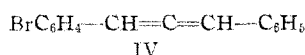
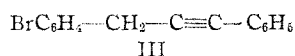


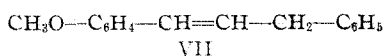
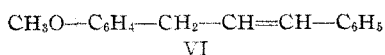
be taken as further evidence against the allene structure, since allenes of this general type are known to form dimers with great ease.⁴

Oxidation of the hydrocarbon with cold 1% potassium permanganate solution gave a large amount of benzoic acid (0.96 equivalent) and a much smaller quantity of phenylacetic acid (0.15 equivalent). Ozonation of the hydrocarbon and hydrolysis of the ozonide gave benzoic acid (1.2 equivalents) and phenylacetic acid (0.10 equivalent). Treatment of the ozonide with aqueous potassium iodide, followed by sodium thiosulfate, gave benzyl phenyl diketone in 25% of the theoretical yield.⁸ The allene form would have been expected to give benzaldehyde upon ozonolysis, but it is not certain that a small quantity of benzaldehyde would have survived the experimental procedure.

The chemical evidence indicates that 1,3-diphenylpropyne exists largely, if not entirely, in the acetylene form but the possibility of a small proportion of the allene form is not excluded. Conclusive evidence on this point was obtained through the study of a pair of isomeric derivatives of 1,3-diphenylpropyne, in which the terminal aryl groups were not identical. Owing to the circumstance that both of the isomeric propynes (III and V) would give rise to the same



allene (IV), it is evident that active prototropy in the system would result in an interconversion of the two propynes. Prototropic change in the 1,3-diarylpropenes and 1,3-diarylmethylene-azomethines has been investigated in this way by Ingold and his collaborators,⁹ who found that isomeric diarylpropenes possessing structures VI and VII existed as separate static individuals.



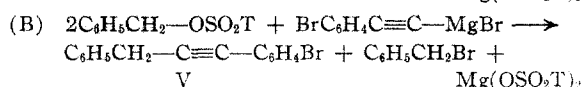
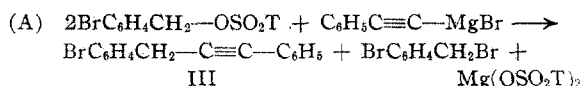
Each gave rise only to its own oxidation products but interconversion (equilibration) could be ef-

(8) Jacobs, *THIS JOURNAL*, **58**, 2272 (1936).

(9) For an excellent survey of this subject, and a discussion of electronic theories of tautomeric change, see J. W. Baker, "Tautomerism," George Routledge and Sons, Ltd., London, 1934.

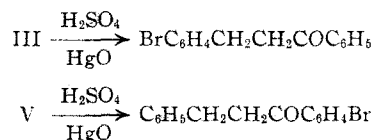
fect by heating with alcoholic sodium ethoxide at 85°.¹⁰

The compounds chosen for the present study were *p*-bromobenzylphenylacetylene (III) and benzyl-*p*-bromophenylacetylene (V). If interconversion did not occur, the former should result from the interaction of *p*-bromobenzyl *p*-toluenesulfonate and phenylethyne magnesium bromide (reaction A) and the latter from benzyl *p*-toluenesulfonate and *p*-bromophenylethyne magnesium bromide (reaction B).



The two syntheses were carried out successfully, and the products were examined carefully to establish their constitution and to discover whether interconversion had occurred.

The compound (III) obtained by reaction A was a crystalline solid which melted at 42–44°. It gave a dibromide, m. p. 108–108.5°, and on hydration produced a ketone which was shown to be *p*-bromobenzylacetophenone, m. p. 68.5–69°. The isomer (V) obtained by reaction B was a



liquid that could not be crystallized. Its dibromide melted at 87°, and the ketone obtained by hydration was identified as benzyl-*p*-bromoacetophenone, m. p. 98–99°. The structure of the isomeric ketones was established by the synthesis of authentic specimens, and mixed melting point determinations with the ketones and with suitable derivatives.

