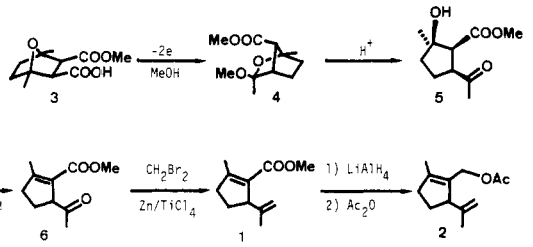
Scheme I



to the protected form 4 of methyl hydroxynepetonate (5) in good yield via Wagner–Meerwein rearrangement. This compound was chosen as a starting material for the present synthesis.

Methyl hydroxynepetonate (5), obtained by acidic hydrolysis of 4,[3] was dehydrated by phosphoryl chloride/pyridine to give a mixture of olefinic isomers. Treatment of the mixture with sodium methoxide in methanol gave a single isomer, 6. The reaction of 6 thus obtained with a reagent consisting of dibromomethane/zinc/titanium tetrachloride[4] afforded the diene 1 in excellent yield. It should be noted that the ester group does not interfere with this carbonyl methylenation reaction, which is not the case if the conventional Wittig methylenation procedure[5] is employed.

Lithium aluminum hydride reduction of 1 followed by acetylation gave 2 in high yield.

Since 1 and 2 can be readily transformed into a variety of iridoid monoterpenes such as matatabiether, neonepetalactone, and so on,[2] the synthesis by the above procedure constitutes a new and efficient route to these interesting substances.[6]

Experimental Section[7]

Methyl (±)-2-Methyl-5-acetylcyclopentene-1-carboxylate (6). To a stirred solution of 1.157 g (5.78 mmol) of methyl 2-hydroxy-2-methyl-5-acetylcyclopentane-1-carboxylate (methyl hydroxynepetonate) (5) in 20 mL of dry pyridine at 0 °C was added dropwise 4 mL (6.58 g, 42.9 mmol) of phosphoryl chloride. After being stirred at room temperature until the starting material disappeared, the reaction mixture was poured into ice water and extracted with dichloromethane. The organic layer was washed successively with dilute HCl, saturated aqueous $NaHCO_3$ solution, and brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to yield 0.984 g (93%) of an oil, GLC analysis of which showed two peaks.[8]

A solution of the above oily mixture (0.110 g, 0.60 mmol) in dry MeOH was stirred with a catalytic amount of sodium methoxide overnight at room temperature under a nitrogen atmosphere. After the solution was neutralized with aqueous AcOH, the solvent was removed in vacuo. The residue was dissolved in water, extracted with dichloromethane, and dried over anhydrous Na_2SO_4. Removal of the solvent gave 0.090 g (82%) of pure 6: IR (neat) 1710, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.90 (m, 1 H), 3.75 (s, 3 H), 2.40–2.70 (m, 2 H), 1.70–2.00 (m, 2 H), 2.25 (s, 6 H, $COCH_3$ and $=CHCH_3$); ^{13}C NMR ($CDCl_3$) δ 210.2 (s), 165.7 (s), 159.6 (s), 126.9 (s), 58.8 (d), 51.1 (q), 39.8 (t), 28.5 (q), 25.9 (t), 16.4 (q). Anal. Calcd for $C_{10}H_{14}O_3$: C, 73.30; H, 8.95. Found: C, 73.50; H, 9.17.

Methyl (±)-Isopropenyl-2-methyl-1-cyclopentene-1-carboxylate (1). To a suspension of Zn dust (0.392 g, 6.00 mmol) and dibromomethane (0.522 g, 3.00 mmol) in 10 mL of freshly distilled dry tetrahydrofuran was added a solution of $TiCl_4$ (2.20 mL of a 1.0 M dichloromethane solution, 2.20 mmol) at room temperature under nitrogen atmosphere. Instantaneous exothermic reaction occurred, and the color of the reaction mixture changed rapidly to dark brown. After the mixture was stirred for 15 min, a solution of 0.182 g (1.00 mmol) of 6 in 3 mL of tetrahydrofuran was added dropwise, and the mixture was stirrred overnight. The mixture was diluted with 10 mL of ether, washed with 20 mL of 1 N HCl and subsequently with 20 mL of brine and finally dried over anhydrous Na_2SO_4. Removal of the solvent gave 0.156 g (94%) of an oil. Spectroscopic data were identical with those reported:[2a] ^{13}C NMR ($CDCl_3$) δ 166.6 (s), 156.5 (s), 148.1 (s), 129.7 (s), 109.2 (t), 53.4 (q), 50.9 (d), 39.4 (t), 28.8 (t), 20.7 (q), 16.4 (q).

