Umlagerungsreaktion des 24-Methylencholesterylacetates mit Jod——2 g 24-Methylencholesterylacetat (Ib) wurden zusammen mit 150 cc Benzol und 120 mg Jod 13 Std. unter Rückfluß erhitzt. Die übliche Aufarbeitung ergab 2 g des rohen Produktes, die nach Chromatographieren mit 20 g Al_2O_3 und Hexan-Benzol (2:1) anschließend aus EtOH mehrmals umkristallisiert wurden. Blättchen vom Schmp. 143~144°. $[\alpha]_D^{30}$ (c=1.005, $CHCl_3$). $C_{30}H_{48}O_2$ (24-Methylcholesta-5,24-dien-3β-ol-acetat IIb)—Ber.: C, 81.76; H, 10.98. Gef.: C, 81.86; H, 11.13. Sterin: Schmp. 141.5~142.5°. Blättchen aus EtOH. $[\alpha]_D^{30}$ $-36.1°$(c=1.028, $CHCl_3$). $C_{28}H_{46}O$—Ber.: C, 84.35; H, 11.63. Gef.: C, 84.16; H, 11.39. Benzoat: Schmp. 145~146°. Blättchen aus EtOH-Benzol. $[\alpha]_D^{30}$ $-20.5°$(c=1.039, $CHCl_3$). $C_{35}H_{50}O_2$—Ber.: C, 83.61; H, 10.02. Gef.: C, 83.60; H, 10.13.

Ozonisierung des Sterinacetates: 210 mg Acetat (IIb) wurden nach der gleichen Methode ozonisiert und das flüchtige Reaktionsprodukt in 2,4-Dinitrophenylhydrazon vom Schmp. 125~126° überführt. Ausbeute 56 mg (65%). Es war identisch mit Aceton-2,4-dinitrophenylhydrazon.

Nach dem Abschluß des Redaktionsgeschäfts hat der Autor an dem kürzlich erschienen Bericht von Briggs, *et al.* gemerkt, daß eine ähnliche Umlagerungsreaktion mittels Jod bei Kauren bzw. Phyllocladen ausgeführt worden ist. Siehe L.H. Briggs, B.F. Cain, R.C. Camble, B.R. Davis, P.S. Rutledge: J. Chem. Soc., **1962**, 1850.

Zusammenfassung

Es wird eine Umlagerungsreaktion der Doppelbindung an $C_{24(28)}$ der Sterinseitenkette beschrieben. Die Doppelbindung an $C_{24(28)}$ des Fucosterylacetates bzw. des 24-Methylencholesterylacetates läßt sich durch Einwirkung von Jod in die 24(25)-Stellung umlagern.

(Eingegangen am 25. September, 1962)

UDC 547.661.07

131. Akihiro Ohta,[*1, *2] Yukio Ogihara,[*1] Kiyoshi Nei,[*3] and Shoji Shibata[*1]: On Methylphenylnaphthalenes. I. Syntheses of Methylphenylnaphthalenes.

(*Faculty of Pharmaceutical Sciences, University of Tokyo*[*1])

Phenylnaphthalenes having methyl group in the 2′-, 3′-, 4′-, 2-, 2,2′-, 2,3-, 3,4-, and 4′,7-positions[*4] have been reported in the literatures.

Some of the new compounds of this series have now been prepared as reference compounds for certain investigation.

1-Phenylnaphthalene derivatives are generally synthesized using α-tetralone and bromobenzene substituted with methyl group(s) in the appropriate position(s) as the starting materials, which are subjected to the Grignard reaction followed by dehydration and subsequent dehydrogenation.

α-Tetralone and alkylated α-tetralone employed were grouped as bellow (i~vii), which were synthesized by the different appropriate processes.

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[*4] The numbering of the phenylnaphthalene nucleus used in this series of studies is indicated in the formula (V).

