of the reaction mixture and second, to increase the ease of recovery of the product indole during workup from the mixture of silica gel and iron-derived solid byproducts. The amount of silica gel required for the optimum yields of the indoles depended upon the polarity of the nonpolar solvent system. For example, use of benzene alone in place of 1:3 benzene-cyclohexane required larger amounts of silica gel. The type of nonpolar solvent system required, in turn, was dictated by the nature of the dinitrostyrene. Thus the use of cyclohexane alone as the nonpolar solvent system was quite effective for the synthesis of the methoxy and (methylenedioxy)indoles but not for the (benzyloxy)indoles.

It is surprising that application of the reaction conditions, which furnished 5,6-bis(benzyloxy)indole (2H) in 94% yield, gave 5,7-bis(benzyloxy)indole (2J) in only 40-45% yield. With toluene as the nonpolar solvent and at reflux temperature, the yield of 2J could be increased to 75% (Table I). Interestingly, synthesis of 4-methyl-, 6-methyl-, and 4,6-dimethyl-5,7-bis(benzyloxy)indoles also required toluene under reflux; however, the yields were 92%, 78%, and 90%, respectively.¹⁹ It is possible that the presence of a methyl group ortho to the nitrovinyl moiety minimizes, through steric hindrance, by productformation arising from Michael addition at the carbon β to the nitro group.

The above results, including the observation that no dimer was formed in the conversion of 1A to 2A, lend support to our original premise for using silica gel.²⁰ The efficacy of silica gel, when used together with a nonpolar solvent system, in preventing byproduct formation is undoubtedly due to its ability to bind polar (neutral or charged) intermediates, which minimizes intermolecular reactions involving these intermediates.²¹

Experimental Section

General Methods. Iron powder (reduced, N.F. IX electrolytic) was purchased from Mallinckrodt. Silica gel used for the reactions as well as for chromatography was 70-270 mesh (silica gel 60, Brinkmann). The $2,\beta$ -dinitrostyrenes were synthesized by the literature methods (see Table I). Melting points were determined in a Thomas-Hoover capillary melting point apparatus and are uncorrected.

General Procedure for the Silica Gel Assisted Reductive Cyclization. A mixture of the 2,\beta-dinitrostyrene 1 (2 mmol), silica gel (see Table I for amounts), reduced iron powder (1.7 g for 1A-I, 2.1 g for 1J), glacial HOAc (12 mL), and 20 mL of the nonpolar solvent system (see Table I) were refluxed under N_2 for 1 h with efficient mechanical stirring. In each case a vigorous exothermic reaction ensued within 5 min of reflux, and the mixture turned dark (color varied). (The dark color disappeared after 15-20 min, indicating essential completion of reaction.) The mixture was then cooled to 25 °C, diluted with CH₂Cl₂, and filtered. The filter cake was washed thoroughly with 10% Et_2O in CH_2Cl_2 (for 2A-**E**,**I**) or with CH_2Cl_2 (for 2**F**-**H**,**J**). The combined filtrates were washed with sodium metabisulfite solution, NaHCO₃ solution (until aqueous layer was basic), and brine, dried (Na_2SO_4) , and then evaporated in vacuo to dryness. Indoles 2A-E were quite pure at this stage except for traces of colored impurities whereas indoles 2F-J were less pure. The crude indoles were chromatographed on a column of silica gel (3-6 g/mmol of 1 cyclized) with CH_2Cl_2 (for 2A-E,I) or CH_2Cl_2 -hexane (for 2F-H,J) to give

solid product, pure by TLC (silica gel, Analtech; solvent CH₂Cl₂). The yields and melting points of the indoles are reported in Table

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Registry No. 1A, 86712-40-5; 1B, 16551-84-1; 1C, 80547-82-6; 1D, 80547-83-7; 1E, 15794-43-1; 1F, 2426-89-3; 1G, 4775-68-2; 1H, 4790-17-4; 1I, 86712-41-6; 1J, 50545-13-6; 2A, 57330-45-7; 2B, 14430-23-0; 2C, 80547-84-8; 2D, 80547-85-9; 2E, 267-48-1; 2F, 2426-59-7; 2G, 4790-04-9; 2H, 4790-19-6; 2I, 27508-85-6; 2J, 50545-14-7; iron, 7439-89-6; HOAc, 64-19-7.

