Benzylation of Allylbenzene. Formation of 3,4-Diphenyl-1-butene and 3-Benzyl-3,4-diphenyl-1-butene

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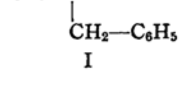
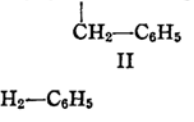
(Received July 2, 1958)

In the preceding papers[1,2] the authors reported the formation of 3,4-diphenyl-1-butyne (I), 3,4-diphenyl-1,2-butadiene (II), and 3-benzyl-3,4-diphenyl-1-butyne (III) by the reaction of benzyl chloride and sodium acetylide in liquid ammonia.



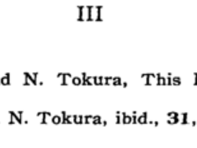
$C_6H_5-\underset{\displaystyle CH_2-C_6H_5}{\underset{|}{CH}}-C\equiv CH$

I



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

II



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

III

It is assumed that 3-phenyl-1-propyne (i.e. propargylbenzene) (IV) is formed as an intermediate at the first stage.

$C_6H_5-CH_2-C\equiv CH$ IV

$C_6H_5-CH_2-CH=CH_2$ V

In 1952, Young, Kosmin, Mixer and Campbell[3] reported on methylation and allylation of allylbenzene (V) in liquid ammonia. More recently, Mixer and Young[4] conducted the same reactions in *n*-pentane. Herbrandson and Mooney[5] reported the isomeric transformation.

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

[2] T. Ando and N. Tokura, ibid., **31**, 351 (1958).

[3] W. G. Young, M. Kosmin, R. Y. Mixer and T. W. Campbell, *J. Am. Chem. Soc.*, **74**, 608 (1952).

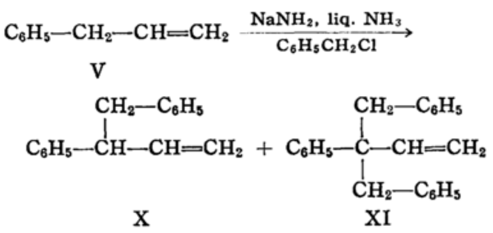
[4] R. Y. Mixer and W. G. Young, ibid., **78**, 3379 (1956).

[5] H. F. Herbrandson and D. S. Mooney, ibid., **79**, 5809 (1957).

[6] W. v. Miller and G. Rohde, *Ber.*, **25**, 2015 (1892).

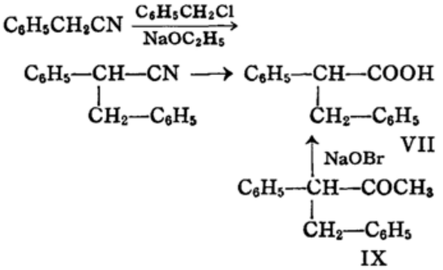
between allylbenzene and propenylbenzene in the presence of butyllithium or lithium amide.

Since allylbenzene (i. e. 3-phenyl-1-propene) (V) is closely related to IV in its structure, it was also expected that the benzylation of V in liquid ammonia would afford mono- and di-benzyl derivatives of V, corresponding to I and III in the benzylation of acetylene. The present paper, records the results of the study on the benzylation reaction which was observed to occur as expected. The structures of the products formed in this reaction and the relations among the products from benzylation of allylbenzene, benzyl cyanide and acetylene have been established unequivocally.



When V was allowed to react with an equi-molecular amount of benzyl chloride in the presence of sodium amide in liquid ammonia, two fractions were obtained, A, b. p. 160～162°C (17 mm.), and B, b. p. 191～192°C (2 mm.).

