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.

Acknowledgment.—This work was supported in part by the U. S. Air Force under contract no. AF 33(657)-7833. Dr. Franz Kasler performed the reported analyses.

Polycyclic Musks. I. Acyl- and Dinitropolyalkyltetralin Derivatives

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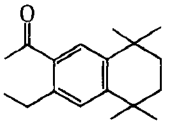
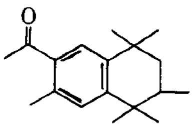
The synthesis of twenty-seven polyalkyltetralin hydrocarbons is described. Acyl and dinitro derivatives of these, which were checked for musk odor, are reported. Contrary to the literature, acetylation of 6-*t*-butyl-1,1,4,4-tetramethyltetralin produces 6-acetyl-1,1,4,4-tetramethyltetralin. The acid-catalyzed 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 co-workers; 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).

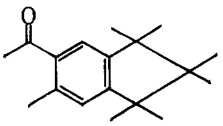
(10) R. O. Roblin, Jr., D. Davidson, and M. T. Bogert, *J. Am. Chem. Soc.*, **57**, 151 (1935).

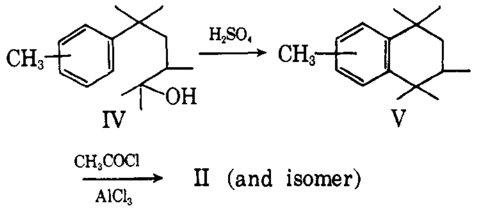
(11) Arabic numerals refer to the hydrocarbons that are listed in Table I (p. 2251).

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

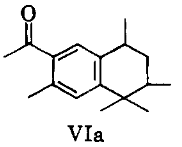
as the 6-*t*-butyl homolog (**26**),[13] were prepared by the cyclialkylation reaction, starting from toluene, ethylbenzene, cumene, and *t*-butylbenzene respectively. Experimental details including acetylations are given in a recent patent.[12] Contrary to the teaching of this patent we have now found that acetylation of 6-*t*-butyl-1,1,4,4-tetramethyltetralin resulted in debutylation giving a product identical with the ketone derived from benzene, 6-acetyl-1,1,4,4-tetramethyltetralin, a compound nearly devoid of musk odor. It was found also that replacement of the acetyl group in this series of musks by either propionyl or isobutyryl results in almost total loss of musk odor while replacement by formyl still results in strong musks.[1,14]

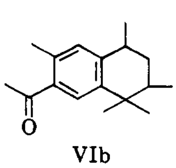
It has been reported[1] that a very outstanding musk was prepared by acetylation of the hydrocarbon formed by the reaction of *p*-cymene with tetramethylene. This compound was erroneously assigned the indan structure (III) probably for the reason that it was known that *p*-cymene reacts generally with olefins to yield indan derivatives.[2] Subsequent work with III, however, has revealed the structure as that of the acetylated tetralin (II). The initial synthesis involved a straightforward approach for the preparation of a tetralin derivative: ethyl α-methallyl-α-methylacetoacetate was prepared and cleaved to produce ethyl 2,4-dimethyl-4-pentenoate. Condensation of this ester with toluene in the presence of anhydrous aluminum chloride produced ethyl 2,4-dimethyl-4-*m*,*p*-tolylpentanoate. Treatment of this compound with methylmagnesium iodide gave the carbinol mixture (IV). Cyclodehydration, followed by acetylation of the resulting mixture (V), gave a viscous oil of strong musk odor which partially solidified upon long storage. The solid fraction was separated and purified by recrystallization yielding a colorless product (II), m.p. 56–57°.


III

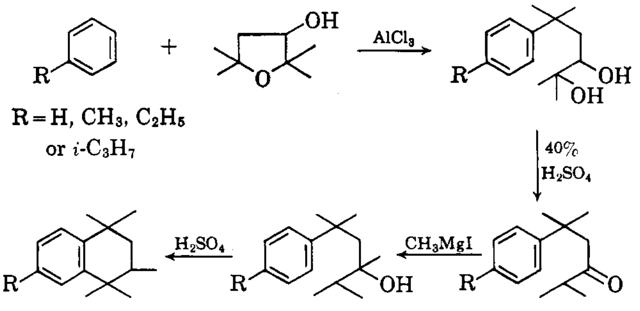


7-Acetyl-1,3,4,4,6-pentamethyltetralin (VIa) and isomer VIb, lower homologs of II, obtained in a viscous liquid mixture of strong musk odor, were synthesized by an analogous sequence of reactions starting with the readily available[15] α-allylacetoacetic ester.


VIa


VIb

Another novel procedure involves a sequence of reactions starting with 2,2,5,5-tetramethyltetrahydro-3-furanol and was employed for the preparation of II, and also a number of its homologs.[16a]



VIIIa, R = H (**12**)
b, R = CH_3 (**17**)
c, R = C_2H_5 (**22**)
d, R = i-C_3H_7 (**25**)

VII, R = CH_3

Acetylation and nitration of all of the hydrocarbons of this series gave derivatives of musk odor (Table II). The maximum musk odor was observed in II, the acetyl derivative of VIIIb (**17**), which previously was reported as a colorless, viscous liquid of persistent, musk-like odor.[16a,b] Compounds **22** and **25** and their derivatives have not been described previously.

Both methods for the preparation of II, described earlier, suffer the disadvantage of leading to isomeric mixtures. This is due to formation of *meta* isomers in the aluminum chloride-catalyzed steps. The formation of isomers was minimized by starting with β-methallyl chloride which may be condensed with either benzene, toluene, ethylbenzene, or cumene in the presence of concentrated sulfuric acid, thus extending the method of Whitmore[17,18] for the preparation of neophyl chloride.

The derivatives thus obtained were converted easily to their Grignard reagents which added readily to methyl isopropyl ketone to produce the desired carbinols. The advantages of this method are substantiated by the fact that the hydrocarbons produced by cyclodehydration (**12**, **17**, **22**, and **25**) were obtained in higher yields and purity as shown by vapor phase chromatography and melting points.

It is noteworthy that the two isomeric carbinols IV and VII each yield the same hydrocarbon **17** as the principal product. This is in harmony with the observation of Price, Davidson, and Bogert[19] that cyclodehydration of 1-phenyl-3,4-dimethyl-3-pentanol gave principally 1,1,2-trimethyltetralin.

The sulfuric acid-catalyzed reaction between *p*-cymene and 2,3-dimethylbutene (or 2,3-dimethyl-2-butanol) gave the hydrocarbon **17** identical with the products synthesized from toluene by the methods discussed before. The most straightforward mechanism requires the *p*-cymylcarbonium ion as intermediate.

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[13] The synthesis and proof of structure of this hydrocarbon has been published by P. C. Myhre and W. M. Schubert, *J. Org. Chem.*, **25**, 708 (1960).

[14] M. S. Carpenter, W. M. Easter, Jr., and T. F. Wood, U. S. Patent 2,800,511 (July 23, 1957); *Chem. Abstr.*, **52**, 1256b (1958).

[15] Food Machinery and Chemical Corporation, Chemicals and Plastics Division, Research Department, New York 17, N. Y.

[16] (a) M. S. Carpenter, W. M. Easter, Jr., and T. F. Wood, U. S. Patent 2,915,561 (December 1, 1959); (b) D. Davison and R. M. Lusskin, U. S. Patent 3,045,047 (July 17, 1962).

