tomaceous earth (Super Cel), Pyrex glass wool, powdered soft glass, barium carbonate and barium hydroxide, catalyzed nitrogen evolution even if previously wetted with ethylene glycol. The surface of glass reaction vessels caused slow evolution of nitrogen from rough spots or scratches.

No difficulty was experienced in reproducing the conventional[2] procedure for conversion of N′-benzenesulfonylbenzhydrazide to benzaldehyde. However, if the sodium carbonate was added as a solution in ethylene glycol essentially no nitrogen was evolved even though the ratio of sodium carbonate to hydrazide was the same. Again the addition of solids initiated nitrogen evolution. Supersaturation by nitrogen was ruled out by the fact that no nitrogen was evolved when the solid was not added until after the solution had been cooled to room temperature and by the fact that the hydrazide could be recovered from heated solutions from which nitrogen had not been evolved.

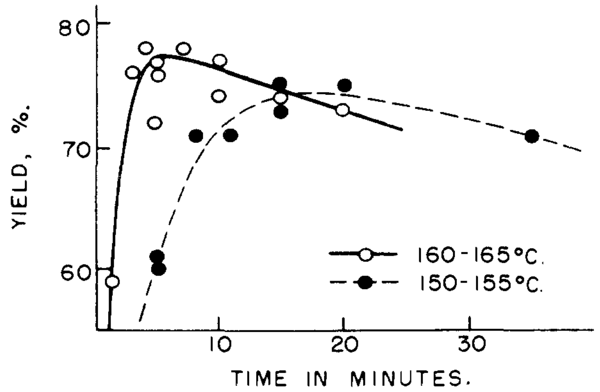


Fig. 1.

Surface-catalyzed Pyrolysis of Sodium N′-Benzenesulfonylbenzhydrazide.—A series of experiments were made to determine yields of benzaldehyde. One procedure was to add 0.6 g. (0.002 mole) of sodium N′-benzenesulfonylbenzhydrazide into 5 ml. of hot ethylene glycol in a test-tube and to stir with a wad of glass wool. At the end of the reaction period the test-tube was quickly transferred from the heating bath to an ice-bath. The reaction mixture was then washed through a sintered glass filter with methanol into a 0.05 *M* solution of 2,4-dinitrophenylhydrazine in 0.5 *M* methanolic hydrochloric acid. After several hours the precipitate was washed with 5–10 ml. of acidic methanol and dried to constant weight. An alternate procedure was to add water to the cooled reaction mixture, extract the benzaldehyde with ether, concentrate the extract and determine the yield by the Bryant–Smith titration.[8] Results are plotted in Fig. 1.

Improved Procedure for Benzaldehyde.—To a stirred hot mixture of 0.5 g. of N′-benzenesulfonylbenzhydrazide, 0.2 g. of powdered soft glass (finer than 30 mesh) and 5 ml. of ethylene glycol in a test-tube was added anhydrous sodium carbonate. The reaction mixture was then worked up as above with the 2,4-dinitrophenylhydrazine reagent and the results are shown in Table I.

2,4,6-Trimethylbenzaldehyde.—N′-Benzenesulfonyl-2,4,6-trimethylbenzhydrazide was treated with sodium carbonate, 0.05 g. of powdered soft glass and 1.5 ml. of ethylene glycol in a manner similar to the above preparation of benzaldehyde. After recrystallization from alcohol, 2,4,6-trimethylbenzaldehyde 2′,4′-dinitrophenylhydrazone was obtained as a red solid, m.p. 256–257°.

Anal. Calcd. for $C_{16}H_{16}N_4O_4$: N, 17.5. Found: N, 17.1.

Pyridine-3-carboxaldehyde.—N′-Benzenesulfonylpyridine-3-carbohydrazide, 0.27 g., was treated with sodium carbonate, 0.1 g. of powdered soft glass and 3 ml. of ethylene glycol as above. The pyridine-3-carboxaldehyde 2′,4′-dinitrophenylhydrazone[9] was obtained as an orange solid, m.p. 258.5–259.5°, after recrystallization from alcohol.

