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THE REARRANGEMENT OF ARYL-SUBSTITUTED PROPYNES TO ALLENES¹

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It is well known that 1,3-diarylpropenes such as I and II exist as separate individuals and can be interconverted to an equilibrium mixture by heating at 85° with alcoholic sodium ethoxide (1).

$$\begin{array}{ccc} p\text{-}\mathrm{CH}_3\mathrm{OC}_6\mathrm{H}_4\mathrm{CH}_2\mathrm{CH}_{=}\mathrm{CHC}_6\mathrm{H}_5 &\rightleftharpoons p\text{-}\mathrm{CH}_3\mathrm{OC}_6\mathrm{H}_4\mathrm{CH}_{=}\mathrm{CHCH}_2\mathrm{C}_6\mathrm{H}_5\\ \mathrm{I} & \mathrm{II} \end{array}$$

In the acetylene series a similar prototropy is complicated by the appearance of an intermediate allene, IV.

$$\begin{array}{ccc} \text{RC} = \text{CCH}_2\text{R}' \rightleftharpoons \text{RCH} = \text{C} = \text{CHR}' \rightleftharpoons \text{RCH}_2\text{C} = \text{CR}' \\ \text{III} & \text{IV} & \text{V} \end{array}$$

1-Pentyne, 2-pentyne, and 1,2-pentadiene form such an equilibrium mixture when heated with alcoholic potassium hydroxide (2). Among aromatic compounds of this sort both phenylallene (3, 5) and benzylacetylene (4, 5, 6) have been isomerized to methylphenylacetylene; the reverse transformation by the action of sodamide has also been reported (5). No 1,3-diarylallenes have been synthesized, and suitable diarylacetylenes (III and V, $R = C_6H_5$, R' = p-BrC₆H₄) were not interconverted (7) by the alkaline reagents tried. Other acetylenes of this type have therefore been synthesized in an attempt to find compounds which melt in a more convenient range and with which an investigation of the isomerization would be easier.

The synthesis of 1-(*p*-bromophenyl)-3-(β -naphthyl)-1- and 2-propynes (III and V, R = *p*-bromophenyl, R' = β -naphthyl) was accomplished by the method described earlier (7) which involves the reaction of an acetylenic Grignard reagent with a *p*-toluenesulfonic acid ester.

$$p\text{-}BrC_{6}H_{4}C \equiv CMgBr + 2\beta\text{-}C_{10}H_{7}CH_{2}OSO_{2}C_{6}H_{4}CH_{3} \longrightarrow$$
$$p\text{-}BrC_{6}H_{4}C \equiv CCH_{2}C_{10}H_{7} + C_{10}H_{7}CH_{2}Br + (CH_{3}C_{6}H_{4}SO_{3})_{2}Mg$$

Yields of the crude acetylenes were moderately good, but purification was difficult. A persistent yellow impurity was finally removed by rapid chromatography on alumina and the acetylenes were isolated as white, crystalline solids, m.p. $118-119^{\circ}$ and $99-100^{\circ}$ respectively. Their structures were proved by hydrogenation to 1-(p-bromophenyl)- $3-(\beta$ -naphthyl)propane and by hydration to 1-(p-bromophenyl)- $3-(\beta$ -naphthyl)-1- and 3-propanones respectively.

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An attempt was also made to prepare 1-phenyl-3- $(\beta$ -naphthyl)-1- and 2-propynes but only the second was obtained in pure, crystalline condition, m.p. 60.5-61.0°.

