Benzylation of Acetylene. I. Formation of 3,4-Diphenyl-1-butyne and 3,4-Diphenyl-1,2-butadiene

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Vaughn, Hennion, Vogt, and Nieuwland[1], in an attempted alkylation of acetylene by treating alkali metal acetylide (I) with various alkyl chlorides in liquid ammonia, observed that benzylacetylene (III) was not formed when benzyl chloride (II) was allowed to react with the acetylide.

The present writers carried out the same benzylation reaction and found that, instead of benzylacetylene (III), 3,4-diphenyl-1-butyne (IV) and an allenic compound, 3,4-diphenyl-1,2-butadiene (V), were formed.

To prepare the metal acetylide, lithium or sodium metal was dissolved in liquid ammonia and purified acetylene was passed through the solution until the blue color of the metal disappeared. The acetylide was allowed to react with benzyl chloride, the reaction product was taken up in ether, and the residue from the ethereal solution was fractionated under reduced pressure. The initial fraction of a small amout of unchanged benzyl chloride was followed by fractions A of b. p. 135°C (2 mmHg) and B of b. p. 190°C (2 mmHg) (total yield 10.3–34.6%), leaving a large amount of a residue which consisted of a viscous polymerized substance.

When lithium was used, the yields of A and B were 12.2% and 34.6% respectively, while sodium gave lower yields, A 0–5.2%

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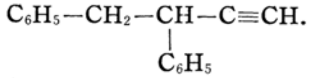
[1] T. H. Vaughn, G. F. Hennion, R. R. Vogt and J. A. Nieuwland, *J. Org. Chem.*, 2, 1 (1938).

and B 10.3–17.8%.

B is a yellowish, viscous liquid and forms a complex salt with silver nitrate, through which it can be purified and estimated. Thus, it has a terminal group $-C{\equiv}CH$ and the determination of residual silver in the complex salt and the liberated nitric acid during the complex formation gave a molecular weight 206 as a monoacetylenic compound. The structure of this substance was assumed to be



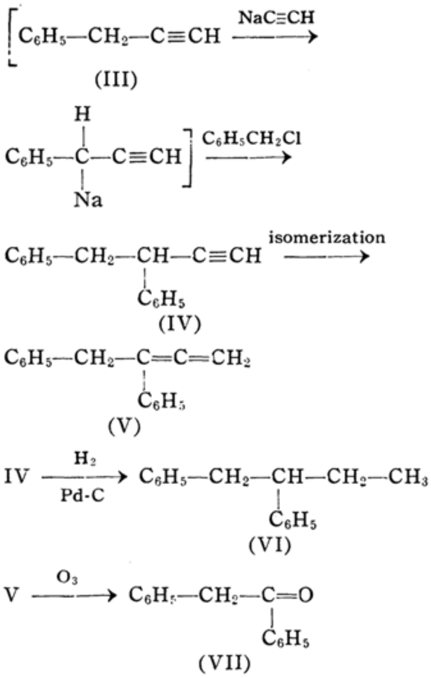
$$C_6H_5-CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{CH}}-C{\equiv}CH. \qquad \text{(IV)}$$

Its infrared absorption spectrum exhibited a strong maximum at 3320 cm^{-1} due to stretching vibration of the terminal acetylenic bond and a weak one at 2120 cm^{-1} for a monosubstituted acetylene[2]. Catalytic reduction of B in the presence of palladium carbon proceeded through a rapid absorption of 1 mole of hydrogen, and then a very slow absorption of one further mole of hydrogen. The product showed physical constants in good agreement with those of 1, 2-diphenylbutane (VI)[3]. The infrared absorption for the unsaturated side-chain disappeared and a new absorption appeared at 1380 cm^{-1} due to methyl deformation[4]. Both the elementary analysis and the molecular refraction agreed with the theoretical values. Thus the structure of 3, 4-diphenyl-1-butyne (IV) for B was concluded.

A is a colorless, clear, easily flowing liquid; it discolors bromine and potassium permanganate, but does not form a complex salt with silver nitrate. Its strong infrared absorptions at 1950, 1680, and 850 cm^{-1} showed it is an allene derivative[5]. As described in the experimental part, A is formed by the isomerization of B and this may be explained by assuming a structure of 3, 4-diphenyl-1, 2-butadiene (V) for A, which was ascertained by the oxidation of A with ozone to desoxybenzoin (VII).

