Preparation of 2-Substituted 1,3,5-Hexatrienes

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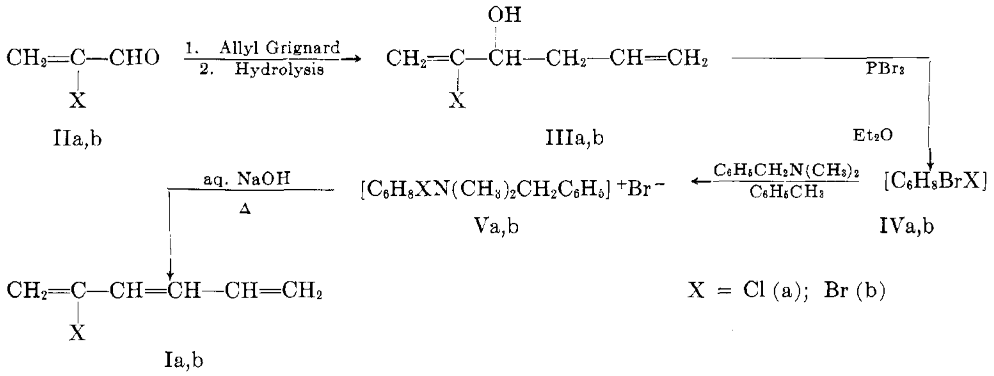
A recently reported method of preparation of 1,3,5-hexatriene[1] has now been utilized for the synthesis of 2-chloro-, 2-bromo-, and 2-methyl-1,3,5-hexatriene. The synthesis consists of (1) reaction of an allylic Grignard reagent with the appropriate unsaturated aldehyde, (2) conversion of the resulting dienol to a dienic bromide by means of phosphorus tribromide, (3) reaction of the dienic bromide with N,N-dimethylbenzylamine to yield a quaternary ammonium bromide, and (4) decomposition of the quaternary ammonium bromide in boiling aqueous sodium hydroxide. The resulting trienes are free of the contaminants derived principally from an internal Diels–Alder reaction of the hexatrienes.

Hwa, de Benneville, and Sims[1] prepared 1,3,5-hexatriene by a Hofmann elimination reaction. Their process has now been modified to synthesize 2-chloro- and 2-bromo-1,3,5-hexatriene as shown by the reactions given in Chart I. Previous preparations of hexatrienes have involved mainly catalytic dehydrations over alumina of the appropriate hexadienols[2-6] as well as a few other methods[2,7-9] involving dehydrations. There has been some question as to the state of purity of several of these substituted hexatrienes.

CHART I



2-Halo-1,5-hexadien-3-ol (III) was prepared by the reaction of α-haloacrolein[10,11] with allylmagnesium bromide. The structures of the halo alcohols (III) were partially established by catalytic reduction which yielded, in both instances, 3-hexanol (hydrogenolysis of the halogen atom occurred). The alcohol was oxidized to 3-hexanone, which was identified as the 2,4-dinitrophenylhydrazone derivative. 2-Bromo-1,5-hexadien-3-ol was quite unstable in contrast to the corresponding chloro compound. The dibromide IVb was too unstable to be isolated in a pure state, in contrast to IVa, the chloro bromide, which was obtained in a satisfactory state for analysis. No attempt was made to isolate Va or Vb, but these substances were directly converted to the corresponding 2-halo-1,3,5-hexatriene. Both of these trienes quantitatively absorbed four moles of hydrogen upon catalytic hydrogenation. Data on these two trienes are presented in Table I.

2-Chloro-1,3,5-hexatriene decomposes slowly in solution or at low temperatures, rapidly at temperatures above 0°, while 2-bromo-1,3,5-hexatriene is less stable. The only halohexatriene reported prior to the present work was impure 3-bromo-1 3,5-hexatriene, prepared by Woods and Temin[3] by catalytic dehydration of 3-bromo-3,5-hexadien-2-ol. They reported that the product was extremely unstable. Apparently 2-bromo-1,3,5-hexatriene behaves much as the previously reported 3-bromo-1,3,5-hexatriene.

