Relative Migratory Aptitudes of the Methyl and Ethyl Groups in a σ Complex Intermediate[1]

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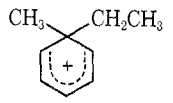
4-Ethyl-4-methyl-1-keto-1,4-dihydronaphthalene (**2**) was synthesized and subjected to the dienone–phenol rearrangement. The sole identifiable product was that formed by rearrangement of the ethyl group, namely, 3-ethyl-4-methyl-1-naphthyl acetate (**4**). No trace of the isomeric 3-methyl-4-ethyl-1-naphthyl acetate (**5**) could be detected by vpc or nmr. The structure of **4** was strongly suggested by its nmr spectrum and proved by converting it to 1-methyl-2-ethylnaphthalene (**10**), identified by comparison of its vpc and nmr characteristics with those of an independently synthesized specimen and shown by the same means to differ from 1-ethyl-2-methylnaphthalene (**11**) and to contain no detectable amounts of the latter. The investigation accords with previously published observations that ethyl migrates in preference to methyl in structures in which the two groups compete for access to an adjacent electron-pair-deficient carbon atom but contrasts with one report of a preferential methyl migration in another dienone–phenol rearrangement.

Interpretation of observations made in the course of another investigation required information about the relative migratory aptitudes of methyl and ethyl groups in σ complex intermediates of general structure **1**.



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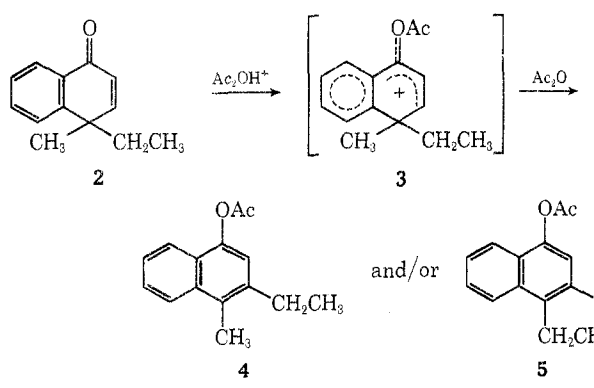
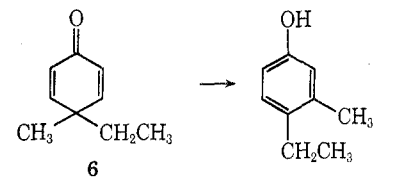
The literature contains a substantial weight of evidence suggesting that the relative rates of alkyl migration in the rearrangement of alkylaromatics follows the order *t*-butyl > *i*-propyl > ethyl > methyl, but a precise interpretation of the data is obstructed by the intervention of intermolecular processes involving all alkyl groups but methyl.[2] Furthermore, although σ complexes seem to be generally accepted as intermediates in the rearrangement of alkylaromatics, no case clearly involving one containing a quaternary carbon atom of type **1** can be identified. The work of Stiles and Meyer[3] showed a strong preference for 1,2 rearrangements of ethyl over methyl in pinacol systems, but steric factors not present in sigma complexes render uncertain the relationship between alkyl migration behavior in pinacol-derived ions and in σ complexes.

The dienone–phenol rearrangement seemed to offer a satisfactory reaction matrix from which to derive the required information, since σ complexes (*e.g.*, **3**) are considered to be intermediates in this process,[2] starting materials such as **2** are accessible synthetically, and the potential products **4** and **5** should be separable and subject to structure proof. If the relative alkyl migratory aptitudes in **3** are those observed in the pinacol rearrangement, as Arnold suggested,[4] then **4** should be the major product. In fact the extensive literature on the dienone–phenol rearrangement contains but two examples of structural systems such as **2**, in which methyl and ethyl groups are in migratory competition, and these are contradictory. Burnell[5] reported only methyl migration in **6**, whereas Miller and Marguiles[6] reported only ethyl migration in **7**. The



2 **3** **4** **5**



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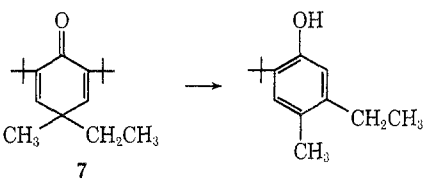

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work hereinafter reported was undertaken in an effort to help resolve the contradiction, as well as to provide data for use in our other investigation.

A satisfactory synthesis of **2** followed the pathway formulated in Scheme I. All products were characterized by analysis and ir and nmr spectroscopy, and the uv spectra of the final three products also were measured. The Experimental Section gives the pertinent data, all of which accord with the structures assigned.

An effort to synthesize **2** by a simpler scheme, patterned after that employed by Arnold[7] for the preparation of the 4,4-dimethyl-1-keto-1,4-dihydronaphthalene (**9**), lower homolog of **2**, failed when γ-ethyl-γ-methyl-butyrolactone reacted with benzene in the presence of aluminum chloride to produce in less

(1) (a) From the doctoral thesis by K. P. Sivaramakrishnan, Carnegie-Mellon University. (b) This work was supported by Grant GP-1948 from the National Science Foundation.

