

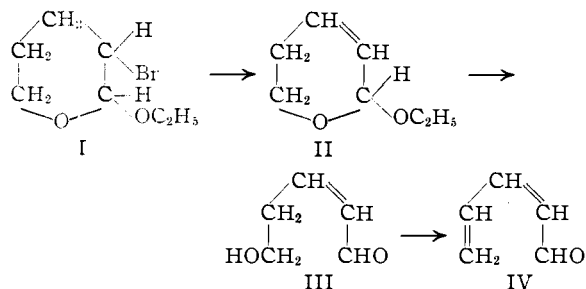
[CONTRIBUTION FROM THE LABORATORIES OF THE UNIVERSITY OF MARYLAND]

Some Reactions of 2,4-Pentadienal

BY G. FORREST WOODS AND HERMAN SANDERS

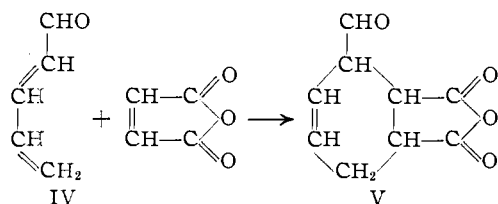
The preparation of 2,4-pentadienal, the aldehyde of butadiene, was reported by us in an earlier paper.¹ We have continued the study of this substance and herein report on the further characterization of this compound, its utilization in the Diels-Alder reaction, and its reaction with phenylmagnesium bromide.

2,4-Pentadienal is obtained by the following sequence of reactions in which we have been unable to isolate the unsaturated aldehyde (III). We



wished to exclude the possibility that the product (IV) might be a cyclobutenal. It was found that 2,4-pentadienal was reduced, although sluggishly, at room temperature with Raney nickel at 2-3 atmospheres of hydrogen. Valeraldehyde and *n*-amyl alcohol were the products identified. These results would seem to exclude a cyclobutenal since the cyclobutane ring is not opened under these mild conditions but requires a temperature considerably above those used here.²

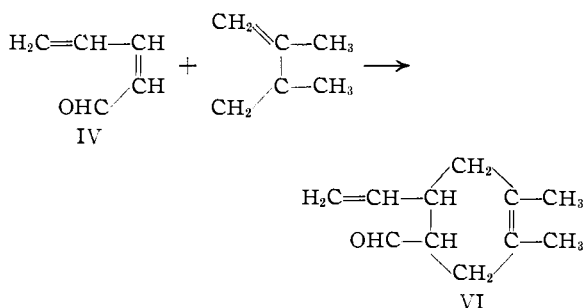
2,4-Pentadienal can be considered as the aldehyde derivative of butadiene and as such it would be expected to enter into the Diels-Alder reaction with maleic anhydride as shown below



3-Aldehyde- Δ^4 -tetrahydrophthalic anhydride (V) was readily obtained when 2,4-pentadienal was refluxed in toluene with maleic anhydride.

In the reaction just described 2,4-pentadienal functioned as a diene. Since it contains an ethylenic linkage activated by both an aldehydic carbonyl group and a vinyl group, 2,4-pentadienal would also be expected to act as a dienophile. This it does in the reaction with 2,3-dimethyl-

butadiene which leads to 4-aldehydro-5-vinyl-1,2-dimethyl- Δ^1 -cyclohexene (VI). This was accomplished by heating the reactants in a sealed tube at 150°



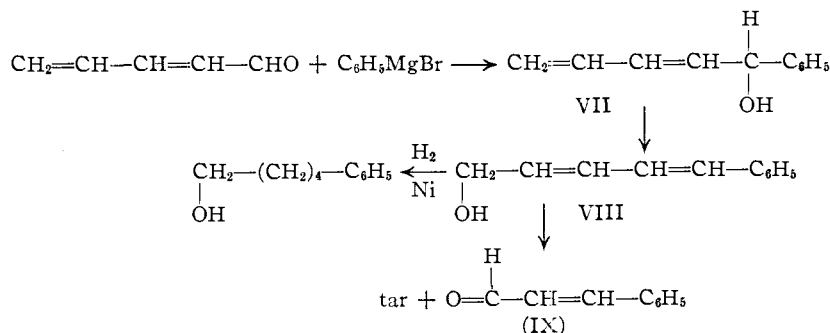
The reaction of phenylmagnesium bromide with 2,4-pentadienal was expected to proceed by 1,2-addition although the possibility of a 1,4- or 1,6-addition mechanism was recognized. The product isolated was a white crystalline substance, an alcohol, which readily yielded a phenylurethan under the usual conditions. Further, we were not able to detect any evidence for 1,4- or 1,6-addition. However, the alcohol was noticeably unstable in air, rapidly degenerating into a viscous mass with noticeable development of an aldehyde odor. That an aldehyde was generated was proved by the isolation of the 2,4-dinitrophenylhydrazone of cinnamaldehyde from the ethanol washings which were obtained from the trituration of the gummy mass from a sample of the solid alcohol which had been deliberately exposed to air. We have been unable to elucidate the nature of this reaction leading to cinnamaldehyde. It is not facilitated by either acid or base.