It follows, therefore, that the reaction of the metal acetylide and benzyl chloride takes the following routes:

$$\underset{\text{(II)}}{C_6H_5CH_2Cl} + \underset{\text{(I)}}{NaC{\equiv}CH} \xrightarrow{\text{Liq. NH}_3}$$



$$\left[\underset{\text{(III)}}{C_6H_5-CH_2-C{\equiv}CH} \xrightarrow{NaC{\equiv}CH} C_6H_5-\overset{\displaystyle H}{\underset{\displaystyle Na}{C}}-C{\equiv}CH\right] \xrightarrow{C_6H_5CH_2Cl}$$

$$\underset{\text{(IV)}}{C_6H_5-CH_2-\underset{\displaystyle C_6H_5}{CH}-C{\equiv}CH} \xrightarrow{\text{isomerization}}$$

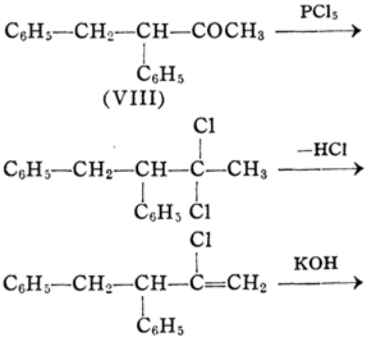
$$\underset{\text{(V)}}{C_6H_5-CH_2-\underset{\displaystyle C_6H_5}{C}{=}C{=}CH_2}$$

$$\text{IV} \xrightarrow[\text{Pd-C}]{H_2} \underset{\text{(VI)}}{C_6H_5-CH_2-\underset{\displaystyle C_6H_5}{CH}-CH_2-CH_3}$$

$$\text{V} \xrightarrow{O_3} \underset{\text{(VII)}}{C_6H_5-CH_2-\underset{\displaystyle C_6H_5}{C}{=}O}$$

It is known that allenic compounds are formed in general in small amounts on heating acetylenic compounds with alkali hydroxide around 170°C[6], and a phenylbenzylallene, such as V, is comparatively easily formed from the isomeric acetylene at the room temperature even in the presence of such a weak base as ammonia.

Treatment of 3, 4-diphenyl-2-butanone (VIII)[7] with phosphorus pentachloride followed by dehydrochlorination with potassium hydroxide[8] did not afford the acetylenic compound (IV) but almost the whole product was the allenic compound (V), which readily polymerized during distillation to give a large amount of a distillation residue.



$$\underset{\text{(VIII)}}{C_6H_5-CH_2-\underset{\displaystyle C_6H_5}{CH}-COCH_3} \xrightarrow{PCl_5}$$

$$C_6H_5-CH_2-\underset{\displaystyle C_6H_5}{CH}-\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{C}}-CH_3 \xrightarrow{-HCl}$$

$$C_6H_5-CH_2-\underset{\displaystyle C_6H_5}{CH}-\overset{\displaystyle Cl}{C}{=}CH_2 \xrightarrow{KOH}$$

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

[3] A. Klages and S. Heilmann, *Ber.*, **37**, 1452 (1904).

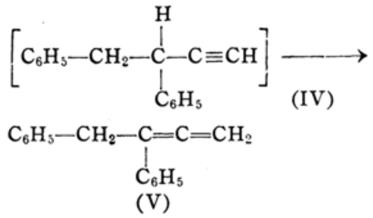
[4] R. S. Rasmussen, *J. Chem. Phys.*, **16**, 712(1948).

[5] W. J. Bailey and C. R. Pfeiffer, *J. Org. Chem.*, **20**, 97 (1955).

[6] E. R. H. Jones, G. H. Whitham and M. C. Whiting, *J. Chem. Soc.*, **1954**, 3201; I. L. Jacobs, R. Akawie and R. G. Cooper, *J. Am. Chem. Soc.*, **73**, 1273 (1951).

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

[8] C. Dufraisse and J. F. Viel, ibid., **37**, 817 (1925).

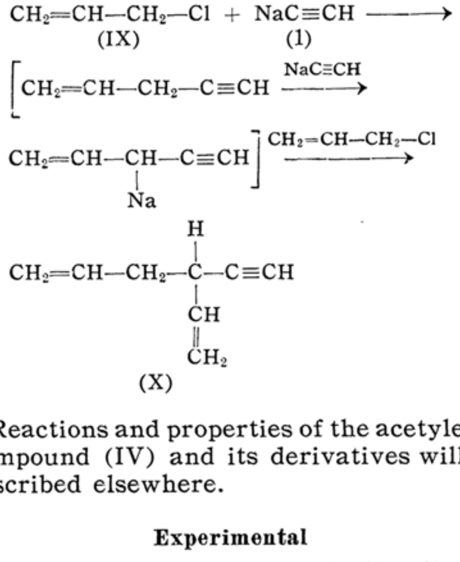


$$\left[C_6H_5-CH_2-\underset{C_6H_5}{\overset{H}{C}}-C\equiv CH\right] \longrightarrow \quad (IV)$$

$$C_6H_5-CH_2-\underset{C_6H_5}{C}=C=CH_2 \quad (V)$$

It was observed that 3,4-diphenyl-1-butyne (IV) was changed into 3,4-diphenyl-1,2-butadiene (V) merely by dissolving it in liquid ammonia and allowing the solution to stand overnight at the room temperature.