(2) *Cf.* H. J. Shine, "Aromatic Rearrangements," Elsevier, New York, N. Y., 1967, Chapter 1.

(3) M. Stiles and R. P. Meyer, *J. Amer. Chem. Soc.*, **81**, 1497 (1959).

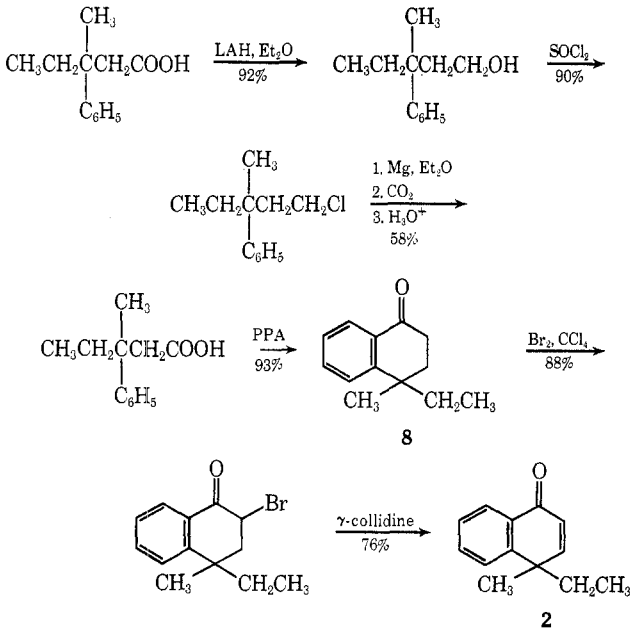
(4) R. T. Arnold and J. S. Buckley, Jr., *ibid.*, **69**, 2322 (1947).

(5) R. H. Burnell, *J. Chem. Soc.*, 1307 (1958).

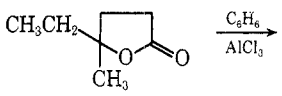
(6) B. Miller and H. Marguiles, *J. Amer. Chem. Soc.*, **87**, 5706 (1965).

(7) R. T. Arnold, J. S. Buckley, Jr., and J. Richter, *ibid.*, **69**, 2322 (1947).

SCHEME I



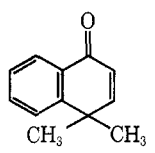
than 40% yield a ketone mixture that contained only about 30% 4-methyl-4-ethyl-1-tetralone (**8**), the intended product. The separation from and identifica-



8 (<12%) + unidentified ketonic material (<30%)

tion of **8** in the product mixture were accomplished by vpc, but its clean separation on a preparative scale could not be effected by convenient means, including fractional crystallization of the semicarbazone mixture. No effort was made to identify the remaining 70% of the isolated product, which appeared as a single peak on the vpc trace, with a shorter retention time than that from **8**. By contrast, the reaction of γ,γ-dimethyl-γ-butyrolactone with benzene afforded, in our hands as in those of Arnold,[7] an essentially homogeneous 4,4-dimethyl-1-tetralone in nearly 60% yield.

The latter was converted to 4,4-dimethyl-1-keto-1,4-dihydronaphthalene (**9**), by procedures reported by Arnold,[7] which employed the same reactions formulated



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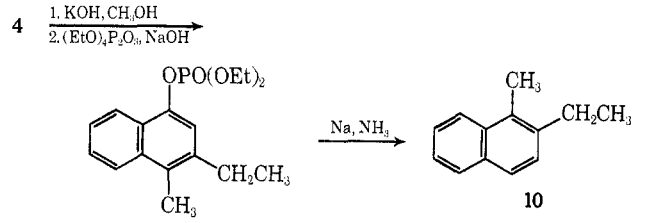
in Scheme I for the conversion of **8** to **2**. This known substance, and its previously reported[7] dienone–phenol rearrangement products, were prepared for comparison of their spectra, especially nmr, with those of **2** and its rearrangement product(s).

Treatment of **2** at room temperature with acetic anhydride containing a little sulfuric acid gave a crystalline product in 92% yield which afforded but one vpc peak. Analysis and spectroscopic properties showed it to be an ethylmethylnaphthyl acetate. The nmr spectrum provided strong evidence for (1) assignment of the ethyl and methyl groups to the 3 and 4 positions, respectively; and (2) establishing the substantial absence of the isomer with the alkyl groups reversed in position. Part of the supporting evidence is based on the observations of Yew, Kurland, and Mair,[8] who showed that nmr signals from methyl groups in the α position of naphthalene in polymethylnaphthalenes usually appear in the τ 7.40–7.50 region, whereas β-methyl signals are normally located in the τ 7.52–7.65 region. The sharp singlet assigned to aromatic methyl in the nmr spectrum of the rearrangement product appeared at τ 7.47 characteristic of α-methyl, and no singlet signal could be detected in the β-methyl region. The remaining nmr evidence was adduced by comparing the spectrum of the rearrangement product from **2** with that of the known 3,4-dimethyl-1-naphthyl acetate, which yielded singlet aromatic methyl signals at τ 7.50 and 7.58, and a singlet assigned to acetate methyl at τ 7.66. The acetate methyl signal from the rearrangement product of **2** appeared at τ 7.65.

