Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.83; H, 9.97.

Chloranil Dehydrogenation of β-Tetramer.—An anhydrous benzene solution (250 ml) of β-tetramer (3.00 g, 0.0187 mole) and sublimed chloranil (15.0 g, 0.0525 mole) was gently refluxed under dry nitrogen for 36 hr. Periodically, samples were removed and analyzed by gas chromatography on a DEGS column. Only the tetramer was detected initially, but within 1 hr several substances had formed with longer retention times. The most abundant of these new materials had a retention time identical with that of either of the dimethyltetralins. At the end of 4 hr a third product with a retention time equal to that of either of the dimethylnaphthalenes was present to the same extent as the tetralin; the amount of unreacted tetramer still exceeded their combined amounts. After 10 hr the ratio of tetramer to tetralin to naphthalene was about 2:1:1. By the end of 36 hr the naphthalene peak was the only one present, although the chromatogram suggested the presence of trace amounts of both tetramer and tetralin. The cooled, brown reaction solution was filtered, the solvent was removed *in vacuo*, and the residual solid was triturated with hot *n*-pentane. The combined extracts were taken to dryness and the tan, semisolid (3.2 g) was placed directly on an alumina column (activity I, neutral, 125 g, packed in hexane). Elution with *n*-hexane (500 ml) gave an off-white, naphthalenic material (1.12 g), which was sublimed twice: mp 70–85°; infrared spectrum, 3040 and 3010 w, 2900 m, 1630 and 1600 mw, 1505 mw, 960 and 905 mw, 882 m, 830 and 815 s, and 632 mw cm^{-1}; ultraviolet spectrum, 228 mμ (log ε 5.03), 273 (3.69), 302 (2.64), 309 (2.69), 317 (2.56), and 323.5 (2.75). Gas chromatography at 179° on a 12-ft column packed with 15% Bentone-34 combined with 5% SE-30 methyl silicone gum using a hydrogen flame detector resolved the product into two components (44:56) with retention times of 53.7 and 57.1 min, respectively.

A 52:48 mixture of 2,6-dimethylnaphthalene and 2,7-dimethylnaphthalene possessed an infrared spectrum almost identical with that exhibited by the naphthalenic material isolated from the dehydrogenation of the β-tetramer. A 1:1 mixture of both dimethylnaphthalenes closely approximated the ultraviolet spectrum of the dehydro-β-tetramer. Both 2,6- and 2,7-dimethylnaphthalene individually have similar, but different infrared and ultraviolet spectral patterns. On the Bentone-34 column, the retention times for 2,6- and 2,7-dimethylnaphthalene are 53.4 and 57.1 min, respectively.[24] A 1:1 mixture gave a resolution pattern and retention times identical with that of the dehydro-β-tetramer sample.

Another portion (0.080 g) of the dehydro-β-tetramer was dissolved in ethanol (5.0 ml) containing picric acid (0.150 g) and on standing gave yellow needles (0.180 g), mp 124–130°. The naphthalene mixture (0.075 g) recovered from decomposition of the picrate on an alumina column (activity I, basic, 5 g) with ether elution gave a product, which, on sublimation, possessed properties identical with those described previously for dehydro-β-tetramer. An equal mixture of 2,6- and 2,7-dimethylnaphthalenes (0.050 g) was used to prepare a picrate analogous to the above procedure (yellow needles), mp 120–130°. In one experiment, repeated recrystallization, rechromatography, and resublimation of the picrate (0.785 g) derived from dehydro-β-tetramer gave a small amount of 2,7-dimethylnaphthalene, mp 93–94°; the picrate had mp 131–133° and depressed melting points with 2,6-dimethylnaphthalene and the corresponding picrate.

