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ARYLALLENES—III

TRIPHENYLALLENE AND 1-(*p*-BIPHENYL)-1,3-DIPHENYLALLENE[1,2]

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Abstract—1,1,3-Triphenylallene and 1-(*p*-biphenyl)-1,3-diphenylallene have been prepared by rearrangement of 1,3,3-triphenylpropyne and 3-(*p*-biphenyl)-1,3-diphenylpropyne on basic alumina. Triphenylallene was also obtained by rearrangement of triphenylpropyne in a hydrocarbon solution with solid sodium hydroxide. Treatment of triphenylallene in glacial acetic acid with hydrogen chloride converted it to the dimer which had been isolated in earlier attempts by others to synthesize the allene.

THERE have been a number of attempts to synthesize triphenylallene[4–7] or other triarylallenes[5,8] by elimination of HX from $\text{Aryl}_2\text{CXCH{=}CHAryl}$ or $\text{Aryl}_2\text{C{=}CHCHXAryl}$ ($X = Cl, OH, OCH_3$) under conditions which give good yields of tetra-arylallenes from $\text{Aryl}_2\text{C{=}CHCXAryl}_2$. The first such attempt[4] was reported to yield triphenylallene, but the product was later reported to be a dimer on the basis of a Rast molecular weight determination. Most of the elimination reactions mentioned yield products with the composition of allenes but molecular weights corresponding to dimers. Some uncertainty was created about the dimeric nature of these compounds when it was observed[2] that diarylallenes, shown by low-temperature molecular weight determinations to be monomeric, gave molecular weights corresponding to dimers by the Rast method because dimerization occurred at the high temperatures of the determination.

We reported[2] the synthesis of 1,3-diarylallenes by rearrangement of the corresponding 1,3-diarylpropynes on the surface of basic alumina, solid sodium hydroxide or solid potassium hydroxide. These methods have now been used to synthesize triphenylallene and 1-(*p*-biphenyl)-1,3-diphenylallene. The yield of triphenylallene was high and was slightly better with mildly basic alumina than with sodium hydroxide pellets as the reagent. The product which we obtained was different from the material previously reported as the dimer. Rearrangement of 3-(*p*-biphenyl)-1,3-diphenylpropyne to 1-(*p*-biphenyl)-1,3-diphenylallene required alumina impregnated with 20% sodium hydroxide as the reagent and then gave 62% of only moderately pure product.

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[2] For previous papers see T. L. Jacobs and S. Singer, *J. Org. Chem.* **17**, 475 (1952); T. L. Jacobs and D. Dankner, *J. Org. Chem.* **22**, 1424 (1957).

[3] Rocket Power Research Laboratories, Pasadena, California.

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The structure of the triphenylallene was assigned on the basis of composition, molecular weight (determined cryoscopically in benzene), hydrogenation to 1,1,3-triphenylpropane, and spectra. The infrared spectrum has a strong band at 1944 cm^{-1} characteristic of allenes. Substituted benzene derivatives have a series of weak bands between 1650 and 2000 cm^{-1} [9]. There are usually four such bands in monosubstituted benzenes and the one at shortest wavelength is usually very near the position of the allene band. If one compares these bands in the spectra of triphenylallene and 1,3,3-triphenylpropyne there is close similarity except that the 1944 cm^{-1} band for the allene is much stronger than the corresponding absorption (1956 cm^{-1}) for the acetylene. The acetylene also shows bands characteristic of carbon-carbon triple bond stretching (2242 (m), 2232 (w) cm^{-1}) which are absent in the allene.

The UV absorption spectrum of triphenylallene is characterized by a strong peak at 259 mμ, two poorly defined peaks of slightly lower intensity at 234 and 240 mμ, and a shoulder at 289 mμ. As with 1,3-diphenylallene[2] the strongest peak lies at somewhat longer wavelengths than the most intense peak for styrene (246 mμ) or 1,1-diphenylethylene (240 mμ) and the extinction coefficient for this allene peak is higher than for either of the olefins (but less than the sum of the two).

Treatment of triphenylallene in glacial acetic acid with dry hydrogen chloride or with a few drops of conc. sulfuric and hydrochloric acids produced the dimer reported earlier.[4,6,7] These experiments make it probable that in the earlier attempts to synthesize triarylallenes, monomers were actually produced, and that they dimerized under the reaction conditions. The structure of this and related dimers will be discussed later.

