

was 53.4% of the total. When corrected for recovered starting material the over-all yield was 89.5% and the yields of **4** and **3** were 34.2 and 47.9%, respectively.

**Reaction of 2 with Magnesium Bromide Etherate. Ammonium Chloride Work-Up.**—Magnesium bromide etherate was prepared by the method of Storfer and Becker<sup>16</sup> from 30.5 g. of magnesium and 235 g. of ethylene bromide in a total of 2500 ml. of anhydrous ether. The lower, pale yellow, layer contained 2.55 mmoles of  $MgBr_2$ /ml. by titration for bromide. To a mixture of 200 ml. of this solution and 200 ml. of anhydrous ether was added, at a rapid dropwise rate, an ether solution of 42 g. (0.25 mole) of **2** in 100 ml. of anhydrous ether. The mixture was refluxed 3 hr. after addition during which time a precipitate separated. The mixture was poured into cold ammonium chloride solution, and the resulting mixture was extracted with ether. The combined ether extracts were dried over anhydrous sodium sulfate. After filtering free of drying agent, the ether was removed by distillation at atmospheric pressure through a 12-in. Vigreux column. A residue of 29 g. of light oil remained. This oil exhibited infrared absorption at 2720, 1738, 1715  $cm^{-1}$  and no peaks at 2820 and 2780  $cm^{-1}$  (dimethylamino group).<sup>17</sup> The oil was distilled at 75 mm.; 24 g. were collected at a bath temperature of 40°. This was redistilled through a 6-in. Vigreux column at 125–126° at 760 mm. The pure liquid was identified as diisopropyl ketone by comparison of its infrared spectrum to a known sample, refractive index,  $n_D^{20}$  1.3988 (lit.<sup>18</sup>  $n_D^{20}$  1.4001), and melting point of its 2,4-dinitrophenylhydrazone, 95.5–96° (lit.<sup>18</sup> m.p. 94–98°). The residue from the vacuum distillation was distilled at 75 mm. to give 3.1 g. of the keto aldehyde identified in the next experiment.

**Acid Work-Up.**—The reaction mixture from 0.48 mole of magnesium bromide etherate and 0.24 mole of **2** was poured into 1 l. of cold 1 *N* hydrochloric acid. A residue of 27.4 g. of oil remained following extraction and evaporation of the ether at 760 mm. through a 12-in. Vigreux column. A sample, gas chromatographed on 10% Carbowax 20M at 100°, was shown to be about 95% of the keto aldehyde previously obtained, retention time 15.5 min., and 5% diisopropyl ketone. The oil was distilled at 75 mm. through a 6-in. Vigreux column and a middle cut of 13 g. of 2-formyl-2,4-dimethylpentanone-3 (**5**) boiling at 103.5° was collected. Pertinent infrared peaks (smear) are 2720 m 1738 s, 1703 s, 1395 m, 1385 s, 1367 s, 1350 m  $cm^{-1}$ ; n.m.r.

(16) S. Storfer and E. I. Becker, *J. Org. Chem.*, **27**, 1868 (1962).

(17) W. B. Wright, Jr., *ibid.*, **24**, 1362 (1959).

(18) "Dictionary of Organic Compounds," Vol. 1, I. M. Heilbron and H. M. Bunbury, Eds., Oxford University Press, New York, N. Y., 1943, p. 875.

doublet (6H) at 1.00 and 1.12 [ $(CH_3)_2CH$ ], singlet (6H) at 1.32 [ $(CH_3)_2C=O$ ], multiplet (1H) at 2.7–3.2 [ $CH(CH_3)_2$ ], singlet (1H) at 8.81 p.p.m. ( $HC=O$ ).

*Anal.* Calcd. for  $C_8H_{14}O_2$ : C, 67.57; H, 9.93. Found: C, 67.20; H, 9.71.

**Conversion of 5 to Diisopropyl Ketone.**—A two-phase system of 0.5 g. of **5** and 50 ml. of 1 *N* sodium hydroxide was stirred vigorously at room temperature for 1 hr. The system was extracted with ether, and the ether extract was dried over anhydrous sodium sulfate. The drying agent was filtered. Gas chromatography of the ether solution on 10% Carbowax 20M at 90° showed the sample to be pure diisopropyl ketone. The ether was removed by distillation at 760 mm. through a 6-in. Vigreux column and the residue was distilled to give 0.3 g. of diisopropyl ketone, b.p. 125–126°.

**Treatment of Tetramethylcyclobutane-1,3-dione with Magnesium Bromide Etherate.**—After refluxing 35 g. (0.25 mole) of tetramethylcyclobutane-1,3-dione with 0.5 mole of magnesium bromide etherate for 1 hr. and pouring the reaction mixture into ice, 34.5 g. of starting material was recovered.