Supplementary Material Available: Full ¹H NMR spectral data for indoles 2A-J (1 page). Ordering information is given on any current masthead page.

On the Aprotic Robinson Annelation of Dihydrocarvone and 2-Methylcyclohexanone with Methyl and Ethyl Vinyl Ketone

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The Robinson annelation reaction is a time-tested method for ring construction. It is generally conceded that the reaction of cyclohexanone enolates and simple alkyl vinyl ketones in an aprotic medium cause polymerization.¹ McQuillin was able to achieve annelation of dihydrocarvone (33%) using sodamide/ether and the "slow" ethyl vinyl ketone releasing reagent diethylmethyl(3-oxopentyl)ammonium iodide.² Marshall and Fanta sought to obviate this difficulty by employing base catalysis in protic medium with subsequent isolation of the resultant ketol prior to dehydration. Application of this technique to dihydrocarvone and ethyl vinyl ketone provided a 49% yield of ketols 1a/1b (7/3) (Chart I) derived from the thermodynamic enolate.³ Stork and Ganem have demonstrated that α -trialkylsilyl vinyl ketones permit the first step of the Robinson sequence, namely, the Michael addition, to be accomplished in both protic and aprotic media.⁴ When applicable, the Robinson annelation sequence can be conducted in acid medium.⁵

Because we had a need for an efficient preparation of (+)-6-epi- α -cyperone, we chose to reinvestigate the aprotic annelation sequence of the thermodynamic enolates of 2-methylcyclohexanones with simple alkyl vinyl ketones.

Reduction of (+)-carvone with lithium bronze⁷ provided (-)-dihydrocarvone, which was converted into its thermodynamic enolate by exposure to 0.9 equiv of lithium diisopropylamide (LDA) in THF at 20 °C for 24 h. Treatment of the enolate with ethyl vinyl ketone (EVK) at -78 °C followed by warming to ambient temperature provided, after chromatography, the known crystalline ketol la in

- (2) McQuillin, F. J. J. Chem. Soc. 1955, 528. Howe, R.; McQuillin, F. J. Ibid. 1955, 2423.
- (3) Marshall, J. A.; Fanta, W. I. J. Org. Chem. 1964, 29, 2501.
 (4) Stork, G.; Ganem, B. J. Am. Chem. Soc. 1973, 95, 6152.
 (5) Heathcock, C. H.; Ellis, J. E.; McMurry, J. E.; Coppolino, A. Tetrahedron Lett. 1971, 4995.
- (6) Professor Ganem has informed us that the aprotic reaction proceeds in 75% yield.
 - (7) Mueller, R. H.; Gillick, J. G. J. Org. Chem. 1978, 43, 4647.

⁽¹⁹⁾ Sinhababu, A. K.; Borchardt, R. T., unpublished observations. (20) In recent years many applications of silica gel as a support for reagents have been made. For an excellent review on this and related topics see: McKillop, A.; Young, D. W. Synthesis 1979, 401-422, 481-500. The manner in which silica gel has been used in the present study does

not, however, qualify silica gel as a support for a reagent, but there are certain similarities

⁽²¹⁾ Cf.: (a) Sinhababu, A. K.; Borchardt, R. T. Tetrahedron Lett. 1983, 24, 227-230. (b) Sinhababu, A. K.; Borchardt, R. T. J. Labelled Compd. Radiopharm., in press.

⁽¹⁾ Gawley, R. E. Synthesis 1976, 777.



92% yield. The purity of the thermodynamic enolate was assessed by quenching aliquots of the reaction mixture with acetic anhydride and by monitoring the disappearance of 90% of the high-field methyl doublets in the ¹H NMR spectrum. Subsequent to the addition of EVK and at temperatures below -20 °C, the major product of the reaction was the intermediate diketone. At 0 °C, ketol was the exclusive product. As has been noted,³ base catalysis of this reaction in protic medium provided diastereomers during the Michael addition. Conversion of ketol 1a into (+)-6-epi- α -cyperone (2) was efficiently accomplished (93% yield) in refluxing KOH/EtOH. The overall sequence provided the target substance in 85% yield.