Registry No.—Allene, 463-49-0; 2,6-dimethylenebicyclo[4.4.0]dec-9,10-ene, 13064-99-8; 2,7-dimethylenebicyclo[4.4.0]dec-9,10-ene, 13065-00-4; 2,6-dimethyl-[4.4.0]dec-9,10-ene, 13065-01-5; 2,7-dimethyl[4.4.0]dec-9,10-ene, 13065-02-6; 2,6-dimethyl[4.4.0]decane, 1618-22-0; 2,7-dimethyl[4.4.0]decane, 3868-66-4; 2-methylene-6-methyl[4.4.0]dec-9,10-ene, 13065-04-8; 2-methylene-7-methyl[4.4.0]dec-9,10-ene, 13065-05-9; 2,6-dimethyl-1,2,3,4-tetrahydronaphthalene, 7524-63-2; 2,7-dimethyl-1,2,3,4-tetrahydronaphthalene, 13065-07-1.

Acknowledgment.—Appreciation is expressed to the William Nichols Fellowship Fund and the Dow Chemical Co. for financial assistance to A. H. Fenselau.

Aryl-Substituted Propargyl Alcohols and Related Compounds. II. 1-Mesityl-1,3-diphenyl-2-propyn-1-ol and 1-(α-Naphthyl)-1,3-diphenyl-2-propyn-1-ol[1,2]

THOMAS L. JACOBS, CALVIN HALL, DONALD A. BABBE, AND PAIROJE PREMPREE

Contribution No. 2011 from the Department of Chemistry, University of California at Los Angeles, Los Angeles, California

Received December 9, 1966

An acetylene–allene rearrangement occurs during conversion of 1-mesityl- and 1-(α-naphthyl)-1,3-diphenyl-2-propyn-1-ol to chlorides; the latter have allenyl structures. The relative ease of attack at the propargyl and allenyl positions of the carbonium ions (IV) formed from these and related alcohols and chlorides appears to depend on the hindrance around the unsaturated system. The mesityl chloro compound yields allenyl ethers with sodium alkoxides but in the α-naphthyl series only propargyl ethers were isolated although with sodium ethoxide some of the allene was probably formed. All of the compounds are readily converted to α,β-unsaturated ketones. Infrared spectra in the region 1000–1300 cm^{-1} are not very useful to distinguish propargyl from allenyl ethers and are worthless to show that a given reaction mixture has both such ethers present.

It was suggested earlier[1] that reactions of aryl-substituted propargyl alcohols such as I are best understood on the basis of carbonium ion intermediates such as IV. Reversible reactions were generally found to yield allenic products such as II or products expected from further reactions of the allenes (*e.g.*, VII). Attack on IV appeared to occur more rapidly at the propargyl position unless that position was hindered. The present work was undertaken to show the generality of these suggestions and to explore more carefully the effect of hindrance around the carbon adjacent to the acetylenic group.

Most of the halides described in the first paper[1] had been reported earlier to have propargyl structures (IIIa, b, and b′) but all in fact were allenyl halides (IIa, b, and b′) and infrared spectral studies failed to show that the propargyl halides were present in the crude reaction mixtures. Repeated attempts to obtain halides of propargyl structures were unsuccessful; it was suggested that, with a leaving group as good as

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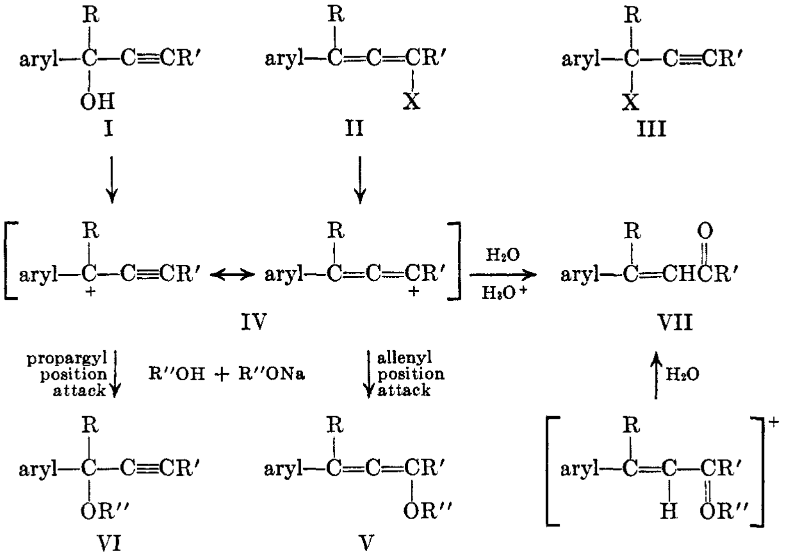
[1] For part I, see T. L. Jacobs and D. M. Fenton, *J. Org. Chem.*, **30**, 1808 (1965), where references are given to earlier work on compounds of the type discussed in the present paper.

