[Contribution from the Department of Chemistry, The University of California, Los Angeles]

Arylallenes. II. Synthesis of Diarylallenes. Partial Asymmetric Synthesis of Allenes*[1,2]

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1,3-Diphenylallene and 1-(*p*-biphenyl)-3-phenylallene have been synthesized by prototropic rearrangement of 1,3-diphenylpropyne and 1-(*p*-biphenyl)-3-phenyl-1-propyne by adsorption on basic alumina. The second of these allenes was also prepared by rearrangement in an inert solvent in the presence of solid alkali. These methods appear to be general for the synthesis of such unstable allenes. A partial asymmetric synthesis of these allenes was accomplished by carrying out the rearrangement with brucine or quinine adsorbed on alumina.

The rearrangement of 1-(*p*-bromophenyl)-3-(β-naphthyl)-1- and 2-propynes (I and II, R = *p*-BrC_6H_4, R′ = β-$C_{10}H_7$) to 1-(*p*-bromophenyl)-3-(β-naphthyl) allene (III, R = *p*-BrC_6H_4, R′ = β-$C_{10}H_7$) by adsorption on activated alumina was reported earlier.[2] It was of interest to examine the isomerization more closely and to extend it to other diarylallenes because no others have been reported.

$$\underset{\text{I}}{RC{\equiv}CCH_2R'} \longrightarrow \underset{\text{III}}{RCH{=}C{=}CHR'} \longleftarrow \underset{\text{II}}{RCH_2C{\equiv}CR'}$$

This paper describes the synthesis of 1,3-diphenylallene and 1-(*p*-biphenyl)-3-phenylallene; a rearrangement of the corresponding propynes by brucine or quinine adsorbed on alumina has resulted in a partial asymmetric synthesis of these allenes.

It was found that a highly active, basic alumina was required to accomplish the isomerization of 1,3-diarylpropynes to allenes. Harshaw's 80-mesh activated alumina was effective only after heating for some time. This alumina is basic (*p*H∼9); when it was treated with ethyl acetate, which gave a more nearly neutral material, and activated by heat, it would no longer cause isomerization. It was found that the yield of allene was improved if the time of residence on the adsorption column was reduced; thus the yield of 1-(*p*-bromophenyl)-3-(β-naphthyl)allene was improved from 50%[2] to 82% by reducing the time on the column from 8 hr. to the minimum time required for elution (∼20 min.). This did not result in recovery of unreacted acetylene, but did reduce the amount of non-crystalline, by-product material, apparently formed by further rearrangement of the allene. The yield of such by-products was also increased by using too long a column. With each new propyne examined, some experimentation was usually necessary to find the correct column length, basicity of adsorbent, and time of residence on the column for optimum yields. With 1,3-diphenylpropyne, which rearranges somewhat slowly, the yield of 1,3-diphenylallene was 52% when ordinary Harshaw alumina was simply activated by heat and used with rapid elution and a short column, but rose to 75% when alumina impregnated with potassium hydroxide was used. The rearrangement of 1-(*p*-biphenyl)-3-phenyl-1-propyne was accomplished in 69% yield on the ordinary, heat-activated alumina.

The nature of the by-products formed from the allenes is under investigation and will be reported in a separate paper.

An easier method of isomerization which permitted the preparation of larger amounts of the allenes was realized by shaking substituted propynes in an inert solvent with pellets of sodium hydroxide or potassium hydroxide at room temperature for a number of hours. This method failed with 1,3-diphenylpropyne, and appeared to give slightly lower yields with other propynes.

Partially asymmetric rearrangements of 1,3-diphenylpropyne and 1-(*p*-biphenyl)-3-phenyl-1-propyne to the corresponding allenes were accomplished by adsorbing the acetylenic compounds on columns of neutral, activated alumina which had been impregnated with brucine or quinine. The products with the brucine-impregnated columns were levorotatory and the maximum specific rotations were −1.24° and −7.0° respectively. With quinine-impregnated columns, dextrorotatory products were obtained with maximum specific rotations of +2.48° and +8.57° respectively. Infrared spectra of the products sometimes indicated a mixture of the starting acetylene with allene, but in other experiments the products appeared to be pure allenes; in every instance however the products had broad melting points. Attempts to isolate a pure enantiomer were unsuccessful although it was possible to increase the specific rotation slightly by fractional crystallization; these allenes are not easy to recrystallize, and during manipulation, dimers and other transformation products form readily.