By oxidizing A with potassium permanganate, a white crystalline substance (VI), m. p. 88～89°C, was obtained. Miller and Rohde[6] reported on the synthesis of 2, 3-diphenylpropionic acid (VII), and it was observed that the substance exists in three isomers, m. p. 82°C, and 95～96°C[7,8]; the present authors prepared 2, 3-diphenylpropionic acid (VII) by hydrolyzing 2, 3-diphenylpropionitrile (VIII), obtained by the reaction of benzyl cyanide with an equi-molecular amount of benzyl chloride in the presence of sodium alcoholate according to the method of Miller and Rohde[6].



In this case two kinds of crystalline product having melting points 82°C and 88～89°C, respectively, were isolated, but the one having the highest melting point, 95～96°C, was not isolated. A mixture of the crystalline product having m. p. 88～89°C and VI gave no lowering of the melting point. By oxidizing the known compound, 3, 4-diphenyl-2-butanone[9] (IX), with sodium hypobromite, an acid showing an m. p. and a mixed m. p. with VI of 88～89°C was also obtained.

Infrared spectra in potassium bromide disks and carbontetrachloride solution of two specimens of 2, 3-diphenylpropionic acid having m. p. 82～82.5°C and 88～89°C were measured. The spectra in the disks gave different curves, while those in the solution gave the same. (Compare Fig. 1 and the experimental part.).

Thus, the structure of VI being established as 2, 3-diphenylpropionic acid, A is regarded as 3, 4-diphenyl-1-butene (X), which is further supported by the elementary analysis (molecular formula: $C_{16}H_{16}$), and infrared spectrum.

The boiling point, the molecular formula $C_{23}H_{22}$ and the infrared spectrum of B were almost coincident with those of the partially hydrogenated product of III, 3-benzyl-3, 4-diphenyl-1-butene (XI). The structure of XI for B was proved by several reactions as follows. Oxidation of B with potassium permanganate afforded an α-keto acid (XII), m. p. 138.5～139.5°C, which showed no depression of the mixed melting point with an authentic phenyldibenzylpyruvic acid[2]. Furthermore, oxidation of XII with potassium permanganate or hydrogen peroxide gave an acid (XIII), m. p. 122～123°C, a mixture of which with the α-form of 2-benzyl-2, 3-diphenylpropionic acid[2] obtained previously gave no melting point lowering. As was already reported[2], this acid showed a polymorphic transformation and the melting point was raised to 153～154°C after standing for two months.

No material to be considered as derived from propenylbenzene was isolated in this reaction. Therefore, in the metallation of allylbenzene(V) with sodium amide in liquid ammonia, the carbon atom adjacent

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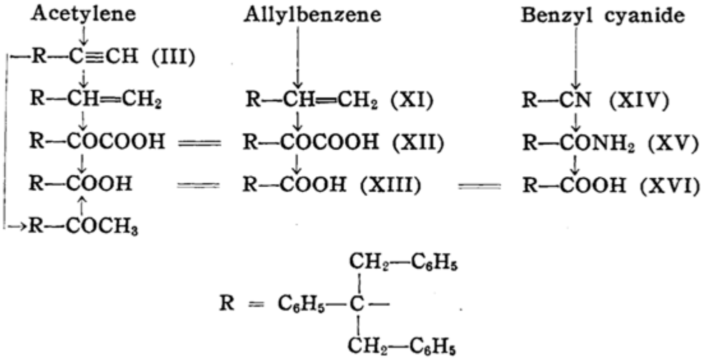
[7] C. R. Hauser and W. J. Chambers, *J. Am. Chem. Soc.*, **78**, 4942 (1956).

[8] N. Campbell and E. Ciganck, *J. Chem. Soc.*, **1956**, 3834.

[9] M. M. Tiffeneau and M. J. Levy, *Bull. soc. chim. France*, **33**, 779 (1923).

TABLE I

BENZYLATION OF ACETYLENE, ALLYLBENZENE, AND BENZYL CYANIDE



to the benzene ring was metallated, and the action of benzyl chloride afforded the mono- or di-benzyl compounds, 3, 4-diphenyl-1-butene (X) (40 percent) and 3-benzyl-3, 4-diphenyl-1-butene (XI) (30 percent).

