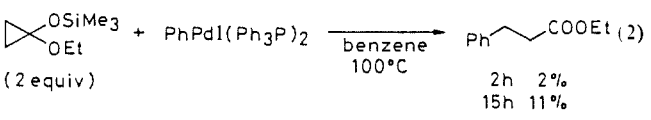
(25% in THF, 37% in PhCl at 50 °C), indicating that the cleavage of the C-C bond by an electron-demanding cationic complex is a remarkably facile process.

Halobenzenes (PhX) failed to react with **1a**, due to the inability of the $PhPdXL_n$ complex generated in situ to activate the C-C bond. In fact, **1a** was phenylated in very poor yield even by a stoichiometric amount of $PhPdI(Ph_3P)$[13] (eq 2). In addition, the



presence of either LiCl (3 equiv) or Bu_4NBr (1 equiv), which converts a tetracoordinated platinum triflate complex to the halide complex,[14] almost completely inhibited the reaction of **1a** with the aryl triflate. These observations indicate that the high electron-demanding nature of the intermediary arylpalladium complex[11] (cf. eq 1) is essential for the desired C-C bond cleavage.

In addition to the siloxycyclopropanes **3** and **4** that generate ester homoenolates, the siloxycyclopropanes **5-9** that produce ketone and aldehyde homoenolates also cleanly reacted with various aryl triflates.[15] Tables I and II show the examples, which demonstrate the utility of the reaction for the functionalization of various aromatic nuclei including coumarin and pyridine. The high functional group selectivity (e.g., aldehyde, ketone, ester, and nitro groups remaining intact) of this reaction stands in contrast to the limited selectivity of the standard, classical Umpolung-counterpart[7] such as the conjugate addition of aryl cuprates to unsaturated carbonyl compounds.[16] Substituted siloxycyclopropanes **4**, **5**, **7**, **8**, and **9** underwent exclusive cleavage of the less substituted C-C bond connected to the siloxy group. *tert*-Butyldimethylsiloxycyclopropane **8** also gave the arylation product in good yield.

It should be noted that *p*-methoxyphenyl triflate (Table I, entry 6) fails to arylate the cyclopropane **3**, which makes sharp contrast to the result with the *m*-methoxy derivative (entry 5). The deactivating effect of the *p*-methoxy group gives strong supporting evidence for the presumed importance of the electron-demanding nature of the metal in this reaction (vide supra).[17]

In summary, it is demonstrated that *the combination of an electron-rich C-C bond and an electron-demanding metal complex provides a viable protocol for catalytic C-C bond cleavage for organic synthesis*. In addition, the successful use of the highly labile, nucleophilic homoenolates of ketone and aldehyde provides a significant addition to the repertory of homoenolate chemistry.[18]

Acknowledgment. E.N. thanks Professors J. Halpern and I. Ojima for helpful discussion, Asahi Glass Foundation for partial financial support, and Central Glass Co. for a gift of trifluoromethanesulfonic acid.

