cis-1,3,5-Hexatriene and Chloro- and Methyl-1,3,5-hexatrienes

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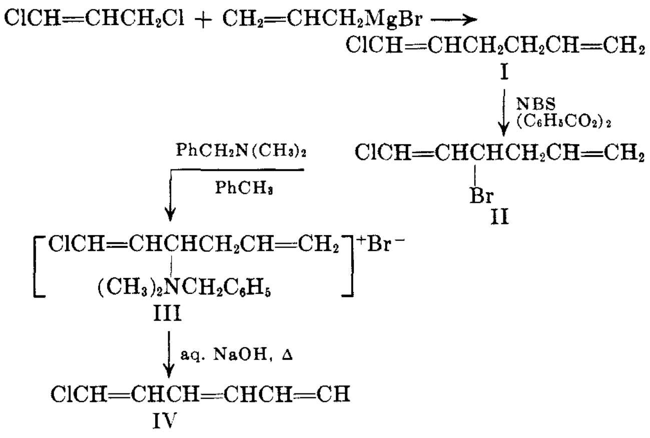
The three positional isomers of the chloro-1,3,5-hexatrienes and the methyl-1,3,5-hexatrienes have been prepared and examined by gas–liquid chromatography. The geometric configurational assignment of the isomers of 1,3,5-hexatriene can now be made, on a chemical basis, as a result of a stereospecific synthesis of *cis*-1,3,5-hexatriene. This chemical assignment agrees with the previous assignment based on infrared and Raman spectroscopy.

1,3,5-Hexatriene may be substituted in any of three positions (designated as the 1-, 2-, or 3-positions). An earlier paper from this laboratory[1] reported the preparation of 2-methyl-, 2-bromo-, and 2-chloro-1,3,5-hexatrienes. We now report the preparation of 1-chloro- and 3-chloro-1,3,5-hexatrienes along with 3-methyl- and 1-methyl-1,3,5-hexatrienes.

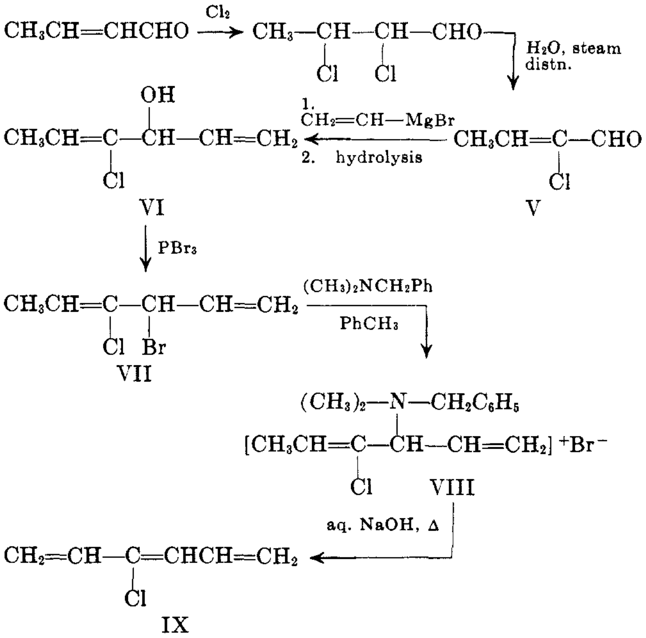
The synthesis of 1-chloro-1,3,5-hexatriene (IV) is shown by equations in Scheme I. The first step in the reaction scheme, which yielded 1-chloro-1,5-hexadiene (I), was accomplished in high yield. Bromination of I led to a bromochlorohexadiene, for which the structure II is written with no justification, since the position of the bromine atom with respect to the two saturated methylene groups is unknown. It was not feasible to attempt characterization of this substance, as it is quite unstable. Conversion of the bromine-containing compound to the quaternary salt III was readily accomplished. Here again, the attachment of the nitrogen atom to the chlorodienic system is arbitrarily assigned. However, decomposition of III in boiling aqueous sodium hydroxide provided 1-chloro-1,3,5-hexatriene (IV). The assignment of the trienic structure to IV is based on the following: (1) a typical trienic ultraviolet absorption spectrum and (2) the absence of allenic or acetylenic links in its infrared spectrum.