2-Methyl-1,5-hexadien-4-ol (VII) was utilized in the synthesis of 2-methyl-1,3,5-hexatriene. The dienol was prepared by reaction of acrolein with methallylmagnesium chloride (Chart II). Examination of VII by vapor phase chromatography indicated a single substance. VII absorbed quantitatively two moles of hydrogen and oxidation of the resulting product provided ethyl isobutyl ketone. This was isolated and identified as the semicarbazone derivative. VII with phosphorus tribromide gave a high yield of crude 2-methylbromohexadiene (IVc) which could not be isolated in an analytically pure condition. This material proved satisfactory for the subsequent preparation of ammonium salt Vc, which was handled in an aqueous solution. Hwa, *et al.*,[1] reported that 1,5-hexadien-3-ol and phosphorus tribromide gave a mixture of the allylic isomers 1-bromo-2,5-hexadiene and 3-bromo-1,5-hexadiene. 2-Methylbromohexadiene (IVc) also might be an allylic mixture; vapor phase chromatography of IVc on a silicone column was inconclusive, since thermolysis of the product occurred yielding some 2-methyl-1,3,5-hexatriene. The nature

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(1) J. C. H. Hwa, P. L. de Benneville, and H. J. Sims, *J. Am. Chem. Soc.*, **82**, 2537 (1960).

(2) G. F. Woods and H. Fleischacker, *ibid.*, **78**, 3436 (1956).

(3) G. F. Woods and S. Temin, *ibid.*, **72**, 139 (1950).

(4) G. F. Woods and A. Viola, *ibid.*, **78**, 4380 (1956).

(5) G. F. Woods and L. H. Schwartzman, *ibid.*, **71**, 1396 (1949).

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

(7) E. A. Braude and C. J. Timmons, *J. Chem. Soc.*, 2007 (1950).

(8) E. H. Farmer, *et al.*, *ibid.*, 2937, 2948 (1927).

(9) L. W. Butz, *et al.*, *J. Am. Chem. Soc.*, **64**, 1978 (1942); *J. Org. Chem.*, **5**, 171 (1940).

(10) F. Stitz, *Österr Chemiker-Ztg.*, **48**, 186 (1947).

(11) R. H. Baker, *et al.*, *J. Am. Chem. Soc.*, **72**, 393 (1950).

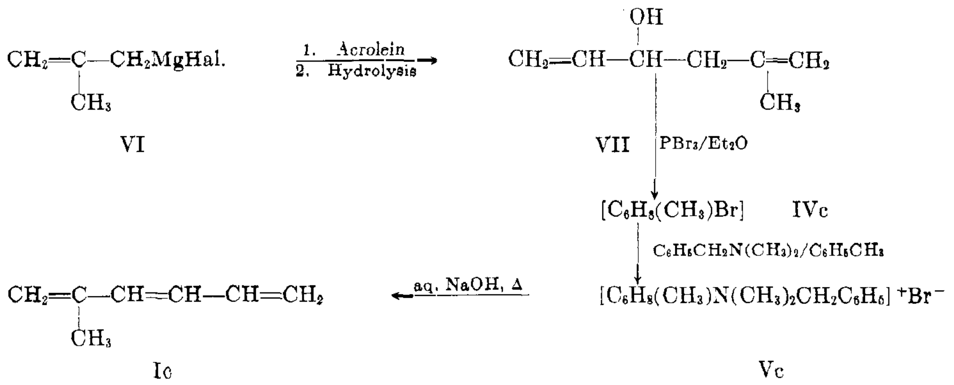
TABLE I

PHYSICAL DATA FOR 2-SUBSTITUTED 1,3,5-HEXATRIENES[a]

			2-Methyl	
	2-Bromo	2-Chloro	This work	Reported
B.p., °C. (mm.)	50–52 (20)	39–40 (20)	108 (760) 30–32° (20)	27 (14)[b] 48–52° (52)[c]
Refractive index		$n^{23}\text{D}$ 1.5395	$n^{27}\text{D}$ 1.5075	$n^{26}\text{D}$ 1.491[b] $n^{16}\text{D}$ 1.5127[c]
Density (g./ml.)		d^{23} 0.9706	d^{26} 0.7632	
Molar refraction (exhaltation)		37.0 cc. (3.6 cc.)	36.7 cc. (3.5 cc.)	
Ultraviolet spectrum, $\epsilon \times 10^{-4}$	3.25 (268 mμ); 4.00 (257.5 mμ); 2.95 (248 mμ);	3.02 (267 mμ); 3.61 (256.5 mμ); 2.49 (247.5 mμ); 1.35 (239.5 mμ) (sh)	2.85 (267 mμ); 3.58 (256.5 mμ); 2.57 (247.5 mμ); 1.39 (239.5 mμ) (sh)	2.20 (267 mμ)[c]; 2.80 (257 mμ); 2.60 (248 mμ) 2.14 (267.5 mμ)[b]; 2.65 (257.5 mμ); 2.02 (248.0 mμ)