[17] F. C. Whitmore, C. A. Weisgerber, and H. C. Shabica, Jr., *J. Am. Chem. Soc.*, **65**, 1469 (1943).

[18] W. T. Smith, Jr., and J. T. Sellas, *Org. Syn.*, **32**, 90 (1952).

[19] D. Price, D. Davidson, and M. T. Bogert, *J. Org. Chem.*, **2**, 540 (1938).

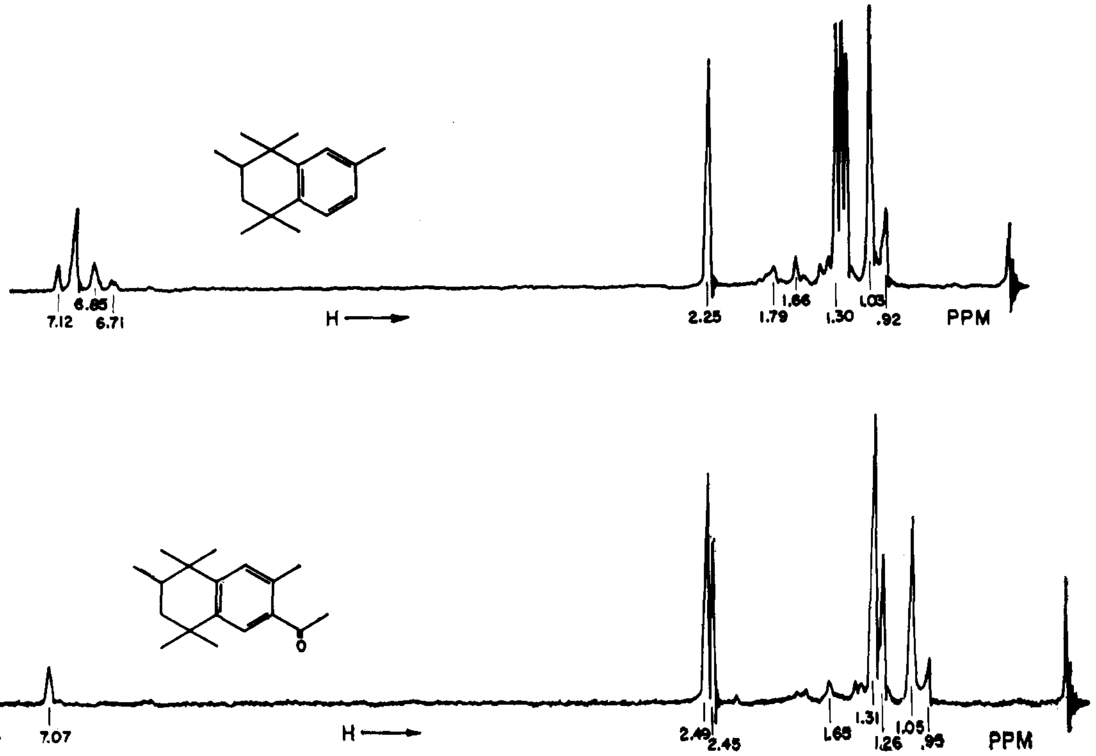
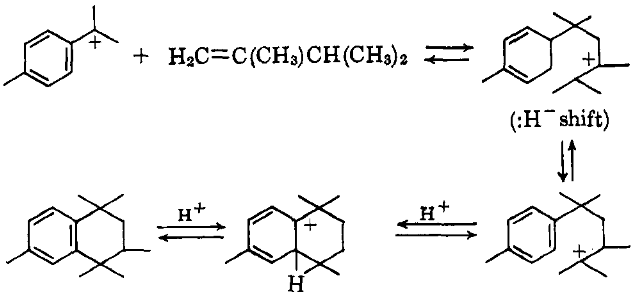


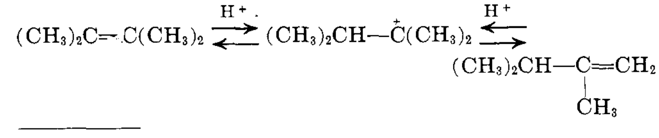
Fig. 1.—The proton magnetic resonance spectra of 1,1,3,4,4,6-hexamethyltetralin and its acetyl derivative at 60 Mc. Tetramethylsilane used as internal reference at 0 with respect to the observed resonance peaks.

This is produced in accordance with the well known reaction where hydride transfer takes place from *p*-cymene to a tertiary carbonium ion.[3,20] In our case the by-product is 2,3-dimethylbutane. The *p*-cymylcarbonium ion then reacts with 2,3-dimethyl-1-butene to produce VIIIb (**17**).



VIIIb (**17**)

This proposed mechanism requires participation of the energetically less stable 1-butene derivative, which may not seem unusual if it is recalled that the mixture of diisobutylenes, formed from the intermediate carbonium ion, $(CH_3)_3C—CH_2\text{-}\overset{+}{C}(CH_3)_2$, consists of 80% of the 1-pentene and 20% of the 2-pentene derivative, in spite of the fact that the 2-pentene is thermodynamically more stable. This may be due to the fact that the proton acceptor may be sterically hindered in removing methylene protons, or that there are more (six) methyl protons. In strong sulfuric acid it seems quite reasonable to expect in the equilibrium mixture (col. 2, bottom) substantial amounts of the 1-butene, which is then attacked preferentially by the *p*-cymylcarbonium ion, because the 1-butene derivative is much less sterically hindered than the 2-butene, and it is much more polar.[21] Alternate syntheses of VIIIb (**17**) permit the substitution of either dimethyl-*p*-tolylcarbinol or α,*p*-dimethylstyrene for *p*-cymene, as sources of the *p*-cymylcarbonium ion.



$$(CH_3)_2C{=}C(CH_3)_2 \overset{H^+}{\rightleftarrows} (CH_3)_2CH{—}\overset{+}{C}(CH_3)_2 \overset{H^+}{\rightleftarrows} (CH_3)_2CH{—}\underset{CH_3}{\underset{|}{C}}{=}CH_2$$

Recent patents[22] disclose a procedure for the synthesis of indans from a number of styrenes and certain olefins in the presence of sulfuric acid. One example describes the reaction of α,*p*-dimethylstyrene and 2,3-dimethyl-2-butene to produce a hydrocarbon, m.p. 65-66°, designated as 1,1,2,2,3,3,5-heptamethylindan, which is reported to yield an acetyl derivative of strong musk odor. Following the given procedure, we obtained a hydrocarbon identical with VIIIb (**17**) as shown by mixture melting point and infrared spectra comparisons. The tetralin structure was confirmed by analysis of its n.m.r. and infrared spectra.[23] The n.m.r. spectrum of the acetyl derivative (II) is in harmony with that of the hydrocarbon (Fig. I). The quartet produced by the ring protons is replaced by two unsplit peaks at 7.07 and 7.55 p.p.m. for two remaining *para*-situated protons. An additional peak appears at 2.49 p.p.m. for the acetyl methyl group next to the aromatic-ring methyl at 2.45 p.p.m.[24]

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[20] V. N. Ipatieff, H. Pines, and R. C. Olberg, *J. Am. Chem. Soc.*, **70**, 2123 (1948).

