5. A sample of *l*-acid dissolved in 0.1 *N* sodium hydroxide solution did not change in rotation upon standing for twenty-four hours at room temperature, nor upon heating for two hours at 80°. The solution was then refluxed but due to the small rotation in sodium hydroxide the rotations were taken on the free acid in methyl alcohol.

Rotation. 0.1140 g. made up to 15 cc. with 0.1 *N* NaOH at 20° gave $\alpha_D = +0.19°$, $l = 2$; $[\alpha]^{20}_D +12.6°$.

Time in minutes	$[\alpha]^{20}_D$ in CH_3OH	*k*	Av. *k*
0	−67.7°	....	
120	−50.6°	0.0011	0.00115
300	−29.0°	.0012	

Half-life period = 262 minutes = 4.5 hrs.

Summary

1. The compound 2-methyl-6-nitro-2′-carboxydiphenyl has been prepared and resolved.

2. The active forms racemize slowly in boiling alkali and still more slowly in neutral or acid solvents.

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

HEXA-OMEGA-TERTIARY-BUTYLPROPINYLETHANE AND SOME NEW ACETYLENIC CARBINOLS

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In attempting to find some aliphatic unsaturated hydrocarbons which would resemble the hexa-arylethanes, several tetra- and hexa-acetylenic ethanes have been prepared in this Laboratory.[1] All of the compounds which have been described heretofore have had as the acetylenic group the radical *tert.*-butylethinyl, $(CH_3)_3C—C{\equiv}C—$. In order to learn more about compounds of this general type, the work has now been extended to cover hydrocarbons in which other than tertiary alkyl groups are attached to the ethinyl group. It has been shown[2] that a tertiary alkyl group directly attached to the central carbon of a hexasubstituted ethane has a greater effect in producing dissociation than does a secondary alkyl group, and this in turn has a greater effect than does a primary alkyl group. It has seemed of interest to determine whether this effect is transmitted through the acetylenic structure to the central ethane carbon. As the first step in this study, the preparation and properties of a hexa-

[1] The publications describing these compounds are Salzberg and Marvel, THIS JOURNAL, **50**, 1737, 2840 (1928); Rossander and Marvel, *ibid.*, **51**, 932 (1929); Gillespie and Marvel, *ibid.*, **52**, 3368 (1930).

[2] Conant, Small and Sloan, *ibid.*, **48**, 1743 (1926); Conant and Bigelow, *ibid.*, **50**, 2041 (1930).

acetylenic ethane which has a primary alkyl group attached to the ethinyl group are described in this communication.

The synthesis of hexa-ω-*tert.*-butylpropinylethane was accomplished in the following manner

$$\mathrm{(CH_3)_3CMgCl + BrCH_2CBr{=}CH_2 \longrightarrow \underset{I}{(CH_3)_3CCH_2CBr{=}CH_2} \xrightarrow{NaNH_2}}$$

$$\mathrm{\underset{II}{(CH_3)_3CCH_2C{\equiv}CH} \xrightarrow[CO(OC_2H_5)_2]{C_2H_5MgBr} \underset{III}{[(CH_3)_3C{-}CH_2{-}C{\equiv}C]_3COH} \xrightarrow[Ag]{CH_3COBr}}$$

$$\mathrm{\underset{IV}{[(CH_3)_3CCH_2C{\equiv}C]_3C{-}C[C{\equiv}CCH_2C(CH_3)_3]_3}}$$

The first two compounds in this series, 4,4-dimethyl-2-bromopentene-1 (I) and 4,4-dimethylpentine-1 (II) were prepared according to the general method of Lespieau and Bourguel.[3] The carbinol (III) was prepared by the method described by Salzberg and Marvel[1] for tri-*tert.*-butylethinylcarbinol. It was impossible to convert this carbinol to a crystalline bromide which could be purified. However, the desired hydrocarbon (IV) was obtained by treating the carbinol with acetyl bromide and then with metallic silver. The same product was obtained when these two reactions were carried out in separate operations that was obtained when all of the reagents were mixed together and the synthesis accomplished in one step.