[2] This research was supported by grants from the National Science Foundation and the U. S. Army Research Office (Durham). Calvin Hall received support from the National Science Foundation Undergraduate Research Participation Grant.

SCHEME I



a, aryl = R = R' = C_6H_5; X = Br or Cl; R'' = CH_3 or C_2H_5
b, aryl = R' = C_6H_5; R = $C(CH_3)_3$; X = Br or Cl; R'' = CH_3
b', aryl = C_6H_5; R = R' = $C(CH_3)_3$; X = Br or Cl
c, aryl = mesityl; R = R' = C_6H_5; X = Cl; R'' = CH_3 or C_2H_5
d, aryl = α-naphthyl; R = R' = C_6H_5; X = Cl; R'' = CH_3 or C_2H_5

halide ion, propargyl halides such as III, even if formed more rapidly, would rearrange under the reaction conditions to allenyl halides which would be expected to be more stable because the aryl group (or groups) could conjugate with the double bonds.

The compounds reported in the present paper are 1-mesityl-1,3-diphenyl-2-propyn-1-ol (Ic), 1-(α-naphthyl)-1,3-diphenyl-2-propyn-1-ol (Id), and compounds derived from them. The chlorides from both of these alcohols are sharp-melting solids which have infrared spectra compatible only with structure II. The crude reaction mixtures gave no evidence for the presence of the propargyl isomers (III). Carbinol Ic and the compounds derived from it are new, but Id was prepared earlier[3] and converted to a chloride.

In earlier work[1] it was found that 1,1,3-triphenyl-2-propyn-1-ol (Ia) and the corresponding allenyl bromide were readily converted to ethers of propargyl structure VIa, but that 1-bromo-4,4-dimethyl-1,3-diphenyl-1,2-pentadiene (IIb, X = Br) gave an allenyl ether, Vb (R = CH_3), by reaction with sodium methoxide (Scheme I). This observation was the basis for the suggestion that the relative ease of attack on IV at the propargyl and allenyl positions could be controlled by the hindrance at these positions. An S_N2 displacement of halide ion by alkoxide ion was regarded as an unlikely mechanism for formation of Vb because sodium iodide in acetone fails to attack IIb (X = Br).

The present work also supports the idea that the position of attack on the carbonium ion depends upon hindrance. Allenyl chloride IIc gave only allenyl ether Vc (R'' = CH_3), by reaction with sodium methoxide; there was no spectral evidence for the presence of the propargyl ether VIc (R'' = CH_3) in the crude reaction mixture, but the band near 2240 cm^{-1} is often weak and small amounts of VIc could have escaped detection. Compound Vc (R'' = CH_3) is a solid which melts sharply; IIc (X = Cl) was also allowed to react with sodium ethoxide and gave a sharp-melting solid which was presumed to be the allenyl ethyl ether Vc (R = C_2H_5), on the basis of its infrared spectrum; this compound was not completely characterized.