Both of the bromophenylnaphthylpropynes rearranged to 1-(*p*-bromophenyl)- $3-(\beta-naphthyl)$ allene when adsorbed on activated alumina and left for some time. Optimum conditions for the isomerization were probably not realized. The allene was isolated in 19-50% yield; none of either acetylene could be recovered and the other products were yellow, amorphous solids or oils. The allene had the correct composition and was shown to have the correct molecular weight by a comparative vapor pressure method (8). When melted, the allene turned yellow and could not be obtained again in a crystalline state. Apparently dimerization was occurring, because attempts to apply the Rast molecular weight method gave yellow solutions and values corresponding to a dimer. Mixtures of the allene with either acetylene showed melting point depressions. The allene absorbed two moles of hydrogen over Adam's catalyst and gave 1-(p-bromophenyl)- $3-(\beta-naphthyl)$ propane identical with a sample formed by hydrogenation of the acetylenes. The reaction of the allene with acidic reagents will be described later, but it can be mentioned that under the conditions used for hydration of the acetylenic isomers, only recovered starting material was isolated at low temperatures and only sticky gums at higher temperatures. No ketonic material was obtained.

The synthesis of the allene was attempted by a standard method as detailed in the experimental part, but failed at the final stage which consisted of an attempt to remove bromine from 1-(p-bromophenyl)-2,3-dibromo-3-(β -naphthyl)-1-propene (BrC₆H₄CH=CBrCHBrC₁₀H₇) by zinc and alcohol. The products of this reaction were tars and a yellow oil which had the composition of 1-(pbromophenyl)-2-bromo-3-ethoxy-2-(β -napthyl)-1-propene, [BrC₆H₄CH=CBr-CH(OC₂H₅)C₁₀H₇]. A very small amount of a crystalline solid was separated by chromatography but it was shown to be 3-(p-bromophenyl)-1-(β -naphthyl)-1propanone.

The spectra of the isomeric acetylenes and the allene in the ultraviolet region are given in Figure 1. The absorption of the allene is less intense than that of 1,3-diphenyl-1,3-di-(1-naphthyl)allene (9) but starts at almost the same place. These spectra are rather unsuitable for analysis of a mixture of the compounds. Infrared spectra were determined in carbon tetrachloride. The allene is characterized by a sharp band at 5.22 μ , which is absent in 1-(*p*-bromophenyl)-3-(β -naphthyl)-1-propyne (III, R = BrC₆H₄, R' = C₁₀H₇). There is a rather broad, low intensity band, maximum 5.30 μ , in the spectrum of the other acetylenic isomer (III, R = C₁₀H₇, R' = BrC₆H₄), but it is unlikely that it results from the presence of any of the allenic compound. Many aromatic substances have low intensity bands in this region.

An attempt was made to separate the two acetylenes by chromatography and it was shown that 1-(*p*-bromophenyl)-3-(β -naphthyl)-1-propyne (III, R = BrC_6H_4, R' = C_{10}H_7) was more tightly held on alumina. The method failed as a means of separation because isomerization occurred before the acetylenes could be eluted. Each of the acetylenes was also treated with potassium *tert*-butoxide in *tert*butanol, but the allene could not be isolated from the reaction mixtures. Instead a new compound having the composition of an addition product of *tert*butanol to the starting acetylene was obtained. An investigation of this reaction will be reported later.



FIGURE 1, ULTRAVIOLET ABSORPTION SPECTRA IN *n*-HEPTANE. A, 1-(*p*-bromophenyl)-3-(β -naphthyl)-2-propyne; B, 1-(*p*-bromophenyl)-3-(β -naphthyl)-1-propyne; C, 1-(*p*-bromophenyl)-3-(β -naphthyl)allene.

EXPERIMENTAL PART²

 $1-(p-Bromophenyl)-3-(\beta-naphthyl)-1-propyne.$ β -Naphthylmethyl p-toluenesulfonate was prepared from β -naphthylcarbinol, p-toluenesulfonyl chloride, and powdered potassium hydroxide in ether by the method used for p-bromobenzyl p-toluenesulfonate (7). Benzene was added during washing to bring all of the product into solution, and since removal of the solvent usually resulted in decomposition to a green tar, the yield was estimated on an aliquot and the dried solution used directly in the Grignard reaction. The yield was 75-88%. A small sample was recrystallized in the cold from benzene and ether by addition of petroleum ether, and remained undecomposed long enough for analysis. This sample began to decompose at 61.5° and softened at 135-140°.