An attempt was made to prepare optically active 1-(*p*-biphenyl)-1,3-diphenylallene by asymmetric rearrangement of 3-(*p*-biphenyl)-1,3-diphenylpropyne on alumina impregnated with brucine or quinine as was done with diarylallenes.[2] The acetylene was synthesized from 4-phenylbenzhydryl chloride and phenylethynylmagnesium bromide as for triphenylpropyne, and rearranged to the allene on basic activated alumina. However asymmetric rearrangement failed; either no rearrangement occurred or impure allene of very low rotation was obtained.

EXPERIMENTAL

IR spectra were obtained with a Perkin-Elmer spectrophotometer Model 21 equipped with an NaCl prism. UV spectra were measured with a Beckman Model DU spectrophotometer. M.ps. are corrected except where noted.

Triphenylallene

A solution of 2·06 g. 1,3,3-triphenylpropyne[10] m.p. 78–78·5° (reported m.p. 79°) in 75 ml. *n*-heptane and 25 ml pet. ether (b.p. 20–40°) was passed rapidly through a 1·7 × 10 cm. column of activated alumina[2] which had been dried for 5 days at 160–175°. Elution was carried out at once with *n*-heptane; lower yields were obtained if the column was allowed to stand before elution. The eluate was filtered and the solvent removed at red. press. to give 1·72 g (83·5%) of the allene, m.p. 77·5–79°. The m.p. of a mixture with starting acetylene showed marked depression. Sometimes a yellow impurity was present; this could be removed by rapid chromatography from solution in pet. ether (b.p. 20–40°) on a short column of undried activated alumina. The allene melted to a green liquid which did not resolidify when cooled.. (Found: C, 93·90; H, 6·07; M.W. (cryoscopic in benzene), 260. Calcd. for $C_{21}H_{16}$: C, 93·99; H, 6·01%; M.W., 268·3).

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[9] L. J. Bellamy, *The Infrared Spectra of Complex Molecules* (2nd Ed.) pp. 67–69. John Wiley, New York (1958).

[10] H. Wieland and H. Kloss, *Liebigs Ann.* **470**, 201 (1929).

The equilibrium vapor pressure method used for determination of the mol. wt. of 1-(*p*-bromophenyl)-3-(*β*-naphthyl)-allene[2] proved ineffective with triphenylallene because dimerization or polymerization occurred in the equilibrating solution at r.t.; the mol. wt. calculated from the data rose steadily throughout the experiment and reached 409 after 32 days.

IR spectra (25% *solutions in* CCl_4). Triphenylallene: 3046 (s), 1939 (s), 1887 (m), 1812 (m), 1760 (w), 1687 (w), 1662 (w), 1600 (s), 1487 (s), 1449 (s), 1384 (m), 1326 (m), 1305 (m), 1282 (m), 1271 (m), 1242 (w), 1193 (m), 1176 (m), 1157 (m), 1102 (m), 1093 (m), 1069 (s), 1026 (s), 1000 (w), 965 (w), 908 (s). 1,3,3-Triphenylpropyne: 3054 (s), 2904 (s), 2844 (s), 2332 (w), 2242 (w), 1956 (m), 1880 (m), 1805 (m), 1756 (w), 1673 (w), 1600 (s), 1488 (s), 1451 (s), 1384 (m), 1337 (m), 1324 (m), 1289 (m), 1272 (m), 1235 (w), 1181 (m), 1156 (m), 1097 (w), 1070 (s), 1025 (s), 910 (s), 846 (w and broad).

UV spectra (*in n-heptane*). Triphenylallene: λ_{max}, 234, 240, 260, 289 (shoulder); log ϵ, 4·35, 4·36, 4·50, 3·95. 1,3,3-Triphenylpropyne: λ_{max}, 242, 253, 271 (shoulder), 279; log ϵ, 4·39, 4·34, 2·95, 2·63.

Triphenylallene was obtained in 74% yield when a solution of the propyne in a mixture of heptane and pet. ether was shaken at r.t. for 15 hr in contact with NaOH pellets. No rearrangement occurred when the acetylene was shaken with Na_2CO_3 or when a solution was chromatographed on undried alumina or on alumina treated with ethyl acetate and dried at 160–170°.

Hydrogenation of 500 mg triphenylallene in methanol over 10% Pd–C resulted in absorption of 2 mol. equiv. H_2. Recrystallization of the product from methanol gave 64 mg 1,1,3-triphenylpropane, m.p. 42·5–45°, no depression when mixed with authentic 1,1,3-triphenylpropane,[10] m.p. 44·5–45·5°. A solid, m.p. 202–208° unc., was also isolated in low yield. A mixture of this solid with the triphenylallene dimer, m.p. 218·5–219·5°, gave a large m.p. depression.