Benzylation of allylbenzene, benzyl cyanide and acetylene[1,2], and the relations of the products are schematically represented by Table I.

Experimental[10]

Benzylation of allylbenzene.—Liquid ammonia (700 cc.) was taken in a three-necked flask of 100 cc. capacity equipped with a mechanical agitator, a dry-ice condenser and a dropping funnel, and kept at −50°±5°C in a dry-ice-ethanol bath, and 14 g. of metallic sodium was dissolved in the liquid ammonia. After being mixed with a minute amount of ferric nitrate, the content was agitated for about 20 minutes to produce sodium amide. After another 20 minutes' agitation, 60 g. of allylbenzene (b. p. 47°C/12 mm.) was added in 30 minutes. The solution was tinged with reddish brown color. It was further agitated for 20 minutes and 68 g. of benzyl chloride was added drop by drop in 40 minutes. When the addition of the same mole of benzyl chloride was completed, the color of the solution changed to grayish white. The benzylation reaction was exothermic. The dry-ice bath was removed and the flask was left overnight at room temperature, while liquid ammonia was naturally evaporated off. The residue was extracted with ether, and the ethereal solution was washed with water to neutral reaction and dried with dehydrated Glauber's salt. After the ether was distilled off, the residue was fractionated in vacuo to give two fractions: A fraction, boiling at 150∼155°C/11 mm., (yield 44.2 g.), which was redistilled to give 38.7 g. of b. p. 160∼162°C/17 mm. B fraction, boiling at 175∼200°C/2 mm., (yield 24.6 g.), which gave 18.2 g. of b. p. 191∼192°C/2 mm. by redistillation.

	Molecular formula	Crude (g.)	Distillate (%)	Theoretical yield based on benzyl chloride (%)
A	$C_{16}H_{16}$	44.2	51	40
B	$C_{23}H_{22}$	24.6	28	30

Anal. Found: C, 92.32; H, 7.77. Calcd. for A or $C_{16}H_{16}$: C, 92.26; H, 7.74%. I. R. ν_{max}: 1635, 1452, 1415, 990, and 910 cm^{-1}. *Anal.* Found: C, 92.61; H, 7.39. Calcd. for B or $C_{23}H_{22}$: C, 92.57; H, 7.43%. I. R. ν_{max}: 1634, 1455, 1415, 1005, and 912 cm^{-1}.

Oxidation of A with potassium permanganate. 2, 3-Diphenylpropionic acid (VI). — A (4.1 g.) was dissolved in 300 cc. of acetone in a three-necked flask of 1000 cc. capacity equipped with an agitator. Powdered potassium permanganate (9 g.) was added to the solution little by little with agitation at the room temperature. After 6 hours' agitation, the mixture was left overnight at room temperature, and then the solvent was distilled off. Water was added to the residue and manganese dioxide was dissolved by passing sulfur dioxide gas into the mixture.

The substance in crystalline suspension was extracted with ether and the ethereal solution was washed with aqueous alkali. The aqueous solution was acidified and extracted with ether. The ethereal solution was washed with water until the solution became neutral. After drying with dehydrated Glauber's salt, the solution was evaporated to give 4 g. (88 %) of a white crystalline substance, m. p. 70∼83°C, and recrystallization from petroleum ether (b. p. 60∼80°C) gave VI, m. p. 88∼89°C. A mixture of VI and 2, 3-diphenylpropionic acid (VII), m. p. 88∼89°C, prepared by the method given by Miller and Rohde[6], gave no melting point lowering.

Anal. Found: C, 79.81; H, 6.30. Calcd. for 2, 3-diphenylpropionic acid (VI) or $C_{15}H_{14}O_2$: C, 79.62; H, 6.24%.