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(2) For paper I see T. L. Jacobs and S. Singer, *J. Org. Chem.*, **17**, 475 (1952).

Although the observed rotations are small it appears very unlikely that they result from impurities. The products were carefully washed in ether under nitrogen with aqueous hydrochloric acid to remove any traces of active base. When attempts were made to rearrange the propynes with brucine or quinine by shaking in solution in the absence of alumina, only inactive starting material was isolated; the purification was the same as used to insure the absence of optically active bases from the products of successful rearrangements. Isolation of dimeric material from successful rearrangements gave an inactive, crystalline dimer. Finally it was found that the broad-melting, *levo*-1-(*p*-biphenyl)-3-phenylallene was hydrogenated to an inactive product (no activity in the crude sample) with absorption of two molecular equivalents of hydrogen. Pure 1-(*p*-biphenyl)-3-phenylpropane was isolated without difficulty from the hydrogenation product.

The allenes were characterized by analysis, molecular weight determination, hydrogenation to the propane derivatives (also obtained from the starting propynes), and especially by infrared spectroscopy. Although the aryl groups in both the starting propynes and in the allenes give a series of small bands[3,4] between 1650 cm.$^{-1}$ and 2000 cm.,$^{-1}$ one of which usually has a maximum near 1950 cm.$^{-1}$ where the characteristic strong absorption which results from the antisymmetrical C=C=C stretching vibration is observed,[4,5] the allene absorption is so much stronger that it is easily distinguishable. The starting propynes showed a characteristic C≡C absorption in the 2200–2250 range[4] where the allenes did not absorb. All three of the allenes prepared during this investigation are solids, and it was necessary to observe the spectra in rather concentrated solutions to bring out the characteristic absorptions.

The ultraviolet absorption spectra of the allenes are interesting. Celmer and Solomons[6] pointed out that very little conjugation across the allene system would be expected since the orbitals of the π electrons are at right angles to each other. Each double bond of the allene group conjugates independently with the groups attached to it and the spectrum of each allene should be approximately equivalent to a summation of the spectra of the two corresponding olefins. In general, however, λ_{max} for the most intense absorption of the allenes appears to occur at slightly longer wavelengths. Thus styrene[7] shows λ_{max} 244 while 1,3-diphenylallene has λ_{max} 255. As would be expected the extinction coefficients are higher for the allenic systems.

The starting propynes were prepared by conventional methods[2,8] as detailed in the experimental part. The final step in this synthesis is the reaction of an acetylenic Grignard reagent with benzyl *p*-toluenesulfonate. The *p*-toluenesulfonate is unstable and must be used in double the molecular amount of the acetylenic compound because the first equivalent reacts with the Grignard reagent to give benzyl bromide. An attempt was made therefore to alkylate the Grignard reagent with benzyl bromide in the presence of cuprous chloride.[9] With phenylethynylmagnesium bromide a 35% yield of 1,3-diphenylpropyne was obtained, whereas benzyl *p*-toluenesulfonate gave 72% yield.[8] With *p*-phenylphenylethynylmagnesium bromide no 1-(*p*-biphenyl)-3-phenyl-1-propyne was isolated when benzyl bromide was used, but benzyl *p*-toluenesulfonate gave 33% of the desired propyne.

An investigation of the reactions of the allenes obtained in this work is underway and will be reported in a separate paper.

EXPERIMENTAL

All melting points were taken on a Hershberg[10] immersion apparatus. Infrared spectra were determined on a Model 21 Perkin-Elmer instrument using a sodium chloride prism.

1,3-Diarylpropynes. 1-(*p*-Bromophenyl)-3-(β-naphthyl)-1-propyne was a sample prepared by S. Singer.[2] 1,3-Diphenylpropyne was prepared from benzyl *p*-toluenesulfonate and phenylethynylmagnesium bromide as described earlier,[8] $n_D^{19.8}$ 1.5995. It was also prepared by the method of Gensler and Thomas[9b] for coupling acetylenic Grignard reagents with propargyl bromides. Phenylacetylene (22.6 g.; 0.22 mole), dissolved in dry ether was added dropwise to a stirred, ethereal solution of ethylmagnesium bromide (0.2 mole). The solution was refluxed for 1 hr. and cuprous chloride (0.4 g.) as well as cupric chloride (0.4 g.) were added. The solution was refluxed for another 30 min. Benzyl bromide (34.3 g.; 0.2 mole) dissolved in ether was added dropwise with stirring to the reaction mixture. The stirred reaction mixture was refluxed for 46 hr.; a heavy yellow precipitate formed. The reaction mixture was decomposed with cold aqueous hydrochloric acid solution. The organic layer was washed with cold water, neutralized with cold aqueous sodium bicarbonate solution and finally washed with cold water. It was dried over anhydrous magnesium sulfate. On distillation phenylacetylene (3.83 g.) and benzyl bromide (13.31 g.) were recovered. 1,3-Diphenylpropyne (13.78 g.: 35.6%) distilled at 140–145°C/3 mm.