An alternative route was also employed. The thermodynamic enolate of (-)-dihydrocarvone, formed in situ by the lithium bronze reduction of (+)-carvone, was trapped with EVK. Overall conversion to 2 was achieved in 67% yield.

Treatment of the thermodynamic enolate (LDA route) derived from the less expensive (+)-dihydrocarvone with methyl vinyl ketone (MVK) was not as clean as the EVK experiment. Some MVK polymer was observed. Three products could be isolated from the reaction mixture. A Michael adduct (homogeneous, but of undefined stereochemistry) was obtained in 12% yield in addition to ketols 3a (53%) and 3b (12%). The relative configuration of the angular methyl and isopropenyl groups was assigned on the basis of a comparison of the chemical shift of the angular methyl group with that of ketol la and the knowledge that the principal diastereomer from the protic³ and aprotic² reactions has the angular methyl and isopropenyl group trans to one another. In addition, dehydration of ketol 3a provided enone 4a (70% yield) while ketol 3b, contaminated with MVK polymer, afforded enone 4b in 60% yield.

When the thermodynamic enolate of 2-methylcyclohexanone was annelated with EVK, the Michael adduct was isolated (27%) in addition to two ketols (27%), (cis fused), 31% (trans fused)). The diketone (Michael adduct) was aldolized and dehydrated to afford enone 5a in 60% yield while the ketols provided the enone 5a in >90% yield. These yields translate to a 70% yield in the annelation sequence.

The yields in the aprotic annelation were poorest with 2-methylcyclohexanone and MVK. The enone **5b** (17%) and a ketol contaminated with MVK polymer were obtained. Dehydration of the ketol (8% KOH/EtOH; 20 °C) permitted the isolation of an additional 15% of enone **5b** (total, 32%). Under protic conditions (NaOEt/EtOH/-10 °C), a cis-fused ketol was reported to be formed in 50–55% yield.³ Annelation of 2-methylcyclohexanone with 3-(triethylsilyl)-3-buten-2-one (KOBu-t/t-BuOH) has been reported to afford **5b** in 60% yield while no yield was specified for the aprotic reaction.^{4,6}

Although the present study is not extensive, it does reveal that the aprotic Robinson annelation with reactive enones such as EVK and MVK may not be as poor a reaction as has been implied. In instances where the cyclohexanones are readily available, coupled with the commercial availability of EVK and MVK, this methodology may prove to be the method of choice.

Experimental Section

Ether and tetrahydrofuran were dried over sodium benzophenone ketyl under nitrogen. Diisopropylamine was distilled from CaH_2 . Ethyl and methyl vinyl ketone (Aldrich) were used as received.

1(S),4a(S)-Dimethyl-8a(S)-hydroxy-7(S)-isopropenyl-1,4,4a,5,6,7,8,8a-octahydronaphthalen-2(3H)-one (1a). LDA Method. To a stirred solution of 10.4 g (0.10 m) of dry diisopropylamine in 100 mL of dry THF (0 °C, argon) was added over 20 min 45.4 mL (2.2 M in hexane, 0.1 mol) of n-butyllithium (Alfa), followed by stirring for 1 h. The solution was added over 7 min to a stirred solution of 16.7 g (0.11 mol, 93% pure) of (-)-dihydrocarvone (from (+)-carvone⁷) in 30 mL of THF at 0 °C. After the addition was completed, the yellow solution was allowed to warm to 20 °C and stirred at that temperature for 24 h. The solution was cooled to -78 °C (dry ice-acetone) followed by the addition of 12.6 g (0.15 m) ethyl vinyl ketone in 10 mL of THF over a period of 20 min, after which the reaction mixture was allowed to warm to 20 °C. After 4 h at ambient temperature, the reaction mixture was poured onto 70 mL of 3 N HCl and 70 g of ice, and was extracted with ether $(4 \times 100 \text{ mL})$. The combined extracts were washed with water (50 mL) and brine (100 mL), dried (MgSO₄), filtered, and concentrated to give 34 g of oil. A portion of this mixture (21.1 g) was subjected to flash chromatography⁸ (20% ethyl acetate-hexanes) to afford 13.0 g (92% yield, based upon 93% purity of (-)-dihydrocarvone and including remaining 12.9 g of oil) as a crystalline materal suitable for subsequent reactions. A sample recrystallized from petroleum ether displayed the following data: mp 108 °C [lit.² mp 106 °C (petroleum ether)]; $[\alpha]^{22}_{D}$ -54.6° (c 3.2, methanol) [lit.² $[\alpha]_{5461}$ -54° (c 3.0)]; ¹H NMR (CDCl₃, 90 MHz) δ 1.00 (3 H, d, J = 7.00 Hz), 1.20 (3 H, s), 1.40-3.00 (13 H, m), 1.64 (3 H, s), 4.64 (2 H, br s); IR (CHCl₃) 3550, 1700 cm⁻¹. Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.22; H, 10.24. Found: C, 76.20; H, 10.23.

