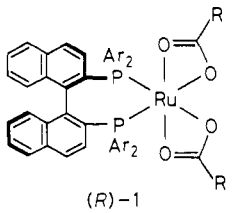
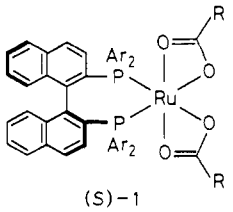


(R)-1



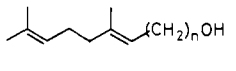
(S)-1

a, Ar = C_6H_5; R = CH_3 c, Ar = p-$CH_3C_6H_4$; R = CH_3

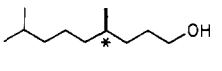
b, Ar = C_6H_5; R = $C(CH_3)_3$

avoiding hydrogenation of the C(6)=C(7) bond, (3) lack of double-bond migration[3] or E/Z isomerization, (4) high substrate/catalyst (S/C) mole ratio, and (5) easy recovery or reusability of the catalysts.

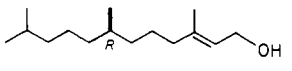
BINAP-based Ru(II) dicarboxylate complexes (**1**) were found to serve as efficient catalyst precursors, meeting all the above described criteria. Some representative results obtained under varying reaction conditions are summarized in Table I. (*R*)- or (*S*)-Citronellol, **4**, was obtained in nearly quantitative yield and with 96–99% enantioselectivity. The allylic and nonallylic double bonds in **2** and **3** can be clearly differentiated; the product was accompanied by less than 0.5% of, if any, dihydrocitronellol.[11] Initial hydrogen pressure higher than 30 atm afforded satisfactory enantioselectivities. The S/C mole ratio is extremely high and, in certain cases, the efficiency of the chiral multiplication, defined as [major stereoisomer − minor stereoisomer (in mol)]/chiral source in mol, approaches 48 500! The catalyst can be recovered, if one desires, by simple distillation of the product under reduced pressure (35 °C/1.5 × 10^{-5} mmHg); the air-sensitive BINAP-Ru complex residue acts as a catalyst for further runs without substantial loss of activity and selectivity. The stereochemical outcome outlined in Scheme I implies that the BINAP-Ru species differentiates the C(2) enantiofaces at a certain stage of the catalysis. Thus, both *R* and *S* enantiomers are accessible by either variation of allylic olefin geometry or choice of handedness of the catalysts. The relative position of the hydroxyl group and olefinic bond strongly affects the reactivity and selectivity. Hydrogenation of homogeraniol (**5**) aided by (*S*)-**1a** (S/C = 200, CH_3OH, 30 °C, 3 h, 100 atm) occurred regioselectively to produce (*R*)-**7** in 96% yield and in 92% ee.[10] Sense of the asymmetric induction was identical with that of the reaction of **2**. However, the higher homologue **6** was inert to the comparable hydrogenation conditions.



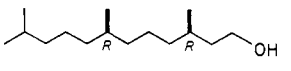
5, n = 2
6, n = 3



7



8



9

High levels (>90%) of enantioselective hydrogenations have been attained only with α-acylaminoacrylic acids or esters[2] and related substrates.[7] The present result marks the first example of the high enantioselection with simple prochiral unsaturated alcohols, providing a new, powerful means in the synthesis of optically active terpenes and related compounds. Indeed, this procedure has been successfully applied to the asymmetric synthesis of (3*R*,7*R*)-3,7,11-trimethyldodecanol (**9**),[13] a versatile intermediate for convergent synthesis of α-tocopherol (vitamin E). When the pure *R*,*E* allylic alcohol **8**, derived from homochiral isopulegol,[14] was hydrogenated in the presence of (*S*)-**1a** (S/C = 520, CH_3OH, 20 °C, 3.5 h, 100 atm), the desired saturated alcohol **9** was obtained in 99% yield. The diastereomeric purity of the 3*R*,7*R* alcohol, $[\alpha]^{25}_D$ +3.19° (*c* 3.76, $CHCl_3$), was determined to be 99% by HPLC analysis of the amide,[13c] derived from the oxidized 3,7,11-trimethyldodecanoic acid and (*R*)-1-(1-naphthyl)ethylamine.[10,15] Since the requisite **8** now becomes obtainable in 98% ee in a practical manner starting from (*R*)-citronellal, synthesized by the BINAP–Rh^+-catalyzed asymmetric isomerization of diethylgeranylamine (1,3-hydrogen shift) followed by hydrolysis,[6c] combination of the chiral C_{15} building block, **9**, and readily accessible (*S*)-chroman-2-carboxylic acid[16] opens a promising, straightforward way to α-tocopherol.[17]

