chloro derivative of this is inactive, but the hydroxylamine without the methyl group, N-carbethoxy-*m*-chlorophenylhydroxylamine, affected the growth of grasses but was inactive when applied to dicotyledonous plants.

COLLEGE PARK, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

Base-Catalyzed Condensations of Aldehydes with α,β-Unsaturated Ketones[1]

BY SARGENT G. POWELL AND WILLIAM J. WASSERMAN[2]

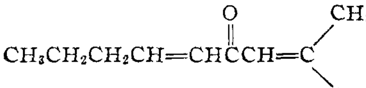
RECEIVED JUNE 19, 1956

Condensations of α,β-unsaturated ketones with aldehydes were studied in an attempt to determine the site of condensation in the ketones. Butyraldehyde condensed with mesityl oxide to give 2-methyl-2,5-nonadien-4-one, the result of condensation with the α-methyl group. The condensation of benzaldehyde with 2,2-dimethyl-4-hexen-3-one gave 2,2-dimethyl-7-phenyl-4,6-heptadien-3-one, the product resulting from condensation in the vinylogous γ-position.

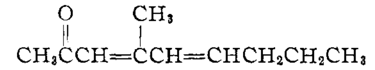
In the past 75 years since Claisen and Claparede[3] first studied the condensation of benzaldehyde with mesityl oxide many condensations of aldehydes and ketones with α,β-unsaturated carbonyl compounds have been observed, but very few have been investigated sufficiently to elucidate the nature of the condensation products. Where condensation was possible on both the vinylogous γ-carbon and on the α-methyl or methylene group of the α,β-unsaturated ketone (1-acetyl-2-methylcyclohexene,[4] 3,5-dimethyl-2-cyclohexen-1-one[5] and 3,4,5,6-tetrahydroacetophenone),[6] investigation of the condensation product showed the condensation to have occurred on the α-methyl or methylene group.

Butyraldehyde was condensed with mesityl oxide in dioxane using potassium hydroxide as the catalyst. Besides the 2-ethyl-2-hexenal resulting from self condensation of butyraldehyde, two products were isolated.

The lower boiling product (I) was found to have a molecular weight of 151 corresponding to either Ia or Ib.



Ia



$CH_3\overset{\overset{O}{\|}}{C}CH=\overset{\overset{CH_3}{|}}{C}CH=CHCH_2CH_2CH_3$

Ib

Hydrogenation of I gave II which was identical with a sample of 2-methyl-4-nonanone prepared by an authentic method, and did not agree in properties with a sample of 4-methyl-2-nonanone prepared by an authentic method. In this case, therefore, the condensation had occurred with the α-methyl group in preference to the vinylogous carbon.

The other product, b.p. 125–127° (5 mm.), was not satisfactorily identified. Cryoscopic determination of its molecular weight gave a value of 178 as compared to an expected value of 180 for 2,4-diethyl-2,4-octadienal[7] ($C_{12}H_{20}O$, arising from a condensation of 2-ethyl-2-hexenal and butyraldehyde). Analysis of a 2,4-dinitrophenylsemicarbazone supported the presumed structure. Hydrogenation data seemed to indicate the presence of impurities. The product of the platinum-catalyzed hydrogenation gave a 2,4-dinitrophenylsemicarbazone which analyzed correctly for 2,4-diethyloctanal 2,4-dinitrophenylsemicarbazone.

Since only a small sample of the highest boiling product had been obtained, it seemed profitable to examine the contents of the residue of the distillation of the C.P. butyraldehyde used in the condensation. The lower boiling constituents of the residue were identified as 2-ethyl-2-hexenal, butyric acid and butyraldol. Another fraction, b.p. 97–100° (0.5 mm.), was identified as 2-ethyl-3-hydroxy-1-hexyl butyrate.[8] The hydroxyester was conclusively identified by saponification and identification of the butyric acid and 2-ethyl-1,3-hexanediol produced. The presence of the hydroxyester in the butyraldehyde residues is difficult to explain since the ordinary Tischenko reaction is promoted by basic catalysts.[9] Since the formation of the hydroxyester probably occurred in an acid medium (assuming the auto-oxidation of butyraldehyde to butyric acid to be the initial reaction) it is most likely that the hydroxyester was formed by some type of acid-catalyzed Tischenko reaction from butyraldehyde and butyraldol.

After determining that the methyl group in the α-position is preferred as a condensation site to the vinylogous position, it seemed desirable to extend the comparison to other groups placed in the α-po-

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[1] Abstracted from a dissertation submitted by William J. Wasserman to the University of Washington in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Division of Natural Sciences, Humboldt State College, Arcata, Calif. Please address all inquiries to this author.

[3] L. Claisen and A. Claparede, *Ber.*, **14**, 349 (1881).

[4] R. B. Turner and D. M. Voitle, THIS JOURNAL, **72**, 4166 (1950); W. S. Johnson, J. Szmuszkovicz and M. Miller, *ibid.*, **72**, 3726 (1950).

[5] E. Knoevenagel, *Ann.*, **281**, 117 (1894).

[6] R. E. Christ and R. C. Fuson, THIS JOURNAL, **59**, 893 (1937).

