[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, THE UNIVERSITY OF IDAHO, PURDUE UNIVERSITY AND RUTGERS, THE STATE UNIVERSITY]

The Base-catalyzed Self-condensation of 2-Ethyl-2-hexenal. I. Formation of a Cyclic Aldol, $C_{16}H_{28}O_2$[1]

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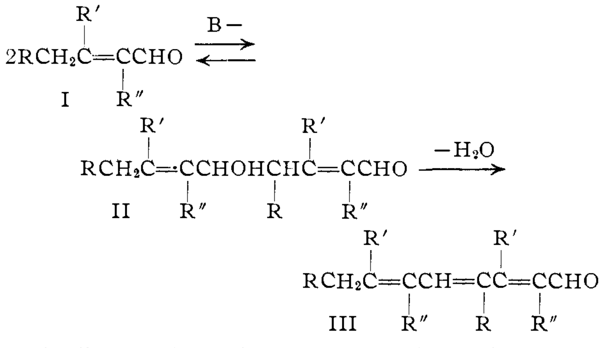
2-Ethyl-2-hexenal has been self-condensed in the presence of methanolic potassium hydroxide to yield a cyclic aldol dimer VIII. Two independent degradation paths were followed to establish the structure of this new type of condensation product. It is concluded that the "cyclic dimerization" reaction of α,β-unsaturated aldehydes is a more general base-catalyzed reaction of these compounds than is their condensation to linear products, since none of the latter were obtained in the present investigation.

There are reports in the literature of the base-catalyzed self-condensation of α,β-unsaturated aldehydes to either cyclic or linear products. The latter compounds are believed to arise from an aldol condensation, involving carbonyl attack at the γ-carbon, which generally produces a conjugated trienal III.[3–5] A weakly basic catalyst (usually piperidine acetate) is employed in this reaction, the intermediate aldol II seldom being isolated because of its ease of dehydration. Mixed condensations of this type, employing two different aldehydes, also have been reported.[3,4b,6]

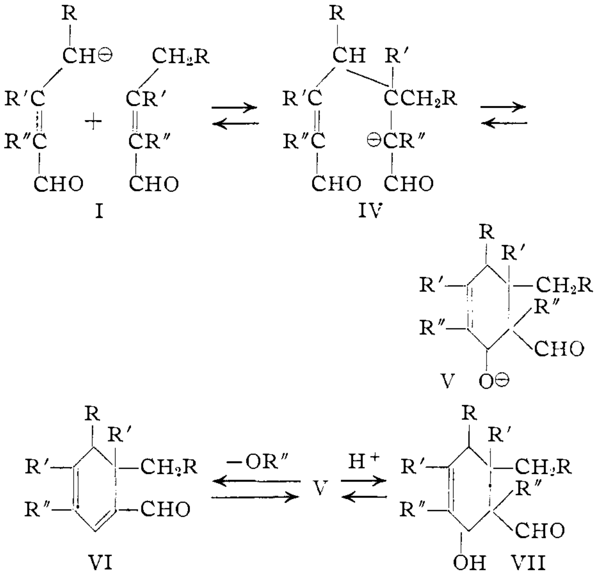


$$2RCH_2\overset{R'}{C}=\underset{R''}{C}CHO \overset{B-}{\rightleftharpoons} \quad \text{I}$$

$$RCH_2\overset{R'}{C}=\underset{R''}{C}CHOH\underset{R}{CH}\overset{R'}{C}=\underset{R''}{C}CHO \xrightarrow{-H_2O} \quad \text{II}$$

$$RCH_2\overset{R'}{C}=\underset{R''}{C}CH=\underset{R}{C}\overset{R'}{C}=\underset{R''}{C}CHO \quad \text{III}$$

Cyclic condensation products have been obtained from crotonaldehyde,[3,4b,7] 3-methyl-2-butenal[3,8] and citral,[3] stronger basic catalysts being employed here than in the corresponding linear condensation. The cyclization is believed to involve a Michael addition as indicated (I → V → VI or VII).[8] In the previously reported examples (R″ = H) the cyclic products isolated were dienals (type VI), not cyclic aldols (VII).



In the present work the self-condensation of 2-ethyl-2-hexenal, in the presence of methanolic potassium hydroxide catalyst, has been investigated. Although no previous study of this condensation had been reported at the time this work was initiated, there appeared independently, subsequent to our first report,[9] patents disclosing some of these preliminary results.[10] The present paper presents a more detailed study of the reaction. The base-catalyzed self-condensation of 2-ethyl-2-hexenal was also studied recently by Häusermann.[11] However, with the elevated temperatures which he employed, the condensation products obtained were different from those reported herein.

On the basis of previously reported work one would expect 2-ethyl-2-hexenal to self-condense,

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[1] Presented at the 127th American Chemical Society Meeting, Cincinnati, Ohio, April, 1955.

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[3] 3-Methyl-2-butenal, for example, yields 3,7-dimethyl-2,4,6-octatrienal (III, R and R″ = H; R′, = CH_3); (a) F. G. Fischer and K. Löwenberg, *Ann.*, **494**, 263 (1932); (b) F. G. Fischer and K. Hultzsch, *Ber.*, **68**, 1726 (1935).

[4] (a) T. Reichstein, C. Ammann and G. Trivelli, *Helv. Chim. Acta*, **15**, 261 (1932); (b) K. Bernhauer, K. Irrgang, K. Adler, M. Mattauch, P. Miller and F. Neiser, *Ann.*, **525**, 43 (1936); (c) F. G. Fischer, K. Hultzsch and W. Flaig, *Ber.*, **70**, 370 (1937); (d) R. Kuhn and C. Grundmann, *ibid.*, **71**, 2274 (1938); (e) C. Grundmann, *Chem. Ber.*, **81**, 510 (1948).

[5] The self-condensation of 2-methyl-2-pentenal in the presence of ethanolic potassium hydroxide has been reported to yield a linear glycol, $C_{12}H_{22}O_2$, possibly derived from an aldol such as II; A. von Lenz, *Monatsh.*, **24**, 155 (1903). J. Ducasse (*Bull. soc. chim. France*, [5] **11**, 333 (1944)) obtained this same glycol from propanal using sodium ethoxide catalyst.

[6] Yields in these reactions range 10–50%; (a) E. Barraclough, J. W. Batty, I. M. Heilbron and W. E. Jones, *J. Chem. Soc.*, 1549 (1939); (b) R. Kuhn and C. J. O. Morris, *Ber.*, **70**, 853 (1937); P. Karrer and A. Rüegger, *Helv. Chim. Acta*, **23**, 284 (1940).

[7] K. Bernhauer and G. Neubauer, *Biochem. Z.*, **251**, 173 (1932).

[8] The cyclization of 3-methyl-2-butenal has previously been pictured as a diene addition (*cf.* refs. 3 and 7). E. A. Braude, B. F. Gofton, G. Lowe and E. S. Waight (*J. Chem. Soc.*, 4054 (1956)) concur with this mechanism in the cases of their reported lithium-catalyzed cyclization of 3-methyl-2-butenal and dimerization of mesityl oxide to the cyclic ketol, 2-acetyl-1,3,3,5-tetramethyl-5-cyclohexen-1-ol. On the other hand, the postulated mechanism for the self-condensation of 1-acetylcyclohexene is in agreement with the one shown here (*cf.* E. R. H. Jones and H. P. Koch, *J. Chem. Soc.*, 393 (1942)).

