4-Phenyl-2-bromo-1-butene.—Although the synthesis of this compound has been reported,[31] the difference in boiling points observed makes it desirable to give the details of this synthesis. Benzylmagnesium chloride, made from 25.3 g. (0.20 mole) of distilled benzyl chloride (b. p. 72–73° (24 mm.)) and 4.9 g. (0.20 atom) of magnesium in 100 ml. of absolute ether, was added to 40 g. (0.20 mole) of 2,3-dibromo-1-propene[32] (b. p. 73–76° (75 mm.)) in 100 ml. of absolute ether so as to maintain a slow reflux. The mixture was then refluxed for two hours, followed by hydrolysis in 80 ml. of saturated ammonium chloride solution and 120 g. of ice. The ether layer was washed, dried, etc., and vacuum distilled; the forerun consisted of 12 g. of 2,3-dibromo-1-propene and the 4-phenyl-2-bromo-1-butene distilled at 85–87° (4–5 mm.). A residue of 11.1 g. was crystallized from methyl alcohol and shown to be bibenzyl by a mixed melting point. After twice redistilling the product, a fraction boiling 90–91° (4–5 mm.) showed d^{25}_{4} 1.2860 and n^{25}_{D} 1.5467. Previously reported[31]: b. p. 77–78° (5 mm.), d^{20}_{4} 1.2901, n^{20}_{D} 1.5450.

Anal. Calcd. for $C_{10}H_{11}Br$: C, 56.89; H, 5.25; Br, 37.86. Found: C, 56.48; H, 5.16; Br, 38.02 (Carius).

4-Phenyl-1-butyne.—Sodamide was prepared from 3.1 g. (0.133 atom) of sodium by the method of Murray and Cloke,[33] and the reaction with 10 g. (0.0474 mole) of 4-phenyl-2-bromo-1-butene was carried out according to Johnson and McEwen.[31] The product distilled at 72–78° (11 mm.) and weighed 3.9 g. (64%); n^{25}_{D} 1.5192. The mercury derivative, bis-(4-phenyl-1-butynyl)-mercury, melted 83.5–84.5°; reported, 83.5–84.5°.[31]

2,3,4,5-Tetraphenylbibenzyl from Tetracyclone and 4-Phenyl-1-butyne.—A solution of 1.0 g. (7.68 millimoles) of the acetylenic compound and 2.88 g. (7.50 millimoles) of tetracyclone in 15 ml. of *p*-cymene was refluxed under a slow current of nitrogen until carbon monoxide was no longer evolved (about five and one-half hours). The product was isolated by steam distillation and crystallization from a solution of 10 ml. of benzene and 50 ml. of petroleum ether (60–70°) to give 2.44 g. (67%) of fine, colorless crystals melting 135–137°. A mixed melting point with compound (E) gave 135–137°.

Anal. Calcd. for $C_{38}H_{30}$: C, 93.79; H, 6.21; mol. wt., 487. Found: C, 93.57; H, 6.42; mol. wt. (Rast camphor), 476.

With dioxane substituted for *p*-cymene as the solvent, the condensation required 204 hours and the yield of product melting 135–137° was 57%.

2,3,4,5-Tetraphenylbibenzyl from Tetracyclone and 4-Phenyl-2-bromo-1-butene.—A solution of 0.78 g. (3.70 millimoles) of the butene derivative and 1.36 g. (3.54 millimoles) of tetracyclone in 15 ml. of cymene was refluxed under a slow current of nitrogen for twenty-nine and one-half hours. During this time carbon monoxide and hydrogen bromide were evolved. The product was isolated as before. The yield was 1.04 g. (60%) melting 135–137°. A mixed melting point with a 2,3,4,5-tetraphenylbibenzyl prepared above showed no depression.