Ultraviolet absorption spectrum of 1,3-diphenylpropyne, in 95% ethanol: λ_{inf} 232, $\epsilon = 16{,}650$; λ_{max} 240, $\epsilon = 25{,}200$; λ_{max} 251, $\epsilon = 22{,}900$; $\lambda_{shoulder}$ 264, $\epsilon = 1400$; $\lambda_{shoulder}$ 267.5, $\epsilon = 1100$; λ_{max} 272, $\epsilon = 1050$; λ_{max} 279, $\epsilon = 800$; $\lambda_{shoulder}$ 287, $\epsilon = 480$; λ_{max} 305, $\epsilon = 460$; λ_{max} 326, $\epsilon = 370$.

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(3) C. W. Young, R. B. Du Vall, and N. Wright, *Anal. Chem.*, **23**, 709 (1951).

(4) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley and Sons, Inc., New York (1954).

(5) J. H. Wotiz and D. E. Mancuso, *J. Org. Chem.*, **22**, 207 (1957).

(6) W. D. Celmer and I. A. Solomons, *J. Am. Chem. Soc.*, **75**, 1372 (1953).

(7) A. E. Gillam and E. S. Stern, *An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry*, Edward Arnold Ltd., London, 1954, p. 126.

(8) J. R. Johnson, T. L. Jacobs and A. M. Schwartz, *J. Am. Chem. Soc.*, **60**, 1885 (1938).

(9) (a) J. P. Danehy, D. B. Killian, and J. A. Nieuwland, *J. Am. Chem. Soc.*, **58**, 611 (1936); (b) W. J. Gensler and G. R. Thomas, *J. Am. Chem. Soc.*, **73**, 4601 (1951); (c) W. J. Gensler and A. P. Mahadevan, *J. Am. Chem. Soc.*, **77**, 3076 (1955); (d) W. R. Taylor and F. M. Strong, *J. Am. Chem. Soc.*, **72**, 4263 (1950).

(10) E. B. Hershberg, *Ind. Eng. Chem., Anal. Ed.*, **8**, 312 (1936).

The infrared spectrum of 1,3-diphenylpropyne shows a medium absorption peak at 2217 cm.,$^{-1}$ attributed to the internal acetylenic bond. Likewise it shows several phenyl bands betwen 1650 cm.$^{-1}$ and 2000 cm.$^{-1}$ The principal peaks are at 1665 cm.$^{-1}$, 1743 cm.$^{-1}$, 1795 cm.$^{-1}$, 1868 cm.$^{-1}$, and 1944 cm.$^{-1}$.

p-Biphenylacetylene. To 156 g. (0.75 mole) of phosphorus pentachloride in 200 ml. of dry benzene in a 2-l., round-bottomed, 3-neck flask equipped with stirrer, condenser, and dropping funnel was added dropwise a solution of 98.5 g. (0.5 mole) of methyl-(*p*-biphenyl)-ketone[11] in dry benzene containing a few crystals of 4-*tert*-butylcatechol. The flask was wrapped to exclude light. Evolution of hydrogen chloride began at once. After addition was completed the yellow solution was refluxed for 3.5 hr., stirred overnight at room temperature, and poured into ice water. A white suspension formed and was stirred for 40 min.; it was then left in the hood for several hours until all of the benzene had evaporated. The organic chloride was taken up in ether, which left behind a considerable amount of solid soluble neither in ether nor in chloroform; the ether solution was washed with water and dried over anhydrous magnesium sulfate. The ether was removed and the residue added to 1.5 moles of sodamide in a liter of liquid ammonia. The dark brown solution was stirred for several hours, neutralized with ammonium chloride (80.3 g., 1.5 moles), diluted with ether and concentrated by allowing the ammonia to evaporate. The ether solution was washed with cold, dilute hydrochloric acid, 1*N* aqueous sodium carbonate and water, dried over anhydrous magnesium sulfate, and concentrated to leave a dark brown solid. Recrystallization from ethanol (decolorizing), then from carbon tetrachloride gave white crystals of *p*-biphenylacetylene, m.p. 86–87°. The yield was 38.8 g. (43.4%). In one instance the acetylene was purified by making the silver salt.

