white powder, m.p. 230–235°, which was not identified. The ethereal extract was evaporated to 0.84 g. of clear sirup. This was dissolved in several ml. of dry ether, treated to incipient turbidity with *n*-pentane, seeded and cooled. The first crop, 0.28 g., had m.p. 54–58°. On two recrystallizations from ether and *n*-pentane this was raised to 73.5–74°, and $[\alpha]^{22}\text{D}$ was 37.8° (chloroform; *c*, 0.850). The product showed no m.p. depression when mixed with authentic tetraacetyl-1,5-anhydro-D-glucitol.

Action of Bromine on II.—II (1.5 g.) was suspended in acetic acid (15 ml.). Bromine (1.9 ml., 12 equiv.) was added, causing immediate solution of II. After 2.5 hours the mixture was poured into water, extracted with ether and the extract washed with bisulfite solution, water and bicarbonate solution. After drying and evaporation, 0.32 g. of amber sirup resulted, crystallizing readily on scratching. Two recrystallizations, with Norit decolorization on the first, gave white crystals, m.p. 108–110°, $[\alpha]^{25}\text{D}$ 94.0 (chloroform; *c*, 1.078), showing no m.p. depression when mixed with α-D-glucose pentaacetate.

Kinetic Studies.—Tetraacetyl-α-D-glucosyl bromide (I) (0.411 g.) in warm 2-propanol (10 ml.) was cooled and placed in a 2-dcm. polarimeter tube. The rotation changed from 15.30° to only 14.39° in 1020 minutes, indicating the negligible rate of reaction between I and solvent.

Similarly, II (0.2435 g.) was dissolved in 10 ml. of 2-propanol containing 5% water. The rotation in a 2-dcm. tube of the cooled 0.05 *M* solution, −1.26°, was unchanged on standing overnight, establishing the irreversibility of the reaction and the indifference of II to the solvent.

In the rate studies, the requisite quantity of I was dissolved in hot 2-propanol (5 ml.), the requisite quantity of thiourea similarly treated, the two solutions cooled, mixed and poured into a 10 ml. 2-dcm. jacketed polarimeter tube held thermostatically at 25.0 ± 0.1°. Rotation and time readings were taken at one-half to one hour intervals throughout the first day. Generally, by the second day II began to crystallize in the tube, and further observation was impossible.

Calculation on the usable data was made as follows. The rotation of the system containing two optically active components may be expressed by

$$R = \lambda(a - x) + \mu x$$

where a is the original concentration of I, x the amount of II and $(a - x)$ the amount of I present at time t, λ a constant applying to I, and μ a constant applying to II. The numerical value of λ was established as 160.0 by extrapolation of the mutarotation curves to $t = 0$ and $x = 0$. That of μ was determined as −25.2 by employing the data in the second paragraph above applying to II. Thus the value of x calculated from the relation

$$x = \frac{R - 160.0a}{-185.2}$$

was used in determining the rate constants at each point in each run according to equation (1) or (2). The average values of the rate constants so obtained appear in Table II.

Polarographic Reduction.—10^{-3} *M* solutions of the acetylated thiuronium halides of glucose, mannose, xylose and cellobiose were made in phosphate buffer of *p*H 6.0 containing 2–3 drops of 6% gum arabic solution as maximum suppressor. Electrolysis was conducted automatically in a E. A. Sargent model XXI polarograph. Curves similar to Fig. 2 were obtained in each case, although the first break in the curve for the xylose salt was rather less pronounced than that for the others.

Infrared Absorption Spectra.—These were determined by using a suspension of each salt in mineral oil, according to the procedure of Kuhn.[11] A Perkin–Elmer Infrared Spectrophotometer was used in the measurements, which were kindly made by Dr. John H. Wise.

Ultraviolet Absorption Spectra.—The data in Fig. 4 were obtained in 95% ethanol using a Beckman model DU quartz spectrophotometer.

Rotatory Dispersion.—The curves obtained in Fig. 5 are based on rotatory dispersion data obtained in the region 4990 to 6670 Å. using a Rudolph precision polarimeter and spectroscope monochromator. The solutions observed were the salts dissolved in ethanol at concentrations of 1.4 to 4.4%.