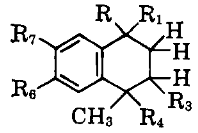
[21] The analogy between the well known formation of 2,4,4-trimethyl-1-pentene in the dimerization of isobutylene and the formation of 2,3-dimethyl-1-butene in our reaction was pointed out by Professor J. L. E. Erickson, Louisiana State University.

[22] G. Benz and E. H. Polak, U. S. Patent 2,851,501 (September 9, 1958); British Patents 796,129 and 796,130 (both published June 4, 1958).

[23] T. F. Wood and J. Angiolini, *Tetrahedron Letters*, No. **1**, 1 (1963).

[24] We are indebted to Dr. Martin Saunders of Yale University for the n.m.r. determination and interpretation.

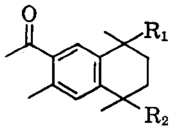
TABLE I
POLYALKYLTETRALINS



No.	Formula	R	R₁	R₃	R₄	R₆	R₇	B.p., °C. (mm.)	n^{20}D or m.p., °C.	d^{20}_4	Method[a]	Yield, %[b]
1	$C_{12}H_{16}$	H	H	H	CH_3	H	H	78.5(4)	1.5278	0.9440	CD[c]	98.0
2	$C_{13}H_{18}$	CH_3	H	H	CH_3	H	H	74(2)	1.5245	0.9375	CD[d]	93.2
3	$C_{13}H_{18}$	CH_3	H	H	H	CH_3	H	82–84(1.8)	1.5314	0.9465	CD[e]	67.8
4	$C_{13}H_{18}$	H	H	H	CH_3	CH_3	H	74–76(1.5)	1.5261	0.9353	CD[f]	89.5
5	$C_{13}H_{18}$	H	H	H	CH_3	H	CH_3	107–108(10)	1.5230	0.9341	CD[g]	80.0
6	$C_{14}H_{20}$	CH_3	CH_3	H	H	CH_3(H)	H(CH_3)	82–84(2)	1.5244	0.9321	CD[h]	78.5
7	$C_{14}H_{20}$	CH_3	CH_3	H	CH_3	H	H	74(0.5)	1.5180, 6.5–7.0	0.9280	CD, CA-1[i]	80, 16.0
8	$C_{14}H_{20}$	CH_3	H	H	CH_3	CH_3(H)	H(CH_3)	86(2)	1.5300	0.9410	CD[j]	88.5
9	$C_{14}H_{20}$	CH_3	H	H	C_2H_5	H	H	86(2)	1.5250	0.9398	CD[k]	95.0
10	$C_{14}H_{20}$	H	H	H	CH_3	H	C_2H_5	94(1.5)	1.5220	0.9303	CD[l]	64.0
11	$C_{15}H_{22}$	H	i-C_3H_7	H	CH_3	H	H	89(1.5)	1.5200	0.9320	CD	63.5
12	$C_{15}H_{22}$	CH_3	CH_3	CH_3	CH_3	H	H	88–89(2.5)	1.5204	0.9325	CD	93.5
13	$C_{15}H_{22}$	CH_3	CH_3	H	CH_3	CH_3	H	66–67(1.5)	35–35.5[m]	0.9235	CA-1	97.5
14	$C_{15}H_{22}$	CH_3	H	CH_3	CH_3	CH_3(H)	H(CH_3)	90–92(2)	1.5267	0.9373	CD	86.5
15	$C_{15}H_{22}$	CH_3	H	H	C_2H_5	CH_3(H)	H(CH_3)	84(0.5)	1.5337	0.9446	CD[n]	88.7
16	$C_{16}H_{24}$	i-C_3H_7	H	H	CH_3	H(CH_3)	CH_3(H)	96(1.5)	1.5209	0.9289	CD	91.2
17	$C_{16}H_{24}$	CH_3	CH_3	CH_3	CH_3	CH_3	H	90(1.5)	66–67		CD, PCC[o]	77, 73.4
18	$C_{16}H_{24}$	CH_3	CH_3	H	CH_3	CH_3	CH_3	95–97(1.5)	85–86		CA-1	98.5
19	$C_{16}H_{24}$	CH_3	CH_3	H	CH_3	C_2H_5	H	90–91(1.5)	1.5165	0.9200	CA-2[p]	96
20	$C_{16}H_{24}$	CH_3	CH_3	H	C_2H_5	CH_3(H)	H(CH_3)	99(2)	1.5200	0.9272	CD[q]	87.5
21	$C_{17}H_{26}$	CH_3	C_2H_5	H	C_2H_5	CH_3	H	108(2)	1.5201	0.9248	CA-1	91.2
22	$C_{17}H_{26}$	CH_3	CH_3	CH_3	CH_3	C_2H_5	H	100–101 (1.5)	1.5158	0.9265	CD	88
23	$C_{17}H_{26}$	CH_3	CH_3	H	CH_3	i-C_3H_7	H	100(1.5)	26–27		CA-1[p]	85
24	$C_{18}H_{28}$	CH_3	C_2H_5	H	C_2H_5	C_2H_5	H	112(1.5)	1.5181	0.9203	CA-2	95
25	$C_{18}H_{28}$	CH_3	CH_3	CH_3	CH_3	i-C_3H_7	H	107–108(1)	1.5140	0.9156	CD	79.5
26	$C_{18}H_{28}$	CH_3	CH_3	H	CH_3	t-C_4H_9	H	108(2)	62–63		CA-1[p,q]	41.7
27	$C_{19}H_{30}$	CH_3	C_2H_5	H	C_2H_5	i-C_3H_7	H	118(1.5)	1.5146		CA-1	70.0

[a] Method relates to final cyclization step. CD is cyclodehydration. CA-1 is cyclialkylation with $AlCl_3$ and CA-2 with $FeCl_3$. [b] Yields are given in per cent based on the cyclization step. [c] Method of M. T. Bogert, D. Davidson, and P. M. Apfelbaum, *J. Am. Chem. Soc.*, **56**, 962 (1934), except that the carbinol was added slowly to the cold sulfuric acid. [d] Method of J. Colonge and L. Pichat, ref. 25, p. 857, except the final cyclodehydration step was modified by reversing the mode of addition of the reactants. Hydrocarbon also was synthesized by M. C. Kloetzel, *ibid.*, **62**, 3409 (1940), starting with 4-phenylpentanoic acid. [e] Ref. 25, p. 857. [f] Synthesis started with 3-*p*-tolylpropan-1-ol and was analogous to that of compound **1**. [g] Method of M. T. Bogert and V. G. Fourman, *J. Am. Chem. Soc.*, **55**, 4674 (1933); see also footnote *c*, p. 961. [h] Synthesis was analogous to that of compound **3** except that toluene was condensed with methallylacetone instead of allylacetone in the first step. [i] First synthesized by Bruson and Kroeger, ref. 9. [j] Ref. 25, p. 857. [k] Starting materials were benzene and allylacetone. [l] Ref. 29, p. 97. [m] Bruson and Kroeger, ref. 9, p. 44, described this material as a liquid, b.p. 95° (4 mm.). [n] Ref. 26. [o] PCC refers to *p*-cymene condensation (see Experimental section). [p] Ref. 12. [q] Recently prepared and studied by P. C. Myhre and W. M. Schubert, ref. 13.