Allenyl chloride IId appeared to give a mixture of allenyl and propargyl ethers, Vd and VId (R'' = C_2H_5), by reaction with sodium ethoxide. The evidence for Vd is tenuous however because the infrared band at 1940 cm^{-1} was not enough stronger than the aryl band in that region to make the presence of an allene certain; moreover, some starting chloride may have remained. A pure, crystalline compound could not be isolated by simple crystallization, but the pure propargyl ether VId (R = C_2H_5) was obtained by chromatography. Reaction of Id with ethanol in the presence of concentrated sulfuric acid also gave a mixture which contained VId and possibly Vd, but this reaction gave some of the α,β-unsaturated ketone VIId as well and left some unchanged starting material; small amounts of VId were isolated. The evidence for Vd (R = C_2H_5) in this acidic ethanol reaction consisted of an infrared band at 1940 cm^{-1} which appeared to be stronger than the aryl band expected at about that position. It would be expected that Vd (R = C_2H_5) would be hydrolyzed rapidly to VIId. Compound IId (X = Cl) was also allowed to react with sodium methoxide in dry methanol. A crystalline solid of sharp melting point was obtained by concentration of the reaction mixture; this was the methyl propargyl ether VId (R'' = CH_3). There was no evidence of Vd (R'' = CH_3) in this experiment.

An attempt was made to show that allenyl ethers were present in the products from IId and alkoxides by examination of the infrared bands in the 1000- to 1300-cm^{-1} region. Unsaturated ethers containing the grouping =CO give[4] strong bands in the range 1270–1230 cm^{-1}. The allenyl ether Vc (R'' = CH_3) has a very strong band at 1240 cm^{-1} and weaker bands (but still strong) at 1023, 1081, 1125, 1171, and 1187 cm^{-1}. The propargyl ether VId (R'' = CH_3) has a fairly

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(3) A. Willemart, *Ann. Chim.* (Paris), [10] **12**, 379 (1929).

(4) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, p 115.

strong band at 1250, but the band at 1065 is much stronger and there are bands at 1023, 1167, and 1224 which are approximately as strong as that at 1250 cm^{-1}; a band at 1202 cm^{-1} is only slightly weaker. 1-Methoxy-1,1,3-triphenyl-2-propyne (VIa, $R'' = CH_3$) has a somewhat similar (but simpler) spectrum with a very strong band at 1072, a medium band at 1257, and bands of moderate strength at 1025 and 1172 cm^{-1}; there is also a weak band at 1212 cm^{-1}. Apparently it is common for propargyl ethers or ethers with the grouping $=C\overset{|}{\underset{|}{C}}O$ to have fairly strong absorption in the range 1200–1300 cm^{-1}. For example, dibenzyl ether[5] absorbs strongly at 1097, 1074, and 1029, but has peaks that are quite strong at 1253, 1271, and 1208 cm^{-1}. Thus the 1000- to 1300-cm^{-1} region is not very useful to distinguish propargyl from allenyl ethers, and is worthless to show that a given reaction mixture has both such ethers present.

The rearrangement of almost any of these compounds to an α,β-unsaturated ketone (VII) occurs readily. In the mesityl series for example VIIc was easily prepared from Ic in acidic, aqueous methanol. Even when Ic in anhydrous methanol containing a little concentrated sulfuric acid was stirred at 0° in an attempt to prepare an ether, the solution became bright yellow and only VIIc could be isolated although no water was used in the work-up. Conversion of Ic to IIc by thionyl chloride and pyridine was successful only when water was very carefully excluded. The allenyl ethers (Vc) would be expected to protonate very rapidly on the central carbon of the allenyl system in the presence of even weak acids and the ion formed should yield VIIc rapidly on contact with water. Compound Vc ($R'' = CH_3$) seemed to be very sensitive to water and was never obtained in analytically pure condition (see the Experimental Section). Compound VIIc was formed immediately when an aqueous suspension of Vc ($R'' = CH_3$) was warmed. In the α-naphthyl series both Id and IId ($X = Cl$) gave VIId when treated with acid in 96% alcohol.