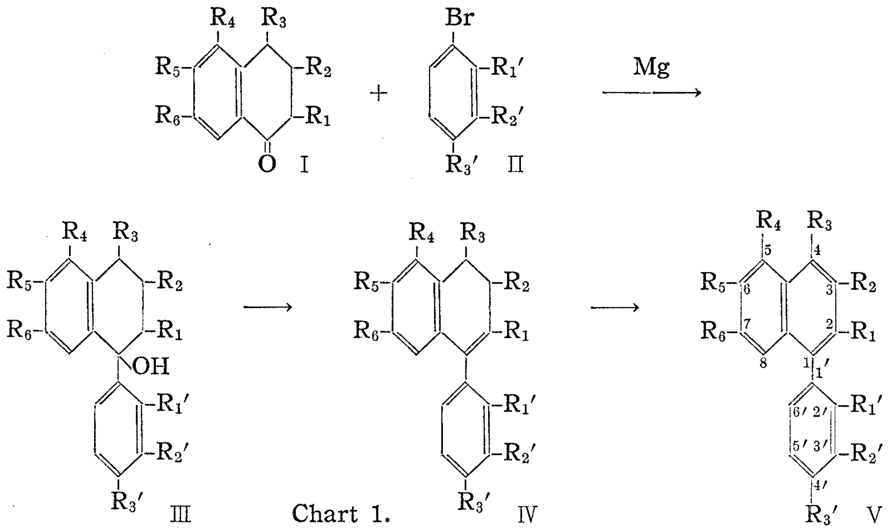

Chart 1.

i) α-Tetralone[1] (I : $R_1 \sim R_6 = H$) was reacted with 4-bromo-1,2-dimethylbenzene (II: R_2', $R_3' = CH_3$, $R_1' = H$) to afford 3′,4′-dimethyl-1-phenylnaphthalene (V : R_2', $R_3' = CH_3$, $R_1 \sim R_6$, $R_1' = H$); 4-Methyl-α-tetralone (I : $R_3 = CH_3$, R_1, R_2, R_4, R_5, $R_6 = H$) was condensed with bromobenzene (II : R_1', $R_3' = H$) or 1-bromo-4-methylbenzene (II : $R_3' = CH_3$, R_1', $R_2' = H$) to give 4-methyl- (V : $R_3 = CH_3$, R_1, R_2, R_4, R_5, R_6, $R_2' = H$), and 4,4′-dimethyl (V : R_3, $R_3' = CH_3$, R_1, R_2, R_4, R_5, R_6, R_1', $R_2' = H$)-1-phenylnaphthalene, respectively.

ii) 3-Methyl-(I : $R_2 = CH_3$, R_1, R_3, R_4, R_5, $R_6 = H$) 3,6-dimethyl-(I : R_2, $R_5 = CH_3$, R_1, R_3, R_4, $R_6 = H$) and 3,7-dimethyl-(I : R_2, $R_6 = CH_3$, R_1, R_3, R_4, $R_5 = H$)-α-tetralones which were synthesized by several steps starting from toluene, *m*- or *p*-xylene were subjected to condensation with bromobenzene (II : R_1', $R_3' = H$), or 1-bromo-2-methylbenzene (II: $R_1' = CH_3$, R_2', $R_3' = H$) to afford 3-methyl-(V : $R_2 = CH_3$, R_1, R_3, R_4, R_5, R_6, R_1', R_2', $R_3' = H$)

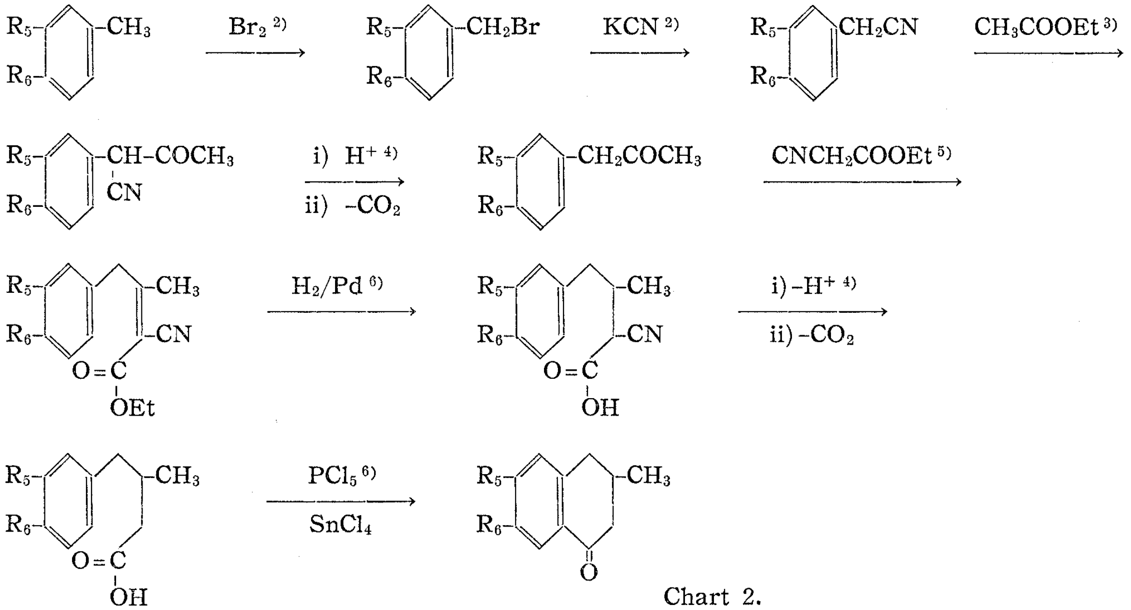

Chart 2.

