5-Methyl-2,3,4-hexatrienal and Related Compounds

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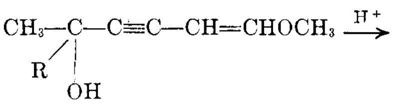
Received June 28, 1962

The preparation of a new type of compound, a cumulene with a functional group has been accomplished. The aldehyde, 5-methyl-2,3,4-hexatrienal, can be obtained in 10–15% yield from the readily available $(CH_3)_2C(OH)-C{\equiv}CCH{=}CHOCH_3$ by treatment with a trace of potassium acid sulfate under carefully controlled conditions. The physical and some chemical properties of the cumulenal are described along with its proof of structure. An infrared band characteristic of cumulenes is found at 2066 cm.$^{-1}$. Two other new compounds are obtained with different conditions for the acid treatment. In aqueous systems a dihydropyrone (**4**) is obtained in good yield while a methoxyallenal is found on treatment with large amounts of potassium acid sulfate. N.m.r., ultraviolet, infrared, and analytical data are used to establish the structures of these compounds.

Our interest in obtaining the acetylenic aldehyde (**2**) ($R = CH_3$) led us to attempt the synthesis reported[2] for the compound with $R = CH_3CH_2$. Although the desired compound was not produced, three different carbonyl compounds could be isolated, depending on the conditions of the reaction. All three compounds were new, and one, 5-methyl-2,3,4-hexatrienal (**3**) represented a previously unknown compound type, a cumulene bearing a functional group.



$$CH_3-\underset{OH}{\overset{R}{C}}-C{\equiv}C-CH{=}CHOCH_3 \xrightarrow{H^+}$$

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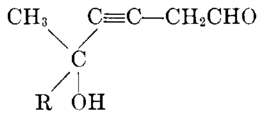

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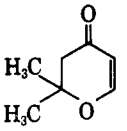
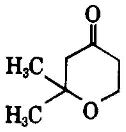
Results

Treatment of the alcohol (**1**) ($R = CH_3$) with two mole per cent *p*-toluenesulfonic acid in tetrahydrofuran–water at reflux led to a 78% yield of a new compound, for which the structure **4** seems most consistent with the evidence.

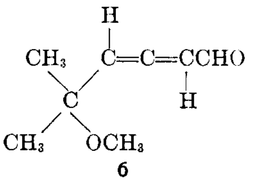




Infrared maxima at 1672 cm.$^{-1}$ and 1595 cm.$^{-1}$ were best explained by a conjugated carbonyl group. An intense solvent-sensitive ultraviolet absorption[3] intermediate in position between that of an α,β- and an $\alpha,\beta,\gamma,\delta$-unsaturated carbonyl compound suggested that a strong electron-donating substituent (*e.g.*, oxygen) was the β-substituent in an α,β-unsaturated carbonyl system. The lack of hydroxyl absorption in the infrared consideration of possible structures led to the formulation of the compound as **4**. The n.m.r. spectrum was in complete agreement with this structure with peaks centered at 8.57 τ (*gem*-dimethyl), 7.57 τ (methylene), 4.86 τ (alkene hydrogen, doublet, $J = 6$ c.p.s.), and 2.86 τ (alkene hydrogen, doublet, $J = 6$ c.p.s.) in the ratio 6:2:1:1. Reduction of **4** with hydrogen over palladium on carbon gave 40% of the saturated ketone (**5**), 2,2-dimethyltetrahydro-4-pyrone. The physical constants for **5** and its semicarbazone are in reasonable agreement with those reported.[4]

In an effort to derive other products of acid-catalyzed rearrangement, the acetylenic alcohol (**1**. $R = CH_3$) was mixed with powdered potassium acid sulfate. After an exothermic reaction, volatile material was removed under reduced pressure and found to possess the strong infrared absorption characteristic of allenes at 1945 cm.$^{-1}$. A rather laborious separation procedure (see Experimental) yielded a sufficient quantity of pure material for structural determination. No effort was made to isolate more than a small portion of the allene derivative formed.

The pure allene possessed a strong sharp infrared absorption band at 1938 cm.$^{-1}$ along with a conjugated carbonyl band at 1688 cm.$^{-1}$. A small sharp peak at 2778 cm.$^{-1}$ suggested the presence of an aldehyde group, and the compound did, in fact, reduce diammino silver(I) ion. Analysis of the n.m.r. spectrum with peaks centered at *ca.* 9.50 τ (*gem*-dimethyl), *ca.* 7.59 τ (methoxyl), *ca.* 5.00 τ (two alkene hydrogens), and *ca.* 1.33 τ (aldehyde hydrogen, doublet, $J = 7$ c.p.s.) suggested the structure **6**. (Area ratios of the peaks were approximately 9:4:2:1.)[5] Carbon–hydrogen analysis confirmed the empirical formula.



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The most interesting product of the acid-catalyzed rearrangement of (**1**. $R = CH_3$) was formed by treatment with a trace of potassium acid sulfate under very carefully controlled conditions. The separation of the

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[1] (a) To whom requests for reprints should be addressed at the Department of Chemistry, State University of New York, Long Island Center, Stony Brook, N. Y.; (b) Present address: Department of Chemistry, University of Alberta at Calgary, Calgary, Alberta, Canada; (c) The authors are grateful for the support of the National Institutes of Health through research grant E-1608; (d) A preliminary report of this work was presented at the National Meeting of the American Chemical Society in Washington, D. C., March 22, 1962, Abstracts 141, p. 21-O.