Hydrolysis of allenyl chloride IId ($X = Cl$) in the presence of moist silver oxide in acetone represents an especially interesting reaction because it gave a mixture of the propargyl alcohol Id and the α,β-unsaturated ketone VIId, the latter predominating. This hydrolysis is believed to occur through carbonium ion IVd and separate experiments indicate that Id is not rearranged to VIId under these nonacidic conditions; thus, the distribution of products should reflect the relative rates of attack at the propargyl and allenyl positions of IVd. The hydrolysis conditions were the same as those used to hydrolyze IIb' ($X = Br$)[6] which was reported to give only Ib'. In IVb' there is a tertiary butyl group at each end of the three-carbon propargyl–allenyl system and the relative ease of attack at the two positions might be expected to be greater at the propargyl position by comparison with IVd. Compound IId ($X = Cl$) also presents a contrast with IIa ($X = Cl$) which was reported[7] to yield Ia when refluxed with aqueous acetone. The conditions in this hydrolysis were different because no silver oxide was included and the solution would have become acidic as the reaction proceeded; neither is it certain that VIIa was not produced, although one would have expected it to be mentioned and the description is sufficiently detailed to imply a high yield of Ia. It is significant that even under these conditions which might have caused rearrangement of Ia to VIIa the propargyl derivative is the product. These experiments support the suggestion that position of attack on carbonium ions such as IV does depend on hindrance, but more carefully controlled experiments are needed and will be reported later.

Experimental Section

All nmr spectra were taken on a Varian A-60 instrument; compounds were dissolved in carbon tetrachloride, and tetramethylsilane was used as an external standard. Infrared spectra were taken on Perkin-Elmer 421 or 21 spectrophotometers. Melting points are uncorrected. Analyses were carried out by Miss Heather King in the University of California at Los Angeles laboratories except as noted.

1-Mesityl-1,3-diphenyl-2-propyn-1-ol (Ic).—Mesityl phenyl ketone, bp 135–139° (1 mm) was prepared in 81% yield from benzoyl chloride, mesitylene, and aluminum chloride by the Perrier[8] modification of the Friedel-Crafts reaction. Phenylethynylmagnesium bromide was prepared under nitrogen from 0.15 mole of ethylmagnesium bromide and 15.3 g (0.15 mole) of phenylacetylene in 75 ml of di-*n*-butyl ether. The solution was refluxed while 22.4 g (0.10 mole) of mesityl phenyl ketone was added during 2 hr, then refluxed for 36 hr; a dark red color developed. The mixture was decomposed with aqueous ammonium chloride and ice. The organic layer was separated, washed in the usual manner, and dried over anhydrous sodium sulfate. Solvent was removed under reduced pressure leaving a viscous oil which was taken up in 96% ethanol; cooling gave 9.1 g (28% yield) of dark brown crystals. The crystals were decolorized and recrystallized from 96% ethanol to give light yellow crystals, mp ~65°. An analytical sample was obtained by chromatography on activated alumina, grade I/II (elution with 50:50 benzene–ether). Solvent was removed from the eluate and the residue was recrystallized from petroleum ether (bp 40–60°) to yield small, white crystals, mp 66–67°. The infrared spectrum showed absorption at 3570 (hydroxyl), 2220 (internal triple bond), and around 1670 cm^{-1} (aromatic); there was no carbonyl absorption.

Anal. Calcd for $C_{24}H_{22}O$: C, 88.31; H, 6.79. Found: C, 88.21; H, 6.70.

1-Chloro-1,3-diphenyl-3-mesitylpropadiene (IIc).—All apparatus for the synthesis was dried at 120° and kept in a vacuum desiccator until use. The liquid reagents were distilled from a dried apparatus immediately before use. All solutions were added to the reaction flask by means of a hypodermic syringe.