SCHEME I



For the synthesis of 3-chloro-1,3,5-hexatriene, the following reaction sequence was utilized: (1) α-chlorocrotonaldehyde (V), prepared by the addition of chlorine to crotonaldehyde followed by dehydrohalogenation, was treated with vinylmagnesium bromide, yielding 4-chloro-1,4-hexadien-3-ol (VI); (2) VI was converted to 3-bromo-4-chloro-1,4-hexadiene (VII) with phosphorus tribromide; (3) VII was converted to the quaternary ammonium compound (VIII) by reaction of VII with N,N-dimethylbenzylamine; and finally (4) VIII was decomposed in boiling aqueous sodium hydroxide to provide the desired product (IX). This reaction scheme is shown in Scheme II. The assignment of the structure is based upon the same type of data as was utilized for 1-chloro-1,3,5-hexatriene with the added fact that reaction of IX with hydrogen in the presence of palladium consumed four molecules of hydrogen (hydrogenolysis of the carbon–chlorine bond and addition of three molecules of hydrogen).

SCHEME II



Physical data for 1-, 2-, and 3-chloro-1,3,5-hexatrienes are given in Table I. 1-Chloro-1,3,5-hexatriene is considerably less stable than either the corresponding 2-chloro or 3-chloro compounds. Satisfactory carbon–hydrogen analyses were obtained for

TABLE I

PHYSICAL DATA FOR CHLORO-1,3,5-HEXATRIENES

	2-Chloro[a]	3-Chloro	1-Chloro
B.p., °C. (mm.)	39–40 (20)	40 (25)	40–42 (25)
n_D (°C.)	1.5395 (23)	1.5470 (24)	1.5329 (27)
d_4, g./ml. (°C.)	0.9706 (23)	0.9994 (23)	...
Molar refraction, ml. (exaltation, ml.)	37.0 (3.6)	36.3 (3.0)	...
λ_{max}, mμ (ϵ_{max} × 10^{-4})	239.5 (1.35) (sh)	244.0 (1.70) (sh)	255.5 (3.20)
	247.5 (2.49)	252.5 (2.98)	265.0 (4.35)
	256.5 (3.61)	262.5 (4.35)	275.5 (3.46)
	267.0 (3.02)	273.5 (3.60)	

[a] See ref. 1.

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(1) C. W. Spangler and G. F. Woods, *J. Org. Chem.*, **28**, 2245 (1963).

TABLE II

PHYSICAL DATA FOR METHYL-1,3,5-HEXATRIENES

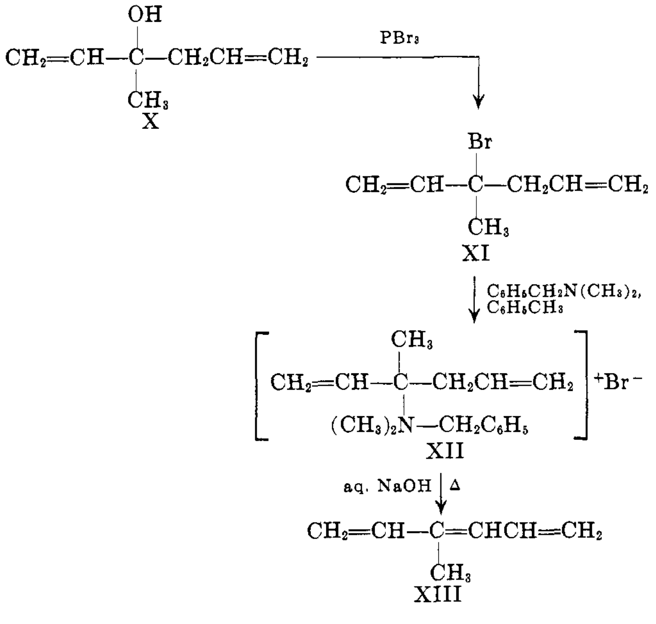
	2-Methyl		3-Methyl		1-Methyl	
	Previous paper[a]	Reported	This work	Reported[b]	This work	Reported[b]
B.p., °C. (mm.)	108 (760)	27 (14)[b]	74 (50)	28 (25)	115 (760)	114–115 (760)
		48–52 (52)[c]				
n_D (°C.)	1.5075 (27)	1.491 (26)[b]	1.5198 (26)	1.492 (28)	1.5239 (24)	1.5239 (28)
		1.5127 (16)[c]				
d_4, g./ml. (°C.)	0.7632 (24)	...	0.7633 (26)	...	0.7631 (22)	...
Molar refraction, ml. (exaltation, ml.)	36.7 (3.5)	...	37.6 (4.5)	...	37.6 (4.5)	...
λ_{max}, mμ ($\epsilon_{max} \times 10^{-4}$)	239.5 (1.39) (sh)	248.0 (2.02)[b]	251.0 (2.75)	253.0 (1.55)	250.0 (3.33)	251.0 (3.42)
	247.5 (2.75)	257.5 (2.65)	260.5 (3.70)	262.5 (2.14)	260.0 (4.45)	260.5 (4.68)
	256.5 (3.58)	267.5 (2.14)	271.0 (2.86)	272.5 (1.65)	270.0 (3.56)	271.0 (3.81)
	267.0 (2.85)					
		248 (2.60)[c]				
		257 (2.80)				
		267 (2.20)				

[a] See ref. 1. [b] See ref. 2. [c] E. A. Braude and C. J. Timmons, *J. Chem. Soc.*, 2007 (1950).