[2] Th. Herbertz, *Ber.*, **85**, 475 (1952).

[3] E. M. Kosower, G.-S. Wu, and T. S. Sorensen, *J. Am. Chem. Soc.*, **83**, 3151 (1961).

[4] I. N. Nazarov, I. B. Torgov, and L. N. Terekhova, *Bull. Acad. Sci. URSS, Classe Sci. Chim.*, 43 (1943); *Chem. Abstr.*, **38**, 1729 (1944); A. N. Elizarova and I. N. Nazarov, *Bull. Acad. Sci. URSS, Classe Sci. Chim.*, 223 (1940); 423 (1941); *Chem. Abstr.*, **36**, 747, 1295 (1942).

[5] It was difficult to obtain accurate values for the vinyl and aldehyde hydrogens with the spectra available. The positions of the peaks are at unusually high field (except for the allenic hydrogens) when calculated by the addition of 3.52 to chemical shifts measured from a benzene capillary reference. The n.m.r. pattern, however, is entirely consistent with the structure as are all other data.

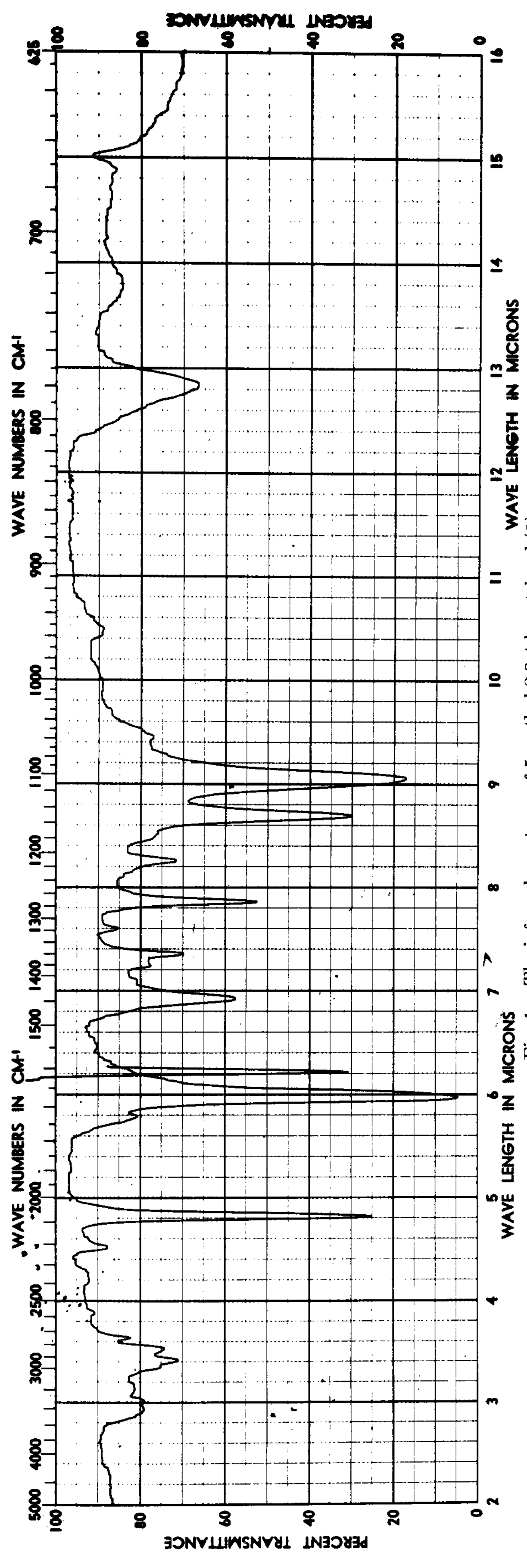
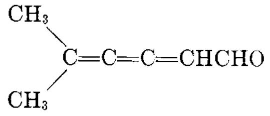


Fig. 1.—The infrared spectrum of 5-methyl-2,3,4-hexatrienal (3).

new material was followed with the aid of an unusual sharp and strong infrared band at 2066 cm.$^{-1}$ (Fig. 1). The pure substance had the composition C_7H_8O and a simple n.m.r. spectrum (Fig. 2). With ordinary resolution, three peaks centered at *ca.* 7.82 τ (*gem*-dimethyl), *ca.* 4.41 τ (alkene hydrogen, doublet, J = 8.2 c.p.s.) and *ca.* 0.80 τ (aldehyde hydrogen, doublet, J = 7.6 c.p.s.). The fine structure revealed by the first two peaks under high resolution (see Fig. 2) is discussed below.

Reduction of the compound results in a small yield of isoheptyl alcohol. The n.m.r. spectrum indicates that the original compound is a cumulenal **3**. No previous examples of compounds bearing a functional group directly attached to a cumulene system have been reported.[6] The unusual ultraviolet absorption of **3** has already been reported.[3]



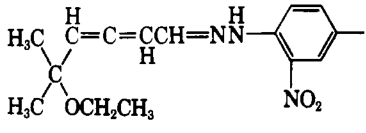
$$(CH_3)_2C{=}C{=}C{=}CHCHO$$

3

A few chemical reactions were carried out with each new compound. The lithium aluminum hydride reduction of **4** will be described separately.[7] The allenal (**6**) is converted to the dihydropyrone (**4**) in over 50% yield on refluxing with acidic aqueous tetrahydrofuran. The allenal reacts immediately with *n*-butylamine and aqueous hydroxide; the product of the amine reaction has strong infrared absorption between 1587 and 1612 cm.$^{-1}$, probably due to the grouping N—C=C—CHO.