Had the crude rearrangement product from **2** contained an appreciable amount of the isomer **5**, the nmr spectrum should have included a sharp singlet signal in the τ 7.55–7.58 region. In fact the spectrum showed only a scarcely discernible shoulder at the base of the τ 7.65 acetate methyl signal which is probably an artifact. However, even if this shoulder is assumed to be a singlet signal owing to a 3-methyl from traces of **5**, this isomer could not comprise more than 3–4% of the crude mixture. The failure of the vpc trace to show more than one sharp peak also suggests that any **5** actually present probably amounted to much less than 3–4% of the whole. The vpc evidence cannot be considered wholly reliable, however, since **5** was not actually prepared, isolated, and shown to be separated from **4** by vpc. Thus, we are able to conclude with some assurance only that the **4**:**5** ratio in crude product from **2** must be at least 25.

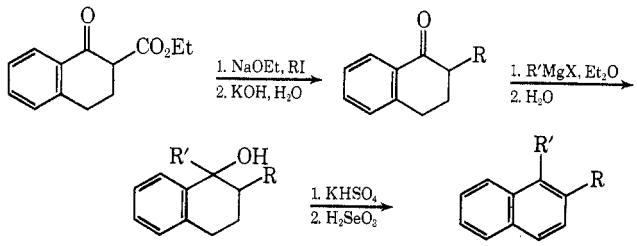
Confirmation of the structure **4** for the sole identifiable product of the dienone–phenol rearrangement of **2** was provided by its conversion through the corresponding naphthol to the diethyl phosphate derivative and then reduction of the latter by sodium and ammonia in tetrahydrofuran[9] to 1-methyl-2-ethylnaphthalene (**10**). The latter was identified with a sample prepared



by independent synthesis and shown to be different from 1-ethyl-2-methylnaphthalene (**11**) by comparison of the nmr spectra and by vpc. The hydrocarbon **10** obtained from the dienone–phenol rearrangement product contained no trace of **11** detectable by nmr or vpc.

Both ethylmethylnaphthalenes **10** and **11** were synthesized from ethyl-1-tetralone-2-carboxylate, as follows.

(8) F. F. Yew, R. J. Kurland, and B. J. Mair, *Anal. Chem.*, **36**, 843 (1964).
(9) G. W. Kenner and N. R. Williams, *J. Chem. Soc.*, 523 (1956).



10, R = C_2H_5; R' = CH_3
11, R = CH_3; R' = C_2H_5

Since nmr data for di- and polyalkylnaphthalenes containing ethyl groups have not hitherto been reported, it may be useful here to observe that the chemical shifts of the alkyl group signals in the nmr spectra of **10** and **11** also accorded with the generalizations of Yew, Kurland and Mair.[8] The 1- (α-) methyl signal from **10** appeared at τ 7.47, whereas that of the 2- (β-) methyl from **11** occurred upfield at τ 7.68. Furthermore, the quartet signal from the ring-bound methylene group of 1- (α-) ethyl in **11** was centered at τ 7.06, while that of the 2- (β-) ethyl in **10** had its center upfield at τ 7.23. The upfield position of the signal from the methylene protons of **10** relative to those of **11** is particularly significant in the light of the observation that the triplet signal from **10** owing to the methyl not joined to the ring is actually centered downfield (τ 8.81) compared with that from **11** (τ 8.89).

This investigation has therefore disclosed only ethyl migration in the postulated σ complex **3** derived from **2**; no methyl migration product could be detected; and nmr data preclude its occurrence to the extent of more than 1 part in 25. This new evidence therefore accords with that of Miller and Marguiles[6] but not with that reported by Burnell;[5] it is also consistent with the results of the quantitative study of the pinacol system reported by Stiles and Meyer.[3] We now consider it reasonable to suppose that the ethyl group will migrate substantially more rapidly than methyl in σ complexes of general structure **1**.

Experimental Section

A Cary automatic recording spectrophotometer was used to measure uv spectra. Some infrared spectra were measured with an Infracord double-beam instrument and some with a Perkin-Elmer 21 spectrophotometer. All nmr spectra were measured with a Varian A-60 spectrometer on samples dissolved in deuteriochloroform with tetramethylsilane as an internal standard. Vapor phase chromatograms were obtained by means of a Wilkens Aerograph Model 328, equipped with a Hy-Fl Model 600D hydrogen flame detector, with nitrogen as the carrier gas. Chemical analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn.

