the several attempts, the following proved satisfactory. Mono-*t*-butylacetylene (I), prepared from pinacolone dichloride,[4] was converted to *t*-butylethynyldimethylcarbinol (II) via addition to acetone by the Grignard method. The carbinol was then converted to the corresponding tertiary chloride (III) by reaction with hydrogen chloride and the product alkylated with methylmagnesium bromide to complete the synthesis (IV).

$$(CH_3)_3C—C{\equiv}CH \xrightarrow{C_2H_5MgBr}$$
(I)
$$(CH_3)_3C—C{\equiv}C—MgBr \xrightarrow{CH_3COCH_3}$$
(II)
$$(CH_3)_3C—C{\equiv}C—C(CH_3)_2OH \xrightarrow{HCl}$$
(III)
$$(CH_3)_3C—C{\equiv}C—C(CH_3)_2Cl \xrightarrow{CH_3MgBr} (CH_3)_3C—C{\equiv}C—C(CH_3)_3$$
(IV)

About 10% of the final product was a hydrocarbon boiling higher than di-*t*-butylacetylene. This byproduct seemed to polymerize partially during each distillation and exact identification could not be made. The complete removal of this material from the di-*t*-butylacetylene proved troublesome and could be accomplished only by repeated fractional distillation and fractional freezing.

Due to the compactness and symmetry of the di-*t*-butylacetylene molecule, the boiling point is unusually low (112.5° at 760 mm.), and the freezing point high (19.4°). Perhaps of greater interest is the fact that the molecular refraction shows an apparent exaltation of 1.26 units[5] when calculated in the usual manner. It was thought desirable, therefore, to establish the structure of di-*t*-butylacetylene beyond question. This was accomplished partly by hydrogenation to the known *sym*-di-*t*-butylethane[6] and further by its Raman spectrum as well as the spectra of its precursors (II) and (III).[7]

An alternative synthesis of di-*t*-butylacetylene by methylation of *bis*-(2-chloroisopropyl)-acetylene (V) failed. The latter compound, prepared from tetramethylbutynediol, reacted with an excess of methylmagnesium bromide to yield a solid polymer insoluble in all ordinary solvents.

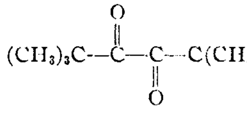


$$\underset{OH}{(CH_3)_2C}—C{\equiv}C—\underset{OH}{C(CH_3)_2} \xrightarrow{HCl}$$
$$\underset{Cl}{(CH_3)_2C}—C{\equiv}C—\underset{Cl}{C(CH_3)_2} \xrightarrow{CH_3MgBr} \text{Polymer}$$

(V)

The hydrogenation of di-*t*-butylacetylene to the corresponding olefin, likely the *cis*-isomer, was accomplished with Raney nickel in accordance with directions of Campbell and Eby.[8] About twice the usual time was required for the absorption of two atoms of hydrogen and the resulting olefin showed no tendency to hydrogenate further under these conditions. The olefin also failed to absorb hydrogen in the presence of platinum oxide; the reaction was successful, however, with finely divided palladium, yielding *sym*-di-*t*-butylethane.[6] Attempts to reduce the acetylene to the *trans*-olefin with sodium and liquid ammonia failed.[8,9] On account of the high freezing point, the acetylene solidified in the liquid ammonia and the failure to reduce may be due to this fact. Use of ether as a cosolvent also was unsuccessful.

The oxidation of di-*t*-butylacetylene with aqueous permanganate proved of interest because di-*t*-butyldiketone (VI) was formed rather than pivalic acid. According to the Fisher–Hirschfelder model, only the *trans* form of the diketone



$$(CH_3)_3C—\overset{O}{\overset{\|}{C}}—\underset{O}{\underset{\|}{C}}—C(CH_3)_3$$

(VI)

may exist without excessive molecular strain. Despite the successful oxidation, attempts to hydrate the triple bond catalytically[10] to form *t*-butyl neopentyl ketone met with no success.

