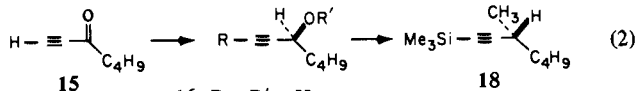

15 16, R = R′ = H 17, R = Me_3Si, R′ = CO_2Me 18 (2)

(prepared from 92% ee (−)-α-pinene and 9-BBN) according to the procedure of Midland[16] gave (*S*)-1-heptyn-3-ol[7] (**16**, 82 ± 3% ee by 250-MHz ^1H NMR analysis of the MTPA ester[17]) in 60–74% yield. Conversion of **16** to silyl carbonate **17**[7] and organocuprate coupling (CH_3MgBr, 4 equiv; CuI, 2 equiv; THF; 25 °C) according to Macdonald and Brinkmeyer[18] gave silylalkyne **18**,[7] $[\alpha]^{25}_D$ −27.7° (*c* 2.0, $CHCl_3$), in 50% yield from **16**. We anticipated[19] that propargylic coupling would occur with inversion of configuration, and our subsequent use of **18** for the synthesis of 251D rigorously establishes this stereochemical outcome.[20]

The conversion of **18** to 251D (Scheme I) proceeded along the lines utilized to prepare **14**. Thus sequential treatment of (*R*)-silylalkyne **18** with *i*-Bu_2AlH (1 equiv), CH_3Li (1 equiv), and chiral epoxide **8** afforded carbamate **19**[7] and its C-11 epimer in a 13:1 ratio[21ab] (41% yield). Chromatographic separation of the minor diastereomer was difficult at this stage, and consequently this intermediate was directly hydrolyzed to give a crystalline mixture of **20**[7] and its C-11 epimer, in 81% yield. Cyclization was best accomplished by converting amino alcohol **20** to the corresponding oxazolidine (paraformaldehyde, 1 equiv; EtOH; 80 °C), and subsequently heating this intermediate (0.1 M) in refluxing ethanol in the presence of 1 equiv of *d*-10-camphorsulfonic acid. After chromatographic purification (silica gel, 800:20:1 $CHCl_3$–*i*-PrOH:NH_4OH) to remove the unwanted C-11 epimer and crystallization from hexane–ethyl acetate, pure[21a] (+)-251D hydrochloride, mp 205–206 °C (evacuated capillary), $[\alpha]^{25}_D$ + 31.4° (*c* 0.62, CH_3OH),[22] was isolated in 60% yield. The ^1H NMR (250 MHz) and ^{13}C NMR spectra of synthetic (+)-251D hydrochloride in CD_3OD (and the free base in $CDCl_3$) as well as the EI mass spectra were identical with those of the natural material[1], and synthetic (+)-251D hydrochloride was indistinguishable by capillary GLC[21a] and TLC (in three solvent systems) with an authentic sample of 251D hydrochloride kindly furnished by Dr. John Daly.[23]

The synthetic sequence reported here provides a highly convergent, concise, and *practical* route for the chemical synthesis of the pumiliotoxin A alkaloids. The enantiospecific total synthesis of 251D was achieved in *10 total steps* from 1-heptyn-3-one and *N*-carbobenzyloxy-L-proline methyl ester (**6**). The overall yield was ~6% from proline ester **6**. Efforts to improve the yields of individual steps, develop a stereospecific synthesis of epoxide **8**, and prepare pumiliotoxin B by this sequence are in progress. The results of those investigations as well as other synthesis applications of iminium ion–vinylsilane cyclizations will be reported in due course.

Acknowledgment. Financial assistance from the National Institutes of Health (HL 25854) and the Camille and Henry Dreyfus Foundation (teacher-scholar award to L.E.O.) is gratefully acknowledged. We particularly thank Dr. Barney Kane of SCM Organics for a generous sample of (−)-β-pinene, Professor T. L. Macdonald for a preprint of ref 18b, and Dr. John Daly for providing a comparison sample of 251D hydrochloride and copies of its ^{13}C NMR spectra. NMR and mass spectra were determined with spectrometers purchased with the assistance of NSF instrumentation grants.