3-chloro-1,3,5-hexatriene and 2-chloro-1,3,5-hexatriene (reported[1] earlier), but apparently hydrogen chloride is eliminated readily from the 1-chloro compound, which could not be obtained in a state satisfactory for analysis.

3-Methyl-1,3,5-hexatriene had been prepared earlier,[2] in an impure state, by the phosphorus pentoxide dehydration of 3-methyl-1,5-hexadien-3-ol (X), prepared by the addition of allylmagnesium halide to methyl vinyl ketone. In this work, the same alcohol (X) was utilized as starting material. A procedure, similar to that described above for the preparation of 3-chloro-1,3,5-hexatriene, for the conversion of X to 3-methyl-1,3,5-hexatriene (XIII) is shown in Scheme III.

SCHEME III



A pure geometrical isomer of 1,3,5-heptatriene (1-methyl-1,3,5-hexatriene), one of the four possible isomers, has been reported earlier.[2] This isomer was obtained by catalytic dehydration over alumina of 3,5-heptadien-2-ol. A different synthesis of 1,3,5-heptatriene, now reported, was examined in order to establish the validity of the method of Hwa, de Benneville, and Sims[3] for 1-substituted trienes, and also to determine whether more than one geometrical isomer of the triene could be obtained. The Hwa method consists of the conversion of an allylic dienol to a bromide, conversion of the bromide to a quaternary ammonium salt, and decomposition of this salt to the triene. This was the method utilized above for the syntheses of 3-chloro-1,3,5-hexatriene and 3-methyl-1,3,5-hexatriene. This method, applied to 1,5-heptadien-4-ol, provided 1,3,5-heptatriene (1-methyl-1,3,5-hexatriene). Examination of the material so obtained by g.l.c. showed but one peak, corresponding to the 1,3,5-heptatriene previously reported. The physical data obtained for methyl-1,3,5-hexatrienes are incorporated in Table II. Similar g.l.c. examination of 1-chloro-, 3-chloro-, and 3-methyl-1,3,5-hexatrienes showed but single peaks. The fact that single peaks were observed does not establish isomeric purity for these compounds, however, the *cis–trans* isomers of the parent 1,3,5-hexatriene were readily resolved under identical conditions.

It is our opinion that these samples represent single entities, but of unknown geometric configuration.

The assignment of geometrical isomerism to the simple, parent hydrocarbon 1,3,5-hexatriene has been a rather vexing problem. The earlier geometrically pure isomer of 1,3,5-hexatriene prepared in this laboratory[4,5] was examined by Lippincott, White, and Sibilia.[6] On the application of selection rules to the infrared and Raman spectra, and with certain assumptions, these workers assigned (now known to be correct) the *trans* configuration and linear-extended conformation to it. Hwa, *et al.*,[3] isolated a mixture of the two geometrical isomers of 1,3,5-hexatriene. One isomer was removed by reaction with maleic anhydride (presumably the *trans*) providing the second pure isomer. This second isomer was assigned the *cis* configuration, primarily on the basis of Lippincott's work. Further, this second isomer is a liquid even at reasonably low temperatures, and is the more unstable isomer in that it is readily converted, by iodine catalysis, to the solid

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[2] G. F. Woods and H. Fleischacker, *J. Am. Chem. Soc.*, **78**, 3436 (1956).

[3] J. C. H. Hwa, P. L. de Benneville, and H. J. Sims, *ibid.*, **82**, 2537 (1960).

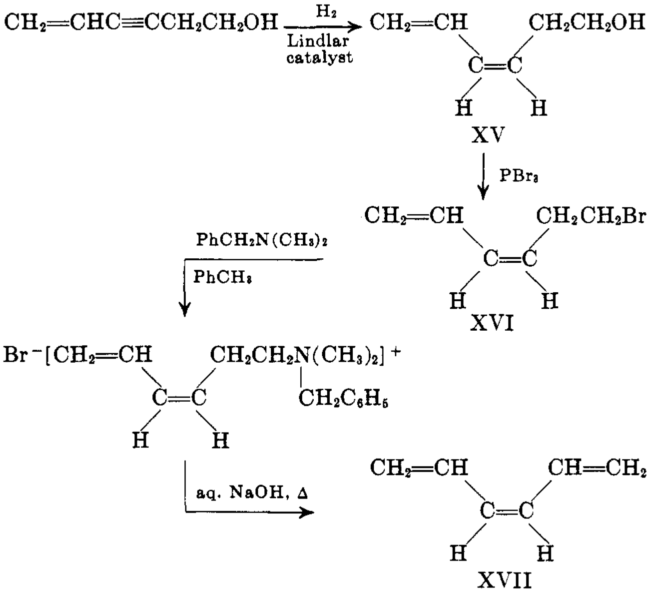
[4] G. F. Woods and L. Schwartzman, *ibid.*, **70**, 3394 (1948).