² All melting points are corrected.

Anal. Calc'd for C₁₈H₁₆O₂S: C, 69.21; H, 5.16. Found: C, 69.27; H, 5.16.

p-Bromophenylethynylmagnesium bromide (0.108 mole) (7) was added to a stirred, refluxing solution of β -naphthylmethyl p-toluenesulfonate (0.23 mole) during two hours and refluxing was continued for seven hours. After hydrolysis (7) and removal of solvent, the red oil (65.6 g.) was mixed with 400 ml. of dry pyridine with slight cooling. After 2½ hours, water was added to dissolve the pyridinium salt and the sticky red solid that separated was taken up in ether. The aqueous layer was further diluted, acidified with dil. sulfuric acid, and extracted with ether. Evaporation of the ether solutions gave 30 g. of dark, semicrystalline product that could be decolorized in ether with carbon and purified by recrystallization from ethanol, methanol, or various ligroin fractions. A low yield of white crystals, m.p. 116.5–118° was obtained in this way. Improved results were obtained by passing a nearly-saturated solution of the acetylene in petroleum ether (b.p. 60–70°) rapidly through a short column of activated alumina (-80 mesh, not dried before use).³ The method is not suitable for large amounts of material because long contact with the adsorbent produces isomerization and the acetylene has only limited solubility in the solvent (roughly 1 g. in 300 ml.). Evaporation of the colorless eluate gave white crystals m.p. 118–119°.

Anal. Calc'd for C19H13Br: C, 71.04; H, 4.08.

Found: C, 71.01, 70.81; H, 4.52, 4.25.

The acetylene (33.7 mg.) was hydrogenated over Adam's catalyst in alcohol and absorbed 2.06 molecular equivalents of hydrogen (15 minutes). 1-(p-Bromophenyl)-3-(β -naphthyl)propane was isolated, yield 23 mg., m.p. 50-50.5° with slight softening at 49.5°.

Hydration of 3 g. of the crude acetylene with mercuric oxide and sulfuric acid (7) gave 2 g. of 1-(p-bromophenyl)-3-(β -naphthyl)-1-propane, m.p. after several recrystallizations from alcohol, 96–97.5°. Oxime, m.p. 151–152.5°. Mixture melting points with authentic samples of the ketone and oxime gave no depression.

 β -Naphthal-p-bromoacetophenone was prepared by condensation of 2-naphthaldehyde and p-bromoacetophenone in alcohol with 10% sodium hydroxide. The product was crystallized from ethyl acetate, m.p. 192–193° (yellow crystals).

Anal. Cale'd for C₁₉H₁₃BrO: C, 67.67; H, 3.89.

Found: C, 67.57; H, 4.19.

Oxime, m.p. 154.5-155.5° from mixtures of alcohol and ethyl acetate.

Anal. Calc'd for C₁₉H₁₄BrNO: C, 64.78; H, 4.01.

Found: C, 64.46; H, 3.89.

 $1-(p-Bromophenyl)-3-(\beta-naphthyl)-1$ -propanone was prepared by hydrogenation of the unsaturated ketone in dioxane over Adam's catalyst; colorless crystals, m.p. 99.0-99.5° from ethanol alone or mixed with ethyl acetate.

Anal. Cale'd for C₁₉H₁₅BrO: C, 67.27; H, 4.46.

Found: C, 67.45; H, 4.57.

Oxime, m.p. 151-152.5° from dil. alcohol.

Anal. Cale'd for C₁₉H₁₆BrNO: C, 64.42, H, 4.53.

Found: C, 64.61; H, 4.88.