(15) Prepared in high yield by Jones oxidation of commercially available 1-heptyn-3-ol: Joss, U.; Schaltegger, H. *Helv. Chim. Acta* **1969**, *52*, 2465.

(16) Midland, M. M.; McDowell, D. C.; Hatch, R. L.; Tramontano, A. *J. Am. Chem. Soc.* **1980**, *102*, 867.

(17) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543.

(18) (a) Brinkmeyer, R. S.; Macdonald, T. L. *J. Chem. Soc., Chem. Commun.* **1978**, 876. (b) Macdonald, T. L.; Reagan, D. R.; Brinkmeyer, R. S. *J. Org. Chem.* **1980**, *45*, 4740.

(19) See: Whitesides, G. M.; Fischer, W. F.; San Filippo, J.; Basche, R. W.; House, H. O. *J. Am. Chem. Soc.* **1969**, *91*, 4871. Johnson, C. R.; Dutra, G. A. *Ibid.* **1973**, *95*, 7783. Fouquet, G.; Schlosser, M. *Agnew Chem., Int. Ed. Engl.* **1974**, *13*, 82.

(20) Inversion of configuration in this reaction has been independently demonstrated by T. L. Macdonald et al.: Brinkmeyer, R. S.; Macdonald, T. L.; Reagan, D. R., in press; personal communication from T.L.M.

(21) (a) A 12-m, SE-30 glass capillary column (4000 plates per m) was used for this analysis. (b) The large ratio of diastereomers produced in this reaction indicates that the optical yield for the conversion of **17** to silylalkyne **18** was high.

(22) The free base is apparently levorortatory. A synthetic sample of 251D which was contaminated[21a] with 3.6% of the C-11 epimer and 1% of the oxazolidine derived from **20** showed $[\alpha]^{25}_D$ −3.1° (*c* 1.6, $CHCl_3$).

(23) The comparison of mp and optical rotation must await the isolation of additional natural 251D.

Tandem Cope-Claisen Rearrangements for the Construction of (*E*,*E*)-1,6-Cyclodecadienes. Effect of Ketene Acetal Substituents on $\Delta G^{\ddagger}_{Claisen}$[1]

Stanley Raucher,*† John E. Burks, Jr., Ki-Jun Hwang, and Dana P. Svedberg

Department of Chemistry, University of Washington Seattle, Washington 98195

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The development of methods for the construction of 10-membered rings[2] is of paramount importance in strategies for the synthesis[3] of germacrane sesquiterpenes.[4] Although the interconversion of germacrane and elemane sesquiterpenes via Cope rearrangement has been well documented,[5] efforts to synthesize germacrane sesquiterpenes from 1,2-divinylcyclohexanes have met with only limited success[6] due to the reversible nature of the Cope rearrangement.[7]

For some time now, we have been intrigued with the possibility of stereospecifically and enantiospecifically[8] preparing (*E*,*E*)-1,6-cyclodecadiene (**4**) via a strategy which involves shifting the unfavorable Cope equilibria between **1** or **2** and **3** with a Claisen rearrangement[7] that irreversibly removes the 1,5-cyclodecadiene (**3**) from the Cope energy surface. An (*E*,*E*)-1,6-cyclodecadiene with the absolute stereochemistry shown in **4** was desired in connection with efforts directed toward the total synthesis of (+)-costunolide.

As shown in Scheme I, it should be possible to stereospecifically and enantiospecifically prepare the desired (*E*,*E*)-1,6-cyclo-

† Fellow of the Alfred P. Sloan Foundation, 1980–1982.

(1) Synthesis via Sigmatropic Rearrangements. 5. For the previous paper in this series, see: Raucher, S.; Macdonald, J. E.; Lawrence, R. F. *Tetrahedron Lett.* **1980**, 4335.

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(3) For an up-to-date list of germacrances prepared by total synthesis, see: Wender, P. A.; Lechleiter, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 6340; footnote 6.