The formation of 3,4-diphenyl-1-butyne (IV) and of no benzylacetylene (III) in the reaction of metallic compounds of acetylene and benzyl chloride is analogous to the formation of 3,4-divinyl-1-butyne (X) in the reaction of a metal acetylide and allyl chloride (IX) in liquid ammonia.



$$\underset{(IX)}{CH_2=CH-CH_2-Cl} + \underset{(1)}{NaC\equiv CH} \longrightarrow$$

$$\left[CH_2=CH-CH_2-C\equiv CH \xrightarrow{NaC\equiv CH} CH_2=CH-\underset{Na}{CH}-C\equiv CH\right] \xrightarrow{CH_2=CH-CH_2-Cl}$$

$$CH_2=CH-CH_2-\underset{\underset{CH_2}{\overset{\|}{CH}}}{\overset{H}{C}}-C\equiv CH \quad (X)$$

Reactions and properties of the acetylenic compound (IV) and its derivatives will be described elsewhere.

Experimental

Benzylation of Acetylene.—(1) Reaction of Lithium Acetylide and Benzyl Chloride.—Metallic lithium (1.7 g., 1/4 mole) was dissolved in 400 cc. of liquid ammonia, contained in a three-necked flask provided with a dry-ice reflux condenser and a stirrer, and maintained at −50° ±5°C in a dry-ice-ethanol bath. Acetylene, dried and purified by passage through concentrated sulfuric acid, soda lime, and phosphorus pentoxide, successively, was introduced into the solution with stirring until the blue color faded. It required about ten minutes. After stirring the solution for further ten minutes or so, 31 g. (1/4 mole) of benzyl chloride was added from a dropping funnel during about twenty-five minutes. The solution gradually acquired a pale pink color. When the mixture was stirred for 2.5 hr., it gradually became pale pinkish orange in color with increasing amount of a white precipitate. After allowing the mixture to stand in an ice bath overnight, ammonia was allowed to evaporate and 100 cc. of water was added to the residue to dissolve the greyish white solid. Then an excess of 4 N hydrochloric acid was added to transform the by-product amine into the hydrochloride insoluble in ether, and the mixture was extracted with 200 cc. of ether. After filtration, the ethereal solution was washed successively with 4 N HCl and with water and dried over anhydrous sodium sulfate overnight. A small amount of hydroquinone was added to the ethereal solution, the ether was evaporated, and the residue was submitted to a low-pressure distillation in a nitrogen stream. Besides 1 g. of recovered benzyl chloride, b. p. 39–41°C/2 mmHg, the following fractions were obtained:

(A) Pale yellow liquid, b. p. 135–143°C/2 mmHg. 3.1 g. (12.2%).

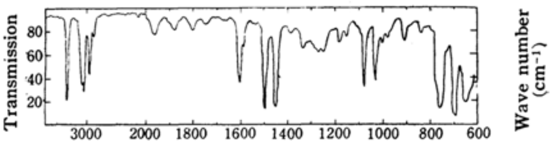
(B) Yellowish brown viscous liquid, b. p. 185–190°C/2 mmHg, 8.9 g. (34.6%).

(C) Distillation residue, ca. 15 g.

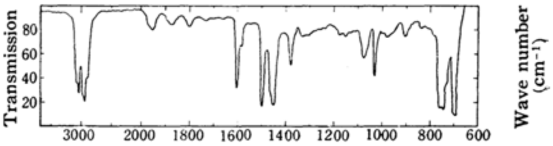
B was identified with 3,4-diphenyl-1-butyne (IV) and A with 3,4-diphenyl-1,2-butadiene (V).