2, 3-Diphenylpropionic acid (VII)[6].—Metallic sodium (12 g.) was dissolved in 100 g. of absolute ethanol in a flask of 300 cc. capacity, and 58 g. of benzyl cyanide and 69 g. of benzyl chloride were added and the mixture was refluxed for 4 hours. Sodium chloride was filtered off and

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[10] Melting points and boiling points were not corrected.

the solution was evaporated. Vacuum distillation of the residue gave 33 g. (48%) of unchanged benzyl cyanide and 10 g. (15.7%) of diphenylpropionitrile, m. p. 57.5∼58.5°C (recrystallized from alcohol). The nitrile (1 g.) was heated with 2 cc. of concentrated hydrochloric acid in a sealed tube at 130°C for 5 hours. After the reaction was completed, the product was made alkaline and the unchanged nitrile and the intermediate acid amide were removed with ether. The remaining aqueous solution was acidified and extracted with ether. The crystalline substance from the ethereal solution was recrystallized from petroleum ether (b. p. 60∼80°C). Needles, m. p. 82∼82.5°C. Recrystallization of the needles from water gave small white plates, m. p. 88∼89°C. Melting points of the two crystalline specimens were coincident with those of 2, 3-diphenylpropionic acid. 82°C and 88∼89°C, given in the literature[6].

Anal. Found: C, 86.75; H, 6.43; N, 6.67. Calcd. for 2, 3-diphenylpropionitrile (VIII) or $C_{15}H_{13}N$: C, 86.92; H, 6.32; N, 6.76%. Found: C, 79.74; H, 6.73; N, 6.06. Calcd. for 2, 3-diphenylpropionamide or $C_{15}H_{15}ON$: C, 79.97; H, 6.71; N, 6.22%. Found: C, 79.56; H, 6.22. Calcd. for 2, 3-diphenylpropionic acid (VII) or $C_{15}H_{14}O_2$: C, 79.62; H, 6.24%.

Crystals having m. p. 82∼82.5°C: I. R. crys. ν_{max}: 3300∼2300, 1700, 1688, and 940 cm^{-1}, I. R. CCl_4 soln. ν_{max}: 3300∼2300 and 1708 cm^{-1}, U. V. λ_{max}: 258 mμ (log ε: 2.76) and 265 mμ (log ε: 2.65).

Crystals having m. p. 88∼89°C: I. R. crys. ν_{max}: 3180, 1724, 1677, and 1173 cm^{-1}, I. R. CCl_4 soln. ν_{max}: 3300∼2400, and 1705 cm^{-1}, U. V. λ_{max}: 258 mμ (log ε: 2.68), and 265 mμ (log ε: 2.61).

Synthesis and oxidation of 3, 4-diphenylbutanone (IX). — According to Tiffeneau and Lévy[9], phenylacetone was metallated with sodium alcoholate and then refluxed with the same mole of benzyl chloride for 2 hours. The product boiled at 188∼189°C/20 mm. and melted at 31∼32°C after recrystallization from petroleum ether (b. p. 40°C). The same m. p. was given by the literature[9]. Its oxime, m. p. 138∼138.5°C. (literature[9]: 134∼135°C) semicarbazone, m.p. 169∼170°C. (literature[9]: 168°C).

Anal. Found: C, 85.77; H, 6.94. Calcd. for 3, 4-diphenyl-2-butanone (IX) or $C_{16}H_{16}O$: C, 85.68; H, 6.84%. I. R. oil ν_{max}: 1700, 1351, 1148, 1088, and 1030 cm^{-1}, U. V. λ_{max}: 268 mμ (log ε: 2.78), 265 mμ (log ε: 2.74) and 288 mμ (log ε: 2.70).

Sodium hypobromite[11] was prepared by adding 5 cc. of bromine to an aqueous solution of 15 g. of sodium hydroxide in 50 cc. water cooled in ice. It was added to a solution of 5 g. of the above substance of m. p. 31∼32°C in 50 cc. of 1, 4-dioxane with vigorous agitation and the mixture was kept at the room temperature for 2 days. On concentration, the aqueous layer gave a grayish-white semi-solid, from which the unchanged substance was removed with ether. After acidifying with hydrochloric acid, the product was extracted with ether. The ethereal solution gave 1.8 g. (36.4%) of a crystalline substance, m. p. 82∼82.5°C. Recrystallization from petroleum ether (b. p. 60∼80°C) gave white crystals, m. p. 88∼89°C. A mixture of the acid and VI showed no lowering of the melting point.