[a] It is interesting to observe that λ_{max} for the three 2-substituted hexatrienes are essentially identical in contrast to the 3-substituted hexatrienes wherein a 5-mμ shift is seen. 3-Bromo-1,3,5-hexatriene,[3] λ_{max} 278.5, 267.5, 258 mμ; 3-methyl-1,3,5-hexatriene,[2] λ_{max} 272.5, 262.5, 253 mμ. [b] See ref. 2. [c] See ref. 7.

CHART II



of IVc was not investigated further for the following reasons: (1) either or both isomers could yield 2-methyl-1,3,5-hexatriene *via* the Hofmann elimination route; (2) its instability; (3) the observation of Hwa, *et al.*,[1] that their mixture of bromohexadienes provided as satisfactory yields of 1,3,5-hexatriene as did their purified bromohexadienes; and (4) the potentiality of an allylic rearrangement in the next step of quaternary ammonium salt formation. Crude product IVc was, therefore, submitted to the quaternary ammonium salt formation, V, which itself was not investigated further, but in turn was treated with boiling aqueous alkali to effect the Hofmann elimination whereby 2-methyl-1,3,5-hexatriene was obtained.

2-Methyl-1,3,5-hexatriene (Ic) was quite stable at 0° and could be kept at room temperature for two or three days with no evidence of decomposition. Impure 2-methyl-1,3,5-hexatriene has been prepared earlier by Woods and Fleischaker[2] and by Braude and Timmons.[7] The former workers dehydrated 2-methyl-1,5-hexadien-3-ol by two methods: (1) catalytically over alumina and (2) the use of phosphorus pentoxide, while Braude and Timmons[7] employed an aqueous acid-catalyzed dehydration of 2-methyl-3,5-hexadien-2-ol. The ultraviolet spectrum of Ic was similar to that reported by the earlier workers for impure 2-methyl-1,3,5-hexatriene except that the new extinction coefficients for the absorption bands were considerably larger. This seems to indicate that Ic is of a much higher degree of purity than has been obtained to date. The infrared spectrum of 2-methyl-1,3,5-hexatriene (and also of 2-chloro- and 2-bromo-1,3,5-hexatriene) resembles that of *trans*-1,3,5-hexatriene more closely than that of *cis*-1,3,5-hexatriene, as reported by Hwa, *et al.*[1] Attempts to prepare a Diels–Alder adduct with maleic anhydride did not yield a crystalline derivative; however, a reaction did occur as evidenced by the evolution of heat. Woods and Fleischaker[2] reported that the Diels–Alder adduct obtained from 2-methyl-1,3,5-hexatriene was a liquid, b.p. 140–141° (0.1 mm.), which could not be induced to crystallize and could not be further characterized. The present work seems to bear out their observations.

An attempt was made to determine if both isomers (*cis* and *trans*) of 2-methyl-1,3,5-hexatriene were present. Hwa, *et al.*,[1] used the preferential Diels–Alder reaction with *trans*-1,3,5-hexatriene as a method for obtaining the pure *cis* form. When 2-methyl-1,3,5-hexatriene was submitted to vapor phase chromatography on both silicone and carbowax columns, two peaks, very close together, were observed, whose areas were in the ratio of 1:9 (first peak to second peak). These two substances could not be separated by fractional crystallization, since 2-methyl-1,3,5-hexatriene could not be induced to crystallize down to Dry Ice temperatures. The method Hwa, *et al.*,[1] was attempted by reaction of 2-methyl-1,3,5-hexatriene with 0.25 equivalent of sublimed maleic anhydride. If the larger peak corresponded to the *trans* isomer, one would expect the ratio (1:9) of hexatrienes present to increase as the *trans* isomer would be preferentially removed from the medium. If anything, the ratio decreased slightly. Further reaction with another 0.25 equivalent of maleic anhydride did not cause a further discernible increase or decrease in the peak area ratio. It would seem from these results that the separation of these two geometrical isomers will prove more difficult than for the isomers of the parent 1,3,5-hexatriene. Data on 2-methyl-1,3,5-hexatriene are presented in Table I.