STANFORD, CALIF. RECEIVED OCTOBER 2, 1950

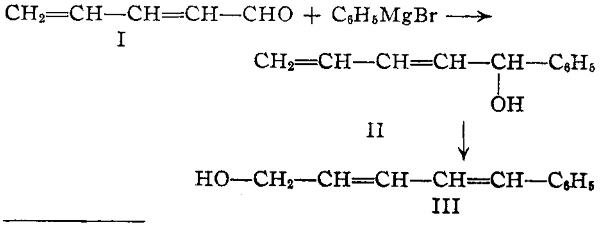
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF MARYLAND]

The Chemistry of Pentadienal and its Derivatives

BY G. FORREST WOODS AND HENRY F. LEDERLE

An attempt was made to prepare 1,3,5,7,9-decapentaene. 2,4-Pentadienal was reduced to 2,4-pentadienol-1. Treatment of this dienol with thionyl chloride afforded a pentadienyl chloride. The product of the reaction of 2,4-pentadienal with the Grignard reagent prepared from the pentadienyl chloride was shown to be 3-vinyl-1,5,7-octatrien-4-ol. 2,4-Pentadienyl acetate and 2,4-pentadienyl 2,4-pentadienoate were formed from pentadienyl chloride on treatment with a salt of the organic acid.

The reaction of 2,4-pentadienal[1] with Grignard reagents has been studied in this Laboratory. A 1,2-addition occurs followed by an allylic rearrangement when phenylmagnesium bromide is the Grignard reagent.[2]



$$\underset{\text{I}}{CH_2{=}CH{-}CH{=}CH{-}CHO} + C_6H_5MgBr \longrightarrow \underset{\text{II}}{CH_2{=}CH{-}CH{=}CH{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}C_6H_5} \Big\downarrow \underset{\text{III}}{HO{-}CH_2{-}CH{=}CH{-}CH{=}CH{-}C_6H_5}$$

With the Grignard reagents, methylmagnesium bromide and allylmagnesium chloride, the addition is 1,2 and no rearrangement takes place. The product of these reactions, the unsaturated alcohols, (IV) and (VI), were readily converted to 1,3,5-hexatriene[3] (V) and 1,3,5,7-octatetraene[4] (VII).

$$\underset{\text{I}}{CH_2{=}CH{-}CH{=}CH{-}CHO} + CH_3MgBr \longrightarrow \underset{\text{IV}}{CH_2{=}CH{-}CH{=}CH{-}CHOH{-}CH_3} \longrightarrow \underset{\text{V}}{H{-}(CH{=}CH)_3{-}H}$$

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

(2) Woods and Sanders, *ibid.*, **69**, 2926 (1947).

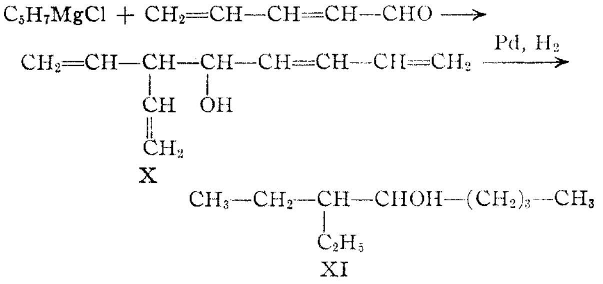
(3) Woods and Schwartzman, *ibid.*, **70**, 3394 (1948).

(4) Woods and Schwartzman, *ibid.*, **71**, 1396 (1949).

$$CH_2{=}CH{-}CH{=}CH{-}CHO + \text{allylMgCl} \longrightarrow \underset{\text{VI}}{CH_2{=}CH{-}CH{=}CH{-}CHOH{-}CH_2{-}CH{=}CH_2} \longrightarrow \underset{\text{VII}}{H{-}(CH{=}CH)_4{-}H}$$

It seemed possible to prepare the next higher member of the highly unsaturated series, 1,3,5,7,9-decapentaene, by similar steps, provided 1-chloro-2,4-pentadiene could be synthesized.