A solution of 0.41 g (0.035 mole) of thionyl chloride and 0.55 g (0.070 mole) of dried pyridine was placed in a 50-ml, three-necked flask fitted with syringe cap, magnetic stirrer, and reflux condenser with attached drying tube. The solution was cooled to 0° and stirred rapidly as 1.14 g (0.035 mole) of Ic in 20 ml of carefully dried ether was added. A flocculent, white precipitate formed immediately and prevented further stirring. The reaction mixture was allowed to warm to room temperature and stand for 15 hr; it was cooled to 0°, filtered, and concentrated on a hot plate to leave a viscous oil. Solution of the oil in warm ether–ethanol and cooling gave crystals. Several recrystallizations gave material: mp 124–125°; infrared absorption at 1925 (allene), no absorption at 2220 cm^{-1}. The nmr spectrum showed only peaks corresponding to aromatic hydrogens (τ 2 to 3), and two peaks at 7.7 and 7.8 corresponding to the three methyls of the mesityl group.

Anal. Calcd for $C_{24}H_{21}Cl$: C, 83.58; H, 6.14; Cl, 10.28. Found: C, 83.39; H, 6.29; Cl, 9.87.

1-Methoxy-3-mesityl-1,3-diphenylpropadiene (Vc, $R'' = CH_3$).

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[5] R. Mecke and F. Langenbucher, "Infrared Spectra of Selected Chemical Compounds," Heyden and Sons Ltd., London, 1965.

[6] J. H. Ford, C. D. Thompson, and C. S. Marvel, *J. Am. Chem. Soc.*, **57**, 2619 (1935).

[7] C. Moureu, C. Dufraisse, and C. Mackall, *Bull. Soc. Chim. France*, [4] **33**, 934 (1923).

[8] G. Perrier, *ibid.*, [3] **31**, 859 (1904); L. F. Fieser, "Experiments in Organic Chemistry," 2nd ed, D. C. Heath and Co., Boston, Mass. 1941, pp 192–196.

—Reagent grade methanol was refluxed over sodium methoxide and distilled; the fraction boiling at 64–65° was used. A solution of sodium methoxide was prepared from 10 mg of sodium and 10 ml of methanol. To this was added 100 mg of allenyl chloride IIc in 5 ml of methanol. The mixture was concentrated to 7 ml and allowed to stand in a refrigerator overnight. Small, white crystals formed, mp 107–110°, strong infrared band at 1920 cm^{-1}. These crystals contained considerable sodium chloride; analysis gave the correct carbon–hydrogen ratio but values for both elements were low and the sodium chloride remained as a residue in the boat.

Anal. Calcd for $C_{25}H_{24}O$: C, 88.19; H, 7.11; C/H, 12.39. Found: C, 70.58; H, 5.67; C/H, 12.45.

When Vc was prepared from 0.36 g (0.00105 mole) of IIc in 20 ml of methanol by addition of 0.063 g (0.00118 mole) of sodium methoxide in 10 ml of methanol (overnight shaking at room temperature), concentration to 5 ml and standing at −20° gave small, faintly yellow crystals. These were redissolved in dry ether, the solution was filtered to remove sodium chloride, and solvent was removed. The residue was taken up in warm methanol, concentrated, and allowed to crystallize in a refrigerator. Small, pale yellow crystals (0.146 g, 41% yield) were obtained, mp 105°. The nmr spectrum showed peaks between τ 2 and 3 (aromatic hydrogens), at 7.7–7.8 (three methyl groups, nine protons), and at 6.3 (singlet corresponding to the methoxyl group, three protons). The infrared spectrum showed a strong allenic absorption at 1920, strong bands at 1240 and 1020 as expected for =COC, and no absorption at 2240 cm^{-1}. There was also a weak band at 1670 cm^{-1} attributable to small amounts of the unsaturated ketone VIIc; this band was absent in the spectrum of the solid obtained directly from the reaction mixture. The analysis of these crystals was carried out by Elek Laboratories which entailed a delay of several days. The analysis is in better agreement with values for ketone VIIc and it is presumed that conversion to the ketone occurred during exposure to the laboratory atmosphere.