Experimental

2-Methyl-1,5-hexadien-4-ol.—Acrolein (60 g., 1.1 moles) in 200 ml. of dry ether was added slowly to the methallylmagnesium chloride solution prepared from 136 g. of methallyl chloride. The addition complex was decomposed with ammonium chloride. The product, 2-methyl-1,5-hexadien-4-ol (92.5 g., 77%), was isolated in the usual manner, b.p. 76–78° (75 mm.). A small sample was redistilled through an 8-in. Vigreux column and the product was collected, b.p. 145.5–146°, n^{27}D 1.4498.

Anal. Calcd. for $C_7H_{12}O$: C, 74.95; H, 10.79. Found: C, 75.09; H, 10.95.

2-Methyl-1,5-hexadien-4-ol (4.44 g., 0.0393 mole) in 40 ml. of ethanol absorbed 1805 ml. of hydrogen at 24° with 1 g. of 5% palladium–charcoal catalyst (calculated for the reduction of two ethylenic links is 1918 ml.). This corresponds to 95% of the theoretical uptake. The catalyst was removed by filtration, and after evaporation of the solvent crude 2-methyl-4-hexanol was obtained by distillation. 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 solvent of the ether extract was evaporated and the residue reacted with semicarbazide reagent from which the semicarbazone of 2-methyl-4-hexanone (m.p. 150–152°; lit.[12] m.p. 152°) was obtained. Admixture with an authentic sample gave no depression in melting point.

2-Methyl-1,3,5-hexatriene.—2-Methyl-1,5-hexadien-4-ol (112 g., *ca.* 1 mole) in 50 ml. of dry ether was added dropwise during a period of 3 hr. to phosphorus tribromide (135 g., 0.5 mole), with cooling. After standing for 12 hr., the product was decanted into water and the resulting mixture was neutralized with saturated sodium carbonate solution. The organic product was extracted with ether, and the ether extract washed with water and dried with anhydrous magnesium sulfate. Ether was removed and the product, crude 2-methyl-4-bromo-1,5-hexadiene (149 g., 85%), was obtained. Distillation of a portion of this product was attempted at reduced pressure. After a small forerun, liquid distilled at 59–60° (35 mm.) which, however, was cloudy, presumably from polymeric material. Successive fractions, although distilling at a constant boiling point, were also cloudy. A clear sample was obtained from filtration. Analysis indicated high carbon and hydrogen composition, probably resulting from the loss of hydrogen bromide in the polymeric material (dissolved in the liquid).

A solution of the above crude 2-methyl-4-bromo-1,5-hexadiene (87.0 g., 0.50 mole), N,N-dimethylbenzylamine (82.0 g., 0.60 mole), and 0.2 g. of hydroquinone in 900 ml. of dry toluene was heated for 3 hr. at 55°. After refrigerating for 12 hr. at 0°, the organic solution was decanted and discarded. The gummy brown residue was dissolved in water, and the resulting solution was extracted several times with ether to remove suspended organic matter. 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 for several weeks.

The above aqueous solution of the N,N-dimethylbenzylammonium salt was added dropwise to a solution of sodium hydroxide (64 g. in 400 ml. of water) which was in the process of being distilled. The distillate, which was collected in a flask which was being 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, then with water until neutral, and finally dried with anhydrous magnesium sulfate and distilled. 2-Methyl-1,3,5-hexatriene (8.2 g., 17% over-all yield based on 2-methyl-4-bromo-1,5-hexadiene) was obtained, b.p. 30–32° (20 mm.). Redistillation through a 4-in. Vigreux column yielded pure 2-methyl-1,3,5-hexatriene, b.p. 108°.

Anal. Calcd. for C_7H_{10}: C, 89.29; H, 10.71. Found: C, 89.12; H, 11.00.