Anal. Calcd. for $C_{12}H_9N_5O_4$: C, 50.2; H, 3.1; N, 24.4. Found: C, 50.2; H, 3.1; N, 23.8.

---

(8) W. M. D. Bryant and D. M. Smith, This Journal, **57**, 57 (1935).

(9) J. P. Wibaut and R. Huls, *Rec. trav. chim.*, **71**, 1021 (1952); S. J. Angyal, G. B. Barlin and P. C. Wailes, *J. Chem. Soc.*, 1740 (1953).

Columbus 10, Ohio

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

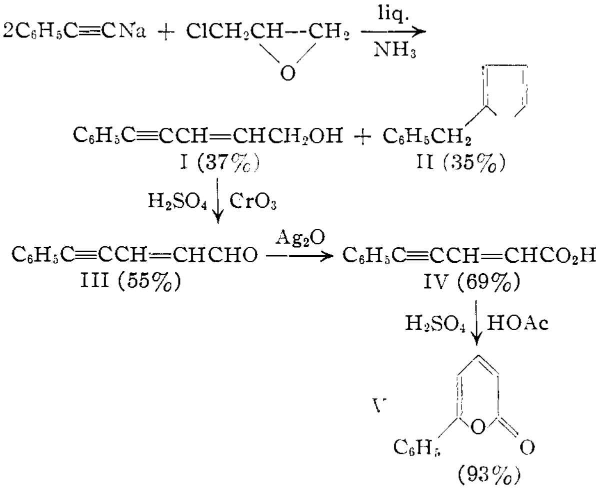
5-Phenyl-2-penten-4-yn-1-ol and Related Compounds[1]

By Thomas L. Jacobs, David Dankner and Arlyn R. Dankner

Received September 6, 1957

The synthesis of 5-phenyl-2-penten-4-yn-1-ol from sodium phenylacetylide and epichlorohydrin was repeated and the by-product shown to be α-benzylfuran. The alcohol was oxidized to the corresponding aldehyde and acid; the latter was cyclized to phenylcoumalin.

The physiological activity of highly unsaturated systems containing acetylenic and allenic bonds, such as Mycomycin,[2] $HC{\equiv}CC{\equiv}CCH{=}C{=}CH\text{-}CH{=}CHCH{=}CHCH_2CO_2H$, and Diatretyne 2,[3] $N{\equiv}CC{\equiv}CC{\equiv}CCH{=}CHCO_2H$, suggested an investigation of more stable and more readily available related compounds. As part of this general program 5-phenyl-2-penten-4-yn-1-ol and compounds easily derived from it were submitted[4] for screening and certain of them were found to possess interesting physiological properties.



---

(1) This work was supported by a grant from the Los Angeles County Tuberculosis and Health Association.

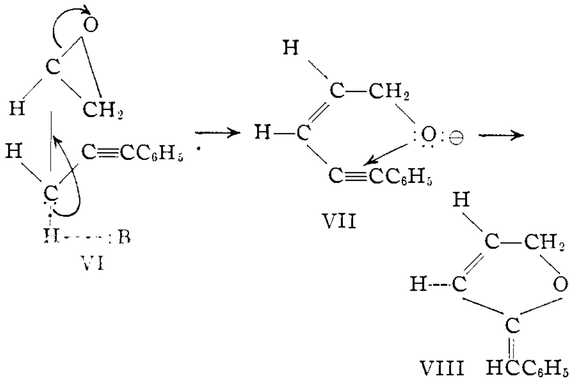
(2) W. D. Celmer and I. A. Solomons, This Journal, **74**, 1870, 2245, 3838 (1952); **75**, 1372 (1953).

(3) M. Anchel, *Science*, **121**, 607 (1955).