The chemical evidence therefore indicates that the three-carbon system of the simple 1,3-diarylpropynes is not actively prototropic, and that these compounds are distinct individuals which do not exist in dynamic equilibrium with the isomeric allenes. Proton mobility in the 1,3-diarylpropyne system is evidently quite low, since the isomeric bromodiphenylpropynes were not interconverted by contact with a Grignard re-

(10) Ingold and Piggott, *J. Chem. Soc.*, **121**, 2381 (1922); Ingold and Shoppee, *ibid.*, **447** (1929). See also Shoppee, *ibid.*, 968 (1930); 1225 (1931).

Benzyl-*p*-bromophenylacetylene

Preparation.—*p*-Bromophenylacetylene was obtained conveniently from *p*-bromoacetophenone by the procedure of Dufraisse and Desquesnes.¹² The product boiled at 71–72° (3 mm.) and melted at 62–63°.

p-Bromophenylacetylene (64 g., 0.35 mole) was converted to the bromomagnesium derivative by warming with a slight excess of ethylmagnesium bromide, and the resulting homogeneous solution was added slowly to an excess (185 g., 0.7 mole) of benzyl *p*-toluenesulfonate in ether solution. The procedure was essentially the same as that employed for benzylphenylacetylene. There was obtained 25 g. (26% yield) of crude benzyl-*p*-bromophenylacetylene, b. p. 170–180° (3 mm.); redistillation gave a pale yellow liquid, b. p. 175–180° (3 mm.). The product was characterized by means of the solid dibromide, and by hydration to a solid ketone.

A solution of 2 g. of the acetylene in 10 cc. of carbon tetrachloride was treated with slightly more than two equivalents of bromine in the same solvent. The solvent was evaporated at 20° and the crude product recrystallized from ethyl alcohol. There was obtained 2 g. (63% yield) of the dibromide; white needles, m. p. 87°.

Anal. Calcd. for C₁₅H₁₁Br₂: Br, 55.66. Found: Br, 55.70, 55.71.

Hydration to Benzyl-*p*-bromoacetophenone.—In the usual way 5 g. of benzyl-*p*-bromophenylacetylene was treated with sulfuric acid and mercuric oxide, in the presence of ethyl alcohol. The resulting ketone after crystallization from ethyl alcohol weighed 2 g.; white leaflets, m. p. 98–99°. The semicarbazone of the ketone crystallized from alcohol in white needles, m. p. 163–164°. The ketone formed an oxime which crystallized readily from alcohol but showed a wide melting range; m. p. 115–125°. The ketone produced in the hydration reaction was shown to be the expected compound, benzyl-*p*-bromoacetophenone, by direct comparison with an authentic specimen, as described below.

Synthesis of Benzyl-*p*-bromoacetophenone.—A solution of 18.2 g. (0.1 mole) of pure *p*-bromobenzonitrile in absolute ether was added with stirring to a solution of 2-phenyl ethylmagnesium bromide (0.1 mole) and the mixture was refluxed gently for three hours. The reaction mixture was treated with a large excess of cold 15% sulfuric acid and the ether was distilled off without separating the aqueous acidic layer. The oily reaction product crystallized on cooling and after recrystallization from ethyl alcohol formed glistening white plates, m. p. 98–99°. The melting point was not changed by admixture with the ketone obtained by hydration of benzyl-*p*-bromophenylacetylene.

Anal. Calcd. for C₁₅H₁₃OBr: Br, 27.67. Found: Br, 27.62, 27.65.

The semicarbazone of the synthetic ketone melted at 164–165°, and showed no depression when mixed with the specimen obtained from the acetylene.

p-Bromobenzylphenylacetylene

Preparation.—A mixture of 54 g. (0.3 mole) of pure *p*-bromobenzyl alcohol (m. p. 77–78°), 54.5 g. (0.3 mole)

(12) Dufraisse and Desquesnes, *Bull. soc. chim.*, [4] **49**, 1880 (1931).

of redistilled and recrystallized *p*-toluenesulfonyl chloride, and 500 cc. of anhydrous ether was cooled to –10° and treated with 24 g. (0.43 mole) of finely powdered potassium hydroxide, in small portions and with good stirring. The mixture was stirred vigorously for several hours, removed from the cooling bath, and treated with water. The ethereal layer was washed with water, dried over anhydrous potassium carbonate, and concentrated under reduced pressure. The crude *p*-bromobenzyl *p*-toluenesulfonate was precipitated by the addition of petroleum ether and was purified by recrystallization from ether and petroleum ether. The purified product (55% yield) formed large transparent plates, m. p. 74–75°.