Registry No. 2 (R = O-*i*-Pr; Ar = C_6H_5), 22767-95-9; **2** (R = O-*i*-Pr; Ar = *o*-FC_6H_4), 113777-12-1; **2** (R = O-*i*-Pr; Ar = *p*-$CH_3C(=O)C_6H_4$), 113777-13-2; **2** (R = O-*i*-Pr; Ar = *o*-$CH_3C(=O)OC_6H_4$), 113777-14-3; **2** (R = O-*i*-Pr; Ar = *m*-$CH_3OC_6H_4$), 113777-15-4; **2** (R = O-*i*-Pr; Ar = 1-$C_{10}H_7$), 113777-16-5; **2** (R = O-*i*-Pr; Ar = 4-coumarinyl), 113777-17-6; **3**, 84098-44-2; **4**, 113777-08-5; **5**, 38858-74-1; **6**, 60068-19-1; **7**, 113777-09-6; **8**, 113777-10-9; **9**, 113777-11-0; $[PdCl(\eta^3\text{-}C_3H_5)]_2$, 12012-95-2; PPh_3, 603-35-0; C_6H_5OTf, 17763-67-6; *o*-FC_6H_4OTf, 113777-27-8; *p*-$CH_3C(=O)C_6H_4OTf$, 109613-00-5; *o*-$CH_3C(=O)OC_6H_4OTf$, 113777-28-9; *m*-$CH_3OC_6H_4OTf$, 66107-33-3; *p*-$CH_3OC_6H_4OTf$, 66107-29-7; 1-$C_{10}H_7OTf$, 99747-74-7; ethyl 2-methyl-3-(1-naphthyl)propionate, 113777-18-7; 2-(1-naphthylmethyl)-cyclohexanone, 113777-19-8; 2-(4-nitrophenylmethyl)cyclohexanone, 113777-20-1; 2-(4-acetylphenylmethyl)cyclohexanone, 113777-21-2; 2-(2-pyridylmethyl)cyclohexanone, 113777-22-3; 1-(4-methoxyphenyl)-3-phenyl-1-propanone, 5739-38-8; 1-(4-methoxyphenyl)-3-(1-naphthyl)-1-propanone, 113777-23-4; 2-(1-naphthylmethyl)-3-pentanone, 113777-24-5; 2-(1-naphthylmethyl)nonanone, 113777-25-6; 2-(4-acetylphenylmethyl)nonanal, 113777-26-7; 4-coumarinyl triflate, 113777-29-0; 4-nitrophenyl triflate, 17763-80-3; 4-acetylphenyl triflate, 109613-00-5; 2-pyridyl triflate, 65007-00-3.

Supplementary Material Available: A typical procedure of arylation of ketone and aldehyde homoenolates and physical properties of new compounds (5 pages). Ordering information is given on any current masthead page.

(13) Fitton, P.; Johnson, M. P.; McKeon, J. E. *J. Chem. Soc., Chem. Commun.* **1968**, 6.

(14) (a) Kowalski, M. H.; Stang, P. J. *Organometallic* **1986**, *5*, 2392. Scott, W. J.; Crisp, G. T.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 4630.

(15) Stang, P. J.; Hanack, M.; Subramanian, L. R. *Synthesis*, **1982**, 85.

(16) Cf. Posner, G. H. *Org. React.* **1972**, *19*, 1.

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A Solution to the *in,out*-Bicyclo[4.4.1]undecan-7-one Problem Inherent in Ingenane Total Synthesis

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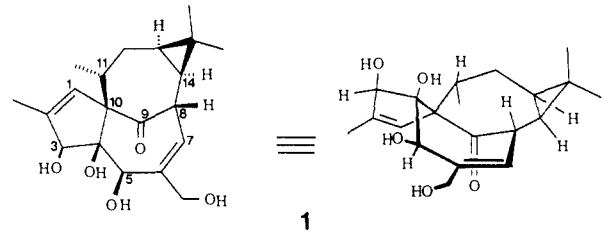
In 1968 Hecker reported the isolation and chemical characterization of a new irritant and cocarcinogenic substance, ingenol 3-hexadecanoate, from the latex of *Euphorbia ingens* and from the seed oil of *Euphorbia lathyris*.[2] It is now known that ingenol 3-hexadecanoate is one member of a structurally diverse group of compounds which are believed to promote tumor formation by activating protein kinase C.[3] Moreover, this natural product



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embodies a rare example of in,out-bridged bicyclic topological isomerism.[4] In most of the previously reported routes to ingenol, including one of our own, a solution to the in,out-stereochemical

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(2) (a) Hecker, E. *Cancer Res.* **1968**, *28*, 2338. (b) Hecker, E.; Opferkuch, H.; Adolf, W. *Fette, Seifen, Anstrichmittel* **1968**, *70*, 850. (c) Hoppe, W.; Brandl, F.; Zechmeister, K.; Adolf, W.; Opferkuch, H. J.; Hecker, E. *Tetrahedron Lett.* **1970**, 4075.