(4) The physiological testing of these compounds is being carried out by Dr. Charles M. Carpenter, Mr. A. W. C. Naylor-Foote and their colleagues in the Department of Infectious Diseases, University of California at Los Angeles Medical Center.

The synthesis of 5-phenyl-2-penten-4-yn-1-ol (I) from phenylacetylene and epichlorohydrin as described by Heilbron, Jones and co-workers[5] was improved and the product which accompanied the desired alcohol was shown to be α-benzylfuran (II) on the basis of analysis, molecular weight and infrared and ultraviolet spectra. The refractive index agrees with that reported for the by-product obtained earlier[5] and reported for α-benzylfuran prepared from α-bromomethylfuran and phenylmagnesium bromide.[6] A similar cyclization of related alcohols, $RCHOHCH{=}CHC{\equiv}CR'$, has been reported[7] under acid conditions and dihydrofurans have been isolated from the reaction of 4-pentyn-1-ol with sodamide[8,9] and as by-products in the reaction of phenylethynylmagnesium bromide with ethylene oxide.[10]

If 5-phenyl-1,2-epoxy-4-pentyne is an intermediate in the reaction[5,11] and this undergoes opening to 5-phenyl-2-penten-4-yn-1-ol by removal of a proton from carbon 3, one might expect that both the *cis* and *trans* forms of this alcohol would be formed, because the phenylethynyl group would hardly interfere in a significant way with the number 1 carbon of the epoxide ring in the transition state leading to the *cis*-alcohol even though these two groups had departed from the *gauche* conformation shown in VI in the direction of coplanarity.


VI

VII

VIII

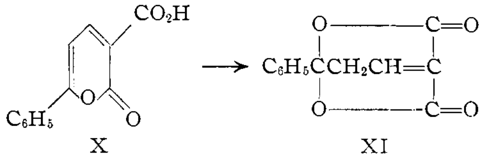
The resulting anion of the *cis*-alcohol VII should close readily to VIII which would be expected to rearrange rapidly to II. This suggests that the surviving 5-phenyl-2-penten-4-yn-1-ol should be *trans*. The alcohol is a liquid and may be a mixture of stereoisomers; however, it does exhibit a strong infrared band at 950 cm.$^{-1}$. This is somewhat lower than the 990–965 range expected for a compound containing a *trans*-$CH{=}CH$—,[12] but some lowering might be expected to result from conjugation with the triple bond; there is also a band at 990 cm.$^{-1}$. The alcohol also displays a band at 690 cm.$^{-1}$ where one might expect to find absorption characteristic of *cis*-$CH{=}CH$—, but such a band is also found in the spectra of monosubstituted benzene derivatives.[12] When the alcohol was converted to the corresponding acid IV, a solid, the infrared spectrum indicated the double bond to be *trans*, but some rearrangement during the oxidation might have occurred. It also has been reported[11] that both *cis*- and *trans*-crotyl alcohols absorb near 970 cm.$^{-1}$.

Chromic acid oxidation of 5-phenyl-2-penten-4-yn-1-ol (I) under conditions which have led to the conversion of 2-penten-4-yn-1-ol to the corresponding acid gave instead an aldehyde III as well as a small amount of phenylpropiolic acid; III was converted to the acid IV by oxidation with silver oxide and liberation from the silver salt. The spectra of III and IV were in agreement with the structures given.

Phenylcoumalin (V) was obtained in excellent yield by cyclizing IV with sulfuric acid. This naturally occurring material was first synthesized in poor yield by cyclizing with sulfuric acid, the condensation product from phenylpropargyl aldehyde and malonic acid.[13] Kalff[13] suggested structure X for the condensation product, m.p. 208–218°, which was soluble in sodium bicarbonate solution and which underwent the cyclization to phenylcoumalin, and structure XI for a second condensation product obtainable from the first by heating or simple recrystallization. The second product was insoluble in sodium bicarbonate solution and failed to yield phenylcoumalin when treated with sulfuric acid.