An ethereal solution of 79.5 g. (0.23 mole) of *p*-bromobenzyl *p*-toluenesulfonate was treated with 0.115 mole of phenylethynylmagnesium bromide, and the reaction and purification were carried out as described for benzylphenylacetylene. There was obtained 15.5 g. (50% yield) of a pale yellow liquid boiling at 167–171° (1–2 mm.). Redistillation gave 12.5 g. of pure *p*-bromobenzylphenylacetylene; b. p. 166–169° (1–2 mm.), m. p. 42–44°.

Anal. Calcd. for C₁₅H₁₁Br: Br, 29.49. Found: Br, 29.88, 30.05.

Treatment of the acetylene with two equivalents of bromine in carbon tetrachloride gave a crystalline dibromide, which melted at 108–108.5° after two crystallizations from ethyl alcohol.

Hydration to *p*-Bromobenzylacetophenone.—To a solution of 5.8 g. of *p*-bromobenzylphenylacetylene in 10 cc. of ethyl alcohol, 2 g. of yellow mercuric oxide was added and 15 g. (8 cc.) of concd. sulfuric acid was introduced dropwise, with cooling and stirring, over a period of ten minutes. The temperature of the flask was raised to 50° for thirty minutes and finally to 95° for fifteen minutes. The reaction mixture was cooled and poured into 250 cc. of cold water. The crude ketone (5.2 g.) was recrystallized from ethyl alcohol and finally from methyl alcohol; m. p. 68.5–69°. The semicarbazone melted at 161–162°. A mixture of this compound with the semicarbazone of the isomeric ketone from benzyl-*p*-bromophenylacetylene, m. p. 163–164°, was found to melt at 133–142°.

The identity of the product of hydration of *p*-bromobenzylphenylacetylene was established by comparison of the ketone and of its semicarbazone with a synthetic specimen of *p*-bromobenzylacetophenone and its semicarbazone.

Synthesis of *p*-Bromobenzylacetophenone.—Several methods were investigated before a satisfactory synthesis of this ketone was found. The preparation was finally effected in an unequivocal manner by the interaction of *p*-bromophenylpropionyl chloride and diphenylzinc. We are greatly indebted to Mr. Stephen Hubard for carrying out the following preparations.

β-Phenylpropionic acid was brominated according to the general directions of Göring¹³ and the mixture of brominated products was crystallized three times from 50% alcohol and once from a 1:1 mixture of benzene and petroleum ether. The resulting *p*-bromophenylpropionic acid melted at 131.5–134° (reported, 135°). The constitution of the acid was confirmed by oxidation with aqueous

(13) Göring, *Chem. Centr.*, (3) **8**, 795 (1877); Glaser, *Ann.*, **143**, 341 (1867).

potassium permanganate, which produced *p*-bromobenzoic acid, m. p. 245–246.5°.

Twenty-five grams of *p*-bromophenylpropionic acid was refluxed gently for five hours with four equivalents of thionyl chloride, and the excess of thionyl chloride was removed by distillation. The residual acid chloride was taken up in 75 cc. of benzene and the solution was added slowly, with stirring, to an excess of diphenylzinc. The latter was prepared by the addition of 27 g. (0.2 mole) of anhydrous zinc chloride in 25 cc. of absolute ether, to 0.45 mole of phenylmagnesium bromide.¹⁴ After the reaction had been completed the mixture was hydrolyzed with dilute acid; the benzene-ether layer was separated, washed with dilute alkali, and finally with water. After removal of the solvent the crude product was recrystallized from ethyl alcohol, and finally from methyl alcohol. The purified ketone formed white needles, m. p. 68–69°. This material was identical with a small sample of the ketone which had been obtained by treating the sodium derivative of ethyl benzoylacetate with *p*-bromobenzyl bromide and saponifying the resulting ethyl benzoyl-*p*-bromobenzylacetate.