1,4a(S)-Dimethyl-7(S)-isopropenyl-4,4a,5,6,7,8-hexahydronaphthalen-2(3H)-one ((+)-6-Epi- α -cyperone, 2). A solution of 440 mg (1.86 mmol) of ketol 1a in 5 mL of 8% KOH/EtOH was refluxed for 1 h. The mixture was diluted with water (15 mL) and extracted with ether (3 × 10 mL). The combined extracts were washed with water and brine, dried (MgSO₄), filtered, and evaporated to afford 390 mg of oil. Flash chromatography (20% ethyl acetate-hexanes) provided 390 mg (94% yield) of 2 whose spectroscopic data were in accord with literature values:² ¹H NMR (90 MHz, CDCl₃) δ 1.20 (3 H, s), 1.32–2.00 (6 H, m), 1.68 (3 H, s), 1.80 (3 H, s), 2.20–3.00 (5 H, m), 4.70 (2 H, br s); IR (neat) 1680, 890 cm⁻¹; MS (20 eV), m/e 218.2 (M⁺, 45.5), 203.2 (33), 190.2 (42.5) 175.2 (50.1), 147.2 (73.0), 132.0 (100).

⁽⁸⁾ Still, W. C.; Kahn, M.; Mitra, A. J. Org. Chem. 1978, 43, 2923.

Lithium Bronze Route to (+)-6-Epi- α -cyperone (2). Into a three-necked flask equipped with a stirrer, dry ice condenser, and 760 mg (0.11 mol) of lithium wire under argon was distilled 11 mL (0.44 m) of liquid ammonia (from sodium). After the lithium bronze had formed, 30 mL of dry THF was added. To the stirred mixture was added, dropwise at gentle reflux, a solution of 7.5 g (50 mmol) of (+)-carvone and 3.7 g (50 mmol) of tert-butyl alcohol in 20 mL of dry THF. After the addition was complete, the dry ice condenser was removed, and the ammonia was allowed to evaporate under a stream of N_2 . The mixture was cooled to -78 °C (dry ice-acetone) followed by the addition of 6.72 g (80 mmol) of ethyl vinyl ketone via syringe over 3 min. After the addition was complete, the reaction mixture was allowed to warm to 20 °C at which temperature it was maintained for 1 h. The reaction mixture was quenched with 50 mL of saturated NH₄Cl solution, diluted with water (200 mL), and extracted with ether $(3 \times 100 \text{ mL})$. The combined extracts were washed with 1 N HCl (50 mL), water (50 mL), and brine $(2 \times 50 \text{ mL})$, dried (MgSO₄), filtered, and concentrated to give 11.2 g of residue. TLC and GC analysis indicated the presence of ketol 1a and dihydrocarvone. The residue was dehydrated with 8% KOH/EtOH (vide supra) to provide 9.5 g of crude product. Fractional distillation provided dihydrocarvone [1.5 g (20%); bp 49-50 °C (0.17 mmHg) and 2 [5.3 g (49%); bp 80-81 °C (0.01 mmHg)]. The pot residue was chromatographed to give an additional 2.0 g (18%) of the desired enone

1,4a-Dimethyl-4,4a,5,6,7,8-hexahydronaphthalen-2(3H)-one (5a). To a solution of LDA (5.0 mmol, generated from 524 mg of diisopropylamine and 2.12 mL of 2.35 M n-butyllithium in 5 mL of THF at 0 °C) was added 627 mg of 2-methylcyclohexanone (5.6 mmol) at 0 °C followed by stirring of the solution for 3 h at 20 °C. The reaction mixture was cooled to -78 °C followed by the addition of 672 mg (8.0 mmol) ethyl vinyl ketone over a period of 1 min. The mixture was allowed to warm to 20 °C over 1.5 h and then worked up as described above, providing 1.5 g of oil. Flash chromatography (20% ethyl acetate-hexanes) afforded diketone and two ketols, A and B.