[7] Similar products had reportedly been isolated from butyraldehyde self-condensations. F. Bauer (*Monatsh.*, **25**, 1 (1904)) obtained $C_{12}H_{20}O$, b.p. 200° (20 mm.). A. Gorhan (*ibid.*, **26**, 73 (1905)) and C. Weizmann and S. F. Garrard (*J. Chem. Soc.*, **117**, 324 (1920)) obtained $C_{12}H_{22}O_2$, b.p. 160–162° (12 mm.) which the latter believed to be 2,4-diethyl-3-hydroxy-4-octenal.

[8] This compound had previously been observed by V. Grignard and M. Fluchaire (*Ann. chim.*, [10] **9**, 18 (1928)) and F. J. Villani and F. F. Nord (THIS JOURNAL, **69**, 2605 (1947)), to be among the base-catalyzed self-condensation products of butyraldehyde. It had also been identified by J. von Braun and G. Manz (*Ber.*, **67**, 1696 (1934)) among the products resulting from the heating of butyraldehyde in an inert atmosphere.

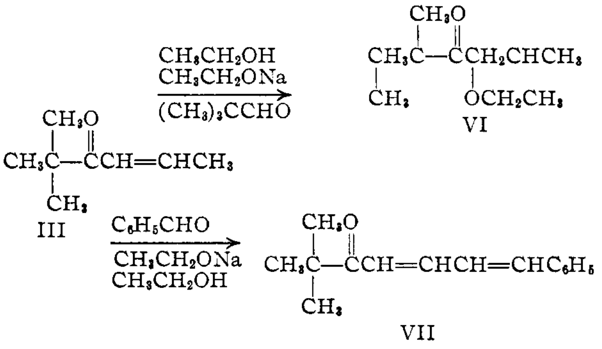
[9] T. A. Geissman, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 102; W. A. Waters, "Organic Chemistry," H. Gilman, editor, Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 1244.

sition. Therefore, as our second unsaturated ketone we chose 2,2-dimethyl-4-hexen-3-one (III) in which the α-position is blocked, thus forcing any condensation which might occur into the vinylogous γ-position. Since we were unable to synthesize III by the condensation of acetaldehyde with pinacolone it was necessary to choose a more roundabout route. The reaction of *t*-butylmagnesium chloride with butyryl chloride gave 2,2-dimethyl-3-hexanone (IV), butyl butyrate and, principally, 2,2-dimethyl-3-hexyl butyrate (V). Saponification of V gave an alcohol which was oxidized to IV with chromic acid. Bromination of IV in dilute acetic acid gave 4-bromo-2,2-dimethyl-3-hexanone which could be dehydrohalogenated with the aid of collidine to give III in varying yield. An easier route to III was developed later. The method of Stevens[10] was used to produce 2,2-dimethyl-4-hexen-3-ol and 3,4,4-trimethylpentanal from crotonaldehyde and *t*-butylmagnesium chloride, and the unsaturated alcohol was oxidized to III with the aid of the chromium trioxide–pyridine complex.

In attempting to effect the condensation of butyraldehyde with III, the only products obtained were the self-condensation products of butyraldehyde, *i.e.*, 2-ethyl-2-hexenal and butyraldol.

To avoid the possibility of self-condensation, the condensation of pivalaldehyde with III was attempted. Since pivalaldehyde does not undergo the Cannizzaro reaction in dilute basic solution[11] and has been shown to give aldol type condensations with 2-butanone[12] and acetophenone,[13] it seemed likely that this aldehyde would be more apt to undergo aldol condensation than the Cannizzaro reaction and, thus, would be a good test of the ability of aliphatic aldehydes to condense in the vinylogous position of III. An attempted condensation of pivalaldehyde with III in ethanolic solution using sodium ethoxide as the basic catalyst resulted in the addition of ethanol to the double bond of III giving 2,2-dimethyl-5-ethoxy-3-hexanone (VI). The infrared absorption spectrum of VI showed peaks at 8.80 μ corresponding to the frequency characteristic of saturated ether linkages and at 5.87 and 9.05 μ corresponding to the frequencies attributed to the carbonyl group.[14] No other product was found. Michael additions of alcohols to the double bond of unsaturated carbonyl compounds have been observed previously.[15] Attempts to condense pivalaldehyde with III in tetrahydrofuran yielded only starting materials.

Since our attempts to condense aliphatic aldehydes with III were unsuccessful we shifted to the use of benzaldehyde. The sodium ethoxide catalyzed condensation of benzaldehyde with III gave 2,2-dimethyl-7-phenyl-4,6-heptadien-3-one (VII) which was found to be identical with authentic VII prepared by the condensation of cinnamaldehyde with pinacolone. Aldol-type condensation in the vinylogous γ-position was thus clearly demonstrated.