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(4) We are aware of only one other natural product which possesses an in,out bridged bicycloalkane ring system, see: (a) Kato, T.; Hirukawa, T.; Uyehara, T.; Yamamoto, Y. *Tetrahedron Lett.* **1987**, *28*, 1439. For a review and recent papers concerning in,out bridged bicycloalkanes, see: (b) Adler, R. *Acc. Chem. Res.* **1983**, *16*, 321. (c) Gassman, P.; Hoye, R. *J. Am. Chem. Soc.* **1981**, *103*, 2498. (d) McMurry, J.; Hodge, C. *Ibid.* **1984**, *106*, 6450. (e) Winkler, J.; Hey, J.; Williard, P. *Ibid.* **1986**, *108*, 6425.

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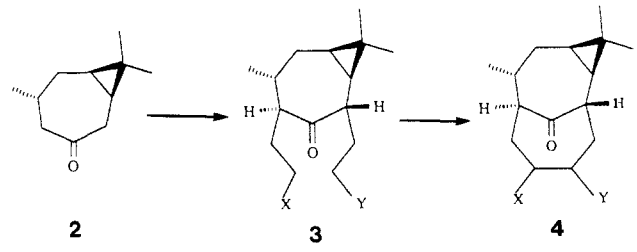
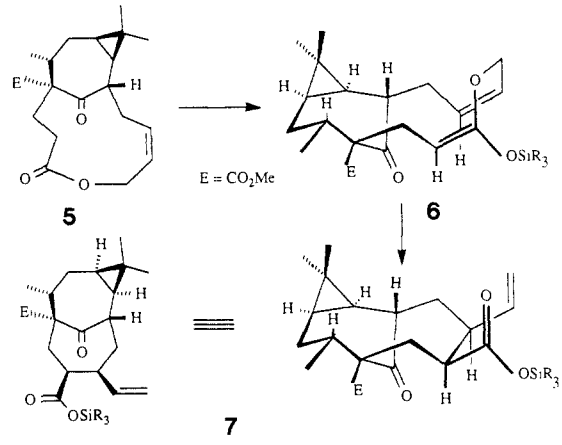
Scheme I



Scheme II

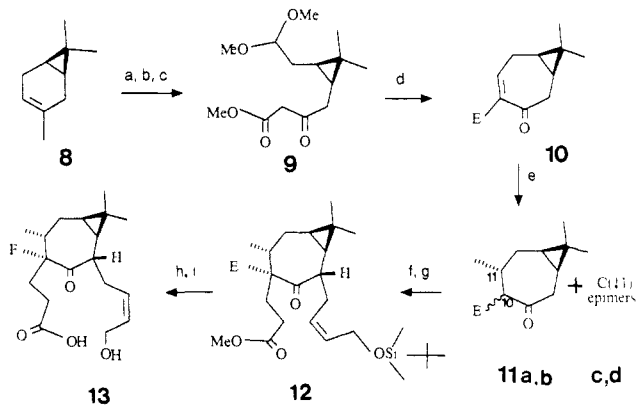


problem has been postponed.[5,6] Instead, the isoingenane ABC tricarbocyclic ring system has been assembled and in one case highly functionalized.[5f] While this strategy may ultimately prove practicable, we thought it prudent to pursue a synthesis which addresses the central issue of in,out stereoisomerism at the outset. We describe herein an effective solution to this challenging problem which may be adaptable to the preparation of optically pure ingenol and its analogues.

Our concept is summarized in Scheme I. It was envisioned that the substituents on a cycloheptanone such as **2** could be used to direct the stereoselective attachment of two side chains possessing the trans stereorelationship depicted in **3**. Subsequent bond formation between these side chains facilitated by groups X and Y would complete the formation of the remaining seven-membered ring and, hence, the *trans*- or *in,out*-bicyclo[4.4.1]undecan-7-one substructure **4** present in ingenol. MM2 calculations suggested that it would be advantageous to perform this connection with the carbonyl present as shown rather than in the form of various synthetic equivalents.[7]