2-Methyl-1,3,5-hexatriene (0.65 g., 0.0069 mole) in 75 ml. of methanol absorbed 480 ml. of hydrogen at 23° with 0.5 g. of 5% palladium–charcoal catalyst (theoretical absorption calculated for the presence of three ethylenic links is 501 ml.). This represents an absorption of 95.5% of theoretical.

2-Chloro-1,5-hexadien-3-ol.—α-Chloroacrolein[10] (68.7 g., 0.76 mole) in 200 ml. of dry ether was added slowly to a cooled allylmagnesium bromide solution prepared from 160 g. of allyl bromide in 700 ml. of ether. The addition complex was decomposed with ammonium chloride, and the product was isolated in the usual manner. 2-Chloro-1,5-hexadien-3-ol (73 g., 73%), b.p. 76–80° (18 mm.) was obtained. The product was redistilled through an 8-in. Vigreux column for an analytical sample of 2-chloro-1,5-hexadien-3-ol; b.p. 76° (20 mm)., n^{27}D 1.4715.

Anal. Calcd. for C_6H_9ClO: C, 54.35; H, 6.84. Found: C, 54.60; H, 7.10.

2-Chloro-1,5-hexadien-3-ol (3.31 g., 0.0249 mole) in 50 ml. of methanol absorbed 1835 ml. of hydrogen at 24° with 1 g. of 5% palladium–charcoal catalyst (theoretical absorption calculated for two ethylenic links and hydrogenolysis of one chlorine atom is 1820 ml.). This represents 101% of theoretical. The isolation and subsequent oxidation of 3-hexanol from the hydrogenation product followed the general procedure as outlined for 2-methyl-4-hexanol. The steam distillate obtained from the oxidation of 3-hexanol was also treated in like manner, yielding 3-hexanone (isolated as the 2,4-dinitrophenylhydrazone, m.p. 130–132°; lit.[12] m.p. 132°.) Admixture with an authentic sample produced no depression in melting point.

2-Chloro-3-bromo-1,5-hexadiene.—2-Chloro-1,5-hexadien-3-ol (75 g., 0.56 mole) in 100 ml. of dry ether was added dropwise with cooling during 1–1.5 hr. to phosphorus tribromide (70 g., 0.26 mole). The reaction product was treated as has been described for 2-methyl-4-bromo-1,5-hexadiene. Crude 2-chloro-3-bromo-1,5-hexadiene (81.2 g., 74%) was obtained. Distillation of a small sample of this product yielded a clear yellow liquid, b.p. 82–84° (45 mm.), n^{23}D 1.5110

Anal. Calcd. for C_6H_8BrCl: C, 36.86; H, 4.12. Found: C, 37.10; H, 4.29.

This liquid was extremely unstable and darkened rapidly at temperatures above 0°.

2-Chloro-1,3,5-hexatriene.—A solution of crude 2-chloro-3-bromo-1,5-hexadiene (75.0 g., 0.38 mole), N,N-dimethylbenzylamine (56.7 g., 0.42 mole), and 0.2 g. of hydroquinone in 700 ml. of dry toluene was heated at 55° for 3 hr. The product was treated as has been described for 2-methyl-4-bromo-1,5-hexadiene. A clear, pale yellow solution was obtained which was stable at room temperature for several weeks.

The aqueous solution of the N,N-dimethylbenzylammonium salt prepared from 2-chloro-3-bromo-1,5-hexadiene (75.0 g., 0.38 mole) was added dropwise to a boiling solution of sodium hydroxide (32 g. of sodium hydroxide in 300 ml. of water). The distillate was treated as has been described for 2-methyl-1,3,5-hexatriene. The product was distilled at reduced pressure, and 2-chloro-1,3,5-hexatriene was obtained, b.p. 39–40° (20 mm.) (6.7 g., 16% over-all yield from 2-chloro-3 bromo-1.5-hexadiene).

Anal. Calcd. for C_6H_7Cl: C, 62.89, H, 6.17. Found; C, 62.85; H, 6.60.

2-Chloro-1,3,5-hexatriene (0.74 g., 0.0065 mole) in 75 ml. of methanol absorbed 620 ml. of hydrogen at 23° with 0.5 g. of 5% palladium–charcoal catalyst (theoretical absorption calculated for the presence of three ethylenic links and hydrogenolysis of one chlorine atom is 632 ml.). This represents an absorption of 98% of theoretical.