The structure of the new hydrocarbon was not as easily determined as was that of hexa-*tert.*-butylethinylethane. Treatment of hexa-ω-*tert.*-butylpropinylethane with liquid sodium–potassium alloy gave a colored alkali metal derivative that reacted with dry carbon dioxide to give an acidic compound which could not be purified. Oxidation of the hydrocarbon with ozone gave about 30% of the calculated amount of *tert.*-butylacetic acid. These facts are in agreement with the structure which has been proposed for the hydrocarbon.

The hydrocarbon was not cleaved by 1% sodium amalgam and hence is more stable in this respect than hexa-*tert.*-butylethinylethane. It is less stable in air and does not keep well. After it is a few hours old it begins to develop a yellow color and in one day turns brown due to decomposition or polymerization. The nature of the change has not been determined.

Several other intermediate compounds containing primary alkyl groups attached to an acetylenic linkage have been obtained and are described in the experimental part. However, their conversion to hexasubstituted ethanes has not been accomplished. One hydrocarbon has been described as di-ω-*tert.*-butylpropinyl-tetraphenylethane but this structure is only supported by the method of synthesis.

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[3] Lespieau and Bourguel, "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., **1926**, Vol. VI, pp. 20, 26.

Experimental Part

4,4-Dimethyl-2-bromopentene-1.—In a three-liter, three-necked flask fitted with a mechanical stirrer, a reflux condenser and a separatory funnel, was placed 200 g. of bromo-allyl bromide and 200 cc. of anhydrous ether. The flask was placed in an ice-bath, and through the separatory funnel was added an ether solution of 1.33 moles of *tert.*-butylmagnesium chloride which had been prepared and titrated previously. The Grignard reagent was added at such a rate that the ether boiled gently. The addition required about thirty to forty-five minutes. After the addition was complete, the ice-bath was removed and the mixture was gently refluxed on a water-bath for about two hours in order to insure completion of the reaction.

The mixture was then cooled and the excess Grignard reagent was decomposed by adding slowly a solution of 35 cc. of concentrated hydrochloric acid in 350 cc. of water through the separatory funnel. The ether layer was separated, washed with a saturated solution of sodium bicarbonate, dried over calcium chloride and distilled. After the ether was removed, the 4,4-dimethyl-2-bromopentene-1 was collected at 135–138°. The yields varied from 80 to 110 g. (45–62% of the theoretical amount); d_4^{20} 1.030, n_D^{20} 1.4630.

Anal. Subs., 0.1930: 26.26 cc. of 0.04137 *N* $AgNO_3$. Calcd. for $C_7H_{13}Br$: Br, 45.2. Found: Br, 45.0.

In order to obtain a pure product it was always necessary to use an excess of the Grignard reagent so that no unreacted bromoallyl bromide (b. p. 140°) remained in the mixture.

4,4-Dimethylpentine-1.—Sixty-two grams of sodamide was ground in a mortar with 104 cc. of purified high-boiling mineral oil until a fine suspension was obtained. This was transferred to a 1-liter round-bottomed three-necked flask fitted with a reflux condenser protected with a calcium chloride tube, a 500-cc. separatory funnel, and an efficient mechanical stirrer. An additional 125 cc. of mineral oil was used in transferring the suspension from the mortar to the reaction flask. The mixture was heated in an oil-bath at 160–165°, the stirrer was started, and 92 g. of 4,4-dimethyl-2-bromopentene-1 was added from the dropping funnel.

The reaction started at once and ammonia was evolved. Heating and stirring were continued for two hours after the addition of the bromo compound was complete. The mixture was then cooled, diluted with 250 cc. of xylene and this solution was poured onto about 700 g. of cracked ice to which had been added 140 cc. of concentrated hydrochloric acid (sp. gr. 1.19). The oil layer was separated, washed with a saturated solution of sodium bicarbonate, dried over calcium chloride and distilled from a modified Claisen flask.[4] In the first fractionation the material boiling between 50 and 100° was saved. On redistillation the product boiling at 73–75° at ordinary pressures was collected. The yield was 18 g. (37% of the theoretical amount). There was some loss in the preparation due to the heptine passing off with the ammonia. By using ice water in the condenser and washing the ammonia which escaped with the xylene which was used to dilute the reaction mixture, the yield was increased to 45% of the theoretical amount. The new acetylene has the following constants: d_4^{20} 0.7154, n_D^{20} 1.4028.