Anal. Calcd. for $C_{14}H_{10}$: C, 94.34; H, 5.66. Found: C, 94.29; H, 5.85.

1-(p-Biphenyl)-3-phenyl-1-propyne was synthesized from *p*-phenylphenylethynylmagnesium bromide (0.027 mole) and benzyl *p*-toluenesulfonate (0.06 mole) according to the directions used for 1,3-diphenylpropyne.[8] The product was purified by rapid chromatography on a very short column of activated, undried alumina and recrystallized from petroleum ether (b.p. 20–40°) or methanol to give white crystals, m.p. 75.4–76.6°, yield 2.4 g. (33%).

Anal. Calcd. for $C_{21}H_{16}$: C, 93.99; H, 6.01; mol. wt., 268.3. Found: C, 94.01; H, 6.19. Mol. wt., (Signer method[12]) 302.

Hydrogenation of the acetylene (100 mg.) in 10 ml. of methanol over palladium-on-carbon resulted in absorption of 2 molecular equivalents of hydrogen. The product was recrystallized from methanol to give 32 mg , m.p. 40–41.6°.

The infrared spectrum of 1-(*p*-biphenyl)-3-phenyl-1-propyne was determined in carbon tetrachloride solution (25% by weight) with a cell thickness of 0.4 mm. Even at this concentration the characteristic acetylenic bond (2242 cm.$^{-1}$) shows 64% transmission. The phenyl bonds between 1650 cm.$^{-1}$ and 2000 cm.$^{-1}$ are all stronger; the principal peaks are at 1668 cm.$^{-1}$, 1687 cm.$^{-1}$, 1700 cm.$^{-1}$, 1795 cm.$^{-1}$, 1870 cm.$^{-1}$, 1902 cm.$^{-1}$ and 1942 cm.$^{-1}$

Ultraviolet absorption spectrum, in 95% ethanol: $\lambda_{\max}$ 273, ϵ = 45,060.

Basic activated alumina. Harshaw's 80-mesh alumina of the sort commonly used for chromatography was found to be slightly basic. It was dried for 5 days at 160–170° before use and was then effective for the acetylene-allene rearrangement. It will be referred to as alumina A. With the compounds examined in this work the undried alumina of this grade did not effect the rearrangement, nor would alumina treated with ethyl acetate and then dried as above give successful results.

A more basic alumina was prepared by shaking 1 kg. of Harshaw's 80-mesh activated alumina with 250 g. of potassium hydroxide or sodium hydroxide in 750 ml. of water in a 3 l., round-bottomed flask heated with a heating mantle until most of the water was evaporated. Evaporation was interrupted before the mixture became completely dry in order to prevent cake formation. The alumina was stored under nitrogen; just before use it was dried at 160° at 3 mm. for a period of 14 hr. The dried alumina absorbs carbon dioxide rather rapidly from the air and is then less effective for the rearrangement. No attempt was made to study the effect of varying the quantity of the base on the activity of the alumina for the rearrangement. This alumina will be referred to as alumina B.

To prepare alumina impregnated with an optically active base 650 g. of Harshaw's 80-mesh alumina was heated with an open flame for 1 hr., soaked in 815 ml. of ethyl acetate for 24 hr., washed on a Buchner funnel first with 1630 ml. of water, then with 1630 ml. of methanol and dried in a desiccator under vacuum overnight; it was finally dried at 250° for 4 hr. Fifty grams of this neutral alumina was stirred for 2 hr. with a solution of 5 g. of anhydrous quinine or anhydrous brucine in about 70 ml. of chloroform, filtered, and finally dried at 135° under 5 mm. pressure. This will be referred to as alumina C. When an attempt was made to impregnate with twice the amount of quinine, a column of the alumina became gelatinous during use with pentane, and elution was difficult.

1,3-Diphenylallene. A solution of 0.68 g. of 1,3-diphenylpropyne in 20 ml. of *n*-pentane was placed on a 2.7 × 10 cm. column of alumina A and eluted at once with *n*-pentane. The first 150 ml. of *n*-pentane coming through the column contained neither allene nor starting material; from the next fractions was isolated 0.35 g. (51.5% yield) of 1,3-diphenylallene, m.p. 43–48°C. Some greenish oil, apparently decomposition product, was also collected.