(2) Reaction of Sodium Acetylide and Benzyl Chloride.—Metallic sodium was dissolved in liquid ammonia under the same conditions as above and benzyl chloride was allowed to react with sodium acetylide so obtained. The yields of A and B from this reaction were as follows:

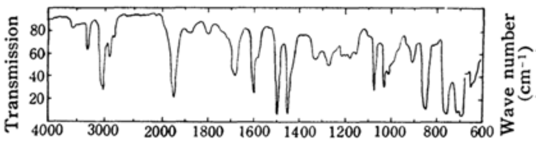
Expt. No.	Na (g.)	$PhCH_2Cl$ (g.)	Molar ratio Na/$PhCH_2Cl$	Yield A (g.)	Yield A (%)	Yield B (g.)	Yield B (%)
1	46	253	1/1	0	0	35	16.9
2	12	126	1/2	5.4	5.2	10.6	10.3
3	12	31	2/1	0.8	3.1	4.6	17.8



3,4-Diphenyl-1-butyne



1,2-Diphenylbutane



3,4-Diphenyl-1,2-butadiene

Fig. 1. Spectra were taken by a Perkin-Elmer Model 21 Infrared Spectrophotometer.

Purification of Fraction B (3, 4-Diphenyl-1-butyne (VI))10).—To a solution of 5.5 g. of Fraction B, b. p. 185–190°C/2 mmHg, dissolved in 20 cc. of ethanol, a solution of 10 g. of silver nitrate dissolved in a mixture of 20 cc. of water and 40 cc. of ethanol was added, and the mixture was warmed for about 40 minutes on a water bath and allowed to stand overnight. The white precipitate was collected by filtration, washed with water to remove excessive silver nitrate and then with ethanol to remove the unchanged materials, and dried in a desiccator. Yield, 12 g.

A suspension of 12 g. of the silver complex salt in a 10% potassium cyanide solution was refluxed by heating on an oil bath, when an oily layer separated as the reaction proceeded. In ten hours' refluxing, the complex salt disappeared completely. After cooling, the mixture was extracted with ether, the ethereal layer was washed with water to neutral reaction, dried over anhydrous sodium sulfate and concentrated. The residue was distilled under a reduced pressure in nitrogen stream and in the presence of hydroquinone, to give 4.5 g. of a colorless, clear, viscous liquid, b. p. 190–192°C/2 mmHg, n_D^{25} 1.6040, d_{25}^{25} 1.0646. Mole Ref. Found: MR_D, 66.78. Calcd: 66.87.

Anal. Found: C, 92.86; H, 6.87. Calcd. for $C_{16}H_{14}$: C, 93.16; H, 6.84%. IR ν_{max}: 3320 and 2120 cm^{-1}. Silver determination of the complex salt: 4.350 mg. of the substance gave an ignition residue (Ag) 1.988 mg. Calcd. for $C_{16}H_{13}Ag.AgNO_3$: 1.939 mg. Mol. wt., Found 194. Calcd. for $C_{16}H_{14}$: 206. Determination of HNO_3 produced during formation of silver complex salt11): 0.1691 g., and 0.1743 g. of the substance gave nitric acid equivalent to 10.67, and 11.00 cc., respectively, of 0.1 N NaOH. (f=0.7691). Mol. wt., Found: 206,206. Calcd. for $C_{16}H_{14}$: 206.

Catalytic Reduction of IV (Formation of 3, 4-Diphenylbutane (VI).—A solution of 2 g. of IV in 100 cc. of methanol with the addition of 0.3 g. of palladium-carbon was submitted to reduction at ordinary temperature and pressure in a Willstätter apparatus. One mole of hydrogen was absorbed in twenty-five minutes while another mole of hydrogen in a longer time, fifteen hours being required in total. After removal of the catalyst, the solvent was evapolated, and the residue was submitted to vacuum distillation. The fraction of b, p. 153°C/11.5 mmHg, n_D^{17} 1.5882, agreed with the values of b. p. 152°C/11 mmHg and n_D^{18} 1.587 given for 1, 2-diphenylbutane in the leterature3). Yield, 1.7 g.

Formation of 3, 4-Diphenyl-1, 2-butadiene (V) from 3, 4-Diphenyl-2-butanone (VIII).—In order to change VIII, prepared by the method of Tiffeneau7), to the acetylenic compound (IV) by the method of Dufraisse and Viel8), VIII was treated successively with phosphorus pentachloride and with ethanolic potash. A solution of 17.4 g. of VIII dissolved in 35 cc. of petroleum ether was dropped into 25 g. of phosphorus pentachloride covered with 35 cc. of petroleum ether with stirring and the mixture was heated at 60°C for thirty hours. The mixture was then poured into ice water, extracted with ether, and ethereal layer was washed with water. After drying over anhyd. sodium sulfate, ether was evaporated and the residue was distilled under a reduced pressure, affording 10.3 g. of an oily substanc b. p. 156–158°C/5 mmHg. The oil was heated with 10% ethanolic potassium hydroxide for fifteen hours, and cooled, and ethanol was evaporated under a reduced pressure. The residue was extracted with ether, and the ethereal layer was washed with water to neutral reaction and dried over anhyd. sodium sulfate.

