Benzylation of Acetylene. II. On the Structure and Oxidation of 3-Benzyl-3,4-diphenyl-1-Butyne

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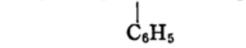
We reported the formation of 3,4-diphenyl-1-butyne (I) and its isomer, 3,4-diphenyl-1,2-butadiene (II), by the reaction of benzyl chloride and sodium or lithium acetylide in liquid ammonia[1], whereas formation of benzylacetylene had been expected[2]. In the present paper, we report the formation and the structure of 3-benzyl-3,4-diphenyl-1-butyne (III).

It is particularly interesting that III was produced in addition to I and II in the reaction using an equimolar ratio of benzyl chloride to a metallic acetylide and that III resisted oxidation.

$$\mathrm{C_6H_5{-}CH_2{-}\underset{\underset{\displaystyle C_6H_5}{|}}{CH}{-}C{\equiv}CH}$$

I



$$\mathrm{C_6H_5{-}CH_2{-}\underset{\underset{\displaystyle C_6H_5}{|}}{C}{=}C{=}CH_2}$$

II

III was obtained as a fraction distilling at 207°C (4.5 mmHg) and following the fraction of I and II from the reaction mixture. III was a yellowish, viscous liquid and formed complex salts with silver nitrate and with alkaline mercuric iodide[3,4], showing the presence of an ethynyl group $-C\equiv CH$. The presence of the terminal acetylenic bond was reassured by a strong absorption maximum at 3320 cm.$^{-1}$ due to stretching vibration of the bond and a weak one at 2120 cm.$^{-1}$ for a monosubstituted acetylene[5]. The

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[1] T. Ando and N. Tokura, This Bulletin, **30**, 259 (1957).

[2] T. H. Vaughn, G. F. Hennion, R. R. Vogt and J. A. Nieuwland, *J. Org. Chem.*, **2**, 1 (1938).

[3] J. R. Johnson and W. L. McEwen, *J. Am. Chem. Soc.*, **48**, 469 (1926).

[4] B. B. Elsner and P. F. M. Paul, *J. Chem. Soc.*, **1951**, 893.

[5] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules", John Wiley and Sons, Inc., New York (1954), p 49.

ethynyl group of III resisted strongly against oxidizing agents, as compared with a double bond between ordinary aliphatic carbon atoms⁶⁾. Namely, (1) by passing air into a solution of III for many hours at room temperature, III was not oxidized and was completely recovered. (2) When an alkaline aqueous solution of III (a part was dissolved but most part remained as a suspension) was agitated with 30% aqueous hydrogen peroxide and the solution was left to stand for one night, the substance was not oxidized. Even when the alkaline solution was mixed with an excess of hydrogen peroxide and the solution was heated on a water bath, it remained without being oxidized. (3) When 5% ozone was introduced into a solution of III in ethyl acetate for 30 minutes at −10°C, a minute amount of benzoic acid was produced, but the main part remained without being oxidized. The above results well coincided with the experiment of Criegee and Lederer⁷⁾ on an ethynyl compound. III was oxidized with potassium permanganate either in neutral, alkaline or acidic solution at room temperature. The oxidation in an acidic medium gave a white crystalline substance (A), m.p. 139~140°C, in a low yield, but the yield was increased to 92% in a neutral solution. The aqueous solution of A was acidic. When a piece of A was dropped into concentrated sulfuric acid, instant vesication was observed, showing A was an α-keto acid. An absorption of carboxyl ion $-COO^{-}$⁸⁾ was observed at 1370 cm.$^{-1}$ in infrared spectrum of A. Absorptions at 1711 cm.$^{-1}$ and 1722 cm.$^{-1}$ showed that the substance was a derivative of pyruvic acid, according to Icherweed⁹⁾ and Jones¹⁰⁾. In addition to the above I.R. spectra, elementary analysis of A corresponded to $C_{23}H_{20}O_3$. This acid (A) is therefore considered to be phenyldibenzylpyruvic acid (IV).

By either decarbonylation by heat or oxidation with hydrogen peroxide or potassium permanganate, IV always gave a white crystalline substance (B), melting at 122~123°C. When III was reduced with hydrogen and palladium carbon, a colorless, slightly viscous oil (C), b.p. 192~194°C (3 mmHg), was produced through absorption of one mole of hydrogen. In C, the absorptions of the ethynyl group (3320 cm.$^{-1}$) disappeared, but stretching vibration of C=C (non-conjugate)¹¹⁾ newly appeared at 1668 cm^{-1}. Absorption maxima at 1430 cm.$^{-1}$ and 912 cm.$^{-1}$ showed the presence of a vinyl group ($-CH=CH_2$). C was therefore assumed to be 3-benzyl-3,4-diphenyl-1-butene (V).