This requirement imposes severe restrictions on the selection of a protocol to effect closure to this strained ring system since many conceivable reaction conditions are either incompatable with this functionality or would induce epimerization prior to closure and deliver the less strained out,out isomer. Our methodology for the preparation of carbocycles, Claisen rearrangement mediated ring contraction of macrocyclic lactones,[8] is well suited for this key bond formation. The in,out bridged *macrobicyclic* lactone **5** (Scheme II) does not suffer from the bending strain present in the smaller bicyclo[4.4.1]undecanone ring system and, consequently, should be accessible without diversion to the out,out isomer. The derived ketene acetal **6** was then expected to preferentially rearrange through a boatlike transition state arising from the conformer shown to afford the desired multisubstituted *in,out*-bicyclo[4.4.1]undecane carboxylate **7**.[9]

Scheme III



[a] Reagents: (a) O_3, CH_2Cl_2/MeOH; Me_2S; 70%; (b) $CeCl_3$, 5 equiv of $HC(OMe)_3$, of MeOH, 25 °C, 2 h; 90%; (c) 1.2 equiv, 5 equiv of $CO(OMe)_2$, xylenes, reflux, 1 h; 55%; (d) 1 equiv of $TiCl_4$, CH_2Cl_2, −25 °C, 1 h; 84%; (e) 1.4 equiv of LiMeCuCN, Et_2O, −78 °C, 0.5 h; 86%; (f) 2.25 equiv of LDA, 1 equiv of HMPA, THF, −78 °C → 30 °C, 3 h; 2 equiv of *cis*-1-(*tert*-butyldimethylsilyloxy)-4-chloro-2-butene, −78 °C → −30 °C, 4 h; 64%; (g) 10 equiv of CH_2CHCO_2Me, 1 equiv of Triton-B, dioxane, 10 °C, 30 min; 85%; (h) 1.2 equiv of Bu_4NF, THF, 0 °C, 2 h; 90%; (i) 2 equiv of K_2CO_3, MeOH/H_2O, 25 °C, 48 h; 94%.

A synthesis of the optically pure lactone **5** precursor, hydroxy acid **13**, from (+)-carene (**8**) is illustrated in Scheme III. Ozonolysis (O_3, CH_2Cl_2/MeOH; Me_2S) of carene provided a keto aldehyde (70%) which was selectively protected as the keto acetal by using the Luche procedure[10] (1 equiv of $CeCl_3$, 5 equiv of $HC(OMe)_3$, MeOH, 25 °C, 2 h; 90%). The keto aldehyde was then converted to the desired β-keto ester **9** upon treatment with potassium hydride (1.2 equiv) and dimethyl carbonate (5 equiv) in refluxing xylenes (1 h; 55%). Acylation of the keto aldehyde at lower temperatures, e.g., refluxing toluene, afforded a mixture of **9** and the regioisomeric β-keto ester (2:1). Although transformation of the keto ester **9** to the cycloheptenone **10** could conceivably be accomplished by a classical Knovenagel condensation on the derived aldehyde, we were gratified to discover that the β-keto ester **9** underwent a direct $TiCl_4$ catalyzed internal aldol reaction (1 equiv of $TiCl_4$, CH_2Cl_2, −25 °C, 1 h) to provide the cycloheptenone **10** [84%, mp 67–67.5 °C, $[\alpha]_D^{25}$ = +168° (*c* 0.1, $CHCl_3$)].[11] Conjugate addition of LiMeCuCN (1.4 equiv, −78 °C, Et_2O) to the enone **10**[13] provided a mixture of four separable

(5) (a) Satoh, T.; Kaneko, Y.; Okieda, T.; Uwaya, S.; Yamakawa, K. *Chem. Pharm. Bull. Jpn.* **1984**, *32*, 3452. (b) Paquette, L.; Nitz, T.; Ross, R.; Springer, J. *J. Am. Chem. Soc.* **1984**, *106*, 1446. (c) Funk, R. L.; Bolton, G. *Ibid.* **1986**, *108*, 4655. (d) Rigby, J.; Moore, T.; Rege, S. *J. Org. Chem.* **1986**, *51*, 2398. (e) Mehta, G.; Pathak, V. P. *J. Chem. Soc., Chem. Commun.* **1987**, 876. (f) Paquette, L. A.; Ross, R. J. *J. Org. Chem.* **1987**, *52*, 5499.

(6) The clever approach by Winkler is the exception. Winkler, J. D.; Henegar, K. E.; Williard, P. G. *J. Am. Chem. Soc.* **1987**, *109*, 2850.