3-Methyl-3-phenyl-1-pentanol.—A solution of 80 g (0.416 mol) of 3-methyl-3-phenylpentanoic acid[10] in 300 ml of anhydrous ether was added to a solution of 18 g (0.515 mol) of lithium aluminum hydride in 300 ml of anhydrous ether at such a rate that the solution refluxed spontaneously. The slurry was stirred for 24 hr and treated with 60 ml of aqueous sodium sulfate; then the ether solution was filtered and dried over anhydrous sodium sulfate. Removal of the ether and distillation of the residue afforded 68.0 g (92%) of 3-methyl-3-phenyl-1-pentanol, a colorless liquid: bp 133° (2 mm); $n^{24.4}D$ 1.5195; ir (neat) 2.95 (OH), 6.23 μ (C_6H_5); nmr τ 2.75 (s, 5, C_6H_5), 6.58 (t, 3, CH_2OH), 7.96–8.55 (m, 4, CH_2CCH_2), 8.72 (s, 3, CCH_3), 9.33 (t, 3, CH_2CH_3).

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 81.04; H, 10.18.

1-Chloro-3-methyl-3-phenylpentane.—A mixture of 135 g (0.757 mol) of 3-methyl-3-phenyl-1-pentanol and 180 g (1.514 mol) of thionyl chloride was stirred and heated at reflux for 24 hr. Removal of volatile material and distillation of the residual brown liquid afforded 132 g (90%) of 1-chloro-3-methyl-3-phenylpentane as a colorless liquid: bp 115–116° (3 mm); $n^{24.4}D$ 1.5182; nmr τ 2.70 (s, 5, C_6H_5), 6.55–7.0 (m, 2, CH_2Cl), 7.67–8.09 (m, 2, CH_2CH_2Cl), 8.20–8.58 (m, 2, CH_2CH_3), 8.72 (s, 3, CCH_3), 9.33, (t, 3, J = 7 Hz, CH_2CH_3).

Anal. Calcd for $C_{12}H_{17}Cl$: C, 73.26; H, 8.71. Found: C, 73.16; H, 8.76.

4-Methyl-4-phenylhexanoic Acid.—A solution of 66.0 g (0.32 mol) of 1-chloro-3-methyl-3-phenylpentane in 500 ml of anhydrous ether was added gradually to 8.99 g (0.37 g-atom) of magnesium turnings being stirred in 250 ml of anhydrous ether, after the reaction was initiated by an iodine crystal. The mixture was boiled for 2 hr after addition of the halide was complete, then treated with 500 g of powdered Dry Ice and stirred for an hour. The mixture was stirred with 5% aqueous sulfuric acid, the aqueous layer was extracted with ether and the latter combined with the original ether solution. The combined ether solution was washed with water, dried over anhydrous sodium sulfate and concentrated. Distillation afforded 39.8 g (58%) of 4-methyl-4-phenylhexanoic acid as a colorless liquid: bp 136° (2 mm); $n^{24.4}D$ 1.5165; ir (neat) 3.6–3.8 (OH), 5.83 (C=O), 6.23 μ (C_6H_5); nmr τ −1.40 (s, 1, COOH), 2.52 (s, 5, C_6H_5), 7.80–8.00 (m, 2, CH_2COOH), 8.10–8.50 (m, 4, CH_2CH_2COOH, CH_2CH_3), 8.71 (s, 3, CH_3), 9.30 (t, 3, J = 7 Hz, CH_2CH_3).

Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.90; H, 8.94.

4-Ethyl-4-methyl-1-tetralone (8).—The procedure was adapted from that reported by Cromwell and Bell[11] for the preparation of 4,4-dimethyl-1-tetralone. A 27.8-g (0.135 mol) sample of 4-methyl-4-phenylhexanoic acid was warmed to 65° and added in one portion to 80 g of polyphosphoric acid which had been preheated to 90°. The mixture was stirred for 5 min, warmed on the steam bath, and then treated with an additional 40 g of polyphosphoric acid. The temperature of the mixture was maintained at 90° while it was stirred for 35 min; then it was cooled and stirred into ice water. When the color of the viscous, water-immiscible oil had completed its change from brown to yellow, it was extracted into three 250-ml portions of ether. The combined ether extracts were washed successively with 300 ml of water, 200 ml of 5% aqueous sodium hydroxide, 300 ml of water, 200 ml of 3% aqueous acetic acid, and finally with 200 ml of water. The solution was dried over anhydrous sodium sulfate, the ether was removed, and the residual oil distilled to yield 23.5 g (93%) of 4-ethyl-4-methyl-1-tetralone (**8**) as a colorless oil: bp 112–113° (4 mm); $n^{24.4}D$ 1.5487; uv max (95% EtOH) 247 mμ (ϵ 12,760), 290 (2145); ir (neat) 5.93 (C=O), 6.23 μ (C_6H_5); nmr τ 1.91 (complex d, 1, J = 7 Hz, C_8H), 2.4–2.8 (m, 3, C_5H, C_6H, C_7H), 7.29 and 7.96 (A_2X_2 mult, 4, $COCH_2CH_2$, respectively), 8.3–8.48 (m, 2, CH_2CH_3), 8.66 (s, 3, CCH_3), 9.15 (t, 3, J = 7.5 Hz, CH_2CH_3).