(±)-2-(Acetoxymethyl)-3-isopropenyl-1-methylcyclopentene (2). To a stirred suspension of 0.061 g (1.61 mmol) of $LiAlH_4$ in 10 mL of dry ether was added 0.114 g (0.63 mmol) of 1 in 10 mL of dry ether. After 3 h the reaction was quenched with saturated aqueous Na_2SO_4 solution. The mixture was filtered and the organic layer was dried over Na_2SO_4. Removal of the solvent gave an oily alcohol. The alcohol was dissolved in 20 mL of acetic anhydride and 4 drops of pyridine was added. The mixture was kept overnight at room temperature, then poured into water, and stirred. The mixture was extracted with ether and the organic layer was washed with water, saturated aqueous $NaHCO_3$ solution, and brine. Removal of the ether left 0.119 g (97%) of the acetate 2. Spectroscopic data were identical with those reported:[2b] ^{13}C NMR ($CDCl_3$) δ 171.0 (s), 147.6 (s), 141.2 (2 s), 110.8 (t), 59.5 (t), 48.0 (d), 37.8 (t), 27.9 (t), 20.8 (q), 18.9 (q), 14.1 (q).

Registry No. (±)-1, 73136-32-0; (±)-2, 73136-33-1; (±)-5, 73136-34-2; (±)-6, 73089-87-9; methyl 2-methyl-5-acetyl-2-cyclopentene-1-carboxylate, 73089-88-0; methyl 2-methylene-5-acetylcyclopentanecarboxylate, 73089-89-1.

(4) K. Takai, Y. Hotta, K. Oshima, and H. Nozaki, *Tetrahedron Lett.*, 2417 (1978).

(5) Attempted Wittig methylenation of 6 required preparative GLC separation and gave 1 only in 22% yield.

(6) Financial support of this work was provided by a Grant-in-Aid for Scientific Research from the Ministry of Education of Japan (No. 347074) (to M.K.) and by the Kawakami Foundation (to T.A.).

(7) IR spectra were determined with a Shimadzu IR-27 spectrometer. ^1H NMR spectra were measured with Varian EM-360 and EM-390 spectrometers and ^{13}C NMR spectra with a Varian CFT 20 spectrometer. Chemical shifts are given with reference to internal tetramethylsilane. GLC analyses were conducted with a PEG 20 M column (1 m) at 150 °C.

(8) Preparative LC separation [SiO_2; PhH/AcOEt (4:1) as eluant] gave pure 6 and another component in a ratio of 85:15. NMR spectral analyses of the latter enabled us to estimate that it was a mixture of methyl 2-methyl-5-acetyl-2-cyclopentene-1-carboxylate [^1H NMR δ 5.38 (1 H, m); ^{13}C NMR δ 125.6 (d)] and methyl 2-methylene-5-acetylcyclopentanecarboxylate [^1H NMR δ 5.02 and 5.10 (1 H each, both q of 2.3-Hz spacing); ^{13}C NMR δ 108.8 (t)] in a ratio of 4:3 (^1H NMR assay).

Cyclization–Rearrangement of Alkylstyrenes. 1. A. 1-Phenyl-1-pentene and Homologues. B. A Short Synthesis of Calamenene

Francis E. Condon* and David L. West

Department of Chemistry, The City College of the City University of New York, New York, New York 10031

Received August 8, 1979

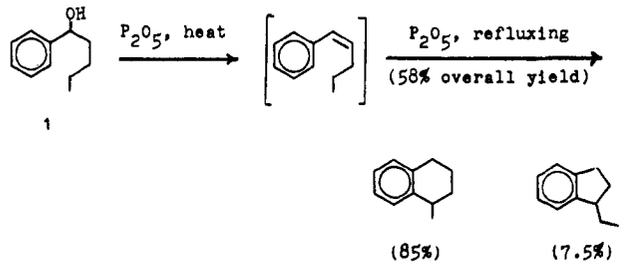
The preparation of 1,2,3,4-tetrahydronaphthalenes (tetralins) and indans by cyclodehydration of alcohols[1] or by acid-catalyzed ring closure of arylalkenes having a rationally placed double bond (e.g., 5-aryl-1- or -2-pentenes)[1c,2] is well-known. In pioneer work in this area, however, Bogert and co-workers obtained only polymer and

(1) (a) M. T. Bogert and D. Davidson, *J. Am. Chem. Soc.*, **56**, 185 (1934); (b) M. T. Bogert, D. Davidson, and P. M. Apfelbaum, *ibid.*, **56**, 959 (1934); (c) R. O. Roblin, Jr., D. Davidson, and M. T. Bogert, *ibid.*, **57**, 151 (1935); (d) D. Price, D. Davidson, and M. T. Bogert, *J. Org. Chem.*, **2**, 540 (1937).