The spatial arrangement of di-*t*-butylacetylene permits the *trans* addition of two bromine atoms.

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[1] Paper XLIX on the chemistry of substituted acetylenes; previous paper, THIS JOURNAL, **67**, 282 (1945).

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[3] Picon, *Compt. rend.*, **168**, 825 (1919).

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

[5] This point is discussed elsewhere, THIS JOURNAL, **68**, 1381 (1946).

[6] Whitmore, *et al.*, *ibid.*, **61**, 1616 (1939); **63**, 124 (1941).

[7] We are indebted to Dr. M. J. Murray of the Illinois Institute of Technology, Chicago, for the Raman spectra of these compounds. An early sample of the di-*t*-butylacetylene, freezing (low) at 15.7–15.2°, was reported to contain 5–10% of an olefin or aromatic compound, no doubt the byproduct described above.

[8] Campbell and Eby, THIS JOURNAL, **63**, 216 (1941).

[9] Henne and Greenlee, *ibid.*, **65**, 2020 (1943).

[10] Thomas, Campbell and Hennion, *ibid.*, **60**, 718 (1938).

Addition did occur slowly in carbon disulfide, though incompletely, and with evolution of some hydrogen bromide. A poor yield of product analytically in agreement with $C_{10}H_{18}Br_2$ was obtained.

While the higher acetylenes do not polymerize on standing, they do peroxidize in contact with air and acquire a yellow-orange color and unpleasant odor. Di-*t*-butylacetylene has been kept in a partially filled bottle at room temperature for over a year with but very little discoloration.

Experimental

***t*-Butylethynyldimethylcarbinol** (II) —One hundred and ninety-four grams (2.37 moles) of *t*-butylacetylene[4] diluted with an equal volume of dry ether was added dropwise with mechanical stirring to 2.4 moles of ethylmagnesium bromide in 500 ml. of anhydrous ether. The mixture was refluxed for thirty minutes and allowed to stand overnight. About 200 ml. of dry ether was then added to loosen the insoluble *t*-butylethynylmagnesium bromide and facilitate stirring. A solution of 145 g. (2.5 moles) of purified acetone in an equal volume of dry ether was added slowly while the flask was cooled in a water-bath. When the addition of acetone was completed the mixture was stirred for two hours with gradual heating to a temperature of 40°. The product was treated with dilute iced hydrochloric acid and worked up in the ordinary manner. The yield of carbinol was 266 g. (81%), boiling at 84–86° (60 mm.). After fractionation through a helix-packed column it boiled at 85° (60 mm.), 150° (743 mm.); freezing point, 32.0–31.8°; n^{38}_{D} 1.4222; d^{38} 0.8064.

Anal. Calcd. for $C_9H_{16}O$: C, 77.09; H, 11.50. Found:[11] C, 76.64; H, 11.08.

***t*-Butylethynyldimethylcarbinyl Chloride** (III).—A mixture of 266 g. (1.9 moles) of the carbinol (II), 300 ml. of purified low boiling ligroin, and 60 g. of solid calcium chloride was stirred mechanically at near 0° while dry hydrogen chloride was admitted continuously for five hours. The liquid layer was decanted from the pasty calcium chloride underlayer and shaken with anhydrous potassium carbonate until neutral. The ligroin was distilled off and the residue fractionated to yield 239 g. (80%) of the chloride (III); b. p. 81–81.5° (100 mm.), f. p. 15.2–15.0°, n^{20}_{D} 1.4343, d^{20} 0.8585. As proof of structure a small sample was hydrolyzed back to the carbinol (II) with dilute aqueous potassium carbonate.

Anal. Calcd. for $C_9H_{15}Cl$: Cl, 22.37; mol. wt., 158.7. Found: Cl, 22.1; mol. wt., 154.