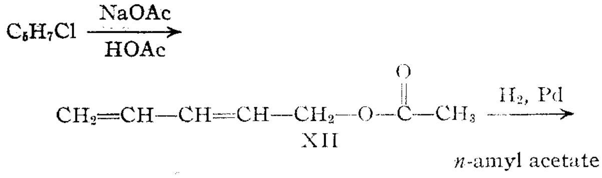
Reduction of 2,4-pentadienal with aluminum isopropoxide yielded 2,4-pentadien-1-ol (VIII), whose structure was confirmed by reduction to *n*-amyl alcohol. The properties of our sample of 2,4-pentadien-1-ol are in good agreement with those reported by Heilbron,[5a,b] *et al.* Treatment of 2,4-pentadien-1-ol with thionyl chloride yielded a pentadienyl chloride (IX), whose structure could not be determined, but which readily formed a Grignard reagent. Reaction of this Grignard reagent with 2,4-pentadienal yielded a decatetraenol. To establish the identity of this unsaturated alcohol, it was hydrogenated and compared with isomeric decanols, which were prepared by standard Grignard reactions. It proved to be 3-ethyloctan-4-ol (XI). These reactions may be formulated



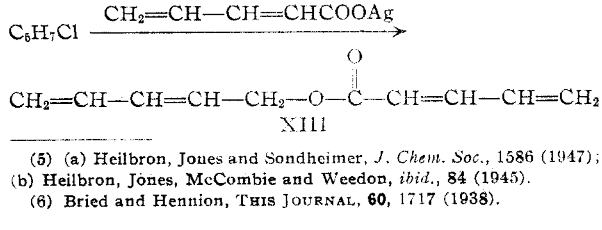
$$C_5H_7MgCl + CH_2{=}CH{-}CH{=}CH{-}CHO \longrightarrow \underset{\text{X}}{CH_2{=}CH{-}\underset{\underset{CH_2}{\|}}{\underset{|}{CH}}{-}\underset{OH}{\underset{|}{CH}}{-}CH{=}CH{-}CH{=}CH_2} \xrightarrow{\text{Pd, }H_2} \underset{\text{XI}}{CH_3{-}CH_2{-}\underset{C_2H_5}{\underset{|}{CH}}{-}CHOH{-}(CH_2)_3{-}CH_3}$$

Only one derivative of the decanol (XI) could be prepared so the various decanols were oxidized to the corresponding ketones. These ketones failed to form solid 2,4-dinitrophenylhydrazones and the semicarbazones were formed very slowly; ten days to two weeks was generally required. Bried and Hennion[6] have reported that decanone-5 does not yield any of the common carbonyl derivatives. The structure of the pentadienyl chloride (IX) is uncertain since the step resulting in rearrangement has not been identified.

Pentadienyl chloride reacted smoothly with sodium acetate to yield the acetate (XII) which was reduced to *n*-amyl acetate.



$$C_5H_7Cl \xrightarrow[\text{HOAc}]{\text{NaOAc}} \underset{\text{XII}}{CH_2{=}CH{-}CH{=}CH{-}CH_2{-}O{-}\overset{\overset{O}{\|}}{C}{-}CH_3} \xrightarrow{H_2,\text{ Pd}} n\text{-amyl acetate}$$



$$C_5H_7Cl \xrightarrow{CH_2{=}CH{-}CH{=}CHCOOAg} \underset{\text{XIII}}{CH_2{=}CH{-}CH{=}CH{-}CH_2{-}O{-}\overset{\overset{O}{\|}}{C}{-}CH{=}CH{-}CH{=}CH_2}$$

The same ester was produced by the action of acetyl chloride on pentadienol.

Pentadienyl pentadienoate (XIII) was prepared by the reaction of pentadienyl chloride with the silver salt[7] of pentadienoic acid.[8] This ester, which was very unstable and could be distilled only with considerable loss, was identified by reduction to *n*-amyl valerate.

Experimental

All analyses were performed by Mrs. Mary Aldridge and Mr. Byron Baer of this Laboratory.

2,4-Pentadien-1-ol (VIII).—To a boiling solution of 122 g. of aluminum isopropoxide in 600 ml. of isopropyl alcohol was slowly added 18 g. of pentadienal. The reaction and isolation of the product, 2,4-pentadien-1-ol, was carried out in the usual manner; yield 46 g. (55%); b.p. 55° (8 mm.); $n^{26}_{\rm D}$ 1.4857. *Anal.* Calcd. for C_5H_8O: C, 71.39; H, 9.59. Found: C, 71.39, 71.42; H, 9.73, 9.70. On prolonged standing the compound formed a clear, transparent polymer. A phenylurethan, m.p. 62.5–63.5°, was prepared from the compound in the usual manner. *Anal.* Calcd. for $C_{12}H_{13}O_2N$: C, 70.91; H, 6.45. Found: C, 71.09, 71.17; H, 6.64, 6.64. The α-naphthylurethan melted at 96.5–97.5°. (Heilbron, *et al.*[5] report 97.5°.) *Anal.* Calcd. for $C_{16}H_{15}O_2N$: C, 75.86; H, 5.97. Found: C, 75.84, 76.20; H, 6.01, 5.99.