(4) (a) Devon, T. K.; Scott, A. I. "Handbook of Naturally Occurring Compounds"; Academic Press: New York, 1972; Vol. II, pp 77–83. (b) Sörm, F. *J. Agric. Food Chem.* **1971**, *19*, 1081. (c) Fischer, N. H.; Olivier, E. J.; Fischer, H. D. *Fortschr. Chem. Org. Naturst.* **1979**, *38*, 47.

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(6) (a) Grieco, P. A.; Nishizawa, M. *J. Org. Chem.* **1977**, *42*, 1717. (b) Still, W. C. *J. Am. Chem. Soc.* **1977**, *99*, 4186. (c) *Ibid.* **1979**, *101*, 2493.

(7) For reviews of the Cope and Claisen rearrangements, see: (a) Rhoads, S. J.; Raulins, N. R. *Org. React.* **1975**, *22*, 1; (b) Ziegler, F. *Acc. Chem. Res.* **1977**, *10*, 227; (c) Bennett, G. B. *Synthesis* **1977**, 589.

(8) All structures in this paper represent the single enantiomer depicted. All new compounds exhibited satisfactory infrared, proton magnetic resonance, GC, and mass spectroscopic data; yields refer to isolated, chromatographically homogeneous material. Purified on 40–60-μm silica gel.[15] GC analyses were performed on a Hewlett-Packard 5880A Level Three FID Gas Chromatrograph equipped with a SP 2100 12 meter fused silica capillary column. Ratios are calculated directly from peak integrations.

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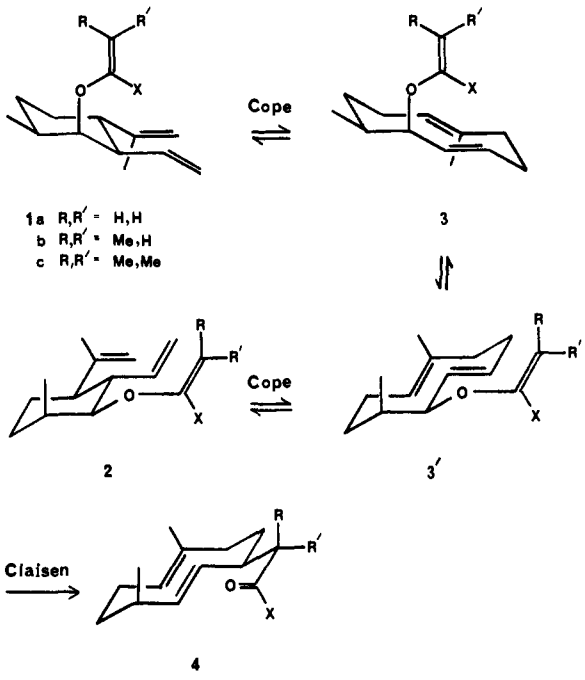
Scheme I



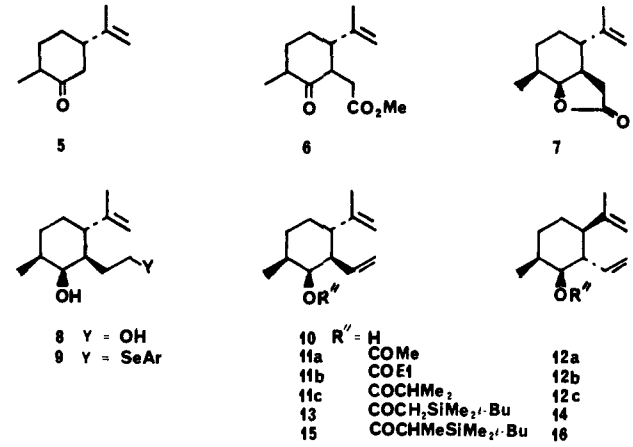
decadiene (**4**) either from **1** or from **2** via interconnected pathways on the Cope–Claisen energy surface. Thus, Cope rearrangement of **1** through a chair-like transition state should produce the (*E*,*E*)-1,5-cyclodecadiene in conformation **3**. Although Claisen rearrangment of conformation **3** appears to be precluded by the orthogonal relationship of the C–O bond and π orbitals of the allyl moiety, **3** may undergo a conformational flip to **3′** which then may either be reversibly converted to **2** via Cope rearrangement or be transformed irreversibly to **4** via Claisen rearrangement through a chair-like transition state.