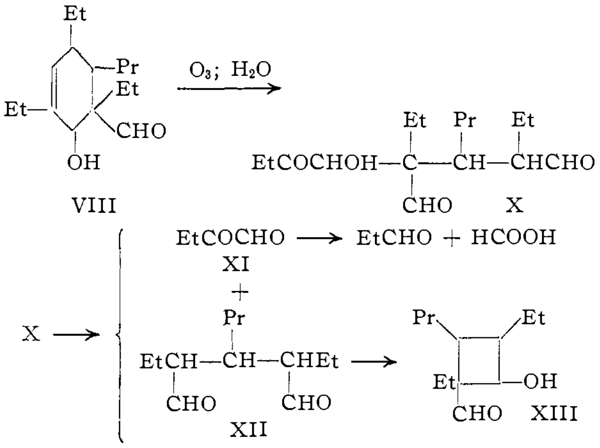
[9] A. T. Nielsen, Ph.D. Thesis, University of Washington, June, 1947.

[10] (a) R. H. Hall and K. H. W. Tuerck, British Patent 608,985, Sept. 23, 1948; *C. A.*, **44**, 4493 (1950); (b) R. H. Hall and K. H. W. Tuerck, U. S. Patent 2,528,592, Nov. 7, 1950; *C. A.*, **45**, 3686 (1951).

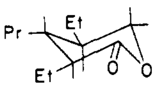
[11] M. Häusermann, *Helv. Chim. Acta*, **34**, 1482 (1951).

initially to either a linear or a cyclic aldol dimer (II or VII). It was found, however, that unlike other α,β-unsaturated aldehydes previously studied, it failed to react in the presence of weak bases. On the other hand, when treated with aqueous methanolic potassium hydroxide, there was produced a 40% yield[12] of a dimer, $C_{16}H_{28}O_2$, as indicated by analysis and molecular weight data. Strong infrared absorption at 3.0 and 5.9 μ and a Zerewitinoff determination indicated the presence of one hydroxyl and one carbonyl group. The absence of olefinic conjugation with the carbonyl group was apparent from the ultraviolet spectrum which showed a low intensity carbonyl band at 320 mμ but no maximum in the region 200–270 mμ. The compound formed a monoöxalomonophenyldihydrazone and a 2,4-dinitrophenylhydrazone and gave a Schiff aldehyde reaction. Quantitative hydrogenation and bromination data indicated the presence of only one olefinic double bond. Reduction with lithium aluminum hydride gave a glycol, $C_{16}H_{30}O_2$ (IX), also having one double bond. The above data are in agreement with a cyclic aldol structure for the dimer (*i.e.*, VIII; VII, R′ = H, R = R″ = Et); such a compound cannot, of course, dehydrate to VI.

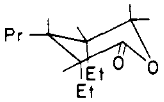
Since no cyclic aldol had been reported previously as a product of the self-condensation of an α,β-unsaturated aldehyde, it was felt that additional evidence in support of structure VIII was required, particularly in view of the limited number of examples of this cyclization reaction.[3,4b,7,14] Such evidence was first obtained by ozonolysis of the dimer to yield the following products[15]: formic acid (38%), propionic acid (30%), propionaldehyde (8%), carbon dioxide (3%) and a neutral, steam-volatile compound, $C_{12}H_{22}O_2$ (XIII), (*ca.* 30% yield, crude). The latter substance showed strong infrared absorption at 2.9 and 5.8 μ assigned to one hydroxyl and one carbonyl group, respectively; a Zerewitinoff determination supported this assignment. The ozonolysis products readily can be rationalized on the basis of structure VIII by the equations shown. Under the reaction conditions the intermediate X (not isolated) is cleaved, by dealdolization, to 2-ketobutanal (XI) and the dialdehyde XII which readily cyclizes to the aldol XIII.[16-18]



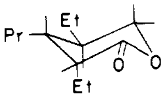
Aldol XIII when treated with methanolic potassium hydroxide led to the lactone XIV, a compound previously reported by Häusermann.[11,19,20]



XIV



XIVa



XIVb

By direct titration with 0.5 *N* sodium hydroxide XIV was easily saponified to regenerate its precursor, the anion of 2,4-diethyl-5-hydroxy-3-propylpentanoic acid (XV). Oxidation of XV with permanganate led to a high melting *meso* isomer of 2,4-diethyl-3-propylpentanedioic acid (XVI), m.p. 151–151.5°,[21] which was found, by mixture melting point determination, to be identical with an authentic sample of this acid kindly provided by Dr. Häusermann.[11]

Because the ozonolysis gave products somewhat indirectly derived from VIII, more direct evidence for the presence of a six-membered ring was sought by chromic acid oxidation. This reaction produced equal molar amounts of carbon dioxide and a neutral compound $C_{15}H_{26}O$. The same product was obtained by oxidizing VIII with permanganate and decarboxylating the crude acid (XVII) formed thereby. The presence of one double bond in the product was demonstrated by quantitative hydrogenation. That this bond was conjugated with a carbonyl group was indicated

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[12] The maximum yield (40%) was obtained using 0.6 mole-equivalent of potassium hydroxide per mole of aldehyde (25°, 30 minutes reaction time); under these same conditions, shorter or longer reaction periods gave a lowered yield. At the longer reaction times (1–2 hr.) large amounts of an acidic compound, $C_{16}H_{30}O_3$, were produced (ref. 13). Increasing or decreasing the reaction temperature or alkali concentration did not increase the yield.

[13] A. T. Nielsen, THIS JOURNAL, **79**, 2524 (1957).

[14] The structure of the product has been established in two of the three reported cases of self-condensation to a cyclic dienal, *viz.*, 3-methyl-2-butenal[3a] and crotonaldehyde.[7] The reaction has perhaps not been recognized as a general one because of the paucity of examples (*cf.* ref. 8).

[15] Yields in parentheses are based on the assumption that one mole-equivalent of each compound is formed from VIII.

[16] The formation of a four-membered cyclic aldol is believed to be favored by the buttressing effect of adjacent alkyl substituents; (a) R. C. Fuson in H. Gilman, "Organic Chemistry," 2nd Ed., Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 81; (b) S. Winstein and E. Grunwald, THIS JOURNAL, **70**, 828 (1948).

[17] Under the conditions of the experiment, none of the 2-ketobutanal was isolated, since it decomposed, apparently completely, into formic acid and propionaldehyde. For similar cleavages of 2-ketoaldehydes *cf.* (a) R. Pummerer, O. Guyot and L. Birkofer, *Ber.*, **68**, 480 (1935); (b) C. Harries and H. O. Türk, *Ann.*, **374**, 338 (1910) and (c) W. G. Young, A. C. McKinnis, I. D. Webb and J. D. Roberts, THIS JOURNAL, **68**, 293 (1946); refs. b and c refer to ozonolysis experiments.

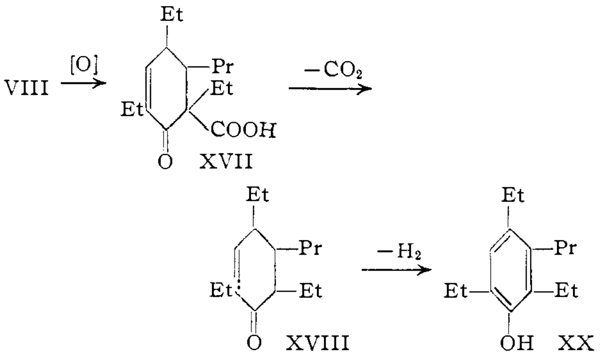
[18] Only an 8% yield of propionaldehyde was obtained (as its 2,4-dinitrophenylhydrazone), since the major portion was oxidized to propionic acid (30% yield); T. E. Friedemann (*J. Biol. Chem.*, **73**, 331 (1927)) observed pyruvaldehyde to be very rapidly oxidized by hydrogen peroxide at *p*H 7 or less to formic and acetic acids.

[19] See H. Meerwein, *Ber.*, **53**, 1829 (1920), for other examples of disproportionation of 1,5-dialdehydes.