(7) For example, the global minimum energy conformers of *out,out*- and *in,out*-bicyclo[4.4.1]undecane differ in strain energy by 6.3 kcal/mol, whereas the analogous *out,out*- and *in,out*-bicyclo[4.4.1]undecan-7-one conformers differ in strain energy by only 3.3 kcal/mol. In each case, the in,out isomer is the more strained. It is also of interest to note that we calculate ingenol (**1**) to be more strained than its C(8) configurational out,out isomer, isoingenol, by 5.9 kcal/mol. Thus, ingenol is most likely the contrathermodynamic isomer.

(8) (a) Funk, R. L.; Abelman, M. M.; Munger, J. D. *Tetrahedron* **1986**, *42*, 2831. (b) Funk, R. L.; Abelman, M. M. *J. Org. Chem.* **1986**, *51*, 3247. (c) Funk, R. L.; Munger, J. D. *Ibid.* **1985**, *50*, 707.

(9) Inspection of molecular models clearly indicates that the alternative boatlike transition state, which would give rise to the diastereomer epimeric at both the carboxyl- and vinyl-substituted centers, would be higher in energy due to serious transannular interactions between the C(9) carbonyl (ingenane numbering) and the allylic C–O bond. Moreover, Matthew M. Abelman of these laboratories had previously demonstrated that the rearrangement of a lactone without the methyl or isopropylidene substituents followed the desired stereochemical course. The details of this initial investigation will be reported in the full paper.

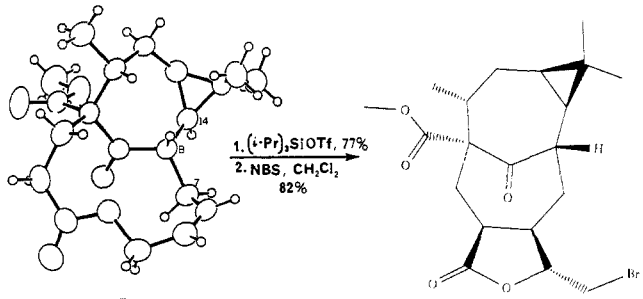
(10) Luche, J.-L.; Gemal, A. L. *J. Org. Chem.* **1979**, *47*, 2572.

(11) To the best of our knowledge, this is the first example that employs a β-keto ester as the enol participant in intramolecular Mukaiyama type condensations with acetals.[12] For intramolecular condensations with enol silyl ethers, see: (a) Mukaiyama, T. *Org. React.* **1982**, *28*, 241. (b) Posner, G. H.; Alexakis, A.; Chapdelaine, M. J.; Runquist, A. W. *Tetrahedron Lett.* **1978**, 4205. (c) Smith, A. B., III; Guaciaro, M. A.; Schow, S. R.; Wovkulich, P. M.; Toder, B. H.; Hall, T. W. *J. Am. Chem. Soc.* **1981**, *103*, 219. (d) Smith, A. B., III; Taylor, M. D.; Minaskanian, P.; Winzenberg, K. N.; Santone, P. *J. Org. Chem.* **1982**, *47*, 3960. (e) Kocienski, P.; Isaac, K. *J. Chem. Soc., Chem. Commun.* **1982**, 460. (f) Cockerill, G. S.; Kocienski, P. *Ibid.* **1983**, 705.

diastereomeric β-keto esters (9.5:6.6:4.5:1; 86%). The two major isomers (**11a,b**) were shown to be epimeric at C(10) (ingenane numbering) upon equilibration with NaOMe/MeOH and to possess the desired C(11) β-methyl substituent by decarbomethoxylation (NaCN, HMPA) to the known cycloheptenone **2**.[5a]