Catalytic reduction of the phenylpentadiene alcohol obtained from the reaction of phenylmagnesium bromide and 2,4-pentadienal was accomplished at room temperature and 2-3 atmospheres of pressure with Raney nickel as the catalyst. Isolation of the product yielded a phenylpentanol which was shown to be different from 1-phenylpentanol-1, the expected product, an authentic sample of which was prepared by the reaction of *n*-butylmagnesium bromide and benzaldehyde. Subsequently, our product was proved to be identical with 5-phenylpentanol-1. An authentic sample of this compound was prepared by the following sequence of reactions: a Friedel-Craft reaction of glutaric anhydride with benzene, the keto acid product was reduced by the Clemmensen method and the acid so obtained esterified. The phenylvaleric ester was reduced by the Bouveault-Blanc method. We found that 5-phenylpentanol-1 readily formed a white crystalline

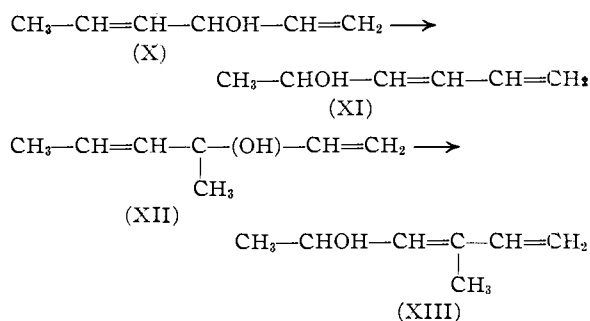
(1) Woods and Sanders, *THIS JOURNAL*, **68**, 2483 (1946).

(2) Fuson, "Organic Chemistry," Vol. 1, 2nd ed., Henry Gilman, editor-in-chief, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 103.

phenylurethan by operating in the usual manner.³ The solid 3,5-dinitrobenzoate of 5-phenylpentanol-1 was also prepared for further characterization. We therefore consider the reaction of phenylmagnesium bromide and 2,4-pentadienal to proceed by a 1,2-addition mechanism to yield compound (VII). This latter substance undergoes immediately a 1,5-rearrangement of the hydroxyl group (double allylic) to yield compound (VIII). Further, 5-phenyl-2,4-pentadien-1-ol (VIII) undergoes a molecular scission to yield cinnamaldehyde (IX)



That the 1-phenyl-2,4-pentadien-1-ol (VII) rearranges to 5-phenyl-2,4-pentadien-1-ol is not too surprising. For instance, Heilbron and co-workers⁴ have shown that the dienols (X) and XII readily rearranged to yield products XI and XIII, respectively:



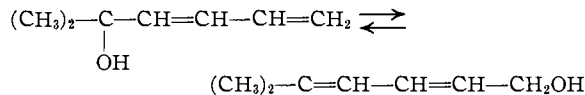
In these rearrangements a secondary alcohol is formed; the direction of the migration of the hydroxyl group is explained by the "electron repelling tendency of the methyl group."^{4a} The migration of the hydroxyl group in 1-phenyl-2,4-pentadien-1-ol (VII) is in the opposite direction which would then infer that the phenyl group is "electron attracting." Nazarov and Fisher⁵ reported a migration of this type in which the hydroxyl group migrates from a secondary to a primary position in the equilibrium reaction

(3) Von Braun reported that he could not prepare a crystalline phenylurethan of 5-phenylpentanol-1; *Ber.*, **44**, 2873 (1911).

(4a) Heilbron, Jones, McCombire and Weedon, *J. Chem. Soc.*, **84** (1945).

(4b) Cymerman, Heilbron and Jones, *ibid.*, **93** (1945).

(5) Nazarov and Fisher, *Bull. acad. sci. U. R. S. S., Classe Sci. chim.*, **631** (1945); *C. A.*, **40**, 4657 (1946).



Zal'kind and Kulikov⁶ prepared 1-phenyl-2,4-pentadien-1-ol by the reduction of 1-phenyl-2-pentyne-4-ene-1-ol. They stated that their alcohol rearranged to yield mostly 1-phenyl-1,4-pentadien-3-ol, and only a trace of the product (VIII) that we have obtained. They based their conclusions on the results of ozonization products. Our results are not in accord with these findings, but the difference may be explicable on the basis of geometrical isomers.