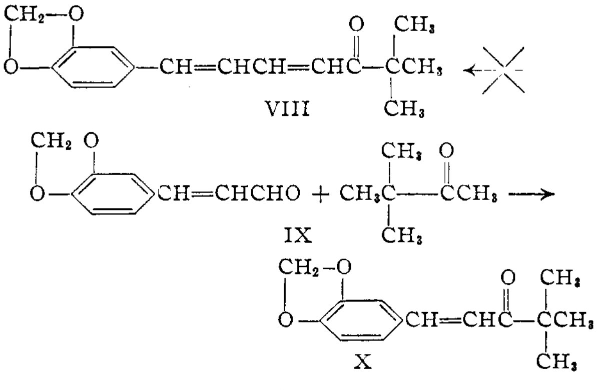
$$\mathrm{CH_3\underset{CH_3}{\overset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}CH{=}CHCH_3 \xrightarrow[(CH_3)_3CCHO]{CH_3CH_2OH,\ CH_3CH_2ONa} CH_3\underset{CH_3}{\overset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}CH_2\underset{OCH_2CH_3}{CH}CH_3}$$

III VI

$$\mathrm{III \xrightarrow[CH_3CH_2ONa,\ CH_3CH_2OH]{C_6H_5CHO} CH_3\underset{CH_3}{\overset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}CH{=}CHCH{=}CHC_6H_5}$$

VII

Our first studies of VII had indicated that it would be difficult to utilize because of its semi-solid characteristics. Therefore an attempt to prepare 2,2-dimethyl-7-(3,4-methylenedioxyphenyl)-4,6-heptadien-3-one (VIII) was made. 3-(3,4-Methylenedioxyphenyl)-2-propenal (IX) was condensed with pinacolone in the presence of sodium ethoxide giving 4,4-dimethyl-1-(3,4-methylenedioxyphenyl)-1-penten-3-one (X) instead of the expected VIII. The authentic material prepared by the condensation of piperonal with pinacolone was found to be identical with X, and both showed approximately the same melting points as X prepared in a different manner by Pace.[16] Apparently X had resulted from an initial reverse aldol reaction of IX giving piperonal and acetaldehyde, followed by condensation of the piperonal with pinacolone.



VIII

IX

X

Experimental[17]

Condensation of Mesityl Oxide with Butyraldehyde.—A solution of 32 g. of potassium hydroxide in 25 ml. of water, 800 ml. of dioxane and 940 ml. (810 g., 8.2 moles) of mesityl oxide was stirred vigorously while 368 ml. (300 g., 4.17

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(10) P. G. Stevens, This Journal, 56, 1425 (1934); 57, 1112 (1935).

(11) T. A. Geissman, ref. 9, p. 99; J. B. Conant, C. N. Webb and W. C. Mendum, This Journal, 51, 1246 (1929).

(12) C. A. Friedman, Dissertation, University of Washington, 1938, p. 25.

(13) B. Rowland, University of Washington, private communication.

(14) F. A. Miller, "Organic Chemistry," Vol. III, H. Gilman, editor, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 122.

(15) B. Puetzer, C. H. Nield and R. H. Barry, This Journal, 67, 832 (1945); F. Weisenborn, Dissertation, University of Washington, 1950, p. 83; C. F. Koelsch, This Journal, 65, 437 (1943); R. C. Fuson, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 470.

(16) E. Pace, *Atti acad. Lincei*, [6] 9, 778 (1929); *C. A.*, 23, 4942 (1929).

(17) All melting points and boiling points are uncorrected. A Fisher melting point block was employed for the melting point measurements. Ultraviolet absorption spectra were observed with a Beckman DU spectrophotometer with 1.00-cm. fused quartz absorption cells. A Perkin–Elmer model 21 recording spectrophotometer with sodium chloride prism and cells was employed for the infrared absorption spectra measurements. Analyses were performed by B. J. Nist, H. L. Pan and M. E. Taylor of the University of Washington Analytical Laboratories.

moles) of butyraldehyde was added dropwise over a period of 13 hours. The reaction mixture remained basic to phenolphthalein throughout the addition, and was neutralized upon completion of the addition with 160 g. of tartaric acid. After removal of the precipitated salt the solution was concentrated under reduced pressure, dried over anhydrous magnesium sulfate and distilled through a 25-plate stainless steel gauze packed column under reduced pressure. Three fractions were obtained: (1) 2-ethyl-2-hexenal, b.p. 62–63° (14 mm.), $n^{26}\mathrm{D}$ 1.4398, 36.7 g. (14%); (2) 2-methyl-2,5-nonadien-4-one, b.p. 92–94° (12 mm.), $n^{26}\mathrm{D}$ 1.4798, 141 g. (22%); (3) 2,4-diethyl-2,4-octadienal (?), b.p. 125–127° (5 mm.), $n^{26}\mathrm{D}$ 1.4790, 3.9 g. (1.6%); residue, 100 g.

(1) **Identification of 2-Ethyl-2-hexenal.**—The reported boiling point of 2-ethyl-2-hexenal is 65–66° (14 mm.).[18] After one recrystallization from ethanol the 2,4-dinitrophenylhydrazone ($\epsilon_{\max}$ 28,500, $\lambda_{\max}$ 380 mμ in ethanol) melted at 122–123°, reported m.p. 122°.[19]

Quantitative hydrogenation with 10% palladium-on-barium sulfate catalyst in ethanol required 1.01 moles of hydrogen per mole of 2-ethyl-2-hexenal. The 2,4-dinitrophenylhydrazone of 2-ethylhexanal melted at 120–121°, reported m.p. 120–121°.[20]

(2) **Identification of 2-Methyl-2,5-nonadien-4-one (I).**—Cryoscopic determination of the molecular weight in benzene gave a value of 151; calculated value 152. The ultraviolet absorption spectrum in ethanol showed $\epsilon_{\max}$ 13,000, $\lambda_{\max}$ 248 mμ.

The 2,4-dinitrophenylhydrazone formed red-brown needles from ethanol, m.p. 138–139°.

