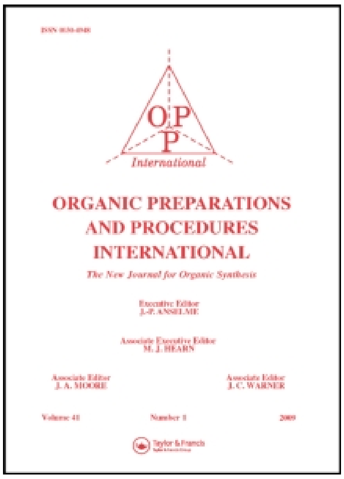

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J. W. Burnham[a]; W. P. Duncan[a]; E. J. Eisenbraun[a]; G. W. Keen[b]; M. C. Hamming[b]
[a] Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma [b] Research and Development Department, Continental Oil Company, Ponca City, Oklahoma

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THE SYNTHESIS OF 5-*TERT*-BUTYL-1,2,3,4-TETRAHYDRONAPHTHALENE

J. W. Burnham,[1a] W. P. Duncan,[1b] and E. J. Eisenbraun*

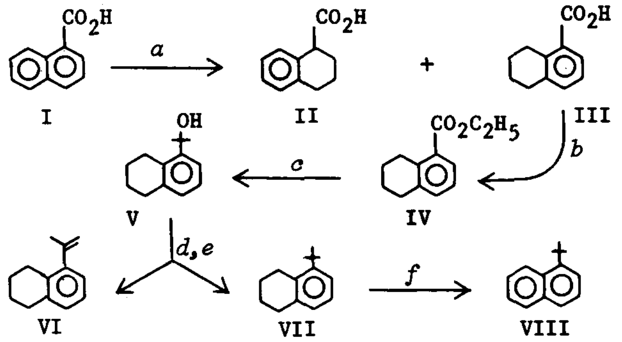
Department of Chemistry, Oklahoma State University
Stillwater, Oklahoma 74074

and

G. W. Keen and M. C. Hamming

Research and Development Department, Continental Oil Company
Ponca City, Oklahoma 74074

The direct preparation of 5-*tert*-butyl-1,2,3,4-tetrahydronaphthalene (VII) from 1-*tert*-butylnaphthalene (VIII)[2] by catalytic hydrogenation[3] is not feasible since reduction occurs exclusively in the substituted ring. Sodium-ammonia reduction[4] of VIII leads to a mixture of products in low yield, a large portion of starting material being recovered.



^{a}H$_2$, Pd/C, CH$_3$CO$_2$H. ^{b}H$_2$SO$_4$, C$_2$H$_5$OH, C$_6$H$_6$. ^{c}CH$_3$MgCl in THF. ^{d}HCl, Et$_2$O. ^{e}CH$_3$MgBr in Et$_2$O. ^{f}Pd/C, Δ.

In order to avoid the problems associated with catalytic and chemical reduction of VIII to VII, we decided to prepare VII by hydrogenation of the ring at an early stage, separation of products and then generation of the *tert*-butyl group in the final stages. The hydrocarbon VII was required for a study of effects of alkyl substituents in the chromic acid oxidation of tetralins. This synthesis utilizes a series of convenient steps which yield VII, a new hydrocarbon, as shown in the scheme in 32% overall yield of purified material. Although VII is accompanied by 5-isopropenyl-1,2,3,4-tetrahydronaphthalene (VI) in the ratio 2.9:1.0 (VII:VI), these hydrocarbons may be separated by distillation; furthermore, the olefin VI may be utilized by recycling to V or the corresponding chloride. An advantage of this synthesis of VII is that there is no contamination of the compounds shown in the scheme by impurities with substituents at the 2- or 6-position if pure I is used. To confirm the position of attachment of the *tert*-butyl group of VII and as a further check on its purity, VII was dehydrogenated to VIII.