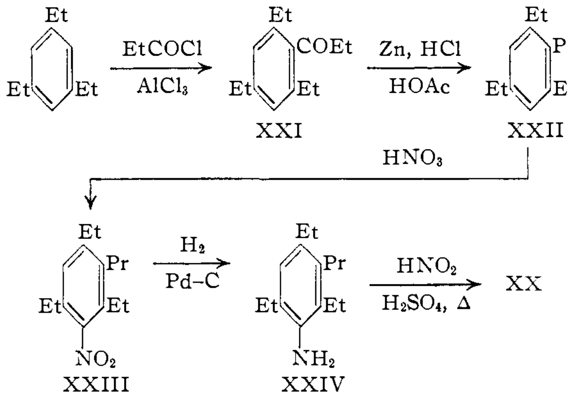
[20] The dialdehyde XII should readily equilibrate to the most stable conformation in the presence of base, thus leading to the equatorial form XIV. The alternate structure (XIVa) which could lead to a *meso*-acid may be considered unstable relative to XIV. The possibility of epimerization at the position alpha to the carbonyl group occurring readily as a result of the mild saponification conditions (direct titration with 9.5 *N* sodium hydroxide) appears unlikely; the lactone structure XIVb (which would lead to racemic XVI in the absence of epimerization) is therefore excluded.

[21] The racemic isomer melts at 98–99° (ref. 13).

by the strong ultraviolet absorption maximum at 242 mμ (log ϵ 3.75).[22] Although neither this compound nor its dihydro derivative XIX gave carbonyl-group reactions,[23] its structure was shown to be XVIII by aromatization to 3-propyl-2,4,6-triethylphenol (XX).



(This phenol, being insoluble in hot 50% aqueous potassium hydroxide, but soluble in Claisen alkali,[24,25] may be classified as a "cryptophenol."[26,27]) An authentic specimen of XX was obtained by an unambiguous route shown below (XXI-XXIV).[28]



The reaction of 2-ethyl-2-hexenal to form VIII provides the first reported example of the dimerization of an α,β-unsaturated aldehyde to yield a cyclic aldol which is incapable of dehydration; in previously reported cases cyclization has always led to cyclic dienals.[8] It should be emphasized that 2-ethyl-2-hexenal, unlike its lower homologs, failed to yield any linear condensation product. Thus, it would appear that the "linear aldol condensation" discussed above is limited to suitably unhindered aldehydes (I, R, R′ and R″ no larger than methyl); also, it requires a milder basic catalyst than the corresponding condensation to cyclic products. The position of the equilibrium I $\rightleftarrows$ II evidently is determined to some extent by steric factors. In cases where the formation of II is unfavorable, the "cyclic dimerization" is realized (assisted by the formation of a six-membered ring) and would appear to be possible for all examples, including higher homologs of 2-ethyl-2-hexenal having γ-hydrogens, and to be a typical, general reaction of these compounds.

Experimental[29]

2-Ethyl-2-hexenal.—Preliminary experiments indicated that purified, freshly distilled, samples of 2-ethyl-2-hexenal were required for maximum yields of condensation products. Traces of peroxide or acidic impurities in the aldehyde had no effect on the reaction, but in larger amounts these substances caused much resin formation with resulting lowered yields of condensation products. Peroxide-free 2-ethyl-2-hexenal was prepared by the self-condensation,[30] in a nitrogen atmosphere, of peroxide-free butanal, b.p. 70–72° (690 mm.), n^{25}_D 1.3770.[31] The pure 2-ethyl-2-hexenal obtained (71% yield) was distilled under nitrogen; b.p. 81° (34 mm.), n^{25}_D 1.4504. It was found to contain no peroxide[32] and 0.1% of an acidic impurity[33] by direct titration with 0.1 *N* sodium hydroxide It was found unnecessary, however, to employ this highly purified material, since samples of aldehyde which had been purified by the following procedure gave equally good results. A 423-g. sample of Carbide 2-ethyl-2-hexenal[34] was washed successively with five 100-ml. portions of *N* sodium hydroxide solution and then with *N* hydrochloric acid and water. After drying over anhydrous magnesium sulfate in a nitrogen atmosphere, the aldehyde was distilled *in vacuo* under nitrogen; b.p. 67° (18 mm.), yield 368 g.; peroxide and acidic impurities were 0.6 and 0.3%, respectively.[32,33]

Self-condensation of 2-Ethyl-2-hexenal: Preparation of 2-Hydroxy-6-propyl-1,3,5-triethyl-3-cyclohexene-1-carboxaldehyde (VIII).—2-Ethyl-2-hexenal (160 g., 1.27 moles), purified by the alkali extraction procedure described above, was freshly distilled, under nitrogen, directly into the reaction flask. A solution of 48 g. of potassium hydroxide (85% assay, 0.73 mole) in 25 ml. of water and 65 ml. of methanol was then added during 1.5 minutes with vigorous stirring while a nitrogen atmosphere was maintained and the temperature held at 25° by ice-bath cooling. The color quickly changed to orange while the alkali was being added, and after a total reaction time of 30 minutes (temp. 25°), 500 ml. of water was added rapidly to the mixture with stirring. The oily layer which formed was separated, the aqueous layer extracted four times with ether and the extracts combined with the main portion. The ether solution was washed with water and dried over magnesium sulfate.

After distilling the ether on the steam-bath, the residue was distilled *in vacuo* to yield the following fractions: (1) 56 g., b.p. 60–61° (14 mm.), 2-ethyl-2-hexenal (35% recovery); (2) 72 g. (45%), b.p. 114–115° (0.12 mm.), n^{25}_D 1.4885, crude aldol VIII; (3) residue, 8 g. Redistillation of fraction 2 gave 63.5 g. (40% yield) of pure VIII, b.p. 114–116° (0.16 mm.), n^{25}_D 1.4893.

Anal. Calcd. for $C_{16}H_{28}O_2$: C, 76.14; H, 11.18; mol. wt., 252.4. Found: C, 76.27; H, 11.39; mol. wt., 250, 253.[35]

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[22] R. B. Woodward, This Journal, **63**, 1123 (1941); **64**, 76 (1942).

[23] *Cf.* R. Cornubert, C. Borel, M. De Demo, J. Garnier, R. Humeau, H. Le Bihan and G. Sarkis, *Bull. soc. chim. France*, [5] **2**, 195 (1935).

[24] L. Claisen, *Ann.*, **418**, 69, 96 (1919); **442**, 210, 224 (1925).

[25] G. H. Stillson, This Journal, **68**, 722 (1946).

[26] K. Auwers, *Ber.*, **39**, 3160, 3167 (1906).

[27] G. H. Stillson, D. W. Sawyer and C. K. Hunt, This Journal, **67**, 303 (1945).

[28] When 2,4,6-triethylpropiophenone (XXI) was reduced to the hydrocarbon XXII (27% yield) by a forcing Clemmensen procedure, deacylation also occurred with the formation of 1,3,5-triethylbenzene in 24% yield. This appears to be the first reported case of deacylation accompanying a Clemmensen reduction.

[29] All melting points are corrected. Boiling points are uncorrected.

[30] C. Weizmann and S. F. Garrard, *J. Chem. Soc.*, **117**, 324 (1920).

[31] *Cf.* F. E. McKenna, E. C. Lingafelter and H. V. Tartar, This Journal, **71**, 2263 (1949), on purification and peroxide formation of propanal.

[32] Procedure of K. Nozaki, *Ind. Eng. Chem., Anal. Ed.*, **18**, 583 (1946).

[33] Acidic and peroxide impurity each assumed to have a molecular weight of 142, for purposes of calculating percentage by weight present.