To show that the hydrogen bromide was eliminated from the adduct and not from the 4-phenyl-2-bromo-1-butene, a model experiment was run in which a solution of 0.78 g. of the butene derivative in 15 ml. of *p*-cymene was refluxed for sixteen hours. No hydrogen bromide was evolved during this time. The easy elimination of hydrogen bromide from the addition compound is due to the reactivity of the tertiary bromine atom and is comparable to the behavior of Diels–Alder addition compounds of chloromaleic anhydride.[34]

Summary

1-Phenyl-1,3-butadiene can be synthesized from cinnamaldehyde and methylmagnesium bromide in 70–80% yields. Phenyl-β-naphthylamine is an effective polymerization inhibitor for this hydrocarbon. 1-Phenyl-1,3-butadiene and 2,3,4,5-tetraphenylcyclopentadienone react in a 1/1 mole ratio to give 2,3,4,5-tetraphenyl-1-(β-phenylethenyl)-7-keto-bicyclo[2,2,1]3-heptene. The structure of the adduct was proven by degradation to 2,3,4,5-tetraphenylbibenzyl. The latter compound was synthesized independently from tetracyclone and 4-phenyl-1-butyne or 4-phenyl-2-bromo-1-butene. This reaction demonstrates further that the preferred mode of addition to 1-phenyl-1,3-butadiene is 3,4. This process is the result of steric hindrance by the phenyl group and of polarization throughout the butadienyl side chain by electron displacements away from the ring.

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[31] Johnson and McEwen, THIS JOURNAL, **48**, 469 (1926).

[32] Lespieau and Bourguel, "Organic Syntheses," Coll. Vol. I, 209 (1941).

[33] Murray and Cloke, THIS JOURNAL, **58**, 2014 (1936).

[34] Synerholm, THIS JOURNAL, **67**, 1229 (1945).

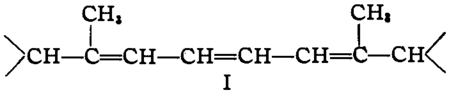
CLEVELAND, OHIO RECEIVED JULY 24, 1947

[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, UNIVERSITY OF WISCONSIN]

Acetylenic Glycols Related to Natural Polyenes[1]

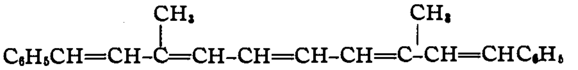
BY LENA F. DEEMER, LEO LUTWAK AND F. M. STRONG

In connection with the general problem of the synthesis of carotenoid pigments and related compounds, it seemed of interest to attempt to prepare substances corresponding in structure to the central ten carbon atoms common to nearly all the natural carotenoids (formula I). Substances of this type



I

bearing terminal substituents which would facilitate further lengthening of the carotenoid chain were desired. As far as the authors are aware the only previously synthesized compound having the carbon skeleton in question is 3,8-dimethyl-1,10-diphenyldeca-1,3,5,7,9-pentaene (II), which was prepared by Kuhn and Wallenfels in 1938.[2]



$$C_6H_5CH{=}CH{-}\overset{CH_3}{\overset{|}{C}}{=}CH{-}CH{=}CH{-}CH{=}\overset{CH_3}{\overset{|}{C}}{-}CH{=}CHC_6H_5$$

II

The recent work of Heilbron and collaborators

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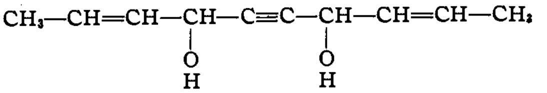
[1] Published with the approval of the Director of the Wisconsin Agricultural Experiment Station. Supported in part by a grant from the Winthrop Chemical Company.

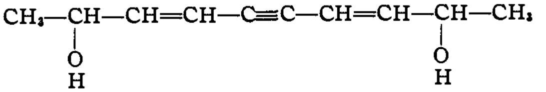
[2] Kuhn and Wallenfels, *Ber.*, **71**, 1891 (1938).

on the anionotropic rearrangement of certain acetylenic glycols[3] as typified, for example, by the ready conversion of III to IV appeared to offer a possible route to substances of the desired structure.



$$\mathrm{CH_3{-}CH{=}CH{-}\underset{\underset{\displaystyle H}{|}\atop\displaystyle O}{CH}{-}C{\equiv}C{-}\underset{\underset{\displaystyle H}{|}\atop\displaystyle O}{CH}{-}CH{=}CH{-}CH_3}$$

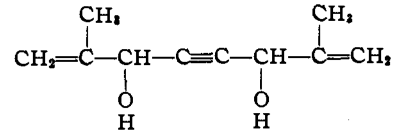
III



$$\mathrm{CH_3{-}\underset{\underset{\displaystyle H}{|}\atop\displaystyle O}{CH}{-}CH{=}CH{-}C{\equiv}C{-}CH{=}CH{-}\underset{\underset{\displaystyle H}{|}\atop\displaystyle O}{CH}{-}CH_3}$$