Experimental⁷

2,4-Pentadienal¹ (IV).—To a solution of 80 ml. of 85% phosphoric acid in 400 ml. of water was added with stirring 80 g. of 2-ethoxy- Δ^3 -dihydropyran. After a few minutes the homogeneous solution which formed was added dropwise to a solution of 80 ml. of phosphoric acid in 400 ml. of water which was already undergoing steam distillation. Steam

distillation was discontinued when the distillate no longer had the characteristic odor of 2,4-pentadienal: The distillate was saturated with potassium chloride and extracted three times with ether. After drying over sodium sulfate the solvent was removed under reduced pressure and the residue rapidly fractionally distilled, b. p. 38–40° (20 mm.), yield 24 g. (47%).

Catalytic Hydrogenation of 2,4-Pentadienal.—A suspension of 13.3 g. of 2,4-pentadienal in 150 ml. of distilled water and 3 g. of Raney nickel as catalyst was subjected to reduction at room temperature and 2–3 atmospheres of pressure. The rate of hydrogen absorption was very slow and at the end of six hours when the hydrogen uptake was somewhat in excess of that required for the two ethylenic links, the reduction was discontinued. The catalyst was removed by filtration and the filtrate was extracted with ether. The ether extract was dried over sodium sulfate. After removal of the solvent the residue was distilled. Three fractions were obtained (1) b. p. 85–105° (3 g.); (2) b. p. 105–125° (4 g.) and (3) b. p. 125–130° (2 g.). Fraction 1 yielded a yellow 2,4-dinitrophenylhydrazone, as did fraction 2 (although in smaller quantity), which melted at 105.5–106.5° after recrystallization from alcohol-water. This is in accord with the melting point of the 2,4-dinitrophenylhydrazone of valeraldehyde.⁸ *Anal.* Calcd. for $\text{C}_{11}\text{H}_{14}\text{ON}_4$: C, 49.61; H, 5.30. Found: C, 49.02; H, 5.21.

An α -naphthylurethan was prepared from fraction 3, by operating in the usual manner, which melted at 68° after recrystallization from petroleum ether, and which gave no depression in a mixed melting point determination with an authentic sample of the α -naphthylurethan of *n*-amyl alcohol. *Anal.* Calcd. for $\text{C}_{16}\text{H}_{19}\text{O}_2\text{N}$: C, 74.68; H, 7.47. Found: C, 74.71; H, 7.42.

Reaction of 2,4-Pentadienal with Maleic Anhydride.—A solution of 10 g. of 2,4-pentadienal and 13 g. of maleic anhydride in 60 ml. of dry toluene was refluxed for four hours. The toluene was decanted from a large amount of oil which had formed and the toluene solution was diluted with 120 ml. of anhydrous ether. Upon standing, 2 g. of a white crystalline material precipitated; after recrystalli-

(6) Zal'kind and Kulikov, *J. Gen. Chem. (U. S. S. R.)*, **15**, 643 (1945).

(7) All microanalyses by Miss Eleanor Werble of this Laboratory.

(8) Airs, Firth and Garner, *J. Chem. Soc.*, 1089 (1946).

zation from petroleum ether (80–100°) the Diels–Alder product melted at 153–154°. *Anal.* Calcd. for $C_9H_8O_4$: C, 60.00; H, 4.47. Found: C, 60.10, 60.19; H, 4.82, 4.75.

Reaction of 2,4-Pentadienal with 2,3-Dimethylbutadiene.—Ten grams of 2,4-pentadienal and 20 g. of 2,3-dimethylbutadiene were heated in a Carius tube at 150° for six hours. The liquid product was distilled to yield 7 g. of 4-aldehydro-5-vinyl-1,2-dimethyl- Δ^1 -cyclohexene, b. p. 121–128° (12 mm.). A sample, redistilled, b. p. 117–118° (8 mm.) was used for analysis, n_D^{20} 1.5100. *Anal.* Calcd. for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.39; H, 9.94.

The yellow 2,4-dinitrophenylhydrazone of this substance prepared in the usual manner melted at 179–180° after recrystallization from alcohol–water. *Anal.* Calcd. for $C_{17}H_{20}O_4N_4$: C, 59.29; H, 5.85. Found: C, 59.31; H, 5.85.

The semicarbazone of this compound was prepared and crystallized in glistening white platelets from alcohol–water, m. p. 202°. *Anal.* Calcd. for $C_{12}H_{19}ON_3$: C, 65.09; H, 8.65. Found: C, 64.96; H, 8.70.