(8) (*S*)-(−)-Citronellol of optical purity up to 92% can be obtained in a limited quantity from rose oil. (*R*)-(+)-Citronellol has been obtained by hydrogenation of naturally occurring citronellal of <85% optical purity. Enantiomerically pure (*R*)-(+)-citronellol has been obtained by a microbiological reduction of geraniol.[9]

(9) Gramatica, P.; Manitto, P.; Maria Ranzi, B.; Delbianco, A.; Francavilla, M. *Experientia* **1982**, *38*, 775.

(10) Bergot, B. J.; Anderson, R. J.; Schooley, D. A.; Henrick, C. A. *J. Chromatogr.* **1978**, *155*, 97.

(11) The hydrogenation of **2** using $[Ru_2((R)\text{-binap})_2Cl_4]N(C_2H_5)_3$[12] as catalyst (6:1 ethanol–methylene chloride, H_2 40 atm, 24 °C, 90 h) gave (*S*)-**4** in 47% yield and in 93% ee (92% conversion) in addition to dihydrocitronellol (40% yield).

(12) Ikariya, T.; Ishii, Y.; Kawano, H.; Arai, T.; Saburi, M.; Yoshikawa, S.; Akutagawa, S. *J. Chem. Soc., Chem. Commun.* **1985**, 922.

(13) (a) Valentine, D., Jr.; Chan, K. K.; Scott, C. G.; Johnson, K. K.; Toth, K.; Saucy, G. *J. Org. Chem.* **1976**, *41*, 62. (b) Chan, K.-K.; Cohen, N.; De Noble, J. P.; Specian, A. C., Jr.; Saucy, G. *J. Org. Chem.* **1976**, *41*, 3497. (c) Fujisawa, T.; Sato, T.; Kawara, T.; Ohashi, K. *Tetrahedron Lett.* **1981**, *22*, 4823. (d) Koreeda, M.; Brown, L. *J. Org. Chem.* **1983**, *48*, 2122. (e) Fujiwara, J.; Fukutani, Y.; Hasegawa, M.; Maruoka, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1984**, *106*, 5004. (f) Takabe, K.; Uchiyama, Y.; Okisaka, K.; Yamada, T.; Katagiri, T.; Okazaki, T.; Oketa, Y.; Kumobayashi, H.; Akutagawa, S. *Tetrahedron Lett.* **1985**, *26*, 5153. (g) Kallmerten, J.; Balestra, M. *J. Org. Chem.* **1986**, *51*, 2855.

(14) Sully, B. D.; Williams, P. L. *Perfum. Essent. Oil Rec.* **1968**, *59*, 365.

(15) The reduction of **8** catalyzed by (*R*)-**1a** gave the 3*S*,7*R* isomer with equal (99%) selectivity.

(16) Cohen, N.; Lopresti, R. J.; Neukom, C. *J. Org. Chem.* **1981**, *46*, 2445.

(17) (a) Barner, R.; Schmid, M. *Helv. Chim. Acta* **1979**, *62*, 2384. (b) Cohen, N.; Lopresti, R. J.; Saucy, G. *J. Am. Chem. Soc.* **1979**, *101*, 6710.

Enantioselective Total Synthesis of Aphidicolin

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Tallahassee, Florida 32306

Received November 17, 1986

The diterpene tetraol aphidicolin (**1**), isolated from *Cephalosporium aphidicolia* petch,[2] has been found to reduce the mitotic rate of mouse L cells and to inhibit the growth of *Herpes simplex* Type I.[3] The strong in vitro activity of aphidicolin against herpes virus is presumed to arise through inhibition of virus DNA synthesis.[4] Its structure was first elucidated by chemical and spectroscopic means, and the structure and absolute configuration were confirmed by X-ray crystal analysis.[2a]

(1) A portion of this work was carried out at Virginia Polytechnic Institute and State University.