Anal. Calcd. for $C_{16}H_{20}O_4N_4$: N, 16.86. Found: N, 16.74.

A solution of 45 g. (0.30 mole) of Ia in 100 ml. of ethanol was reduced with 0.1 g. of platinum oxide at room temperature in a Parr hydrogenation apparatus. After 0.59 mole of hydrogen had been absorbed the catalyst was removed by filtration and the solvent distilled under reduced pressure. A careful fractionation with the previously described column gave a fraction, b.p. 88–89° (18 mm.), 32 g. (71%), which was used for comparison with authentic 2-methyl-4-nonanone and 4-methyl-2-nonanone.

The oxalomonophenyldihydrazone[21] of 2-methyl-4-nonanone formed colorless needles from benzene, m.p. 125–127°.

4-Methyl-2-nonanone[22] **(IIb, and 3-Carbethoxy-4-methyl-2-nonanone).**—An ethyl sodioacetoacetate solution prepared from 150 ml. of absolute ethanol, 6.9 g. (0.3 mole) of sodium and 39 ml. (39 g., 0.3 mole) of ethyl acetoacetate was refluxed and stirred vigorously while 31.8 ml. (36 g., 0.2 mole) of 2-bromoheptane[23] was added dropwise over a period of one hour. After 18 hours at reflux temperature the mixture was cooled, the precipitated salt removed by filtration and the solution concentrated at atmospheric pressure. The residue was refluxed for 2 hours with 200 ml. of a 10% sodium hydroxide solution. Following acidification the mixture was steam distilled until 500 ml. of distillate had been collected. The organic layer was dried with anhydrous magnesium sulfate and distilled giving recovered 2-bromoheptane, b.p. 80–95° (42 mm.), 3 g.; 4-methyl-2-nonanone, b.p. 108–112° (39 mm.), yield 5 g. (16%); and 3-carbethoxy-4-methyl-2-nonanone, b.p. 142–142.5° (11 mm.), yield 6.1 g. (13%). Venable[22] reported the boiling points of the latter two compounds at atmospheric pressure as 196–198° and 250–260°, respectively.

Attempts to prepare a 2,4-dinitrophenylhydrazone of the ketone gave oils from which a crystalline product could not be obtained.

The 2,4-dinitrophenylsemicarbazone of the ketone was prepared by refluxing 1 g. of the ketone with 1.7 g. of 2,4-dinitrophenylsemicarbazide and 1 ml. of pyridine in 10 ml. of ethanol for 2.5 hours. The pale yellow product from a benzene–hexane mixture melted at 182–183°.

Anal. Calcd. for $C_{17}H_{25}O_5N_5$: N, 18.46. Found: N, 18.59.

The oxalomonophenyldihydrazone[21] formed colorless needles from benzene, m.p. 124.5–125.5°.

Anal. Calcd. for $C_{18}H_{28}O_2N_4$: N, 16.86. Found: N, 17.14.

2-Methyl-4-nonanone (IIa).[24] **The semicarbazone** gave colorless needles from ethanol, m.p. 55–56°.

Anal. Calcd. for $C_{11}H_{23}ON_3$: N, 19.70. Found: N, 19.95.

The 2,4-dinitrophenylsemicarbazone prepared as described above proved to be unstable with its m.p. range becoming wider and lower with the passage of time.

The oxalomonophenyldihydrazone gave colorless needles from benzene, m.p. 128–129°.

Anal. Calcd. for $C_{18}H_{28}O_2N_4$: N, 16.86. Found: N, 17.27, 17.32.

Mixed Melting Points of Oxalomonophenyldihydrazone Derivatives: II, *127–129°*; IIa, *128–129°*; IIb, 124.5–125.5°; II with IIa, 124–126°; II with IIb, 110–114°.

Comparison of Infrared Absorption Spectra.—II and IIa showed the following peaks in the absorption spectrum which were not shown by IIb (wave length of maxima are given in μ): 2.45 (shoulder), 3.70 (very weak), 7.62 (shoulder), 8.19 (very weak), 8.75 (strong), 8.92 (weak), 9.56 (strong), 10.01 (very weak), 10.84 (medium), 11.45 (weak), 12.10 (weak). In addition IIb showed the following peaks not shown by II or IIa: 3.89, 5.97, 6.11, 7.87, 8.88, 10.41, *10.68, 11.10, 11.18, 11.77, 12.57, 13.03.*

(3) **Identification of 2,4-Diethyl-2,4-octadienal.**—Cryoscopic determination of the molecular weight in benzene gave a value of 178; calculated for $C_{12}H_{20}O$, 180.

Attempts to prepare a 2,4-dinitrophenylhydrazone resulted in the formation of oils from which no crystalline product could be obtained.

The 2,4-dinitrophenylsemicarbazone was prepared by the method previously described and gave pale yellow needles from a benzene–hexane mixture, m.p. 102–103°.

Anal. Calcd. for $C_{19}H_{25}O_5N_5$: N, 17.36. Found: N, 17.29.

When reduced in the presence of 10% palladium-on-barium sulfate, the octadienal absorbed 0.81 molar equivalent of hydrogen per mole; with platinum oxide, 1.65 molar equivalents per mole. The 2,4-dinitrophenylsemicarbazone prepared in the manner previously described from an ethanolic solution of the latter hydrogenation product gave short yellow needles from ethanol, m.p. 150–151°.