The cumulenal (**3**) does not react at room temperature with maleic anhydride but yields a black tar on heating with tetracyanoethylene. Measurement of the ultraviolet spectra in methanol and water[3] was complicated by the reaction of the solvent with the cumulenal, resulting in diminution of absorption with a half-life of *ca.* thirty minutes. Ultraviolet data were corrected to zero time, but no correction was necessary for tetrafluoropropanol (TFP).

Reaction of the cumulenal with an acidic ethanol solution of 2,4-dinitrophenylhydrazine forms a derivative of the ethoxyallenal (**7**), identified by analysis and the presence of an allene band at 1941 cm.$^{-1}$. Like the



allenal, the cumulenal forms the dihydropyrone on heating with acid in aqueous tetrahydrofuran.

The cumulenal undergoes slow polymerization at room temperature and is best stored at −78°. However, the infrared spectrum of the gel formed in a number of instances indicated that most of the material was monomeric. A sample kept under nitrogen for one month at room temperature lost most of its cumulene infrared absorption, with new absorption at 1640 cm.$^{-1}$ and 3333 cm.$^{-1}$. The latter band might represent water, formed by aldol condensation.

The dihydropyrone (**4**) reacts with *n*-butylamine on refluxing in methanol or benzene to form 5-methyl-5-hydroxy-1-butylaminohex-1-en-3-one (**8**, R = $CH_3CH_2CH_2CH_2$—), λ_{max} 3048 (ϵ 22,000) (95% ethanol).

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(6) P. Cadiot, W. Chodkiewicz, and J. Rauss-Godineau, *Bull. soc. chim. France*, 2176 (1961).

(7) E. M. Kosower and T. S. Sorensen, *J. Org. Chem.*, **28**, 692 (1963).

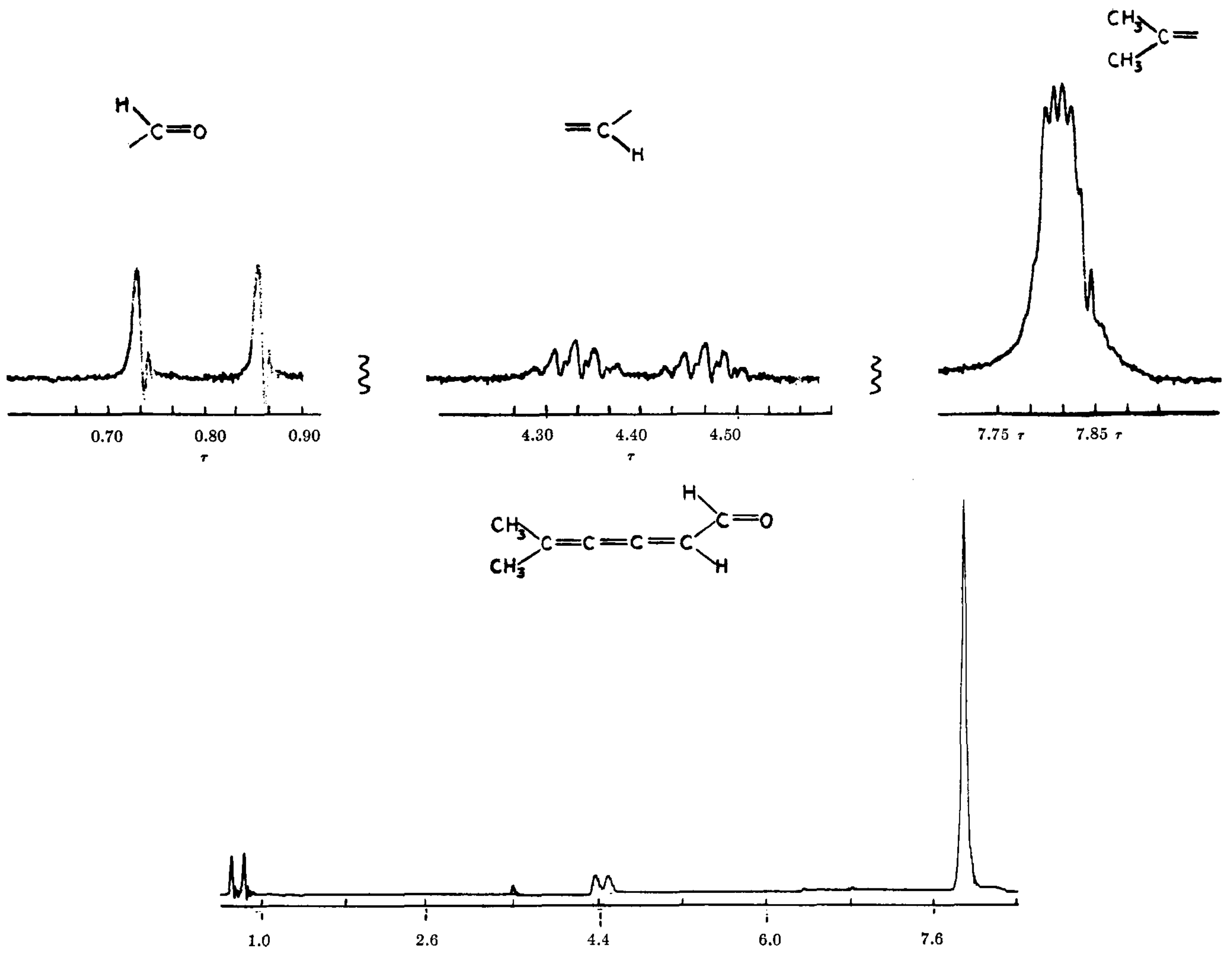
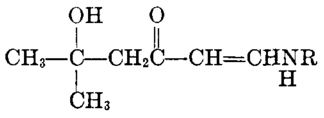