Oxidation of B with potassium permanganate. — *Phenyldibenzylpyruvic acid (XII).* — B (4.2 g.) was dissolved in 400 cc. of acetone in a three-necked flask of 2 liter capacity equipped with an airtight agitator and a reflux condenser. To the solution 8 g. of potassium permanganate dissolved in 400 cc. of water was added and the mixture was agitated for 48 hours at the room temperature. After removal of acetone, sulfur dioxide gas was introduced into the residue under cooling in ice and then the solution was made alkaline with dilute aqueous caustic soda. The unchanged neutral part was extracted with ether and the remaining alkaline layer was acidified with hydrochloric acid and extracted with ether. The ethereal solution gave 4.3 g. of a crystalline substance, m. p. 138∼139.5°C, in a yield of 88%. The melting point of the keto acid (XII) did not change on admixture with phenylbenzylpyruvic acid obtained by oxidation of III.

Anal. Found: C, 79.92; H, 5.98. Calcd. for phenyldibenzylpyruvic acid (XII) or $C_{23}H_{20}O_3$: C, 80.21; H, 5.85%. I. R. ν_{max}: 1722, 1711, and 1370 cm^{-1}.

The α-form of 2-benzyl-2, 3-diphenylpropionic acid (XIII).—*a) Oxidation of XII with potassium permanganate.*—XII (0.5 g.) was dissolved in 100 cc. of 2% aqueous sodium hydroxide in a round-bottom 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 overnight. It was then neutralized with dilute sulfuric acid, treated with sulfur dioxide gas to dissolve manganese dioxide, and extracted with ether. The white crystalline substance from the ethereal solution was recrystallized from ligroin (b. p. 80∼100°C). White scales m. p. 121∼122°C. (α-form) (XIII). Yield 0.2 g. (43.5%).

b) Reaction of XII with hydrogen peroxide.— In a beaker of 200 cc. capacity, 1.5 g. of XII was mixed with 20 cc. of 10% sodium hydroxide and 30 cc. of 10% sodium hydrogen peroxide and the mixture was allowed to stand overnight in an ice box. Then 10 cc. more of hydrogen peroxide was added to the mixture with agitation. After 8 hours, the mixture was acidified and extracted with ether. The ethereal solution gave 0.4 g. (87%) of fine scales, m. p. 118∼120°C, and recrystallized from ligroin (b. p. 80∼100°C). White scales (α-form, XIII), m. p. 122∼123°C. Yield 3 g. No melting point depression was observed on admixture of the acid (XIII) with α-form of 2-benzyl-2, 3-diphenylpropionic acid, obtained by the oxidation of III.

Anal. Found: C, 83.32; H, 6.42. Calcd. for 2-benzyl-2, 3-diphenylpropionic acid (XIII) or

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11) W. S. Johnson, C. D. Gutsche and R. D. Offenhauer, *J. Am. Chem. Soc.*, **68**, 1648 (1946).

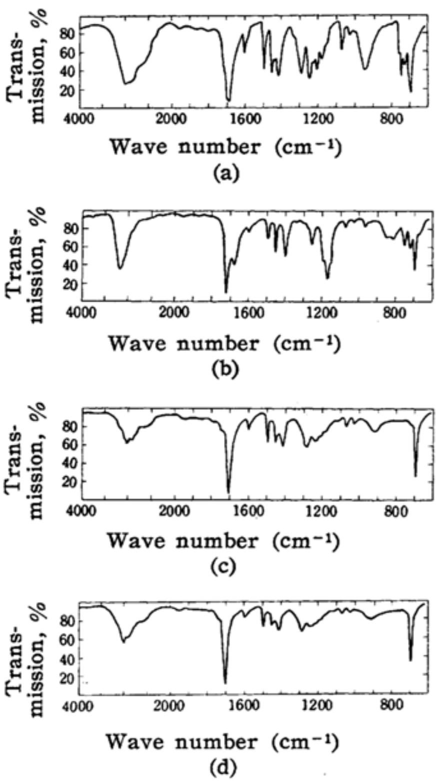

Fig. 1.