[5] G. F. Woods, N. C. Bolgiano, and D. E. Duggan, *ibid.*, **77**, 1800 (1955).

[6] E. R. Lippincott, C. E. White, and J. P. Sibilia, *ibid.*, **80**, 2926 (1958).

isomer. Lippincott and Kenney[7] found this liquid isomer to have infrared and Raman spectra consistent with the postulated *cis* extended form. One is dealing, in the 1,3,5-hexatrienes, with a difficult situation where the *trans* configuration might be, but is not necessarily, more stable than the *cis* configuration. We do not yet know, for either isomer, the magnitude of the steric interference or resonance stability, particularly in the *cis* form. It therefore appeared desirable to attempt an assignment of isomerism by chemical, rather than instrumental, means. Accordingly, a stereospecific synthesis of *cis*-1,3,5-hexatriene was accomplished, as shown by the equations in Scheme IV.

SCHEME IV



The final product (XVII) was isolated and examined by g.l.c. and one major peak and three lesser peaks were observed. Of these, the major peak (approximately 60% of the total area under the peaks) corresponded to the *cis* peak observed by Hwa, *et al.*,[3] and one of the lesser peaks corresponded to the isomer previously assigned the *trans* configuration. This latter peak was eliminated by the addition of maleic anhydride to the mixture as a consequence of Diels–Alder adduct formation (which the more stable isomer forms). Also, the larger peak, attributable to the less stable isomer, was likewise almost completely removed by equilibration with a catalytic amount of iodine. Concurrent with the decrease in this peak was an increase of the peak assigned to the more stable isomer.

The above observations are only consistent if the reduction of the acetylenic link provided, as expected, a *cis* configuration which was maintained throughout the remaining reaction scheme (IV).

Experimental

1-Chloro-1,5-hexadiene (I).—Allylmagnesium bromide was prepared from allyl bromide (240 g., 2 moles) and magnesium turnings (130 g., 5.4 g.-atoms). After the reaction was complete, the Grignard reagent was decanted from the excess magnesium and reacted with a solution of 1,3-dichloropropane (189 g., 1.6 moles) in 200 ml. of dry ether. This reaction was slightly exothermic. After the addition of the halide was complete, the product was allowed to stand at room temperature for 12 hr., during which time it solidified to a pasty gray mass. A dilute solution of sulfuric acid (10% by volume) was added dropwise to this mass until a separation took place, yielding a white sludge and a yellow ethereal solution. This solution was decanted from the sludge into a mixture of ammonium chloride and ice. The ether solution of the product was separated, and the aqueous portion was extracted with a further quantity of ether. The combined ether solutions were dried with anhydrous magnesium sulfate, filtered, and distilled at reduced pressure. 1-Chloro-1,5-hexadiene (149 g., 78%) was obtained as a clear, colorless liquid, b.p. 78° (130 mm.) $n^{25}\text{D}$ 1.4476 [lit.[8] b.p. 82° (200 mm.), $n^{20}\text{D}$ 1.450].

Anal. Calcd. for C_6H_9Cl: C, 61.81; H, 7.78. Found: C, 62.06; H, 7.70.

1-Chloro-1,3,5-hexatriene (**IV**).—1-Chloro-1,3,5-hexadiene (107 g., 0.9 mole) was dissolved in 600 ml. of chloroform. To this solution was added N-bromosuccinimide (164 g., 0.9 mole) and benzoyl peroxide (1 g.). This mixture was heated under reflux for 4 hr., then refrigerated for 16 hr. The cold chloroform solution was washed thoroughly with water and dried with anhydrous magnesium sulfate. After filtration, the product was distilled under reduced pressure to effect solvent removal, finally yielding crude 3- (or 4-) bromo-1-chloro-1,5-hexadiene (134.5 g., 70%) as an orange, lachrymatory liquid. Further purification was not attempted, and the crude product was used directly in the next step.

Crude 3- (or 4-) bromo-1-chloro-1,5-hexadiene (135 g., 0.7 mole) and N,N-dimethylbenzylamine (125 g., 0.9 mole) were dissolved in 500 ml. of toluene. The resulting mixture was allowed to stand at room temperature for 6 hr. and then heated at 60° for an additional 3 hr. After refrigeration for 12 hr., the organic solution was decanted from the precipitated gummy brown residue and discarded. The residue was dissolved in water, and the resulting solution was extracted several times with ether to remove suspended organic material. The aqueous solution was then heated to boiling to remove dissolved ether. Upon cooling, a clear amber solution was obtained which was stable on storage at room temperature.