EXPERIMENTAL[5]

Hydrogenation of 1-Naphthoic Acid (I) to 1,2,3,4-Tetrahydro-1-naphthoic Acid (II) and 5,6,7,8-Tetrahydro-1-naphthoic Acid (III).— 1-Naphthoic acid (129 g., 0.75 mole), mp. 161-162°, was dissolved in 750 ml. of acetic acid and hydrogenated in the presence of 8 g. of 10% Pd/C catalyst at 50 psi and 75° for 60 hr. The ratio of the product mixture II:III (1.0:1.4) was determined by glc[5a] of the methyl esters. The acids II and III were separated by two recrystallizations from a hot saturated ethyl acetate solution, III being the less soluble one. The overall yield of III was 61 g. (47% amounting to 79% of the III present in the mixture), mp. 148.5-150° [lit.[6a] 150.0-151.5°,[6b] 146-150°]; mass spectrum (70 eV) *m/e* (rel intensity) 176 M^+ (75), 158 (71), 131 (100), 130 (36), 115 (36), 91 (41), pmr ($CDCl_3$) δ 7.94-7.78 (m, 1, isolated ArH at C-2), 7.34-7.02 (m, 2, ArH at C-3 and C-4), 3.32-2.97 (m, 2, $ArCH_2$ at C-8), 2.95-2.64 (m, 2, $ArCH_2$ at C-5), 2.00-1.55 (m, 4, $ArCH_2\underline{H}_2\underline{H}_2$).

The isomer II, mp. 81-84°,[6b] may be obtained from the mother liquor by evaporation and recrystallization from hot petroleum.[5b]

Esterification of III to Ethyl 5,6,7,8-Tetrahydro-1-naphthoate (IV).— The acid III was esterified by azeotropic removal of water (Dean-Stark trap) from a mixture of 95% ethanol and benzene using sulfuric acid catalyst. Distillation gave IV (94%), bp. 110-111° (0.9 mm) [lit.[7] 124.5-127.5° (2 mm)]; mass spectrum (70 eV) *m/e* (rel intensity) 204 M^+ (63), 175 (72), 159 (56), 158 (95), 131 (100), 91 (53); pmr (CCl_4) δ 7.72-7.52 (m, 1, isolated ArH at C-2), 7.14-6.86 (m, 2, ArH at C-3 and C-4), 4.22 (q, 2, CO_2CH_2, J = 7Hz), 3.20-2.89 (m, 2, $ArCH_2$ at C-8), 2.84-2.58 (m, 2, $ArCH_2$ at C-5), 1.90-1.55 (m, 4, $ArCH_2\underline{CH_2}\underline{CH_2}$), 1.29 (t, 3, $CO_2CH_2\underline{CH_3}$, J = 7Hz).

Conversion of IV to 5,6,7,8-Tetrahydro-α,α-dimethyl-1-naphthalenemethanol (V).— To a stirred solution of 1.05 mole of methylmagnesium chloride in 750 ml. of tetrahydrofuran (THF) was gradually added 72 g. (0.35 mole) of IV in 400 ml. of THF. A nitrogen atmosphere was maintained during the reaction. During the addition (90 min.) the temperature rose until reflux resulted. After addition, reflux was continued for 6 hr. Saturated aqueous ammonium chloride solution (400 ml.) was added dropwise, with cooling, over a 1-hr. period. The product mixture was filtered and the filtrate was washed and dried ($MgSO_4$). Concentration gave 79 g. of yellow oil, which was made to crystallize by dilution with 225 ml. of petroleum ether[5b] and cooling to -20°. Filtration gave 54 g. (80%) of colorless V. Recrystallization from petroleum ether gave the final product, mp. 56-57°; ir 3370 cm^{-1} (OH); mass spectrum (70 eV) *m/e* (rel intensity) 172 (100), 157 (89), 129 (60), 128 (40), 115 (32), 43 (10); pmr ($CDCl_3$) δ 7.36-7.21 (m, 1, isolated ArH at C-2), 7.14-6.97 (m, 2, ArH at C-3 and C-4), 3.20-2.98 (m, 2, $ArCH_2$), 2.91-2.66 (m, 2, $ArCH_2$), 2.14 (s, 1, OH), 1.89-1.58 (m, 4, $ArCH_2\underline{CH_2}\underline{CH_2}$), 1.64 (s, 6, *gem* methyls).

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.06; H, 9.54. Found: C, 81.91; H, 9.51.