[34] A generous supply of 2-ethyl-2-hexenal was provided us by the Carbide and Carbon Chemicals Corp., South Charleston, West Va.

[35] The procedure of R. E. Kitson, A. N. Oemler and J. Mitchell (*Anal. Chem.*, **21**, 404 (1949)) was used, with slight modifications, for this molecular weight determination.

The aqueous alkaline solution above, remaining after extraction with ether, was acidified with concd. hydrochloric acid. The oil which formed was separated and the aqueous part extracted three times with ether. The ether extracts and the oil were combined and dried over magnesium sulfate. After distilling the ether, the residue was distilled to give (1) 1.4 g., b.p. 85–142° (0.25 mm.); (2) 9.2 g., b.p. 142–155° (0.25 mm.), $n^{25}\text{D}$ 1.4764 and 1.0 g. of residue.

Attempts were made to increase the yield of VIII by varying the experimental conditions. It was found that, under the conditions of the above experiment, either longer or shorter reaction periods gave lower yields of VIII. At shorter reaction times than 30 minutes, larger amounts of unreacted 2-ethyl-2-hexenal were recovered; at longer reaction times (1–2 hr.) less unreacted aldehyde was recovered; but greater amounts of acidic material were obtained. Higher reaction temperatures or alkali concentrations produced a less pure aldol in lowered yield, whereas lower temperatures or alkali concentrations made necessary a prolonged reaction time without increasing the yield.[13]

Quantitative hydrogenation of a 0.5-millimole sample of the aldol VIII at 689 mm. and 23° (acetic acid solvent containing a few drops of concd. hydrochloric acid, 5% palladium–charcoal catalyst) resulted in absorption of 1.00 mole-equivalent of hydrogen in 300 minutes, after which time hydrogenation continued extremely slowly (*ca.* 0.065 mole-equivalent per hour). On quantitative bromination with a 5% solution of bromine in carbon tetrachloride, 1.07 mole-equivalents of bromine were absorbed, with some hydrogen bromide evolution. A Zerewitinoff determination showed 1.03 active hydrogens and 1.04 additional mole-equivalents of methylmagnesium iodide reacted. The compound gave a positive Schiff aldehyde test. A sample of the aldol, b.p. 132–135° (0.5 mm.), $n^{25}\text{D}$ 1.4894, showed a broad ultraviolet maximum at 320 mμ (log ε 2.1), a minimum at 270 mμ (log ε 1.85) (95% ethanol solvent). There was no maximum in the range 200–270 mμ. The infrared spectrum showed bands at 3.0m, 3.5, 3.6, 5.9, 6.9, 7.3m, 9.4m, 9.75 and 13.0 μ.

The oxalomonophenyldihydrazone[36] separated from dilute aqueous ethanol or from ligroin as a cream-colored amorphous powder, m.p. 95–97°. The derivative was contaminated with a small amount of less soluble impurity which could not be removed by crystallization.

Anal. Calcd. for $C_{24}H_{36}N_4O_3$: C, 67.26; H, 8.47. Found: C, 68.6; H, 8.9.

A 2,4-dinitrophenylhydrazone derivative was prepared, m.p. 40–62°. It could not be purified to constant melting point by recrystallization.

6-Hydroxymethyl-5-propyl-2,4,6-triethyl-2-cyclohexen-1-ol (IX).—To a solution of 1.1 g. (0.029 mole) of lithium aluminum hydride in 80 ml. of ether was added, with stirring, a solution of 13.0 g. (0.0515 mole) of the aldol VIII dissolved in 35 ml. of dry ether, during 30 minutes[37]; stirring was continued for 10 minutes longer. The solution was then treated successively with 45 ml. of water and 50 ml. of 10% sulfuric acid. The ether layer was separated, washed with water and dried over magnesium sulfate. After distilling the ether there was obtained 9.7 g. (74% yield) of the extremely viscous glycol, b.p. 133–135° (0.36 mm.), $n^{25}\text{D}$ 1.4930[38]; infrared bands at 2.78m, 2.92m, 3.40, 3.48, 6.05w, 6.85, 7.26, 8.1w, 8.67w, 9.20w, 9.68, 10.02, 10.60w, 11.20w, 11.52w and 11.95w μ (chloroform solvent).

Anal. Calcd. for $C_{16}H_{30}O_2$: C, 75.53; H, 11.89. Found: C, 75.49; H, 12.12.

On quantitative hydrogenation of the glycol (under conditions identical with those employed with the above aldol VIII) 0.95-mole-equivalent of hydrogen was absorbed in 120 minutes, after which time hydrogenation ceased. A Zerewitinoff determination indicated 1.98 active hydrogens and an additional 0.1 mole-equivalent of methylmagnesium iodide reacted.

The bis-*p*-nitrophenylurethan was prepared as pale yellow crystals from high boiling ligroin, m.p. 76.5–78.5°.

Anal. Calcd. for $C_{30}H_{38}N_4O_8$: C, 61.84; H, 6.57. Found: C, 62.29; H, 6.9.

Ozonolysis of 2-Hydroxy-5-propyl-2,4,6-triethyl-3-cyclohexene-1-carboxaldehyde (VIII).—A 25.3-g. (0.10 mole) sample of the aldol VIII was dissolved in 100 ml. of chloroform and the solution chilled to −15°; oxygen containing ozone was passed through the cold solution at a rate of 0.014 mole of ozone per hour until the exit gases rapidly caused a solution of potassium iodide to turn red (8 hr.; 0.11 mole of ozone used). After distilling the chloroform, 150 ml. of water and 6.6 g. of zinc dust were added to the ozonide and the mixture steam distilled. The receiver was arranged to permit the exit vapors to pass through (1) a washing bottle containing water, (2) a Drierite packed tube and (3) a weighed Ascarite tube. A total of 4040 ml. of distillate was collected, a large amount of oil distilling with the first liter. Concentrated sulfuric acid, 10 ml., was added to the aqueous mixture remaining in the distilling flask and the steam distillation continued, 2350 ml. of additional distillate being collected; very little oil distilled with the last portion of water collected. Throughout the distillation, aliquot portions of the distillate, taken at intervals, were titrated with 0.1 *N* sodium hydroxide to determine the rate of distillation of water-soluble acid; of the total acid collected (0.068 mole) 65% of this amount (0.044 mole) distilled after adding the sulfuric acid.

The Ascarite tube gained 0.14 g. in weight, corresponding to a 3.2% yield of carbon dioxide. A blank determination showed such minute amounts of carbon dioxide in the steam which was used that no correction of this value was necessary.

The total combined aqueous steam distillate obtained was found to contain 0.068 mole of water-soluble acid; aliquot samples of the distillate were analyzed as follows: Formic acid was determined quantitatively by a modification of the procedure of Reid and Weihe.[39] The total amount obtained was found to be 0.038 mole (56% of the total water-soluble acid).

One aliquot portion of the distillate was neutralized with dilute sodium hydroxide solution, evaporated to dryness, diluted with water and acidified with sulfuric acid. In order to decompose the formic acid, the solution was refluxed with mercuric oxide until no more carbon dioxide was evolved. The acid which remained gave Duclaux numbers 12.2, 11.9, 11.5 on distillation (reported[40] for propionic acid, 11.9, 11.7, 11.3). The *p*-phenylphenacyl ester of this acid, m.p. 102.5°, showed no depression in melting point when mixed with an authentic sample of *p*-phenylphenacyl propionate, m.p. 102–103°.