IV

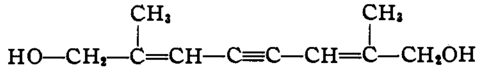
Accordingly, 2,7-dimethyl-octa-1,7-diene-4-yn-3,6-diol, V, was prepared by condensation of 2-methylacrolein with acetylene, and was subjected to rearrangement by acidic reagents. Jones and



$$\mathrm{CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}\underset{\underset{\displaystyle H}{|}\atop\displaystyle O}{CH}{-}C{\equiv}C{-}\underset{\underset{\displaystyle H}{|}\atop\displaystyle O}{CH}{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2}$$

V

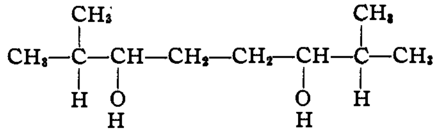
McCombie observed that the allylic shift occurred less readily with substances having terminal vinyl groups,[4] and similar behavior was encountered in the present instance. Nevertheless, the isomeric glycol, 2,7-dimethyl-octa-2,6-diene-4-yn-1,8-diol, VI, was obtained, albeit in poor yield.



$$\mathrm{HO{-}CH_2{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH{-}C{\equiv}C{-}CH{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}CH_2OH}$$

VI

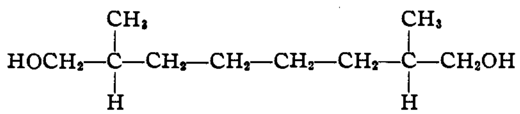
The structure of V was confirmed by an independent synthesis of the saturated glycol, VII,



$$\mathrm{CH_3{-}\underset{\underset{\displaystyle H}{|}}{\overset{\displaystyle CH_3}{\overset{|}{C}}}{-}\underset{\underset{\displaystyle H}{|}\atop\displaystyle O}{CH}{-}CH_2{-}CH_2{-}\underset{\underset{\displaystyle H}{|}\atop\displaystyle O}{CH}{-}\underset{\underset{\displaystyle H}{|}}{\overset{\displaystyle CH_3}{\overset{|}{C}}}{-}CH_3}$$

VII

and the corresponding diketone, which were identical with the reduction product of V and the corresponding diketone, respectively. A similar check on the structure of VI failed, since no solid reduction product or derivative thereof was obtained to compare with the saturated glycol, VIII, which was prepared by another method. How-



$$\mathrm{HOCH_2{-}\underset{\underset{\displaystyle H}{|}}{\overset{\displaystyle CH_3}{\overset{|}{C}}}{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}\underset{\underset{\displaystyle H}{|}}{\overset{\displaystyle CH_3}{\overset{|}{C}}}{-}CH_2OH}$$

VIII

ever, the ultraviolet absorption spectrum of VI (Fig. 1) is convincing evidence that the three unsaturated linkages in V have actually been brought into conjugation. As expected, V showed no selective absorption in the ultraviolet.

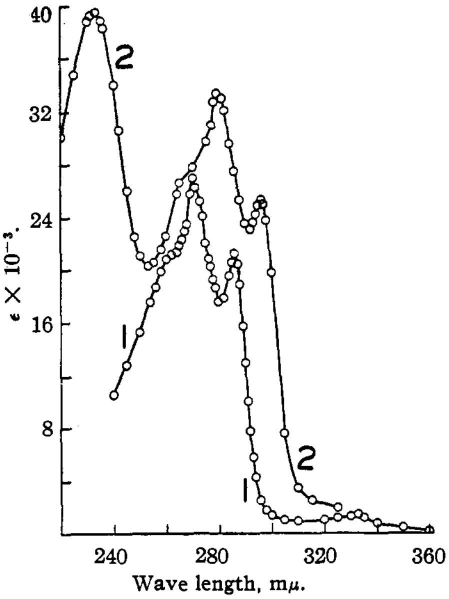


Fig. 1.—Curve 1, absorption spectrum of VI in alcohol solution; curve 2, dibenzoate of VI in alcohol solution.