During the course of our investigations, Ziegler reported both the first example of a tandem Cope–Claisen rearrangement[9a] and a more detailed study[9b] of the Cope–Claisen rearrangement of four diastereomeric 2-vinyl-3-isopropenylcyclohexyl vinyl ethers. It was demonstrated that Cope–Claisen rearrangement of the two *cis*-2-vinyl-3-isopropenylcyclohexyl diastereomers occurs readily at 255 °C to give a (*Z*,*Z*)-1,6-cyclodecadiene; in contrast, the two *trans*-2-vinyl-3-isopropenylcyclohexyl diastereomers, though interconvertible through Cope rearrangement at 255 °C, required considerably higher temperatures in order to undergo Claisen rearrangement via a crossover which led to the formation of the same (*Z*,*Z*)-1,6-cyclodecadiene obtained from the cis diastereomers.[9b] These observations were attributed to $\Delta G^{\ddagger}_{\text{Claisen}} \gg \Delta G^{\ddagger}_{\text{Cope}}$ for the trans diastereomers.[9b]

We now wish to report the first successful application of the tandem Cope–Claisen rearrangement with a *trans*-2-vinyl-3-isopropenylcyclohexyl system which results in the stereospecific and enantiospecific formation of an (*E*,*E*)-1,6-cyclodecadiene via a transformation for which $\Delta G^{\ddagger}_{\text{Claisen}} \simeq \Delta G^{\ddagger}_{\text{Cope}}$.

The diminution of $\Delta G^{\ddagger}_{\text{Claisen}}$ appeared to be crucial for the success of the desired transformations; thus, we chose to examine the Claisen rearrangement of **1a–c**, X = $OSiMe_2$-*t*-Bu,[8] since allyl silyl ketene acetals undergo [3,3]-sigmatropic rearrangements at considerably lower temperatures than the corresponding allyl vinyl ethers.[10,11]

Scheme II



The requisite esters **11a–c** were prepared stereo- and enantiospecifically as shown in Scheme II.[8] Alkylation of 5-(*S*)-dihydrocarvone (**5**)[12] (LDA, $ICH_2CO_2CH_3$) and epimerization ($NaOCH_3$, 25 °C) gave **6** as a mixture of four diastereomers (85:9:6:trace) in an 80% isolated yield with the all-equatorial isomer predominating. Reduction of **6** with lithium tri-*sec*-butylborohydride[13] produced the crystalline lactone **7** (mp 80 °C) in 73% yield; GC and ^{13}C NMR analysis indicated that **7** was completely free of other stereoisomers. Reduction of **7** ($LiAlH_4$) to **8** (98% yield), followed by reaction with *o*-nitrophenyl selenocyanate and Bu_3P[14] afforded **9** (93% yield); oxidative elimination (H_2O_2) gave **10** in 85% yield. Esterification of **10** (1.1 equiv of RR′CHCOCl, pyridine) gave the esters **11a–c** (>95% yield).

Prior to examination of the crucial tandem Cope–Claisen rearrangement, preliminary experiments to determine the facility of the Cope rearrangement and conformational interconversion of these systems were conducted. Heating a dilute solution of **11a** in *o*-dichlorobenzene at 178 °C led to the formation of the diastereomers **11a** and **12a** in the following ratios as indicated by GC analysis: 2 h (89:11), 5 h (79:21), 18 h (64:36). Likewise, in 1,2,4-trichlorobenzene at 214 °C an equilibrium ratio of **11a**/**12a** (62:38) was attained in 40 min.