Diketone: 270 mg (27%); ¹H NMR (90 MHz, CDCl₃) δ 0.99 $(3 \text{ H}, \text{t}, J = 8.2 \text{ Hz}, CH_2CH_3), 1.00 (3 \text{ H}, \text{s}), 1.20-2.00 (8 \text{ H}, \text{m}),$ 2.20-2.92 (6 H, m); IR (neat) 1705, 1720 cm⁻¹

Ketol A: 303 mg (31%); mp 106-108 °C (lit.⁹ mp 109-110 °C; trans-fused ketol); ¹H NMR (90 MHz, CDCl₃) δ 0.95 (3 H, d, J = 6.8 Hz), 1.25 (3 H, s), 1.40–2.12 (11 H, m), 2.20–2.80 (3 H, m); IR (neat) 3500, 1725 cm⁻¹.

Ketol B: 262 mg (27%); ¹H NMR (90 MHz, CDCl₃) δ 0.99 (3 H, d, J = 6.9 Hz), 1.04 (3 H, s), 1.40–2.00 (10 H, m), 2.00–2.60 (3 H, m), 2.92 (1 H, q, J = 5.6 Hz); IR (neat) 3500, 1725 cm⁻¹.

Exposure of ketol A (98 mg, 0.5 mmol) to 1 mL of 8% KOH/EtOH for 10 min at 25 °C followed by a workup (vide supra) and flash chromatography (20% ethyl acetate-hexanes) afforded 81 mg (91% yield) of 5a: ¹H NMR (90 MHz, $CDCl_3$) δ 1.20 (3 H, s), 1.40-2.28 (12 H, m), 1.76 (3 H, s); IR (neat) 1678 cm⁻¹.

A 260-mg sample of ketol B was converted to 5a in 94% yield by using the above procedure.

7(R)-Isopropenyl-4a(R)-methyl-4,4a,5,6,7,8-hexahydronaphthalen-2(3H)-one (4a). A solution of LDA (5.0 mmol) in THF (4 mL) was prepared as described at 0 °C. After 10 min, 845 mg (+)-dihydrocarvone (5.5 mmol, from (-)-carvone) in 1 mL of THF was added and allowed to warm to 25 °C. After 2 h, the mixture was cooled to -78 °C, and methyl vinyl ketone was added dropwise via syringe over a period of 1 min. The cooling bath was removed as the temperature was allowed to warm to 25 °C. The workup (vide supra) gave 1.7 g of oil. Flash chromatography (30% ethyl acetate-hexanes) provided the following substances after the initial removal of dihydrocarvone.

Diketone: 133 mg (12%); ¹H NMR (90 MHz, CDCl₃) δ 0.96 (3 H, s), 1.12-1.88 (4 H, m), 1.72 (3 H, s, vinylic CH₃), 2.08 (3 H, s, COCH₃), 2.20-2.44 (4 H, m), 4.68 (1 H, br s), 4.76 (1 H, br s).

Ketol 3a: 595 mg (53%); ¹H NMR (90 MHz, CDCl₃) δ 1.17 (3 H, s), 1.40-2.88 (14 H, m), 1.66 (3 H, s), 4.68 (2 H, br s); IR (neat) 3500, 1710 $\rm cm^{-1}$.

Ketol 3b: 128 mg (12%); ¹H NMR (90 MHz, CDCl₃; partial) δ 1.04 (3 H, s), 1.64 (3 H, s), 4.62 (2 H, br s).