Preliminary attempts selectively to hydrogenate VI to the corresponding triene and to oxidize it to the dialdehyde by Oppenheimer's method have been unsuccessful.

Experimental

α-Methylacrolein.—The commercial product[5] was distilled shortly before use, and yielded about 50% of a water-white product, b.p. 61–68° (741 mm.) plus higher boiling material. Operations involving this substance or its unsaturated condensation products were carried out under nitrogen and in peroxide-free solvents previously saturated with nitrogen. Usually a trace of hydroquinone was also added.

2,7-Dimethyl-octa-1,7-diene-4-yn-3,6-diol, V.—A solution of ethylmagnesium bromide in ether was prepared from 24 g. (1.0 gram atom) of magnesium turnings in a 1-liter, three-necked, round-bottom flask fitted with a stirrer, reflux condenser, dropping funnel and gas inlet tube. Tank acetylene purified by successive passage through water, concentrated sulfuric acid, calcium chloride and magnesium perchlorate was bubbled through the solution with continuous stirring for twenty-four hours at room temperature. Ether was added as necessary to maintain the volume at approximately 200 cc. At the end of this period analysis of the reaction mixture, by decomposing a small aliquot in water and measuring the proportion of the resulting gas absorbed by ammoniacal cuprous chloride solution, indicated that approximately 80% of the theoretical amount of acetylene di-magnesium bromide had been formed.

A solution of 70 g. (1.0 mole) of α-methylacrolein in 50 cc. of ether was then introduced over a period of one hour, and stirring was continued for two hours longer. Careful addition of 250 cc. of 10% sulfuric acid, followed by filtration, shaking out with ether, drying over "Drierite," and removing the solvent gave 69 g. of a red-brown, viscous liquid. This was distilled from a Claisen flask and yielded 7.2 g. of a pale yellow, mobile liquid, b.p. 30–110° (0.6 mm.) and 42.9 g. (52%) of a yellow, viscous oil, b. p. 135–140° (0.4 mm.). Earlier attempts to distil the crude product through a Vigreux column led to de-

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[3] Heilbron, Jones and Raphal, *J. Chem. Soc.*, 268 (1943).

[4] Jones and McCombie, *ibid.*, 262 (1943).

[5] Obtained from Eastman Kodak Company, *cf.* Hearne, Tamele and Converse, *Ind. Eng. Chem.*, **33**, 805 (1941).

composition with formation of water and much lower yields.

Redistillation of the lower-boiling material gave a colorless oil, b. p. 165–170° (741 mm.), which formed a semicarbazone, m. p. 169–170°. The same substance was obtained from the higher boiling fraction of the commercial α-methylacrolein. It does not appear to be identical with the hydrate or dimer studied by Gilbert and Donleavy.[6]

The higher boiling fraction crystallized almost completely on standing at 0°. The solid was washed free from oil with benzene, and on recrystallization from benzene formed colorless rectangular crystals, m. p. 70.5–71.5°.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 71.9; H, 8.49.

On quantitative microhydrogenation 10.45 and 8.30 mg. absorbed 5.90 and 4.60 cc. of hydrogen (S. T. P.), respectively. *Anal.* Calcd. for $C_{10}H_{14}O_2$: 4 moles of hydrogen per mole. Found: 4.19, 4.12.

The glycol showed no appreciable light absorption in the range 2200–4000 Å. Although attempts to prepare the diacetate, dibenzoate and diphenylurethan were made, no derivative was obtained, and no esterification appeared to occur.

In one preparation the product was found to melt at 88–91°. *Anal.* Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C. 71.8; H, 8.01. The lower melting isomer was also obtained in this case by redistillation of the mother liquors.

In other runs the product did not always crystallize. Redistillation of one such product gave a colorless, viscous oil, b. p. 126–130° (0.04 mm.). *Anal.* Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.26; H, 8.47.

2,7-Dimethyl-octa-4-yn-3,6-diol.—A solution of 36 g. of isobutyraldehyde in 20 cc. of ether was added dropwise with stirring during one hour to an ether solution of acetylene dimagnesium bromide prepared from 12 g. (0.5 gram-atom) of magnesium. After two hours of additional stirring the reaction mixture was worked up as described for compound V. Removal of the solvent left 30 g. of a reddish-yellow, viscous oil which largely solidified at 0°. The solid, recrystallized from benzene, formed colorless diamond-shaped crystals, m. p. 104–105°. A second product, flat plates, m. p. 61–63°, was obtained from the mother liquors. Two isomers, m. p. 69–70° and 105–106°, have been reported.[7] The total yield of the purified products was 27% of the theoretical. The higher melting product was analyzed. *Anal.* Calcd. for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 69.97; H, 10.61.