Since the Cope rearrangement for this system occurs with relative ease, we sought to examine the effect of ketene acetal substituents on $\Delta G^{\ddagger}_{\text{Claisen}}$. Ireland has demonstrated that substituents on the silyl ketene acetal have a pronounced effect on the rate of rearrangement,[11] namely, dramatic increases in the rate of rearrangement for the series of silyl ketene acetals derived from (*E*)-crotyl acetate, (*E*)-crotyl propionate, and (*E*)-crotyl isobutyrate have been reported.[11b] Thus, the silyl ketene acetals **1a–c** (X = $OSiMe_2$-*t*-Bu) were prepared from the corresponding esters by established procedures,[11] isolated by brief aqueous workup[11d] (>90%), shown by GC and NMR analysis to be >90% pure, containing only small amounts of unreacted **11**, and used without further purification.

Thermolysis of **1a**, X = $OSiMe_2$-*t*-Bu, [84 mg in 2.5 mL of hexadecene, 205 °C, 1.7 h, 10 equiv of *O*,*N*-bis(trimethylsilyl)-acetamide, argon] followed by aqueous workup and flash chromatography[15] gave a mixture of compounds (61 mg) which was shown by GC to be comprised of 70% of the diastereomeric *C*-silyl esters **13** and **14** (64:36),[8,16] 20% of the diastereomeric acetates

(9) (a) Ziegler, F. E.; Piwinski, J. J. *J. Am. Chem. Soc.* **1979**, *101*, 1611. (b) *Ibid.* **1980**, *102*, 880. (c) *Ibid.* **1980**, *102*, 6576.

(10) (a) For a recent review of the synthesis and reactions of *O*-silylated enolates see: Rasmussen, J. K. *Synthesis* **1977**, 91. (b) See also: Baukov, Y. I.; Lutsenko, I. F.; Baukov, Y. I.; Burlachenko, G. S.; Khasapov, B. N. *J. Organomet. Chem.* **1966**, *5*, 20. (d) Ainsworth, C.; Chen, F.; Kuo, Y.-N. *Ibid.* **1972**, *46*, 59. (e) Rathke, M. W.; Sullivan, D. F. *Synth. Commun.* **1973**, *3*, 67.

(11) (a) Ireland, R. E.; Mueller, R. H. *J. Am. Chem. Soc.* **1972**, *94*, 5897. (b) Ireland, R. E.; Willard, A. K. *Tetrahedron Lett.* **1975**, 3975. (c) Ireland, R. E.; Mueller, R. H.; Willard, A. K. *J. Org. Chem.* **1976**, *41*, 986. (d) Ireland, R. E.; Mueller, R. H.; Willard, A. K. *J. Am. Chem. Soc.* **1976**, *98*, 2868. (e) Ireland, R. E.; Thaisrivongs, S.; Vanier, N.; Wilcox, C. S. *J. Org. Chem.* **1980**, *45*, 48. (f) Danishefsky, S.; Funk, R. L.; Kerwin, J. F., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 6889. (g) Danishefsky, S.; Tsuzuki, K. *Ibid.* **1980**, *102*, 6891.

(12) Raucher, S.; Hwang, K.-J. *Synth. Commun.* **1980**, *10*, 133.

(13) Brown, H. C.; Krishnamurthy, S. *J. Am. Chem. Soc.* **1972**, *94*, 7159.

(14) Grieco, P. A.; Gilman, S.; Nishizawa, M. *J. Org. Chem.* **1976**, *41*, 1485.

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

11a and **12a** (72:28),[16] and 10% of an unidentified substance of considerably longer retention time. Formation of the diastereomers clearly demonstrates that Cope rearrangement had occurred under the reaction conditions; however, there was no evidence for the desired tandem Cope–Claisen rearrangment. Since *O*- to *C*-silyl migration is not normally observed in the Claisen allyl silyl ketene acetal rearrangement,[17] it is especially noteworthy, and perhaps indicative of the energy barrier for Claisen rearrangement in this system.