Oxidation of V with potassium permanganate gave an acid, m.p. 139~140°C, and no lowering of the melting point of a mixture of this acid and IV was observed. It was supposed that, when gently oxidized with potassium permanganate, III and V gave the same keto-acid owing to the degradation of ethynyl and vinyl group, respectively. When oxidized with ozone, V gave an acid, m.p. 122~123°C, which was identified as B by the mixed melting point.

Treatment of III with sulfuric acid in the presence of mercuric sulfate gave a crystalline substance (VI) in a yield of 78%, b.p. 230~240°C (6 mmHg), m.p. 84~84.5°C. I.R. spectrum of VI showed carbonyl stretching vibration in open chain ketones¹¹⁾ at 1700 cm.$^{-1}$ and methyl deformation of methyl ketone¹²⁾ at 1354 cm.$^{-1}$. From the above I.R. spectral analyses and a positive iodoform reaction, it should have a methyl ketone group, but it has not yet yielded oxime, hydrazone nor semicarbazone. We suppose that this ketone is difficult to react with the carbonyl reagents on account of the steric hindrance by the three phenyl groups.

Furthermore, an attempt to reduce VI by Clemmensen's method failed. When oxidized with hypobromite¹³⁾, VI gave an acid of m.p. 122~123°C, which was identified as B by the mixed melting point.

When B was allowed to stand about two months at room temperature, the melting point was raised to 153~154°C from 122~123°C, but I.R. and U.V. spectra did not change. We call the higher melting substance α-form and the lower melting one β-form tentatively.

Hauser and Brasen¹⁴⁾, and Baker¹⁵⁾ reported the benzylation of benzyl cyanide in liquid ammonia. We carried out the same reaction and prepared 2-benzyl-2,3-diphenylpropionitrile (VII). Hydrolysis

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6) F. Bohlmann and J. Sinn, *Ber.* **88**, 1869 (1955).
7) R. Criegee and M. Lederer, *Ann.* **583**, 29 (1953).
8) M. st. C. Flett, *J. Chem. Soc.*, **1951**, 962.
9) F. A. Icherweed, *Nature*, **195**, 419 (1955).
10) R. L. Jones, ibid., **173**, 121 (1954).
11) R.B. Barmes, R.C. Gore, U. Lidded and V.Z. Williams, "Infra-red Spectroscopy", Reinhold Publishing Co. (1944).
12) J.A. Anderson and W.D. Seybried, *Anal. Chem.*, **20**, 998 (1948).
13) W. S. Johnson, C. D. Gustsche and R. D. Offenhauer, *J. Am. Chem. Soc.*, **68**, 1648 (1946).
14) C. R. Hauser and W. R. Brasen, ibid., **78**, 494 (1956).
15) R. H. Baker, ibid., **70**, 3857 (1948).

of this nitrile to an acid amide (VIII) by refluxing for four days with sulfuric acid in glacial acetic acid, followed by treatment with sodium nitrite, gave 2-benzyl-2,3-diphenylpropionic acid (IX), m.p. 153~154.5°C, which on admixture with the β-form (m.p. 153~154.5°C) showed no depression of the melting point.

It is also of interest that Hauser's[14] acid, obtained by the same procedure as above, showed the same melting point 124~125°C, as our α-form.

When we compared melting points of nitrile VII, amide VIII and acid IX to those of Hauser's[14] and Baker's[15] substance, respectively (Table I), we found that our values resembled Baker's closely except acid IX.

TABLE I

	Author	Hauser et al.[14]	Baker[15]
Nitrile VII	81~83°C	92~92.5°C	82°C
amide VIII	112.7~114°C	—	111~112°C
acid IX	α 122~123°C	124~125°C	131~132°C
	β 153~154.5°C		

It was observed that nitrile VII affords two forms, m.p. 92°C and 82°C. We concluded the α-form and the β-form are polymorphs of 2-benzyl-2,3-diphenylpropionic acid (IX). Such cases often occur in sterically hindered systems[16].

It appears likely that Baker's acid was a mixture of the α- and the β-form. Table II shows a series of compounds derived from III was described above. Since the structure of IX has been thus decided, the structure of III, IV, V and VI are established, as already assumed, as 3-benzyl-3,4-diphenyl-1-butyne, phenyldibenzylpyruvic acid, 3-benzyl-3,4-diphenyl-1-butene and 3-benzyl-3,4-diphenyl-2-butanone, respectively.

