acid washings gave the crude tributyltin acetate, which was recrystallized from petroleum ether (bp 60–80 °C) to give the pure product (79%), mp 84–85 °C, identical (mixed melting point and IR) with a prepared authentic sample.[23]

Registry No.—Norcamphor, 497-38-1; 3-cholestanone, 15600-08-5; methyl naphthyl ketone, 93-08-3; benzophenone, 119-61-9; benzaldehyde, 100-52-7; octanal, 124-13-0; nitrobenzene, 98-95-3; *trans*-stilbene epoxide, 1439-07-2; phenyl benzoate, 93-99-2; diphenylmethyl benzoate, 7515-28-8; 1-chloro-2-phenylethane, 622-24-2; diphenyl sulfoxide, 945-51-7; benzyl chloride, 100-44-7; phenyl bromide, 108-86-1; benzonitrile, 100-47-0; 1-(β-naphthyl)ethanol, 7228-47-9; diphenylmethanol, 91-01-0; benzyl alcohol, 100-51-6; 1-octanol, 111-87-5; aniline, 62-53-3; 1,2-diphenylethanol, 614-29-9; phenol, 108-95-2; cyclohexanone, 108-94-1; *n*-decanal, 112-31-2; 4-*tert*-butylcylohexanone, 98-53-3; tributyltin hydride, 688-73-3; tributyltin acetate, 56-36-0; *exo*-norborneol, 497-37-0; *endo*-norborneol, 497-36-9; 3α-cholestanol, 516-95-0; 3β-cholestanol, 80-97-7.

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Improved Routes to Phenalene and Phenalanone. Alane, Borane, and Silane Reductions of Phenalenone

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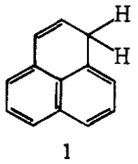
Phenalene (1) has enjoyed considerable attention from chemists because of its ability to generate an anion, neutral radical, and cation, all of which are aromatic and stable in solution.[1] Because earlier reported methods of making and isolating 1 and its precursors are generally tedious[2] and work in our laboratories required ready access to 1, we investigated ways of improving its yield and purification.



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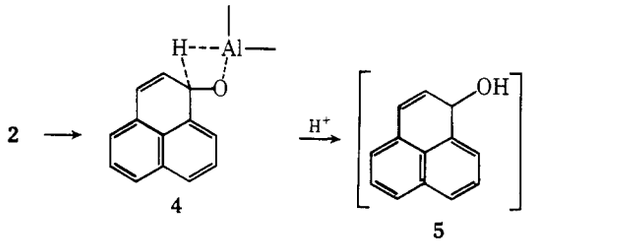
Recently, it was reported that $LiAlH_4/AlCl_3$ reduced phenalenone (2) to 1 and phenalanone (3).[3] The yields varied over a wide range, however, and were markedly affected by the purity of the $LiAlH_4$ and $AlCl_3$, the recommended procedure calling for newly opened bottles of these reagents. Furthermore, the isolation of 1 required large amounts of solvent and is often accompanied by oxidation of the very sensitive 1 on silica gel.

The active agents in the reduction of 2 to 1 by the $LiAlH_4/AlCl_3$ mixture were probably $HAlCl_2$ and H_2AlCl.[4] This suggested to us that diisobutylaluminum hydride (DIBAL-H) might also be effective in reducing 2. We found that DIBAL-H will convert 2 to 1 in high net yields (>85%) and that 1 can be isolated easily in high purity from the product mixture. DIBAL-H is commerically available as a 1 M solution in hexane (Aldrich) and is handled conveniently and precisely by syringe technique. The reagent also has a long shelf-life, even after it has been sampled. These are distinct advantages over $LiAlH_4/AlCl_3$ mixtures.

The sensitivity of 1 to silica gel led us to try other solid supports, and we found that Florisil, a much more acidic absorbent than silica gel,[5] gave very satisfactory results. Phenalene is the first compound eluted from the column and is well separated from the only other product, phenalenone. Moreover, a shorter column and much less solvent are required than when we used silica gel. No significant decomposition of 1 during the chromatography was observed. Scaling up the reaction presented no handling problems, and yields were unchanged.

The production of 1 from 2 and DIBAL-H probably arises from a 1,2 addition of the metal hydride across the C=O bond. Hydrolysis of the resulting alkoxide would give phenalenol 5, which is known to undergo a facile irreversible disproportionation to 1 and 2.[6] Consistent with this scheme is the fact that we recover ~50% of the amount of 2 that we start with regardless of reaction time and the number of equivalents of DIBAL-H used. Reaction times ranged from 4 h to 2 days, and ratios of metal hydride to 2 were varied from 1 to 5 equiv. The addition of aluminum powder or aluminum chloride as potential deoxygenating agents did not change the yield of 1.