The β-keto esters **11a,b** are perfectly functionalized for the regio- and stereoselective attachment of the two side chains required to complete the *in,out*-bicyclo[4.4.1]undecan-7-one ring system. To that end, the β-keto esters **11a,b** were converted to the dianion[14] (2.25 equiv of LDA, 1 equiv of HMPA, THF, −78 °C → 0 °C, 3 h) and then alkylated with *cis*-1-(*tert*-butyldimethylsilyloxy)-4-chloro-2-butene (2 equiv, −78 °C → 30 °C, 4 h) to give one major product (>18:1) in 64% yield after column chromatography. Treatment of the alkylation product with methyl acrylate (10 equiv) in the presence of Triton-B (1 equiv, 0 °C dioxane, 30 min) gave a single Michael reaction adduct (85%). We tentatively assigned the stereochemistry shown in **12** based on the expected approach of the electrophiles from the enolate face opposite the substituents on the carbon β to the C(9) carbonyl (ingenane numbering). The stereochemical assignment was quickly confirmed by straightforward transformation of **12** to hydroxy acid **13** (Bu_4NF, THF, 0 °C; 90%; 2 equiv of K_2CO_3, MeOH, H_2O, 25 °C, 48 h; 94%) and subsequent lactonization (6 equiv of *N*-methyl-2-chloropyridinium iodide, 8 equiv of NEt_3, CH_3CN)[15] to provide the crystalline lactone **5** [62%; mp = 153–154.5 °C; $[a]_D^{25}$ = 256° (*c* 0.1; $CHCl_3$)] whose structure was solved by single-crystal X-ray analysis. As indicated in the ORTEP drawing below, the in,out-macrobicyclic [8.4.1] lactone possesses the desired relative stereochemistry, and the C(7)–C(8)–C(14) bond angle of 113.2° indicates minor bending deformation relative to that present in ingenol [C(7)–C(8)–C(14) bond angle = 126.5°].

Addition of triisopropylsilyl triflate (4 equiv) to a refluxing benzene solution of lactone **5** in the presence of triethylamine (8 equiv)[16] gave one major rearrangement product **7** (R = Si(*i*-Pr)$_3$; >15:1) after chromatography on Florisil. The stereochemical assignment for the two newly created stereogenic centers was based on the previously mentioned transition-state analysis and verified by single-crystal X-ray analysis of the bromolactone derivative **14** (mp 204–206.5 °C).



5 **14**

In conclusion, this concise, stereoselective synthesis of the BCD ring system of ingenol further illustrates the versatility of macrocyclic Claisen rearrangements for the rapid assemblage of strained ring systems.[8b,c] We are currently addressing the introduction of the A ring; our progress will be reported in due course.

Acknowledgment. We appreciate the financial support provided by the National Institutes of Health (Grant GM 28663), Eli Lilly and Company, and Alfred P. Sloan Foundation. High field (360 MHz) ^1H NMR and ^{13}C NMR spectra were obtained on a spectrometer purchased with funds provided, in part, by the National Science Foundation (Grant CHE-80-24328). Mass spectra were obtained through the National Science Foundation Regional Mass Spectroscopy Center at the University of Nebraska (Grant CHE-82-11164).

Supplementary Material Available: X-ray crystallographic data for compounds **5** and **14** (16 pages). Ordering information is given on any current masthead page.

(12) However, the intermolecular Knovenagel condensations of β-keto esters and malonates with aldehydes have been catalyzed by $TiCl_4$. (a) Lehnert, W. *Tetrahedron Lett.* **1970**, 4723. (b) Lehnert, W. *Tetrahedron* **1972**, *28*, 663. (c) Lehnert, W. *Tetrahedron* **1973**, *29*, 635.

(13) For a study of the stereochemistry of cuprate addition to 4-, 5-, and 6-alkylcycloheptenones, see: Heathcock, C. H.; Germroth, T. C.; Graham, S. L. *J. Org. Chem.* **1979**, *44*, 4481.

(14) Weiler, L.; Huckin, S. N. *J. Am. Chem. Soc.* **1974**, *96*, 1082.

(15) Mukaiyama, T.; Usui, M.; Saigo, K. *Chem. Lett.* **1976**, 49.