The acetylene was not analyzed as such, but was converted to the diacetylenic mercury compound $[(CH_3)_3CCH_2C{\equiv}C]_2Hg$ according to the general method recently described by Johnson and McEwen.[5] The mercury derivative melted at 125–126.5° (corr.).

Anal. Subs., 0.1924: Hg, 0.1000. Calcd. for $C_{14}H_{22}Hg$: Hg, 51.28. Found: Hg, 51.9.

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[4] "Organic Syntheses," John Wiley and Sons, Inc., New York, **1921**, Vol. I, p. 40.

[5] Johnson and McEwen, This Journal, **48**, 469 (1926).

Tri-ω-*tert*.-butylpropinylcarbinol.—To 166 cc. of a 3.0 *N* solution of ethylmagnesium bromide in dry ether was added 48 g. of 4,4-dimethylpentine-1. The ethane generated by the reaction was led out through a well-cooled condenser to avoid loss of the acetylene. When this reaction was complete, 19.7 g. of diethyl carbonate was slowly added. After about fifteen hours the reaction mixture was decomposed with an aqueous ammonium chloride solution which contained a little hydrochloric acid. The ether layer was separated, washed with water and sodium bicarbonate solution and dried over anhydrous sodium sulfate.

The ether was evaporated and the carbinol was distilled under reduced pressure. The product boiled at 140–142° at 0.7 mm. The yield of distilled product was 42 g. The distillate solidified and was recrystallized from petroleum ether. The yield of recrystallized material was 32.3 g. (68% of the theoretical amount) of a product which melted at 50–51°.

Anal. Subs., 0.1853: CO_2, 0.5704; H_2O, 0.1805. Calcd. for $C_{22}H_{34}O$: C, 84.07; H, 10.82. Found: C, 83.95; H, 10.90.

Hexa-ω-*tert*.-butylpropinylethane.—A solution of 1.5 g. of the carbinol and 0.2 cc. of acetyl bromide in about 10 cc. of dry petroleum ether was allowed to stand for about ten minutes. The petroleum ether and excess acetyl bromide were then removed by evaporating under reduced pressure. A few drops of methyl alcohol were added to decompose any excess acetyl bromide and the mixture was evaporated again under reduced pressure. The residue was taken up in dry ether, 0.5 g. of molecular silver added and the mixture shaken overnight. After filtering, the solvent was evaporated and the residue was recrystallized from a mixture of methyl alcohol and ether. There were thus obtained crystals which melted at 127.5–128.5°.

The same hydrocarbon was obtained more readily by shaking a solution of carbinol and acetyl bromide in petroleum ether with molecular silver. To an ice-cold solution of 1.66 g. of carbinol in 20 cc. of petroleum ether was added 1.7 g. of molecular silver and 0.5 cc. of acetyl bromide. The flask was swept out with dry nitrogen and sealed. The mixture was shaken for eighteen hours. It was then filtered and the solvent evaporated. The residue on recrystallization yielded 0.4 g. (24% of the theoretical amount) of a product of m. p. 127.5–128.5°. A mixed melting point showed this product to be identical with the one obtained above.

Anal. Subs., 0.1986: CO_2, 0.6455; H_2O, 0.1985. Calcd. for $C_{44}H_{66}$: C, 88.88; H, 11.11. Found: C, 88.65; H, 11.08.

This hydrocarbon turns yellow on standing in the air for a few hours. In one day the color deepens to brown. If kept at 0° it remains colorless for over a week. A dry ether solution of the ethane reacted almost instantly with liquid sodium–potassum alloy to give a red metal alkyl. The ethane did not react with 1% sodium amalgam. The result with 40% sodium amalgam was inconclusive. It was not possible to convert the metal alkyl to a crystalline acid by the action of dry carbon dioxide followed by mineral acid. Evidence was obtained repeatedly that an acidic compound was produced but it seemed very unstable and turned to a brown tarry product.