2,7-Dimethyloctane-3,6-diol, VII.—A solution of 2.12 g. of V, m. p. 70.5–71.5°, in 10 cc. of ethanol was shaken with 100 mg. of platinum oxide catalyst in an atmosphere of hydrogen until no further absorption of hydrogen occurred. Removal of the catalyst and solvent left 1.8 g. of a light amber viscous oil which possessed a distinct lemon odor. The oil partly solidified at 0° forming two types of crystals which were separated mechanically after triturating the pasty mass with a little cold benzene. Needles, m. p. 79–80°, and flat hexagons, m. p. 124–125°, were obtained.

2,7-Dimethylocta-4-yn-3,6-diol was similarly reduced, and formed an oil also possessing a lemon odor which on standing deposited needle crystals, m. p. 68–70°. Recrystallization from benzene raised the m. p. to 79–81.5°, and a mixture with the lower melting isomer above showed no depression. None of the higher melting isomer was obtained.

Anal. Calcd. for $C_{10}H_{22}O_2$: C, 68.9; H, 12.7. Found: C, 69.12; H, 12.74.

2,7-Dimethyloctane-3,6-dione.—To a solution of 2.0 g. of VII (mixed isomers) obtained from the reduction of V, in 20 cc. of benzene was added with continuous stirring over a period of one hour a mixture of 12.8 g. of sodium dichromate, 9 cc. of concentrated sulfuric acid, 30 cc. of water and 5 cc. of glacial acetic acid. The temperature was maintained at 5° during this time. The mixture was stirred for six hours longer at room temperature, the organic product collected in benzene, the extract washed with 5% sodium bicarbonate solution, then with water, dried over "Drierite" and the solvent removed. Since the oily product, 1.18 g., showed no tendency to crystallize, the dioxime was prepared. It separated from dioxane in irregular flat plates, m. p. 174–175°.

Anal. Calcd. for $C_{10}H_{20}O_2N_2$: C, 59.97; H, 10.07. Found: C, 60.5; H, 10.03.

The oily mixture of isomers resulting from the hydrogenation of 2,7-dimethylocta-4-yn-3,6-diol was similarly oxidized, and converted to the dioxime, which melted at 173.5–175° and gave no depression when mixed with the dioxime from V and VII. The literature reports the m. p. of this dioxime as 173–174°.[8]

2,7-Dimethylocta-2,6-diene-4-yn-1,8-diol, VI.—A mixture of 3 g. of V, m. p. 70.5–71.5°, 40 cc. of 95% ethanol and 160 cc. of 5% sulfuric acid was stirred under reflux for seven hours at 55° (±2°). The mixture was cooled, extracted with ether, washed with 5% sodium bicarbonate solution, then with water and dried over "Drierite." Removal of the solvent left 2.8 g. of a red-brown viscous oil. Molecular distillation at 1×10^{-4} mm. from a pot-type still gave 2.65 g. of a pale yellow, oily product which partially crystallized on standing. The solid after repeated crystallizations from benzene, weighed 0.29 g. and melted at 109–110°.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.8; H, 8.24.

The absorption spectrum in absolute ethanol was measured with a Beckman Universal spectrophotometer. Maxima were observed at 2700, 2860 and 3330 Å. with molecular extinction coefficients, at these wave lengths of 27,020, 21,140 and 1,430, respectively (Fig. 1, curve 1).

The dibenzoate was obtained readily and was crystallized from alcohol as needles, m. p. 108.5–109°.

Anal. Calcd. for $C_{24}H_{22}O_4$: C, 77.0; H, 5.92; saponification equivalent, 187.2. Found: C, 77.6; H, 5.72; saponification equivalent, 187.4.

The absorption curve of the dibenzoate is given in Fig. 1, curve 2.