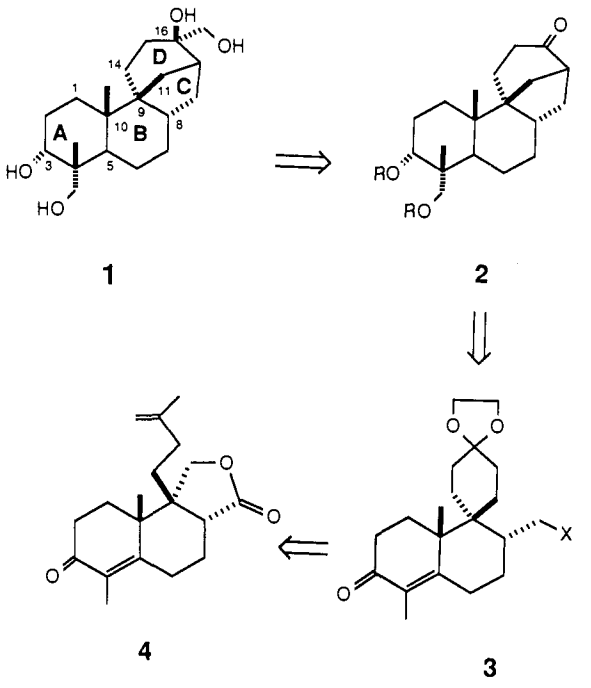
(2) (a) Bundret, K. M.; Dalziel, W.; Hesp, B.; Jarvis, J. A. J.; Neidle, S. *J. Chem. Soc., Chem. Commun.* **1972**, 1027. (b) Dalziel, W.; Hesp, B.; Stevenson, K. M.; Jarvis, J. A. J. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2847.

(3) Bucknall, R. A.; Moores, H.; Simms, R.; Hesp, B. *Antimicrob. Agents Chemother.* **1973**, *4*, 294.

(4) (a) Starrett, A. N.; Loshiavo, S. R. *Can. J. Microbiol.* **1974**, *20*, 416. (b) Kawada, K.; Kimura, Y.; Katogiri, K.; Suzuki, A.; Tamura, S. *Agric. Biol. Chem.* **1978**, *42*, 1611. (c) Ohashi, M.; Taguchi, T.; Ikegami, S. *Biochem. Biophys. Res. Commun.* **1978**, *82*, 1084.

0002-7863/87/1509-1597$01.50/0

Scheme I

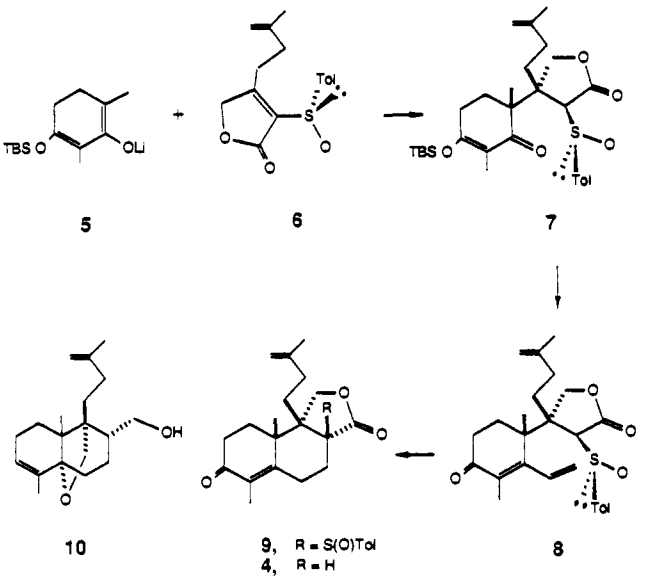


In recent years there has been great interest in this unusual structure. Eight synthetic routes to **1** have been described,[5] and six of these have resulted in successful total syntheses.[5a-f] Despite the elegance of some of these approaches, the most efficient produces racemic **1** in modest overall yield. We report here the first enantioselective total synthesis of aphidicolin.

Our retrosynthetic analysis is shown in Scheme I. Aphidicolinone (**2**, R = H) has been the objective of several total syntheses,[5a-c] has been prepared from aphidicolin,[2b] and has been converted back to the natural product,[2b,5c] albeit with poor stereoselectivity. We planned to construct **2** by formation of the C ring last, with the aim of preparing a known intermediate in Corey's total synthesis.[5c] We envisioned several routes to **3**, and the one reported here employs the keto lactone **4**. A primary goal of this work was to overcome the major difficulty shared by most of the existing total syntheses: construction of the C-9, C-10 contiguous quaternary centers. Therefore, our approach addresses formation of the quaternary centers in the first stage of the synthesis.