The original distillate was found to contain 0.0079 mole of total carbonyl compounds. (Carbonyl analysis was made by reaction of an aliquot sample with hydroxylamine hydrochloride and titration of the liberated hydrochloric acid with 0.1 *N* sodium hydroxide.) An aliquot portion was neutralized with dilute sodium hydroxide and this solution refluxed gently while nitrogen was passed slowly through it. The exit gases when passed into a solution of 2,4-dinitrophenylhydrazine in dilute phosphoric acid formed an orange precipitate, m.p. 153–155°, after recrystallization from dilute ethanol. This compound showed no depression in melting point when mixed with an authentic sample of propionaldehyde 2,4-dinitrophenylhydrazone, m.p. 154–155°.

Thus from the ozonolysis of VIII there were produced a 38% yield of formic acid, 30% propionic acid, 8% propionaldehyde, 3% carbon dioxide and 30% (crude) of the aldol XIII (see below). The remainder of the ozonolysis products were 1.4 g. of steam-volatile oil produced after acidification of the zinc salts with sulfuric acid, 5.7 g. of neutral and 2.9 g. of acidic, non-steam-volatile, undistillable residue. The total weight of ozonolysis products obtained was 22.7 g. (from 25.3 g. of VIII).

1,3-Diethyl-2-hydroxy-4-propylcyclobutanecarboxaldehyde (XIII).—In the above ozonolysis experiment, the oil which distilled before adding the sulfuric acid was separated and the aqueous part extracted twice with ether, the ether

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[36] P. P. T. Sah and H. Wang, *J. Chinese Chem. Soc.*, **14**, 39 (1946); *C. A.*, **43**, 6971 (1949).

[37] R. F. Nystrom and W. G. Brown, THIS JOURNAL, **69**, 1197 (1947).

[38] Hall and Tuerck (ref. 10) reduced the aldol VIII to an unsaturated glycol, $C_{16}H_{30}O_2$, by hydrogenation with Raney nickel catalyst, 74% yield, b.p. 149–151° (2 mm.), $n^{30}\text{D}$ 1.4966, bis-3,5-dinitrobenzoate m.p. 178°. Attempts to prepare a 3,5-dinitrobenzoate of the above glycol resulted in the formation of a gum which failed to crystallize.

[39] J. D. Reid and H. D. Weihe, *Ind. Eng. Chem., Anal. Ed.*, **10**, 271 (1938).

[40] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 147.

extracts being combined with the main portion. After drying and distilling the ether, there was obtained on distillation a forerun, 0.7 g., b.p. 72–78° (0.3 mm.); 6.3 g. of crude compound XIII, b.p. 78–113° (0.3 mm.); and 1.1 g. of residue. On redistillation 3.7 g. (19% yield) of the light yellow, nearly odorless aldol was produced, b.p. 84–92° (0.3 mm.), n^{25}D 1.461–1.463.

Anal. Calcd. for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18; mol. wt., 198.3. Found: C, 72.46; H, 10.99; mol. wt. (Rast), 194, 195.

The infrared spectrum showed bands at 2.90m, 3.38, 3.45, 3.64w, 5.80, 6.85, 7.30, 7.90m, 8.05m, 9.1, 10.4 and 12.90m μ.

A Zerewitinoff determination showed 0.72 active hydrogen and 1.37 mole-equivalents additional methylmagnesium iodide reacted. Oxidation of the compound with alkaline or acid potassium permanganate under various conditions failed to yield a compound which could be isolated in pure form.

2,4-Diethyl-3-propyl-1,5-pentanolactone (XIV).—To a solution of 15.3 g. (0.077 mole) of XIII in 100 ml. of methanol was added, in small portions, a solution of 24 g. of potassium hydroxide (85%) in 60 ml. of methanol and 20 ml. of water (temperature, 10–15°). The orange solution which formed was allowed to stand 24 hr. at 3°, 24 hr. at room temperature (solution became dark red) and then refluxed gently for 1 hr. The methanol was then distilled and the residue diluted with 500 ml. of water. The resulting mixture was extracted five times with ether to remove neutral material. The aqueous solution remaining was acidified with hydrochloric acid and extracted three times with ether. The resulting ether solution of acidic material was extracted with saturated sodium bicarbonate solution, *N* hydrochloric acid and water and dried over magnesium sulfate. Distillation gave: (1) 1.9 g., b.p. 140–152° (10 mm.), n^{25}D 1.4617; (2) 2.6 g. (17%) of XIV, b.p. 152–156° (10 mm.), n^{25}D 1.4613; (3) 1.5 g., b.p. 161–164° (9 mm.), n^{25}D 1.4636; and 2.0 g. of residue. (Häusermann[11] reported b.p. 147–149° (11 mm.), n^{18}D 1.4660 for XIV.) The infrared spectrum of fraction 2, above, showed bands at 3.53, 3.60, 5.85, 6.90, 7.30, 7.95, 8.15m, 8.45, 8.75, 8.95, 9.50m, 10.60w and 13.0w μ.

Anal. Calcd. for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18; mol. wt., 198.3. Found: C, 72.77; H, 11.13; sapn. equiv., 199.

The dried ether solution above, containing neutral material, was distilled to yield the following fractions: 1.4 g., b.p. 120–135° (13 mm.), n^{25}D 1.4702; 2.3 g., b.p. 135–145° (13 mm.), n^{25}D 1.4808; and 1.5 g. of residue; these fractions were not investigated further.

2,4-Diethyl-3-propylpentanedioic Acid (XVI).[11]—A small sample of fraction 2 above (XIV) was saponified, by direct titration, with 0.5 *N* sodium hydroxide; the resulting solution was treated with potassium permanganate to yield the acid XVI, m.p. 151–151.5°, after one recrystallization from water (lit.[11] m.p. 149–150°).[21] When this material was mixed with an authentic sample (m.p. 151–151.5°), kindly provided by Dr. Häusermann, the melting point was not depressed.

5-Propyl-2,4,6-triethyl-2-cyclohexen-1-one (XVIII).—A solution of 33 g. (0.33 mole) of chromic anhydride in 40 ml. of water and 40 ml. of acetic acid was added during 1 hr., with stirring, to a solution of 61.3 g. (0.244 mole) of VIII. The temperature was maintained below 25° during the addition. After 3.5 hr., the solution was warmed to 70–80° and the stirring continued for 25 additional hr. A slow stream of nitrogen was continuously passed through the apparatus, the exit gases being conducted through a purifying train and finally through an Ascarite packed tube. The Ascarite tube gained in weight 2.21 g., corresponding to a 20.6% total yield of carbon dioxide; the yield was *ca.* 19% in 15 hr.

After adding 340 ml. of 6 *N* sodium hydroxide solution and extracting with ether, the ether extracts were washed with water, *N* sodium hydroxide solution, water and dried. After distilling the ether, the residue was fractionally distilled to yield 11.2 g. (20.7% yield) of the unsaturated ketone XVIII, having a faint fruity odor, b.p. 94–96° (0.2 mm.), n^{25}D 1.4829; 29.0 g., b.p. 113–140° (0.20 mm.), partly oxidized and unchanged material; and 7.2 g. of residue. From the alkaline aqueous portion remaining after the ether extractions there was isolated, after acidification, 4.6 g. of a viscous oil which did not liberate carbon dioxide when heated strongly. The yield of crude ketone and of carbon dioxide could be increased to 50% by using a 75% excess of chromic anhydride; however, in this case, the ketone could not be obtained in a pure state by redistillation, and the use of a smaller excess of oxidizing agent was found to be more desirable.