Acetylation of a number of tetralin derivatives made by the procedure of Colonge and Pichat[25] gave homologs of I. Four of these exhibited musk odor.



IX

IX	R₁	R₂	Table II no.
a[26]	H	CH_3	**8**
b	CH_3	H	**6**
c[26]	H	C_2H_5	**15**
d[27]	CH_3	C_2H_5	**20**

The property of musk odor in compounds VIa, b, IXa, b, and c shows that, in some cases, one of the quaternary carbons at positions 1 and 4, as is found in I and II, may be replaced by a tertiary carbon without loss of the musk odor. The technique was extended to cover the condensations of methallylacetone and 6-methyl-5-hepten-2-one with benzene and with toluene using aluminum chloride catalyst and the reaction proceeded equally as well. Although it was reported[25] that the toluene–allylacetone derivative is the *para* isomer we have found that considerable *meta* isomer is produced in aluminum chloride-catalyzed condensations of this type. In the condensations with methallylacetone, methylheptenone, or other compounds where the product has a quaternary carbon, with attached *gem*-methyls, joined to the aromatic ring, no *ortho* isomer formed because of steric hindrance. Here the vapor phase chromatograms show only two isomers. In the condensation of methylheptenone with toluene there were formed nearly equimolar amounts of *meta* and

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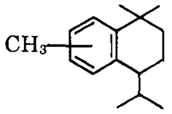
(25) J. Colonge and L. Pichat, *Bull. soc. chim. France*, 855 (1949).

(26) L. Givaudan and Cie, S. A., British Patent 785,410 (October 30, 1957); German Patent 1,017,162 (March 20, 1958); French Patent 1,148,500 (December 10, 1957).

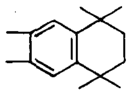
(27) L. Givaudan and Cie, S. A., British Patent 787,300 (December 4, 1957); Geman Patent 1,018,055 (April 3, 1958); French Patent 1,141,714 (September 6, 1957).

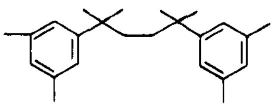
para isomers as shown by infrared spectrum and vapor phase chromatogram of the liquid product. Treatment of the mixture of the isomeric 2-methyl-2-*m,p*-tolyl-6-heptanones with methylmagnesium iodide followed by cyclodehydration of the resulting carbinols yielded a mixture (X) of isomers in nearly equimolar ratio as shown by vapor phase chromatography.


X

Acetylation of this mixture gave a viscous liquid product which was devoid of musk odor. Nitration gave an oil having no musk odor.

An attempt to prepare isomers of I starting from the xylenes was not successful. Reaction of 2,5-dichloro-2,5-dimethylhexane with each of these using aluminum chloride catalyst gave the same tetralin hydrocarbon (XI). The yields of this from *o*-xylene were nearly quantitative but from *m*- and *p*-xylene were only 27% and 10.5%, respectively, with side reactions predominating. The by-product from the *m*-xylene reaction was a diphenylbutane derivative (XII) and that from the *p*-xylene reaction was 1,1,4,4,5,5,8,8-octamethyl-1,2,3,4,-5,6,7,8-octahydroanthracene[9,28] (XIII) which was produced by the reaction of two moles of the dichloride with one mole of *p*-xylene with elimination of the xylene–methyl groups. XI did not undergo acetylation, however, under any of the conditions tried.


XI (**18**)


XII

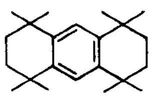

XIII

Table I lists all of the polyalkyltetralins which were synthesized as intermediates for this study. Some of these have been described previously as indicated, mainly in the patent literature, but in Table II are reported new derivatives of these. In Table II are listed all of the acyl and dinitro derivatives which were checked for musk odor. In the latter group are only two musks which have been previously described,[29] namely, 5,7-dinitro-1,1,6-trimethyltetralin "dinitroionene" and 5,7-dinitro-1,1-dimethyl-6-ethyltetralin. In this paper it was stated that "the *gem*-dimethyl group in the tetralin molecule (with its attached quaternary carbon) plays an important role in the production of the musk odor in this type of compound." The dinitro musks prepared in the present study extend the series and lend strong support to this idea.

Subsequent papers will summarize additional findings in the field of the polycyclic musks which, in conjunction with the present paper, should contribute data useful in the continuing efforts to correlate odor with chemical structure.

Experimental

Polyalkylated Tetralin Hydrocarbons.—The two most widely used methods for the synthesis of these hydrocarbons were the cyclialkylation procedure of Bruson and Kroeger[9] and the cyclodehydration method of Bogert, Davidson, and Roblin.[10] In the table the cyclialkylation with aluminum chloride is designated as method CA-1 and with ferric chloride as method CA-2. The cyclodehydration method is designated as CD.

Compounds **1** to **10** inclusive were synthesized by known methods as indicated in Table I (*c* to *l*). Compounds **13**, **19**, **23**, and **26** were prepared according to the procedures given in U. S. Patent 2,897,237 (July 28, 1959). These illustrate the CA-1 and CA-2 techniques of cyclialkylation. Compounds **7**, **18**, **21**, **24**, and **27** were prepared by similar techniques using the designated modifications. For the cyclialkylation reactions the required dichlorides, 2,5-dichloro-2,5-dimethylheptane and 3,6-dichloro-3,6-dimethyloctane, were prepared from the corresponding commercially available ditertiary glycols[30] using the techniques of Bruson and Kroeger.

Compounds **11** and **16**, 1-isopropyl-4,4-dimethyltetralin and 1-isopropyl-4,4,7-trimethyltetralin [admixed with isomeric 1-isopropyl-4,4,6-trimethyltetralin (X)], were prepared by the following sequence.

(a) **6-Methyl-6-phenyl-2-heptanone.**—Freshly distilled methylheptenone, 126 g. (1 mole) (Givaudan) was added dropwise over a 1-hr. period with stirring to 146 g. of aluminum chloride (1.1 mole) in 500 g. of benzene and with cooling to maintain the temperature at 25 to 27°. Stirring was continued at 25 to 30° for 6 hr. longer. The reaction mixture was decomposed on ice. The resulting benzene solution was washed with 5% hydrochloric acid, 5% sodium hydroxide, and then with water to neutrality. The benzene was distilled and the residue vacuum-distilled to yield 138 g. (68.5%) of a colorless liquid, b.p. 132–133° (4 mm.), n^{20}_{D} 1.5020, d^{20}_{4} 0.9559.

Anal. Calcd. for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.12; H, 9.98.

(b) **6-Methyl-6-*m,p*-tolyl-2-heptanone.**—This product was synthesized in similar fashion by the reaction of toluene and methylheptenone and obtained in 80.5% yield. It was a colorless, nearly odorless liquid, b.p. 118–120° (2 mm.), n^{20}_{D} 1.5050, d^{20}_{4} 0.9456. The infrared spectrogram and vapor phase chromatogram showed it to be a mixture of the *meta* and *para* isomers in about equal amounts.

Anal. Calcd. for $C_{15}H_{22}O$: C, 82.51; H, 10.16. Found: C, 82.30; H, 10.45.