It was found that the yield of VI, as measured by spectrophotometric analysis of the reaction mixtures, could be considerably improved by rearranging V with dry hydrogen chloride in absolute ethanol.[9] When held for one to two hours at 50–55° in a solution containing 1 g. of V and 100–200 milliequivalents of hydrogen chloride in 125 cc., the yield of VI was increased to approximately 45%. However, the product from such runs could not be induced to crystallize.

α,α-Dimethylsuberic Acid.—This substance was prepared by the method of Steele[10] from diethyl methylmalonate and 1,4-dichlorobutane. The crude dibasic acid, b. p. 150–160° (5 mm.) was crystallized from chloroform, m. p. 133.5–134°.

Anal. Calcd. for $C_{10}H_{18}O_4$: C, 59.4; H, 8.91; neutral equivalent, 101.1. Found: C, 59.2; H, 9.43; neutral equivalent, 100.8.

A second isomer was obtained from the mother liquors by crystallization from Skellysolve "B," m. p. 88.5–90°. *Anal.* Calcd. for $C_{10}H_{18}O_4$: C, 59.4; H, 8.91; neut. equiv., 101.1. Found: C, 58.9; H, 9.08; neut. equiv., 101.0.

Steele[10] likewise obtained two isomers melting at 132–133° and 91–92°, respectively.

The higher melting isomer formed a diamide, m. p. 214–215°. (*Anal.* Calcd. for $C_{10}H_{20}O_2N_2$: C, 59.96; H,

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[6] Gilbert and Donleavy, THIS JOURNAL, **60**, 1737 (1938).

[7] Krestinskii and Mariin, *Ber.*, **60**, 1866 (1927).

[8] Spasov, *Bull. soc. chim.*, [5] **4**, 1658 (1937).

[9] Heilbron, Jones, McCombie, Lacey and Raphel, *J. Chem. Soc.*, 77 (1945).

[10] Steele, THIS JOURNAL, **55**, 4939 (1933).

10.07. Found: C, 60.3; H, 9.99), and a bis-*p*-bromophenacyl ester, m. p. 125–126° (*Anal.* Calcd. for $C_{26}H_{28}O_6Br_2$: C, 52.38; H, 4.73. Found: C, 52.38; H, 4.71).

2,7-Dimethyloctane-1,8-diol, VIII.—Thirteen grams of α,α-dimethylsuberic acid, m. p. 133.5–134°, was esterified with methanol and concentrated sulfuric acid in the usual manner and yielded 12.5 g. of the dimethyl ester, b. p. 128° (3–5 mm.). *Anal.* Calcd. for $C_{12}H_{22}O_4$: sapon. equiv., 115.2. Found: sapon. equiv., 117.3. This ester was dissolved in alcohol and hydrogenated in a high pressure bomb over 2.5 g. of copper chromite catalyst at 200–250°.[11] Removal of the catalyst and solvent left 7.98 g. of a colorless, viscous oil, which could not be crystallized. It was characterized by preparation of the bis-3,5-dinitrobenzoate, which was recrystallized from benzene, m. p. 175–176°. *Anal.* Calcd. for $C_{24}H_{26}O_{12}N_4$: C, 51.24; H, 4.66. Found: C, 52.19; H, 4.62.

A sample of VI, 0.0528 g., m. p. 108.5–109.5°, was hydrogenated in alcohol solution with platinum oxide catalyst. The theoretical amount of hydrogen was absorbed. Removal of the catalyst and solvent left 0.0506 g. of a colorless, viscous oil. Several such preparations were converted to the bis-3,5-dinitrobenzoate. The products were oily and resisted all attempts at crystallization.

Summary

Acetylene and α-methylacrolein have been condensed to yield 2,7-dimethylocta-1,7-diene-4-yn-3,6-diol, which was rearranged to 2,7-dimethyl-octa-2,6-diene-4-yn-1,8-diol.

MADISON, WIS. RECEIVED JULY 25, 1947

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[11] The assistance of Prof. Homer Adkins in carrying out this hydrogenation is gratefully acknowledged.