Reduction of 2,4-Pentadien-1-ol to *n*-Amyl Alcohol.—Pentadienol (12 g.) was catalytically hydrogenated with Pd–charcoal in methanol solvent; yield 5.7 g. of *n*-amyl alcohol (44%), b.p. 137°. An α-naphthylurethan of the *n*-amyl alcohol was prepared in the usual manner, m.p. 64–66°. (No depression with an authentic sample.) The 3,5-dinitrobenzoate prepared in the usual manner melted at 45°.

Pentadienyl Chloride (IX).—2,4-Pentadienol (42 g.) was added slowly to thionyl choride (66 g.) with stirring and the gaseous reaction products were swept out of the flask by means of an aspirator. After standing for ten minutes the reaction mixture was distilled under reduced pressure in a nitrogen atmosphere. After a small forerun pentadienyl chloride (30 g., 58%) was collected distilling at 24° (13 mm.). Refractive indices showed considerable variation, the values lying between 1.4696 and 1.4919; one sample, after four redistillations, had $n^{25}_{\rm D}$ 1.4701. *Anal.* Calcd. for C_5H_7Cl: C, 58.55; H, 6.88. Found: C, 58.51, 58.38; H, 7.18, 7.04.

3-Vinyl-1,5,7-octatrien-4-ol (X).—A Grignard reagent was prepared by the slow addition of 12 g. of pentadienyl chloride in 330 ml. of ether to 8.8 g. of powdered magnesium in 25 ml. of ether to which was then added 7.6 g. of 2,4-pentadien-1-al in 20 ml. of dry ether. The ethereal solution of the Grignard addition complex was decanted from the excess magnesium and decomposed with aqueous ammonium chloride. The ether layer was shaken with water, dilute sodium bicarbonate, and again with water and dried over magnesium sulfate. After removal of the ether by distillation under reduced pressure in a nitrogen atmosphere 3-vinyl-1,5,7-octatrienol (10 g., 71%) was obtained boiling at 75–95° (8 mm.). A carefully purified sample boiled at 90–92° (8 mm.); $n^{25.5}_{\rm D}$ 1.5042. *Anal.* Calcd. for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.47, 80.04; H, 9.38, 9.34. On prolonged standing the compound formed a clear transparent polymer.

Reduction of 3-Vinyl-1,5,7-octatrien-4-ol to 3-Ethyloctan-4-ol (XI).—3-Vinyl-1,5,7-octatrien-4-ol (15 g.) in methanol was catalytically hydrogenated at room temperature and atmospheric pressure with Pd–charcoal. Absorption of hydrogen was very rapid and stopped at 93% of the theoretical value. The catalyst was removed by filtration. After removal of the solvent, 13 g. of 3-ethyloctan-4-ol (83%) was obtained, b.p. 92–95° (10 mm.), $n^{28.0}_{\rm D}$ 1.4385. *Anal.* Calcd. for $C_{10}H_{22}O$: C, 75.88; H, 14.01. Found: C, 76.02, 75.86; H, 13.26, 13.47. The α-naphthylurethan of 3-ethyloctan-4-ol was prepared in the usual fashion, m.p. 79–80°. (No depression with sample whose preparation is given below.) *Anal.* Calcd. for $C_{21}H_{29}O_2N$: C, 77.02; H, 8.93. Found: C, 77.48, 77.35; H, 9.20, 9.08.

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[5] (a) Heilbron, Jones and Sondheimer, *J. Chem. Soc.*, 1586 (1947); (b) Heilbron, Jones, McCombie and Weedon, *ibid.*, **84** (1945).

[6] Bried and Hennion, This Journal, **60**, 1717 (1938).

[7] Doebner, *Ber.*, **35**, 1136 (1902).

[8] Kohler and Butler, This Journal, **48**, 1041 (1926).