(c) **2,6-Dimethyl-6-phenyl-2-heptanol and 2,6-dimethyl-6-*m,p*-tolyl-2-heptanol mixture** were prepared by treating the preceding ketones with methylmagnesium iodide. The products were obtained as viscous liquids, b.p. 121–123° (3 mm.), n^{20}_{D} 1.5034 (yield 92.3%), and b.p. 125° (3 mm.), n^{20}_{D} 1.5038 (yield 90.2%), respectively. The tertiary carbinols were subjected to the cyclodehydration procedure, feeding each with good agitation into an equal volume of cold (0°) 90% sulfuric acid to produce the desired tetralin derivatives, compounds **11** and **16**.

Compounds **12**, **17**, **22**, and **25**, in addition to the method of U.S. Patent 2,915,561 (ref. 16), were prepared conveniently in good purity by a sequence of reactions starting with β-methallyl chloride. Preparation of compound **22** illustrates the method.

(a) **1-Chloro-2-methyl-2-*p*-ethylphenylpropane.**—β-Methallyl chloride (201 g., 2.22 moles) was added dropwise into a rapidly stirred mixture of 665 g. (6.27 moles) of ethylbenzene and 40.0 g. of concentrated sulfuric acid (Sp. Gr. 1.84) over a 7-hr. period while the temperature was kept at 20°. Stirring at 20° was then continued for 17 hr. After allowing to settle, the lower, dark-colored sulfuric acid layer was separated and discarded. The remaining solution was washed six times with hot water (400 ml. each time).

The reddish color disappeared with the first wash. Salt was added to the washes to facilitate separations. The excess ethylbenzene was distilled at 38 mm. The remainder was vacuum-distilled at 2.5 mm. giving the desired product in a yield of 83.7%. It was a colorless, mild smelling liquid, b.p. 102° (2.5 mm.), n^{20}_{D} 1.5197.

Anal. Calcd. for $C_{12}H_{17}Cl$: C, 73.26; H, 8.71; Cl, 18.02. Found: C, 73.13; H, 8.93; Cl, 17.77.

(b) **2,3,5-Trimethyl-5-*p*-ethylphenyl-3-hexanol.**—A solution of 393 g. of 1-chloro-2-methyl-2-*p*-ethylphenylpropane (2 moles) in 400 ml. of anhydrous dibutyl ether was fed dropwise with stirring into a warm (40°) mixture of 48 g. of magnesium turnings, 150 g. of anhydrous dibutyl ether, and 2 ml. of methyl iodide. The reaction was exothermic and occasional cooling was required to hold the temperature at 40 to 50°. Then stirring and heating

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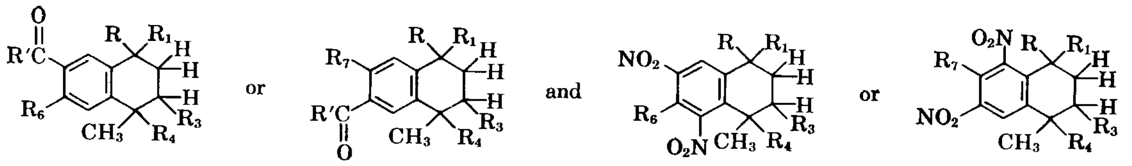
[28] L. R. C. Barclay and E. E. Betts, *J. Am. Chem. Soc.*, **77**, 5735 (1955).

[29] M. S. Carpenter and W. M. Easter, Jr., *J. Org. Chem.*, **19**, 90 (1954).

[30] Air Reduction Chemical and Carbide Co., New York 17, N. Y.

TABLE II

ACYL AND DINITRO DERIVATIVES OF POLYALKYLTETRALINS



	Acyl Derivative										Dinitro derivative								
							Analysis							Analysis					
							Calcd.		Found					Calcd.			Found		
Parent hydrocarbon[a]	R′	B.p., °C. (mm.)	$n^{20}D$ or m.p., °C.	d^{20}_4	Formula	Odor	C	H	C	H	M.p., °C.	Odor	Formula	C	H	N	C	H	N
1	CH_2	122 (1.5)	1.5494	1.0340	$C_{14}H_{18}O$		83.12	8.97			Oil								
2	CH_3	122 (1.5)	1.5430	1.0078	$C_{15}H_{20}O$		83.30	9.32	83.13	9.11	Oil	Faint musk							
3	CH_3	125–127 (2)	33–34		$C_{15}H_{20}O$		83.30	9.32	83.30	9.17									
4	CH_3	125–128 (2)	1.5411	0.9913	$C_{15}H_{20}O$		83.30	9.32			Oil								
5	H	112–114 (1)	1.5618	1.0294	$C_{14}H_{18}O$		83.12	8.97			103	Weak musk[b]	$C_{13}H_{16}N_2O_4$	59.06	6.11	10.61	58.97	6.18	10.72
	CH_3	117–122 (1)	75.5–77		$C_{15}H_{20}O$		83.30	9.32	83.45	9.11									
6	CH_3	128 (1.75)	1.5432, 13	1.0044	$C_{16}H_{22}O$	Weak musk	83.40	9.63	83.54	9.44									
7	H	112–115 (2)	53–54		$C_{15}H_{20}O$		83.30	9.32	83.37	9.09	201–202.5	Odorless	$C_{14}H_{18}N_2O_4$	60.41	6.52	10.07	60.62	6.49	9.86
	CH_3	127–128 (1.5)	1.5372	0.9971	$C_{16}H_{22}O$		83.40	9.63	83.55	9.40									
8	CH_3	120–122 (1)	1.5452	1.0060	$C_{16}H_{22}O$	Musk[c]	83.40	9.63	83.37	9.28									
9	CH_3	130 (1.5)	1.5433	1.0039	$C_{16}H_{22}O$		83.40	9.63	83.52	9.47	Oil								
10	CH_3	133–135 (1.5)	1.5437	1.0171	$C_{16}H_{22}O$		83.40	9.63			112–113	Musk[b]	$C_{14}H_{18}N_2O_4$	60.41	6.52	10.07	60.48	6.35	10.18
11	CH_3	135 (1.5)	1.5380	0.9938	$C_{17}H_{24}O$		83.54	9.90	83.69	9.64	Oil								
12	CH_3	125–127 (2)	1.5360	0.9894	$C_{17}H_{24}O$	Musk[d]	83.54	9.90	83.48	9.74	181.5–182.5	Musk	$C_{15}H_{20}N_2O_4$	61.61	6.89	9.58	61.78	6.89	9.42
13	H		85–91		$C_{16}H_{22}O$	Strong musk[e]	83.40	9.63	83.26	9.41	110–111	Musk	$C_{15}H_{20}N_2O_4$	61.61	6.89	9.58	61.28	6.90	9.33
	CH_3	130–134 (2)	62–63.5		$C_{17}H_{24}O$	Musk[f]	83.54	9.90	83.64	9.63									
	C_2H_5	129–130 (1.25)	1.5330	0.9893	$C_{18}H_{26}O$	Weak musk	83.68	10.14	83.94	10.10									
14	CH_3	145–146 (2)	1.5443	1.0038	$C_{17}H_{24}O$	Strong musk	83.54	9.90	83.44	9.68									
15	CH_3	126–128 (1)	1.5468	1.0066	$C_{17}H_{24}O$	Weak musk[c]	83.54	9.90	83.53	9.54									
16	CH_3	138–139 (1.5)	1.5382	0.9872	$C_{18}H_{26}O$		83.68	10.14	83.60	9.84	77–86								
17	CH_3	144 (2.5)	56–57		$C_{18}H_{26}O$	Strong musk[d]	83.68	10.14	83.87	9.80	113–114	Musk	$C_{16}H_{22}N_2O_4$	62.70	7.24	9.15	62.70	7.20	9.20
18[g]	CH_3										95.5–96.5[g]	Odorless	$C_{16}H_{23}NO_2$	73.51	8.87	5.36	73.31	8.71	5.14
19	H	138–139 (3)	28–31		$C_{17}H_{24}O$	Strong musk[e]	83.54	9.90	83.37	9.63	112–113	Musk	$C_{16}H_{22}N_2O_4$	62.70	7.24	9.15	62.60	7.21	9.20
	CH_3	130 (2)	45–46		$C_{18}H_{26}O$	Strong musk[f]	83.68	10.14	83.53	9.90									
	C_2H_5	132 (1.5)	46–48		$C_{19}H_{28}O$	Weak musk	83.78	10.36	84.01	10.50									
	i-C_3H_7	145–146 (2.5)	58–60		$C_{20}H_{30}O$	V. weak musk	83.83	10.55	84.22	10.36									
20	CH_3	130 (1)	1.5381	0.9895	$C_{18}H_{26}O$	Musk[h]	83.68	10.14	83.80	10.08									
21	CH_3	139–141 (1)	1.5369	0.9831	$C_{19}H_{28}O$		83.78	10.36	83.75	10.28	Oil								
22	CH_3	143–145 (1)	62.5–63.5		$C_{19}H_{28}O$	Musk	83.78	10.36	84.05	10.23	108.5–109.8	Musk	$C_{17}H_{24}N_2O_4$	63.72	7.55	8.74	63.86	7.59	8.48
23	H	133–135 (2)	61.5–63		$C_{18}H_{26}O$	Musk[e]	83.68	10.14	83.76	9.92	119–122	Musk	$C_{17}H_{24}N_2O_4$	63.72	7.55	8.74	64.01	7.40	8.72
	CH_3	118–125 (1.5)	84.5–85.5		$C_{19}H_{28}O$	Musk[f]	83.78	10.36	83.87	10.14									
24	CH_3	141–144 (1)	1.5324	0.9730	$C_{20}H_{30}O$		83.83	10.55	84.14	10.64	Oil	Weak musk							
	C_2H_5	161–170 (2)	1.5286	0.9768	$C_{21}H_{32}O$		83.92	10.74	84.35	10.74									
25	CH_3	143–144 (1)	108–109		$C_{20}H_{30}O$	Weak musk	83.83	10.55	84.08	10.57	182–182.5[i]								
26	CH_2	127–128 (1.5)	1.5372	0.9975	$C_{16}H_{22}O$[j]		83.40	9.63	83.55	9.40	Oil	Musk							
27	CH_2	164–165 (2)	1.5272	0.9707	$C_{21}H_{32}O$		83.92	10.74	84.19	10.51									
	C_2H_5	140–160 (2)	1.5221	0.9639	$C_{22}H_{34}O$		84.02	10.90	84.30	10.68									