The above aqueous solution of the N,N-dimethylbenzylammonium salt was added dropwise to a solution of sodium hydroxide (64 g. in 1 l. of water) which was in the process of being distilled. The distillate, which was collected in a flask chilled by means of an ice bath, was extracted with ether. The ether layer was washed several times with 3 *N* hydrochloric acid to remove amine and then with water until neutral, dried with anhydrous magnesium sulfate, and distilled at reduced pressure. 1-Chloro-1,3,5-hexatriene was obtained (1 g., 2% over-all yield based on crude 3- (or 4-) bromo-1-chloro-1,5-hexadiene), b.p., 40–42° (25 mm.); a large quantity of material was lost owing to decomposition in the distillation flask. The product began decomposing almost immediately if brought to room temperature, although it could be stored at −20° for periods of up to 12 hr. with little or no evident decomposition.

4-Chloro-1,4-hexadien-3-ol.—α-Chlorocrotonaldehyde (90.5 g., 0.86 mole) dissolved in 200 ml. of dry ether was added to a vinylmagnesium bromide solution prepared from magnesium and 118 g. of vinyl bromide in 600 ml. of tetrahydrofuran. The addition complex was decomposed with ammonium chloride and ice, and the product was isolated in the usual manner. 4-Chloro-1,4-hexadien-3-ol (82.5 g., 73.5%), b.p. 74° (20 mm.), $n^{26}\text{D}$ 1.4821, was obtained as a clear, colorless liquid.

Anal. Calcd. for C_6H_9ClO: C, 54.35; H, 6.84. Found: C, 54.39; H, 6.70.

4-Chloro-1,4-hexadien-3-ol (3.20 g., 0.024 mole) in 50 ml. of ethanol absorbed 1790 cc. of hydrogen at 21° and atmospheric pressure with 1 g. of 5% palladium-on-carbon catalyst (absorption calculated for the reduction of two ethylenic links and hydrogenolysis of one chlorine atom is 1745 cc.). This corresponds to 103% of the theoretical uptake. The catalyst was removed by filtration, and after evaporation of the solvent, crude 3-hexanol was obtained. This product was oxidized in the usual manner with sodium dichromate in glacial acetic acid. The resulting reaction medium was diluted with water and submitted to steam distillation. The distillate was made alkaline and extracted with ether. The ether was evaporated and the residue was reacted with 2,4-dinitrophenylhydrazine reagent. The 2,4-

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[7] E. R. Lippincott and T. E. Kenney, *J. Am. Chem. Soc.*, **84**, 3641 (1962).

[8] L. M. Porter and F. F. Rust, *ibid.*, **78**, 5571 (1956).

dinitrophenylhydrazone of 3-hexanone was obtained (m.p. 130–132°, lit.[9] m.p. 132°). Admixture with an authentic sample gave no depression in melting point.

3-Chloro-1,3,5-hexatriene (IX).—4-Chloro-1,4-hexadien-3-ol (75 g., 0.56 mole) in 100 ml. of dry ether was added dropwise during a period of 2 hr. to phosphorus tribromide (66 g., 0.25 mole), with cooling. After standing for 12 hr., the product was decanted into a mixture of ice and water, and the resulting mixture was neutralized with saturated sodium carbonate solution. The organic product was extracted by a further 200 ml. of ether, and the ether extract was washed with water and dried with anhydrous magnesium sulfate. Most of the ether was removed by evaporation under reduced pressure and the residue, crude 3-bromo-4-chloro-1,5-hexadiene (97 g., 88%), a yellow, lachrymatory liquid, was obtained.

A mixture of the above crude chloro bromide (97 g., 0.49 mole) and N,N-diethylbenzylamine (81 g., 0.60 mole) in 500 ml. of toluene was allowed to stand at room temperature for 6 hr. during which time a brown glass gradually settled out of solution. This product was then treated as has been described above for 1-chloro-1,3,5-hexatriene, resulting in an amber aqueous solution of the quaternary ammonium salt.

The solution of the ammonium salt was added dropwise to a solution of sodium hydroxide (64 g. in 1200 ml. of water) undergoing distillation. The distillate was treated as has been described above for 1-chloro-1,3,5-hexatriene. 3-Chloro-1,3,5-hexatriene (14.3 g., 25% over-all yield based on 3-bromo-4-chloro-1,5-hexadiene) was obtained, b.p. 40° (25 mm.).