(2) (a) I. Oka, T. Urasaki, T. Shima, and W. Funakoshi, German Offen. 2 242 777 (1973); *Chem. Abstr.*, **79**, P126152 (1973); (b) S. L. Thompson, U.S. Patent 3 775 497 (1973); *Chem. Abstr.*, **80**, P47705 (1974); (c) I. Oka, T. Urasaki, M. Ogasawara, and T. Shima, Japanese Kokai **73** 75 557 (1973); *Chem. Abstr.*, **80**, 70602 (1974); (d) T. F. Wood, W. M. Easter, Jr., M. S. Carpenter, and J. Ariglione, *J. Org. Chem.*, **28**, 2248 (1963).

0022-3263/80/1945-2006$01.00/0

Scheme I



no tetralin from attempted sulfuric acid catalyzed cyclodehydration of 1-phenyl-1-pentanol.[1c] More recently, in a study of the action of phosphorus pentoxide on a series of β-alkylstyrenes at elevated temperatures, Dumontet[3] found that 1-phenyl-1-pentene gave 46% of a saturated isomer with characteristics "le font assimiler au phenylcyclopentane".

We have reinvestigated the action of phosphorus pentoxide on 1-phenyl-1-pentene, as it seemed unlikely it would give phenylcyclopentane under such treatment. An isomer fraction with characteristics similar to those reported by Dumontet, and obtained in 48% yield, was found to be largely (89%) 1-methyltetralin and 1-ethylindan (9%).

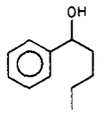
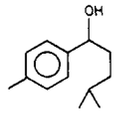
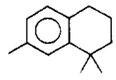
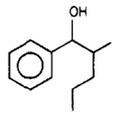
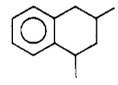
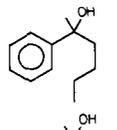
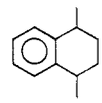
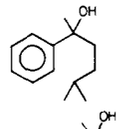
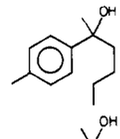
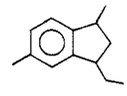
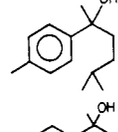
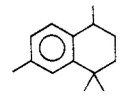
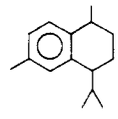
In an experiment comprising P_2O_5-catalyzed dehydration of 1-phenyl-1-pentanol (accompanied by ether formation) and further heating with fresh P_2O_5, without separation of 1-phenyl-1-pentene from the ether formed, we have obtained the bicyclic products in 58% overall yield from the alcohol (Scheme I). Evidently the ether underwent acid-catalyzed cleavage and furnished additional styrene under these conditions.[4]

This cyclization–rearrangement of alkylstyrenes appears to have synthetic utility as one step in a new route to certain indans, tetralins, naphthalenes, and related compounds. In an exploration of its scope and utility, we have carried out the transformations summarized in Table I.[5] (For details of the procedure, the Experimental Section should be consulted.)

These examples demonstrate that the process is broadly applicable. Fair to good yields of cyclization products were obtained from benzyl alcohols via acid-catalyzed dehydration followed by heating the resulting alkylstyrene (or alkylstyrene–benzyl ether mixture) at its boiling point with phosphorus pentoxide. Coupled with modern chromatographic separation techniques, the process could provide a shortcut to an intermediate for synthesis of more complex substances.

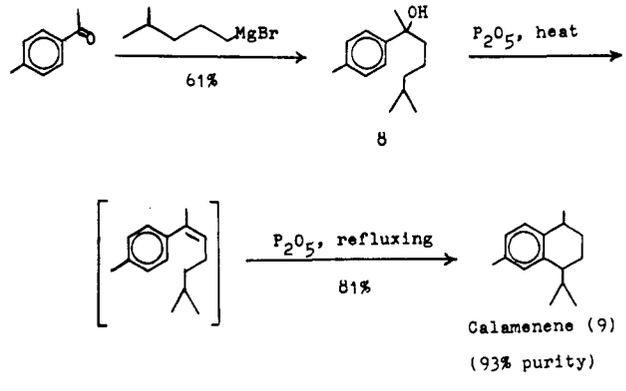
Cyclization was accompanied by some polymerization, as had been observed earlier.[1c,3] The cyclization products were separated from polymer by distillation at reduced pressure and were examined by GLC and NMR spectroscopy. They were usually complex mixtures, with the expected tetralin and indan being the major components. Confirmatory evidence for the structure of the major component (Table I) was obtained in most cases by catalytic dehydrogenation to a substituted naphthalene-rich mixture, which was separated by fractional distillation and in some cases by small-scale preparative GLC into concentrates which were examined by GLC and NMR spectroscopy. In some cases, a picrate of the substituted naphthalene was prepared.