A 12.5-g. sample of VIII, suspended in a solution of 100 ml. of 5 *N* sulfuric acid and 20 ml. of acetic acid was stirred with 11 g. of potassium permanganate for 2.5 hr. at 25°. After adding sodium bisulfite to dissolve the manganese dioxide, the oxidation product was separated into neutral and acidic portions in the usual manner. The acid product was a viscous oil, 3.7 g., containing crude 2-oxo-6-propyl-1,3,5-triethyl-3-cyclohexene-1-carboxylic acid (XVII). [No attempt was made to characterize this acid, since it decarboxylated so readily; on warming slightly on the steam-bath it rapidly evolved carbon dioxide.] Distillation of this material gave 1.0 g. of the neutral, unsaturated ketone XVIII, b.p. 120–127° (0.5 mm.), n^{25}D 1.4807, and 1.6 g. of residue. The neutral fraction from the oxidation was distilled to yield 0.8 g., b.p. 60–130° (0.8 mm.); 3.6 g., b.p. 130–139° (1.0 mm.), n^{25}D 1.4859; and 1.9 g. of residue.

The ketone XVIII was found to react with bromine in carbon tetrachloride solution very slowly without evolution of hydrogen bromide. Quantitative hydrogenation of a small sample in isoamyl alcohol solvent containing a few drops of hydrochloric acid (platinum catalyst, 25°, 690 mm.) showed 0.9 mole-equivalent of hydrogen absorbed in 1.5 hr., after which time hydrogenation continued very slowly (1.0 mole-equivalent total absorbed in 3 hr.). The ultraviolet spectrum showed maxima at 242 mμ (log ϵ 3.75) and 293 mμ (log ϵ 2.79) and a minimum at 281 mμ (log ϵ 2.76) (95% ethanol solvent). Attempts to prepare a carbonyl derivative of this ketone, using a variety of carbonyl reagents, failed, the original reactants being recovered in each case; infrared bands at 2.90w, 3.40, 3.50, 5.82m, 5.98, 6.85, 7.28m, 11.10w and 11.50 μ.

Anal. Calcd. for $C_{15}H_{26}O$: C, 81.02; H, 11.79; mol. wt., 222.4. Found: C, 80.26; H, 11.48; mol. wt., 227, 228.5.[35]

3-Propyl-2,4,6-triethylcyclohexanone (XIX).—An 11.6-g. sample of the above unsaturated ketone XVIII (0.052 mole) dissolved in a solution of 50 ml. of acetic acid, 10 ml. of water and 1 ml. of concd. hydrochloric acid was hydrogenated at 690 mm. (0.87 g. of platinum oxide and 4 g. of 5% palladium-on-charcoal catalysts) until one mole-equivalent of hydrogen was absorbed (64 hr.). After filtering the catalyst, the filtrate was diluted with 350 ml. of water and extracted with ether. The ether extracts were washed with *N* sodium hydroxide solution, then with water and dried. After distilling the ether, the residue was distilled to yield 0.7 g., b.p. 80–89° (0.6 mm.); 4.7 g. of crude XIX, b.p. 88–93° (0.35 mm.), n^{25}D 1.4668; 2.8 g., b.p. 94–95° (0.2 mm.), n^{25}D 1.4700; and 0.7 g. residue. Redistillation of the second fraction gave 2.6 g., b.p. 78–82° (0.17 mm.), n^{25}D 1.466, having a faint sweet odor, which was used for elemental analysis; infrared bands at 3.0w, 3.40, 3.48, 5.83, 6.85, 7.27, 8.85w and 9.10w μ.

Anal. Calcd. for $C_{15}H_{28}O$: C, 80.29; H, 12.58. Found: C, 79.91; H, 12.39.

Attempts to prepare a carbonyl derivative of this ketone failed, the original reactants being recovered in each case.[23]

2,4,6-Triethyl-3-propylphenol (XX) from XVIII.—A 0.70-g. (3.16 millimoles) sample of 5-propyl-2,4,6-triethyl-2-cyclohexen-1-one (XVIII) was refluxed with 0.35 g. of 5% palladium–charcoal catalyst for 1 hr., during which time 0.71 mole-equivalent of hydrogen was collected. After filtering, the residue was distilled through a small Emich tube, to yield 0.32 g. (45%) of the yellow phenol, b.p. 262–266° (690 mm.), n^{25}D 1.506–1.510. Redistillation gave a sample which was used for analysis, n^{25}D 1.5086. The compound rapidly became dark orange in the presence of air, but could be stored under nitrogen without change. The ultraviolet spectrum showed a broad maximum at 281 mμ (log ϵ 3.22) (95% ethanol solvent); infrared bands at 2.87, 3.47, 3.53, 5.95w, 6.22w, 6.37w, 6.87, 7.30m, 7.70m, 7.93, 8.25, 8.45, 9.05 (shoulder), 9.15–9.20, 9.40m, 10.1w, 11.4m, 11.6m and 12.1m μ.

Anal. Calcd. for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.69; H, 11.21.

The phenol was insoluble in 50% aqueous potassium hydroxide solution but soluble in Claisen alkali.[24,25] It reacted with sodium metal but gave a negative ferric chloride test in alcohol. The infrared spectrum showed some absorption at 5.95 μ which was absent in the authentic sample of XX (see below) and which is believed to be due to the presence of a small amount of carbonyl compound (XIX or XVIII) which could not be removed by distillation; in all other respects the two samples were spectroscopically identical.

The phenylurethan derivative was prepared by refluxing a solution of 0.44 g. of the above phenol XX from the condensation, 4 ml. of phenyl isocyanate and 5 ml. of pure diethylene glycol dimethyl ether for 22 hr. After distilling the solvent and excess phenyl isocyanate, the residue was extracted with boiling hexane and filtered hot to remove insoluble material. From the filtrate, by fractional crystallization from hexane, there was obtained 0.14 g. of the crude crystalline derivative, m.p. 111–119°. Three recrystallizations from petroleum ether gave long white needles, m.p. 120–121°; when mixed with an authentic sample of 2,4,6-triethyl-3-propylphenol phenylurethan derivative, m.p. 122–122.5° (see below), the melting point was not depressed. When the ether solvent was omitted from the procedure, no derivative could be isolated.

Anal. Calcd. for $C_{22}H_{29}NO_2$: C, 77.84; H, 8.61. Found: C, 77.77; H, 8.59.

2,4,6-Triethylpropiophenone (XXI).—To a solution of 58.7 g. (0.362 mole) of purified 1,3,5-triethylbenzene (b.p. 101° (21 mm.), $n^{25}D$ 1.4934[41]) and 37.2 g. (0.40 mole) of freshly distilled propionyl chloride, b.p. 76–78°, in 50 ml. of dry tetrachloroethane was added, with stirring, during 1 hr., 66 g. (0.50 mole) of anhydrous aluminum chloride (temp. 26–35°). After addition of approximately one-third of the aluminum chloride, the solution became deep red in color. The solution was held at 40° with continuous stirring for 30 minutes after addition of the aluminum chloride. It was then poured into 400 g. of ice and stirred until all of the complex was dissolved. The oil was separated with the aid of ether and washed successively with *N* sodium hydroxide, *N* hydrochloric acid and water. After drying over magnesium sulfate and distilling the solvents, there was obtained 12 g., b.p. 80–109° (5 mm.), containing mainly unreacted 1,3,5-triethylbenzene (20% recovery) and 60 g. (77%) of colorless, odorless 2,4,6-triethylpropiophenone, b.p. 109–110° (4 mm.), $n^{25}D$ 1.5040, and 1.0 g. of residue; infrared bands at 3.42, 5.90, 6.20, 6.35, 6.90, 7.10, 7.28, 7.48, 7.57 (shoulder), 7.90m, 8.25, 8.68, 9.30, 9.47, 9.88, 10.56, 11.48, 12.40m, 12.69m, 13.15m and 13.84w μ.

The Perrier modification[42] gave a low yield of the propiophenone compound in addition to higher boiling material believed to contain much diacylated product.

Anal. Calcd. for $C_{15}H_{22}O$: C, 82.51; H, 10.16. Found: C, 82.27; H, 10.07.