Di-*t*-butylacetylene (IV).—A solution of 1.75 moles of methylmagnesium bromide was prepared with 300 ml. of dry ether and the solution transferred under nitrogen pressure to a three-liter, three-necked, round-bottom flask fitted with a mechanical stirrer, dropping funnel, and reflux condenser protected with a Gilman bridge. The Grignard reagent was cooled to about 0° and 222 g. (1.4 moles) of the chloride (III) diluted with 100 ml. of ether was added over a period of fifteen hours with continuous stirring. When addition of the chloride was completed, the temperature was gradually raised to 45° over a period of three hours. The flask was again cooled with ice and 300 ml. of cold 10% hydrochloric acid added slowly. The ether solution was separated, washed with dilute sodium carbonate solution, and dried over anhydrous potassium carbonate. Distillation through a Whitmore–Fenske column (packed section 35 cm. × 8 mm.) gave 135 g. (70%) of di-*t*-butylacetylene, b. p. 111–115° (748 mm.), and 14 g. of a hydrocarbon by-product boiling at 85–93° (130 mm.). There was also 18 g. of still residue. Several fractionations of the acetylene gave 106 g. (55%), b. p. 111.7–112.2° (742 mm.). After two fractional freezings and redistillation of the solid portions, the following physical properties were observed: b. p. 111.1° (730 mm.), 111.9° (746 mm.); f. p. by cooling curve 19.4°; n^{20}_{D} 1.4055, n^{25}_{D} 1.4026, d^{20} 0.7120, d^{25} 0.7080.

Anal. Calcd. for $C_{10}H_{18}$: C, 86.88; H, 13.12; mol. wt., 138.24; MR_{D}, 46.38. Found: C, 87.29; H, 12.54; mol. wt., 138; MR_{D}, 47.64.

By-product from Di-*t*-butylacetylene Synthesis.—About 56 g. of higher boiling material, accumulated from several preparations, was fractionated three times. There was obtained 8.4 g. of a hydrocarbon, b. p. 75–77° (100 mm.), n^{20}_{D} 1.4385, d^{20} 0.7575. Analysis showed 85.78% C and 12.57% H. Hydrogenation in ethyl alcohol with palladized carbon proceeded smoothly. The hydrogenated material had b. p. 142–144° (747 mm.), n^{20}_{D} 1.4242, d^{20} 0.7465. The analysis gave 85.70% C and 14.08% H.

Di-*t*-butylethylene.—A mixture of 27.6 g. (0.2 mole) of di-*t*-butylacetylene, 120 ml. of 95% alcohol, and about 4 g. of Raney nickel was subjected to an average pressure of 40 lb./sq. in. of hydrogen in a Parr machine. After three hours the alcoholic solution was filtered and poured into water. The oil was separated, washed with water, and dried over anhydrous potassium carbonate. The recovery amounted to 25 g. After several fractionations, 13.8 g. (49%) of *sym*-di-*t*-butylethylene was obtained; b. p. 144.2–144.4° (748 mm.), n^{20}_{D} 1.4271, d^{20} 0.7439. It did not solidify at −65°.

Anal. Calcd. for $C_{10}H_{20}$: C, 85.64; H, 14.36; mol. wt., 140.26; MR_{D}, 47.91. Found: C, 85.69; H, 14.33; mol. wt., 137.6; MR_{D}, 48.42.

Di-*t*-butylethane.—A mixture of 24.2 g. (0.173 mole) of di-*t*-butylethylene, 100 ml. of 95% alcohol, and 0.05 g. of platinum oxide was shaken for four hours under hydrogen at a pressure of 58 lb./sq. in. Since no hydrogenation occurred, the catalyst was filtered off and replaced with 0.20 g. of palladized carbon. Shaking for three hours at an initial pressure of 54 lb./sq. in. consumed 0.17 mole of hydrogen. The crude product weighed 21.4 g. and was purified by two fractionations; yield, 18.3 g. (75%), b. p. 136.2–136.4° (739 mm.), f. p. −13°, n^{20}_{D} 1.4060, d^{20} 0.7189.