Table I. Cyclization–Rearrangement of Alkylstyrenes

source alcohol no.	source alcohol formula	procedure[a]	cyclization product yield,[b] %	cyclization product major comp	cyclization product purity by GLC, %
1		A (B)	34 (58)		89 (85)
2		A (B)	49 (72)		(73)[c]
3		A	27[d]		67
4		A	65		60
5		B	50		95
6		A	72		48
7		A	71		50
8		B	81		93

[a] See Experimental Section for details of procedure. [b] Overall yield of cyclization–rearrangement products from the source alcohol shown. [c] Composition not determined for procedure A. [d] Overall yield impaired by much ether formation during dehydration of the alcohol.

Scheme II



In a further test of its scope and utility, we have used the process to synthesize the sesquiterpene calamenene (9) [*cis*- and *trans*-1,6-dimethyl-4-(1-methylethyl)-1,2,3,4-tetrahydronaphthalenes], in accordance with Scheme II, that is, in two steps from *p*-methylacetophenone. Much longer syntheses of calamenene have been described.[6]

(3) J. Dumontet, *C. R. Hebd. Seances Acad. Sci.*, **234**, 1173 (1952).

(4) Recently in this laboratory, Mr. Conrad Santini has obtained a good yield of cyclization product from an ether isolated as a dehydration product of 5-methyl-1-(4-methylphenyl)-1-hexanol. The ether [bp 195–200 °C (2 torr), 31.8 g] was refluxed 3 h with 1 g of P_2O_5, magnetic stirring, and removal of water. There was recovered 23.3 g (76.5%) of cyclization product, largely 4-(1-methylethyl)-6-methyl-1,2,3,4-tetrahydronaphthalene, bp 103 °C (2.6 torr).

(5) See also F. E. Condon and G. Mitchell, *J. Org. Chem.*, following paper in this issue.

The calamenene obtained in this way gave an NMR spectrum that was qualitatively identical with a recorded spectrum of calamenene from Cade oil (71% trans isomer)[7] but which indicated a trans/cis isomer ratio near 2:1. These isomers are not separable by chromatography.[7] Gas chromatography of our calamenene revealed about 7% of an impurity with a shorter retention time, which was not identified. An isomeric indan or benzsuberane[8] are possibilities.

A carbonium ion mechanism is probably involved.[1d] The alkylstyrene may be converted first to a benzylic carbonium ion by the phosphorus pentoxide, aided by a trace of water as a proton source. At the high temperature involved, the benzylic carbonium ion may rearrange by a series of 1,2 hydride shifts to a carbonium ion that can effect ring closure by way of an intramolecular Friedel–Crafts-type alkylation so that a five- or six-membered ring may be formed. In the case of styrenes from 8, a seven-membered ring compound, a benzsuberane,[8] may be formed also. Also, because of the high temperature involved, isomerization is given a kinetic advantage over entropy-decreasing polymerization, which is favored by low temperatures.

Experimental Section

Materials and Equipment. Reagents used in syntheses were commercially available pure-grade materials and were used without prior treatment unless otherwise stated. NMR spectra were obtained on Varian A-60 and Jeolco MH-100 instruments. Gas chromatographic analyses were done with a Varian A-90P instrument equipped with a 460 × 0.635 cm stainless-steel column packed with 25% SE-30 on 45/60-mesh A/W dmcs-treated (silanized) Chromosorb P.