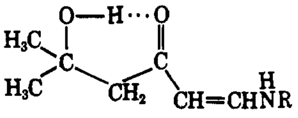
Fig. 2.—The n.m.r. spectrum of 5-methyl-2,3,4-hexatrienal (**3**).

The structure was assigned on the basis of an analysis, infrared and ultraviolet spectra. The corresponding methyl derivative (**8**. R = CH_3) was prepared by the reaction of **4** with methylamine in a sealed tube at 100°.



$$\mathrm{CH_3{-}\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}{-}CH_2\overset{\overset{O}{\|}}{C}{-}CH{=}CH\underset{H}{N}R}$$

The ultraviolet maxima for both ketones are shifted to slightly longer wave lengths in isooctane, suggesting that the ground state is more polar than the excited state for these π → π* transitions. However, it seems more likely that internal hydrogen bonding in isoöctane (as in **8**A) is responsible for the small solvent sensitivity.



Discussion

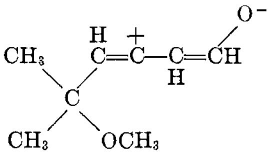
Ultraviolet Spectra.—Absorption data for the allenal (**6**) are listed in Table I for various solvents. The solvent sensitivity of the π → π* transition is quite low, a fact which might be explained by the inability of the β-carbon to accommodate an increase in positive charge in the excited state (**9**).

TABLE I

ULTRAVIOLET MAXIMA FOR THE ALLENAL (6)

Solvent	(Z)[a]	π—π* transition λ_{max}, Å. (ϵ_{max})	n—π* transition λ_{max} (ϵ_{max})
Isoöctane	(60.1)[a]	2268 (10,400)	3030 (34)
Acetonitrile	(71.3)	2289 (12,000)	. . .
Methanol	(83.6)	2288 (9,800)	2800-3000 sh (240)
Water	(94.6)	2297 (12,500)	. . .

[a] See ref. 8.



The cumulenal (**3**) exhibited ultraviolet absorption suggestive of a solvent-sensitive equilibrium between *s-cis* and *s-trans* forms.[3]

Infrared Spectra.—The infrared bands assigned to C=C stretching show an orderly progression to higher frequencies with increasing stiffness of the group concerned. Thus, unconjugated double bonds absorb

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(8) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253 (1958).

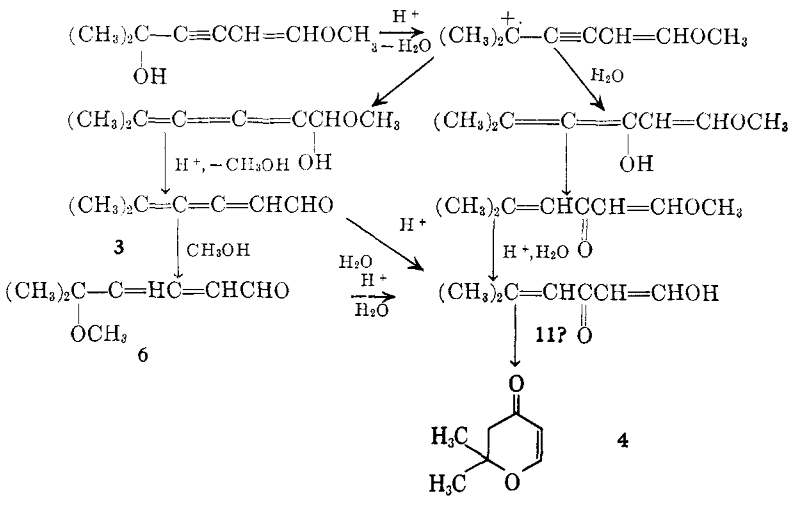
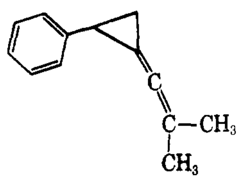


Chart I

between 1680–1620 cm.$^{-1}$, the intensity being weak when little change in dipole moment occurs with vibrational motion.[9] Allenes possess a characteristic infrared band near 1960–1940 cm.$^{-1}$, while disubstituted acetylenes absorb between 2260–2190 cm.$^{-1}$.[9] The symmetrical molecule 1,2,3-butatriene has absorption bands at 1708 and 1610 cm.$^{-1}$ corresponding to double bond stretching, but does not have a characteristic cumulene band.[10] The surprising report that two 1,2,3,4-tetraenes had infrared absorption at 1940 cm.$^{-1}$ [11] has been cleared up by the finding that the compounds were actually allenes.[12] We now find that a strong absorption, probably characteristic of 1,2,3-trienes appears in infrared spectrum of the cumulenal (**3**) at 2066 cm.$^{-1}$. It is interesting to note that the unusually rigid allene system (**10**) has a band at 2020 cm.$^{-1}$.[13]



N.m.r. Spectrum of Cumulenal.—There has been considerable recent interest in long range coupling of proton spins and experiments have shown that appreciable spin–spin couplings occur through many π-bonds.[14–17] Theoretical studies of the expected coupling[18,19] have suggested that cumulene systems should have a large coupling constant for the hydrogens at the ends.