A similar benzylation of allylbenzene in liquid ammonia has given 3-benzyl-3,4-diphenyl-1-butene (V) in a good yield, as will be reported later.

Experimental[17]

3-Benzyl-3,4-diphenyl-1-butyne (III).— Metallic sodium was dissolved in liquid ammonia and to this solution acetylene gas was introduced to form sodium acetylide, and the product was added to an equimolar amount of benzyl chloride in liquid ammonia, for the mixture to be treated as reported in the preceding paper[1]. Following the fraction of I and II, 3-benzyl-3,4-diphenyl-1-butyne (III) distilled at 207°C (4.5 mmHg), a pale yellow oil; yield, 15.3% or 30 g. from 252 g. of benzyl chloride.

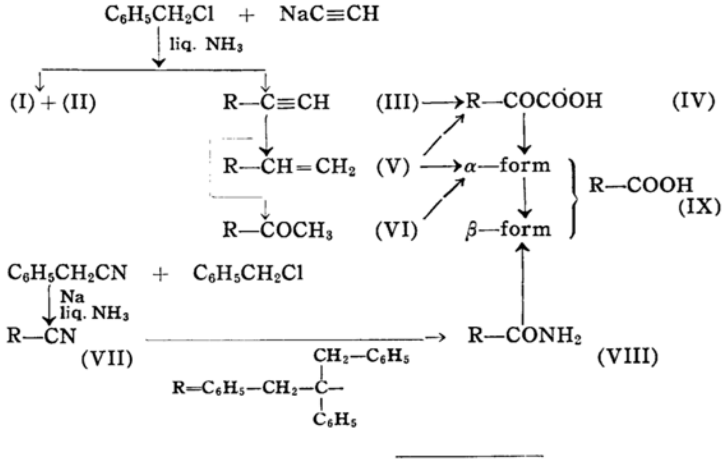
Anal. Found: C, 93.48; H, 6.64. Calcd. for $C_{23}H_{20}$: C, 93.20; H, 6.80%. I.R. ν max: 3320 and 2120 cm.$^{-1}$ Mol. wt.: Found, 296; Calcd. for $C_{23}H_{20}$: 296.

A mercuric complex[3] was given as white fine needles from petroleum ether (b.p. 40~60°C), m.p. 159~159.5°C.

Mercury determination of the complex salt: 4.093 mg. of the substance gave 1.0379 mg. or 25.36% of Hg. Calcd. for $C_{46}H_{38}Hg$: Hg, 25.36%.

Oxidation of III with Potassium Permanganate. Phenyldibenzylpyruvic Acid (IV).— (*a*). *Oxidation in a neutral medium.* A three necked flask of two litre capacity equipped with an air-tight agitator and a reflux condenser are used as the reaction vessel. III (4.2 g.) was dissolved in 400 cc. of acetone and to the solution 8 g. of potassium permaganate dissolved in 400 cc. of water was added and the mixture was agitated for 48 hours at room temperature. After distilling off acetone, sulfur dioxide gas cooled with ice

TABLE II



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16) W. V. Miller and G. Rohde, *Ber.*, **25**, 2017 (1892).

17) Melting points were not corrected.

was introduced into the residue and then the solution was made basic with dilute aqueous sodium hydroxide. Unchanged neutral part was extracted with ether and the remaining alkaline layer was acidified with hydrochloric acid and extracted with ether. After removal of ether, 4.5 g. of crystals melting at 139.51~40°C were obtained in a yield of 92%.

Anal. Found: C, 80.68; H, 5.92. Calcd. for $C_{23}H_{20}O_3$: C, 80.21; H, 5.85%. I.R. ν max: 1722, 1711, and 1370 cm.$^{-1}$

In other experiments oxidation was carried out for 100 hours at room temperature and 8 hours at boiling water bath temperature, the yields of IV being depressed to 17.2 and 21%, respectively, when the precipitate of manganese dioxide was not decomposed with sulfur dioxide.

(*b*) *Oxidation in an alkaline medium.* One gram of III was vigorously agitated and emulsified with 150 cc. of water and 20 cc. of 2N potassium hydroxide solution. To the emulsion 200 cc. of 1% aqueous potassium permanganate was added and then agitation was continued for 150 hours at room temperature. Then the solution was treated as stated above yielding 0.1 g. (8.6%) of crystals (IV), m.p. 139.5~140°C.