Anal. Calcd. for $C_{19}H_{29}O_5N_5$: N, 17.19. Found: N, 17.28.

Identification of Butyraldehyde Residue.—The residue, amounting to approximately one-third of the original material, remaining after the separation of the butyraldehyde from the commercial product was distilled, giving three fractions: a mixture of 2-ethyl-2-hexenal and butyric acid, b.p. 75–80° (25 mm.); butyraldol, b.p. 120–126° (25 mm.); and 2-ethyl-3-hydroxy-1-hexyl butyrate, b.p. 97–100° (0.5 mm.), $n^{24.8}\mathrm{D}$ 1.4428, reported[25] b.p. 148–149° (15 mm.), $n^{15}\mathrm{D}$ 1.4452.

The hydroxyester (14 g., 0.065 mole) was saponified by refluxing overnight in 100 ml. of 10% ethanolic potassium hydroxide. Water was added, and the solution was extracted with ether. The ether was evaporated under reduced pressure, the residue dried over anhydrous magnesium sulfate and distilled giving 2-ethyl-1,3-hexanediol, b.p. 129–129.5° (11 mm.), $n^{24.5}\mathrm{D}$ 1.4521, yield 6 g. (63%), reported[25] b.p. 133–134° (15 mm.), $n^{15}\mathrm{D}$ 1.4535. The basic aqueous solution was acidified with hydrochloric acid and extracted with ether. Ether was removed under reduced pressure, and butyric acid was obtained, b.p. 80–83° (25 mm.), yield 4 g. (70%).

The *p*-phenyl phenacyl ester was recrystallized from aqueous ethanol, m.p. 80–81°, mixed m.p. with authentic material, m.p. 78–80°, 79–80°.

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[18] A. Gorhan, *Monatsh.*, **26**, 73 (1905).

[19] M. Baches, *Compt. rend.*, **196**, 277 (1933).

[20] C. Weizmann, E. Bergmann and L. Haschelberg, *Chemistry & Industry*, **587** (1937).

[21] Oxalomonophenyldihydrazide was prepared by the method of P. P. T. Sah and H. Wang (*J. Chinese Chem. Soc.*, **14**, 39 (1946)), and the procedure of A. T. Nielsen, C. Gibbons and C. A. Zimmerman (THIS JOURNAL, **73**, 4696 (1951)), was used for the preparation of derivatives with this reagent.

[22] F. P. Venable (*Ber.*, **13**, 1651 (1880)), had observed the reaction of 2-bromoheptane with ethyl sodioacetoacetate, but neglected to report the experimental details.

[23] M. L. Sherrill, THIS JOURNAL, **52**, 1989 (1930).

[24] Carbide and Carbon Chemicals Corporation, French Patent 799,037, May 30, 1936; *C. A.*, **30**, 7581 (1936).

[25] V. Grignard and M. Fluchaire, *Ann. chim.*, [10] **9**, 18 (1928).

2,2-Dimethyl-4-hexen-3-one (III).—Attempts to prepare this compound by the condensation of acetaldehyde with pinacolone failed. Two successful synthetic routes to this ketone were found.

A. *Via* **2,2-Dimethyl-3-hexanone.**—The method of Whitmore, *et al.*,[26] was employed for the reaction of butyryl chloride and *t*-butylmagnesium chloride.[27] The only modification in the procedure was the addition of the butyryl chloride to the Grignard reagent instead of the inverse addition method used by Whitmore, *et al.* The products were 2,2-dimethyl-3-hexanone, b.p. 138–149°, $n^{24.5}\mathrm{D}$ 1.4098, yield 5% (reported b.p. 138–142°, $n^{20}\mathrm{D}$ 1.4097, yield 21%); *n*-butyl butyrate, b.p. 149–164°, $n^{24.5}\mathrm{D}$ 1.4033, yield 8% (reported 11%); and 2,2-dimethyl-3-hexyl butyrate, b.p. 203–206°, $n^{24.5}\mathrm{D}$ 1.4224, yield 50% (reported 37%).

Saponification of 2,2-Dimethyl-3-hexyl Butyrate.—The ester (143 g., 0.72 mole) was refluxed with a solution of 60 g. of potassium hydroxide in 200 ml. of ethanol and 20 ml. of water for 16 hours, and the solution was then poured into water, saturated with sodium chloride. The separated 2,2-dimethyl-3-hexanol was washed with water, dried with anhydrous magnesium sulfate, and distilled, b.p. 153–155°, $n^{24.5}\mathrm{D}$ 1.4528, yield 75 g. (83%), reported[28] b.p. 153–156°.

2,2-Dimethyl-3-hexanone was prepared from the alcohol by the method of Leroide,[28] b.p. 142–145°, $n^{24.5}\mathrm{D}$ 1.4102, yield 73%, reported b.p. 145–148°, $n^{17}\mathrm{D}$ 1.4148.

The 2,4-dinitrophenylhydrazone gave yellow-orange needles, m.p. 118–120°, reported[26] 119–120°.