The high resolution n.m.r. spectrum of the cumulenal reveals a complex methyl band consisting of four main peaks, spaced about 0.55 c.p.s. apart. The vinyl hydrogen bands (a wide doublet resulting from coupling to the aldehyde hydrogen) are further split into quintets in which the couplings to the methyl groups are about 1.2 c.p.s. The peak ratios (9:14:20:16:10) suggest that the bands are, in fact, heptets. (Peak ratios expected—quintet 1:4:6:4:1; heptet 1:6:15:20:15:6:1.) The nature of the vinyl hydrogen band indicates that the two methyl groups are not coupled equally to the vinyl hydrogen and that the spectrum is more complex than would be the case for an A_6X spectrum.

The magnitude of the coupling is much less than that predicted for strictly cumulene systems but it is well known that the methyl couplings are indeed smaller.[18] The order of magnitude of the constant seems reasonable in relation to that reported for methyldiacetylene (J = 1.3 c.p.s.)[15] for which the separation of the coupled portions is similar to that in the cumulenal.

Mechanisms.—Reasonable mechanisms can be written for the transformations described in this paper (Chart I). It is worth noting that a base-soluble compound was present in some of the dihydropyrone (**4**) preparations. The structure was not investigated but might well be **11**.

Experimental

5-Methyl-5-hydroxy-1-methoxyhex-1-en-3-yne (1. R = CH$_3$). A solution of *n*-propyl Grignard reagent was prepared by the addition of *n*-propyl bromide (185 g., 1.5 moles) in ether (1 l.) to magnesium turnings (37 g., 1.5 g.-atoms). Redistilled 1-methoxy-1-buten-3-yne (Aldrich Chemical Co., Milwaukee) (b.p. 51°/55–60 mm.) (122 g., 1.5 moles) in ether (400 ml.) was added over a 1-hr. period. During addition a white precipitate developed. The solution was stirred for an additional hour, then cooled to *ca.* 5° in an ice bath. Acetone (dried over potassium carbonate, distilled) (87 g., 1.5 moles) in ether (100 ml.) was added over a 1-hr. period; cooling was discontinued at the beginning of the addition. The precipitate gradually disappears, leaving a dark-colored solution which was stirred for 1 hr. after addition. Some precipitate appeared immediately after addition was complete. Saturated ammonium chloride solution (1.1 l.) was added, the ether layer separated, washed with saturated sodium bicarbonate solution (1.1 l.) and dried over magnesium sulfate. Distillation of the residue under nitrogen after removal of the ether yielded 5-methyl-5-hydroxy-1-methoxyhex-1-en-5-yne, b.p. 68–74°/0.3 mm., n^{25}D 1.498; yield 142 g. (68%) (reported b.p. 117°/5 mm., n^{20}D 1.478).[2]

2,2-Dimethyl-3,4-dihydro-4*H*-pyran-4-one (4).—A solution of 30.7 g. (0.219 mole) of the alcohol (1. R = CH$_3$), 0.75 g. (0.00395 mole) of *p*-toluenesulfonic acid monohydrate and 23 ml.

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[9] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958.

[10] W. M. Schubert, T. H. Liddicoet, and W. A. Lanka, *J. Am. Chem. Soc.*, **76**, 1929 (1954).

[11] M. Nakagawa, K. Shingu, and K. Naemura, *Tetrahedron Letters*, No. **22**, 802 (1961).

[12] R. Kuhn and B. Schulz, *Angew. Chem.*, **74**, 292 (1962).

[13] H. D. Hartzler, *J. Am. Chem. Soc.*, **83**, 4990 (1961).

[14] R. A. Hoffman and S. Gronowitz, *Arkiv. för Kemi*, **16**, 471 (1960).

[15] E. I. Snyder and J. D. Roberts, *J. Am. Chem. Soc.*, **84**, 1582 (1962).

[16] E. I. Snyder, L. J. Altman, and J. D. Roberts, *ibid.*, **84**, 2004 (1962).

[17] R. C. Hirst and D. M. Grant, *ibid.*, **84**, 2009 (1962).

[18] M. Karplus, *ibid.*, **82**, 4431 (1960).

[19] R. A. Hoffman and S. Gronowitz, *ibid.*, **83**, 3910 (1961).

of water in 225 ml. of peroxide-free tetrahydrofuran was refluxed for 12 hr. Most of the tetrahydrofuran was distilled and replaced with diethyl ether. The ether solution was separated from a small amount of water and dried over anhydrous magnesium sulfate. Evaporation of the ether *in vacuo* left 24.9 g. of a light red oil. The oil was distilled under nitrogen to give 21.6 g., (78%) of fairly pure 2,2-dimethyl-3,4-dihydro-4*H*-pyran-4-one (**4**). The product was redistilled through a 15 × 1.2 cm. straight tube to give pure **4**, b.p. 67–68°/8 mm., n^{25}_{D} 1.4770, d_4^{20} 1.024. The liquid solidifies when cooled in Dry Ice.

Anal. Calcd. for $C_7H_{10}O_2$: C, 66.64; H, 7.99. Found: C, 66.89; H, 8.05.