The 2,4-dinitrophenylhydrazone crystallized from ethyl acetate as reddish needles, mp 183–184°.

Anal. Calcd for $C_{19}H_{20}N_4O_4$: C, 61.94; H, 5.47; N, 15.21. Found: C, 61.75; H, 5.61; N, 15.00.

2-Bromo-4-ethyl-4-methyl-1-tetralone.—A solution of 16 g (0.1 mol) of bromine in 80 ml of carbon tetrachloride was added with stirring over a period of 45 min to a solution of 18.8 g (0.1 mol) of 4-ethyl-4-methyl-1-tetralone in 200 ml of carbon tetrachloride; then the solution was stirred for an additional 30 min. Removal of solvent left 26 g of a viscous oil which afforded 23.41 g (88%) of crystalline 2-bromo-4-ethyl-4-methyl-1-tetralone, mp 73–75°, when triturated with petroleum ether (bp 65–110°). Recrystallization from the same solvent afforded white crystals: mp 74–75°; uv max (95% EtOH), 251 mμ (ϵ 11,200), 294 (1747); ir 5.91 μ (C=O), 6.23 (C_6H_5).

The nmr spectrum revealed the presence of two stereoisomers: τ 2.0 (complex d, 1, J_{78} = 7 Hz, C_8H), 2.4–2.8 (m, 3, C_5H, C_6H, C_7H), 4.90 and 4.99 (two overlapping "X" quartets of ABX systems, 1, $COCHBrCH_2$), 7.08–7.91 (two overlapping "AB" multiplets of ABX systems, 2, $COCHBrCH_2$), 8.20 and 8.31 (two overlapping quartets, 2, J = 7 Hz, CH_2CH_3), 8.61 and 8.63 (both s, 3, CCH_3), 9.07 and 9.19 (two overlapping triplets, 3,

(10) N. Rabjohn, Ed., "Organic Syntheses," Coll. Vol. IV, Wiley, New York, N. Y., 1963, p 97.

(11) N. H. Cromwell and V. Bell, *J. Org. Chem.*, **23**, 789 (1953).

J = 7 Hz, CH_2CH_3). The τ values for CHBr suggested axial bromine for both isomers.[12]

Anal. Calcd for $C_{13}H_{15}BrO$: C, 58.44; H, 5.66; Br, 29.90. Found: C, 58.69; H, 5.87; Br, 29.71.

4-Ethyl-4-methyl-1-keto-1,4-dihydronaphthalene (2).—A solution of 20.037 g (0.075 mol) of 2-bromo-4-ethyl-4-methyl-1-tetralone in 65 ml of γ-collidine was boiled for 75 min, cooled to 0°, and diluted with 300 ml of ether. The solution was filtered free of 12 g of precipitated γ-collidine hydrobromide and washed successively with 5% aqueous hydrochloric acid, 5% aqueous sodium hydroxide, and finally water. The liquid remaining after removal of the ether solvent was distilled to afford 10.54 g (76%) of **2** as a colorless liquid: bp 150° (4 mm); $n^{24.4}$D 1.5649; uv max (95% EtOH) 242 mμ (ϵ 10,820); ir (neat) 6.04 (C=C—C=O), 6.24 μ (C_6H_5); nmr τ 1.82 (doublet of quartets, 1, J_{78} = 8 Hz, C_8H), 2.42–2.83 (m, 3, C_5H, C_6H, C_7H), 3.24 (d, 1, J = 10 Hz, COCH=CH), 3.56 (d, 1, J = 10 Hz, COCH=CH), 8.04 and 8.13 (minor and major overlapping quartets, 2, J = 7 Hz, CH_2CH_3), 8.57 and 8.67 (major and minor singlets, 3, CCH_3), 9.51 (t, 3, J = 7 Hz, CH_2CH_3).

The 2,4-dinitrophenylhydrazone was obtained as scarlet needles from ethyl acetate: mp 195–196°; uv max (95% EtOH) 391 mμ (ϵ 39,270).

Anal. Calcd for $C_{19}H_{18}N_4O_4$: C, 62.98; H, 4.95; N, 15.29. Found: C, 62.51; H, 5.19; N, 15.10.