Anal. Calcd. for C_6H_7Cl: C, 62.89; H, 6.17. Found: C, 63.15; H, 5.95.

3-Chloro-1,3,5-hexatriene (1.09 g., 0.0095 mole) in 75 ml. of ethanol absorbed 900 cc. of hydrogen at 23° and atmospheric pressure with 1 g. of 5% palladium-on-carbon catalyst (absorption calculated for the reduction of three ethylenic links and hydrogenolysis of one chlorine atom is 920 cc.). This represents 98% of the theoretical uptake.

Benzyldimethyl-3-(3-methyl-1,5-hexadienyl)ammonium Bromide (XII).—3-Methyl-1,5-hexadien-3-ol[2] (75 g., 0.67 mole) in 100 ml. of dry ether was added dropwise, with cooling, to phosphorus tribromide (80 g., 0.3 mole) over a period of 2 hr. The reaction product was treated as has been described. Crude 3-bromo-3-methyl-1,5-hexadiene was obtained as an unstable yellow, lachrymatory liquid (97 g., 82.5%). The above crude bromide (97 g., 0.55 mole) and N,N-dimethylbenzylamine (75 g., 0.56 mole) were mixed in 700 ml. of toluene, and the resulting mixture was allowed to stand at room temperature for 20 hr. The resulting crystalline product (147 g., 85.5%) was filtered and washed with ether. A small portion was recrystallized from ethyl acetate–ethanol, m.p. 135–137°.

Anal. Calcd. for $C_{16}H_{24}BrN$: C, 61.93; H, 7.79. Found: C, 61.67; H, 7.95.

3-Methyl-1,3,5-hexatriene (XIII).—The aqueous solution of benzyldimethyl-3-(3-methyl-1,5-hexadienyl)ammonium bromide (147 g., 0.47 mole) in 1 l. of water was added dropwise to a solution of sodium hydroxide (70 g. in 1200 ml. of water) undergoing distillation. The distillate was treated as has been described for 1-chloro-1,3,5-hexatriene. 3-Methyl-1,3,5-hexatriene (30 g., 73%) was obtained as a clear colorless liquid, b.p. 74° (50 mm.).

Anal. Calcd. for C_7H_{10}: C, 89.29; H, 10.71. Found: C, 89.07; H, 10.98.

3-Methyl-1,3,5-hexatriene (0.75 g., 0.008 mole) in 75 ml. of ethanol absorbed 550 cc. of hydrogen at 22° and atmospheric pressure with 1 g. of 5% palladium-on-carbon catalyst (absorption calculated for the reduction of three ethylenic links is 580 cc.). This represents 95% of the theoretical uptake.

1,3,5-Heptatriene (1-Methyl-1,3,5-Hexatriene).—1,5-Heptadien-4-ol[10] (89 g., 0.80 mole) dissolved in 100 ml. of dry ether was added dropwise, with cooling, to phosphorus tribromide (90 g., 0.33 mole) over a period of 2 hr. The product was isolated as has been described above for 3-chloro-1,3,5-hexatriene, yielding crude 4-bromo-1,5-heptadiene (126.5 g., 91%) as a yellow, lachrymatory liquid.

Crude 4-bromo-1,5-heptadiene (150 g., 0.86 mole) and N,N-dimethylbenzylamine (125 g., 0.93 mole) were dissolved in 700 ml. of toluene, and the resulting mixture, after standing for 15 min. at room temperature, was heated at 60–70° for 4 hr. The reaction mixture, treated as described above for 3-chloro-1,3,5-hexatriene, yielded a dark amber solution stable at room temperature.

The above aqueous solution of the quaternary ammonium salt was added dropwise to a solution of sodium hydroxide (50 g. in 600 ml. of water) in the process of being distilled. The product was isolated from the distillate as has been described for 1-chloro-1,3,5-hexatriene. 1,3,5-Heptatriene (31 g., 38% over-all yield based on 4-bromo-1,5-heptadiene) was obtained by distillation at reduced pressure, b.p. 30–32° (25 mm.). Redistillation at atmospheric pressure through a 4-in. Vigreux column provided an analytical sample, b.p. 115° (760 mm.).

Anal. Calcd. for C_7H_{10}: C, 89.29; H, 10.71. Found: C, 89.19; H, 10.89.

1,3,5-Heptatriene (0.65 g., 0.0069 mole) in 50 ml. of methanol absorbed 500 cc. of hydrogen at 23° and atmospheric pressure with 0.5 g. of 5% palladium on carbon (absorption calculated for the reduction of three ethylenic links is 501 cc.). This represents 99.9% of the theoretical uptake.