The preparation of keto lactone **4** is outlined in Scheme II. This sequence is based upon three studies that we have recently described: (1) the formation of contiguous quaternary centers via the kinetic Michael addition,[6] (2) a new stereospecific annulation employing tandem Michael additions,[7] and (3) a simple preparation of chiral *p*-tolylsulfinyl butenolides.[8] Michael addition of lithium dienolate **5**, from deprotonation of 2,6-dimethyl-3-(*tert*-butyldimethylsiloxy)-2-cyclohexenone with LDA in THF at −78 °C, to (*S*)-(+)-sulfinyl butenolide **6**[8] in THF at −95 °C for 2 h gave a 7.4:1 mixture of diastereomeric sulfinyl lactones in 75% yield. Recrystallization of this mixture afforded **7**,[9,10] mp

Scheme II



138–140 °C, $[\alpha]^{25}_{Hg}$ + 132° ($CHCl_3$, *c* 0.12). Addition of vinyllithium (7 mol equiv, toluene, 25 °C, 20 min) to **7** was followed by treatment with HF (1 M in methanol) at 25 °C for 20 min to provide **8**,[10] mp 145–147 °C, $[\alpha]^{25}_{Hg}$ +172° ($CHCl_3$, *c* 0.09), in 76% yield. In the presence of sodium methoxide in methanol containing a trace of water at 0 °C for 2.5 h, **8** smoothly cyclized to give **9**,[10] mp 135–137 °C, $[\alpha]^{25}_{Hg}$ +116° ($CHCl_3$, *c* 0.11), quantitatively. This sequence could be carried out in a single synthetic operation. For this purpose **6** was added to a solution of **5** in toluene at −78 °C. The solution was slowly warmed to 0 °C, 7 mol equiv of vinyllithium in pentane was added, and after 1 h the mixture was diluted with methanolic HF. After 20 min at 25 °C, the solution was cooled to 0 °C, made basic with methanolic sodium methoxide, and stirred at 0 °C for 1.5 h to give, after chromatography, enone **9** in 45% yield.[11]

The cis relationship of the C-10 methyl and the C-9 methylbutenyl substituents in **9** was verified as follows. Reductive desulfurization (Zn/NH_4Cl)[12] provided **4**,[10] mp 144–145 °C, $[\alpha]^{25}_{Hg}$ +34° ($CHCl_3$, *c* 1.02), in 94% yield. Reduction of **4** with lithium aluminum hydride in THF gave a triol which cyclized (PPTS, acetone, 25 °C) quantitatively to the ether **10**. Although this experiment made certain the relative stereochemistry at C-9 and C-10 in **7**–**9** and **4**, the absolute configuration of these compounds, as well as the stereochemistry at C-9 and C-10 relative to that at sulfur in **7**–**9** remained unknown at this stage.

The conversion of **4** into pivalyl aphidicolinone (**17**) is outlined in Scheme III. We had hoped, based upon experience with a model system,[13] to be able to introduce A ring functionality through lithium–ammonia reduction of **4**. However, this reduction produced only the cis AB ring fused material.[14] Therefore, we

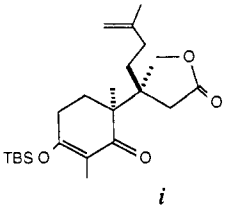
(5) (a) McMurry, J. E.; Andrus, A.; Musser, J. H.; Johnson, M. A. *Tetrahedron* **1981**, *37*, 319. (b) Trost, B. M.; Nishimura, Y.; Yamamoto, K. *J. Am. Chem. Soc.* **1979**, *101*, 1328. (c) Corey, E. J.; Tius, M. A. Das, J. *Ibid.* **1980**, *102*, 1742. (d) Ireland, R. E.; Godfrey, J. D.; Thaisrivongs, S. *Ibid.* **1981**, *103*, 2446. (e) van Tamelen, E. E.; Zawacky, S. R., Russel, R. K.; Carlson, J. G. *Ibid.* **1983**, *105*, 142. (f) Bettollo, R. M.; Tagliatesta, P.; Lupi, A. Bravetti, D. *Helv. Chem. Acta* **1983**, *66*, 1922. (g) Kametani, T.; Honda, T.; Shiratori, Y.; Fukumoto, K. *Tetrahedron Lett.* **1980**, 1665. (h) Cargill, R. L.; Bushey, D. F.; Dalton, J. R.; Prasad, R. S.; Dyer, R. D.; Bonder, J. *J. Org. Chem.* **1981**, *46*, 3389.