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2′,3-dimethyl-(V : R_2, :$R_1'=CH_3$, R_1, R_3, R_4, R_5, R_6, R_1', $R_3'=H$) 3,6-dimethyl-(V : R_2, $R_5=CH_3$, R_1, R_3, R_4, R_6, R_1', R_2', $R_3'=H$) and 3,7-dimethyl-(V : R_2, $R_6=CH_3$, R_1, R_3, R_4, R_5, R_1', R_2', $R_3'=H$)-1-phenylnaphthalene.

iii) 5-Methyl-(I : $R_4=CH_3$, R_1, R_2, R_3, R_5, $R_6=H$) and 6-methyl-(I : $R_5=CH_3$, R_1, R_2, R_3, R_4, $R_6=H$)-α-tetralones were condensed with bromobenzene to yield 5-methyl-(V : $R_4=CH_3$, R_1, R_2, R_3, R_5, R_6, R_1', R_2', $R_3'=H$) and 6-methyl-(V : $R_5=CH_3$, R_1, R_2, R_3, R_4, R_6, R_1', R_2', $R_3'=H$)-1-phenylnaphthalene, respectively.

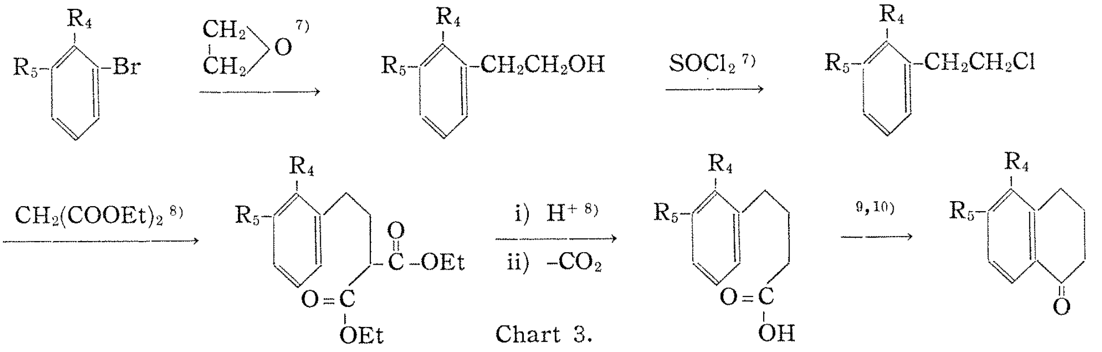

Chart 3.

iv) 7-Methyl-α-tetralone (I : $R_6=CH_3$, $R_1\sim R_5=H$) was employed to react with bromobenzene to afford 7-methyl-1-phenylnaphthalene (V : $R_6=CH_3$, $R_1\sim R_5$, $R_1'\sim R_3'=H$).

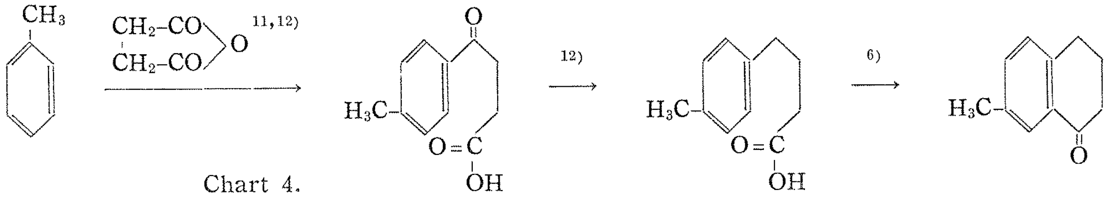

Chart 4.

v) 2-Methyl-α-tetralone[6] (I : $R_1=CH_3$, $R_2\sim R_6=H$) was condensed with *m*-bromotoluene (II : $R_2'=CH_3$, R_1', $R_3'=H$) to give 2,3′-dimethyl-1-phenylnaphthalene (V : R_1, $R_2'=CH_3$, $R_2\sim R_6=H$). In this case, organolithium condensation was employed instead of the Grignard reaction, which was shown to be useful for the synthesis of the sterically hindered alkylated 1-phenylnaphthalenes.

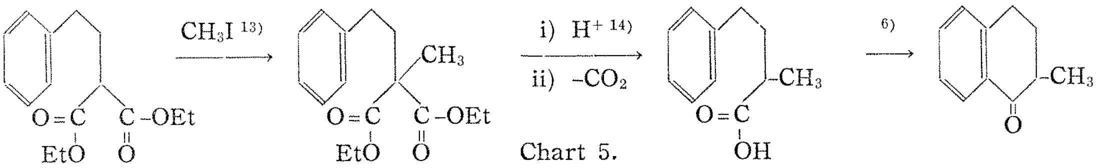

Chart 5.

vi) 4,6-Dimethyl-α-tetralone[6] (I : R_2, $R_5=CH_3$, R_1, R_2, R_4, $R_6=H$) was subjected to condensation with bromobenzene to yield 4,6-dimethyl-1-phenylnaphthalene (V : R_3, R_5 $=CH_3$. R_1, R_2, R_4, R_6, $R_1'\sim R_3'=H$).

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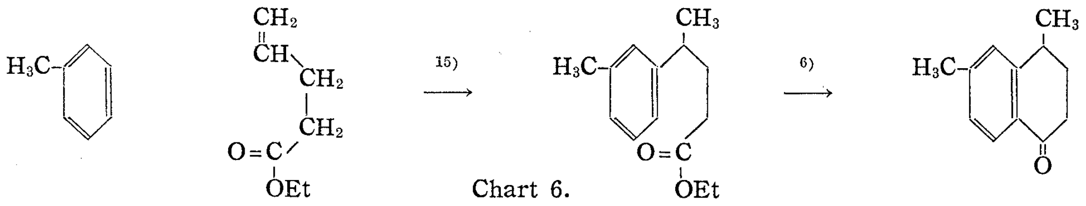

Chart 6.

vii) 4,7-Dimethyl-α-tetralone[6] (I : $R_3, R_6=CH_3$, $R_1, R_2, R_4, R_6=H$) was reacted with bromobenzene to afford 4,7-dimethyl-1-phenylnaphthalene (V : $R_3, R_6=CH_3$, $R_1, R_2, R_4, R_5, R_1'\sim R_3'=H$).

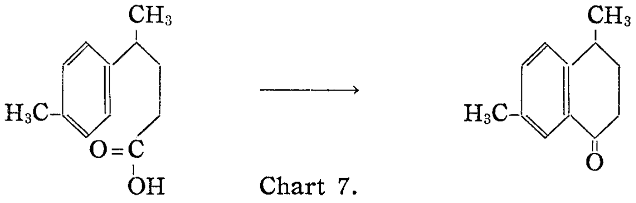

Chart 7.

Benzotrifuroxan was recently employed for characterization of aromatic hydrocarbons by the formation of complex compounds.[17] Some of the phenylnaphthalene derivatives were characterized as the yellow crystalline benzotrifuroxan complex compounds.

Experimental

The general procedure of condensation for α-tetralone and bromobenzene components and the subsequent processes to obtain alkylated 1-phenylnaphthalene derivatives are given as follows.

1) An ethereal solution (15 cc.) of α-tetralone (12 g.) was slowly added to a solution of phenylmagnesium bromide, prepared from Mg (2.2 g.) and bromobenzene (15 g.) in abs. Et_2O (30 cc.). After refluxing for 30 min., the reaction mixture was decomposed by the addition of dil. HCl and ice. The ethereal layer was separated and distilled off on a bath, and the residue was extracted with Et_2O. To the ethereal extract, after removing the solvent, Ac_2O (about 10 cc.) was added. The mixture was warmed at 100° for 30 min., and the reaction mixture was evaporated under reduced pressure.

The yellowish residue mixed with S (1.5 g.) was subjected to dehydrogenation by heating in a metal bath for 30 min. at 200~250°. The reaction mixture was chromatographed to separate S on alumina column using hexane or petr. ether as the developing solvent, and the product, 1-phenylnaphthalene, was finally purified by distillation.

2) To *o*-tolyllithium prepared from dried *o*-bromotoluene (5 g.) and Li (0.47 g.) in the usual method an ethereal solution (20 cc.) of 3-methyl-α-tetralone (4.2 g.) was added dropwise, and the mixture was refluxed for 1 hr. under the stream of N_2 gas. The resulted complex compound was decomposed with dil. H_2SO_4 and ice, and the subsequent treatment for dehydration and dehydrogenation was carried out in the same way as mentioned above.

The analytical figures of alkylated 1-phenylnaphthalene derivatives newly prepared in the present study, and the physical properties of new compounds and some of known compounds of this series are tabulated below.