***cis*-3,5-Hexadien-1-ol (XV).**—5-Hexen-3-yn-1-ol[11] (7.50 g., 0.0718 mole) dissolved in 50 ml. of methanol was hydrogenated with 1 g. of Lindlar catalyst at 23° and atmospheric pressure. Absorption did not stop after 1 equiv. of hydrogen was absorbed; it was interrupted after 1920 cc. had been absorbed (absorption calculated for the reduction of one acetylenic link is 1900 cc.). This represents 101% of the theoretical uptake. The catalyst was removed by filtration and the product was fractionally distilled through an 8-in. Vigreux column. A clear liquid was obtained, b.p. 78–81° (30 mm.), $n^{28}D$ 1.4714, λ_{max} 225–227 mμ.

Anal. Calcd. for $C_6H_{10}O$: C, 73.49; H, 10.20. Found: C, 72.34; H, 10.42.

Comparison of the infrared spectrum with that of 5-hexen-5-yn-1-ol showed the destruction of the acetylenic link.

An α-naphthylurethan was prepared in the usual manner and was recrystallized from *n*-hexane, m.p. 71–73°.

Anal. Calcd. for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.40. Found: C, 76.49; H, 6.30.

cis-3,5-Hexadien-1-ol (3.50 g., 0.357 mole) in 50 ml. of *n*-hexane absorbed 1615 cc. of hydrogen at 21° and atmospheric pressure with 1 g. of 5% palladium-on-charcoal catalyst (absorption calculated for the reduction of two ethylenic links is 1720 cc.). This corresponds to 94% of the theoretical uptake. Suction filtration was used to remove the catalyst. The α-naphthylurethan of 1-hexanol was prepared by addition of α-naphthyl isocyanate to the filtered solution. The derivative was recrystallized from *n*-hexane, m.p. 56–70 (lit.[12] m.p. 59°). Admixture with authentic sample gave no depression in melting point.

***cis*-1,3,5-Hexatriene (XVIII).**—Crude *cis*-3,5-hexadien-1-ol (86.5 g., 0.88 mole) dissolved in 100 ml. of dry ether was added dropwise with cooling, over a period of 2 hr., to phosphorus tribromide (105 g., 0.39 mole). The reaction product was treated as described above for 3-chloro-1,3,5-hexatriene to yield crude *cis*-1-bromo-3,5-hexadiene (101 g., 72%), a yellow lachrymatory liquid.

Crude *cis*-1-bromo-3,5-hexadiene (101 g., 0.63 mole) and N,N-dimethylbenzylamine (103 g., 0.76 mole) were dissolved in 600 ml. of toluene, and the resulting solution was allowed to stand at room temperature for 12 hr. The mixture was heated at 75° for an additional 12 hr., and then refrigerated. The reaction product was treated as described for 3-chloro-1,3,5-hexatriene yielding a clear yellow solution.

The above aqueous solution of the quaternary ammonium salt was added dropwise to a solution of sodium hydroxide (45 g. in 1 l. of water) which was undergoing distillation. The distillate was treated as described above for 1-chloro-1,3,5-hexatriene, and the product was distilled through an 8-in. Vigreux column at atmospheric pressure. Crude *cis*-1,3,5-hexatriene (6 g., 12%) was obtained, b.p. 78–80°, $n^{29}D$ 1.4836. The ultraviolet spectrum was determined in the usual manner, λ_{max} 265, 255, 245 mμ (lit.[4] λ_{max} 265, 255, 245 mμ). This product was submitted to g.l.c. examination on a 12-ft. 15% silicone column (as were all the hexatrienes in this work); four peaks were observed. Com-

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[9] "Tables for Identification of Organic Compounds," Chemical Rubber Publishing Co., Cleveland, Ohio, 1960, p. 84.

[10] I. N. Nazarov and A. I. Kakhniashvili, *Sb. Statei Obshch. Khim. Akad. Nauk SSSR*, **2**, 919 (1954); *Chem. Abstr.*, **49**, 6845*d* (1955).

[11] W. J. Croxall and J. O. Van Hook, *J. Am. Chem. Soc.*, **76**, 1700 (1954).

[12] N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," Interscience Publishers, Inc., New York, N. Y., 1957, p. 568.

parison of the retention times with an authentic *cis–trans*-1,3,5-hexatriene mixture[8] indicated that the second and third peaks emanating from the chromatograph corresponded to *trans*- and *cis*-1,3,5-hexatrienes, respectively. Equilibration of the crude product with iodine resulted in the almost total conversion of the area of the third peak to that of the second, while reaction with maleic anhydride resulted in the removal of the second peak altogether, thus establishing the identity of the second and third peaks as *trans*- and *cis*-1,3,5-hexatrienes, respectively. The peak attributable to *cis*-1,3,5-hexatriene represented approximately 60% of the total area and 85% of the trienic component.