Similarly 1.17 g. of 1,3-diphenylpropyne in 20 ml. of *n*-pentane was placed on a 2 × 9 cm. column of alumina B and eluted at once. A deep red band formed at the top of the column as soon as the propyne was added. The allene came off the column in the first 50 ml. of eluate and was isolated by evaporating the solvent at room temperature under nitrogen with a water aspirator to yield 0.87 g. (74.5%) of white crystals, m.p. 46.4–51.4°C. The product was recrystallized from *n*-pentane by cooling the solution in a Dry Ice–acetone bath to −40°C. The recrystallized product melted at 49–51°C.

Anal. Calcd. for $C_{15}H_{12}$: C, 93.71; H, 6.29; Mol. wt., 192.25. Found: C, 93.55; H, 6.07; Mol. wt., (cryoscopic in benzene), 201.

Ultraviolet absorption spectrum in 95% ethanol: $\lambda_{\text{shoulder}}$ 230, ϵ = 14,720; $\lambda_{\max}$ 236.5, ϵ = 20,550; $\lambda_{\max}$ 255, ϵ = 52,200; $\lambda_{\text{shoulder}}$ 279, ϵ = 6,870; $\lambda_{\max}$ 289.5, ϵ = 3,900.

The infrared absorption spectrum of 1,3-diphenylallene shows a strong allene absorption at 1947 cm.$^{-1}$ The characteristic phenyl peaks between 1650 cm.$^{-1}$ and 1900 cm.$^{-1}$ are well defined; however, in comparison with the 1947 cm.$^{-1}$ peak they are extremely weak.

1-(p-Biphenyl)-3-phenylallene. A solution of 0.768 g. of 1-(*p*-biphenyl)-3-phenyl-1-propyne in *n*-pentane was placed on a 1.7 × 11 cm. column of alumina A and eluted after 45 min. with *n*-pentane. The solvent was removed at room temperature under an atmosphere of nitrogen. The yield of 1-(*p*-biphenyl)-3-phenylallene was 0.527 g. (68.6% yield) m.p. 84.8–86.4°C.

1-(*p*-Biphenyl)-3-phenylallene was also prepared by shaking a solution of 0.100 g. of 1-(*p*-biphenyl)-3-phenyl-1-propyne, in 50 ml. of petroleum ether (b.p. 20–40°), with 1 g. of sodium hydroxide pellets, for 11 hrs. at room temperature. The solution was filtered and concentrated. When cooled in an ice bath the concentrated solution deposited white crystals of 1-(*p*-biphenyl)-3-phenylallene (58% yield,

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(11) L. M. Long and H. R. Henze, *J. Am. Chem. Soc.*, **63**, 1939 (1941).

(12) E. P. Clark, *Semimicro Quantitative Organic Analysis*, Academic Press, New York (1943), p. 47.

m.p. 91–94°C.). Further purification was effected by recrystallizing from petroleum ether (b.p. 20–40°). The melting point was raised to 94.6–95.5°C.

Anal. Calcd. for $C_{21}H_{16}$: C, 93.99; H, 6.01; M.W., 268. Found: C, 93.83; H, 6.09; M.W. (cryoscopic in benzene), 242.

The infrared absorption spectrum of 1-(*p*-biphenyl)-3-phenylallene shows a strong allene absorption at 1944 cm.$^{-1}$ Just as in the case of 1,3-diphenylallene, the phenyl peaks between 1650 cm.$^{-1}$ and 1900 cm.$^{-1}$ are well defined, but they are extremely weak in comparison with the 1944 cm.$^{-1}$ peak.

levo-1,3-Diphenylallene. A solution of 1.18 g. of 1,3-diphenylpropyne in 20 ml. of *n*-pentane was placed on a column of alumina C (alumina-brucine mixture, total weight of mixture, 30 g.) and eluted at once with excess *n*-pentane. The solvent was removed at room temperature under an atmosphere of nitrogen, using a water aspirator. The solid residue was taken up in ether and extracted with cold 0.1*N* hydrochloric acid, washed with cold dilute aqueous sodium bicarbonate solution and finally washed with cold water. After drying over anhydrous magnesium sulfate, the ether was removed. The residue, a white solid, weighed 0.94 g. (80% yield), m.p. 41.8–50.6°C. The infrared spectrum of this solid showed a strong allene absorption band at 1940 cm.$^{-1}$ whereas, no acetylene absorption was observed. Rotation was taken in a carbon tetrachloride solution, using a 1 dcm. polarimeter tube. $[\alpha]_D^{23}$ $-1.24°$ (c 10.58); observed rotation α_D^{23} $-0.131° \pm 0.009$. The specific rotation of the allene was increased to $[\alpha]_D^{22.8}$ $-1.82°$ (carbon tetrachloride, c = 3.19) by fractional recrystallization, using *n*-pentane as solvent and cooling the solution in a Dry Ice–acetone bath.