3-Ethyl-4-methyl-1-naphthyl Acetate (4) by Rearrangement of 2.—After standing for 6 hr at room temperature, a solution of 0.93 g (0.005 mol) of **2** in 17.5 ml of acetic anhydride containing 0.25 g of sulfuric acid was poured, with vigorous stirring, into 150 ml of cold water. Continued stirring converted the original water-insoluble oil into 1.05 g (92%) of a white powder, mp 42–43°. Recrystallization from petroleum ether (bp 30–60°) afforded tiny white crystals: mp 43.5–44.5°; uv max (95% EtOH) 227 mμ (ϵ 74,470), 287 (6460), 322 (1188); ir (Nujol) 5.65 μ (ester C=O); nmr τ 1.8–2.65 (complex, 4, C_5H, C_6H, C_7H, C_8H); 2.86 (s, 1, C_2H), 7.17 (q, 2, J = 7 Hz, CH_2CH_3), 7.47 (s, 3, $ArCH_3$), 7.65 [s, 3, $OCOCH_3$ (compare with $OCOCH_3$ signal from 3,4-dimethyl-1-naphthyl acetate, τ 7.66)], 8.76 (t, 3, J = 7 Hz, CH_2CH_3).

The vpc analysis using a Dow-11 column at 150° with N_2 (48 ml/min) as carrier gas and H_2 flow of 33 ml/min afforded a trace showing but one peak, retention time 16.4 min.

Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 79.07; H, 7.25.

3-Ethyl-4-methyl-1-naphthol.—A solution of 0.52 g (0.00238 mol) of **4** in 15 ml of 5% methanolic potassium hydroxide was boiled for 2 hr, and the methanol was removed. Dilution with water and acidification with aqueous hydrochloric acid yielded 0.412 g (99%) of 3-ethyl-4-methyl-1-naphthol, mp 81–82°. Recrystallization from carbon tetrachloride and petroleum ether (bp 65–110°) gave colorless crystals: mp 83–84°; uv max (95% EtOH) 239 mμ (ϵ 40,700), 302 (5327); ir (Nujol) 2.95 μ (OH); nmr τ 1.85–2.25 and 2.6–2.85 (m, 4, ring C_5H, C_6H, C_7H, C_8H), 3.70 (s, 1, ring C_2H), 4.55 (broad, 1, OH), 7.38 (q, 4, J = 7 Hz, CH_2CH_3), 7.55 (s, 3, $ArCH_3$), 8.88 (t, 3, J = 7 Hz, CH_2CH_3).

Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.63; H, 7.66.

1-Methyl-2-ethylnaphthalene (10) by Reduction of (3-Ethyl-4-methyl-1-naphthyl)diethyl Phosphate.—A solution of 0.372 g (0.002 mol) of 3-ethyl-4-methyl-1-naphthol in 2 ml of 1 *N* sodium hydroxide was shaken vigorously with 0.508 ml (0.002 mol) of tetraethyl pyrophosphate. The brown oil that separated was extracted into 25 ml of ethyl acetate, and the solution was washed first with 0.01 *N* sodium hydroxide and then with water. Evaporation of solvent from the dried (K_2CO_3) solution afforded 0.512 g (81%) of the naphthyldiethyl phosphate as a brown oil, which was dissolved in 1.5 ml of dry tetrahydrofuran. The solution, cooled in Dry Ice–acetone, was diluted with 10 ml of anhydrous ammonia, and the new solution maintained just below the boiling point while 75 mg of clean sodium was added in small pieces. After 3 hr, about 1 ml of ethanol was added, and the ammonia was permitted to evaporate. The residue was shaken with chloroform and water, the chloroform solution was washed successively with aqueous sodium bicarbonate, sodium hydroxide, and then water, the solution was dried ($CaCl_2$), the chloroform was removed under reduced pressure, and the residual brown oil was (0.310 g) subjected to vpc analysis. A sample introduced into a Dow-11 column at 150° with N_2 as the carrier gas (33 ml/min) and hydrogen flowing at 33 ml/min gave a trace with a single peak, retention time 7.1 min. A mixture of this oil with an authentic sample of 1-methyl-2-ethylnaphthalene (**10**) (see below), introduced into the same column under the same conditions, again showed a single peak with the same retention time. A mixture of the oil and an authentic sample of 1-ethyl-2-methylnaphthalene (**11**) (see below), on the other hand, afforded 2 peaks with retention times 7.1 and 7.4 min, the latter being the retention time of pure 1-ethyl-2-methylnaphthalene in the same column, under the same conditions.

2-Methyl-1-tetralone was prepared by the method of Bailey and Stavely[13] from ethyl 1-tetralone-2-glyoxalate, which was obtained by the procedure of Huisgen and Rauenbush.[14] The colorless liquid, bp 112° (13 mm), $n^{24.4}$D 1.5558 (lit.[13] n^{26}D 1.5538), gave a 2,4-dinitrophenylhydrazone, scarlet needles from benzene, mp 236°, as reported.[12]

2-Ethyl-1-tetralone, similarly prepared from ethyl-1-tetralone-2-glyoxalate was a colorless liquid, bp 140–141° (13 mm), $n^{24.4}$D 1.5454 (lit.[13] n^{25}D 1.5460).