Anal. Calcd. for $C_{15}H_{13}OBr$: C, 62.30; H, 4.50. Found: C, 61.89; H, 4.78.

(14) Job and Reich, *Bull. soc. chim.*, [4] **33**, 1428 (1923).

The semicarbazone of the synthetic ketone melted at 160–161.5°, and the 2,4-dinitrophenylhydrazone at 67–67.5°. The synthetic ketone and its semicarbazone showed no depression of the melting point when mixed with the specimens obtained from *p*-bromobenzylphenylacetylene.

Summary

1,3-Diphenylpropyne (benzylphenylacetylene) and two isomeric bromo derivatives have been prepared, and their chemical reactions investigated.

It has been shown that active prototropy of the propyne-allene type does not occur in these compounds, and that the 1,3-diarylpropynes exhibit low proton mobility.

Comparison with benzyl cyanide and 3-phenyl-1-propyne indicates that the phenylethynyl group has less activating effect than $-C\equiv N$ or $-C\equiv CH$, which is in agreement with the anticipated order.

ITHACA, N. Y.

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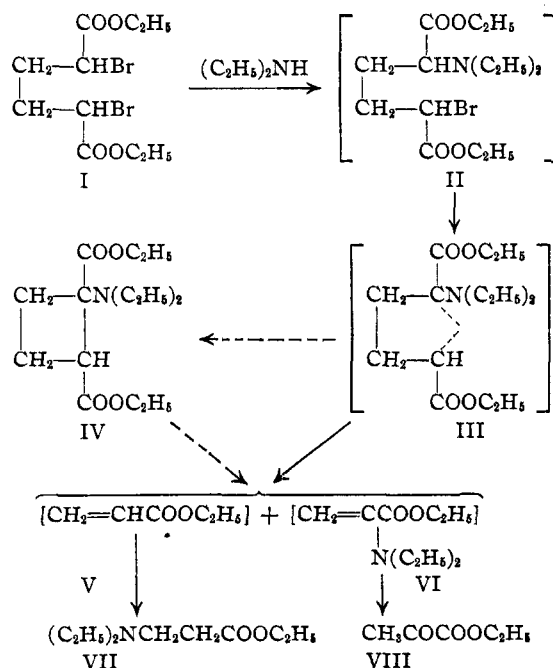
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Mechanism of the Cleavage of Ethyl α,α' -Dibromoadipate by Diethylamine

BY REYNOLD C. FUSON AND WM. E. LUNDQUIST

The cleavage of ethyl α,α' -dibromoadipate (I) by secondary amines, discovered by von Braun, Leistner and Münch,¹ may be interpreted in the light of Criegee's recently proposed theory of chain cleavages.² This postulate suggests that the cleavage may be explained by the formation of a 1,4-biradical. According to Criegee such radicals may stabilize themselves in two ways: (1) by closure to a four-membered ring or (2) by chain fission between atoms 2 and 3 to give two molecules of olefinic character. Applied to the cleavage of ethyl α,α' -dibromoadipate (I) by diethylamine this theory suggests that the biradical (III) may be produced from the intermediate bromoamino ester (II) by the loss of hydrogen bromide. The biradical might be expected to decompose to give ethyl acrylate (V) and ethyl α -diethylaminoacrylate (VI). The products actually isolated were ethyl β -diethylaminopropionate (VII) and ethyl pyruvate (VIII)—compounds which may be regarded as transformation products of V and VI, respectively. The forma-

tion of these compounds constitutes an example of the second mode of stabilization of the biradical.



(1) Von Braun, Leistner and Münch, *Ber.*, **59**, 1950 (1926).

(2) Criegee, *ibid.*, **68B**, 665 (1935).