Di-*t*-butyl Diketone (VI) —An 8.18-g. portion of di-*t*-butylacetylene and 75 ml. of water was refluxed gently with stirring and 17.5 g. of potassium permanganate added in small portions during a period of about thirty hours. Steam distillation gave 6.0 g. of pale yellow oil, b. p. 166–169°. Redistillation of several combined samples gave a fairly pure product, b. p. 168–169° (745 mm.), n^{20}_{D} 1.4157, d^{20} 0.8776. The compound is mentioned in the literature although not well described.[12,13]

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66; mol. wt., 170.2; MR_{D}, 48.40. Found: C, 71.26; H, 10.86; mol. wt., 168; MR_{D}, 48.65.

Reaction of Di-*t*-butylacetylene with Bromine.—A solution of 13.8 g. of the acetylene and 16 g. of bromine in 100 ml. of carbon disulfide was allowed to stand in the dark at about 10° for three days. The solution was washed with dilute sodium bisulfite solution, dilute sodium hydroxide solution, water, and then dried. Distillation yielded 5 g. of unreacted di-*t*-butylacetylene, 4 g. of fairly constant boiling material, 5 g. of high boiling bromides, and 3.2 g. of residue. The 4-g. fraction was redistilled, b. p. 87–89° (4 mm.); n^{20}_{D} 1.521, d^{20} 1.422.

Anal. Calcd. for $C_{10}H_{18}Br_2$: Br, 53.6; mol. wt., 298.1. Found: Br, 53.3; mol. wt., 290.

bis-(**2-Chloroisopropyl**)-**acetylene** (V) —A mixture of 204 g. (1.44 moles) of tetramethylbutynediol,[14] 400 g. of carbon tetrachloride, and 50 g. of calcium chloride was held at 0–3° with stirring while hydrogen chloride was admitted. After nine hours the weight increase was 110

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(11) Grateful acknowledgment is made to Dr. T. S. Ma of the Microchemical Laboratory at the University of Chicago for the various combustion analyses.

(12) Bouveault and Locquin, *Bull. soc. chim.*, (3) **35**, 657 (1906).

(13) Egorova, *J. Russ. Phys.-Chem. Soc.*, **46**, 1327 (1914); Beilstein, 4th ed., vol. I, first supp., p. 410.

(14) Macullum, U. S. Patent 2,162,676 (1939); Froning and Hennion, THIS JOURNAL, **62**, 654 (1940).

g. (theoretical, 105 g.). The liquid layer was decanted from the calcium chloride sludge and neutralized by shaking with anhydrous potassium carbonate. Distillation yielded 108 g. (42%) of the dichloride (V), b. p. 65–70° (25 mm.). Purification was achieved by low temperature crystallization from ligroin followed by one fractionation: b. p. 62° (14 mm.), f. p. 22.5–22.0°, $n^{20}\text{D}$ 1.4605, d^{20} 1.009. Dupont[15] reported b. p. 62–63° (15 mm.); m. p. 29°.

Anal. Calcd. for $C_8H_{12}Cl_2$: Cl, 39.6; mol. wt., 179. Found: Cl, 39.2; mol. wt., 172.

Attempted Methylation of *bis*-2(-Chloroisopropyl)-acetylene.—Ninety-eight grams (0.57 mole) of *bis*-(2-chloroisopropyl)-acetylene (V) in ether was added dropwise to 1.68 moles of methylmagnesium bromide solution. An inflammable gas was evolved continuously from the reaction mixture, even when the flask was packed in crushed ice. After the addition of the halide the flask contents was stirred for six hours as the bath temperature was raised slowly to 50° When the product was poured into dilute iced hydrochloric acid, the ether layer was seen to contain considerable solid matter. After washing, drying and distillation of the ether, 66 g. of a white solid remained. This substance, somewhat waxy in appearance and feel, gave no test for halogen, decomposed without melting, and burned readily though incompletely.