[a] See Table I for structures. [b] Previously reported (ref. 29, pp. 90–91). [c] Ref. 26. Products were each mixtures of two isomers. [d] Ref. 16a products previously reported were each mixtures of two isomers. [e] Ref. 14. [f] Ref. 12. [g] Attempts to acetylate this hydrocarbon failed. Only the mononitro derivative was obtained. [h] Ref. 27. Mixture of two isomers. [i] Nitration removed the isopropyl group giving derivative same as that of hydrocarbon **12**. [j] Acetyl derivative was same as that of hydrocarbon **7**.

were continued for 3 hr. The Grignard solution was cooled to 2°, and there was fed in dropwise over a 50-min. period a solution of 172 g. of methyl isopropyl ketone (2 moles) in 300 ml. of anhydrous dibutyl ether with cooling to maintain the temperature at 2 to 9°. Then stirring was continued at 10° for 30 min. The batch was quenched with good agitation into a mixture of 1600 g. of cracked ice and 200 g. of 37% hydrochloric acid. After being stirred the mixture was allowed to settle overnight. The water layer was removed. The remaining solution was washed with three 400-ml. portions of water and two 400-ml. portions of 5% sodium carbonate solution. The dibutyl ether was distilled and the residual liquid vacuum-distilled to yield a considerable forerun, b.p 57–64° (2.5 mm.), which appeared to be *p-t*-butylethylbenzene, followed by the desired carbinol, b.p. 125–127° (2 mm.), $n^{20}\mathrm{D}$ 1.5066, amounting to 97 g. (19.5%).

Anal. Calcd. for $C_{17}H_{28}O$: C, 82.20; H, 11.36. Found: C, 82.24; H, 11.26.

(c) **6-Ethyl-1,1,3,4,4-pentamethyltetralin.**—The prior tertiary carbinol was cyclodehydrated by dropwise addition with stirring to a cold (0°) 90% sulfuric acid solution. After working up by the usual method, there was obtained an 88% yield of the desired tetralin derivative, a colorless liquid, b.p. 100–101° (1.5 mm.), m.p. 5–8°, $n^{20}\mathrm{D}$ 1.5158, d^{20}_4 0.9265. The purity shown by vapor phase chromatography was 93%.

Anal. Calcd. for $C_{17}H_{26}$: C, 88.62; H, 11.38. Found: C, 88.50; H, 11.23.

Compounds **14** and **17** were synthesized in the following way.

(a) **Ethyl 2,4-Dimethyl-4-pentenoate.**—Ethyl α-methallylacetoacetate[31] (184 g.) was added with stirring and cooling to a solution of 27.5 g. (1.2 g.-atoms) of sodium in 400 ml. of absolute alcohol at 15°. After the feeding, stirring was continued for 1 hr. at 15 to 20°. Then there was added all at once 170 g. of methyl iodide (1.2 moles). A mildly exothermic reaction set in which required occasional water bath cooling to maintain the temperature at 30 to 32° over a 90-min. period. Then after stirring for 2 hr. longer at room temperature (no cooling required), the mixture was stirred and heated at reflux (82°) for 1 hr. After allowing to stand and cool overnight the precipitated sodium iodide was removed by filtration. Toluene (500 ml.) was added and the resulting solution slowly distilled with stirring to remove the toluene–ethanol azeotrope, b.p. 73–78°. After removing 500 ml. of distillate, there was added 250 ml. of toluene; the mixture was stirred, cooled, and filtered. Sodium iodide removed was 164 g. (theory 180 g.). Toluene was distilled and residual liquid vacuum-distilled to yield 111 g. of colorless liquid, b.p. 30–32° (1 mm.), $n^{20}\mathrm{D}$ 1.4230. Analyses indicated that this was the ester resulting from cleavage of the acetoacetic ester derivative, ethyl 2,4-dimethyl-4-pentenoate, sapon. equiv. value, 338.9 (theory, 360). Carbonyl value was 3.6.

Anal. Calcd. for $C_9H_{16}O_2$: C, 69.3; H, 10.24. Found: C, 69.20; H, 10.05.