Bromination of 2,2-Dimethyl-3-hexanone.—A mixture of 29 g. (0.23 mole) of the ketone, 63 ml. of acetic acid and 54 ml. of water was kept at 65° while 12 ml. (37 g., 0.23 mole) of bromine was added dropwise over a period of 2.5 hours while stirring vigorously. After the addition of 50 ml. of water the mixture was cooled to 10°, and sodium carbonate was added until there was no further evolution of carbon dioxide. Water was added to dissolve the precipitated salts, the organic layer separated, washed, dried over anhydrous magnesium sulfate and distilled, b.p. 78–80° (13 mm.), yield 27 g. (69%).[29]

Dehydrobromination of 4-Bromo-2,2-dimethyl-3-hexanone.—The method used by Ungnade and Tucker[30] for the dehydrobromination of several bromodiethylstilbestrol derivatives was employed. The product obtained by refluxing 10.4 g. (0.050 mole) of the bromoketone and 36.3 g. (0.30 mole) of collidine for 2 hours was purified and distilled giving III, b.p. 48–50° (13 mm.), yield 4.6 g. (73%),[31] reported[32] b.p. 52–54° (9 mm.). The ultraviolet absorption spectrum in ethanol showed $\epsilon_{\max}$ 12,700, $\lambda_{\max}$ 229.5 mμ.

The 2,4-dinitrophenylhydrazone formed yellow-orange needles from ethanol, m.p. 132–133°, reported[33] 135–135.5°.

B. *Via* **2,2-Dimethyl-4-hexen-3-ol.**—The reaction of *t*-butylmagnesium chloride with crotonaldehyde was carried out by the method of Stevens.[10] From 249 ml. (210 g., 3.00 moles) of crotonaldehyde, 122.5 g. (5.00 moles) of magnesium turnings and 550 ml. (462 g., 5.00 moles) of *t*-butyl chloride was obtained 152 g. of a mixture consisting mainly of 2,2-dimethyl-4-hexen-3-ol and 3,4,4-trimethylpentanal, b.p. 65–67° (40–23 mm.). The aldehyde was removed with a 10% sodium bisulfite solution. Ethereal washings of the bisulfite addition product were added to the separated organic layer, the solution was concentrated under reduced pressure, dried over anhydrous magnesium sulfate and the hexenol distilled, b.p. 66–70° (30 mm.), $n^{25}\mathrm{D}$ 1.4353, yield 85.5 g. (22%), reported[10] b.p. 75–76° (36 mm.), $n^{25}\mathrm{D}$ 1.4369, yield 36% determined from the crude phthalate prepared from an aliquot of the distilled mixture.

The bisulfite addition compound was treated with saturated sodium carbonate, the product extracted with ether, and the ethereal solution was concentrated and the aldehyde distilled, b.p. 64–67° (31 mm.), $n^{25}\mathrm{D}$ 1.4227, yield 7 g. (2%), reported[10] b.p. 70–72° (36 mm.), yield 20% determined as the crude semicarbazone from an aliquot of the distilled mixture.

The 2,4-dinitrophenylhydrazone gave yellow needles from ethanol, m.p. 112–112.5°.

Anal. Calcd. for $C_{14}H_{20}O_4N_4$: N, 18.16. Found: N, 18.24.

A second run in which Stevens' procedure was modified by an inverse addition of the Grignard reagent to the crotonaldehyde and the purification procedure described above gave 2,2-dimethyl-4-hexen-3-ol in 13% yield, and 3,4,4-trimethylpentanal in 22% yield. The higher boiling products obtained by both procedures were not investigated.

Oxidation of 2,2-Dimethyl-4-hexen-3-ol.—The chromium trioxide–pyridine complex was prepared from 300 g. of chromic acid and 3 l. of pyridine by the method of Poos, *et al.*[34] A solution of 122 g. (0.95 mole) of the hexenol in 900 ml. of pyridine was added to the oxidizing mixture and allowed to stand at room temperature for 60 hours before pouring the suspension into 6 l. of water. The mixture was extracted with ether and the ethereal extracts were washed with 5% hydrochloric acid and water. After concentrating the solution the residue was dried over anhydrous magnesium sulfate and III was distilled, b.p. 74–78° (37 mm.), yield 49 g. (39%).

The 2,4-dinitrophenylhydrazone was recrystallized from ethanol, m.p. 133–134°, mixed m.p. with earlier materials (m.p. 132–133°), 132–133°.

Attempted Condensation of Butyraldehyde with 2,2-Dimethyl-4-hexen-3-one.—A mixture of 75 ml. of tetrahydrofuran,[35] 1 g. of potassium hydroxide in 1 ml. of water and 47 g. (0.37 mole) of III was stirred vigorously while 90 ml. (72 g., 1.00 mole) of butyraldehyde was added dropwise over a period of 75 minutes. After 45 minutes, 1 g. of potassium hydroxide in 1 ml. of water was added to maintain basic conditions. The mixture was allowed to stand for 15 minutes, neutralized with tartaric acid and filtered to remove the precipitated salt. The solution was concentrated, dried over anhydrous magnesium sulfate, and distilled giving III; 2-ethyl-2-hexenal, b.p. 91–95° (39 mm.), yield 12 g. (19%); butyraldol, b.p. 98–102° (10 mm.), $n^{25.5}\mathrm{D}$ 1.4454, yield 32 g. (45%); and residue, 14 g.

To determine whether the butyraldol contained any condensation product of butyraldehyde with III it was refluxed with iodine for one hour, washed with 10% sodium bisulfite, dried over anhydrous magnesium sulfate and distilled, giving only 2-ethyl-2-hexenal, b.p. 67–69° (16 mm.), 22.5 g., residue 3 g.