[CONTRIBUTION FROM THE CHEMOTHERAPY DIVISION, STAMFORD RESEARCH LABORATORIES, AMERICAN CYANAMID COMPANY]

The Iodination of Certain Phenylsulfonamido- and Amino-heterocycles[1]

BY ROBERT G. SHEPHERD AND CATHERINE E. FELLOWS

Introduction

In a study of variously substituted sulfanilamido- and metanilamido-pyrimidines, the unique antimalarial effect of halogen substitution in the 5-position of the pyrimidine ring was discovered.[2] The preparation of iodinated pyrimidines was investigated in this connection and also because of their particular suitability for the preparation of cyano analogs.[2b] A satisfactory preparative method has now been found in the use of iodine and mercuric acetate. Using pyrimidines and other aromatic nuclei, this method was compared with the usual procedures involving iodine chloride and iodine in alkaline solution with the results set forth in the experimental section and Table II. Certain relationships of reactivity to structure were also investigated.

Experimental

The properties and analyses of the new compounds prepared in the subsequent procedures are listed in Table I by the Roman numerals accompanying them in the text.

Iodination of Aminoheterocycles. 2-Aminopyrimidine.—A solution of 23 g. (0.24 mole) of this amine in 200 cc. of water was treated with 32 g. (0.1 mole) of mercuric acetate and the mixture stirred for two minutes on the steam-bath. The initial yellow precipitate quickly turned to a thin white slurry which was treated at 70° with a solution of 50.8 g. (0.2 mole) of iodine in 200 cc. of hot dioxane. All of the iodine reacted during a half hour of stirring during which time considerable evaporation occurred. The thick slurry was poured into several volumes of 15% potassium iodide solution and washed on the filter with fresh iodide solution until white. Recrystallization from absolute alcohol (25 cc./g.) gave mercury-free **2-amino-5-iodopyrimidine** (I). Methanol and acetic acid are equally satisfactory purification solvents.

Iodination in hot acetic acid, as used for the sulfonamides, gave an orange-colored product in only 30% yield along with a large amount of mercury-containing tar.

The structure of the product was determined by conversion into 2-phenylsulfonamido-5-iodopyrimidine, the constitution of which had been previously demonstrated.[2b]

2-Aminopyridine.—The first method applied to this amine gave a 60% yield of product which was separated from the tarry by-product by ethylene dichloride extraction after the potassium iodide treatment. 5-Iodination was established by comparison (mixed m. p.) with **2-amino-5-iodopyridine** prepared according to the literature.[3]

Using two moles of iodine and one of mercuric acetate, **2-amino-3,5-diiodopyridine** (VIII) was obtained by hot ethylene dichloride extraction. After recrystallization from 95% alcohol (10 cc./g.) and ethylene dichloride (*ca.* 3 cc./g.), the melting point was 12° higher than that reported by Caldwell, *et al.*[4] Its identity was confirmed by nitrogen and iodine analyses and by conversion[4] to 2-hydroxy-3,5-diiodopyridine identical (mixed m. p.) with that prepared[4] by iodination of 2-hydroxypyridine. This amine differs from the mono-iodo derivative in being relatively insoluble in dilute acid and less soluble in ether.

Sulfonamides from Aminoheterocycles (Compounds VI, IX, X and XIII).—In this and other reactions of various benzenesulfonyl chlorides with amines in pyridine, the purification of the products has been aided materially by the addition of hot glacial acetic acid to the reaction mixture and isolation by cooling. The colored and alkali-insoluble materials which are thrown down by the usual addition of water remain in solution in this procedure which seems to have general application. The procedure for XIII given below illustrates the method.

A boiling solution of 3.5 g. (0.02 mole) of benzenesulfonyl chloride and 4.4 g. (0.02 mole) of 2-amino-5-iodopyrimidine in 3.2 cc. (0.04 mole) of dry pyridine was heated for fifteen minutes, allowing evaporation of the pyridine, to a final reaction temperature of about 150°. The temperature was then reduced to 105° for forty-five minutes and the crystalline mass was treated with 10 cc. of boiling glacial acetic acid and filtered at 30°. The 2-

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[1] Presented before the Division of Organic Chemistry at the Chicago meeting of the American Chemical Society, September 12, 1946.

[2] (a) English, Clark, Clapp, Seeger and Ebel, THIS JOURNAL, **68**, 453 (1946); (b) English, Clark, Shepherd, Marson, Krapcho and Roblin, *ibid.*, **68**, 1039 (1946).

[3] v. Schickh, German Patent 473,213 (1929).

[4] Caldwell, Tyson and Lauer, THIS JOURNAL, **66**, 1479 (1944).