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Studies on the Azidolysis of 4-Arylidene- and 4-Alkylidene-5-oxazolones

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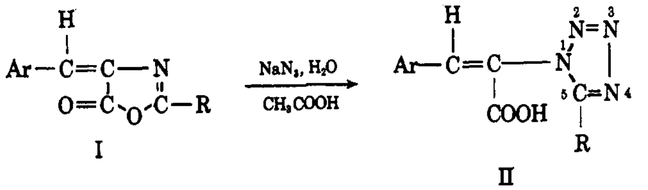
Tetrazolylcinnamic acid derivatives are prepared by a simple method in good yields. Infrared spectra of these acids revealed two types of acids in the solid state: (a) a dipolar type in equilibrium with its monomer, and (b) normal bonded acids. The ultraviolet spectra show that the methyl group in the 5-position has no interaction with the tetrazolyl ring while a phenyl group has. Under similar conditions 4-isopropylidene- and 4-cyclohexylidene-5-oxazolones gave no tetrazolylacrylic acid derivatives and the reaction proceeds *via* another route with decarbonylation to give Va, Vb, and VII. The constitution of these products is discussed in the light of their ultraviolet, infrared, and n.m.r. spectra.

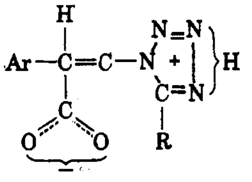
Behringer and Grimure[2] found that 4-arylidene-5-oxazolones react with hydrazoic acid in chloroform in a sealed tube or with a mixture of sodium azide and aluminum chloride in tetrahydrofuran to give α-(1-tetrazolyl)acrylic acid derivatives (II).

In the present investigation a simpler method, giving much better yields (*cf.* Table II), for the preparation of α-(1-tetrazolyl)acrylic acid derivatives has been found, and some new acids have been synthesized according to the following scheme. The structure of these products is established by a study of their infrared and ultraviolet spectra. Thus, the infrared spectra revealed two types of acids: (a) normal acids which show a bonded OH stretching frequency in the region 2700–2500 cm.$^{-1}$ (weak)[3a] (these acids are IIa, c, and g–o); and (b) acids which exist in zwitterionic form (*cf.* III) in equilibrium with the nonpolar monomer form (IIb and d–f) since their infrared spectra show three main bands in the ranges 3500–3450 cm.$^{-1}$ for acidic OH,[3a] 2500–2440 and 1900–1886 cm.$^{-1}$ for $^{+}$NH,[3b] and about 1700 cm.$^{-1}$ for C=O.[3a] The acids that show dipolar character are those having an electron-attracting group in the aromatic moiety of the cinnamyl part of the molecule.



I

II



III

Methylation of IIa (diazomethane) gave the corresponding ester, and its infrared spectrum revealed a shift in the C=O stretching frequency to 1730 cm.$^{-1}$.

The bands in the region 985–1110 cm.$^{-1}$ appear to be characteristic of the tetrazole ring modes.[4]

The ultraviolet spectra of some 1,5-disubstituted tetrazoles were investigated by Roberts, Fanta, and Martin.[5] Cinnamic acid[6a] showed $\lambda_{\max}$ 273 mμ ($\epsilon_{\max}$ 20,000). Most of the acids under investigation (*cf.* Table II) show more than one maximum. The maxima at shorter wave lengths can be attributed to the tetrazolyl moiety and those at longer wave lengths can be attributed to the cinnamyl moiety.

Elpern and Nachod[7] showed that the tetrazolyl ring had little or no absorption in the usual ultraviolet region. In the compounds under investigation (*cf.* Table II), if we compare the ultraviolet spectrum of IIa with that of IIk or the spectrum of IIb with that of IIl where the methyl group replaces a phenyl group in the 5-position, it is only the absorption due to cinnamyl moiety that appears. This favors the conclusion reached by Roberts, *et al.*,[5] and Garbrecht and Herbst.[8]

The values for IIh and IIn are rather similar, and are comparable with those of *p*-methoxycinnamic acid, $\lambda_{\max}$ 224 mμ ($\epsilon_{\max}$ 22,000) and 289 mμ ($\epsilon_{\max}$ 28,000). The values for IIj and IIo can be attributed to the 3,4-methylenedioxycinnamic acid moiety as the values for 3,4-methylenedioxycinnamic acid are: $\lambda_{\max}$ 225 mμ ($\epsilon_{\max}$ 28,900), 283 (26,830), and 313 (26,300). IIf showed only one band, which is actually a broad one and might have masked the band due to the tetrazolyl moiety. The ultraviolet spectra are thus not helpful in distinguishing acids that show dipolar character.[9]

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