The ketone failed to react with 2,4-dinitrophenylhydrazine under forcing conditions.

2-Propyl-1,3,5-triethylbenzene (XXII).[43]—A solution of 39.8 g. (0.182 mole) of the ketone XXI in 400 ml. of acetic acid was added dropwise, during 4.5 hr., to a refluxing mixture of 750 g. of amalgamated zinc and 150 g. of water, while, starting simultaneously, 2500 ml. of concd. hydrochloric acid was added during 7.5 hr.; refluxing was continued 14 hr. after addition of the hydrochloric acid was complete. The mixture was then steam distilled and 2 l. of distillate collected. The distillate was extracted three times with ether and the combined ether extracts washed with *N* sodium hydroxide solution and water and dried over magnesium sulfate. Distillation gave the following fractions: (1) 8.1 g., b.p. 78–85° (6 mm.), $n^{25}D$ 1.4931; (2) 3.6 g., b.p. 92–101° (4 mm.), $n^{25}D$ 1.4930; (3) 15.3 g., b.p. 101–108° (5 mm.), $n^{25}D$ 1.4976; (4) 2.2 g. residue.

Fractions 1 and 2 were combined, distilled from sodium at 760 mm. (b.p. 216–230°) and then *in vacuo* to yield 7.0 g., b.p. 101–102° (21 mm.), $n^{25}D$ 1.4932, of 1,3,5-triethylbenzene (24% yield). The infrared spectrum of this sample was identical with that of an authentic sample of 1,3,5-triethylbenzene; infrared bands at 3.47, 5.62w, 5.70w, 6.23, 6.88, 7.28, 7.58, 8.60w, 9.35, 9.45, 11.35, 11.6, 12.1w, 12.80w and 14.20 μ.

Fraction 3, distilled from sodium at 760 mm., b.p. 252–254°, and redistilled *in vacuo*, gave 10.0 g. (27% yield), b.p. 134–136° (21 mm.), $n^{25}D$ 1.4960, of 2-propyl-1,3,5-triethylbenzene; infrared bands at 3.48, 6.20m, 6.90, 7.28, 7.60w, 9.20w, 9.35m, 9.50, 11.10w, 11.30m, 11.50, 12.90w and 13.7w μ. (The strong band at 14.20 μ found in 1,3,5-triethylbenzene is absent.)

Anal. Calcd. for $C_{15}H_{24}$: C, 88.16; H, 11.84. Found: C, 87.60; H, 11.96.

Nitration of 2-Propyl-1,3,5-triethylbenzene.—To 2-propyl-1,3,5-triethylbenzene (3.06 g., 0.015 mole) was added dropwise, with stirring, a mixture of 2 ml. of fuming nitric acid and 6 ml. of concd. nitric acid during 50 minutes (temperature 3–4°). Stirring was continued at 5° for 5 hr. and then at 24° for 30 minutes. The mixture was then poured into ice-water and extracted with ether. The ether extract was washed four times with water, dried over magnesium sulfate and the ether distilled. Distillation of the residue gave 1.8 g. of crude 1-nitro-3-propyl-2,4,6-triethylbenzene (XXIII), b.p. 117–120° (0.50 mm.), and 1.2 g. of residue. A redistilled sample which was used for analysis had b.p. 109–112° (0.25 mm.), $n^{25}D$ 1.5140; infrared bands at 3.48, 5.95, 6.25m, 6.58, 6.88, 7.30, 7.82, 8.30m, 8.60m, 9.23m, 9.50, 10.50w, 11.37, 12.27, 12.75m and 13.55w μ.

Anal. Calcd. for $C_{15}H_{23}NO_2$: C, 72.25; H, 9.30; N, 5.62. Found: C, 74.97; H, 9.45; N, 4.15.

The poor elemental analysis suggests that the compound probably decomposed on distillation or on standing.

3-Propyl-2,4,6-triethylaniline (XXIV).—A 2.50-g. sample of the above crude nitro compound, dissolved in 100 ml. of acetic acid, was hydrogenated at 50 pounds pressure in the presence of 5.0 g. of 10% palladium-charcoal catalyst until the theoretical amount of hydrogen was absorbed (3 hr.). After filtering the catalyst, the acetic acid was evaporated *in vacuo* leaving a mass of brown crystals. These were suspended in benzene and dry hydrogen chloride gas was passed through the mixture; a few ml. of ethanol was then added and the volatile materials evaporated *in vacuo*. Trituration of the residue with petroleum ether gave 1.4 g. (26% from hydrocarbon XXII) of white crystalline 3-propyl-2,4,6-triethylaniline hydrochloride (neut. equiv. calcd. for $C_{15}H_{26}ClN$: 255.8; found, 255 (by direct titration with 0.1 *N* sodium hydroxide)). Reduction of the nitro compound with tin and hydrochloric acid also was successful and gave a 22% over-all yield of the hydrochloride (from XXII).

The above hydrochloride (1.4 g.) when treated with *N* sodium hydroxide gave an oil which was extracted with ether, dried and distilled under nitrogen to yield 0.5 g. (11% yield from XXII), b.p. 101–102° (0.35 mm.), $n^{25}D$ 1.5265, of 3-propyl-2,4,6-triethylaniline; infrared bands at 2.95w, 3.40, 3.47, 6.15, 6.86, 7.28m, 7.75m, 8.25w, 9.20w, 11.36 and 12.1w μ.

Anal. Calcd. for $C_{15}H_{25}N$: C, 82.13; H, 11.49. Found: C, 82.04; H, 11.49.

3-Propyl-2,4,6-triethylphenol (XX) from 3-Propyl-2,4,6-triethylaniline.—3-Propyl-2,4,6-triethylaniline (0.90 g., 4.1 mmoles) when treated with 10 ml. of 2 *N* sulfuric acid, formed a precipitate of the corresponding sulfate, soluble on warming. To a cold stirred suspension of the finely divided sulfate was added a solution of 0.28 g. (4.1 mmoles) of sodium nitrite in 2 ml. of water (temperature 5–10°). After 20 minutes a gummy solid had formed; 45 ml. of 12 *M* sulfuric acid was then added to the mixture, causing the temperature to rise to 90°. After warming on the steam-bath for a few minutes, the mixture was cooled and allowed to stand 2 hr. at room temperature. The red oil which formed was extracted three times with petroleum ether, the extracts washed with water and sodium bicarbonate solution and dried, under nitrogen, over magnesium sulfate. Dry hydrogen chloride was passed into the solution to precipitate a small amount of black material. The mixture was filtered and the filtrate distilled *in vacuo* under nitrogen through a short column to yield, in addition to 0.30 g. of residue and holdup, 0.24 g. (27%) of 3-propyl-2,4,6-triethylphenol, b.p. 96–98° (0.4 mm.), $n^{25}D$ 1.5181–1.5193; λ_{max} 282 mμ, (log ε 3.31); infrared bands at 2.87m, 3.47, 3.52, 6.10w, 6.25w, 6.37w, 6.85, 7.30m, 7.70m, 7.93, 8.25, 8.45, 9.05m (shoulder), 9.15–9.20, 9.40m, 10.1w, 11.41, 11.62m and 12.1m μ.

Anal. Calcd. for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.50; H, 10.93.

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(41) L. I. Smith and C. O. Guss, THIS JOURNAL, **62**, 2625 (1940).

(42) G. Perrier, *Ber.*, **33**, 815 (1900).

(43) This forcing procedure for the Clemmensen reduction of a hindered ketone was adapted from one by E. Philippi and G. Rie, *Monatsh.*, **42**, 5 (1921).

The phenylurethan derivative was prepared as above, except that diethylene glycol diethyl ether was used as solvent (reaction temperature 165°); small colorless prisms from hexane, m.p. 122–122.5°.