Preparation of Alcohols 1–7. The alcohols were prepared from the appropriate Grignard reagent and aldehyde or ketone by standard procedures. In some cases, examination of the prepared alcohol by NMR spectroscopy revealed the presence of unchanged aldehyde or ketone. This was removed by treatment with semicarbazide, filtration to remove precipitated semicarbazone, and redistillation. **1-Phenyl-1-pentanol (1)** was obtained from *n*-butylmagnesium bromide and freshly distilled benzaldehyde; bp 95–101 °C (2 torr) [lit.[1c] bp 137 °C (21 torr)]. **4-Methyl-1-(4-methylphenyl)-1-pentanol (2)** was obtained from (3-methylbutyl)magnesium bromide and freshly distilled 4-methylbenzaldehyde; bp 110–125 °C (5 torr) [lit.[9] bp 147 °C (15 torr)]. **2-Methyl-1-phenyl-1-pentanol (3)** was obtained from (1-methylbutyl)magnesium bromide and freshly distilled benzaldehyde; bp 100–118 °C (0.9 torr) (lit.[10] boiling point not given). **2-Phenyl-2-hexanol (4)** was obtained from *n*-butylmagnesium bromide and acetophenone; bp 104–115 °C (1.7 torr) [lit.[11] bp 129–130 °C (4 torr)]. **4-Methyl-2-phenyl-2-pentanol (5)** was obtained from isobutylmagnesium bromide and acetophenone; bp 76–108 °C (1.2 torr) (with some decomposition) [lit.[12] bp 112–114 °C (12 torr)]. **2-(4-Methylphenyl)-2-hexanol (6)** was obtained from *n*-butylmagnesium bromide and *p*-methylacetophenone: bp 100–140 °C (2 torr) dec; NMR (CCl_4) δ 7.12 (d, 2, J = 8 Hz, C_2 ArH), 6.92 (d, 2, J = 8 Hz, C_3 ArH), 2.17 (2 s, 4, $ArCH_3$ and OH), 1.64 (t, 2, J = 7 Hz, C_3 H), 1.40 (s, 3, C_1 H), 1.0–1.1 (complex, 4, C_4 H and C_5 H), 0.80 (t, 3, J = 7 Hz, C_6 H). **5-Methyl-2-(4-methylphenyl)-2-hexanol (7)** was obtained from (3-methylbutyl)magnesium bromide and *p*-methylacetophenone: bp 104–124 °C (6 torr) dec; NMR (CCl_4) δ 7.26 (d, 2, J = 8 Hz, C_2 ArH), 6.96 (d, 2, J = 8 Hz, C_3 ArH), 3.14 (br s, 1, OH), 2.18 (s, 3, $ArCH_3$), 1.72 (t, 2, J = 7 Hz, C_3 H), 1.44 (s, 3, C_1 H), 0.9–1.3 (complex, 3, C_4 H and C_5 H), 0.78 (d, 6, J = 7 Hz, C_6 H).

Cyclization Procedures. Experiments were carried out on a scale of 0.13–1.26 mol. **Procedure A.** The alcohol was dehydrated by heating it, neat, with a small amount of *p*-toluenesulfonic acid, while the water and some organic material were removed by distillation. When the temperature of the liquid rose to 150–160 °C and vigorous bumping set in, the distilled organic material was returned to the flask, and the whole was distilled under reduced pressure. Generally, a mixture of styrene isomers was obtained, distilling in the range 100–150 °C at 15–20 torr. Iodine was used as a catalyst for dehydration of some of the tertiary alcohols, in which case zinc dust was added prior to distillation for recovery of the styrenes. The styrene was heated at its boiling point with about 5% by weight of phosphorus pentoxide for several hours to effect cyclization. The progress of the reaction was monitored by NMR spectroscopy, and additional P_2O_5 was added as necessary. When cyclization appeared complete, as evidenced by the disappearance of vinyl proton signals in the NMR spectrum, the cyclization product was recovered by distillation under reduced pressure.

Procedure B. Yields of styrenes in the above procedure were sometimes poor, especially from secondary alcohols, evidently because of formation of a substituted benzyl ether, which appeared as a high-boiling residue after distillation of the styrene. A better overall yield of cyclization product was obtained in those cases by a simplified procedure. In this procedure, phosphorus pentoxide was used as the catalyst for dehydration of the alcohol, which was carried out as described for procedure A. Some of the phosphoric acid, which separated as a lower layer in the flask containing the crude dehydration product, was removed by means of a Pasteur pipet. Fresh P_2O_5 was added, and the crude dehydration product, largely a mixture of styrene isomers and by-product ether, was refluxed as before, with a provision for removal of additional water from the top of an air-cooled reflux condenser. Evidently the benzyl ether underwent acid-catalyzed cleavage and furnished additional styrene under these conditions.[4] (Compare the results of experiments with 1 and 2, Table I.) Severe bumping was encountered in some of these experiments, caused by droplets of water impinging on the surface of the boiling organic liquid. Mechanical or magnetic stirring was used to counter this.