***Tert*.-butylacetic Acid.**—A solution of 30 g. of 4,4-dimethyl-2-bromopentene-1 in 200 cc. of carbon tetrachloride was placed in a wash bottle which was packed with an ice–salt mixture. Ozonized air was passed through the solution at the rate of seven liters per minute for about twelve hours. Additional carbon tetrachloride was added occasionally to replace that swept out by the current of air. Some solid ozonide separated from solution. Dilute aqueous alkali was added and the mixture was heated. The carbon tetrachloride layer was separated and evaporated and the residue was again heated with aqueous alkali. The alkaline solutions were combined and acidified with sulfuric acid and the aqueous solution was distilled until no more oil came over. The distillate was extracted with ether and the ether was removed by evaporation. The residue was distilled under ordinary pressure. There was thus obtained 7 g. of acid which boiled at 186–188° and gave a neutral equivalent of 118.3 instead of the theoretical 116. The *p*-bromophenacyl ester was formed by refluxing an alcohol solution of the sodium salt with *p*-bromophenacyl bromide. After crystallizing repeatedly this product melted at 81–81.5°.

Anal. Subs., 0.3786: 29.56 cc. of 0.04137 *N* $AgNO_3$. Calcd. for $C_{13}H_{17}O_3Br$: Br, 25.56. Found: Br, 25.82.

Ozonization of Hexa-ω-*tert.*-butylpropinylethane.—An ice-cold solution of 2.94 g. of the ethane in 200 cc. of carbon tetrachloride was treated with a current of ozonized air at the rate of about 4 liters per minute for about two hours. The ozonized mixture was treated with a little water and then sodium hydroxide solution was added. The carbon tetrachloride solution was thoroughly extracted with the aqueous alkali. The alkaline solution was separated, acidified with sulfuric acid and distilled. An oily acid came over. This distillate was titrated with standard alkali and assuming that all of the acidity was due to *tert.*-butylacetic acid the yield was 0.965 g. (28% of the theoretical amount). The neutral solution was evaporated to dryness, the residue was taken up in 35 cc. of 95% alcohol and 2.03 g. of *p*-bromophenacyl bromide was added. After boiling to complete the reaction, the derivative was isolated and crystallized. It melted at 80.5–81.5° and was shown by a mixed melting point determination to be identical with the derivative prepared before from *tert.*-butylacetic acid.

ω-*Tert.*-butylpropinyl-diphenylcarbinol.—To 19 cc. of 3.7 *N* ethylmagnesium bromide solution was added 7 g. of 4,4-dimethylpentine-1. The mixture was allowed to stand until no more ethane was evolved and then 7.9 g. of benzophenone was added. The mixture was stirred for about five hours and allowed to stand overnight. On working up the reaction mixture in the usual manner, the carbinol was obtained as a liquid boiling at about 135° under 0.4 mm. pressure. It crystallized readily from petroleum ether and then melted at 55–56°. The yield was 10.3 g. (85% of the theoretical amount).

Anal. Subs., 0.2184: CO_2, 0.6886; H_2O, 0.1556. Calcd. for $C_{20}H_{22}O$: C, 86.33; H, 7.91. Found: C, 85.98; H, 7.96.

ω-*Tert.*-butylpropinyl-diphenyl-bromomethane.—A solution of 0.5 g. of the carbinol in 10 cc. of petroleum ether was treated with 0.2 cc. of phosphorus tribromide. After about one-half hour the solution was washed with sodium bicarbonate solution, dried over sodium sulfate and evaporated under reduced pressure. The residue was a light brown liquid which would not crystallize even when cooled in solid carbon dioxide. This liquid was dried in a vacuum desiccator over phosphorus pentoxide and analyzed.

Anal. (Stepanow) Subs., 0.2040: 6.15 cc. of 0.1000 *N* $AgNO_3$. Calcd. for $C_{20}H_{21}Br$: Br, 23.53. Found: Br, 24.11.