$$C_6H_5C{\equiv}CCHO + CH_2(CO_2H)_2 \xrightarrow{HOAc}$$

$$\underset{IX}{C_6H_5C{\equiv}CCH{=}C(CO_2H)_2} \longrightarrow$$


X

XI

We repeated Kalff's condensation and obtained a solid, m.p. 200–218°, which had a strong infrared peak at 2190 cm.$^{-1}$ characteristic of an internal acetylenic group. This compound had a neutral equivalent indicating 1.74 carboxyl groups per molecule. On this basis it is believed to be impure IX rather than X. When this broad-melting compound was heated as described by Kalff, it gave a compound melting sharply at 218°. This compound showed no infrared absorption in the region 2000–2300 cm.$^{-1}$ and had a neutral equivalent indicating 0.96 carboxyl group per molecule; it is believed to have structure X instead of XI.

The physiological activity of these compounds will be reported later.[4]

Experimental Part

5-Phenyl-2-penten-4-yn-1-ol was synthesized by the following modification of earlier directions.[5] To 2 moles of sodium phenylacetylide in 2.3 liters of liquid ammonia was added dropwise during approximately half an hour 102 g.

---

(5) L. J. Haynes, I. M. Heilbron, E. R. H. Jones and F. Sondheimer, *J. Chem. Soc.*, 1583 (1947).

(6) R. Paul, *Compt. rend.*, **200**, 1481 (1935).

(7) I. M. Heilbron, E. R. H. Jones, P. Smith and B. C. L. Weedon, *J. Chem. Soc.*, 54 (1946).

(8) R. Paul and S. Tchelitcheff, *Compt. rend.*, **230**, 1872 (1950).

(9) G. Eglinton, E. R. H. Jones and M. C. Whiting, *J. Chem. Soc.*, 2873 (1952).

(10) J. P. Danehy, R. R. Vogt and J. A. Nieuwland, THIS JOURNAL, **56**, 2790 (1934).

(11) C. F. Hiskey, H. L. Slates and N. L. Wendler, *J. Org. Chem.*, **21**, 429 (1956).

(12) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 40, 42, 65.

(13) J. Kalff, *Rec. trav. chim.*, **46**, 594 (1927).

(1.1 moles) of redistilled epichlorohydrin and the reaction mixture was stirred for 7 hours at the reflux temperature of liquid ammonia. Ammonium chloride (118 g., 2.2 moles) was then added in 3 portions followed by 1 liter of ether and stirring maintained while the ammonia was allowed to evaporate overnight. The ethereal solution was filtered, the solid residue was washed with ether and then dissolved in water, and the aqueous solution was extracted with ether. The combined ether solution was dried over anhydrous magnesium sulfate, filtered, and the ether removed at room temperature using a water aspirator. Approximately 0.8 mole of phenylacetylene was next recovered by distillation using an oil-pump and products obtained by distillation using a mercury vapor pump. Two fractions were isolated. (1) α-Benzylfuran, 55.2 g., 34.7% yield, b.p. 50–52° (10^{-3} mm.), n^{25}D 1.5411 (lit.[5] b.p. 70–72° (1 mm.), n^{16}D 1.5459, 6.7% yield; from α-bromomethylfuran,[6] b.p. 114–116° (23 mm.), n^{19}D 1.5451).

Anal. Calcd. for $C_{11}H_{10}O$: C, 83.51; H, 6.37; mol. wt., 158.17. Found: C, 83.23; H, 6.38; mol. wt., cryoscopic in benzene, 157.

(2) 5-Phenyl-2-penten-4-yn-1-ol, 58.6 g., 36.8% based on epichlorohydrin, b.p. 92–97° (10^{-3} mm.), n^{25}D 1.6158 (lit.[5] b.p. 94–96° (10^{-3} mm.), n^{24}D 1.6173); yield 24% based on half of the phenylacetylene taken.