1-Ethyl-2-methyl-1-tetralol was prepared by the procedure of Adkins and Davis.[15] It formed white crystals, mp 66–67° (lit.[15] mp 65–67°), from acetone at about −70°.

1-Ethyl-2-methylnaphthalene (11) was prepared in two steps from 1-ethyl-2-methyl-1-tetralol by the procedure of Christol,[16] colorless liquid: bp 133–134° (15 mm) [lit.[15] bp 153° (30 mm)]; uv max (95% EtOH) 225 mμ (ϵ 81,890), 273 (5505), 282 (5937), 306 (958), 321 (718); nmr τ 1.96–2.91 (complex, 6, ArH), 7.06 (q, 2, J = 7.5 Hz, CH_2CH_3), 7.68 (s, 3, $ArCH_3$), 8.89 (t, 3, J = 7.5 Hz, CH_2CH_3); vpc retention time (conditions as described above) 7.4 min, single peak.

1-Methyl-2-ethylnaphthalene (10), prepared from 2-ethyl-1-tetralone as its isomer was from 2-methyl-1-tetralone, was a colorless liquid: bp 150° (30 mm) [lit.[14] bp 155° (30 mm)]; uv max (95% EtOH) 226 mμ (ϵ 91,520), 273 (5334), 282 (5701), 306 (889), 321 (600); nmr τ 1.96–2.91 (complex, 6, ArH), 7.23 (q, 2, J = 7.5 Hz, CH_2CH_3), 7.47 (s, 3, $ArCH_3$, partially obscuring upfield lobe of CH_2 quartet), 8.81 (t, 3, J = 7.5 Hz, CH_2CH_3); vpc retention time (conditions as described above) 7.1 min, single peak. All spectroscopic data, including ir, matched those of the sample obtained by reduction of the rearrangement product (above).

4,4-Dimethyl-1-tetralone, prepared by the method of Arnold,[7] afforded a far simpler nmr spectrum than did its 4-methyl-4-ethyl homolog. Although the aromatic protons gave entirely similar signals, τ 1.95 (doublet of quartets, J_{78} = 7 Hz, 1, C_8H), 2.43–2.81 (complex 3, C_5H, C_6H, C_7H). The methylene groups afforded relatively simple signals, centered at τ 7.28 ($COCH_2$) and τ 8.02 ($COCH_2CH_2$), only slightly more complex than an A_2X_2 triplet pair in which $J_{AX} = J'_{AX}$ = 7 Hz. The geminal methyl groups yielded a lone singlet at τ 8.65.

2-Bromo-4,4-dimethyl-1-tetralone[7] also afforded a much simpler nmr spectrum than did its homolog with an ethyl displacing one of the methyl groups. The aromatic proton signals comprised a doublet of quartets at τ 1.92 (1, J_{78} = 7 Hz, C_8H) and a complex pattern at 2.35–2.83 (3, C_5H, C_6H, C_7H). With methyl groups at both 4 positions, the signals for the protons of the $COCHBrCH_2$ grouping appeared as a triplet and a doublet at 4.88 and 7.43, respectively (J = 9 Hz), an uncomplicated A_2X pattern. By contrast, the ethyl analog gave two overlapping ABX patterns, characteristic of stereoisomers. In both cases the chemical shift associated with the COCHBr signal suggested axial bromine.[12] Finally, the two methyl groups yielded separate signals at τ 8.52 and 8.58, respectively.

4,4-Dimethyl-1-keto-1,4-dihydronaphthalene[7] showed nmr spectral features in common with those of the 4-ethyl homolog (**2**). The aromatic proton signals, τ 1.80 (complex d, 1, J_{78} = 7 Hz, C_8H), and 2.4–2.7 (m, 3, C_5H, C_6H, C_7H), were quite similar to those from **2**, as was the AB quartet with the 1-proton doublets located at τ 3.08 and 3.66 (J = 10 Hz) arising from COCH=CH. Strikingly, major and minor singlets from the methyls appeared in this spectrum (τ 8.56 and 8.64) as they did in that of **2**.

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3,4-Dimethyl-1-naphthyl acetate[7] gave an nmr spectrum whose aromatic portion was substantially superimposable over those of the two methyl ethyl homologs. The three methyl singlets appeared at τ 7.50, 7.58, and 7.66 (4-CH_3, 3-CH_3, and $OCOCH_3$, respectively).