We tried to intercept the disproportionation of 5 by using alcohols in large excess during workup. However, allyl alcohol, glyoxal, and benzoin did not alter the yield or product distribution. The report of successful hydrogenolysis of the magnesium alkoxides of allylic alcohols using complexes derived from adding *n*-propylmagnesium bromide[7] to bis(phosphine)nickel dichlorides suggested that 4 might be similarly reduced. This route also gave 1 and 2 when applied to 4. We also tried reductions of 2 using boranes and found that while $BH_3{\cdot}SMe_2$ is useful for preparing cyclopropane from cyclopropenone,[8] mainly polymeric products are obtained when it is used with 2. 9-Borabicyclononane, on the other hand, does give 1 in net yields of ~90% when stirred overnight at room temperature in THF.

We extended our studies to polymethylhydrosiloxane (PMHS)[9] and tetramethyldisiloxane (TMDS)[9] and found that

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the major product was phenalanone (3). While small amounts of 3 can be obtained from the $LiAlH_4/AlCl_3$ reduction of 2,[3] the best known synthesis is the cyclization of β-1-napthylpropionic acid using anhydrous hydrogen fluoride.[2] The latter route is inconvenient and limited to small scale reactions because of the precautions necessary when using anhydrous HF. This cyclization procedure also gives the isomeric mixture, phenalanone/4,5-benzhydrindone.

We have prepared 3 in ~30% yield using 2 equiv of TMDS and 2 in acidified 95% ethanol in the presence of catalytic amounts of palladium. Although the yield is modest, the simple reaction conditions, ready availability of these inexpensive reagents and ease of product isolation make this an attractive synthesis of 3. PMHS was found to be less effective than TMDS, giving yields of ~20%. No improvement in this yield was observed over the range of 1.1 to 4.4 equiv[9] of PMHS to 2.

Experimental Section

Phenalenone was prepared by the method of Fieser and Hershberg.[10] Benzene and hexane were stirred over H_2SO_4, distilled, and stored in brown bottles until needed. Tetrahydrofuran was refluxed over sodium metal and benzophenone until the blue color of benzophenone ketyl was observed, and then it was distilled just before use. NMR spectra were recorded on a Varian EM-390 spectrometer and correspond to those reported in the literature.[11] Melting points were obtained on a Thomas-Hoover Mel-Temp melting point apparatus and are uncorrected. All glassware was oven-dried, assembled hot, and cooled under a stream of dry nitrogen. The reactions were run under a dry nitrogen atmosphere unless otherwise noted. Florisil was placed in a round-bottom flask, put under vacuum, and purged with N_2. This cycle was repeated several times just before use.

DIBAL-H Reduction of Phenalenone. Excess DIBAL-H (11.2 mL, 1 M in hexane; Aldrich Chemical Co.) was added to a benzene solution (~20 mL) of 2 (1.0 g, 5.5 mmol) over a 30-min period at room temperature. The resulting dark red solution was heated to reflux overnight and cooled to room temperature, and excess DIBAL-H was quenched by the dropwise additon of 2 mL of a saturated NH_4Cl solution. Hexane (50 mL) was added and the mixture filtered. The salts were washed with 1 × 50 mL of hexane. The hexane layers were combined, washed with 1 × 50 mL of the NH_4Cl solution, and dried ($MgSO_4$), and the solvent was removed by rotary evaporation. The oil was deposited on Florisil (100–200 mesh; Matheson, Coleman and Bell) and placed atop a 10 × 5 cm column of Florisil. Elution was with 250 mL of hexane; 50-mL fractions were collected. Fractions 2–4 contained 1 (0.40 g, 2.41 mmol), mp 70–75 °C (lit. mp 85 °C).[2] The column was then eluted with 50 mL of 1:1 hexane/ether, and 2 (0.52 g, 2.88 mmol) was recovered. The isolation of 2 from the product mixture was confirmed by comparison of its melting point and IR and NMR spectra with those of an authentic sample.