**Reaction of Isopropylmagnesium Bromide with 2.**—The Grignard reagent was prepared from 6.1 g. (0.25 mole) of magnesium and 31 g. (0.25 mole) of isopropyl bromide in 75 ml. of anhydrous ether. The gas-collecting system used previously<sup>2</sup> was set up and 16.9 g. (0.1 mole) of **2** in 35 ml. of anhydrous ether were added dropwise. A white precipitate appeared during addition and 1500 cc. of propylene evolved. During the 1-hr. reflux after addition, an additional 50 cc. of propylene was collected. The reaction mixture was poured into cold ammonium chloride solution and worked up in the same fashion as the phenylmagnesium bromide reaction. A crude yield of 11.2 g. of white solid was obtained. The infrared spectrum ( $CCl_4$  solution) was very similar to that of a sample of *trans*-2,2,4,4-tetramethyl-3-dimethylaminocyclobutanol obtained from Tennessee Eastman Co. A very weak  $C=O$  peak was present at 1705  $cm^{-1}$ . The crude material was dissolved in ether and gas chromatographed on 10% Carbowax 20M programmed at 15°/min. from 100 to 240°. It had only one peak with a retention time, 5.2 min., identical with that of the above cyclobutanol. After one recrystallization from petroleum ether (b.p. 30–60°), the infrared spectrum and melting point, 72–73°, were identical with those of the known sample.

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## Aryl-Substituted Propargyl Alcohols and Related Compounds\*<sup>1</sup>

THOMAS L. JACOBS AND DONALD M. FENTON

Contribution 1779 from the Department of Chemistry, University of California, Los Angeles, California

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The halides prepared from aryl-substituted propargyl alcohols Ia, Ib, and Ic, previously reported to have propargyl structures, III, were shown to have allenyl structures, II. Ethers formed from 1,1,3-triphenyl-2-propyn-1-ol (Ib) or from allenyl halide IIb have propargyl structures. Methyl ethers corresponding to both propargyl and allenyl structures were prepared in the 4,4-dimethyl-1,3-diphenyl-1-pentyn-3-ol series (Ic and IIc). The various acetylene-allene rearrangements involved in reactions of these compounds have been explained on the basis of the stabilized carbonium ions, IV.

Investigations of rubenes<sup>2</sup> and of the possibility of dissociation of highly substituted dipropargyl deriva-

tives into radicals<sup>3–10</sup> involved the synthesis of a variety of aryl-substituted, tertiary propargyl alcohols, I, and replacement of the hydroxyls of these alcohols by halogens. The possibility of an acetylene-allene

\* To Professor Louis F. Fieser.

(1) This paper is taken from the Ph.D. Thesis of D. M. Fenton, June 1958. A summary of the work was presented before the Organic Chemistry Division at the 135th National Meeting of the American Chemical Society, Boston, Mass., April 1959; Abstracts, p. 560. This research was supported by the U. S. Army Research Office (Durham).

(2) See A. Willemart, "Traite de chimie Organique," Vol. 17, V. Grignard, G. Dupont, and R. Lorquin, Eds., Maisson et Cie, Paris, 1949, pp. 1241–1298, and also a series of articles by C. Dufraisse [*Bull. soc. chim. France*, [5] **3**, 1847–1913 (1936)] which discusses the revision of the rubene structure from the incorrect biindanyl to the naphthacene. The latter lists, with references, old and new structures for many rubenes (pp. 1866–1871).

(3) K. Hess and W. Weltzien, *Ber.*, **54**, 2511 (1921).

(4) C. Moureu, C. Dufraisse, and A. S. Houghton, *Bull. soc. chim. France*, [4] **41**, 56 (1927).

(5) P. L. Salzberg and C. S. Marvel, *J. Am. Chem. Soc.*, **50**, 2840 (1928).

(6) I. L. Ozanne and C. S. Marvel, *ibid.*, **52**, 5267 (1930).

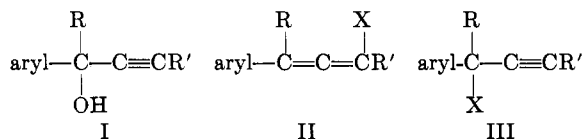
(7) J. G. Stampfi and C. S. Marvel, *ibid.*, **53**, 4057 (1931).

(8) R. S. Sweet and C. S. Marvel, *ibid.*, **54**, 1184 (1932).

(9) J. C. Tsao and C. S. Marvel, *ibid.*, **55**, 4709 (1933).

(10) J. H. Ford, C. D. Thompson, and C. S. Marvel, *ibid.*, **57**, 2619 (1935).

rearrangement to yield II during those displacements was recognized because the halides formed were sometimes less reactive than might have been expected for propargyl compounds III and in some reactions allenyl products were obtained from these chlorides. Never-



a, R = R' = C(CH<sub>3</sub>)<sub>3</sub>  
 b, R = R' = C<sub>6</sub>H<sub>5</sub>  
 c, R = C(CH<sub>3</sub>)<sub>3</sub>; R' = C<sub>6</sub>H<sub>5</sub>  
 aryl = C<sub>6</sub>H<sub>5</sub> (in examples from ref. 2-10 it was sometimes another aryl group)

theless structure III was assigned in the earlier work to all of these halides because hydrolysis under basic, neutral, or very mildly acidic conditions produced the propargyl alcohols I.

In 1957 it was shown<sup>11</sup> that the bromide prepared by Ford, Thompson, and Marvel from 2,2,6,6-tetramethyl-3-phenyl-4-heptyn-3-ol (Ia) with phosphorus tribromide was at least mainly allenic compound IIa. This bromide is a liquid and could have contained an appreciable amount of IIIa which might escape detection because the infrared band at the characteristic acetylenic frequency (2230 cm.<sup>-1</sup>) is often very weak. We have re-examined IIa and confirmed the allenic structure.