2,2-Dimethyltetrahydro-4*H*-pyran-4-one (**5**).—A solution of **4** (10.0 g.) in methanol (200 ml.) was allowed to absorb hydrogen at room temperature with 10% palladium on charcoal as catalyst. Uptake ceased at *ca.* 1.46 moles hydrogen per mole. After filtration and removal of solvent, the residue was distilled to yield 9.3 g. of mixture, boiling range 56–79°/12 mm. The material had little carbonyl absorption in the infrared and was therefore hydrolyzed for 5 min. with 50 ml. of 5% hydrochloric acid. Ether extracts were dried and distilled, yielding 3.9 g. (37%) of the saturated ketone (**5**), a colorless liquid with a menthol-like odor, b.p. 62–65°/12 mm., n^{25}_{D} 1.4431, $\nu_{C=O}$ 1724 cm.$^{-1}$ (reported constants[4] are b.p. 178–179°, n^{18}_{D} 1.4458). The semicarbazide has a m.p. of 168–169.5° from methanol (reported 165.5°).

Anal. Calcd. for $C_8H_{15}N_3O_2$: C, 51.87; H, 8.16. Found: C, 52.24; H, 8.30.

5-Methyl-5-hydroxy-1-butylaminohex-1-en-3-one (**8**. R = $CH_3CH_2CH_2CH_2$—).—The dihydropyrone (**4**) (12.6 g., 0.1 mole) and *n*-butylamine (7.3 g., 0.1 mole) were refluxed in methanol (100 ml.) for 23 hr. The methanol was removed under vacuum and the residue distilled to yield 16.8 g. (84%) of a yellow liquid, b.p. 97–99°/0.03 mm. Redistillation under nitrogen gave a light yellow liquid, b.p. 97–99°/0.05 mm., n^{25}_{D} 1.5183.

Anal. Calcd. for $C_{11}H_{21}NO_2$: C, 66.29; H, 10.62; N, 7.03. Found: C, 66.25; H, 10.36; N, 7.44.

The ultraviolet maximum in 95% ethanol was at 3048 Å. (ϵ 22,000) and in isoöctane at 3062 Å. ($\epsilon \backsim$ 18,000). Infrared spectra indicated NH and/or OH absorption along with a conjugated carbonyl group. (Bands occurred at 3246 cm.$^{-1}$, 1642 cm.$^{-1}$, and 1553 cm.$^{-1}$.)

The corresponding methyl derivative (**8**. R = CH_3) was prepared in 19% yield in a sealed tube reaction at 100° for 22 hr., using Linde molecular sieve 4A as a dehydrating agent. The pure compound was a viscous yellow oil, b.p. 75–77°/0.07 mm., n^{25}_{D} 1.5445.

Anal. Calcd. for $C_8H_{15}NO_2$: C, 61.12; H, 9.62; N, 8.91. Found: C, 61.00; H, 9.54; N, 9.26.

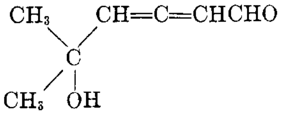
In 95% ethanol, λ_{max} 2999 Å. (ϵ 20,100); in isoöctane, λ_{max} 3048 Å. ($\epsilon \backsim$ 16,700). Infrared bands occurred at 3257 cm.$^{-1}$, 1645 cm.$^{-1}$, and 1553 cm.$^{-1}$.

5-Methyl-5-methoxy-2,3-hexadienal (**6**).—The alcohol (**1**. R = CH_3) (10.098 g.) (0.0721 mole), was put into a 25-ml. pear-shaped flask and 5 g. of powdered potassium acid sulfate added to this. The mixture becomes dark and quite hot. After 5 min., the flask was connected to a small distillation apparatus and the contents rapidly distilled at 6–7 mm. using a nitrogen-fed bleed. A yellow liquid, 6.65 g., n^{25}_{D} 1.487, was collected. The combined product *from three runs* was distilled through a 15 × 1.2 cm. helices-packed column under nitrogen atmosphere to give fractions boiling at 63–70°/6–7 mm. with n^{25}_{D} 1.488–1.480.

These fractions (11.2 g.) were combined (on the basis of infrared data) and 7.9 g. was chromatographed on 100 g. (37.5 × 2.5 cm.) of silicic acid (acetone-washed and dried). Elution with 200-ml. of petroleum ether (b.p. 60–68°), 100 ml. of 10% benzene–petroleum ether and 200 ml. of benzene yielded almost no product. Elution with 150 ml. of 5% ether–benzene gave *ca.* 0.5 g. of oil, while elution with 250 ml. of 10% ether–benzene (50-ml. fractions) gave a total of 5.5 g. of liquid. Elution with 50 ml. 20% ether–benzene gave some additional oil. The middle fraction (*ca.* 1 g.) from 10% ether–benzene (lowest infrared absorption between 6.1 and 6.2 μ) was distilled under nitrogen to give a colorless oil, b.p. 64.5–65°/6 mm., n^{25}_{D} 1.4781. The compound solidifies at Dry Ice temperatures, but has a melting point well below 0°.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.54; H 8.60. Found: C, 68.53; H, 8.75.

The yield of pure material is quite low (∽ 3%) but the crude product contains about 75% (**6** or **6H**) in a yield of roughly 50%. (The allene is easily identified by infrared.) No effort was made to improve the yield or the procedure, but the structure of **6** was firmly established by infrared, ultraviolet, and n.m.r. analysis.