(16) The standard Ireland conditions for ester enolate rearrangement (LDA; $ClSiMe_2$-*t*-Bu) gave a retro-Michael addition product. Consequently, we employed the silyl triflate, triethylamine protocol for the preparation of ketene acetals which may proceed via a silylation and then deprotonation mechanism, see: (a) Simchen, G.; Kober, W. *Synthesis* **1976**, 259. (b) Simchen, G.; Emde, H. *Ibid.* **1977**, 867. (c) Corey, E. J.; Cho, H.; Rücker, C.; Hua, D. H. *Tetrahedron Lett.* **1981**, *22*, 3455. (d) Mander, L. N.; Sethi, S. P. *Ibid.* **1984**, *25*, 5953.

Cyclopentane Synthesis via Free-Radical-Mediated Addition of Functionalized Alkenes to Substituted Vinylcyclopropanes

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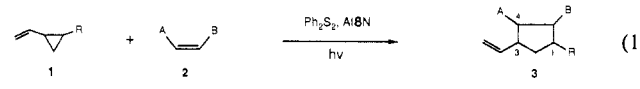
Herein we report a novel [3 atom + 2 atom][1] bond construction strategy for the synthesis of highly functionalized cyclopentane rings. Our approach relies on phenylthio radical catalyzed addition of substituted alkenes to vinylcyclopropane derivatives, eq 1. This



1 2 3 (1)

process transpires under mild experimental conditions, is tolerant of many organic functional groups, occurs with complete regiochemical control, and exhibits moderate stereoselectivity. These characteristics suggest that this chemistry may be broadly applicable to the efficient synthesis of cyclopentanoid natural products.

Treatment of a benzene solution of a vinylcyclopropane **1** and a 10–15-fold excess of an alkene **2** with a phenylthio radical precursor, either at reflux or at low temperature in the presence of Lewis acid, furnishes the vinylcyclopentane **3** in good yield. In addition to cyclopentane formation, varying amounts (5–50%) of the 1,5-phenyl disulfide adduct **17** are produced, presumably through addition of homoallylic radical **14** (vide infra) to phenyl disulfide.[2] Several selected examples are shown in Table I.[3-5]

(1) Other examples of [3 atom + 2 atom] strategies for cyclopentane synthesis can be found in the following: (a) Beal, R. B.; Dombroski, M. A.; Snider, B. B. *J. Org. Chem.* **1986**, *51*, 4391. (b) Demuth, M.; Wictfeld, B.; Pandey, B.; Schaffer, K. *Angew Chem.* **1985**, *97*, 777. (c) Tsuji, J.; Shimizu, I.; Ohashi, Y. *Tetrahedron Lett.* **1985**, *26*, 3825. (d) Molander, G. A.; Shubert, D. C. *J. Am. Chem. Soc.* **1986**, *108*, 4683, and references cited therein. (e) Danheiser, R. L.; Carini, D. J.; Fink, D. M.; Basak, A. *Tetrahedron* **1983**, *39*, 935. (f) Marino, J. P.; Laborde, E. *J. Am. Chem. Soc.* **1985**, *107*, 734. (g) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1, and references cited therein. (h) Beak, P.; Wilson, K. D. *J. Org. Chem.* **1987**, *52*, 218. (i) Boger, D. L.; Brotherton, C. E. *J. Am. Chem. Soc.* **1984**, *106*, 805. (j) Herndon, J. W. *J. Am. Chem. Soc.* **1987**, *109*, 3165. (k) Cekovic, Z.; Saicic, R. *Tetrahedron Lett.* **1986**, *27*, 5893. (l) Little, R. D.; Muller, G. W.; Venegas, M. G.; Carroll, G. L.; Bukhari, A.; Patton, L.; Stone, K. *Tetrahedron* **1981**, *37*, 4371. (m) Curran, D. P.; Chen, M.-H. *J. Am. Chem. Soc.* **1987**, *109*, 6558. (n) Clive, D. L. J.; Angoh, A. G. *J. Chem. Soc., Chem. Commun.* **1985**, 980.

(2) The rate constant for addition of 5-hexenyl radical to phenyl disulfide is 7.6×10^4 l·m^{-1} s^{-1} (80 °C): Russell, G. A.; Tashtoush, H. *J. Am. Chem. Soc.* **1983**, *105*, 1398. This competitive process sets a lower limit on useful rate constants for addition of substituted alkenes to homoallylic radical **14**.

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