This same alcohol prepared in 64% yield by the reaction of *n*-butylmagnesium bromide with 2-ethylbutyraldehyde had the following properties: b.p. 90–93° (9 mm.), $n^{25.3}D$ 1.4362, α-naphthylurethan m.p. 78–80°.

Oxidation of 3-Ethyloctan-4-ol to 3-Ethyloctan-4-one.—3-Ethyloctan-4-ol from each of the above samples was oxidized with sodium dichromate and sulfuric acid in the usual fashion. The product was steam distilled from the reaction mixture and extracted from the distillate; yield, after filtration of ether extract from the drying agent and subsequent distillation: (80%), b.p. 75° (9 mm.), $n^{25.4}D$ 1.4215. The samples of 3-ethyloctan-4-one had a greenish-yellow color which could not be removed on treatment with charcoal or redistillation. The semicarbazone of each sample was prepared in the usual fashion. However, ten days to two weeks were required for crystallization (in the ice-box); melting point 82.5–83° (no depression on mixing). *Anal.* Calcd. for $C_{11}H_{23}N_3O$: C, 61.93; H, 10.87. Found: C, 62.12, 62.02; H, 10.84, 10.86.

Preparation of 3-Decanol, 5-Decanol and 5-Decanone.—The 3- and 5-decanols, which were needed for comparison with the hydrogenated product from the reaction of pentadienylmagnesium chloride and pentadienal, were synthesized by standard Grignard reactions. For the former *n*-valeraldehyde and *n*-amyl bromide and for the latter propionaldehyde and *n*-heptyl bromide were used. The products were isolated in the usual manner.

3-Decanol (b.p. 105–107° (13 mm.), $n^{22.5}D$ 1.4338) was obtained in 82% yield. Our boiling point is in accord with that of Pickard and Kenyon,[9] who prepared this compound by reduction of 3-decanone. The α-naphthylurethan of 3-decanol melted at 60–62°. *Anal.* Calcd. for $C_{21}H_{29}O_2N$: C, 77.02; H, 8.93. Found: C, 77.14, 77.11; H, 8.73, 8.87.

5-Decanol (b.p. 118–120° (30 mm.), $n^{27}D$ 1.4321) was obtained in 89% yield. *Anal.* Calcd. for $C_{10}H_{22}O$: C, 75.88; H, 14.01. Found: C, 75.93, 75.65; H, 13.95, 14.05. The α-naphthylurethan of 5-decanol melted at 55–56°. *Anal.* Calcd. for $C_{21}H_{29}O_2N$: C, 77.02; H, 8.93. Found: C, 76.95, 77.01; H, 9.06, 9.00.

5-Decanone[6] (b.p. 84–86° (8 mm.), $n^{25.2}D$ 1.4225) was obtained by oxidation with Beckmann's solution of 5-decanol, in 92% yield. The semicarbazone melted at 53–54°. *Anal.* Calcd. for $C_{11}H_{23}ON_3$: C, 61.93; H, 10.87. Found: C, 62.13, 61.95; H, 10.97, 10.92. A substituted hydantoin[10] melted at 143–145°. *Anal.* Calcd. for $C_{12}H_{22}O_2N_2$: C, 63.68; H, 9.80. Found: C, 63.68, 63.90; H, 9.84, 9.79.

2,4-Pentadienyl Acetate (XII). **A.**—A mixture of 12 g. of pentadienyl chloride, 12 g. of anhydrous sodium acetate and an equal amount of glacial acetic acid was refluxed for one-half hour, poured into water, and extracted three times with ether. The combined ether layers were washed twice with water, twice with dilute solution of bicarbonate and again twice with water. The ether layer was dried and distilled; yield 8.9 g. of pentadienyl acetate of b.p. 54–55° (8 mm.) (58%). A sample was redistilled four times, $n^{28.0}D$ 1.4598. *Anal.* Calcd. for $C_7H_{10}O_2$: C, 66.64; H, 7.99. Found: C, 66.50, 66.54; H, 8.18, 8.10.

B.—2,4-Pentadien-1-ol (9.6 g.) was slowly added with stirring to 11 g. of acetyl chloride. The gas from the reaction flask was removed by a slight vacuum applied by means of an aspirator. After all the alcohol had been added stirring was continued for ten minutes and the aspirator kept in operation. The mixture was poured into water and twice extracted with ether. The combined ether extract was then washed with 5% potassium carbonate, and again with water. Distillation yielded 10 g. of pentadienyl acetate (70%), b.p. 68–69° (18 mm.).