6H

Small samples of the crude aldehyde reacted rapidly with *n*-butylamine or sodium hydroxide, resulting in a product with reduced infrared allene absorption. Refluxing another sample of the allenal with acidic aqueous tetrahydrofuran gave a product with an infrared spectrum very close to that of the dihydropyrone (**4**).

5-Methyl-2,3,4-hexatrienal (**3**).—The apparatus used for the preparation of this consisted of a 70 × 0.8 cm. straight tube column fitted on the lower end with a 10/18 male joint and sealed on the upper end to a still head-condenser combination. The condenser was connected to a vacuum take-off. The straight tube column was enclosed in a heated jacket within which a thermometer was fixed. Before each run, the internal jacket temperature was adjusted to 72–75°. The reaction vessel was two-necked, the second neck being used to supply nitrogen. A stirred oil bath used for heating the reaction mixture was stabilized at 100° before each run. A good water aspirator (in winter) or a vacuum pump adjusted to hold the system between 5–7-mm. pressure is essential to the success of the preparation. The amount of acetylenic alcohol used each time was about 10 g. along with about 60 mg. of potassium acid sulfate crushed in a mortar and pestle. A typical run was as follows: The alcohol (**1**. R = CH_3) (10.437 g.) (0.0746 mole) was placed in a 25-ml. two-necked distillation flask. Potassium acid sulfate (60 mg.) was added and the flask connected to a vacuum distillation system at 5–7-mm. pressure. The oil bath around the pot was slowly raised to 120°, and column temperature allowed to rise to 78° while the product was distilled as rapidly as it formed. At the end of the distillation, only a black tar remained in the pot. The distilled yellow oil, 2.88 g., n^{22}_{D} 1.538, was dissolved in 60 ml. of pentane, cooled slowly in solid Dry Ice, and allowed to stand for several hours in a Dry Ice–acetone mixture. Most of the liquid was decanted and the rest removed with a filter stick while maintaining the temperature at −78°. The solid was washed twice with pentane (30 ml. at −78°). The material was allowed to come to room temperature under vacuum and transferred to a small distilling flask with pentane. The aldehyde (**3**) was distilled at room temperature at 0.1 mm., using a receiver at −78°. About 1 g. (13%) of **3** was collected. It was recrystallized from 50 ml. of pentane as described, washing twice with 25 ml. of pentane, and redistilled to yield pure aldehyde, a pale yellow liquid with a pungent, lachrymatory vapor, b.p. *ca.* 25°/0.1 mm., m.p. −11 to −9, n^{25}_{D} 1.606 (Abbe refractometer with sodium light source), d_4^{26} 0.920.

Anal.[20] Calcd. for C_7H_8O: C, 77.75; H, 7.46. Found: C, 77.82, 77.90; H, 7.34, 7.27.

Hydrogenation of the Cumulenal (**3**).—The aldehyde (**3**) (0.24 g.) absorbed 2.99 moles of hydrogen per mole using 200 mg. of platinum oxide. After filtration and evaporation, a yellow oil was obtained (0.08 g.) which had hydroxyl absorption in the infrared. The oil was converted to a 3,5-dinitrobenzoate by refluxing with the acid chloride in benzene for 15 min. The ester was isolated by crystallization from chloroform–petroleum ether (b.p. 60–68°) in 14% yield (92 mg.). Several recrystallizations from pentane gave light cream-colored plates, m.p. 52–53.5° (reported for isoheptyl 3,5-dinitrobenzoate, m.p. 54.5–55°[21]).

Anal. Calcd. for $C_{14}H_{18}N_2O_6$: C, 54.19; H, 5.85. Found: C, 54.23; H, 6.04.

Reaction of Cumulenal (3) with 2,4-Dinitrophenylhydrazine.—The aldehyde (0.105 g.) reacted with an acidic ethanol solution of 2,4-dinitrophenylhydrazine. After 1 min., an orange precipitate formed, m.p. 95–103°; weight, 0.201 g. On recrystallization from benzene, a small amount of insoluble oil was noted and discarded. Several recrystallizations produced fine orange plates, m.p. 167.5–168° dec.

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(20) The analytical samples were shipped to Spang Microanalytical Laboratories, Ann Arbor, Mich., packed in Dry Ice.

(21) R. C. Huston and A. H. Agett, *J. Org. Chem.*, **6**, 123 (1941).

Anal. Calcd. for $C_{15}H_{18}N_4O_5$: C, 53.88; H, 5.43. Found: C, 53.99; H, 5.44.

The analysis corresponds to the 2,4-dinitrophenylhydrazone of the ethoxyallenal; λ_{max} 3720 (ϵ 33,100).

Reactions of Cumulenal (3).—The aldehyde (0.12 g.) and maleic anhydride (0.11 g.) were allowed to stand in ethyl ether (10 ml.) for 60 hr. at room temperature. After removal of the solvent, the residual oil had an infrared spectrum characteristic of the two reactants.

The aldehyde was refluxed with a trace of *p*-toluenesulfonic acid in 90% tetrahydrofuran–water for 24 hr. After work-up, the residual oil had an infrared spectrum identical to that of the dihydropyrone (4).

A mixture of tetracyanoethylene and cumulenal in ether shows no apparent color change. Heating at 100° after removal of the solvent produces a black solid with neither cumulene nor allene absorption in the infrared.