The influence of a methyl substituent on the ketene acetal was examined by thermolysis of **1b**, X = $OSiMe_2$-*t*-Bu, 90:10 *E*/*Z* [0.3 M in 1,2,4-trichlorobenzene, 205 °C, 3.5 h, 10 equiv of *O*,*N*-bis(trimethylsilyl)acetamide, argon] followed by treatment with $KF{\cdot}2H_2O$ in HMPA[11d] and extraction with 1 N KOH to give a mixture of carboxylic acids in 51% combined yield. ^1H NMR of this mixture showed a doublet of doublets (J = 15, 4 Hz) at δ 5.80 characteristic of a proton on a *trans*-alkene. Treatment with CH_2N_2 gave a mixture of three methyl esters (20:46:34), all of which showed parent ions at m/e 250 and similar fragmentation patterns on GC/MS analysis. Although the individual components have not yet been separated, the presence of **4b** (X = OMe, one or both α-substituted propionate diastereomers) as a major constituent is strongly suggested by spectral data [inter alia δ 5.60 (dm, J = 16 Hz)]. The formation of compound(s) containing a $>C{=}CH_2$ group via transannular cyclization[18] is also suggested [^1H NMR δ 4.67 (br s); IR 890 cm^{-1}].

In addition to the desired tandem Cope–Claisen rearrangement, the occurrance of *O*- to *C*-silyl migration was also detected by a separate experiment in which neutral byproducts were isolated and characterized. Thus, thermolysis of **1b** [86 mg in 2.5 mL of 1,2,4-trichlorobenzene, 214 °C, 2 h, 5 equiv of *O*,*N*-bis(trimethylsilyl)acetamide, argon], treatment with $KF{\cdot}2H_2O$ in HMPA, and washing with 1 N KOH gave 58 mg of neutral products containing 55% of the diastereomers **15** and **16** (70:30) and 45% of distereomers **11b** and **12b** (76:24). A sample of *C*-silyl esters was obtained by flash chromatography.[8]

Our preliminary investigation concerning the influence of silyl ketene acetal substitution was culminated with the first successful isolation of an (*E*,*E*)-1,6-cyclodecadiene prepared by a tandem Cope–Claisen rearrangement. Thermolysis of **1c**, X = $OSiMe_2$-*t*-Bu [0.1 M in 1,2,4-trichlorobenzene, 214 °C, 2.0 h, 10 equiv of *O*,*N*-bis(trimethylsilyl)acetamide, argon], treatment with $KF{\cdot}2H_2O$ in HMPA, and extraction with 1 N KOH gave a 50% yield of a 9:1 mixture of the (*E*,*E*)-1,6-cyclodecadiene **4c**,[19] X = OH, and an unidentified carboxylic acid.[20] Silylation of the above mixture ($ClSiMe_2$-*t*-Bu, imidazole, DMF) and purification by flash chromatography gave the (*E*,*E*)-1,6-cyclodecadiene **4c**, X = $OSiMe_2$-*t*-Bu, in 82% yield.[21]

In summary, we have demonstrated that the tandem Cope–Claisen rearrangement may be employed for the preparation of (*E*,*E*)-1,6-cyclodecadienes. This transformation appears to occur in a concerted manner through chair-like cyclodecadiene conformations since the (*E*,*E*)-1,6-cyclodecadiene produced is not the thermodynamically most stable isomer.[22] Further, the Claisen rearrangement, indeed the pivotal step in this reaction sequence, is markedly influenced by the substituents on the silyl ketene acetal.[23] The trend observed for **1a–c** may be both a reflection of an electronic effect in which the added methyl substituents accelerate the rate of the Claisen rearrangement[11d] and a result of steric factors in which the added methyl substituents decrease the tendency for *O*- to *C*-silyl migration.[17] Research directed toward the application of this strategy to the total synthesis of germacrane sesquiterpenes is currently in progress.

Acknowledgment. This research was supported by a grant from the National Cancer Institutes, National Institutes of Health (CA 25977). GC/MS data was obtained on a VG 7070 GC/MS and associated VG 2035 F/B data system, funded by NIH Biomedical Research Development Grant 1 S08 RR 09082.