Anal. Calcd for $C_{24}H_{22}O$ (VIIc): C, 88.31; H, 6.79. Found: C, 87.51; H, 6.56.

Attempted purification of Vc by crystallization from ordinary methanol gave VIIc.

1-Ethoxy-3-mesityl-1,3-diphenylpropadiene (Vc).—The first procedure described above was used to prepare the ethyl ether. Small, slightly yellow crystals, mpl 30–133°, were obtained. These displayed very weak carbonyl absorption (1670 cm^{-1}), but were characterized by a strong allenic absorption at 1920 cm^{-1}.

1,3-Diphenyl-3-mesityl-2-propen-1-one (VIIc).—To a cold solution of 2 ml of concentrated sulfuric acid in 10 ml of anhydrous methanol cooled to 0° was added 100 mg of Ic. The mixture was stirred rapidly for 1 hr and became bright yellow. The solution was poured into water and extracted with ether. The product isolated by concentration of the ether solution was recrystallized from ethanol to yield bright yellow crystals, mp 86–87°. The infrared spectrum showed a strong band at 1670 cm^{-1}. The nmr spectrum showed a vinyl proton at τ 3.7, the methyl protons on the mesityl group at 7.8 (9:1 ratio to the vinyl proton), and aromatic protons between 2 and 3.2.

Anal. Calcd for $C_{24}H_{22}O$: C, 88.31; H, 6.79. Found: C, 88.57; H, 6.94.

The ketone was characterized as the 2,4-dinitrophenylhydrazone, mp 235°.

Anal. Calcd for $C_{30}H_{26}N_4O_4$: C, 71.13; H, 5.17. Found: C, 71.21; H, 5.14.

1-Chloro-3-(α-naphthyl)-1,3-diphenylpropadiene (IId).—1-(α-Naphthyl)-1,3-diphenyl-2-propyn-1-ol (Id) was prepared as described by Willemart[3] and converted to IId with phosphorus trichloride. This reagent was also used by Willemart[3] to prepare the chloride, but he reported the product to be far less stable than our chloride although of higher melting point; so the procedure will be given. To 12.4 g (0.037 mole) of Id in 50 ml of anhydrous ether was added 2 g (0.015 mole) of phosphorus trichloride in 10 ml of ether and the solution was stirred at room temperature for 2 hr. A white solid separated and was washed with a little dry ether leaving material, mp 124–125° (yield 50%); recrystallization did not improve the melting point, although Willemart[3] reported that his chloride melted at 130–131° (block Maquenne). Unless care was taken to exclude moisture the chloride precipitated as an impure semisolid. The infrared spectrum of the chloride showed an allenic band at 1935 cm^{-1} (far stronger than the series of weak bands between 2000 and 1700 cm^{-1} which characterize phenyl rings); there was no ketonic band at 1658 nor was there an acetylenic band around 2240 cm^{-1}. Concentration of the mother liquor from the reaction gave an additional 2 g of impure IId, mp 118–120° which contained unsaturated ketone VIId on the basis of its infrared spectrum; there was no spectral evidence for the presence of any acetylenic chloride IIId nor starting carbinol Id, although the acetylenic band at 2240 cm^{-1} for the latter is somewhat stronger than is often encountered with such substituted propargyl alcohols. The chloride appeared to be unchanged after 2 days of standing; its infrared spectrum and melting point remained the same.

Compound IId was also obtained when 2.75 g (0.00824 mole) of Id in 50 ml of dry ether was added in one portion to 1 g (0.0084 mole) of thionyl chloride in 1.3 g (0.0165 mole) of dry pyridine at 0°. The reaction mixture was stirred in an ice bath for 3 hr and overnight at room temperature. A solid (presumably pyridine hydrochloride) was removed by filtration, the filtrate was concentrated, and the residue was taken up in hot ethanol. The ethanol solution was left in a refrigerator and gave 1.2 g (40% yield) of white crystals, mp 122–123°. The infrared spectrum was the same as described above for IId, and the nmr spectrum showed only aromatic protons between τ 2 and 3.