Registry No.—3-Methyl-3-phenyl-1-pentanol, 25594-39-2; 1-chloro-3-methyl-3-phenylpentane, 13556-52-0; 4-methyl-4-phenylhexenoic acid, 25607-04-9; 2-bromo-4-ethyl-4-methyl-1-tetralone, 25607-05-0; 3-ethyl-4-methyl-1-napthol, 25607-06-1; 4,4-dimethyl-1-tetralone, 2979-69-3; 2-bromo-4,4-dimethyl-1-tetralone, 17426-90-3; 4,4-dimethyl-1-keto-1,4-dihydronapthalene, 16020-16-9; 3,4-dimethyl-1-napthyl acetate, 25607-10-7; **2**, 25607-11-8; **2** (2,4-dinitrophenylhydrazone), 25607-12-9; **4**, 25607-13-0; **8**, 25607-14-1; **8** (2,4-dinitrophenylhydrazone), 25607-15-2; **10**, 25607-16-3; **11**, 17057-93-1.

Boron Fluoride Catalyzed Ethylation of Benzene with Radioactive Ethyl Fluoride

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Boron fluoride catalyzed ethylation of benzene was carried out with ethyl-2-^{14}C fluoride in homogeneous solution of nonpolar organic or basic organic solvent. The ethylbenzenes obtained were oxidized with nitric acid. Radioactivity of *p*-nitrobenzoic acid which was found in the *n*-hexane, cyclohexane, or nitromethane system was 47.9, 34.1, or 3.5% of radioactivity of ethyl-2-^{14}C fluoride, respectively. It was confirmed that an electrophile in boron fluoride catalyzed ethylation is either an ethyl carbonium ion in the nonpolar organic solvent or a nonionized complex in the basic organic solvent.

In basic solvent the catalytic activity of Friedel–Crafts catalyst decreases in terms of a competing donor effect of the solvent. Solvated Friedel–Crafts catalyst forms with ethyl fluoride the nonionized complex which is an electrophile of Friedel–Crafts ethylation in basic solvents.[1] In nonpolar solvents a Friedel–Crafts catalyst which does not form a complex with the solvent ruptures a C–X bond of ethyl halide, and an incipient ethyl carbonium ion is an ethylating agent. This was proved by a finding that, when aluminum bromide catalyzed ethylation of benzene with ethyl-2-^{14}C iodide was carried out in the *n*-hexane solution, oxidation of the ethylbenzene with nitric acid gave radioactive *p*-nitrobenzoic acid, indicating the migration of radioactivity from β to α carbon atom of the ethyl group.[2] When the ethyl carbonium ion is an ethylating agent, an anomalous substrate selectivity (a relative rate of toluene to benzene lower than 1) was found.[2]

In this work boron fluoride catalyzed ethylation of benzene with ethyl-2-^{14}C fluoride in the nonpolar solvent has been carried out to obtain an additional evidence for the formation of the incipient ethyl carbonium ion as an ethylating agent.

Results and Discussion

Ethyl fluoride forms a yellow polarized complex with boron fluoride at low temperatures.[3-5] The complex completely dissociates into gaseous components at room temperature. When the gaseous mixture was left for many hours, a yellow-brown oily polymer was formed. The gaseous mixture is soluble in the nonpolar solvent like *n*-hexane or cyclohexane, although the solubility of boron fluoride is low. The colorless solution is thus formed. Also, when the colorless solution was left for many hours, the yellow-brown oily polymer was formed and deposited on the bottom of the vessel. These results suggest that the ethyl carbonium ion is formed as an intermediate.[6] When the gaseous mixture was introduced in the nonpolar solvent with a trace of water, the polymer was immediately formed, and the solution showed a Tyndall effect. The gaseous mixture is very soluble in a basic solvent like nitromethane. Even if the solution was left for many hours, the oily polymer was not formed, indicating the impossibility of formation of the ethyl carbonium ion in the solution.

The gaseous mixture of ethyl fluoride and boron fluoride was dissolved in the nonpolar solvents, in which the aromatics were dissolved. When the homogeneous colorless solution thus formed was left for many hours, the oily polymer was not formed, but the ethylation of aromatics proceeded gradually.[2] However, the materials should be the purest, for when a trace of water exists in the solution, the oily polymer is immediately formed, and the solution shows the Tyndall effect.

Ethylation with Radioactive Ethyl Fluoride.—Boron fluoride catalyzed ethylation of benzene was carried out at room temperature with ethyl-2-^{14}C fluoride in the homogeneous solution of *n*-hexane, cyclohexane, or nitromethane. The ethylbenzenes obtained were oxidized with nitric acid. The *p*-nitrobenzoic acid thus obtained was dissolved in a liquid scintillator, and the radioactivity of the solution was counted.[2,7] The results are summarized in Table I. When the ethylation was carried out in *n*-hexane solution, 47.9% of radioactivity of ethyl-2-^{14}C fluoride was found in the *p*-nitrobenzoic acid obtained, indicating the formation of ethyl-1-^{14}C-benzene and hence the migration of radioactivity from β to α carbon position of the ethyl

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