(a) KBr disk of the specimen of 2, 3-diphenylpropionic acid melting at 82°C.
(b) KBr disk of specimen of the same compound melting at 88~89°C.
(c) A CCl_4 solution of the specimen of the same compound melting at 82°C.
(d) A CCl_4 solution of the specimen of the same compound melting at 88~89°C.

$C_{22}H_{20}O_2$: C, 83.51; H, 6.37%. I. R. crys. ν_{max}: 3200~2300, and 1702 cm^{-1} I. R. CCl_4 soln. ν_{max}: 3300~2400 and 1700 cm^{-1} U. V. λ_{max}: 258 mμ (log ε: 2.67) and 265 mμ (log ε: 2.56).

On standing for about two months at room temperature, the α-form of XIII, m. p. 122~123°C, was changed to the β-form, m. p. 153~154°C. In I. R. and U. V. spectra of the two forms, not even a slight difference was estimated. A mixture of the β-form, m. p. 153~154°C, and the β-form of 2-benzyl-2, 3-diphenylpropionic acid (XVI), synthesized by the method of Hauser and Brasen[12], gave no melting point lowering.

Benzylation of benzyl cyanide. The β-form of 2-benzyl-2, 3-diphenylpropionic acid (XVI).—According to the method of Hauser et al.[12] and Baker[13], 2-benzyl-2, 3-diphenylpropionitrile (XIV) was obtained in a fairly good yield. The product (XIV), m. p. 81~83°C, b. p. 204~205°C/2 mm., was refluxed with 70% sulfuric acid in glacial acetic acid for 4 days, and gave 2-benzyl-2, 3-diphenylpropionamide (XV), m. p. 122.7~124°C. (Baker[11]: m. p. 111~112°C).

Anal. Found: N, 4.20. Calcd. for 2-benzyl-2, 3-diphenylpropionamide (XV) or $C_{22}H_{21}ON$, 4.44%.

Treatment of the amide (XV) with sodium nitrite gave 2-benzyl-2, 3-diphenylpropionic acid (XVI, β-form). The melting point of the substance and of a mixture with an authentic specimen of the β-form was the same, m. p. 154~154.5°C.

Anal. Found: C, 83.51; H, 6.45. Calcd. for 2-benzyl-2, 3-diphenylpropionic acid (XVI) or $C_{22}H_{20}O_2$: 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

When allylbenzene was treated with the same moles of sodium amide and benzyl chloride in liquid ammonia, one or two benzyl radicals were introduced into allylbenzene to produce 3, 4-diphenyl-1-butene and 3-benzyl-1-butene.

The reaction is similar to the well-known reaction[12] of benzyl cyanide and benzyl chloride in liquid ammonia and that[13] of 2-phenyl-1-ethanol and benzyl chloride in benzene.

Two forms of 2, 3-diphenylpropionic acid were isolated and their I. R. spectra were measured. Different curves were obtained in KBr disks, while the identical curves were obtained carbon tetrachloride solution.

Infrared absorption spectra were measured by Professor Kinumaki and his associates of this Institute and the elementary analyses were performed in the laboratory of Shionogi and Company, Ltd., to whom the writers are deeply indebted.

Chemical Research Institute of
Non-aqueous Solutions, Tohoku
University, Katahira-cho, Sendai

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[12] C. R. Hauser and W. R. Brasen, ibid., **78**, 494 (1956).

[13] R. H. Baker, ibid., **70**, 3857 (1948).