(*c*) *Oxidation in an acidic medium.* Two grams of III was dissolved in 500 cc. of glacial acetic acid, and 300 cc. of 1% aqueous potassium permanganate was added to the solution. By 3 hours agitation, reddish violet color disappeared. When the solution was treated as described above, only a minute amount of an acidic part was obtained.

Partial Hydrogenation, 3-Benzyl-3,4-diphenyl-1-butene (V).—Two grams of III was dissolved in 100 cc. of metanol in a reducing flask. In a Willstätter reducing apparatus III was reduced at 15°C in the presence of 0.5 g. of 5% palladium carbon. In 25 minutes, 160 cc. of hydrogen was absorbed. Then the reaction was discontinued and the solvent was distilled off. The residue was distilled under a reduced pressure, and 1.8 g. of V was obtained, b.p. 192~194°C (3 mmHg).

Anal. Found: C, 92.17; H, 7.61. Calcd. for $C_{23}H_{22}$: C, 92.57; H, 7.43%. I.R. ν max: 1668, 1430, 1002 and 912 cm.$^{-1}$

Oxidation of V with Potassium Permanganate.—Two grams of V was dissolved in 500 cc. of acetone in a three-necked flask of 1 liter capacity and to the solution 100 cc. of a 4.2% potassium permanganate solution was added. The mixture was agitated for 48 hours at room temperature, and then for 15 hours at 45°C. After removal of the solvent, sulfur dioxide gas was introduced under cooling with ice. The residue was made basic with dilute caustic alkali and extracted with ether. The aqueous layer was acidified and extracted with ether. After removal of the solvent from the ethereal solution, 0.5 g. (21%) of white globular crystals were obtained; m.p. 138~140°C. It was confirmed that they were identical with IV by a melting point determination of the mixed crystals after recrystallization.

Hydration of III. 3-Benzyl-3,4-diphenyl-2-butanone (VI).—Ten grams of III was dissolved in 200 cc. of methanol in a three-necked flask equipped with a mechanical agitator and a reflux tube. To the solution a mixture of 1.5 g. of mercuric sulfate, 3 cc. of concentrated sulfuric acid and 10 cc. of water was added and agitated under reflux. After 6 days, the reaction was terminated, the insoluble substances were filtered off and the solvent was distilled off from the filtrate. Then the residue was distilled under a reduced pressure. A reddish brown viscous oil was obtained; b.p. 230~240°C (6 mm Hg). On addition of a small amount of ethanol to the oil, white heavy plates were crystallized, m.p. 84~84.5°C; yield, 8.3 g. (78%).

Anal. Found: C, 87.79; H, 7.13. Calcd. for $C_{23}H_{22}O$: C, 87.86; H, 7.05%. I.R. ν max: 1700, 1354, 1152, 1078 and 1031 cm^{-1}.

The α-Form of 2-Benzyl-2,3-diphenylpropionic Acid (IX).—(*a*) *Heat decarbonylation of IV.* IV (0.5 g.) was taken in a small test tube and gradually heated on a sulfuric acid bath. On elevation of the temperature of the bath above the melting point of IV, 140°C, the evolution of a gas from the substance was observed. When the temperature of the bath reached to 220°C, splitting of carbon monoxide occurred very quickly. While the temperature of the bath was elevated to 260°C for 1 hour, the gas evolution was completed. The colorless fused substance changed orange and then to reddish orange in color. After cooling, the product was crystallized form ligroin (b.p. 80~100°C), yielding white crystals, m.p. 122~122.5°C (α-form); yield, 0.1 g. (21.7%).

(*b*) *Reaction of IV with hydrogen peroxide.*—In a beaker of 200 cc. capacity, 1.5 g. of IV was mixed with 20 cc. of 10% sodium hydroxide solution and 30 cc. of 10% hydrogen peroxide, and the mixture was allowed to stand for one night in an ice box. Then another 10 cc. portion of hydrogen peroxide (10%) was added to the mixture with stirring. After 8 hours, the mixture was acidified and extracted with ether. When the ethereal solution was dried and evaporated, fine scales were afforded, m.p. 115~120°C; yield, 0.4 g. (87%). When recrystallized from ligroin (b.p. 80~100°C), 0.28 g. of white scales were obtained, m.p. 122~123°C (α-form).