Identification of the Major Components of the Cyclization Products (Table I). 1-Methyl-1,2,3,4-tetrahydronaphthalene[1c] (from 1): NMR (neat) δ 0.73 (d, 3, J = 7 Hz, 1-CH_3); catalytic dehydrogenation (10% Pd/C, reflux) gave 1-methylnaphthalene,[1c] picrate mp (picrate) 142–143 °C (lit.[1c] mp 141–142 °C). **1,1,7- or 4,4,6-trimethyl-1,2,3,4-tetrahydronaphthalene**[2d] (from 2): NMR (neat) δ 0.90 (s, 6, 1,1-$(CH_3)_2$), 2.17 (s, 3, 7-CH_3). **1,3-Dimethyl-1,2,3,4-tetrahydronaphthalene**[13] (from 3): the NMR spectrum contained three doublets (J = 7 Hz), a large one at 1.05 ppm, assigned to the protons of the 3-CH_3 group, one at 1.26 ppm, with an intensity a little more than half that of the first, assigned to the 1-CH_3 group of the trans isomer, and one at 1.30 ppm, with an intensity a little less than half that of the first, assigned to the 1-CH_3 group of the cis isomer. Dehydrogenation gave 1,3-dimethylnaphthalene:[14] NMR (CCl_4) δ 6.7–7.6 (complex, 6, Ar H), 2.21 (s, 3, 1-CH_3), 2.06 (s, 3, 3-CH_3). **1,4-Dimethyl-1,2,3,4-tetrahydronaphthalene**[13] (from 4): dehydrogenation gave 1,4-dimethylnaphthalene, mp (picrate) 138–139 °C (lit.[15] mp 139–140 °C). **1,1,3-Trimethylindan**[1a] (from 5): NMR (CCl_4) δ 7.04 (br s, 4, Ar H), 3.20 (m, 1, C_3 H), 2.08 (dd, 1, C_2 H syn to C_3 H, dihedral angle about 10°, $J_{2,3}$ = 7 Hz, $J_{2,2}$ = 13 Hz, H–C–H angle about 112°), 1.52 (dd, 1, C_2 H gauche to C_3 H, dihedral angle about 110°, $J_{2,3}$ = 2–3 Hz),[16] 1.08–1.40 (complex, 9, 1,1-$(CH_3)_2$ and 3-CH_3). **3-Ethyl-1,5-dimethylindan** (from 6): the gas chromatogram of the cyclization

(6) (a) F. Sorm, K. Veres, and V. Herout, *Collect. Czech. Chem. Commun.*, 18, 106 (1953); (b) A. Heymes, M. Plattier, and P. Teisseire, *Recherches*, 19, 214 (1974); *Chem. Abstr.*, 83, 43519 (1975).

(7) N. H. Anderson, D. D. Syrdal, and C. Graham, *Tetrahedron Lett.*, 905 (1972).

(8) (a) T. C. Joseph and Sukh Dev, *Tetrahedron Lett.*, 216 (1961); (b) B. N. Joshi, R. Sichadri, K. K. Chakravarti, and S. C. Bhattacharyya, *Tetrahedron*, 20, 2911 (1964).

(9) N. P. Bau-Hoi, N. D. Xuong, and B. K. Diep, *J. Org. Chem.*, 26, 1673 (1961).

(10) Y. Deux, *C. R. Hebd. Seances Acad. Sci.*, 213, 209 (1941).

(11) J. B. Conant and G. H. Carlson, *J. Am. Chem. Soc.*, 54, 4048 (1932).

(12) H. Pines and J. T. Arrigo, *J. Am. Chem. Soc.*, 79, 4958 (1957).

(13) J. P. Quillet and J. Dreux, *Bull. Soc. Chim. Fr.*, 645 (1966).

(14) E. de Barry Barnett and F. G. Sanders, *J. Chem. Soc.*, 434 (1933).

(15) G. Darzens, *C. R. Hebd. Seances Acad. Sci.*, 190, 1562 (1930).

(16) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds", Wiley, New York, 1963, p 79.

product showed six peaks (peak no., relative retention time, percent of total, and probable identity given): 1, 1.00, 48.4, 3-ethyl-1,5-dimethylindan; 2, 1.10, 6.8, unknown; 3, 1.19, 4.0, unknown; 4, 1.31, 26.0, 1,4,6-trimethyltetralin and *x,y,z*-trimethyltetralin; 5, 2.26, 4.2, *x,y,z*-trimethylnaphthalene; 6, 2.38, 10.0, 1,4,6-trimethylnaphthalene. After dehydrogenation GC showed the following (peak no., percent of total, and probable identity given): 1, 46.3, 3-ethyl-1,5-dimethylindan; 2, 6.3, unknown; 3, 3.7, unknown; 4, 0.0, trimethyltetralins; 5, 13.5, *x,y,z*-trimethylnaphthalene; 6, 30.2, 1,4,6-trimethylnaphthalene. Distillation of the dehydrogenation product gave a first fraction that was 69.3% "3-ethyl-1,5-dimethylindan" (peak no. 1). A sample collected from the gas chromatograph gave the following NMR (CCl_4): δ 7.00 (br s, 3, Ar H), 2.58 (m, 2, C_1 H and C_3 H), 2.18 (s, 3, 5-CH_3), 1.52 (m, 2, C_2 H), 1.0–1.3 (m, 2, CH_2CH_3), 1.20 (d, 3, 1-CH_3), 0.84 (t, 3, CH_2CH_3). **1,4,4,6-Tetramethyl-1,2,3,4-tetrahydronaphthalene**[17] (from **7**). A sample collected from the gas chromatograph gave the following NMR (CCl_4): δ 6.7–7.0 (complex, 3, Ar H), 2.70 (m, 1, C_1 H), 2.20 (s, 3, 6-CH_3), 1.3–1.9 (complex, 4, C_2 H and C_3 H), 1.24 (s, 3, 4-CH_3 trans to 1-CH_3), 1.20 (d, 3, 1-CH_3), 1.18 (s, 3, 4-CH_3 cis to 1-CH_3).