 $1-(p-Bromophenyl)-3-(\beta-naphthyl)-2-propyne.$ The Grignard reagent obtained by refluxing 19.7 g. (0.128 mole) of β -naphthylacetylene (10) with an equivalent amount of ethylmagnesium bromide in 100 ml. of ether and 100 ml. of benzene for seven hours was added dropwise with stirring to a refluxing solution of 87 g. (0.255 mole) of p-bromobenzyl p-toluenesulfonate (7) in 150 ml. of benzene and 100 ml. of ether. After an eight hour-period of stirring and refluxing the mixture was hydrolyzed and the extract washed according to the usual procedure. (7).

Steam-distillation with 15% potassium hydroxide to remove p-bromobenzyl bromide caused some darkening and was continued for only 50 minutes. The crude product (51 g.), which still contained p-bromobenzyl bromide, was recrystallized from ethanol to give 27

³ Harshaw Chemical Co., Elyria, Ohio.

g. (66% yield) of non-lachrymatory yellow crystals which still had a broad melting point. Repeated crystallizations from ethanol and from petroleum ether (b.p. $30-60^{\circ}$) gave a low yield of a white product, m.p. 97.0-98.5°. The chromatographic procedure described above was far more effective and gave a product m.p. 99-100°.

Anal. Calc'd for C₁₉H₁₃Br: C, 71.04; H, 4.08.

Found: C, 70.84; H, 4.39.

Hydrogenation of 35.0 mg. of the pure acetylene as above gave 20 mg. of 1-(p-bromophenyl)-3- $(\beta$ -naphthyl)propane, m.p. 50.5-51.5° with absorption of 1.94 molecular equivalents of hydrogen. A mixture m.p. determination indicated the identity of this product with that obtained from the isomeric acetylene.

Hydration of 4 g. of the crude acetylene in a mixture of acetic acid and acetone with sulfuric acid and mercuric oxide gave 2.5 g. of 3-(p-bromophenyl)-1-(β -naphthyl)-1-propanone, m.p. 115-119°. Recrystallization from a mixture of ethyl acetate and alcohol gave colorless prisms, m.p. 118.5-119°. The oxime was recrystallized from dil. alcohol, m.p. 122-123°. These compounds were shown by mixture m.p. to be the same as authentic samples described below.

p-Bromobenzal-\beta-acetonaphthone was prepared in 71% yield from *p*-bromobenzaldehyde and β -acetonaphthone, yellow crystals from ethyl acetate, m.p. 177-177.5°. This ketone turned green on standing in direct sunlight.

Anal. Calc'd for C₁₉H₁₃BrO: C, 67.67; H, 3.89.

Found: C, 67.74; H, 4.16.

The oxime was prepared as usual, m.p. 162-163°.

Anal. Calc'd for C₁₉H₁₄BrNO: C, 64.78; H, 4.01.

Found: C, 64.59; H, 4.34.

 $3-(p-Bromophenyl)-1-(\beta-naphthyl)-1$ -propanone was prepared by hydrogenation of the unsaturated ketone in dioxane over Adam's catalyst and was crystallized from ethyl acetate or a mixture of this and alcohol; white needles, m.p. 118.0-118.5°.

Anal. Calc'd for C₁₉H₁₅BrO: C, 67.27; H, 4.46.

Found: C, 67.66; H, 4.67.

The oxime was prepared as usual, m.p. 122-123° (from dil. alcohol).

Anal. Calc'd for C₁₉H₁₆BrNO: C, 64.42; H, 4.53.

Found: C, 64.32; H, 4.68.

1-Phenyl-3- $(\beta$ -naphthyl)-2-propyne was prepared from β -naphthylacetylene and benzyl p-toluenesulfonate (11, 12) in 75% yield (crude) by the procedure described above. The chromatographic purification was not applied to this compound and great difficulty attended attempts to crystallize the crude, low-melting product. High vacuum-distillation gave improved material with large losses, and crystallization of the distillate from nitromethane gave white crystals, m.p. 60.5-61°. These turned yellow on brief standing.

Anal. Cale'd for C₁₉H₁₄: C, 94.18; H, 5.82. Found: C, 93.67, 93.83; H, 6.19, 6.22.