9-Borabicyclononane (9-BBN) Reduction of Phenalenone. Excess 9-BBN (6 mL, 0.5 M in THF; Aldrich Chemical Co.) was added slowly to a THF solution (~15 mL) of 2 (0.50 g, 2.8 mmol) at 0 °C. The solution was stirred overnight at room temperature. Excess 9-BBN was quenched with 0.5 mL of methanol.[12] NaOH (3 M, 1 mL) and 2 mL of 30% H_2O_2 were added, and the mixture was heated to reflux for 1 h. Anhydrous K_2CO_3 was added to saturate the aqueous phase; the organic layer was decanted, and the K_2CO_3 was extracted with 3 × 20 mL of ether. The organic layers were combined, washed with 4 × 30 mL of H_2O, and dried ($MgSO_4$). The solvent was removed by rotary evaporation, and the oil was deposited on Florisil. This was placed atop a 10 × 2 cm Florisil column. Elution was with 100 mL of hexane. This fraction contained 1 (0.20 g, 1.20 mmol) as pale yellow crystals, mp 65–75 °C. The column was then eluted with 50 mL of 1:1 hexane/ether, and crude 2 (0.26 g, 1.4 mmol, 52%) was obtained.

Purification of Phenalene. Analysis of the chromatographed samples of 1 from the above reductions by NMR spectroscopy showed that the impurities were saturated hydrocarbon residues. However, if 1 must be further purified, the following procedure[13] is recommended.

1 was dissolved in sufficient pentane (~6 mL/g) so that when the resulting solution was chilled to dry ice temperature, a filterable slurry was formed. During the chilling period (~30 min), a Büchner funnel wrapped in aluminum foil and a stoppered flask containing pure solvent were chilled in powdered dry ice. Immediately before use, a conventional filtration assembly was set up using the chilled funnel. The slurry of 1 was filtered and washed with the chilled solvent. An inverted funnel connected to a dry N_2 source was placed over the Büchner funnel, and suction was continued until the apparatus reached room temperature. Phenalene was obtained as a white powder (mp 83–84 °C), and no hydrocarbon residue was visible in the NMR spectrum. The structure was confirmed by comparison of its NMR spectrum [(in $CDCl_3$) δ 2.5–4.1 (m, 8 H), 6.1 (s, 2 H)] with published data.[11]

We have carried out this procedure many times, including runs on as much as 5 g of 2, and in all cases the net yields of 1 exceeded 80% based on recovered 2.

TMDS Reduction of Phenalenone. Palladium on charcoal (5%) (10 mg; Matheson, Coleman and Bell) and a few drops of 12 M HCl were added to a solution of 2 (5.0 g, 27.7 mmol) in 95% ethanol, and the mixture was heated to reflux. TMDS (11.1 mL, 62.3 mmol) was added by syringe through the condenser at a rate to maintain the reflux, which was continued for 1 h after the addition was complete. The mixture was filtered, and the volatile products were removed by rotary evaporation to give ~3 mL of an orange-brown oil. This was dissolved in 50 mL of ether and washed with 3 × 50 mL of H_2O. The H_2O layers were combined and washed with 1 × 50 mL of ether. The ether layers were combined, washed with 1 × 50 mL of a saturated NaCl solution, dried (Na_2SO_4), and filtered, and the ether was removed by rotary evaporation. The residual oil was deposited on alumina (neutral, Alcoa F-20) and placed atop a 25 × 5 cm column of alumina. The product was eluted with 1:1 hexane/ether; 100-mL fractions were collected. Fractions 4 and 5 contained 3 (1.4 g, 7.9 mmol, 28%), mp 80–81 °C (lit.[2] mp 82.6–83.2 °C). No phenalenone was detected in the product mixture. The structure of 3 was confirmed by its NMR [(in $CDCl_3$) δ 1.9–2.7 (m, 6 H), 6.5–7.2 (m, 4 H)] and IR [(in CCl_4) 1700 cm^{-1} (C=O)] spectra, which compare well with the published spectra.[11]

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Registry No.—1, 203-80-5; 2, 548-39-0; 3, 518-85-4.

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Studies with Amino Acids. 1. Synthesis of Valine

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The synthesis of amino acids by the Strecker[1] method is well known and offers one of the best routes available for the preparation of these important compounds. Several modifications have been introduced which increase the yields and safety of the preparation. The method has been of great value in the preparation of carboxyl-labeled amino acids starting with ^{13}C and ^{14}C cyanide, but difficulties arise when synthesizing amino acids labeled with ^{11}C. Compounds labeled with this isotope have great potential for in vivo metabolism studies using nuclear medicine techniques. The short half-life of ^{11}C (20 min) requires considerable modification in existing procedures. The method presented here proceeds smoothly and rapidly without the production of any interfering byproducts. The procedure is described for the synthesis of valine (Scheme I), but may be used for the preparation of other amino acids.

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