(6) Holton, R. A.; Williams, A. D.; Kennedy, R. M. *J. Org. Chem.* **1986**, *51*, 5480.

(7) Krafft, M. E.; Kennedy, R. M.; Holton, R. A. *Tetrahedron Lett.* **1986**, *27*, 2087.

(8) Holton, R. A.; Kim, H. B. *Tetrahedron Lett.* **1986**, *27*, 2191.

(9) Reductive desulfurization (Zn/NH_4Cl)[12] of the minor diastereomer gave a lactone, which we have tentatively identified as i.



i

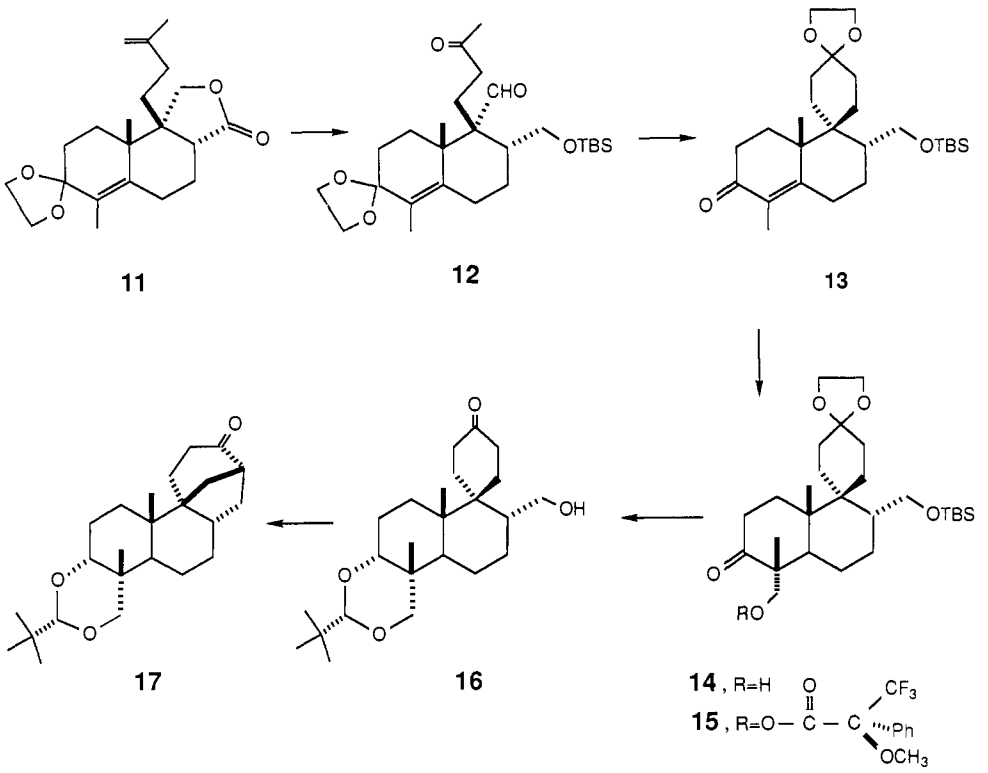
(10) Characterized by either combustion analysis or high-resolution mass spectroscopy.

(11) Determined to be >98% ee by ^1H NMR analysis in the presence of TRIS [3-(heptafluoropropylhydroxymethylene)-*d*-camphorato]europium(III) derivative, Aldrich catalog no. 16,474-7, in $CDCl_3$ solution.

(12) Holton, R. A.; Crouse, D. J.; Williams, A. D.; Kennedy, R. M. *J. Org. Chem.*, in press.

(13) Holton, R. A.; Kennedy, R. M. *Tetrahedron Lett.* **1981**, *28*, 303.