(b) **Ethyl 2,4-Dimethyl-4-*m,p*-tolylpentanoate.**—Ethyl 2,4-dimethyl-4-pentenoate (75 g.) was added dropwise with stirring to a mixture of 400 g. of toluene and 160 g. of powdered aluminum chloride, cooled to 10 to 15°, over a 1-hr. period. After the addition the mixture was stirred for 5 hr. at 10 to 15° and then quenched on 1000 g. of cracked ice. The resulting oil layer was washed successively with 200 ml. of 2% hydrochloric acid, 200 ml. of water, and twice with 200-ml. portions of 2% sodium carbonate solution. Removal of excess toluene and vacuum-distillation yielded 108 g. (90.5%) of the desired ester, a colorless liquid, b.p. 114–115° (1 mm.), $n^{20}\mathrm{D}$ 1.4910.

Anal. Calcd. for $C_{16}H_{24}O_2$: C, 77.37; H, 9.74. Found: C, 77.54; H, 9.63.

(c) **Ethyl 2-Methyl-4-*m,p*-tolylpentanoate.**—This was similarly synthesized starting with ethyl α-allylacetoacetate.[15] The ethyl 2-methyl-4-pentenoate was obtained as a colorless liquid of pleasant odor, b.p. 55–56° (31 mm.), $n^{20}\mathrm{D}$ 1.4170. This was condensed with toluene in the presence of aluminum chloride, as above, to yield the desired product, a colorless liquid, b.p. 106–107° (1 mm.), $n^{20}\mathrm{D}$ 1.4884, d^{20}_4 0.9646, sapon. equiv., 241.9 (theory, 239). The yield was 88%.

Anal. Calcd. for $C_{15}H_{22}O_2$: C, 76.90; H, 9.47. Found: C, 77.04; H, 9.60.

(d) **2,3-Dimethyl-5-*m,p*-tolyl-2-hexanol and 2,3,5-Trimethyl-5-*m,p*-tolyl-2-hexanol** were prepared by the action of methylmagnesium iodide on each of the esters described before in yields of 94.5 and 88.5%, respectively. The two carbinols were obtained as colorless somewhat viscous liquids, the former having b.p. 118–120° (2 mm.), $n^{20}\mathrm{D}$ 1.5080, and the latter, b.p. 124–125° (1.5 mm.), $n^{20}\mathrm{D}$ 1.5080. These were cyclodehydrated by the usual procedure to yield 1,1,2,4,7-pentamethyltetralin (compound **14**) with isomer (yield 86.5%) and 1,1,3,4,4,6-hexamethyltetralin (compound **17**) with isomer (yield, 90%).

Compound **17** also was synthesized conveniently in good purity by processes involving the *p*-cymylcarbonium ion as intermediate.

(a) **From *p*-Cymene.**—2,3-Dimethyl-2-butanol (180 g., 1.53 moles) was added slowly to a rapidly agitated mixture of 420 g. of *p*-cymene (3.14 moles) and 1060 g. of 93% sulfuric acid at 0° over a 1-hr. period. Stirring was continued for 2 hr. at 0°. After settling, the lower acid layer was removed and the remaining oil layer was washed with water and then with 5% sodium hydroxide solution. Vacuum distillation yielded besides 270 g. of recovered *p*-cymene, b.p. 64° (15 mm.), a fraction, b.p. 100–113° (3 mm.), m.p. 56–60°, which amounted to 122 g. (73.4%). Crystallization from isopropyl alcohol gave 97 g. of colorless crystals, m.p. 66–67°, identical with the product made by the cyclodehydration methods. Infrared curves of the hydrocarbons were superimposable. Identical dinitro (m.p. 114°) and acetyl derivatives (m.p. 56–57°) were obtained.

Anal. Calcd. for $C_{16}H_{24}$: C, 88.82; H, 11.18. Found: C, 88.80; H, 11.06.

The preceding experiment was repeated substituting 3,3-dimethyl-2-butanol (pinacolyl alcohol) for 2,3-dimethyl-2-butanol. The product was identical with the preceding product. The yield dropped to 93.7 g. (56.2%) for the vacuum-distilled material.

(b) **From α,*p*-Dimethylstyrene.**—A solution of 116 g. of α,*p*-dimethylstyrene [b.p. 77° (14 mm.), $n^{20}\mathrm{D}$ 1.5325) (0.88 mole)] and 74 g. of 2,3-dimethyl-2-butene[32] (0.88 mole) was treated with a solution of 88 g. of 96% sulfuric acid and 88 g. of glacial acetic acid following the procedure of Example 2 of U.S. Patent 2,851,501 (ref. 22). The yield of product, b.p. 96–98° (2 mm.), m.p. 59–62°, was 59.5 g. (31.3%). Crystallization from isopropyl alcohol gave 42 g. of colorless product, m.p. 66–67°. Mixture melting point and infrared spectra comparison showed it to be identical with compound **17** made by the other procedures listed earlier.

(c) **From Dimethyl-*p*-tolylcarbinol.**—A solution of 75 g. of dimethyl-*p*-tolylcarbinol (0.5 mole) and 56 g. of 2,3-dimethyl-2-butanol (0.5 mole) was slowly dropped into 300 g. of cold agitated 90% sulfuric acid solution over a 45-min. period (temp., −6 to +5°). Stirring was continued 30 min. after the addition. The batch was quenched on cracked ice and the resulting oil in benzene solution washed successively with water and 5% sodium carbonate solution. After distilling the benzene and vacuum-distilling the residue there was obtained 19.5 g. of product, b.p. 115–121° (8 mm.), which solidified. Crystallization from isopropyl alcohol gave 11 g. (10.2%) of colorless product, m.p. 66–67°, which was identical with the other two preparations described earlier.

Compounds **15** and **20** were prepared following the Colonge and Pichat technique[25] by procedures described in the patent literature.[26,27]

Cyclialkylation of the Xylenes. (a) **1,1,4,4,6,7-Hexamethyltetralin.**—A solution of 61 g. (0.333 mole) of 2,5-dichloro-2,5-dimethylhexane in 61 g. (0.575 mole) of *o*-xylene was added dropwise to an agitated mixture of 180 g. (1.70 moles) of *o*-xylene and 5 g. of aluminum chloride powder with the temperature at −10° during the addition. Hydrogen chloride evolution was immediate and brisk. Stirring was continued at 7 to 10° for 50 min. after the addition. The reaction mixture was quenched in water, separated, agitated at 80° with 5% sodium hydroxide, separated, washed neutral with water, and distilled. After recovery of 203 g. of *o*-xylene, b.p. 65–68° (60 mm.), there was obtained 71 g. (98.5%) of crystalline residue. This was crystallized from an equal weight of ethanol to give 63 g. (87.5%) of colorless product, m.p. 84–85°.

Anal. Calcd. for $C_{16}H_{24}$: C, 88.83; H, 11.17. Found: C, 89.10; H, 10.56.

(b) **Compound 18 from *m*-Xylene.**—A solution of 183 g. 2,5-dichloro-2,5-dimethylhexane in 273 g. of *m*-xylene was added with agitation to a mixture of 10 g. of aluminum chloride and 363 g. of *m*-xylene over a period of 1 hr. and 10 min. at 20–25° and then the mixture stirred for 30 min. The solution was quenched

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(31) M. S. Schecter, N. Green, and F. B. LaForge, *J. Am. Chem. Soc.*, **71**, 3168 (1949).