Summary

1. Di-*t*-butylacetylene has been prepared and the structure proved. It was found to have physical properties consistent with its compact, symmetrical structure, and chemical properties influenced by the steric screening of the triple bond.

2. Di-*t*-butylacetylene was hydrogenated to *sym*-di-*t*-butylethylene and thence to *sym*-di-*t*-butylethane.

3. Oxidation of the acetylene gave di-*t*-butyldiketone rather than pivalic acid. Attempts to hydrate the triple bond catalytically were unsuccessful. The sodium in liquid ammonia reduction likewise failed. Bromine added slowly to give a dibromo derivative.

4. A synthesis of *bis*-(2-chloroisopropyl)-acetylene is given. On attempted coupling of this compound with methylmagnesium bromide, a polymer was formed.

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[15] Dupont, *Compt. rend.*, **152**, 198 (1911).

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

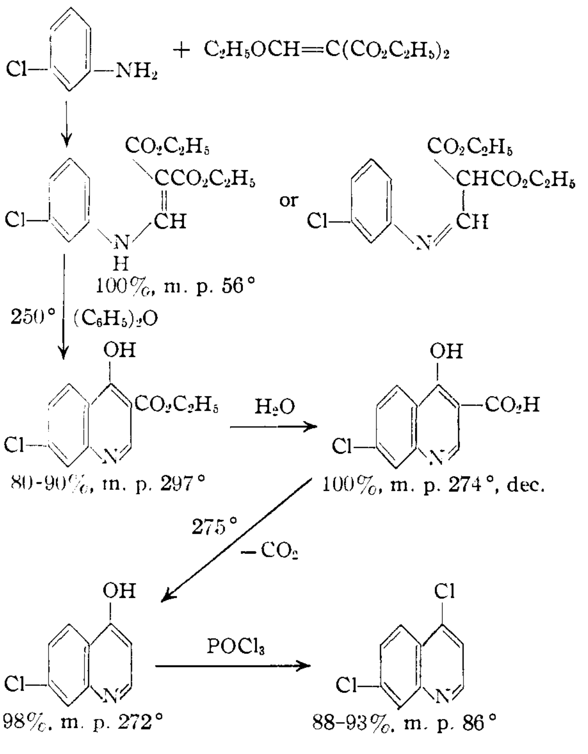
The Synthesis of 4-Hydroxyquinolines.[1] I. Through Ethoxymethylenemalonic Ester

BY CHARLES C. PRICE[2] AND ROYSTON M. ROBERTS[3]

The marked antimalarial activity of a number of quinoline derivatives having an alkylamino side chain attached in the 4-position[4] has led to an investigation of new procedures for the preparation of 4-hydroxyquinolines, which may be readily converted to the desired drugs. It has been found that the reaction reported by Gould and Jacobs,[5] the thermal cyclization of ethyl β-anilino-α-carbethoxyacrylate, is capable of very general application. Furthermore the 4-hydroxy-3-carboxyquinoline derivatives so formed may be readily decarboxylated, producing 4-hydroxyquinolines containing no other substituent in the pyrido-ring.

The procedure is illustrated by the reaction involved in the conversion of *m*-chloroaniline to 4-hydroxy-7-chloroquinoline.

The present paper also describes the preparation of 6-methoxy and 6,7-dimethyl-4-hydroxyquinoline from *p*-anisidine and 3,4-dimethylaniline, respectively. Further examples will be given in the following papers of this series.



The reaction of ethoxymethylenemalonic ester with aromatic amines to form anilinoacrylates takes place readily even at room temperature.

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(1) The work reported in this paper was done under a contract, recommended by the Committee on Medical Research, between the Office of Scientific Research and Development and the University of Illinois.

(2) Present address: University of Notre Dame, Notre Dame, Indiana.

(3) Present address: Merck and Company, Rahway, New Jersey.

(4) Andersag, Breitner and Jung, German Patent 683,792 (1939); *C. A.*, **36**, 4973 (1942).

(5) Gould and Jacobs, THIS JOURNAL, **61**, 2890 (1939).