Hydroxy ketone **3a** (111 mg) was stirred at 25 °C for 2 h in 0.5 mL of 8% KOH/EtOH. The workup afforded 102 mg of yellow oil which, after flash chromatography (30% ethyl acetate-hexane), provided pure enone 4a: 72 mg (70% yield); ¹H NMR (90 MHz, CDCl₃) δ 1.24 (3 H, s), 1.36–2.80 (11 H, m), 1.72 (3H, s), 4.76 (1 H, br s), 4.88 (1 H, br s), 5.76 (1 H, br s); IR (neat) 1670 cm⁻¹; GC/MS (20 ev), m/e 204 (M⁺).

By use of the same procedure, ketol 3b (128 mg) afforded enone **4b**: 60% yield; ¹H NMR (90 MHz, CDCl₃) δ 1.04 (3 H, s) 1.40–3.12 (11 H, m), 1.68 (3 H, s), 4.80 (2 H, br s), 5.80 (1 H, br s); IR (neat) 1680 cm⁻¹; GC/MS (20 eV), m/e 204 (M⁺).

4a-Methyl-4,4a,5,6,7,8-hexahydronaphthalen-2(3H)-one (5b). To a solution of LDA (5.0 mmol) in 5 mL of THF was added 627 mg (5.6 mmol) of 2-methylcyclohexanone at 0 °C. The mixture was stirred for 3 h at 20 °C. After the solution was cooled to -78 °C, 700 mg (1.0 mmol) of methyl vinyl ketone was added. The cooling bath was removed, and the reaction mixture was allowed to warm to 20 °C over 1.5 h. The reaction mixture was cooled to -5 °C and quenched with 5 mL of saturated aqueous NH₄Cl, followed by the workup (vide supra). The resultant oil (1.5 g)was flash chromatographed (30% ethyl acetate-hexanes) to afford the following fractions.

Enone 5b: 135 mg (17%); ¹H NMR (90 MHz, CDCl₃) δ 1.22 (3 H, s), 1.32-2.56 (12 H, m), 5.72 (1 H, s); IR (neat) 1680 cm⁻¹; GC/MS (20 eV), m/e 164 (M⁺)

Ketol 6: 601 mg (contaminated with MVK polymer); ¹H NMR (90 MHz, $CDCl_3$) δ 1.04 (angular methyl). The crude material was exposed to 2 mL of 8% KOH/EtOH at 25 °C for 2 h followed by a workup. The crude residue (470 mg) was subjected to flash chromatography (30% ethyl acetate-hexanes) to provide 119 mg (15%) of enone **5b**. The overall yield was 32%

Registry No. 1a, 86785-82-2; 2, 547-26-2; 3a, 86785-83-3; 3b, 86785-84-4; 4a, 13567-79-8; 4b, 13918-47-3; 5a, 878-55-7; 5b, 826-56-2; 6, 40573-27-1; (-)-dihydrocarvone, 619-02-3; 2methylcyclohexanone, 583-60-8; (+)-dihydrocarvone, 5524-05-0; ethyl vinyl ketone, 1629-58-9; methyl vinyl ketone, 78-94-4; (+)-carvone, 2244-16-8; 2-(3-oxopentyl)-2-methylcyclohexanone, 86785-85-5; 1,4a α -dimethyl-8a α -hydroxydecahydronaphthalen-2-one, 86833-39-8; 1,4a α -dimethyl-8a β -hydroxydecahydronaphthalen-2-one, 86833-40-1; 4(R)-isopropenyl-2-methyl-2(3oxobutyl)cyclohexanone, 66708-16-5.

Examination of (-)- α -Naphthylphenylmethylallylsilane as a **Template for Effecting Chirality Transfer from** Silicon to Carbon¹

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The concept of transferring chirality from asymmetric silicon to carbon, particularly in conjunction with a recyclable chiral silicon pool,¹ holds special interest. We have sought to examine in preliminary fashion the workability of this proposal with $(-)-\alpha$ -naphthylphenylmethylallylsilane (1), the most readily available Si-centered² optically active allylsilane presently known.³ Recent reports have

⁽²⁾ Asymmetric allylsilanes may owe their optical activity to a chiral silicon atom as in I or to a chiral carbon atom as in i. To distinguish simply between these intrinsically different forms of optical activity, we propose use of the qualifying adjectives "Si-centered" and "C-centered", respectively.



⁽¹⁾ Silanes in Organic Synthesis. 19. For part 18, see: Daniels, R. G.; Paquette, L. A. Organometallics 1982, 1, 1449.