Hydration of the crude acetylene gave about 15% of 1-phenyl-3-(β -naphthyl)-3-propanone, m.p. 92.5-94° (reported 93°) (13, 14, 15); oxime, m.p. 125.5-126.5° (reported 120°) (13).

1-(p-Bromophenyl)-3- $(\beta$ -naphthyl)allene. One gram of 1-(p-bromophenyl)-3- $(\beta$ -naphthyl)-1-propyne was adsorbed from its solution in 110 ml. of pure *n*-heptane on a column 1.7 cm. in diameter containing 20 g. of dry, -80 mesh, activated alumina. A little more heptane was added and the column stoppered so that the adsorbant remained covered with solvent during the isomerization. After 74 hours at room temperature, the adsorbed substance was eluted with $60-70^{\circ}$ petroleum ether, then with a mixture of 9 parts of this with 1 part of ether and finally with pure ether. Four eluate fractions were collected during this process. The first two were colorless, but turned yellow after short standing. Evaporation gave a slightly yellow solid which was white after washing with petroleum ether; the yield was 190 mg., m.p. 117-118.5°. The third and fourth fractions gave yellow oils and amorphous solids from which neither acetylene nor allene could be isolated. When the acetylene was left on the alumina for 8 hours instead of 74, a 50% yield of the allene, m.p. $115-118^{\circ}$, was obtained.

One gram of 1-(p-bromophenyl)-3-(β -naphthyl)-2-propyne was adsorbed on a similar column and left for 163 hours. A total of 300 mg. of the crude allene was isolated in several fractions and these gave pure allene, m.p. 117-118.5° on recrystallization with moderate loss; there was no depression of m.p. when mixed with the allene from 1-(p-bromophenyl)-3-(β -naphthyl)-1-propyne. The final eluate gave 180 mg. of a yellow solid, m.p. 80-90° which was not purified successfully.

The allene turned yellow on melting and could not be recovered in crystalline form. It depressed the melting point of either starting acetylene and of 3-(p-bromophenyl)-1- $(\beta$ -naphthyl)-1-propanone, m.p. 117-118.5° as well.

Anal. Calc'd for C₁₉H₁₃Br: C, 71.04; H, 4.08.

Found: C, 71.00; H, 4.31.

The molecular weight was determined in the Signer apparatus (8) using ether as the solvent and azobenzene as the reference compound: Calc'd, 321; Found, 325. The solubility of the allene is only 29 g./liter or 0.09 mole/liter which is a little lower than optimal for the method. It was observed that on long standing in the apparatus the molecular weight rose slowly, suggesting that the allene polymerized under these conditions.

Molecular weight determinations in camphor by the usual Rast technique gave values of 645 and 635 (dimer 642).

1-(p-Bromophenyl)-3- $(\beta$ -naphthyl)propane. Hydrogenation of 34.6 mg. of the allene in alcohol over Adam's catalyst until no more hydrogen was absorbed resulted in an uptake of 5.25 ml. at 25° and 753 mm., corresponding to 1.97 molecular equivalents. The filtrate contained no ionic halogen. There was isolated 25 mg. of 1-(p-bromophenyl)-3- $(\beta$ -naphthyl)propane, m.p. 50-51° (softening at 49.5°). No depression of m.p. resulted in mixtures with the saturated compound from either acetylene.

The various samples of the propane were combined and recrystallized several times from dil. alcohol. The analytical sample had m.p. $51.5-52^{\circ}$ with slight softening at 49.5° .

Anal. Calc'd for C₁₉H₁₇Br: C, 70.16; H, 5.27.

Found: C, 70.19; H, 5.32.