Anal. Calcd. for $C_{22}H_{29}NO_2$: C, 77.84; H, 8.61; N, 4.13. Found: C, 77.74; H, 8.66; N, 4.27.

2,4,6-Triethylphenol was prepared in 86% yield from 2,4,6-triethylaniline[44]; b.p. 104–106° (3 mm.), m.p. 20–21°, n^{25}D 1.5158; λ_{max} 279 mμ, log ε 3.28 (95% ethanol); infrared bands at 2.90, 3.50, 5.70w, 6.25m, 6.90, 7.30w, 7.66m, 7.87m, 8.45, 8.75, 9.40m, 10.0w, 11.5 and 12.5 μ.

The phenylurethan derivative was prepared using the procedure developed for XX, above; plates from hexane, m.p. 117–118°.

Anal. Calcd. for $C_{19}H_{23}NO_2$: C, 76.73; H, 7.80; N, 4.71. Found: C, 76.60; H, 7.88; N, 5.00.

2,4,6-Triethylphenyl Propionate: Attempted Preparation of 3-Hydroxy-2,4,6-triethylpropiophenone.—To 2,4,6-triethylphenol (8.9 g., 0.05 mole) in 30 ml. of nitrobenzene was slowly added 20 g. (0.15 mole) of aluminum chloride, with stirring (temp. below 20°). After 10 minutes, 9.25 g. (0.10 mole) of propionyl chloride was added during 30 minutes (temp. 15–20°). The mixture was stirred 14 hr. at *ca.* 25°, 0.5 hr. at 90° and then poured into ice and hydrochloric acid. The mixture was worked up in the usual manner and twice distilled to yield 9.0 g. (77%) of 2,4,6-triethylphenyl propionate, b.p. 100° (1 mm.), n^{25}D 1.4920; infrared bands at 3.48, 3.54, 5.72, 6.25m, 6.55w, 6.90, 7.40, 7.90, 8.50, 8.80, 9.48, 10.20, 11.30, 11.50 and 12.45m μ. The ultraviolet absorption was weak; λ_{max} 265 mμ, ε 500; 273 mμ, ε 380.

Anal. Calcd. for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 76.93; H, 9.37.

Hydrolysis of the ester (2.32 g.) was effected by refluxing with concd. hydrochloric acid and zinc dust and gave 1.4 g. (78%) of 2,4,6-triethylphenol, b.p. 94–97° (1 mm.); λ_{max} 277 mμ, log ε 3.13.

Reaction of the ester with additional propionyl chloride and aluminum chloride in nitrobenzene gave recovered starting material and no acylated product.

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[44] 1-Nitro-2,4,6-triethylbenzene, b.p. 99° (1 mm.), n^{22}D 1.510, prepared in 83% yield by nitration of 1,3,5-triethylbenzene, was reduced with iron and water to 2,4,6-triethylaniline in 81% yield, b.p. 106–112° (2 mm.), n^{25}D 1.5330; *cf.* W. B. Dillingham and E. E. Reid, THIS JOURNAL, **60**, 2606 (1938).

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, THE UNIVERSITY OF IDAHO AND RUTGERS, THE STATE UNIVERSITY]

The Base-catalyzed Self-condensation of 2-Ethyl-2-hexenal. II. Formation of a Glycol, $C_{16}H_{30}O_2$, and a Lactone, $C_{16}H_{30}O_3$[1]

BY ARNOLD T. NIELSEN[2]

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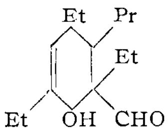
The aldol dimer I of 2-ethyl-2-hexenal undergoes an intramolecular disproportionation in the presence of methanolic potassium hydroxide to form 5,7-dihydroxy-3-propyl-2,4,6-triethyl-1,5-heptanolactone (III). In the presence of 2-ethyl-2-hexenal, I also undergoes a Cannizzaro reaction leading to the glycol II, 2-ethyl-2-hexenoic acid and butyric acid. A mechanism for the formation of III in a preferred conformation is discussed.

2-Ethyl-2-hexenal has been shown to self-condense in the presence of aqueous methanolic potassium hydroxide to yield the cyclic dimer I.[3] It has been observed that the yield of I decreases rapidly as the reaction time is increased while, simultaneously, other products are formed, including a C_{16}-lactone III, a C_{16}-glycol II and 2-ethyl-2-hexenoic and butyric acids (Fig. 1).



I

The preparation of compounds I, II and III has been reported previously,[4,5] although no structures were suggested by Anseln and Nickl or Hall and Tuerck.[5] Häusermann[6] also has studied the self-condensation of 2-ethyl-2-hexenal but under more vigorous reaction conditions (25–50% aqueous sodium hydroxide, *ca.* 200°, 22 hr.) than those of the present investigation. He isolated, among other products, butyric and 2-ethyl-2-hexenoic acids, 2,4-diethyl-3-propyl-1,5-pentanolactone and a C_{16}-glycol, to which no structure was assigned. No C_{16}-lactone was reported by him. There are scattered reports in the literature of the formation of high molecular weight glycols and lactones from various saturated and unsaturated aliphatic aldehydes, in the presence of basic catalysts.[4–7] In most cases, however, the structures of these condensation products have not been established.

The glycol II, formed in 10–30% yields, was found to be identical with the lithium aluminum hydride reduction product of the aldol I.[3] It is believed to have been formed by a Cannizzaro reaction involving reduction of I and oxidation, principally of butanal[8] and 2-ethyl-2-hexenal to butanoic and 2-ethyl-2-hexenoic acids.[9] The linear

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[1] Presented, in part, at the 130th American Chemical Society Meeting, Atlantic City, N. J., September, 1956.

[2] School of Chemistry, Rutgers, The State University, New Brunswick, N. J.

[3] A. T. Nielsen, THIS JOURNAL, **79**, 2518 (1957).

[4] A. T. Nielsen, Ph.D. thesis, University of Washington, 1947.

[5] R. H. Hall and K. H. W. Tuerck, (a) British Patent 608,985, Sept. 23, 1948; *C. A.*, **44**, 4493 (1950); (b) U. S. Patent 2,528,592, Nov. 7, 1950; *C. A.*, **45**, 3866 (1951); (c) H. Anseln and E. Nickl, German Patent 752,482, Feb. 23, 1953; *C. A.*, **50**, 2658 (1956).

[6] M. Häusermann, *Helv. Chim. Acta*, **34**, 1482 (1951).

[7] (a) A. Borodin, *Ber.*, **6**, 982 (1873); (b) A. v. Lenz, *Monatsh.*, **24**, 155 (1903); (c) H. Meerwein, *J. prakt. Chem.*, [2] **97**, 225, 257 (1918); (d) H. Meerwein, *Ber.*, **53**, 1829 (1920); (e) J. Ducasse, *Bull. soc. chim. France*, [5] **11**, 333 (1944); (f) W. Hunter, B. I. O. S. Report No. 1053, Item No. 22. German Acetylenic Chemical Industry, Miscellaneous Organic Compounds, October 13, 1947, pp. 239–241.

[8] Butanal must be formed mainly by hydration of 2-ethyl-2-hexenal to butyraldol, followed by dealdolization. Evidence for formation of butanal from 2-ethyl-2-hexenal (alkaline catalyst) has been reported previously; S. G. Powell and A. T. Nielsen, THIS JOURNAL, **70**, 3627 (1948); Y. Sprinzak, *ibid.*, **74**, 2116 (1952).

[9] The aldol I, itself, is apparently not an important oxidizing agent in this reaction since it was found to be converted solely into lactone III under the milder conditions of the reaction (Fig. 1). However, under more vigorous reaction conditions where the yield of II is higher, some I may be oxidized, leading to a larger amount of