(*c*) *Oxidation of IV with potassium permanganate.* IV (0.5 g.) was dissolved in 100 cc. of 2% aqueous sodium hydroxide in a round flask of 300 cc. capacity, and to the solution 50 cc. of 1% aqueous potassium permanganate was added. The mixture was agitated for 8 hours and left to stand for one night. The mixture was neutralized with dilute sulfuric acid, treated with sulfur dioxide gas to dissolve manganese dioxide, and then extracted with ether. When the ether was distilled off, white crystals remained. On recrystallization from ligroin (b.p. 80~100°C), 0.2 g. (43.5%) of white scales were obtained, m.p. 121~122°C (α-form).

(*d*) *Oxidation of V with ozone.* Two grams of V was dissolved in 100 cc. of ethyl acetate, cooled at -60°C and ozone (0.01 mole/hour) was passed for 50 minutes. The solvent in the reaction mixture was distilled off under a reduced pressure. After decomposition of the ozonide in the residue with ice, 10 cc. of 10% aqueous sodium hydroxide and 5 cc. of 10% hydrogen peroxide were added; the mixture was left to stand for one night, and extracted with ether to remove the neutral part. The residual solution gave 1.5 g. (71%) of an acid, m.p. 119∼121°C, on acidification. When the product was recrystallized from ligroin (b.p. 80∼100°C), crystals (1.2 g.) m.p. 122∼123°C (α-form), were obtained.

(*e*) *Oxidation of VI with sodium hypobromite.* To 50 cc. of 1,4-dioxane containing 5 g. of VI, a sodium hypobromite solution (5 cc. of bromine in 50 cc. of ice-cooled alkali solution containing 15 g. of the alkali hydroxide) was added with vigorous agitation and the mixture was left to stand for two days at room temperature. The dioxane layer was separated and concentrated to a greyish white semisolid, which was dissolved in ether and washed with water. From the ether layer 1.6 g. (yield, 32%) of crystals were obtained, m.p. 118∼120°C. On recrystallization from petroleum ether, white plates were obtained m.p. 122∼123°C (α-form).

Anal. Found: C, 83.51; H, 6.45. Calcd. for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37%. I.R. ν max: 3500, 2200 and 1700 cm.$^{-1}$ U.V. λ max: 258 mμ (log ε: 2.67) and 265 mμ (log ε: 2.56).

The specimens obtained by the above five reactions were confirmed to be the same acid by the melting point determination of mixed crystals.

On standing about two months at room temperature, the melting point of the crystals (IX, α-form) rose to 153∼154°C (β-form) from 122∼123°C (α-form). In I.R. and U.V. spectra of these two forms, no difference was observed.

Benzylation of Benzylcyanide. 2-Benzyl-2,3-diphenylpropionitrile (VII), 2-Benzyl-2,3-diphenylpropioamide (VIII), and the β-Form of 2-Benzyl-2,3-diphenylpropionic Acid (IX).—We carried out the benzylation reaction, as reported by Hauser et al.[14] and Baker[15] to get VII in a fair yield.

The product, 2-benzyl-2,3-diphenylpropionitrile, (VII), m.p. 81∼83°C, b.p. 204∼205°C (2 mm Hg). was mixed with 70% sulfuric acid in glacial acetic acid and the mixture was refluxed for 4 days to afford 2-benzyl-2,3-diphenylpropioamide (VIII), m.p. 122.7∼114°C (Baker[15] reported m.p. 111∼112°C).

Anal. Found: N, 4.20, Calcd. for $C_{22}H_{21}ON$: N, 4.44%.

When amide VIII was treated with sodium nitrite, 2-benzyl-2,3-diphenylpropionic acid (IX) (β-form) was given, m.p. and mixed m.p. with an authentic specimen of β-form, 153∼154.5°C.

Anal. Found: C, 83.51; H, 6.45. Calcd. for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37%. I.R. ν max: 5300, 2200 and 1700 cm^{-1}. U.V. λ max: 258 mμ (log ε: 2.67) and 265 mμ (log ε: 2.56).

Summary

The equimolar reaction between benzyl chloride and sodium acetylide in liquid ammonia resulted in the formation of 3-benzyl-3,4-diphenyl-1-butyne in addition to 3,4-diphenyl-1-butyne and 3,4-diphenyl-1,2-butadiene. This compound resisted various oxidative reagents except potassium permanganate. 2-Benzyl-2,3-diphenylpropionic acid was obtained in two polymorphs.

Infrared absorption sepectra were measured by Professor Kinumaki and his associates of this Institute and the elementary analyses were performed in the Laboratory of Shionogi Drug Manufg. Co., Ltd., to whom the writers are deeply indebted.

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