Reduction of 2,4-Pentadienyl Acetate to *n*-Amyl Acetate.—2,4-Pentadienyl acetate (10 g.) was catalytically hydrogenated at atmospheric pressure and room temperature using Pd-charcoal catalyst and methanol solvent. The calculated amount of hydrogen was very rapidly absorbed. After filtration of the catalyst, the solution was poured into water and a small top layer separated. The bottom layer was twice extracted with ether, and the combined top and ether layers in turn extracted with water to remove as much methanol as possible. The ether layer was dried and distilled to yield 6.3 g. (62%) of *n*-amyl acetate, b.p. 146–149°. Its identity was confirmed by hydrolysis to *n*-amyl alcohol.

2,4-Pentadienyl Ester of 2,4-Pentadienoic Acid (XII).—2,4-Pentadienoic acid (vinylacrylic acid) was prepared by the method of Kohler and Butler.[8] The acid melted at 71°. A modification of the method of Doebner[7] for preparing the silver salt of this acid was made. The acid (6.8 g.) was added slowly to 250 ml. of distilled water, while the solution was vigorously stirred. Any material not dissolved in ten minutes was removed. This material, comprising polymerized pentadienoic acid has a gummy consistency and was discarded. Then 12 g. of silver nitrate in 100 ml. of water (distilled) was added to the solution while stirring was continued. The solution was slowly adjusted to a *p*H of 6 by the dropwise addition of a 3% solution of sodium hydroxide. The silver salt was filtered and partially dried. The salt, though originally white, turns dark brown upon exposure to light or standing.

The salt (18 g.) was placed in a three-neck flask to which was fitted a mechanical stirrer, a separatory funnel and a moisture receiving tube itself connected to a reflux condenser. Benzene (250 ml.) was introduced into the flask and the mixture refluxed with stirring until all the water was removed. Nearly all the benzene was removed by distillation into and through the moisture receiving tube. The tube was removed and dry acetone (200 ml.) added to the flask. Again, under reflux with stirring, pentadienyl chloride (8.5 g.) was added dropwise. The mixture was stirred and heated for an additional 10 minutes, cooled and filtered. The filtrate was poured into water which was then extracted three times with peroxide-free ether. The combined ether extract was washed with dilute sodium bicarbonate solution and finally with water and dried over magnesium sulfate. After removal of the drying agent by suction, filtration and distillation of the ether under reduced pressure in a nitrogen atmosphere, the residue was distilled *as rapidly as possible* using a luminous flame as a source of heat. A considerable amount of material polymerizes, but 3.6 g. (26%) of pentadienyl pentadienoate was obtained, b.p. 80–90° (0.8 mm.), $n^{30.5}D$ 1.5189. A little hydroquinone was added to all ethereal solutions. The instability of the material was too great to obtain a pure sample for analysis.

Pentadienyl pentadienoate (6.0 g.) in methanol, was hydrogenated using a palladium–charcoal catalyst at atmospheric pressure and room temperature (the theoretical amount of hydrogen was absorbed). The solution from which the catalyst had been filtered was poured into water and three times extracted with ether. The combined ether extracts were twice extracted with water and then dried over magnesium sulfate. Fractional distillation of the solution yielded 4.6 g. of *n*-amyl valerate (74%), b.p. 198–208°, $n^{34}D$ 1.4095. *n*-Amyl valerate (6.0 g.) was refluxed for twelve hours with 100 ml. of 25% aqueous solution of sodium hydroxide. Identification of the saponification products in the usual manner established the presence of (1) *n*-amyl alcohol which was obtained in 77% yield and characterized as the 3,5-dinitrobenzoate and (2) *n*-valeric acid (86% yield) which was characterized as the *p*-bromophenacyl ester. Both the derivatives of (1) and (2) were compared with authentic samples.

COLLEGE PARK, MARYLAND RECEIVED AUGUST 29, 1950

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[9] Pickard and Kenyon, *J. Chem. Soc.*, 1945 (1913).

[10] Henze and Speer, THIS JOURNAL, **64**, 522 (1942).