2-Bromo-1,3,5-hexatriene.—α-Bromoacrolein[11] (117.0 g., 0.87 mole) in 200 ml. of dry ether was added slowly to a cooled allylmagnesium bromide solution prepared from 160 g. of allyl bromide in 700 ml. of ether. The addition complex was decomposed with ammonium chloride and 2-bromo-1,5-hexadien-3-ol (35.6 g., 24%) was isolated in the usual manner, b.p. 50–54° (2 mm.). The colorless product rapidly became blue-green at temperatures above that of Dry Ice. Redistillation under nitrogen through an 8-in. Vigreux column yielded a straw-colored liquid, b.p. 40° (0.9 mm.), n^{23}D 1.4900. This material also colored readily above Dry Ice temperatures. This substance readily lost hydrogen bromide

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(12) "Tables for Identification of Organic Compounds," Chemical Rubber Publishing Co., Cleveland, Ohio, 1960, p. 84.

and could not be obtained in a state of purity which was satisfactory for analysis.

2-Bromo-1,5-hexadien-3-ol (3.5 g., 0.20 mole) in 50 ml. of methanol absorbed 1715 ml. of hydrogen at 23° with 1 g. of 5% palladium–charcoal catalyst (theoretical absorption calculated for two ethylenic links and hydrogenolysis of one bromide atom is 1470 ml.). This represents 116% of theoretical. The isolation and oxidation of the saturated alcohol to yield 3-hexanone was carried out in the manner described for 2-chloro-1,5-hexadien-3-ol. 3-Hexanone was isolated as the 2,4-dinitrophenylhydrazone, m.p. 130–132°; lit.[12] m.p. 132°. Admixture with an authentic sample produced no depression in melting point.

Crude 2-bromo-1,5-hexadien-3-ol (71.5 g., 0.40 mole) in 100 ml. of dry ether was added dropwise to phosphorus tribromide (46 g., 0.17 mole) during a period of 1–1.5 hr., with cooling. The reaction product was treated as has been described for 2-methyl-4-bromo-1,5-hexadiene. Crude 2,3-dibromo-1,5-hexadiene (69.5 g., 72%) was obtained as an orange liquid. Distillation was attempted, but the distillate contained a large amount of solid polymer and smelled strongly of hydrogen bromide. The pure compound could not be isolated.

Crude 2,3-dibromo-1,5-hexadiene (60 g., 0.25 mole), N,N-dimethylbenzylamine (41 g., 0.30 mole), and 0.2 g. of hydroquinone in 500 ml. of dry toluene were heated at 55° for 3 hr. The product was treated as has been described for 2-methyl-4-bromo-1,5-hexadiene. A clear yellow solution was obtained which was quite stable.

This solution was then added dropwise to a boiling solution of sodium hydroxide (64 g. of sodium hydroxide in 400 ml. of water). The distillate was treated as has been described for 2-methyl-1,3,5-hexatriene. The product was distilled at reduced pressure, and 2-bromo-1,3,5-hexatriene (5 g., 12% over-all yield from 2,3-dibromo-1,5-hexadiene) was obtained, b.p. 50–52° (20 mm.). The product was very unstable and began decomposing almost immediately when brought to room temperature. Analyses of this sample proved impossible; they were high in carbon and hydrogen which is consistent with the loss of hydrogen bromide.

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Polycyclic Musks. I. Acyl- and Dinitropolyalkyltetralin Derivatives

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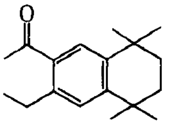
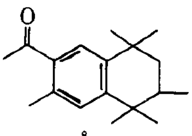
The synthesis of twenty-seven polyalkyltetralin hydrocarbons is described. Acyl and dinitro derivatives of these, which were checked for musk odor, are reported. Contrary to the literature, acetylation of 6-*t*-butyl-1,1,4,4-tetramethyltetralin produces 6-acetyl-1,1,4,4-tetramethyltetralin. The acid-catalyzed reaction of *p*-cymene with 2,3-dimethyl-2-butene, previously reported to yield 1,1,2,2,3,3,5-heptamethylindan, is shown to produce 1,1,3,4,4,6-hexamethyltetralin. The method of Whitmore for neophyl chloride is extended to yield *p*-methyl, *p*-ethyl, and *p*-isopropyl derivatives. The method of Colonge and Pichat for polymethyltetralins is extended to the use of methallylacetone– and of methylheptenone–hydrocarbon condensation reactions. Cyclialkylation of the isomeric xylenes is described.