Attempted Condensation of Pivalaldehyde with 2,2-Dimethyl-4-hexen-3-one.—A solution of 6 g. (0.05 mole) of III and 4.3 g. (0.05 mole) of pivalaldehyde[36] in 50 ml. of absolute ethanol was cooled to 0° and treated with a cooled solution of sodium ethoxide prepared from 1.5 g. of sodium and 25 ml. of absolute ethanol. The mixture was allowed to stand overnight and was then added to 250 ml. of water, extracted with ether and the ethereal extracts were dried over anhydrous magnesium sulfate. After concentration the mixture was distilled yielding III, 1 g., and 2,2-dimethyl-5-ethoxy-3-hexanone (VI), b.p. 73–75° (15 mm.), $n^{24.5}\mathrm{D}$ 1.4237, yield 3.3 g. (48%). The ultraviolet absorption spectrum[37] of VI in ethanol showed a shoulder at 214 mμ (2950) and at 275 mμ (1320) and $\epsilon_{\max}$ 1200, $\lambda_{\max}$ 281 mμ. The infrared absorption spectrum included the following

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[26] F. C. Whitmore, J. S. Whitaker, W. A. Mosher, O. N. Breivik, W. R. Wheeler, C. S. Miner, Jr., L. H. Sutherland, R. B. Wagner, T. W. Clapper, C. E. Lewis, A. R. Lux and A. H. Popkin, THIS JOURNAL, **63**, 643 (1941).

[27] F. C. Whitmore and D. E. Badertscher, *ibid.*, **55**, 1559 (1933).

[28] J. Leroide, *Ann. chim.*, [9] **16**, 369 (1921).

[29] An earlier run in which a nichrome wire stirrer was consumed by the action of the hydrobromic acid formed in the reaction gave an 85% yield of the bromoketone.

[30] H. E. Ungnade and P. W. Tucker, THIS JOURNAL, **71**, 1381 (1949).

[31] A second run with 85 g. (0.41 mole) of the bromoketone and 325 ml. (300 g., 2.48 moles) of collidine gave only a small amount of collidine hydrobromide precipitation in 2 hours, and no apparent increase in the precipitate after 5 hours. This run gave yield 20.8 g. (41%), b.p. 54–57° (27 mm.). The boiling point of the large tarry residue was above 80° (17 mm.), and it was discarded.

[32] J. M. Sprague and H. Adkins, THIS JOURNAL, **56**, 2669 (1934).

[33] P. S. Stutsman and H. Adkins, *ibid.*, **61**, 3303 (1939).

[34] G. I. Poos, G. E. Arth, R. E. Beyler and L. H. Sarett, *ibid.*, **75**, 427 (1953).

[35] Stored as suggested by E. I. du Pont de Nemours and Co. (Electrochemicals Department, Bulletin A-2185-5M-6-51, "Tetrahydrofuran," p. 4) over ferrous sulfate and sodium bisulfate to prevent peroxide formation and distilled immediately preceding use.

[36] K. N. Campbell, THIS JOURNAL, **59**, 1980 (1937).

[37] A Cary, model 10, automatic recording spectrophotometer was used.

maxima: 5.87 μ (very strong), 8.80 μ (very strong) and 9.05 μ (very strong).

Anal. Calcd. for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Found: C, 69.66; H, 10.94.

The 2,4-dinitrophenylhydrazone gave yellow needles from ethanol, m.p. 90–91°.

Anal. Calcd. for $C_{16}H_{24}O_5N_4$: C, 54.53; H, 6.87. Found: C, 54.28; H, 7.03.

Several attempts to condense pivalaldehyde with III in tetrahydrofuran by the method employed above failed, yielding only starting materials.

Condensation of Benzaldehyde with 2,2-Dimethyl-4-hexen-3-one.—A solution of 1.0 g. (0.010 mole) of benzaldehyde and 1.2 g. (0.0095 mole) of III in 10 ml. of absolute ethanol was cooled to 0° and treated with a cooled sodium ethoxide solution prepared from 0.3 g. of sodium and 10 ml. of absolute ethanol and allowed to stand overnight. Water was added and the mixture was extracted with ether. The ethereal extracts were dried over anhydrous magnesium sulfate, concentrated and distilled giving 2,2-dimethyl-7-phenyl-4,6-heptadien-3-one (VII), b.p. 140–142° (1 mm.), yield 0.58 g. (28%).

The 2,4-dinitrophenylhydrazone was recrystallized from ethanol–ethyl acetate, m.p. 202–204°.

Authentic VII was prepared by a similar condensation between 11.9 ml. (13.2 g., 0.10 mole) of cinnamaldehyde and 12.3 ml. (9.8 g., 0.098 mole) of pinacolone in 45 ml. of absolute ethanol using a sodium ethoxide solution prepared from 2.5 g. of sodium and 30 ml. of absolute ethanol. The product, b.p. 137–141° (1.5 mm.), yield 8.0 g. (38%), was crystallized by chilling in an acetone–Dry Ice mixture. After two recrystallizations from ethanol the yellow crystals melted at 56–57°.[38]

Anal. Calcd. for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 83.23; H, 8.66.