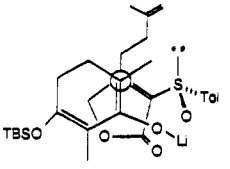
Scheme III



postponed this operation until after construction of the D ring.[5d] The enone **4** was protected (PPTS, benzene, 2-ethoxydioxolane, reflux 8 h, 89%) as the ketal **11**,[10,15] mp 141–143 °C, $[\alpha]^{25}_{Hg}$ +57° ($CHCl_3$, *c* 0.90), in which double-bond migration had not occurred.[16] Selective ozonolysis of the disubstituted olefin[17] (O_3, CH_2Cl_2, −78 °C, $(CH_3)_2S$) was followed by reduction (LAH, THF, 25 °C) to a mixture of diastereomeric triols, selective silylation[18] (TBSCl, DMAP, Et_3N, CH_2Cl_2, −78 °C, 6 h), and oxidation (CrO_3, pyridine, 25 °C, 2.5 h) to provide keto aldehyde **12**,[10] mp 109–111 °C $[\alpha]^{25}_{Hg}$ +80° ($CHCl_3$, *c* 0.31), in 65% yield from **11**. Aldol closure of the D ring was easily accomplished (KO-*t*-Bu, THF, *t*-BuOH, 0 °C, 1 h), and selective hydrogenation of the disubstituted olefin (H_2, 5% Pd/C, EtOH, NaOEt)[19] was followed by ketal exchange (2-methyl-2-ethyldioxolane, $HOCH_2CH_2OH$, *p*-TsOH, 0 °C, 1 h) to give enone **13**,[10] mp 102–103.5 °C, $[\alpha]^{25}_{Hg}$ +88° ($CHCl_3$, *c* 0.36), in 90% yield from **12**. Lithium–ammonia reduction of **13** with in situ formaldehyde trapping produced ketol **14**,[10] mp 113–114 °C, $[\alpha]^{25}_{Hg}$ −14° ($CHCl_3$, *c* 1.51), in 70% yield. ^1H NMR analysis of the (*S*)-(−)-MTPA ester **15**[20] indicated the optical purity of this material to be >99% ee.[21] Reduction of **14** (L-Selectride, THF, −78 → 25 °C, 1 h) gave a diol which was converted directly (pivaldehyde, *p*-TsOH, HF, 0 °C, 20 min) to the Corey intermediate[5c] **16**,[10] mp 118–120 °C, $[\alpha]^{25}_{Hg}$ +8° ($CHCl_3$, *c* 0.45),[22] in 85% yield from **14**. The ^1H and ^{13}C NMR spectra of **16** were identical with spectra of racemic **16** kindly provided by Professor Corey.

At this stage, the synthesis of aphidicolin was formally complete, but the critical question of the absolute configuration of the synthetic material had not been answered. Therefore, following Corey's procedure, **16** was converted (90% yield) to pivalyl aphidicolinone **17**, mp 137–138.5 °C, $[\alpha]^{25}_{Hg}$ −41° ($CHCl_3$, *c* 0.21). An authentic sample of **17**, mp 137–138.5 °C, $[\alpha]^{25}_{Hg}$ −40° (*c* 0.31, $CHCl_3$), was prepared[2a] from natural aphidicolin and was found to be identical (mixture mp 137–138.5 °C) with synthetic **17**.

This result clearly confirms the stereochemical relationship between sulfinyl butenolide **6** and butyrolactone **7** to be as shown in Scheme II.[9] On this basis we formulate the transition state **18** for the Michael addition which provides **7**. Further studies of stereoselectivity in the Michael addition are in progress.[23]



18

In addition to being the first enantioselective total synthesis of aphidicolin, this is also the most efficient synthesis reported to this time, providing pivalyl aphidicolinone in ca. 12% overall yield from **6**. We are still continuing to explore variants of this conceptual approach with the hope of finding an even more efficient synthetic route to **1**.

Acknowledgment. We thank the National Cancer Institute for providing generous finanical support, Dr. Matthew Suffness for

(14) ^1H NMR NOE difference experiments were in accord with the preferred conformation of **11** having ring B in the boat form.

(15) Ketal **11** was found to be very acid labile and subsequent reactions on substrates having this functionality were carried out in base-washed glassware.