Distillation of the residue under a reduced pressure gave about 1 g. of V, b. p. 135–140°C/2 mmHg, and a minute amount of IV, b. p. 170–180°C 0.5 mmHg, with a distillation residue of a polymerized substance. V was identified by its infrared spectrum, exhibiting absorption maxima at 1950, 1680, and 850 cm^{-1}.

Formation of 3, 4-Diphenyl-1, 2-butadiene (V) from 3, 4-Diphenyl-1-butyne (IV).—(a) **Allenation with Potassium hydroxide**12).—A solution of 5 g. of IV dissolved in 100 cc. of 99% ethanol was added to a solution of 10 g. of potassium hydroxide dissolved in 10 g. of water with stirring, and the mixture was refluxed for six hours. Then, ethanol was evaporated under a reduced pressure, the residue was extracted with ether, and the ethereal layer was washed with water to neutral reaction. After drying over anhyd. sodium sulfate, the ether was evaporated and the residue was submitted to low-pressure distillation, giving 1 g. of colorless oil, b. p. 135°C/2 mmHg; I. R. ν_{max} 1950, 1680 and 850 cm^{-1}. The rest remained in the flask as a residue.

(b) **Allenation with Liquid Ammonia**.—A solution of 5 g. of IV dissolved in 100 cc. of liquid ammonia in a pressure bottle was allowed to stand overnight, ammonia was allowed to evaporate, and the residue was extracted with ether. After washing with water and drying over anhyd. sodium sulfate, ether was evaporated and the residue was submitted to low-pressure distillation, giving 0.6 g. (12%) of a fraction, b. p. 135°C/2 mmHg, n_D^{18} 1.5992, 2.2 g. of another fraction, b. p. 140–195°C/2 mmHg, and 2 g. of a residue. The fraction b. p. 135°C/2 mmHg is the allene V, identified by its infrared absorptions at 1950, 1680 and 850 cm^{-1}. The fraction of b. p. 140–185°C/2 mmHg is a mixture of the allene V and the acetylene IV.

Ozonolysis of 3, 4-Diphenyl-1, 2-butadiene (V).—A solution of 2 g. of V dissolved in 100 cc. of ethyl acetate was cooled to -45°C and treated with ozone (0.021 mol./hr.) for one hour. Evaporation of the solvent from the reaction mixture gave a pale yellow oil, which was decomposed with 5 cc. of water and 20 cc. of 10% aqueous

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10) M. Koulkes and I. Marszak, *Bull. soc. chim. France*, **1952**, 556.

11) G. Eglinton and M. C. Whiting, *J. Chem. Soc.*, **1953**, 3055.

12) A. Favorsky, *J. Prakt. Chem.*, **37**, 382 (1888).

sodium hydroxide and further oxidized with 10 cc. of 20% hydrogen peroxide.

On standing in a refrigerator overnight, the mixture gave a pale yellow solid, melting at 54-55.5°C. Yield, 1.2 g. (64%). Recrystallized from petroleum ether, it melted at 55-56°C, and showed no depression of the melting point in admixture with an authentic specimen of desoxybenzoin (VII)[13].

Summary

The reaction between benzyl chlorides and metal acetylides, prepared from metallic lithium and sodium in liquid ammonia resulted in the formation of new compounds, i. e. 3, 4-diphenyl-1-butyne and 3, 4-diphenyl-1, 2-butadiene. The benzylation of acetylene did not stop at benzylacetylene but another benzyl group was introduced to form 3, 4-diphenyl-1-butyne. 3, 4-Diphenyl-1, 2-butadiene was formed by the isomerisation of the butyne. This isomerisation occurred not only by the action of hot ethanolic potash but also in liquid ammonia at the room temperature. 3, 4-Diphenyl-1, 2-butadiene was readily polymerized by heat.

Infrared absorption spectra were measured by Prof. Kinumaki and his associates of this Institutes and the elementary analyses were made in the Laboratory of Shionogi Drug. Manufg. Co., Ltd. to whom the writers are deeply indebted. Thanks are also due to Miss Koko Miyaoka of this Laboratory for technical help.

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[13] C. F. H. Allen and W. E. Barker, *Org. Synth.*, **12**, 16 (1932).