The 2,4-dinitrophenylhydrazone gave red needles from ethanol, m.p. 203–204°, mixed m.p. with derivatives obtained previously (m.p. 202–204°), 202–204°.

Anal. Calcd. for $C_{21}H_{22}O_4N_4$: C, 63.94; H, 5.62. Found: C, 63.87; H, 5.73.

Condensation of 3-(3,4-Methylenedioxyphenyl)-2-propenal (IX) with Pinacolone.—IX was prepared by the method of Ladenburg and Scholtz[39] in 20% yield. A condensation between 4.7 g. (0.027 mole) of IX and 3.7 ml. (3.0 g., 0.030 mole) of pinacolone in 20 ml. of absolute ethanol was catalyzed by a sodium ethoxide solution prepared from 1 g. of sodium and 10 ml. of absolute ethanol as before. After 24 hours 150 ml. of water was added and the crystalline precipitate was recrystallized from ethanol giving 4,4-dimethyl-1-(3,4-methylenedioxyphenyl)-1-penten-3-one (X), m.p. 93–94°, yield 4.5 g. (73%). Pace[16] reported m.p. 98° for X prepared from a piperonal–pinacolone condensation. The ultraviolet absorption spectrum[37] of X in ethanol showed a shoulder at 221 mμ (7900) and at 241 mμ (9000) and ϵ_{max} 9500, λ_{max} 250 mμ and ϵ_{max} 18,000, λ_{max} 339 mμ.

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.36; H, 6.94. Found: C, 71.68; H, 7.05.

The 2,4-dinitrophenylhydrazone gave two varieties of crystals from ethanol–ethyl acetate: fine yellow needles which became orange-red at 120° and melted at 148–155°; and thick shiny red needles, m.p. 148–153°, mixed m.p. of the two forms, 148–155°. Recrystallized from methanol the yellow needles gave orange plates, m.p. 149.5–156°.

Anal. Calcd. for $C_{20}H_{20}O_6N_4$: C, 58.24; H, 4.89. Found: C, 57.94; H, 5.13.

The red needles were recrystallized from ethanol, m.p. 149–156°.

Anal. Calcd. for $C_{20}H_{20}O_6N_4$: C, 58.24; H, 4.89. Found: C, 57.9; H, 4.85.

Both derivatives gave negative Knorr tests[40] indicating that neither possessed a pyrazoline structure. Similar phenomena were observed by Goheen[41] in the preparation of patulin phenylhydrazone.

A condensation of piperonal (4.5 g., 0.030 mole) with pinacolone (3.0 g., 0.030 mole) carried out in the same manner gave 6.6 g. (95%) of X, m.p. 92.5–93.5°, mixed m.p. with previous material (m.p. 93–94°) 92.5–94°.

The 2,4-dinitrophenylhydrazone of authentic X gave the same yellow and red crystalline mixture, m.p. 148–156°, mixed m.p. with previous material 149–156°.

SEATTLE, WASHINGTON

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[38] 4,4-Dimethyl-1-phenyl-1-penten-3-one (colorless), the product of the condensation of benzaldehyde and pinacolone, is reported to have m.p. 43°, b.p. 144–145° (10 mm.) by G. A. Hill, C. S. Spear and J. S. Lachowicz (THIS JOURNAL, **45**, 1559 (1923)).

[39] A. Ladenburg and M. Scholtz, *Ber.*, **27**, 2958 (1894).

[40] L. Knorr. *ibid.*, **26**, 100 (1893).

[41] D. W. Goheen, Dissertation, University of Washington, 1951 p. 144.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Vinyl Alcohols. XX.[1] Reaction with Lead Tetraacetate

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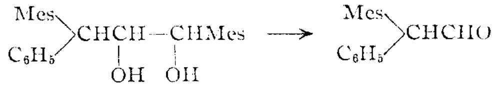
Five 2,2-diarylvinyl alcohols, when treated with lead tetraacetate, have been found to yield the acetates of the corresponding diarylglycolaldehydes.

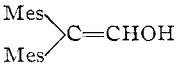
A possible route to diarylacetaldehydes or to the corresponding vinyl alcohols is the cleavage of suitably constituted glycols with lead tetraacetate or with periodic acid. The latter reagent was used successfully to make mesitylphenylacetaldehyde (II) from the glycol I.[1]



$$\mathrm{(Mes)(C_6H_5)CHCH(OH){-}CH(OH)Mes} \longrightarrow \mathrm{(Mes)(C_6H_5)CHCHO}$$

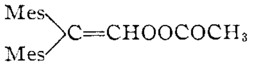
I II

Such a synthesis could not be effected, of course, if the product itself were attacked by the reagent. Experiment showed that lead tetraacetate converted 2,2-dimesitylvinyl alcohol (III) to an acetoxyl derivative which at first was assigned the vinyl peracetate structure IV.



$\mathrm{Mes_2C{=}CHOH}$

III



$\mathrm{Mes_2C{=}CHOOCOCH_3}$

IV

Evidence for this conclusion was the observation that treatment with ethylmagnesium bromide or,

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[1] For the preceding communication in this series see R. C. Fuson and T.-L. Tan, THIS JOURNAL, **70**, 602 (1948).

[2] Rohm and Haas Research Assistant, 1945–1946; du Pont Fellow, 1946–1947.

[3] Standard Oil Co. of Indiana Fellow, 1954–1955; Visking Corporation Fellow, 1955–1956.