(16) For related observations, see: (a) Nitz, T. J.; Paquette, L. A. *Tetrahedron Lett.* **1984**, *25*, 3047. (b) Barton, D. H. R.; Dawes, C. C.; Magnus, P. D. *J. Chem. Soc., Chem. Commun.* **1975**, 432.

(17) This cleavage could also be carried out with $OsO_4/NaIO_4$ in Et_2O/H_2O buffered with NEt_3 to prevent ketal hydrolysis.

(18) Tanis, S. P.; Nakanishi, K. *J. Am. Chem. Soc.* **1979**, *101*, 4398.

(19) Inclusion of sodium ethoxide effectively suppressed competing hydrogenolysis of the unsaturated ketal.

(20) (a) Dale, J. A.; Mosher, H. S. *J. Am. Chem. Soc.* **1973**, *95*, 512 and references contained therein. (b) Yamaguchi, S. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: New York, 1982; Vol. 1, p 125.

(21) ^1H NMR analysis of **15** indicated the presence of a single diastereomer. Another diastereomer could be detected by ^1H NMR analysis of a mixture containing 98% **15** and 2% of the MTPA ester prepared from racemic **14**.

(22) This rotation is too low to be considered reliable.

(23) For other examples of asymmetric Michael additions to vinylic sulfoxides, see: Posner, G. H.; Weitzberg, M.; Hamill, T. G.; Asirvatham, E.; Cun-Heng, H.; Clardy, J. *Tetrahedron* **1986**, *42*, 2919; Posner, G. H.; Switzer, C. *J. Am. Chem. Soc.* **1986**, *108*, 1239.

providing a sample of natural aphidicolin, and Professor E. J. Corey for providing spectra of synthetic **16** and **17**. We are especially grateful to Chris Lovett and Owl Technical Associates, Inc., for their generous loan of a Thorn polarimeter.

Hydrogen Transfer from 1-Naphthol Triplet to Ground-State Benzophenone: Kinetic Evidence against Proposed Exciplex Intermediacy

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Received June 19, 1986

A recent report by Shizuka et al.[1] concerns the transfer of hydrogen from the triplet state of 1-naphthol to the ground state of benzophenone in methanol. Production of the naphthol triplet was by energy transfer from triplet benzophenone, itself formed by pulsed nitrogen laser excitation at 337 nm. The critical mechanistic conclusion of this work was that the H-transfer process takes place within a triplet exciplex, cf. Scheme I. This conclusion was based on curvature observed in plots of the first-order constant for naphthol triplet decay, k', as a function of benzophenone concentration [(1–14) × 10^{-3} mol L^{-1}]. No changes in the absorption characteristics of the naphthol triplet were noted either with time or ketone concentration. This was attributed to lack of $\pi-\pi$ interaction within the exciplex, possibly due to H-bonding-induced association as depicted in Scheme I. Given the assumption of this scheme, standard exciplex kinetic treatments and curve-fitting routines were employed to define rate and activation parameters for the system, an equilibrium constant for exciplex formation of 14.1 L mol^{-1} at 300 K being determined.

We have also examined the 1-naphthol/benzophenone system, albeit in benzene using the pulse radiolysis technique,[2] and have found no evidence for exciplex intermediacy. However, since extrapolation from one medium to another, particularly from aprotic to protic, is clearly not possible, we have carried out experiments essentially identical with those reported by Shizuka et al.; again we find no evidence whatsoever for exciplex intermediacy.

Thus, deaerated methanol solutions of 1-naphthol (3 × 10^{-3} mol L^{-1}) containing various benzophenone concentrations [(3–30) × 10^{-3} mol L^{-1}] were subjected to excitation with the third harmonic (355 nm; 12 ns) of a Q-switched Nd:YAG laser. Transient absorption spectroscopy was in excellent agreement with the overall sequence proposed by Shizuka et al., eq 1. Formation

$$^3Ph_2CO^* \xrightarrow{HO\text{-}Naph} {}^3HO\text{-}Naph^* \xrightarrow{Ph_2CO} \dot{O}\text{-}Naph + Ph_2\dot{C}OH \quad (1)$$