It was reported<sup>10</sup> that Ia did not yield a chloride by reaction with phosphorus trichloride. We prepared IIa (X = Cl) by reaction of Ia with thionyl chloride; the product was a liquid which showed a strong allenic infrared band at 1955 cm.<sup>-1</sup> and no acetylenic absorption.

Triphenyl-2-propyn-1-ol (Ib) was converted to a chloride and a bromide to which structures IIIb were assigned on the basis of hydrolysis experiments.<sup>4,12-15</sup> We have repeated these syntheses and obtained solids with the sharp melting points reported earlier. Infrared spectra established that these compounds have allenic structures IIb. Since our work was first reported<sup>1</sup> the reaction of Ib with thionyl chloride has been re-examined<sup>16</sup>; although the chloride could not be isolated, it was reported on the basis of an infrared band at 1920 cm.<sup>-1</sup> that the allenyl chloride was produced first and that it reacted further by dimerization and loss of hydrogen chloride to form 5-chloro-5,12-dihydro-5,6,11,12-tetraphenylnaphthacene.

Another solid halide, m.p. 65°, was prepared earlier<sup>17</sup> by reaction of phosphorus trichloride with 4,4-dimethyl-1,3-diphenyl-1-pentyn-3-ol (Ic) and assigned structure IIIc. We treated Ic with both phosphorus trichloride and thionyl chloride under a variety of conditions but the product always melted at 38.5-39.5°. This compound is an allenic chloride on the basis of its infrared spectrum. We also prepared the bromide IIc, m.p. 61.5-63.0°. It is possible that Willemart actually had

the propargyl chloride IIIc or that differences in melting point may be attributed to different allotropic modifications. The sample of chloride used for melting point determination might also have hydrolyzed to carbinol (m.p. 68°)<sup>17</sup> or to  $\alpha,\beta$ -unsaturated ketone (m.p. 68°)<sup>17</sup> before the melting point was taken; however the analytical sample had the correct composition. In our experiments the crude reaction mixtures had essentially the same infrared spectra as crystalline products; so it is unlikely that acetylene-allene rearrangements occurred during work-up.

Many attempts to isolate propargyl halides corresponding to IIIa-c were unsuccessful. A likely explanation for this failure is that such aryl-substituted propargyl halides rearrange to II under very mild conditions. One would expect halogens in III to ionize readily and allenyl structures II should be considerably more stable because the double bonds of the allenyl system are stabilized by resonance with the aryl and other groups present. Steric factors also favor II. An attempt to synthesize IIIb from phenylethynylmagnesium bromide and dichlorodiphenylmethane gave only allenyl chloride IIb which suggests that rearrangement of III to II occurs readily.

An alternative explanation for formation of allenyl chlorides involves formation of chlorosulfonates which yield allenyl chlorides by a cyclic (S<sub>N</sub>i') mechanism. This mechanism has been suggested and discussed for conversion of substituted aliphatic propargyl alcohols to allenic chlorides.<sup>18,19</sup> It was impossible to isolate such a chlorosulfonate from the reaction of Ic with thionyl chloride at -78°; however, no reaction occurred unless pyridine was present and this base does not favor a cyclic mechanism. The product of the -78° reaction was chloroallene IIc; some Ic was also recovered. Similar cyclic mechanisms can be written for formation of haloallenes II from propargyl alcohols I with phosphorus trihalides. Although we were unable to obtain IIc from Ic by reaction with hydrogen chloride and pyridine hydrochloride at room temperature, IIb and similar chlorides were prepared from the carbinols with hydrogen chloride in alcoholic solution.<sup>20</sup> In these instances such cyclic mechanisms seem less likely (although still possible if a molecule of hydrogen chloride is hydrogen bonded to the hydroxyl group). Additional discussion of the mechanism must await further experimentation. It should be mentioned that these chlorides are usually quite unstable and crystallize with difficulty.

Hydrolysis of halides with structures II to give carbinol I instead of unsaturated ketone V is readily explained. One need merely assume that hydrolysis involves ionization of II to carbonium ion IV which is attacked at the propargyl position far more rapidly than at the allenyl position. Under conditions which favor irreversibility I would be stable and survive as the main product. Under more strongly acid conditions either I or II yields V. For the carbinol this represents the well-known Meyer-Schuster rearrangement.<sup>21</sup> Under these conditions one would expect

(11) J. Wotiz and D. Mancuso, *J. Org. Chem.*, **22**, 207 (1957).  
 (12) C. Moureu, C. Dufraisse, and C. Mackall, *Bull. soc. chim. France*, [4] **33**, 934 (1923).  
 (13) C. Moureu, C. Dufraisse, and H. Blatt, *ibid.*, [4] **35**, 1412 (1924).  
 (14) C. Moureu, C. Dufraisse, and A. S. Houghton, *ibid.*, [4] **41**, 53 (1927).  
 (15) E. J. Bowen and F. Steadman, *J. Chem. Soc.*, 1098 (1934).  
 (16) P. D. Landor and S. R. Landor, *Proc. Chem. Soc.*, 77 (1962).  
 (17) A. Willemart, *Compt. rend.*, **200**, 561 (1935); *Bull. soc. chim. France*, [5] **2**, 867 (1935).

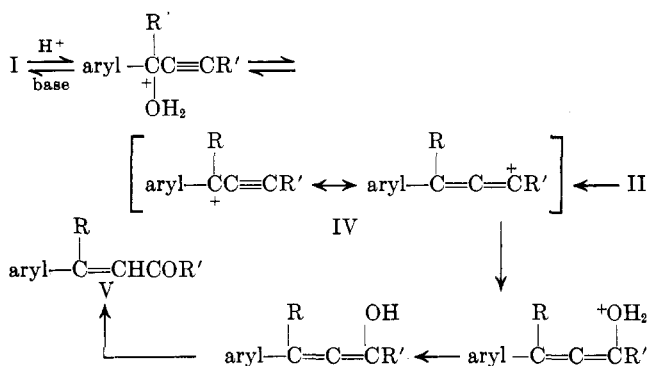
(18) T. L. Jacobs, W. L. Petty, and E. G. Teach, *J. Am. Chem. Soc.*, **82**, 4094 (1960).

(19) Y. R. Bhatia, P. D. Landor, and S. R. Landor, *J. Chem. Soc.*, 24 (1959).

(20) J. Robin, *Ann. chim. (Paris)*, [10] **16**, 421 (1931).

(21) K. H. Meyer and K. Schuster, *Ber.*, **55B**, 819 (1922).

reversible formation of the conjugate acid of I from IV. If IV is attacked even to a small extent at the allenyl position the product would be the conjugate acid of the enol form of V which would be transformed to V readily.



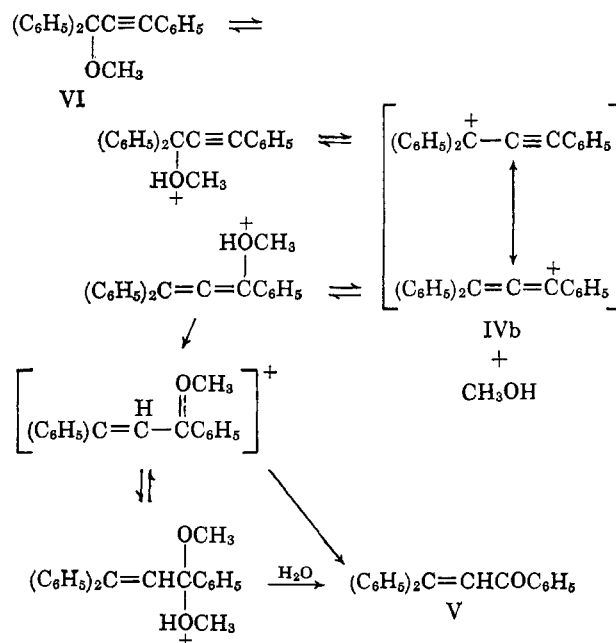
It seems quite probable that the halides obtained from many of the arylated tertiary propargyl alcohols<sup>22</sup> in fact have allenyl structures.

Although haloallene structures were not assigned to the halides obtained from aryl-substituted propargyl alcohols it has been suggested a number of times<sup>2, 16, 23-26</sup> that rubene formation involves rearrangement of an arylated propargyl halide to a haloallene which dimerizes, cyclizes, and loses hydrogen chloride to yield a naphthacene system. Recognition that haloallenes are actually the starting materials for rubene syntheses makes these suggestions more attractive. The precise sequence of events varies in the formulations proposed and further experiments are needed to differentiate between them. An acid-catalyzed reaction involving initial protonation of the center carbon of the allenyl systems<sup>16</sup> seems unlikely in view of the increased yield of rubene which is obtained in the presence of quinoline or sodium bicarbonate.<sup>2</sup> It is attractive to consider rubene formation as a variant of the usual allene dimerization which (except for a small part of the reaction of allene itself) seems always to involve bond formation between the central carbon atoms of the two allenic molecules; this suggestion was first made by Sparks and Marvel.<sup>24</sup> The completely concerted formulation of Dufraisse, Mathieu, and Valls<sup>26</sup> fits into this pattern.

Ethers have been prepared from 1,1,3-triphenyl-2-propyn-1-ol (Ib) by reaction with excess of an alcohol in the presence of concentrated sulfuric acid (cold) or with an alkyl iodide and potassium carbonate.<sup>13</sup> The same ethers were formed when the allenyl chloride IIb was refluxed with an alkoxide in excess of the alcohol.<sup>13</sup> When the sulfuric acid-alcohol solutions of Ib were allowed to stand for longer periods, only 1,3,3-triphenyl-2-propen-1-one (V, aryl = R = R' = phenyl) was isolated. We have repeated the preparations of

methyl and ethyl ethers from Ib and have also prepared them from IIb (X = Br). These ethers have propargyl structures on the basis of their infrared spectra. The reactions may be formulated along the same lines as reactions of the carbinol and halides.

Attempts were made to rearrange the methyl ether VI to the corresponding allenyl ether in anhydrous methanol containing 100% sulfuric acid. An excellent yield of V was obtained along with a small amount of recovered starting material. This suggests that the rearrangement occurred but that the allenyl ether was unstable in the reaction mixture. Sulfuric acid in methanol would be expected to form methylsulfuric acid and water which would probably hydrolyze the allenyl ether very rapidly. Even if the hydrolysis did not occur during the reaction, one would expect rapid protonation of the central carbon of the allenyl system; the conjugate acid of the dimethyl ketal might then form and be hydrolyzed during attempted isolation. Although the reaction mixture was made basic before water was added, it was never possible to isolate the ketal.



Reaction of VI with hydrogen chloride gave allenyl chloride IIb (60%) and V (23%).

Attempts to prepare the *t*-butyl ether from IIb by reaction with potassium *t*-butoxide in *t*-butyl alcohol under the conditions which gave good yields from straight-chain alcohols led to no reaction.

Ether formation took a different course with 1-bromo-4,4-dimethyl-1,3-diphenyl-1,2-pentadiene (IIc, X = Br); an excellent yield of the allenyl ether IIc (X = OCH<sub>3</sub>) was obtained by reaction with sodium methoxide. In this series it was also possible to obtain the propargyl ether by reaction of the potassium derivative of Ic with methyl iodide. Partial cleavage of the carbinol to phenylacetylene and *t*-butyl phenyl ketone in the basic solution reduced the yield of ether. Attempts to prepare ethers in this series from Ic and methyl alcohol-sulfuric acid were unsuccessful although it was reported<sup>17</sup> that a methyl ether, m.p. 46°, was obtained in this way.

(22) In addition to references given in 2 the following describe aryl-substituted halides which may be allenic: A. Willemart, *Compt. rend.*, **188**, 1172 (1929); **200**, 755 (1935); *Ann. chim. (Paris)*, [10] **12**, 345 (1929); N. Drisch, *Compt. rend.*, **194**, 1170 (1932); C. Dufraisse, J. Robin, and D. Bertin, *ibid.*, **229**, 5 (1949); D. Bertin, *ibid.*, **230**, 1356 (1950); *Ann. chim. (Paris)*, [12] **8**, 296 (1953); C. Dufraisse, A. Etienne, and J. Jolly, *Compt. rend.*, **231**, 5 (1950); R. Jaeger, P. Cadot, and A. Willemart, *ibid.*, **239**, 1226 (1954); M. Loury, *Ann. chim. (Paris)*, [12] **10**, 807 (1955).

(23) A. Willemart, *Compt. rend.*, **187**, 385 (1928); *Ann. chim. (Paris)*, [10] **12**, 345 (1929).

(24) W. J. Sparks and C. S. Marvel, *J. Am. Chem. Soc.*, **58**, 865 (1936).

(25) C. F. H. Allen and L. Gilman, *ibid.*, **58**, 937 (1936).

(26) C. Dufraisse, J. Mathieu, and J. Valls, *Compt. rend.*, **246**, 661 (1958).

It seems unlikely that the allenyl ether is formed by direct nucleophilic displacement ( $S_N2$ ) of the bromine in IIc. The failure of sodium iodide in acetone to attack IIc is in accord with this belief. An addition-elimination mechanism also seems improbable because protonation of the central carbon of the allenyl system is unlikely in basic solution. It is more probable that IIc ionizes to carbonium ion IV which reacts preferentially at the allenyl position because attack at the propargyl position is sterically hindered by the *t*-butyl group.

### Experimental

Melting points were taken with total immersion Anschütz thermometers in a stirred bath but were otherwise uncorrected.

Infrared species were obtained with a Perkin-Elmer Model 21 spectrophotometer employing sodium chloride optics. Spectra of solids were determined on 10% solutions in carbon tetrachloride or chloroform. All the compounds examined contained mono-substituted benzene rings and showed the characteristic four-band pattern between 2000 and 1650  $\text{cm}^{-1}$ .<sup>27</sup> Allenic absorption near 1950  $\text{cm}^{-1}$  was usually so close to one of these bands that no resolution was attained. Fortunately the allenic band was strong enough in all but one of the compounds being examined so that there was no question of identification of the allenic system when it was present. This band was weak in 1-methoxy-4,4-dimethyl-1,3-diphenyl-1,2-pentadiene, the allenyl ether from IIc, but in this instance the propargyl ether was also obtained. All of these allenyl bands fell between 1940 and 1970  $\text{cm}^{-1}$ . None of the allenyl compounds gave bands in the acetylene region. All of the acetylenic compounds were characterized by a weak band near 2230  $\text{cm}^{-1}$ . This band was always sharp and distinct, but with Ib and Ic it was especially weak. Values cited for individual compounds are probably no more accurate than  $\pm 5$  wave numbers.

Carbinols Ia,<sup>10</sup> Ib,<sup>3</sup> and Ic<sup>17</sup> were prepared by the methods described earlier in about the yields and with the constants given previously. Infrared bands were observed at 2240 for Ia, 2220 for Ib, and 2230  $\text{cm}^{-1}$  for Ic.

**3-Bromo-2,2,6,6-tetramethyl-5-phenyl-3,4-heptadiene (IIa, X = Br)** was prepared in 80% yield as described earlier<sup>10</sup>: b.p. 107–109° (0.3–0.7 mm.),  $n_D^{20}$  1.5383, infrared absorption at 1958  $\text{cm}^{-1}$ ; reported<sup>10</sup> b.p. 115–117° (1 mm.),  $n_D^{20}$  1.5400, infrared absorption at 1925 (m)  $\text{cm}^{-1}$ .

**3-Chloro-2,2,6,6-tetramethyl-5-phenyl-3,4-heptadiene (IIa, X = Cl)**.—Thionyl chloride (2.46 g., 0.02 mole) was added to 5.0 g. (0.02 mole) of Ia and the solution was warmed to reflux; gas was evolved and the solution turned yellow. The mixture turned magenta in color after 2 hr. standing and was then distilled under reduced pressure. After hydrogen chloride and sulfur dioxide had been removed there remained 4.5 g. (83%) of a light yellow liquid which came over at 105–108° (2–3 mm.):  $n_D^{20}$  1.5215, infrared absorption 1961  $\text{cm}^{-1}$  (infrared absorptions of undistilled material were essentially the same as for purified product throughout the spectrum).

*Anal.* Calcd. for  $C_{17}H_{25}Cl$ : C, 77.69; H, 8.83; Cl, 13.48. Found: C, 77.78; H, 8.96; Cl, 13.26.

**1-Chloro-1,3,3-triphenylpropadiene (IIb,<sup>12,16</sup> X = Cl)**.—To 7.0 g. (0.025 mole) of Ib in ether at 5° was added a mixture of 4.0 g. (0.051 mole) of pyridine and 3.0 g. (0.025 mole) of thionyl chloride in cold ether. The mixture turned dark while standing for 1 hr. Solid material was removed and the filtrate was concentrated to leave 6.7 g. (89%) of a white solid, m.p. 67–69°, which was recrystallized from an ether-ethanol solvent pair. This solid, IIb, had m.p. 68–69°, infrared absorption at 1958  $\text{cm}^{-1}$ , lit. m.p. 70–71°.

*Anal.* Calcd. for  $C_{21}H_{15}Cl$ : C, 83.30; H, 4.99. Found: C, 82.92; H, 5.11.

The same product was obtained when the solvent was petroleum ether or benzene in the presence or absence of pyridine and when phosphorus trichloride was used as in previous directions.<sup>12,15</sup>

**1-Bromo-1,3,3-triphenylpropadiene (IIb, X = Br)**.—To 10 g. (0.035 mole) of Ib in 300 ml. of ether was added dropwise 2.0 ml. (5.7 g., 0.021 mole) of phosphorus tribromide at 0° with stirring.

The yellow, opaque solution was allowed to stand overnight, washed with sodium carbonate solution and with water, and then dried. Solvent was removed, leaving 11.5 g. of light yellow viscous liquid which was chromatographed on neutral activated alumina to give two fractions. The first fraction gave a white solid, 6.8 g. (56%), m.p. 65–67°. Recrystallization from pentane-ether gave white crystals, m.p. 72.5–74°, infrared absorption at 1946  $\text{cm}^{-1}$  (no bands in the hydroxyl, carbonyl, or acetylenic regions), lit.<sup>12</sup> m.p. 72–73°.

*Anal.* Calcd. for  $C_{21}H_{15}Br$ : C, 72.63; H, 4.36. Found: C, 73.20; H, 4.38.

If the crude bromoallene was recrystallized from aqueous methanol, 1,3,3-triphenyl-2-propen-1-one (V) was produced.

The second fraction from the chromatogram was a yellow liquid; its infrared spectrum showed both hydroxyl and  $\alpha,\beta$ -unsaturated carbonyl absorption.

**1-Chloro-4,4-dimethyl-1,3-diphenyl-1,2-pentadiene (IIc, X = Cl)**.—Earlier directions<sup>17</sup> (phosphorus trichloride in petroleum ether, 4 days in sealed tube at room temperature) were followed, but crystals were not obtained when the solvent was evaporated. Distillation (short path below 1 mm.) gave a 74% yield of liquid,  $n_D^{20}$  1.5915, which was chromatographed on activated neutral alumina to yield two fractions. The main fraction was recrystallized from methanol (crystallization difficult) to give a product, m.p. 38.5–39.5°.

*Anal.* Calcd. for  $C_{19}H_{19}Cl$ : C, 80.69; H, 6.77; Cl, 12.54. Found: C, 80.71; H, 7.03; Cl, 12.42.

The second fraction was a liquid, b.p. 145–147° (2–3 mm.),  $n_D^{20}$  1.5940, which gave crystals, m.p. 37–38°, from methanol. The unchromatographed liquid and the two fractions had very similar infrared spectra characterized by an allenic band at 1958  $\text{cm}^{-1}$  and no absorption in the acetylenic range near 2230  $\text{cm}^{-1}$ .

A similar procedure with thionyl chloride gave a liquid, b.p. 155–160° (3–4 mm.),  $n_D^{20}$  1.5917, infrared spectrum very similar to that of the above material.

Experiments involving addition of 100% excess of thionyl chloride in benzene at 0° to Ic in benzene containing excess pyridine hydrochloride gave IIc as a liquid, b.p. 143–144° (1–2 mm.),  $n_D^{20}$  1.5934, yield 95%, which showed a weak  $\alpha,\beta$ -unsaturated ketone band in the infrared spectrum in addition to the allenic absorption. Chromatography gave IIc, m.p. 37–38°, which no longer showed the carbonyl infrared band.

**Attempted Preparation of the Chlorosulfinate of Ic**.—To 10.0 g. (0.038 mole) of Ic in 20 ml. of ether and 3.0 g. (0.038 mole) of pyridine was added 2.25 g. (0.019 mole) of thionyl chloride in 5 ml. of ether during 1 hr. at –78°. A white precipitate formed and was removed by filtration. The filtrate was dried over anhydrous potassium carbonate and magnesium sulfate, solvent was removed under reduced pressure (room temperature), and the residual yellow oil was chromatographed in pentane on activated neutral alumina. Two fractions were obtained: the first, 4.4 g. (38%), was IIc and the second, 2.5 g. (25%), was recovered Ic.

**The Reaction of Diphenyldichloromethane with Phenylethynylmagnesium Bromide**.—To 7.0 g. (0.29 g.-atom) of magnesium in 100 ml. of ether was added 32.0 g. (0.30 mole) of ethyl bromide in 200 ml. of ether. To the gray mixture, after the reaction was over, was added over a 5-hr. period a solution of 30.0 g. (0.29 mole) of phenylacetylene in 150 ml. of ether. The mixture was filtered through a glass-wool plug into a dropping funnel. This solution was added over a 2-hr. period to a solution of 100 g. (0.42 mole) of dichlorodiphenylmethane in 500 ml. of ether. The reaction mixture was magnetically stirred and warmed slightly. A white precipitate formed in the yellow solution. The mixture was stirred for an additional hour and filtered, and to the red-brown filtrate was added 100 ml. of petroleum ether, b.p. 80–100°. The filtrate was concentrated at aspirator pressure and then at full pump to leave 150 ml. of a brown-red oil. Pentane was added and the mixture was filtered. The filtrate was concentrated as before and carbon tetrachloride was added. A light yellow precipitate formed. This was recrystallized from benzene-pentane to give a white powder, m.p. 182–184° dec., 9.6 g. (11%) of 1,1,2,2-tetraphenyl-1,2-dichloroethane (lit.<sup>28</sup> m.p. 186° dec.).

*Anal.* Calcd. for  $C_{26}H_{20}Cl_2$ : C, 77.42; H, 5.00; Cl, 17.58. Found: C, 77.99; H, 5.33; Cl, 16.66.

(27) L. J. Bellamy, "The Infrared Spectra of Complex Molecules" 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 67–68.

(28) W. Madelung and M. Oberwagner, *Ber.*, **60B**, 2469 (1927).

By heating, the 1,1,2,2-tetraphenyl-1,2-dichloroethane was converted to 1,1,2,2-tetraphenylethylene, m.p. 220.5–222° (lit.<sup>29</sup> m.p. 220–221°).

*Anal.* Calcd. for  $C_{28}H_{20}$ : C, 93.93; H, 6.07. Found: C, 93.93; H, 6.31.

The original carbon tetrachloride filtrate was concentrated to leave a red oil, 85 g. An infrared spectrum indicated that this oil was a mixture of dichlorodiphenylmethane and triphenylchloroallene. There was no band around the acetylenic absorption region at 2230  $cm^{-1}$ . A 10.0-g. portion of the red oil was hydrolyzed in alcoholic aqueous sulfuric acid to give 3.1 g. of recovered dichlorodiphenylmethane and 5.4 g. of  $\beta,\beta$ -diphenylacrylophenone. This corresponds to at least a 56% yield of triphenylchloroallene.

**Attempted Rearrangement of Methyl 1,1,3-Triphenylpropargyl Ether (VI).**—The ether was prepared from Ib in methanol-sulfuric acid as reported<sup>13</sup> in 94% yield, m.p. 118–122°, infrared absorption at 2220  $cm^{-1}$ , lit. m.p. 124°.

To a stirred cold solution of 3.0 ml. of 100% sulfuric acid in 200 ml. of anhydrous methanol was added dropwise a solution of 5.0 g. of the ether in 15 ml. of anhydrous benzene.<sup>30</sup> The liquid quickly turned yellow and a white solid formed; this precipitate slowly dissolved as the mixture was stirred for 18 hr. The acid catalyst was then neutralized with anhydrous potassium carbonate and the mixture was partitioned between 500 ml. of water and 500 ml. of ether. The ether layer was separated, dried, and concentrated at reduced pressure to yield 5.5 g. of yellow solid, m.p. 62–72°; infrared indicated this to be mainly  $\beta,\beta$ -diphenylacrylophenone containing a little starting ether. Chromatography gave pure samples of both the ether and ketone. In a similar experiment carried out with concentrated sulfuric acid the neutralization with potassium carbonate was omitted. Chromatography gave 1.2 g. (24%) of recovered starting material and 3.8 g. (76%) of  $\beta,\beta$ -diphenylacrylophenone, m.p. 86–88°, lit.<sup>31</sup> m.p. 89°.

**Ethyl 1,1,3-Triphenylpropargyl Ether.**—A solution of 1.0 g. (0.025 mole) of Ib in 70 ml. of anhydrous ethanol and 10 ml. of concentrated sulfuric acid was stirred for 5 min. at 0°. A mixture of 250 ml. of water and 100 ml. of ether was added and the layers were separated; the ether solution was washed with water, sodium bicarbonate solution, and water and then dried over calcium chloride. Evaporation left a yellow oil which was chromatographed in pentane on neutral activated alumina to yield 5.7 g. (73%) of a colorless oil. Standing for 5 days at 0° in a

little petroleum ether (b.p. 60–70°) gave white crystals, m.p. 49–50°, infrared absorption at 2220  $cm^{-1}$ , lit. m.p. 51°.

*Anal.* Calcd. for  $C_{28}H_{20}O$ : C, 88.34; H, 6.45. Found: C, 88.45; H, 6.37.

An ether with the same melting point (mixture showed no depression) and infrared spectrum was obtained from 0.25 g. (0.00072 mole) of IIb (X = Br) which was allowed to stand for 2 days in 25 ml. of anhydrous ethanol in which had been dissolved 0.5 g. (0.022 g.-atom) of sodium. Purification involved similar chromatography. The yield was 85%, m.p. 49–50°.

**Reaction of VI with Hydrogen Chloride.**—Dry hydrogen chloride was passed into a stirred solution of 3.0 g. (0.01 mole) of VI in 500 ml. of benzene containing 5 g. of calcium chloride. The solution was filtered and concentrated to give a light green liquid. Chromatography in pentane on alumina gave 1.9 g. (60%) of chloroallene IIb, m.p. 60–65°, and 0.7 g. (23%) of  $\beta,\beta$ -diphenylacrylophenone, m.p. 88–89°. Both products showed the expected spectra.

**Methyl 4,4-Dimethyl-1,3-diphenyl-1,2-pentadienyl Ether (IIc, X = OCH<sub>3</sub>).**—A solution of 2.0 g. (0.087 g.-atom) of sodium in methanol was added to 1.0 g. of IIc (X = Br) and the cloudy yellow-green reaction mixture was left overnight at room temperature. Solvent was then removed at reduced pressure on a steam bath, ether was added, and the mixture was filtered. The filtrate was concentrated, diluted with pentane, and chromatographed on basic activated alumina to give IIc (X = OCH<sub>3</sub>), 0.69 g. (80%), as a colorless oil, b.p. 140–141° (1.5 mm.),  $n_D^{25}$  1.5727, infrared absorption at 1960  $cm^{-1}$  (very weak).

*Anal.* Calcd. for  $C_{20}H_{22}O$ : C, 86.28; H, 7.97. Found: C, 86.34; H, 8.06.

**1-*t*-Butyl-1,3-diphenylpropargyl Methyl Ether (IIIc, X = OCH<sub>3</sub>).**—To a benzene solution containing 5.0 g. (0.019 mole) of Ic was added 0.75 g. (0.019 g.-atom) of potassium. Nearly all of the metal was consumed after the mixture was refluxed for 30 min. with vigorous stirring. Methyl iodide (15 g., 0.11 mole) was added and the solution was stirred for 1 hr.; a light tan precipitate formed. Water was added cautiously and the organic layer was washed with water, dried, and concentrated to leave a light yellow oil. Distillation at reduced pressure gave phenylacetylene (caught in a trap at –78°), 1.3 g. (42%) of *t*-butyl phenyl ketone, b.p. 65–66° (1.5 mm.),  $n_D^{25}$  1.5075, strong infrared band at 1675  $cm^{-1}$ , and 2.1 g. (40%) of IIIc (X = OCH<sub>3</sub>), b.p. 145–150° (1.5 mm.). Chromatography of this last fraction gave a single material which was redistilled, b.p. 128–130° (0.9 mm.),  $n_D^{25}$  1.5628; this product could not be induced to crystallize.

*Anal.* Calcd. for  $C_{20}H_{22}O$ : C, 86.28; H, 7.97. Found: C, 86.46; H, 8.13.

The infrared spectrum showed a sharp band at 2220  $cm^{-1}$  and was very different from the spectrum of IIc (X = OCH<sub>3</sub>).

(29) J. Mackenzie, *J. Chem. Soc.*, **121**, 1697 (1922).

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## Internal Strain and Reactivity. Some Reactions of Acenaphthene\*

ERNST BERLINER, DIANE M. FALCIONE,<sup>1</sup> AND JANE L. RIEMENSCHNEIDER<sup>1</sup>

*Department of Chemistry, Bryn Mawr College, Bryn Mawr, Pennsylvania*

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Rates of bromination of acenaphthene in 90% aqueous acetic acid and of the solvolysis of  $\alpha$ -(5-acenaphthyl)ethyl chloride in 90% aqueous acetone were determined at 25°. The rates are faster than can be expected on the basis of reasonable assumptions, and the increase in reactivity is ascribed to internal strain in the acenaphthene molecule.

It has recently been proposed that part of the increased reactivity of fluorene and its derivatives may be due to internal strain.<sup>2</sup> In this connection, we would like to report some data on the reactivity of the acenaphthene system, which is also a strained molecule. The 1,8-distance in naphthalene, to which in acenaphthene the two-carbon bridge is attached, is longer than

2 Å., and in early X-ray investigations abnormally long distances of 2.01,<sup>3</sup> 1.80, and 1.64 Å.<sup>4</sup> were reported for the aliphatic carbon-carbon bond. The results of a more recent X-ray investigation, however, indicate that the acenaphthene molecule is planar with no unusual bond lengths.<sup>5</sup> The carbon-carbon bond has the normal length of  $1.54 \pm 0.014$  Å., but the strain exists in the bond angles and is shared by several

\* To Professor Louis F. Fieser.

(1) Taken from the Senior Honors Theses of D. M. Falcione, 1963, and of J. L. Riemenschneider, 1964.

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