Infrared spectra were determined in carbon tetrachloride in a Beckman Model IR2 infrared spectrophotometer. The solutions of the acetylenes were 4% and of the allene 3% by weight; the solution of 1-(p-bromophenyl)-3-(β -naphthyl)-2-propyne was about 70% of saturation and the other solutions were approximately saturated. The rock salt cell gave a solution layer about 0.2 mm. thick. The spectra of 2-naphthylacetylene and p-bromophenylacetylene were also determined in carbon tetrachloride. The former in 27% solution had sharp bands at 4.8 μ (53% transmission) and 5.3 μ (70% transmission). The latter in 60% solution gave bands at exactly the same wave lengths (69% and 58% transmission respectively).

Ultraviolet spectra were measured in solutions in pure heptane in a Beckman Model DU quartz spectrophotometer. The curves are given in Figure 1.

Attempted synthesis of 1-(p-bromophenyl)- $3-(\beta$ -naphthyl)allene. p-Bromobenzal- β -acetonaphthone dibromide was prepared in 84–87% yield by addition of bromine in chloroform to a chloroform suspension of the unsaturated ketone with stirring. The product was directly pure, m.p. 215–216°d. and recrystallization gave a compound with slightly lower m.p.

Anal. Calc'd for C19H13Br3O: C, 45.91; H, 2.64.

Found: C, 45.84; H, 2.69.

A mixture of 174.5 g. (0.35 mole) of dibromide and 42 g. (0.43 mole) of fused potassium acetate in 1 liter of methanol was stirred and refluxed for 48 hours. The mixture was cooled, poured into 2 liters of water, and extracted with ether. A precipitate of 27 g. of unchanged dibromide remained undissolved and was recovered. The ether extract gave 110 g. of 3-(*p*-bromophenyl)-1-(β -naphthyl)-2-bromo-2-propen-1-one as fine, yellow crystals, 89% yield.

An analytical sample was prepared by successive recrystallizations from methanol, ethanol, and petroleum ether $(30-70^\circ)$, m.p. $89-90.5^\circ$.

Anal. Calc'd for C19H12Br2O: C, 54.84; H, 2.88.

Found: C, 54.78; H, 3.03.

To a boiling solution of 39 g. (0.19 mole) of redistilled aluminum isopropoxide in 300 ml. of 2-propanol was added rapidly 40 g. (0.096 mole) of the unsaturated bromoketone in 450 ml. of 2-propanol. The solution was refluxed for 20 minutes, cooled, poured into an ice slush of 100 ml. of 6 N hydrochloric acid and stirred at 5–10° for three hours. The resulting oil was taken up in ether and dried over potassium carbonate; evaporation gave 35 g. (87%) of yellow solid. Purification was effected by crystallization from ether or petroleum ether $(30-70^\circ)$ with very slow cooling, finally at 0°. Recovery was 85%. A larger excess of aluminum isopropoxide gave a product harder to purify. An analytical sample was prepared by further recrystallization from petroleum ether and melted at 79–80.5°.

Anal. Calc'd for C₁₉H₁₄Br₂O: C, 54.57; H, 3.36.

Found: C, 54.45; H, 3.43.

The hydroxyl of 1-(*p*-bromophenyl)-3-(β -naphthyl)-2-bromo-2-propen-1-ol was replaced by bromine using phosphorus tribromide in ether plus a little pyridine at 0°. The product was obtained in 50–75% yields, m.p. 154–159° with considerable softening as low as 130°, but purification was not successful and the compound was treated with zinc and alcohol directly. Isolation of the desired allene was not successful.

SUMMARY

The isomeric acetylenes 1-(p-bromophenyl)- $3-(\beta$ -naphthyl)-1- and 2-propyne were synthesized by conventional methods. Both were isomerized to 1-(pbromophenyl)- $3-(\beta$ -naphthyl)allene by adsorption on activated alumina. This is the first example of a 1,3-diarylallene to appear in the literature. It could not be obtained by isomerizing the acetylenes under basic conditions or by a standard method of allene synthesis. The allene was identified by hydrogenation to 1-(p-bromophenyl)- $3-(\beta$ -naphthyl)propane, and by its analysis, molecular weight, and infrared spectrum.

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