(16) Authentic sample isolated by preparative gas chromatography.

(17) For references concerning *O*- to *C*-silyl migration, see ref 10c. For alternative reaction pathways available to allyl silyl ketene acetals, see: (a) Arnold, R. T.; Kulenovic, S. T. *J. Org. Chem.* **1980**, *45*, 891. (b) Reference 10d, 11f.

(18) Several studies on the transannular cyclization of 1,5-cyclodecadienes have appeared. (a) Reference 4b. (b) Sutherland, J. K. *Tetrahedron* **1974**, *30*, 1651. (c) Fisher, N. H.; Wiley, R. A.; Perry, D. L. *Rev. Latinoam. Quim.* **1976**, *7*, 87. (d) Hikino, H.; Konno, C.; Nagashima, T.; Kohama, T.; Takemoto, T. *Chem. Pharm. Bull.* **1977**, *25*, 6. For transannular cyclization of 1,6-cyclodecadienes, see: (e) Yosikara, K.; Ohta, Y.; Saki, T.; Hirose, Y. *Tetrahedron Lett.* **1969**, 2263.

(19) Salient spectral features indicative of the (*E*,*E*)-1,6-cyclodecadiene include the following: ^1H NMR (60 MHz, $CDCl_3$) δ 1.50 (br s, *trans*-$CH_3C{=}CH$), 4.77–5.20 (m, $CH(CH_3)CH{=}CH$), 5.02 (dm, J = 9 Hz, $CH_3C{=}CH$), 5.60 (dd, J = 14, 3.5 Hz, $CH(CH_3)CH{=}CH$), 10.9 (br s, CO_2H). The presence of a small amount of compound(s) containing a $>C{=}CH_2$ group[18] is also indicated: δ 4.65 (br s).

(20) Thermolysis of **1c** for longer times results in the formation of a larger percentage of this substance which is presumably a transannular cyclization[18] product.

(21) ^1H NMR (80 MHz, $CDCl_3$) δ 0.25 (s, $>Si(CH_3)_2$, 0.95 (s, $C(CH_3)_3$), 1.02 s, $C(CH_3)_2CO_2$), 1.50 (br s, *trans*-$CH_3C{=}CH$), and 0.67–2.70 (m) (total 37 H), 5.0 (ddd, J = 16, 9, 2 Hz, $CH(CH_3)CH{=}CH$) and 5.02 (dm, J = 9 Hz, *trans*-$CH_3C{=}CH$) (total 2 H), 5.87 (dd, J = 16, 4 Hz, $CH(CH_3)C{-}H{=}CH$,1 H).

(22) (a) Dale, J.; Moussebois, C. *J. Chem. Soc. (C)* **1966**, 264. (b) Dale, J.; Ekeland, T.; Schang, J. *J. Chem. Soc., Chem Commun.* **1968**, 1477.

(23) For Claisen rearrangements facilitated by a substituent on the benzyl moiety, see: (a) Raucher, S.; Lui, A. S.-T. *J. Am. Chem. Soc.* **1978**, *100*, 4902. (b) Raucher, S.; Lui, A. S.-T.; Macdonald, J. E. *J. Org. Chem.* **1979**, *44*, 1885.

Electron-Transfer Photooxygenation. 6. Indirect Sensitized Photooxygenation of Aryl Olefins[1]

Dale S. Steichen and Christopher S. Foote*

Department of Chemistry, University of California Los Angeles, California 90024

Received October 6, 1980

Photooxygenation of aryl olefins sensitized by cyanoaromatics has been shown to proceed by an electron-transfer mechanism with initial formation of the radical anion of the sensitizer and radical cation of the olefin.[2] Quenching of the reaction by electron transfer from aromatic ethers to the substrate radical cation has also been reported.[2,3] Spada and Foote studied these reactions by laser-flash spectroscopy and showed that tetraphenylethylene (TPE) radical cation can also be formed indirectly by electron transfer from TPE to an initially formed *trans*-stilbene (TS) radical cation.[4] