

is directly attached to the asymmetric carbon atom) led to a completely inactive anilide.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

PROPARGYL ETHERS OF PHENOL

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RECEIVED DECEMBER 29, 1930

PUBLISHED MARCH 6, 1931

In contrast to the considerable information concerning the pyrolysis of allyl aryl ethers,¹ little is known concerning the propargyl aryl ethers. Whereas the former type changes on refluxing into *o*-allylphenols, the latter has been reported² to yield nothing but nondescript resins. Thus only tars were found when phenyl propargyl ether or *p*-bromophenyl propargyl ether was refluxed alone or refluxed in diamyl ether.

For the rearrangement of the propargyl ethers to follow the course of the allyl ethers, the anticipated product would be *o*-hydroxyphenylallene, rather than *o*-propargylphenol. It appears to be the gamma carbon of the unsaturated chain which becomes attached to the aromatic nucleus during the rearrangement. Thus, just as $C_6H_5OCH_2CH=C^*H_2$ rearranges into ortho $HOC_6H_4C^*H_2CH=CH_2$, so it might be anticipated that $C_6H_5OCH_2C\equiv C^*H$ would change into ortho $HOC_6H_4C^*H=C=CH_2$. Further-

more, since 2-methylcoumaran, (A) is a by-product from the pyrolysis of the allyl ether, it might be anticipated that 2-methylcoumaron, (B), would result from the propargyl ether. Both hydroxyphenylallene and methylcoumaron are structures which might be expected to polymerize readily. It is conceivable that either or both of these substances were the precursors of the tar which was noticed from the pyrolysis of propargyl phenyl ether.

In extending this subject we endeavored to synthesize the phenyl ethers of the following propargyl alcohols and to study their pyrolysis:

Triphenylpropargyl alcohol
Trimethylpropargyl alcohol
 γ -Methylpropargyl alcohol
1-Phenylethynylcyclohexanol-1

$C_6H_5C\equiv C-C(C_6H_5)_2OH$

$CH_3C\equiv C-C(CH_3)_2OH$

$CH_3C\equiv C-CH_2OH$

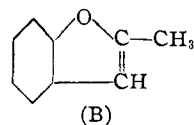
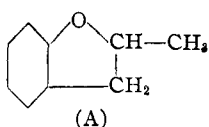
$C_6H_5C\equiv C-C(CH_2)_6OH$

α, γ -Diphenyl- α -*p*-dimethylaminophenylpropargyl alcohol

C_6H_5
|
 $C_6H_5C\equiv C-C-OH$
|
 $C_6H_5N(CH_3)_2$

¹ This topic is summarized in Hurd, "The Pyrolysis of Carbon Compounds," The Chemical Catalog Co., New York, 1929, pp. 214-228.

² Powell and Adams, THIS JOURNAL, 42, 654 (1920).

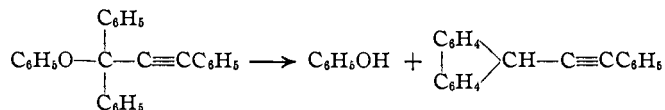


Of these compounds, only the first and third appear to have been described previously.

The first three of these alcohols were converted into the chlorides by phosphorus trichloride. The fourth reacted with phosphorus pentachloride but the reaction product did not analyze correctly for the desired halide. This reaction is being studied further. All attempts to convert the fifth alcohol into its chloride were unsuccessful. Dry hydrogen chloride, concd. or dilute hydrochloric acid, and phosphorus tri- and pentachlorides were all tried with variations in temperature and concentration. It seemed, however, that even small amounts of acid were sufficient to give rise to tarry materials from which nothing could be isolated, not even the original alcohol. In the absence of evidence to the contrary, it has been assumed that the propargyl chlorides, $R-C\equiv C-CR_2Cl$, did not rearrange³ into the chloroallenes, $RCCl=C=CR_2$.

Synthesis of the Phenyl Ethers.—With trimethylpropargyl chloride and with γ -methylpropargyl chloride it was possible to synthesize the respective phenyl ethers by heating in acetone solution with phenol and potassium carbonate. This is analogous to the method which is commonly used in making the allyl ethers. In contrast to this, it was necessary to use sodium phenoxide to effect reaction with triphenylpropargyl chloride. Even more resistant was the material which was considered (temporarily, at least) to be 1-phenylethynylcyclohexyl chloride. In fact, no satisfactory reaction with phenol or sodium phenoxide could be achieved in spite of several modifications of conditions.

Pyrolysis of the Ethers.—All three of the ethers were found to decompose on heating, but none was found to pyrolyze into an ortho substituted phenol. In fact, distinct differences of reaction mechanism were apparent in all three cases. Triphenylpropargyl phenyl ether was the most resistant to heat, but at 300° it pyrolyzed into phenol and 9-phenylethynylfluorene



The yield was about 45%. This reaction is similar evidently to the pyrolysis of triphenylmethyl chloride,⁴ wherein hydrogen chloride was detached at temperatures above 200° and 9-phenylfluorene formed. Similar also is the production of phenyl- α -naphthofluorene by refluxing diphenyl- α -naphthylchloromethane⁵ with zinc chloride in acetic acid.

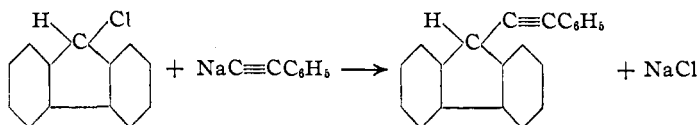
³ See Willemart, *Compt. rend.*, **187**, 385 (1928); **188**, 1172 (1929).

⁴ Hemilian, *Ber.*, **7**, 1208 (1874); **11**, 202, 837 (1878); E. and O. Fischer, *Ann.*, **194**, 257 (1878); Schwarz, *Ber.*, **14**, 1522 (1881); Nef, *Ann.*, **309**, 167 (1899).

⁵ Ullmann and Mourawiew-Winigradoff, *Ber.*, **38**, 2213 (1905).

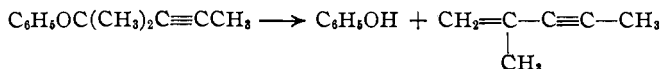
Although it is easy to picture the production of 9-phenylethynylfluorene and 9-phenylfluorene from triphenylpropargyl phenyl ether and triphenylmethyl chloride, respectively, no ready explanation suggests itself as to why other triphenylpropargyl derivatives such as the chloride⁶ or acetate⁷ fail to undergo a similar type of pyrolysis and yield 9-phenylethynylfluorene. Instead, these substances give rubrene, $C_{42}H_{28}$ (m. p. 331°). An intermediate compound, $C_{42}H_{29}Cl$, which is capable of quantitative conversion into rubrene, is isolable from the chloride by careful heating, but no mention has been made of phenylethynylfluorene. Robin reported that traces only of rubrene were obtained on heating triphenylpropargyl benzoate or triphenylpropargyl methyl ether, but that fair amounts of a yellow hydrocarbon of m. p. 245° were isolated from these substances. We found no rubrene in the pyrolytic products of triphenylpropargyl phenyl ether, but we did isolate traces of a solid melting between 240 – 250° , which was presumably the same as Robin's compound.

To prove the structure of 9-phenylethynylfluorene, its synthesis was effected from fluorene through fluorenone, 9-hydroxyfluorene and 9-chlorofluorene. This last was condensed with sodium phenylacetylide



The 9-phenylethynylfluorene thus synthesized was identical with the product of the pyrolysis.

Turning now to trimethylpropargyl phenyl ether, it was found to be much more susceptible to heat. Its temperature of decomposition was 160° , as compared to 300° which was required for the triphenylpropargyl phenyl ether. Tar formation was marked, but there was an appreciable yield of phenol and methyl-2-pentene-1-ine-3, in accordance with the equation



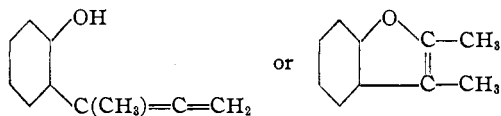
The ene-ine compound, C_8H_8 , was also isolated as a by-product in the synthesis of trimethylpropargyl alcohol and of trimethylpropargyl chloride. Depending on the temperature used, yields of the ene-ine from the alcohol reached as high as 60%. No doubt higher yields could be obtained with facility. This hydrocarbon, b. p. 75 – 77° , represents an extremely interesting type inasmuch as it possesses conjugation of the rare ene-ine type rather than of the common diene type. Its conjugation was attested to by

⁶ Moureu, Dufraisse and Dean, *Compt. rend.*, **182**, 1440 (1926); Moureu, Dufraisse and Robin, *ibid.*, **188**, 1582 (1929).

⁷ Robin, *ibid.*, **189**, 337 (1929).

the fact that sodium caused it to polymerize to a black, rubber-like substance in the course of a few hours.

The pyrolysis of γ -methylpropargyl phenyl ether was necessarily different from the other ethers since it possessed no α -phenyl group to give rise to fluorene formation and no α -methyl group to yield a conjugate enine. Phenol was detected as a reaction product, but only in traces. No gas was evolved. Instead, the chief reaction product was a tar, possessing a molecular weight of about 400. Since the molecular weight of the original ether, or of its isomers such as



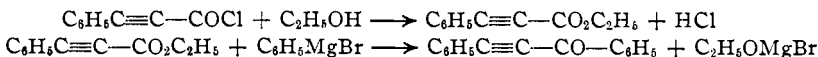
is 146, this suggests a trimer (mol. wt. 438) as the major component of the tarry mixture. In this polymerization process, most of the original unsaturation was consumed since bromine (in chloroform solution) was absorbed only in trivial amounts. Whether or not the tar was produced as the result of prior allene formation cannot be stated, but if such was the case it is fairly certain that none of the allene escaped the polymerization process.

Experimental Part

Phenylacetylene.—This was prepared by the method of "Organic Syntheses," Vol. VI. An alteration, noted in Volume VIII, p. 124, was the use of potassium hydroxide (2 parts) and sodium hydroxide (1 part) for the fused alkali rather than the former alone. The phenylacetylene was carefully fractionated and the fraction boiling at 140–141° (750 mm.) used. For the work described below, this was an essential step. The material was converted into sodium phenylacetylide by Nef's⁸ method. In our use of this salt, it was not removed from the ether wherein it was made.

Phenylethynyl Phenyl Ketone.—Nef's directions⁹ were followed for the synthesis of this ketone from sodium phenylacetylide and benzoyl chloride. After purification by vacuum distillation, for a time the ketone resisted solidification. Finally, a solid, m. p. 53–55°, was obtained in 74% yield. Nef's value was 49–50°. André,¹⁰ who prepared this ketone from benzoyl bromide and sodium phenylacetylide, also reported a melting point of 49°. That the value is higher than any of these, namely 65–66°, is shown below.

To effect another synthesis of this ketone, the following reactions were developed



Ethyl cinnamate was converted into phenylpropionic acid by Perkin's¹¹ method and this acid changed into the acid chloride in 74% yield by thionyl chloride.¹² We found that

⁸ Nef, *Ann.*, **308**, 275 (1899).

⁹ Ref. 8, p. 276.

¹⁰ André, *Ann. chim.*, [8] **29**, 562 (1913).

¹¹ Perkin, *J. Chem. Soc.*, **45**, 172 (1884).

¹² Watson, *ibid.*, **85**, 1324 (1904); Ruhemann and Merriman, *ibid.*, **87**, 1389 (1905).

direct esterification of propiolic acid with ethanol and hydrogen chloride (Perkin's method) was impractical because of low yields (33%). Double this yield was obtained from the acid chloride.

Ethyl Phenylpropiolate.—A solution of phenylpropiolyl chloride (39 g.) in absolute alcohol (80 cc.) was refluxed for four hours. Then the solution was poured into water and an oil separated. This was extracted with ether, washed with dilute sodium carbonate solution, then with water, dried, and fractionally vacuum-distilled. The yield of the ester was 28.4 g., which is 65% of the theoretical.

Phenylethynyl Phenyl Ketone.—A solution of 0.15 mole of phenylmagnesium bromide in 150 cc. of dry ether was prepared. To this, 10 g. of ethyl phenylpropiolate (0.057 mole) in 100 cc. of dry ether was added slowly. After standing for two hours, the solution was poured into cold, dilute sulfuric acid for hydrolysis. The ether layer was separated and allowed to evaporate at room temperature. A very thick oil was obtained. It failed to crystallize by itself in the cold after two days, but the addition of a little petroleum ether to the surface of the oil caused it to set to a solid mass of very fine crystals. These were filtered off and washed with a small amount of petroleum ether. When dry, the crystals of phenylethynyl phenyl ketone weighed 10 g.; this is an 85% yield. These crystals melted at 43–54° and after several recrystallizations from alcohol the melting point was raised to 65–66°. The boiling point at 15 mm. was found to be 200–202°. This confirms André, who reported 200–205° at 14 mm. Inasmuch as the melting point differed from the older value, the pure material was analyzed.

Anal. Subs., 0.1415: CO₂, 0.4513; H₂O, 0.0621. Calcd. for C₁₆H₁₀O: C, 87.4; H, 4.89. Found: C, 87.0; H, 4.87.

Although the yields in this synthesis were quite satisfactory, Nef's method involves the use of simpler intermediates and is to be preferred for that reason. It is interesting to note that Wilson and Hyslop¹³ synthesized triphenylpropargyl alcohol, rather than phenylethynyl phenyl ketone, by the interaction of ethyl phenylpropiolate and phenylmagnesium bromide. In their procedure, the reaction mixture was kept in a freezing solution of ice and salt during the mixing and the duration of the experiment was "overnight" instead of two hours. Otherwise their steps were very similar to ours.

Synthesis of Triphenylpropargyl Alcohol.—In addition to Wilson and Hyslop's method, three other plans have been recorded for the synthesis of this alcohol. (1) Phenylethynyl phenyl ketone¹⁴ plus phenylmagnesium bromide, with a reported yield of "excellent." (2) Benzophenone¹⁵ plus phenylethynylmagnesium bromide, in 79% yield. (3) Benzophenone¹⁶ plus sodium phenylacetylide. Nef's yield in this reaction was 54%.

After using all of these methods we reached a preference for the last. However, with Nef's directions very poor yields (0–10%) were obtained. The trouble seemed to be largely in the purification process. It was found that crystallization was a poor method for removing the impurities so, in order to minimize them, the reacting materials were carefully purified before use. Under these conditions the reaction mixture was almost colorless and subsequent crystallization and purification without distillation of unreacted materials was possible. The yields were increased to 65–70% of the theoretical.

To a mixture of 0.1 mole of freshly prepared sodium phenylacetylide in 100 cc. of

¹³ Wilson and Hyslop, *J. Chem. Soc.*, **123**, 2612 (1923).

¹⁴ Kohler, *Am. Chem. J.*, **38**, 561 (1907).

¹⁵ Hess and Weltzien, *Ber.*, **54**, 2518 (1921).

¹⁶ Nef, *Ann.*, **308**, 282 (1899); Moureu, Dufraisse and Mackall, *Bull. soc. chim.*, **33**, 934 (1923).

dry ether was added 18.2 g. (0.1 mole) of benzophenone. A very slight heat of reaction which seemed to continue for some time was insufficient to keep the ether refluxing. To hasten the reaction, the mixture was refluxed vigorously for six to eight hours. The reaction proceeded smoothly with the formation of the sodium salt of triphenylpropargyl alcohol, which was soluble in ether. When the mixture became a clear solution, the reaction was assumed to be completed but the refluxing was usually continued for an extra hour. The reaction mixture was almost colorless.

After cooling to room temperature, the mixture was poured with stirring into 500 cc. of normal sulfuric acid. Without separating the layers, the ether was allowed to evaporate at room temperature. The light yellow oil which remained was composed of triphenylpropargyl alcohol, phenylacetylene and benzophenone. The mixture was cooled to 0° whereupon the oily layer became a thick sirup. In the course of a few hours at this temperature crystals slowly formed until finally the layer was solid. This solid was broken up and filtered, then washed with petroleum ether and dried. The yield of crude material was 20–22 g., which was 71–74% of the theoretical. One crystallization from benzene and petroleum ether was sufficient to obtain a product which melted at 78–80°. The yield of triphenylpropargyl alcohol thus purified was 16–18 g., or 65–70% of the theoretical.

Trimethylpropargyl Alcohol.—Methylacetylene, prepared from 250 g. of propylene bromide¹⁷ and alcoholic potassium hydroxide, was conducted through a long, well-cooled condenser and then through three cold phosphorus pentoxide traps. The dry gas was then passed into a 500-cc. solution of 1.0 mole of ethylmagnesium bromide in ether. The rate of addition of the methylacetylene was such that a gentle but steady refluxing of the ether was induced, with the formation of ethane and methylethynylmagnesium bromide. Although methylacetylene which is prepared from propylene bromide contains some allene, no trouble is caused thereby since the allene cannot react with ethylmagnesium bromide.

The reaction mixture of ether, methylethynylmagnesium bromide and excess ethylmagnesium bromide was cooled to 0° and to it 1.5 moles (87 g.) of acetone was added slowly. The Grignard addition compound was decomposed by cold dilute hydrochloric acid and the ether layer was washed, dried and distilled under reduced pressure. Methyl-2-pentene-3-ol-2 was isolated as a colorless liquid boiling at 75–77° (15 mm.). The yield was 47 g. (47% of the theoretical). The index of refraction, n_D^{20} , was 1.4193.

Anal. Subs. 0.2041: CO₂, 0.5472; H₂O, 0.1836. Calcd. for C₆H₁₀O: C, 73.4; H, 10.2. Found: C, 73.2; H, 10.2.

Methyl-2-pentene-1-ine-3.—In this synthesis of trimethylpropargyl alcohol, part of the alcohol was always dehydrated with the formation of methyl-2-pentene-1-ine-3, CH₂=C(CH₃)—C≡C—CH₃. The yield of hydrocarbon depended on the temperature at which the reaction occurred, and yields as high as 60% were obtained. No efforts were made to improve this yield. No doubt it would be possible to obtain almost quantitative yields by heating the alcohol with oxalic acid dihydrate, since *t*-butyl alcohol (a related tertiary alcohol) is easily dehydrated in this manner. The methyl-pentenene was also isolated as a by-product in the preparation of methyl-2-chloro-2-pentene-3, but in much smaller amounts. This hydrocarbon was also one of the chief pyrolytic products of trimethylpropargyl phenyl ether (see below). It was a colorless liquid which boiled at 75–77° and which gave a value of 1.4002 for the index of refraction, n_D^{20} .

Anal. Subs., 0.2148, 0.1407: CO₂, 0.7070, 0.4630; H₂O, 0.3800, 0.1254. Calcd. for C₆H₈: C, 89.94; H, 10.06. Found: C, 89.66, 89.75; H, 9.82, 9.94.

¹⁷ Hurd, Meinert and Spence, *THIS JOURNAL*, **52**, 1141, second method (1930).

γ -Methylpropargyl alcohol (butine-2-ol-1) was synthesized by Yvon's¹⁸ method from trioxymethylene and methylethynylmagnesium bromide. It was collected in 16% yield at 137–140°; n_D^{20} 1.4497. Yvon reported a yield of 25%. Various modifications were tried with no better success. These included the use of gaseous formaldehyde, the use of an excess of Grignard reagent, or the variation of temperature or time of reaction.

1-Phenylethynylcyclohexanol-1.—Twenty-five grams of freshly distilled phenylacetylene (0.25 mole) was converted into its sodium salt. To this was then added slowly 25 g. (0.25 mole) of cyclohexanone. A vigorous reaction resulted. Then the mixture was refluxed until a clear solution was obtained after which it was hydrolyzed with dilute hydrochloric acid and the ether layer separated. The water layer was extracted with a small quantity of ether and the ether extracts combined. After drying over sodium sulfate, the solution was fractionated. Eighteen grams of a mixture of phenylacetylene and cyclohexanone was obtained, then 1-phenylethynylcyclohexanol-1 distilled as a thick, colorless sirup, b. p. 166–169° at 14 mm. After several hours at room temperature this material crystallized to a white solid which melted at 58–60°. The yield was 25.1 g., or 50%.

α,γ -Diphenyl- α -*p*-dimethylaminophenylpropargyl Alcohol.—Sodium phenylacetylide was made from 33 g. of phenylacetylene (0.33 mole), and 75 g. (0.33 mole) of *p*-dimethylaminobenzophenone¹⁹ in 150 cc. of benzene was added. The mixture was refluxed until all of the solid had disappeared (four hours). After completion of the reaction, the mixture was poured into cold water and the benzene layer washed to remove the sodium hydroxide formed. The benzene solution was then dried and the solvent distilled. The black, tarry material which remained was extracted with petroleum ether. Most of the impurities were removed by this method. A light colored solid was obtained which, on recrystallization from benzene, gave a fine white crystalline material of m. p. 144–145°. The yield was 55 g., or 50%.

Anal. Subs. 0.2841, 0.4020: 0.100 N HCl, 8.50, 12.20. Calcd. for $C_{23}H_{21}ON$: N, 4.28. Found: N, 4.14, 4.22.

The Propargyl Chlorides.—Triphenylpropargyl chloride was prepared²⁰ from phosphorus trichloride and the alcohol in benzene.

Trimethylpropargyl Chloride.—To a solution of 20.0 g. of trimethylpropargyl alcohol (0.2 mole) in 50 cc. of dry ether was added 13.7 g. of phosphorus trichloride (0.1 mole). The reaction mixture was maintained at 0° for one hour and at room temperature for two hours. After this time the ether solution was decanted from the phosphorous acid and distilled. The fraction which boiled at 35–65° and 47 mm. was collected, washed with cold water, dried and redistilled. Trimethylpropargyl chloride (methyl-2-chloro-2-pentine-3) was obtained as a light yellow liquid, b. p. 57–61° at 47 mm.; n_D^{20} 1.4143. The yield was 6.6 g. (33%).

Anal. Subs., 0.2358, 0.2510: cc. of *N*/10 $AgNO_3$, 19.9, 20.4. Calcd. for C_6H_7Cl : Cl, 30.43. Found: Cl, 30.48, 30.65.

γ -Methylpropargyl Chloride (Chloro-1-butine-2).—To 10.0 g. of butine-2-ol-1 (0.14 mole), dissolved in 50 cc. of dry ether, was added 10.0 g. of phosphorus trichloride (0.07 mole). A vigorous reaction began immediately and in one hour it was completed. After standing for eight hours at room temperature, the ether solution was decanted from the phosphorous acid, washed quickly with cold water, dried and distilled. Chloro-1-butine-2 was obtained as a light yellow liquid, b. p. 81–84°. The yield was 5.4 g., which is 44% of the theoretical.

¹⁸ Yvon, *Compt. rend.*, **180**, 749 (1925).

¹⁹ This material was prepared by Hurd and Webb, *THIS JOURNAL*, **49**, 551 (1927).

²⁰ Moureu, Dufraisse and Mackall, *Bull. soc. chim.*, **33**, 934 (1923).

Anal. Subs. 0.2009, 0.2014: cc. of *N*/10 AgNO₃, 23.4, 23.4. Calcd. for C₄H₅Cl: Cl, 40.34. Found: Cl, 41.28, 41.23.

The Phenyl Ethers

Triphenylpropargyl Phenyl Ether.—Five grams (0.015 mole) of triphenylpropargyl chloride was added to 50 cc. of absolute ether. The chloride was only slightly soluble. To this mixture was then added an ether solution containing the sodium phenoxide obtained by treating 2.5 g. of phenol with a slight excess of sodium. A finely divided precipitate of sodium chloride settled to the bottom and a clear solution was obtained. After filtration the ether was evaporated off, thereby leaving a mass of yellow crystals which was washed with cold water and with cold absolute alcohol. The crystalline material was recrystallized from ether; m. p. 90–90.5°. The yield of the ether was 70% of the theoretical, or 4.3 g.

Anal. Subs., 0.1628: CO₂, 0.5346; H₂O, 0.0901. Calcd. for C₂₇H₂₀O: C, 89.68; H, 5.59. Found: C, 89.54; H, 5.79.

Trimethylpropargyl Phenyl Ether.—An ether solution containing 50 cc. of dry ether, 5 g. (0.04 mole) of trimethylpropargyl chloride and 30 cc. of acetone was made and to it was added 5 g. of potassium carbonate and 3.3 g. (0.04 mole) of phenol. The mixture was refluxed for four hours. Fifty cc. of ether was then added and the ether solution washed with dilute alkali to remove unreacted phenol. The ether solution was dried and fractionally distilled. After removal of the ether and the unreacted trimethylpropargyl chloride, a clear and rather viscous yellow oil remained; n_D^{20} 1.3408. All attempts to purify the oil by distillation brought about pyrolysis. The yield was 4.8 g., which was 69% of the theoretical. For identification, its molecular weight was determined.

Mol. wt. Subs. 0.2040; benzene, 21.96; freezing point lowering, 0.150°. Calcd. for mol. wt. of C₁₂H₁₄O: 174. Found: 340. Subs., 0.1694, 0.2421; acetic acid, 26.23, 26.23; freezing point lowering, 0.150°, 0.220°. Found: mol. wt., 167.9, 168.6.

γ -Methylpropargyl Phenyl Ether.—Four grams (0.055 mole) of chloro-1-butine-2 was dissolved in 50 cc. of absolute ether, and to this solution were added 5.0 g. of potassium carbonate, 10 cc. of acetone and 4.6 g. (0.055 mole) of phenol. After the first vigorous reaction, the mixture was refluxed for six hours. The ether solution was then carefully washed with dilute alkali to remove unreacted phenol. After washing with water and drying, the mixture was fractionally distilled. γ -Methylpropargyl phenyl ether was obtained as a colorless oil, b. p. 123–126° at 25 mm.; n_D^{20} 1.3894. A 57% yield (4.6 g.) was realized in the preparation.

Anal. Subs. 0.1442: CO₂, 0.4340; H₂O, 0.0920. Calcd. for C₁₀H₁₀O: C, 82.13; H, 6.90. Found: C, 82.15; H, 7.08.

Pyrolysis of the Ethers

Triphenylpropargyl Phenyl Ether.—One gram of the pure ether was heated in a test-tube by means of a large salt-bath. The temperature was raised slowly and uniformly to 310°. At 230° the compound darkened appreciably. At a bath temperature of 252° the reaction temperature ascended from 248 to 256°, indicating a slight exothermic reaction. The noticeably vigorous change occurred at 295°, however, when the vapor of phenol was evolved in appreciable amounts (0.12 g.). The temperature of 310° was maintained for about ten minutes, which was about five minutes after the evolution of a gas had ceased. Then the bath was allowed to cool slowly to room temperature.

A red, glassy material was obtained which, on pulverizing, became a light yellow powder which fused between 85–98°. By extraction with petroleum ether a soluble portion was obtained which after recrystallization melted at 98–100°. This was 9-

phenylethynylfluorene, and it was formed in 45–50% yields. The fraction which was insoluble in petroleum ether was crystallized from benzene. Less than 0.01 g. of red crystals was obtained, m. p. 240–250°.

Synthesis of 9-Phenylethynylfluorene.—Fluorene in acetic acid was oxidized²¹ with sodium dichromate to fluorenone, and the latter reduced²² in alkaline alcoholic solution to 9-hydroxyfluorene by zinc dust. Thionyl chloride was then used to effect the change into 9-chlorofluorene.^{22b} Respectively, the yields in the three operations were 50, 87 and 76%.

A slight excess of sodium was added to 3.0 g. of phenylacetylene in 50 cc. of dry ether. The excess of sodium was mechanically removed after completion of the reaction. To the sodium phenylacetylide thus prepared was added three g. of 9-chlorofluorene (0.015 mole). The mixture immediately assumed a dark brown coloration. It was refluxed for three hours and then the solution was filtered to remove the unreacted sodium phenylacetylide and sodium chloride. Evaporation of the filtrate yielded a brown, crystalline solid. The pure 9-phenylethynylfluorene was readily obtained from this as a yellow solid which melted at 98–100° by crystallization from petroleum ether. The yield was 2 g., or 50%.

Anal. Subs., 0.1627: CO₂, 0.5649; H₂O, 0.0750. Calcd. for C₂₁H₁₄: C, 94.69; H, 5.31. Found: C, 94.54; H, 5.19.

Phenylethynylfluorene was also synthesized from the 9-hydroxyfluorene. One gram of the latter was dissolved in 50 cc. of dry ether and to it was added 2 g. of phenylacetylene. The mixture was chilled to 5–10° and 5 cc. of concd. sulfuric acid was added slowly while the solution was stirred vigorously. After washing the solution with a little water to remove the sulfuric acid, the solution was evaporated, leaving crude 9-phenylethynylfluorene as a yellow solid. After recrystallization there was 1 g. of pure product (m. p. 98–100°), which was a 65% yield.

Trimethylpropargyl Phenyl Ether.—In a test-tube which was heated by an oil-bath was placed 3.5 g. of trimethylpropargyl phenyl ether. The test-tube was connected to an efficient condenser and the temperature of the bath was carefully raised. At 160° the substance darkened materially and it was maintained at that temperature for half an hour. A small amount of vapor was at once apparent. This condensed and was collected as a colorless liquid. It proved to be methyl-2-pentene-1-ine-3. The yield of it was 0.8 g., a 43% yield.

The material which remained in the test-tube became a black tar after a few minutes and no further decomposition was evident as the heating was prolonged. Extraction of this tar with alkaline solution yielded 0.35 g. of phenol (as tribromophenol). This was 20% of the theoretical. The tarry, alkali-insoluble residue weighed 2.1 g.

γ-Methylpropargyl Phenyl Ether.—Three grams of γ-methylpropargyl phenyl ether was heated slowly in a test-tube immersed in a large oil-bath. The temperature was raised slowly to 215–220° without any apparent decomposition and at this point a natural reflux seemed to occur. After one-half hour at this temperature, the material had become much darker and after one and a half hours it was black. When cooled, a thick, black and tarry material was obtained.

Extraction of the tar thus formed with dilute alkali gave less than 0.1 g. of phenol as tribromophenol. The tar was but slightly soluble in ether whereas benzene dissolved it readily. To ascertain the complexity of the tar, its molecular weight was taken and found to be about 400.

²¹ Graebe and Rateanu, *Ann.*, **297**, 258 (1894).

²² (a) Barbier, *Compt. rend.*, **80**, 1396 (1875); (b) Werner and Grob, *Ber.*, **37**, 2887 (1904).

Mol. wt. Subs., 0.2638, 0.3018, 0.2833; benzene, 21.96, 21.96, 21.96; freezing point lowering, 0.144, 0.169, 0.164°. *Mol. wt.*, 407, 401, 392.

Summary

New syntheses of phenylethynyl phenyl ketone (benzoylphenylacetylene) and of ethyl phenylpropiolate have been developed.

A homolog of propargyl alcohol, $RC\equiv C-CH_2OH$, and four trisubstituted analogs, $RC\equiv C-CR_2OH$, were synthesized. Three of these were converted into the corresponding propargyl chlorides and then to the phenyl ethers. These ethers were subjected to pyrolysis.

Triphenylpropargyl phenyl ether pyrolyzed into phenol and 9-phenylethynylfluorene, which was synthesized for purposes of identification from fluorene. Both trimethylpropargyl alcohol and trimethylpropargyl phenyl ether decomposed on heating into phenol and a conjugated "ene-ine" hydrocarbon, namely, methyl-2-pentene-1-ene-3. When refluxed, γ -methylpropargyl phenyl ether changed primarily into a tar, the apparent molecular weight of which was 400. No simple allenes were found although they may have been the precursors of the tars. Should propargyl aryl ethers have been found to rearrange like allyl aryl ethers, allenes would have been expected.

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RESEARCHES ON PYRIMIDINES. CXX. THE ACTION OF OZONE ON URACIL

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RECEIVED JANUARY 6, 1931

PUBLISHED MARCH 6, 1931

In order to develop a new technique for determining the constitution of nucleic acids, and also known glucosidic combinations containing pyrimidine and purine cycles, the authors decided to investigate the action of ozone on pyrimidines of the uracil type, and to follow this up later with a study of the behavior of certain purines of biochemical interest toward this same reagent. So far as the authors are aware, the behavior of heterocycles of these two types toward ozone has never been investigated. Since both cycles are characterized structurally by the presence of ethylene or unsaturated groupings, it might be predicted that pyrimidines and purines would be very reactive toward ozone, and be broken down at the double bond by this reagent with formation of unique acyclic, ureide constructions possessing immediate biochemical interest. In this paper we now describe the behavior of the pyrimidine "uracil" I when allowed to interact with ozone in glacial acetic acid at ordinary temperature.

¹ Constructed from a dissertation presented by Robert Barnett Flint to the Graduate School of Yale University in June, 1930, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.