The last decade has seen much activity in the field of the nitrogen-free aromatic musks, especially in the polycyclics. Carpenter[1] reported our early work in this new field covering indan, tetralin (preferred over "1,2,3,4-tetrahydronaphthalene" according to the *Ring Index*. The name "Tetralin" is a registered trademark of the Du Pont Company) and tricyclic derivatives and laid out requirements for musk odor. This was followed by the publications of Grampoloff,[2] Weber and co-workers,[3,4] Beets and co-workers,[5] and Ferrero and Helg.[6] These reported results of others, as well as our subsequent studies, have shown that our early ideas on requirements for musk odor are still valid. The outstanding tetralin musks resulting from our work have the preceding structures (col. 1).


I[7]


II[8]

It is the purpose of this paper to survey the chemistry involved in the preparation of these and a number of homologs and isomers and to list new tetralin hydrocarbons and derivatives prepared in the course of this study. Two cases are reviewed where incorrect structures were assigned originally.

Syntheses of the necessary tetralin hydrocarbon intermediates utilized three methods: the cyclialkylation technique, discovered by Bruson and Kroeger[9]; the cyclodehydration method[10] of Bogert and coworkers; and finally the *p*-cymylcarbonium ion–2,3-dimethyl-1-butene reaction. Some of this chemistry has been published in patent examples, but interesting aspects remain to be disclosed.

Impetus to our studies in the tetralin series was given by the discovery that acetylation of 1,1,4,4,6-pentamethyltetralin (**13**)[11] and its 6-ethyl (**19**) and 6-isopropyl (**23**) homologs produced derivatives of pronounced musk odor.[1,12] These hydrocarbons, as well

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[1] M. S. Carpenter, *Proc. Sci. Sect. Toilet Goods Assoc.*, **23**, 1 (1955).

[2] A. V. Grampoloff, *Helv. Chim. Acta*, **38**, 1263 (1955).

[3] S. H. Weber, D. B. Spoelstra, and E. H. Polak, *Rec. trav. chim.*, **74**, 1179 (1955).

[4] S. H. Weber, J. Stofberg, D. B. Spoelstra, and R. J. C. Kleipool, *ibid.*, **75**, 1433 (1956); S. H. Weber, R. J. C. Kleipool, and D. B. Spoelstra, *ibid.*, **76**, 193 (1957); D. B. Spoelstra, S. H. Weber, and R. J. C. Kleipool, *ibid.*, **76**, 205 (1957).

[5] M. G. J. Beets, H. Van Essen, and W. Meerburg, *ibid.*, **77**, 854–71 (1958); U. S. Patent 2,889,363 (June 2, 1959).

[6] C. Ferrero and R. Helg, *Helv. Chim. Acta*, **42**, 2111 (1959); German Patent 1,059,902 (June 25, 1957).

[7] Versalide® (polycyclic musk) is a product of Givaudan-Delawanna, Inc., New York, N. Y.; U. S. Patent 2,897,237 (July 28, 1959).

[8] Believed to be the same as the product marketed under the trademark "Tonalid" by Polak's Frutal Works, Inc., Middletown, N. Y.; U. S. Patent 2,759,022 (August 14, 1956).

[9] H. A. Bruson and J. W. Kroeger, *J. Am. Chem. Soc.*, **62**, 36 (1940); U. S. Patent 2,198,374 (April 23, 1940).

[10] R. O. Roblin, Jr., D. Davidson, and M. T. Bogert, *J. Am. Chem. Soc.*, **57**, 151 (1935).

[11] Arabic numerals refer to the hydrocarbons that are listed in Table I (p. 2251).

[12] M. S. Carpenter, W. M. Easter, Jr., and T. F. Wood, U. S. Patent 2,897,237 (July 28, 1959).