Dimerization of triphenylallene

Dry HCl was bubbled for 40 min into a stirred solution of 400 mg triphenylallene in 40 ml gl. acetic acid. The white solid which precipitated was collected and recrystallized from ether to give 192 mg (48% yield) of dimer, m.p. 215–216°. About the same yield of this dimer was obtained when a solution of 11·6 mg the allene was heated at 100° for 45 min in 1 ml acetic acid containing 2 drops conc. H_2SO_4 and 1 drop conc. HCl. Recrystallization from benzene gave white crystals, m.p. 218·5–219·5°; a mixture of these with the material m.p. 218·5–220·5° prepared from diphenylstyrylcarbinol[4,6] showed no m.p. depression.

3-*Biphenyl*-1,3-*diphenylpropyne*

4-Phenylbenzophenone was reduced with Zn and NaOH[11] to give a quantitative yield of crude 4-phenylbenzhydrol, m.p. 93–95° (reported m.p. 95–96°[12]). The alcohol was converted to the chloride with thionyl chloride[12]; recrystallization from heptane gave material m.p. 60–65°.

To the stirred Grignard reagent from 2·7 g Mg and 12 g (0·11 mole) C_2H_5Br in 75 ml anh. ether was added dropwise 11·2 g (0·11 mole) phenylacetylene in 75 ml ether. The mixture was stirred for an additional hour and a solution of 27·9 g (0·1 mole) of 4-phenylbenzhydryl chloride dissolved in 25 ml ether and 125 ml benzene was added dropwise. The mixture was then refluxed for 4 hr, poured on ice and worked up as usual with dil. HCl. Some difficulty was experienced in obtaining crystalline material but a total of 18·4 g (54%) of material melting between 110° and 116° was isolated in several fractions. Careful recrystallization from pentane gave white crystals, m.p. 117–118·5°. (Found: C, 93·87; H, 6·13; M.W. (cryoscopic in benzene), 329. Calcd. for $C_{27}H_{20}$: C, 94·15; H, 5·85%; M.W. 344·4).

IR spectrum (25% *solution in* CCl_4): 3036 (s), 2864 (m), 2237 (w), 1956 (m), 1880 (m), 1805 (m) 1756 (w), 1673 (w), 1600 (s), 1570 (m), 1484 (s), 1454 (s), 1409 (s), 1384 (m), 1324 (s), 1292 (s), 1273 (s), 1233 (w), 1176 (m), 1155 (m), 1108 (m), 1067 (s), 1025 (s), 1003 (m), 960 (w), 908 (s), 840 (s and broad). This spectrum is very similar in appearance to that of 1,3,3-triphenylpropyne.

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[11] F. Y. Wiselogle and H. Sonneborn, *Org. Syn.*, Coll. Vol. I (2nd Ed.) pp. 90–91 (directions for benzophenone). John Wiley, New York (1941).

[12] E. Bergmann, *Ber., Dtsch. Chem. Ges.* **63**, 1617 (1930).

1-(p-*Biphenyl*)-1,3-*diphenylallene*

A solution of 474 mg 3-biphenyl-1,3-propyne in pentane was adsorbed on a 2 × 9 cm column of alumina impregnated with 20% by weight of NaOH (column material dried 79 hr at 150°) and eluted with pentane under slight press. The eluate gave 293 mg crude allene, m.p. 105–109°. The remainder was a green oil that refused to crystallize. Purification of the allene by recrystallization from pentane and rapid chromatography on undried alumina gave white needles, m.p. 105·5–107°; a mixture with starting acetylene gave a large melting point depression. (Found: C, 93·96; H, 6·00. Calcd. for $C_{27}H_{20}$: C, 94·15; H, 5·85%).

IR spectrum (11% *solution in* CCl_4); 3036 (s), 1935 (s), 1892 and 1878 (m, doublet), 1804 (m), 1753 (w), 1677 (w), 1600 (s), 1489 (s), 1448 (s), 1410 (s), 1384 (m), 1309 (m), 1272 (m), 1190 (m), 1155 (w), 1101 (m), 1088 (m), 1068 (m), 1025 (m), 1004 (m), 963 (w), 905 (s), 840 (m), 818 (m and broad).