A mixture of cumulenal and methylamine hydrochloride in acetonitrile at room temperature for 3 days in concentrations of *ca.* 0.05 *M* yielded an oil with an infrared spectrum almost identical to that of starting material.

Ultraviolet and Infrared Spectra.—Spectra were measured using 1-cm. cells and a Cary Model 11 spectrophotometer. Infrared spectra were obtained with an Infracord or, in the case of pure compounds, a Baird double beam instrument (Model B or Model 4–55).

Nuclear Magnetic Resonance Spectra.—Measurements were made on a Varian Associates HR-60 instrument at 60 Mc. Spectra were run on dilute carbon tetrachloride solutions (15–20%) and with a benzene capillary for reference except for the dihydropyrone (4) which was measured with a Varian Associates A-60 instrument with tetramethylsilane as reference. Approximate conversion to τ-values was made by the addition of 3.52.

Acknowledgment.—The authors are grateful to Dr. James W. Patton for obtaining many of the n.m.r. spectra and to Dr. S. Seltzer of Brookhaven National Laboratory for the A-60 spectrum. We are indebted to Professor J. D. Roberts, Dr. F. C. Nachod, and Dr. Paul C. Lauterbur for helpful criticism and advice.

Some Unsaturated Imines

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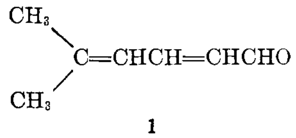
Received July 2, 1962

The synthesis of the unsaturated imines derived from *n*-butylamine and 5-methyl-2,4-hexadienal and 2,4-hexadienal is reported. The former could not be cyclized to a 1,2-dihydropyridine. The *n*-butylimine of crotonylideneacetone is formed in the reaction of crotonaldehyde and the *n*-butylimine of acetone. A large and striking shift of the ultraviolet maximum of the unsaturated imines to longer wave lengths occurs on protonation. The synthesis of 5-methyl-2,4-hexadienal and its formation from 2,2-dimethyl-3,4-dihydro-4*H*-pyran-4-ol as well as another acid-catalyzed reaction of the latter are described. The ultraviolet spectra of the aldehyde and 2,4-hexadienal in solvents of a wide range of **Z**-value are reported.

In connection with some attempted syntheses of 1,2-dihydropyridines, a number of unsaturated imines were prepared. Certain of their properties were investigated and are here reported.

Results

Dienals.—The unsaturated aldehyde, 5-methyl-2,4-hexadienal (1), was synthesized in 71% yield by the lithium aluminum hydride reduction of 5-methyl-5-hydroxy-1-methoxy-3-hexyn-1-ene[2] followed by acid hydrolysis according to the general procedure of Inhoffen and co-workers.[3] The aldehyde was also prepared by the reaction of 1-methoxy-5-methyl-5-hydroxy-1-*trans*,3-*cis*-hexadiene with boron trifluoride. The ultraviolet spectrum of the aldehyde was measured in solvents of different polarity (as measured by **Z**-value).[4,5] Data for the aldehyde (1) and the closely related sorbaldehyde (2) are listed in Table I.



$(CH_3)_2C{=}CHCH{=}CHCHO$

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TABLE I

ULTRAVIOLET ABSORPTION DATA FOR ALDEHYDES

Solvent (Z)[a]	Aldehyde 5-Methyl-2,4-hexadienal[d] (**1**) λ_{max}, Å. (ϵ_{max})	 2,4-Hexadienal[c] (**2**) λ_{max}, Å. (ϵ_{max})
Isoöctane (60.1)	2742 (31,000)	2604 (28,600)
Acetonitrile (71.3)	2838 (30,900)	2690 (31,800)
2-Propanol (76.3)	2858 (29,200)	.. ...
Methanol (83.6)	2866 (29,000)	2712 (30,100)
Water (94.6)	2964 (27,800)	2797 (29,700)
TFP[b] (96.3)[e]	2958 (30,300)	2779 (29,600)
10 *M* LiCl (106.8)[e]	3058 (21,000)	2882 ...

[a] Ref. 4. [b] 2,2,3,3-Tetrafluoropropanol. [c] Sorbaldehyde. [d] $n \rightarrow \pi^*$ transition in isoöctane at 3330 Å. [e] Ref. 5.

The 5-methyl-2,4-hexadienal was formed by heating 2,2-dimethyl-3,4-dihydro-4*H*-pyran-4-ol (3) in tetrahydrofuran saturated with hydrogen chloride, as shown by the infrared spectrum of the product and the isolation of the 2,4-dinitrophenylhydrazone. It was of some interest that the pyranol, which is readily available from the lithium aluminum hydride reduction of the corresponding ketone,[2] did not form the dienal with aqueous hydrochloric acid. Instead, a rapid reaction led to a solution thought to contain 5-hydroxy-5-methyl-*cis*-2-hexenal (4) with λ_{max} 2325 Å. (ϵ 7300). Crotonaldehyde had λ_{max} 2235 Å. (ϵ 16,000) in the same medium. Attempted isolation of the *cis*-aldehyde by extraction with ether led to a material with a camphoraceous odor and negligible ultraviolet absorption past 2100 Å. This material was probably the 2-isomer (5) of the 4-pyranol. The n.m.r. data for the 4-pyranol are tabulated in Table II and the n.m.r. spectrum shown in Fig. 1. The reactions of the pyran-4-ol are shown in equa-

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