The ultraviolet spectrum of the α-benzylfuran showed an unconjugated phenyl group. The infrared spectrum showed the absence of acetylene and hydroxyl groups and confirmed the presence of the phenyl.

5-Phenyl-2-penten-4-yn-1-al (III).—A solution of 15.8 g. (0.158 mole) of chromic anhydride and 25.3 g. of concd. sulfuric acid diluted with water to a total volume of 79 ml. was added dropwise with stirring to 17.9 g. (0.113 mole) of 5-phenyl-2-penten-4-yn-1-ol dissolved in 70 ml. of acetone during 1 hour while keeping the temperature at about 15°. The reaction mixture was stirred for an additional hour at 15°, poured on crushed ice and extracted thoroughly with ether. The ethereal solution was washed with water, extracted with sodium bicarbonate solution, dried over anhydrous magnesium sulfate, filtered, and the ether removed at room temperature. 5-Phenyl-2-penten-4-yn-1-al was distilled under high vacuum, b.p. 62° (10^{-3} mm.), n^{25}D 1.6422, yield 9.7 g. (55%). Light absorption properties (solvent, 95% ethanol): $\lambda_{\max}$ 229 mμ, $\epsilon_{\max}$ 13,600; $\lambda_{\max}$ 238 mμ, $\epsilon_{\max}$ 13,900; $\lambda_{\text{shoulder}}$ 243 mμ, ε 11,850; $\lambda_{\max}$ 249 mμ, $\epsilon_{\max}$ 13,200; $\lambda_{\text{shoulder}}$ 274 mμ, ε 12,000; $\lambda_{\max}$ 289.5 mμ, $\epsilon_{\max}$ 13,800; $\lambda_{\max}$ 308–318 mμ, $\epsilon_{\max}$ 15,950. The infrared spectrum had an exceptionally strong acetylene peak at 2195 cm.$^{-1}$. The expected carbonyl, olefin and phenyl absorption bands were present.

Anal. Calcd. for $C_{11}H_8O$: C, 84.59; H, 5.16. Found: C, 84.29; H, 5.19.

From the sodium bicarbonate solution was isolated phenylpropiolic acid, 0.4 g., m.p. 130–133° (no depression with an authentic sample). None of the acid IV could be obtained.

5-Phenyl-2-penten-4-ynoic acid (IV) was prepared by adding 12.1 g. (0.0775 mole) of 5-phenyl-2-penten-4-yn-1-al in ethanol to a mixture of freshly-prepared, thoroughly-washed silver oxide (from 52.7 g. of silver nitrate and 12.4 g. of sodium hydroxide) in 400 ml. of water and shaking for 22 hours. The silver salt of the acid was converted to the sodium salt with aqueous sodium hydroxide and the free acid liberated with diluted sulfuric acid. The acid was readily soluble in ether or alcohol but relatively insoluble in water; it was recrystallized from pentane as a white solid, m.p. 147–148.6°. Light absorption properties (solvent, 95% ethanol): $\lambda_{\max}$ 220 mμ, $\epsilon_{\max}$ 11,250; $\lambda_{\max}$ 225 mμ, $\epsilon_{\max}$ 11,000; $\lambda_{\max}$ 237 mμ, $\epsilon_{\max}$ 8,100; $\lambda_{\text{shoulder}}$ 250 mμ, ε 9,100; $\lambda_{\max}$ 296 mμ, $\epsilon_{\max}$ 24,300. The infrared spectrum was taken in a potassium bromide disk; it had a strong internal acetylene absorption at 2190 cm.$^{-1}$ and displayed the usual carboxyl, olefin and phenyl absorptions.

Anal. Calcd. for $C_{11}H_8O_2$: C, 76.73; H, 4.68. Found: C, 76.54; H, 4.47.