Preparation of 5-Isopropenyl-1,2,3,4-tetrahydronaphthalene (VI) and 5-*Tert*-Butyl-1,2,3,4-tetrahydronaphthalene (VII) from V.— Anhydrous hydrogen chloride was slowly bubbled through a magnetically stirred solution of 48 g. (0.25 mole) of V in 1.5 ℓ of anhydrous ether at 0-10° for 4 hr. The reaction mixture was poured onto 500 g. of ice, excess ice was allowed to melt, the layers were separated and the ether layer was washed with water, dried ($MgSO_4$), and filtered through additional $MgSO_4$. The filtrate was added dropwise to a stirred solution of 250 ml. (0.75 mole) of methylmagnesium bromide in ether during 90 min. The reaction mixture was heated at reflux for 4 hr. Water (200 ml., was added dropwise to the cooled, stirred reaction mixture over 1 hr. To this suspension, 300 ml. of 15% hydrochloric acid was added to dissolve the basic salts. The resulting layers were separated and the ethereal layer was washed with water, dried ($MgSO_4$), filtered, and concentrated. The resulting yellow oil was diluted with petroleum ether[5b] and filtered through a 2.5 x 5 cm. column of Merck basic alumina. Distillation at 63-66° (0.1 mm.) gave 43 g. of a colorless mixture of VI:VII (1.0:2.9). This mixture was separated by distillation[5c] into fractions. The first major fraction was 8 g. of VI, bp. 88-89° (2.9 mm.); mass spectrum (70 eV) *m/e* (rel intensity) 172, M^+ (98), 157 (100), 143 (31), 129 (74), 128 (49), 115 (36); pmr (CCl_4) δ 7.02-6.70 (m, 3, ArH), 5.18-5.02 (m, 1, vinyl proton E to CH_3), 4.84-4.71 (m, 1, vinyl proton Z to CH_3), 2.84-2.51 (m, 4, $ArCH_2$), 1.96 (s, 3, allylic CH_3), 1.88-1.55 (m, 4, $ArCH_2C\underline{H}_2C\underline{H}_2$).

Anal. Calcd. for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.43; H, 9.29.

The second major fraction was 25 g (53%) of VII, bp. 102-103° (2.9 mm); mass spectrum (70 eV) *m/e* (rel intensity) 188, M^+ (27), 173 (100), 131 (66), 91 (16), 43 (15), 41 (15); pmr (CCl_4) 7.18-6.70 (m, 3, ArH), 2.97-2.56 (m, 4, $ArCH_2$), 1.84-1.58 (m, 4, $ArCH_2C\underline{H}_2C\underline{H}_2$), 1.36 (s, 9, *tert*-butyl). Comparison of this pmr spectrum with that of authentic 6-*tert*-butyl-1,2,3,4-tetrahydronaphthalene[8,9] showed a significant low-field chemical shift (*ca.* 20 Hz) of the C-4 protons of VII compared to those of 6-*tert*-butyl-1,2,3,4-tetrahydronaphthalene.

Anal. Calcd. for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.08; H, 10.63.

Dehydrogenation of VII to 1-*tert*-Butylnaphthalene (VIII).— A 10-g. sample of VII was dehydrogenated in the presence of 10% Pd/C (1 g.) at 275° for 5 min. Filtration and concentration gave 8 g. of colorless liquid. Glc studies[5a] indicated that 2-*tert*-butylnaphthalene was absent.

The crude reaction product was diluted with 15 ml. of hot 95% ethanol and 10 g. of picric acid was added; VIII picrate was filtered and recrystallized twice from abs. ethanol to give yellow crystals, mp. 100-101°; [lit.[2] 101.4-102°]. The picrate was decomposed[10] and the recovered VIII was distilled at 81° (0.3 mm) [lit.[2] 87° (0.4 mm)]: mass spectrum (70 eV) *m/e* (rel intensity) 184, M^+ (36), 169 (100), 141 (34), 129 (18), 128 (17), 41 (15); pmr (CCl_4) δ 8.43-8.24 (m, 1, ArH *peri* to *tert*-butyl), 7.75-7.07 (m, 6, ArH), 1.53 (s, 9, *tert*-butyl).

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*Author to whom correspondence should be addressed.

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(5) (a) The glc studies used a Hewlett-Packard Model 5750 instrument with an 0.25-in. x 12-ft. column of 80-100 mesh Chromosorb G (acid-washed and DMCS-treated) treated with 5% silicone rubber UC W-98. The injector and detector temperatures were 270° and 250° respectively. The column temperatures were I, II, and III as methyl ester and IV at 220°; VI, VII, and VIII at 215°. The helium pressure was 60 psi.
(b) Petroleum ether, bp. 60-68°, was redistilled before use.
(c) A Nester/Faust (NFA-100) auto-annular spinning band column was used.
(d) 1-Naphthoic acid, Aldrich Chemical Co., was used as purchased since a glc analysis[5a] of the methyl ester gave a single peak.

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