Sym.-di-ω-*tert.*-butylpropinyl-tetraphenylethane.—The crude bromide prepared from 2 g. of carbinol and 0.74 g. of phosphorus tribromide in petroleum ether was treated with 1.5 g. of molecular silver and the mixture was shaken for about twelve hours. The mixture was then filtered, the solvent was evaporated and the residue was crystallized from alcohol. There was thus obtained 0.2 g. of a hydrocarbon which melted at 116–118°. Analysis showed that it had the expected composition. It gave a red color when treated in dry ether with liquid sodium–potassium alloy. However, the metal alkyl thus obtained could not be converted into the corresponding acid.

Anal. Subs., 0.1791: CO_2, 0.6000; H_2O, 0.1305. Calcd. for $C_{40}H_{42}$: C, 91.97; H, 8.03. Found: C, 91.38; H, 8.13.

Di-ω-*tert.*-butylpropinyl-phenylcarbinol.—This carbinol was prepared in the same general manner described before. From 18 cc. of 3.6 *N* ethylmagnesium bromide solution, 6.5 g. of 4,4-dimethylpentine-1 and 5.2 g. of ethyl benzoate there was obtained 3.8 g. of a product boiling at 135–137° at 0.4 mm. pressure: d_4^{20} 0.9325; n_D^{20} 1.5080.

Anal. Subs., 0.2139: CO_2, 0.5979; H_2O, 0.1391. Calcd. for $C_{21}H_{28}O$: C, 85.14; H, 9.46. Found: C, 84.60; H, 9.59.

Diphenyl-ω-cyclohexylpropinylcarbinol.—From 21.6 cc. of 3.8 *N* ethylmagnesium bromide solution, 10.5 g. of cyclohexylpropine and 14.5 g. of benzophenone there was obtained 6 g. of product which boiled at 210–215° at 1.1 to 1.3 mm. pressure; d_4^{20} 1.058; n_D^{20} 1.5750. This product was redistilled at 0.003 mm. pressure and then boiled at 165–166°.

Anal. Subs., 0.2043: CO_2, 0.6505; H_2O, 0.1459. Calcd. for $C_{22}H_{24}O$: C, 86.84; H, 7.89. Found: C, 86.85; H, 7.99.

Phenyl-di-ω-cyclohexylpropinylcarbinol.—From 35 cc. of 4.2 *N* ethylmagnesium bromide solution, 18.5 g. of cyclohexylpropine and 11.4 g. of ethyl benzoate there was obtained 4 g. of this carbinol; b. p. 180–185° at 0.017 mm. pressure; d_4^{20} 1.014; n_D^{20} 1.5390.

Anal. Subs., 0.1986: CO_2, 0.6258; H_2O, 0.1635. Calcd. for $C_{25}H_{32}O$: C, 86.20; H, 9.19. Found: C, 85.94; H, 9.21.

Summary

1. Hexa-ω-*tert.*-butylpropinylethane has been prepared and has been found to be less readily cleaved by alkali metals than hexa-*tert.*-butylethinylethane. However, it decomposes with greater rapidity in the air.

2. Some new acetylenic carbinols having primary alkyl groups next to the acetylenic linkage have been described.

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[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

PHOTOCHEMICAL OXIDATION OF LACTIC ACID[1]

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The present study is a development and a continuation of an investigation of the action of ultraviolet radiation on lactic acid. In the absence of oxygen it has been shown that the main products of the decomposition are ethanol and carbon dioxide.[2] It was felt that the conflicting results obtained by other investigators[3] of this decomposition were due to the presence of oxygen dissolved in the solution.

The decomposition of lactic acid in the presence of oxygen has never been fully investigated. Some workers[4] in this field have exposed solutions of lactic acid to sunlight and air and have obtained qualitative tests

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[1] A part of a paper presented at the Cincinnati meeting of the American Chemical Society.

[2] Burns, THIS JOURNAL, **51**, 3165 (1929).

[3] See Neuberg, *Biochem. Z.*, **39**, 163 (1912); Baudisch, *ibid.*, **103**, 59 (1920).

[4] See Ganassini, *Chem. Zentr.*, I, 387 (1913); I, 729 (1910); *Chemical Abstracts*, **5**, 3236 (1911); Ciamician and Silber, *Ber.*, **46**, 1558 (1913).