Reaction of 2,4-Pentadienal with Phenylmagnesium Bromide.—A solution of 14.5 g. (0.18 mole) of freshly distilled 2,4-pentadienal in 50 ml. of ether was added dropwise to the Grignard reagent solution prepared from 39.3 g. (0.25 mole) of bromobenzene and 6.1 g. (0.25 mole) of magnesium in 200 ml. of ether. The Grignard complex which was cooled in an ice-bath was decomposed by dilute aqueous ammonium chloride. The ether layer was first washed with water and then subjected to steam distillation to remove impurities. The oil remaining in the steam distillation pot was extracted with ether. The dried ethereal solution was concentrated to approximately 40 ml. and then cooled over Dry Ice. Crystalline material was formed which was rapidly removed and washed with petroleum ether by suction filtration. The solid was decolorized and recrystallized with Norite from petroleum ether to yield a white crystalline material whose maximum melting point was 78–79°. *Anal.* Calcd. for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.39; H, 7.72. This material should be stored under nitrogen because of its instability in air.

The phenylurethan of 5-phenyl-2,4-pentadien-1-ol prepared in the usual manner was a stable compound which crystallized in white needles from petroleum ether (80–100°) and melted at 99.5–100°. *Anal.* Calcd. for $C_{18}H_{17}O_2N$: C, 77.39; H, 6.14. Found: C, 77.17; H, 6.02.

5-Phenyl-2,4-pentadien-1-ol visibly changes in appearance from a solid to a gummy mass on standing exposed to the air. This process was allowed to proceed in a petri dish for forty-eight hours, at the end of which time the gummy mass was triturated several times with small portions of ethyl alcohol. The 2,4-dinitrophenylhydrazone of the cinnamaldehyde in these alcohol washings was pre-

pared in the usual manner. Red crystals were obtained and melted at 253–254° after 3 recrystallizations from ethyl acetate. *Anal.* Calcd. for $C_{18}H_{12}O_4N_4$: C, 57.69; H, 3.88. Found: C, 57.57; H, 3.71. No depression was observed in a mixed melting point determination with an authentic sample of cinnamaldehyde-2,4-dinitrophenylhydrazone.

Hydrogenation of 5-Phenyl-2,4-pentadien-1-ol.—A solution of 5 g. of 5-phenyl-2,4-pentadien-1-ol in 25 ml. of alcohol was reduced at room temperature and 3 atmospheres pressure with Raney nickel as the catalyst. The reduction required approximately one hour for the theoretical absorption of hydrogen at which time the reaction arrested itself. The catalyst was removed by filtration and the filtrate distilled. 5-Phenylpentanol-1 (3.7 g.) distilled at 133–134° (8 mm.), 150–151° (14 mm.), n_D^{20} 1.5122. These constants are in good agreement with those reported in the literature.^{8,9} *Anal.* Calcd. for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.23; H, 9.96.

This alcohol readily yielded a stable, white, crystalline phenylurethan which melted at 73.5° after recrystallization from petroleum ether (80–100°). *Anal.* Calcd. for $C_{18}H_{21}O_2N$: C, 76.29; H, 7.47. Found: C, 76.39; H, 7.49. This phenylurethan gave no depression in a mixed melting point determination with the phenylurethan prepared from an authentic sample of 5-phenylpentanol-1.

For purposes of further identification, the 3,5-dinitrobenzoate of 5-phenylpentanol-1 obtained from the hydrogenation of 5-phenyl-2,4-pentadien-1-ol was prepared in the usual manner; m. p. 67.5° after two recrystallizations from petroleum ether (80–100°). *Anal.* Calcd. for $C_{18}H_{18}O_6N_2$: C, 60.33; H, 5.06. Found: C, 60.12; H, 5.15. No depression was observed in a mixed melting point determination with the 3,5-dinitrobenzoate prepared from an authentic sample of 5-phenylpentanol-1.

Summary

1. Further characterization of 2,4-pentadienal has been made.

2. It has been shown that 2,4-pentadienal reacts with phenylmagnesium bromide by 1,2 addition, and that this product undergoes a rearrangement. The rearranged product undergoes a decomposition to yield cinnamaldehyde.

3. That 2,4-pentadienal reacts with both 2,3-dimethylbutadiene and maleic anhydride has been shown. Thus, 2,4-pentadienal can function in the Diels–Alder reaction as a diene or a dienophile.

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(9) Roblin, Davidson and Bogert, *THIS JOURNAL*, **57**, 155 (1935).