Anal. Calcd for $C_{25}H_{17}Cl$: C, 85.10; H, 4.86. Found: C, 84.71; H, 5.22.

Ether Formation.—To a solution of 2 g of sodium in 100 ml of anhydrous ethanol was added 1 g of IId; the reaction mixture was stirred for 2 days at room temperature, concentrated at reduced pressure, and extracted with ether. The ether layer was separated, dried, and concentrated to give a broad-melting solid. The infrared spectrum of this product indicated the presence of a propargyl ether (sharp band at 2220 cm^{-1}) but the band at 1940 was not enough stronger than the weak aromatic bands between 2000 and 1660 cm^{-1} to indicate with certainty the presence of an allenyl ether; there was no absorption at 1670 cm^{-1} which indicated that the α,β-unsaturated ketone (VIId) was absent or nearly so.

The crude product was dissolved in pentane and chromatographed on neutral alumina to give a small amount of a light yellow, crystalline material, mp 126.5–127.5°. The infrared spectrum of this solid showed the sharp band at 2220, characteristic of an internal acetylene and only a series of low, broad bands between 1660 and 2000 cm^{-1}. The spectrum also showed a weak band at 1670 cm^{-1} which indicated the presence of a little VIId. It would not be surprising if any allenyl ether present was transformed into VIId on the chromatographic column.

To 0.065 g (0.0012 mole) of sodium methoxide in 40 ml of dry methanol was added 0.36 g (0.001 mole) of IId. The mixture was shaken overnight at room temperature, filtered to remove a small amount of sodium chloride, and concentrated to 10 ml; slow crystallization in a refrigerator gave 0.2 g (56% yield) of a white solid which melted at 101.5–102.5° after washing with a little dry methanol and drying.

Anal. Calcd for $C_{26}H_{20}O$: C, 89.64; H, 5.79. Found: C, 89.23; H, 5.64.

Infrared gave 3050 (m), 2935 (m), 2820 (m), 2220 (w but sharp), 1937, 1865, 1795, 1740 (four small peaks of decreasing intensity characteristic of monosubstituted benzene derivatives; these peaks are complicated by small side peaks or shoulders that seem characteristic of the α-naphthyl group), 1590 (m), 1498 (m), 1480 (s), 1440 (s), 1435 (m), 1387 (m), 1339 (m), 1251 (m), 1223 (m), 1201 (m), 1166 (m), 1060–1090 (s), and 1023 (m) cm^{-1}. Nmr showed τ 6.72 and absorption between 2 and 3.

Hydrolysis of 1-Chloro-3-(α-naphthyl)-1,3-diphenylpropadiene, (IId).—To 7 g (0.02 mole) of IId in 100 ml of acetone was added the moist silver oxide from 17 g (0.1 mole) of silver nitrate, and the suspension was refluxed for 1 hr, then stirred overnight at room temperature. The suspension was filtered and solvent was removed from the filtrate to yield a sticky, yellow solid. An infrared spectrum indicated that IId had reacted completely but both Id and VIId were present. The latter was the main component of the mixture and was isolated by recrystallization from alcohol as a yellow, crystalline compound, mp 106–107° (lit.[3] mp 107–108°). This procedure is the same as was used for hydrolysis of IIb′ (X = Br).[6]

Registry No.—Ic, 13124-90-8; Id, 13124-91-9; IIc, 13124-92-0; IId, 13124-93-1; Vc (R″ = Me), 13124-94-2; VIIc, 13124-95-3; VIIc 2,4-dinitrophenylhydrazone, 13124-96-4; VIId, 13124-89-5.