When 1,3-diphenylpropyne (1 g.) was treated with a solution of anhydrous brucine (6.15 g.) in chloroform (31 ml.) at room temperature, for 11.5 hr., only the starting propyne (0.86 g.) was isolated and it was optically inactive.

dextro-1,3-Diphenylallene was prepared by the method described for the preparation of levo-1,3-diphenylallene, using alumina C (alumina-quinine mixture). The yield of allene was 73.3%. The rotation was taken in carbon tetrachloride solution using a 1 dcm. polarimeter tube. $[\alpha]_D^{23}$ $+2.48°$ (c 10.7); observed rotation α_D^{23} $+0.265° \pm 0.023$. A side-product in this reaction was a white compound m.p. 191.5–194°C. It was found to have twice the molecular weight of 1,3-diphenylpropyne. This compound was optically inactive.

levo-1-(p-Biphenyl)-3-phenylallene was prepared by the method described above for the preparation of levo-1,3-diphenylallene. The yield of allene (m.p. 83–95°C.) was 69.3%. An infrared spectrum of the product was identical with that of racemic 1-(*p*-biphenyl)-3-phenylallene. The rotation was taken in carbon tetrachloride solution using a 1 dcm. polarimeter tube. $[\alpha]_D^{22.8}$ -7.0 (c = 10.35); observed rotation $\alpha_D^{22.8}$ $-0.725 \pm 0.022°$.

Hydrogenation of levo-1-(*p*-biphenyl)-3-phenylallene (m.p. 83–95°C.; $[\alpha]_D^{22.8}$ $-7.0°$) over platinum oxide catalyst at room temperature and atmospheric pressure, using benzene as solvent, indicated an uptake of 2 moles of hydrogen. The isolated crude product was optically inactive. Recrystallization of the product yielded a solid m.p. 37.5–40°C. A mixture melting point of this solid with the hydrogenation product of 1-(*p*-biphenyl)-3-phenyl-1-propyne (m.p. 40–41.6°C.) maintained a sharp melting point, 39–41°C. Platinum oxide was chosen as the catalyst in this experiment because it has been reported[13] to give very little racemization in the reduction of (−)-3-phenyl-1-butene to (−)-2-phenylbutane. In this olefin the double bond is adjacent to the asymmetric center, and there is also a phenyl group on the asymmetric carbon. The possibility that the observed optical activity of our allene might result from the presence, as an impurity, of a compound bearing an asymmetric center appears very unlikely because all activity is destroyed by the hydrogenation.

dextro-1-(p-Biphenyl)-3-phenylallene. A column, 1.7 × 10 cm., of neutral alumina (20 g.)-quinine (4 g.) mixture, prepared as described for the preparation of alumina C, was covered with *n*-pentane. The rate of migration of *n*-pentane on the column was very slow; it could be increased by using a water aspirator. 1-(*p*-Biphenyl)-3-phenyl-1-propyne (0.5 g.), dissolved in *n*-pentane was placed on the column. After 5 days the column was eluted with *n*-pentane and *n*-heptane. The solution was filtered and the solvent removed at room temperature, under an atmosphere of nitrogen and reduced pressure. The solid residue was taken up in ether, washed with cold 0.1*N* hydrochloric acid, dilute aqueous sodium bicarbonate solution and finally with cold water. It was dried over anhydrous magnesium sulfate. The ether was removed at room temperature under an atmosphere of nitrogen, using a water aspirator. Light yellow crystals (0.171 g., 34% yield, m.p. 67.2–82.8°C.) were obtained. An admixture of product and starting material showed a depression of the melting point (54°–75°C.). An infrared spectrum of the product was identical with that of racemic 1-(*p*-biphenyl)-3-phenylallene. The rotation was taken in carbon tetrachloride solution, using a 1 dcm. polarimeter tube. $[\alpha]_D^{24}$ $+8.57°$, (*c* 10.03); observed rotation α_D^{24} $+0.860 \pm 0.029$.

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[13] D. J. Cram, *J. Am. Chem. Soc.*, **74**, 5518 (1952).