Synthesis of Calamenene (9). 4-Methyl-1-pentanol was prepared from isobutylmagnesium bromide and ethylene oxide as described in the literature.[18] It was converted to 4-methyl-1-bromopentane[19] (**10**) by the sodium bromide–sulfuric acid method.[20] The Grignard reagent prepared in ether from 14.6 g (0.60 mol) of Mg and 99.8 g (0.60 mol) of **10** was treated with 80.3 g (0.60 mol) of *p*-methylacetophenone. Worked up in the usual way, the reaction mixture gave 80.7 g (61%) of 6-methyl-2-(4-methylphenyl)-2-heptanol (**8**) distilling with some decomposition in the range 99–137 °C at 3.5 torr: NMR (neat) δ 7.30 (d, 2, J = 8 Hz, C_2 and C_6 Ar H), 7.00 (d, 2, J = 8 Hz, C_3 and C_5 Ar H), 3.42 (br s, 1, OH), 2.22 (s, 3, Ar CH_3), 0.9–1.9 (complex, 7, C_3 H, C_4 H, C_5 H, and C_6 H), 1.50 (s, 3, C_1 H), 0.80 (d, 6, J = 6 Hz, C_7 H). A 62.3-g sample of this alcohol (**8**), containing some dehydration product, was heated with 5 g of P_2O_5, and 4.5 mL of water was removed by distillation. The residual mixture was refluxed for 2 h and then distilled under reduced pressure. After a 3.1-g forerun, material boiling at 130–168 °C at 22 torr was collected and redistilled to give 45.9 g (81%) of **9** distilling at 127–158 °C at 27 torr. GLC analysis revealed about 7% of an impurity with a shorter retention time, which accounts for the wide range in the boiling point. For further analytical details, see the text.

Acknowledgment. George Mitchell[5] carried out the work with alcohols **5**, **6**, and **7**. The senior author is indebted to Berta Anderes, Allen W. Gin, Pi-Chun Jen, Yen-Ping Liu, and Robert Weinberger for literature searches on indans and naphthalenes.

Registry No. **1**, 583-03-9; **2**, 73177-66-9; **3**, 73177-67-0; **4**, 4396-98-9; **5**, 4423-54-5; **6**, 73177-68-1; **7**, 73177-69-2; **8**, 73177-70-5; *cis*-**9**, 72937-55-4; *trans*-**9**, 73209-42-4; **10**, 626-88-0; butyl bromide, 109-65-9; benzaldehyde, 100-52-7; 3-methylbutyl bromide, 107-82-4; 4-methylbenzaldehyde, 104-87-0; 1-methylbutyl bromide, 107-81-3; acetophenone, 98-86-2; isobutyl bromide, 78-77-3; *p*-methylacetophenone, 122-00-9; 1-methyl-1,2,3,4-tetrahydronaphthalene, 1559-81-5; 1-methylnaphthalene picrate, 2798-40-5; 1,1,7-trimethyl-1,2,3,4-tetrahydronaphthalene, 22824-34-6; *trans*-1,3-dimethyl-1,2,3,4-tetrahydronaphthalene, 39172-86-6; *cis*-1,3-dimethyl-1,2,3,4-tetrahydronaphthalene, 39172-85-5; 1,3-dimethylnaphthalene, 575-41-7; 1,4-dimethyl-1,2,3,4-tetrahydronaphthalene, 4175-54-6; 1,4-dimethylnaphthalene, 571-58-4; 1,1,3-trimethylindan, 2613-76-5; 3-ethyl-1,5-dimethylindan, 73177-71-6; 1,4,6-trimethyltetralin, 22824-32-4; trimethyltetralin, 72843-02-8; trimethylnaphthalene, 28652-77-9; 1,4,6-trimethylnaphthalene, 2131-42-2; 1,4,4,6-tetramethyl-1,2,3,4-tetrahydronaphthalene, 1634-12-4; 4-methyl-1-pentanol, 626-89-1.