Phenylcoumalin (V).—A solution of 0.3 g. of 5-phenyl-2-penten-4-ynoic acid in 4.46 g. of glacial acetic acid and 4.46 g. of concentrated sulfuric acid was warmed for 5 hours on a steam-bath, then left overnight at room temperature. Addition of water gave an oil which solidified on cooling and did not dissolve when aqueous sodium carbonate solution was added until the mixture was basic to litmus. The solid was taken up in ether, and the solution was washed with water and dried over anhydrous magnesium sulfate. Evaporation of the ether gave 0.28 g. of white crystals, m.p. 61–66° (93% yield). The product was recrystallized from pentane, m.p. 66–67° (lit.[13] m.p. 68°). Light absorption properties (solvent, 95% ethanol): $\lambda_{\text{shoulder}}$ 221 mμ, ε 7,100; $\lambda_{\text{shoulder}}$ 229 mμ, ε 8,860; $\lambda_{\max}$ 233.5 mμ, $\epsilon_{\max}$ 9850; $\lambda_{\text{shoulder}}$ 243 mμ, ε 8,070; $\lambda_{\max}$ 332 mμ, $\epsilon_{\max}$ 14,100. The infrared spectrum showed the absence of the carboxylic acid group; a strong carbonyl band centered about 1700 cm.$^{-1}$, somewhat lower than less unsaturated δ-lactones.

4-Phenyl-1-buten-3-yne-1,1-dicarboxylic Acid (IX).—Kalff's directions were followed to prepare the so-called "soluble" compound which we obtained with a m.p. of 200–218°. The infrared spectrum of this solid in a potassium bromide disk showed strong absorption at 2190 cm.$^{-1}$ indicative of the acetylenic group. A neutral equivalent in 95% alcohol showed 1.74 carboxyl groups per molecule.

6-Phenylcoumalin-3-carboxylic acid (X) was prepared by refluxing IX in *p*-xylene for 18 hours.[13] The product melted at 218° and its infrared spectrum in a potassium bromide disk showed no absorption in the 2000–2300 cm.$^{-1}$ region. A neutral equivalent indicated 0.96 carboxyl group per molecule.

LOS ANGELES 24, CALIFORNIA

[CONTRIBUTION NO. 1012 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

The Chemistry of Allenic Acids. III.[1] The Acid Behavior of Highly Branched Unsaturated Malonic Acids Prepared by a Novel Method

BY J. H. WOTIZ[2] AND H. E. MERRILL[3]

RECEIVED OCTOBER 9, 1957

The reaction of butylbutadienoic acid with Grignard reagents results in a complex which on hydrolysis yields 2-butyl-3-alkyl-3-butenoic acids, and which on carbonation followed by hydrolysis gives butyl-(1-alkylvinyl)-malonic acids in high yields. They titrate as monobasic acids in 50% ethanol. Butyl-(1-*t*-butylvinyl)-malonic acid has the K_1/K_2 ratio of 57,600,000, which is the highest known.

It has been shown previously[4,5] that Grignard reagents add to allenic acids and α,β-olefinic acids to yield an adduct, which upon hydrolysis gives the corresponding β-substituted acid in high yield. The present paper reports the reaction of various Grignard reagents (I) (R = CH_3, C_2H_5, *i*-C_3H_7, *t*-C_4H_9, $CH_2C_6H_5$ and C_6H_5) with butylbutadienoic acid (II) to give a complex (III) which on hydrolysis results in high yields of 2-butyl-3-alkyl-3-butenoic acids (IV). Reaction of this complex with CO_2 results in

---

[1] The Chemistry of Allenic Acids. II, J. H. Wotiz and N. C. Bletso, *J. Org. Chem.*, **19**, 403 (1954).

[2] Research Center, Diamond Alkali Co., Painesville, Ohio.

[3] Abstracted from a portion of the Ph.D. dissertation of H. E. M., Univ. of Pittsburgh, 1957.

[4] J. H. Wotiz and J. S. Matthews, THIS JOURNAL, **74**, 2559 (1952).

[5] J. H. Wotiz, J. S. Matthews and H. Greenfield, *ibid.*, **75**, 6342 (1953).