(32) Houdry Process Corporation, Commercial Chemical Development Department, Research and Development Laboratories, Marcus Hook, Pa.

in water, separated, heated to 80° with agitation with 5% sodium hydroxide, separated, washed neutral, and distilled. After the distillation of excess *m*-xylene the desired product was obtained in a fraction, b.p. 102–105° (2 mm.), amounting to 152 g. The residue amounting to 84 g. congealed. This was crystallized from methanol–benzene solution yielding 70 g. of a colorless compound, m.p. 106–107°. This product (XIIa) was the condensation product of two moles of *m*-xylene with one mole of 2,5-dichloro-2,5-dimethylhexane.

Anal. Calcd. for $C_{24}H_{34}$: C, 89.37; H, 10.63. Found: C, 89.25; H, 10.20.

The prior fraction, b.p. 102–105° (152 g.), congealed to a semicrystalline mass. It was dissolved in an equal weight of hot benzene, and methanol added until turbidity developed. Chilling with stirring gave 51 g. of crystals, m.p. 85–86°. Reworking the mother liquor yielded an additional 7 g. for a total yield of 58 g. (27%) of product, m.p. 85–86°, which was identical with the compound obtained earlier from *o*-xylene.

(c) **Compound 18 from *p*-Xylene.**—A solution of 183 g. of 2,5-dichloro-2,5-dimethylhexane in 183 g. of *p*-xylene was added with stirring to a mixture of 453 g. of *p*-xylene and 15 g. of aluminum chloride over a period of 1 hr. keeping the temperature at 17 to 21°. Strong evolution of hydrogen chloride was observed. The mixture was stirred for 3 hr. at 21–22°, quenched in water, and washed neutral. Upon vacuum distillation there was obtained, besides recovered *p*-xylene, a fraction, b.p. 101–109° (2.5–3.0 mm.), amounting to 153 g. and 52 g. of semicrystalline residue. The residue, crystallized from ethanol, gave 18 g. of product melting at 219–221° which proved to be identical with 1,1,4,4,5,5,8,8-octamethyl-1,2,3,4,5,6,7,8-octahydroanthracene[9] synthesized by the method of Bruson and Kroeger. The fraction, b.p. 101–109°, amounting to 153 g. was crystallized from an equal weight of ethanol to give 23 g. (10.5%) of colorless product, m.p. 85–86°, identical with the cyclialkylation product obtained from *o*-xylene.

Acetylation of Hydrocarbons.—The same general procedure was used for the preparation of all of these derivatives. A solution of 1 mole of the hydrocarbon and 1.1 moles of acetyl (propionyl or isobutyryl) chloride was added during the course of 30 to 60 min. to a suspension of 1.15 to 1.20 moles of ground (small granules) anhydrous aluminum chloride in 550 to 650 g. of ethylene dichloride with stirring throughout the reaction period and cooling to maintain a temperature of 20–25°. Stirring was usually continued for 1 hr. longer at 25°. The solution was quenched on ice and the resulting ethylene dichloride layer was washed with water to neutrality. The solvent was distilled and the remaining oil distilled *in vacuo*. The products which were found to be crystalline at room temperature were further purified by crystallizing from an equal weight of ethanol with chilling to 0 to 10°.

Formyl Derivatives.—The formyl derivative of hydrocarbon **7** was prepared by the oxidation of hydrocarbon **13**. The derivatives of hydrocarbons **5**, **13**, **19**, and **23**, were prepared by first chloromethylating and then oxidizing by the Sommelet method with hexamethylenetetramine. Procedures for this method are given in detail in U. S. Patent 2,800,511 (ref. 14).

6-Formyl-1,1,4,4-tetramethyltetralin.—A mixture of 96 g. of 1,1,4,4,6-pentamethyltetralin (hydrocarbon **13**), 50 g. of manganese dioxide, and 225 g. of 50% sulfuric acid was agitated at 60° for 30 hr. No apparent reaction occurred. Sufficient 93% sulfuric acid was added to bring the acid concentration to 60% and agitation was continued at 60° for another 30 hr. The cooled mixture was thinned with benzene and filtered. The benzene solution was washed with 5% sodium hydroxide then with water to neutrality and distilled. After recovery of 59 g. of unconverted hydrocarbon, b.p. 81–83° (2 mm.), there was obtained 22 g. of the desired aldehyde, a colorless liquid, b.p. 112–115° (2 mm.), which rapidly congealed. Crystallization, using 22 g. of ethanol, gave 16 g. of product, m.p. 53–54°, having a weak amber-like odor.

Anal. Calcd. for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.37; H, 9.09.

Dinitro Derivatives.—The following general procedure was used for all of the hydrocarbons which were nitrated. One mole of the hydrocarbon was added dropwise with agitation and cooling (15–25°) to a mixed acid composed of 6 moles of 98% nitric acid and 9.5 moles of 93% sulfuric acid. In some cases where the hydrocarbon was a solid, ethylene dichloride was added to the mixed acid and the hydrocarbon added in ethylene dichloride solution. The nitration mixture was quenched on ice, and the product taken up in benzene, washed with water, then with 5% sodium hydroxide until the washes were free of color, then with water to neutrality, and the solvent removed. When these derivatives were obtained as solids, they were purified by crystallizing from ethanol.

The prior procedure led to dinitration in all cases except one. Hydrocarbon **18** gave only a mononitro derivative. Nitration of hydrocarbon **25** resulted in removal of the isopropyl group producing a dinitro derivative identical with the one prepared from hydrocarbon **12**.

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The Pyrolysis of Hexachlorocyclopentadiene[1]

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Slow pyrolysis of hexachlorocyclopentadiene at *ca.* 250° gave octachloroindene, hexachlorobenzene, octachlorocyclopentane, dodecachlorodihydrotrindene, and a chlorocarbon, $C_{20}Cl_{14}$, of unknown structure.

The liquid phase pyrolysis of hexachlorocyclopentadiene (**1**) has been the subject of a brief study.[3] A closer examination of this reaction revealed the formation of not only octachlorocyclopentene (**2**) (11–22% conversion)[3b] and dodecachlorodihydrotrindene (**3**)[3a,4] (30%), but also octachloroindene (**4**) (9%), hexachlorobenzene (**5**) (0.8%), and a chlorocarbon, $C_{20}Cl_{14}$ (**6**) (1.2%), of unknown structure.

The products **4** and **5** were identified by comparison with known samples. A sample of authentic **4** was synthesized according to Eaton and co-workers[5] by the reaction of hexachloroindenone (**7**) with phosphorus pentachloride. Using the same conditions,[5] an appreciable amount of decachloroindan (**8**) was obtained in

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(1) This paper is based on a portion of a thesis submitted by Wendell L. Dilling to the Graduate School of Purdue University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Hooker Chemical Corporation Research Assistant, 1958–1959; National Science Foundation Cooperative Fellow, 1959–1962.

(3) (a) J. D. Idol, Jr., Ph.D. thesis, Purdue University, (1955); (b) R. H. Earle, Jr., Ph.D. thesis, Purdue University, (1957); (c) The gas phase pyrolysis of **1** recently has been reported by A. E. Ginsberg, R. Paatz, and F. Korte, *Tetrahedron Letters*, 779 (1962).

(4) V. Mark, *Tetrahedron Letters*, 333 (1961).

(5) P. Eaton, E. Carlson, P. Lombardo, and P. Yates, *J. Org. Chem.*, **25**, 1225 (1960).