(17) (a) J. Colonge and L. Pichat, *C. R. Hebd. Seances Acad. Sci.*, **226**, 673 (1948); (b) M. S. Carpenter, W. M. Easter, Jr., and T. F. Wood, U.S. Patent 2 815 382 (1957); *Chem. Abstr.*, **52**, P54766 (1958).

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

(19) A. Buelens, *Recl. Trav. Chim. Pays-Bas*, **28**, 113 (1908); *Chem. Abstr.*, **3**, 1746 (1909).

(20) O. Kamm and C. S. Marvel in "Organic Syntheses", Collect. Vol. I, A. H. Blatt, Ed., 2nd ed., Wiley, New York, 1941, p 29.

Cyclization–Rearrangement of Alkylstyrenes. 2. Applications to the Synthesis of Some Naphthalene and Phenanthrene Derivatives

Francis E. Condon* and George Mitchell

Department of Chemistry, The City College of the City University of New York, New York, New York 10031

Received August 8, 1979

It has been shown that alkylstyrenes, upon refluxing with phosphorus pentoxide, undergo a facile rearrangement with cyclization to produce mixtures consisting largely of derivatives of indan and 1,2,3,4-tetrahydronaphthalene.[1] Alkylstyrenes are readily available by dehydration of easily prepared benzyl alcohols. The best yields of cyclization–rearrangement products are obtained, however, if the alkylstyrene is not isolated. A mixture of dehydration products, including a benzyl ether, obtained by heating a benzyl alcohol with a small amount of phosphorus pentoxide, is refluxed with fresh phosphorus pentoxide to effect cyclization. Evidently the ether undergoes acid-catalyzed cleavage and furnishes additional alkylstyrene under these conditions.

The cyclization–rearrangement of alkylstyrenes appears to have promise as a new tool for the synthesis of certain indans, tetralins, naphthalenes, and related compounds, from readily available, relatively inexpensive starting materials. The reactions can be carried out on a large scale, and the procedures are simple. The products are usually mixtures, but they are separable in principle by use of modern chromatographic techniques.

In this paper are described short syntheses of 1,5-dimethylnaphthalene and 1-methylphenanthrene which make use of cyclization–rearrangement of an alkylstyrene as a crucial step. These compounds were chosen to test the utility of the method because they are crystalline solids and were expected to be easily separable from liquid by-products by filtration and purification by recrystallization from a solvent.

1,5-Dimethylnaphthalene was synthesized from 2-methylbenzaldehyde in 15% overall yield in accordance with Scheme I. Essentially three steps are involved, since the alkylstyrene is not isolated. The method compares favorably in ease and number of operations with previously reported syntheses of 1,5-dimethylnaphthalene.[2]

1-Methylphenanthrene was synthesized from 1-bromonaphthalene in three steps and 23% overall yield in accordance with Scheme II. The method compares favorably in ease and number of operations with Haworth's six-step synthesis from naphthalene.[3]

In a similar fashion, we have obtained 1-methylnaphthalene in 95% purity and 35% overall yield from 1-phenyl-1-pentanol and 1,4-dimethylnaphthalene in 99% purity and 11% overall yield from 2-phenyl-2-hexanol by catalytic dehydrogenation of cyclization–rearrangement products described earlier.[1] These liquid naphthalene derivatives were separated by distillation from other components of the reaction mixtures, and the yields were

(1) F. E. Condon and D. L. West, *J. Org. Chem.*, previous paper in this issue.

(2) (a) V. Vesely and F. Stursa, *Collect. Czech. Chem. Commun.*, **3**, 430 (1931); *Chem. Abstr.*, **26**, 721 (1932); (b) A. R. Anderson and W. F. Short, *J. Chem. Soc.*, 485 (1933); (c) R. H. F. Manske and A. E. Ledingham, *Can. J. Res., Sect. B*, **17**, 14 (1939); (d) L. W. Butz, A. M. Gaddis, E. W. J. Butz, and R. E. Davis, *J. Org. Chem.*, **5**, 379 (1940); (e) E. W. J. Butz, *J. Am. Chem. Soc.*, **62**, 2557 (1940); (f) G. G. Eberhardt, U.S. Patent 3 244 758 (1966); *Chem. Abstr.*, **64**, 19517 (1970); (g) P. Canonne and A. Regnault, *Can. J. Chem.*, **47**, 2837 (1969).

(3) R. D. Haworth, *J. Chem. Soc.*, 1125 (1932).

0022-3263/80/1945-2009$01.00/0