of the naphthol triplet (λ_{max} 430 nm) by energy transfer from triplet benzophenone (λ_{max} 525 nm) was essentially complete within 400 ns. Subsequent reaction with ground-state benzophenone gave the corresponding ketyl (λ_{max} 550 nm) and naphthyloxy (λ_{max} 390 nm) radicals, cf. spectra reproduced in Figure 1a. It is clear from these spectra that the radicals exhibit significant absorption at 430 nm, the naphthol triplet maximum. This is confirmed by the decay of transient absorption at 430 nm reproduced in Figure 1b which shows "fast" decay of triplet and "slow" decay of radicals. It is therefore clear that determination of the first-order constant for decay, k', of naphthol triplet as a function of benzophenone concentration, the relationship leading Shizuka et al. to propose exciplex intermediacy, is a nontrivial exercise. Radical decay is kinetically second order. We have therefore analyzed the decay of transient absorption at 430 nm as a combination of independent first- and second-order processes,[3] cf. Figure 1b. This is a sensible procedure because of the large difference in naphthol triplet and radical lifetimes. In the least favorable case, i.e., at the lowest benzophenone concentration, first half-lives were 3.2 and 136 μs, respectively. In addition, to obviate possible problems associated with excited-state concentration changes as a consequence of changing the concentration of the species which absorbs the laser light (benzophenone), the laser energy was suitably attenuated by means of metal-coated filters. Maximum optical densities of naphthol triplet were therefore low and reasonably uniform, 0.028 ± 0.008, and the analyzing light was restricted to a band between 420 and 470 nm (Balzer K45 interference filter); detection system details have been described.[4] In Figure 1 is shown the resulting plot of k' vs. benzophenone concentration, each point corresponding to an average of five shots. The arrows indicate the concentration range over which Shizuka

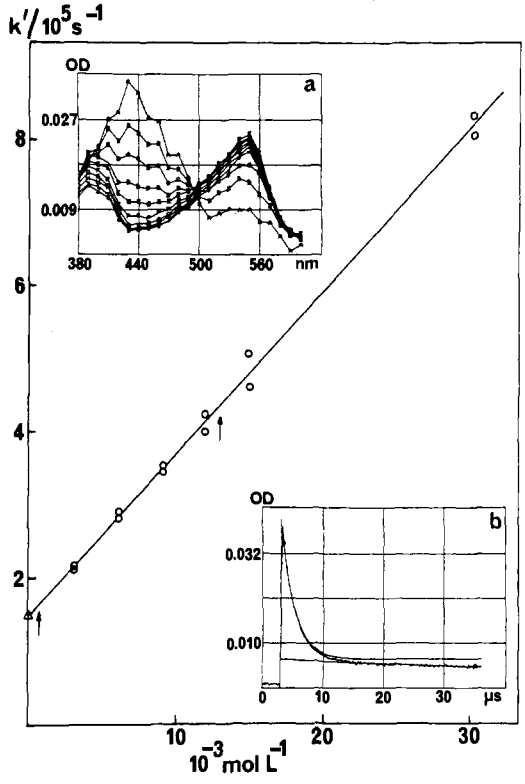
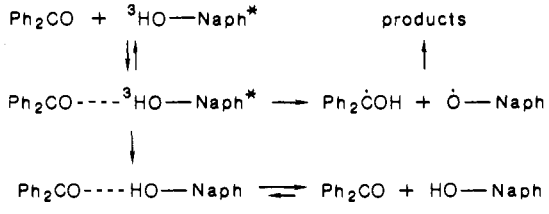


Figure 1. First-order constant, k', for 1-naphthol triplet decay at 298 K, determined at 430 nm, as a function of benzophenone concentration; the data point at zero concentration corresponds to the intercept obtained by Shizuka et al.[1] at 300 K. Insets: (a) transient absorption spectra measured 0.4 (A), 1.0 (B), 1.7 (C), 2.7 (D), 3.7 (E), 5.5 (F), 7.5 (G), 9.5 (H), 11.5 (I), and 13.5 (J) μs after absorption of a 12-ns laser pulse (355 nm) by deaerated methanol containing 1-naphthol (3 × 10^{-3} mol L^{-1}) and benzophenone (1.51 × 10^{-2} mol L^{-1}); (b) decay of transient absorption at 430 nm for a similar experiment with 1-naphthol (3 × 10^{-3} mol L^{-1}) and benzophenone (1.21 × 10^{-2} mol L^{-1}) showing fit for independent first-order (fast) and second-order (slow) processes together with individual components.

Scheme I



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