Formation of Benzotrifuroxan Complex Derivatives

Benzotrifuroxan[17]

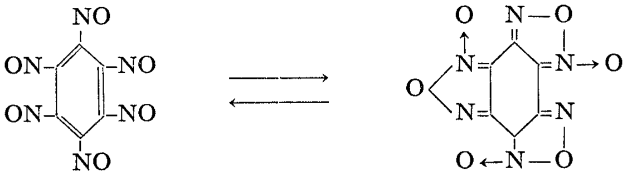

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Table I.

Elemental Analysis of Mono- and Di-methyl-1-phenylnaphthalenes

Anal. Calcd. for $C_{17}H_{14}$: C, 93.53; H, 6.47

Found:	C	H
3-Methyl-1-phenylnaphthalene	93.65	6.46
4-Methyl-1-phenylnaphthalene	93.25	6.32
5-Methyl-1-phenylnaphthalene		
6-Methyl-1-phenylnaphthalene	93.40	6.20
7-Methyl-1-phenylnaphthalene	93.75	6.30

Anal. Calcd. for $C_{18}H_{16}$: C, 93.06; H, 6.94

Found:	C	H
2′,3-Dimethyl-1-phenylnaphthalene	92.93	6.92
3, 6-Dimethyl-1-phenylnaphthalene	93.09	6.94
3, 7-Dimethyl-1-phenylnaphthalene	93.15	6.94
4, 4′-Dimethyl-1-phenylnaphthalene	93.19	7.17
4, 6-Dimethyl-1-phenylnaphthalene	93.05	6.99
4, 7-Dimethyl-1-phenylnaphthalene	92.60	7.41
3′,4′-Dimethyl-1-phenylnaphthalene	92.66	7.29
2, 3′-Dimethyl-1-phenylnaphthalene	92.80	6.71

Physical Properties of Phenylnaphthalene and its Mono- and Di-methyl Derivatives

	m.p.[a] (°C)	b.p. (°C)/mm. Hg
1-Phenylnaphthalene		137∼138/1
2-Methyl-1-phenylnaphthalene		162∼164/3
3-Methyl-1-phenylnaphthalene		141∼143/0.6
4-Methyl-1-phenylnaphthalene		148/0.9
5-Methyl-1-phenylnaphthalene		148/0.9
6-Methyl-1-phenylnaphthalene	59∼60	140∼145/1
7-Methyl-1-phenylnaphthalene		145∼150/1
2′-Methyl-1-phenylnaphthalene	68∼69	136∼137/1
3′-Methyl-1-phenylnaphthalene		140/1
4′-Methyl-1-phenylnaphthalene	52∼54	142∼143/1
2,2′-Dimethyl-1-phenylnaphthalene		129/1.5
2,3′-Dimethyl-1-phenylnaphthalene		145∼146/0.8∼0.9
2′,3-Dimethyl-1-phenylnaphthalene		124/1
3,6-Dimethyl-1-phenylnaphthalene	75∼75.5	195∼200/15
3,7-Dimethyl-1-phenylnaphthalene	47∼48	
4,6-Dimethyl-1-phenylnaphthalene		165∼174/1.7
4,7-Dimethyl-1-phenylnaphthalene		161∼167/2.5
4,4′-Dimethyl-1-phenylnaphthalene	94.5∼95	
3,4′-Dimethyl-1-phenylnaphthalene		

[a] The crystalline products were recrystallized from EtOH.

Yellow leaflets, m.p. 193°, was dissolved in EtOH-AcOH (4:1) and added to the ethanolic solution of phenylnaphthalenes. The complex compounds formed were recrystallized from EtOH or EtOH-AcOH to give yellow crystals.

The benzotrifuroxan compounds of
1-phenylnaphthalene, m.p. 159° (EtOH)
3′-methyl-1-phenylnaphthalene, m.p. 139∼140° (EtOH-AcOH)
4′-methyl-1-phenylnaphthalene, m.p. 134° (EtOH-AcOH)
2-methyl-1-phenylnaphthalene, m.p. 145° (EtOH-AcOH).

The elementary analysis was carried out by the members of Microanalytical Laboratory of this Faculty to whom the authors' thanks are due.

Summary

The 1-phenylnaphthalene derivatives which possess methyl group(s) at the position of 3, 4, 5, 6, 7, 3,2′, 3,6′, 3,7, 4,4′, 4,6, 4,7, 3′,4′, and 2,3′ were prepared by the general procedure involving the Grignard reaction of the α-tetralone derivatives and bromobenzene substituted with methyl group(s) in appropriate position(s).

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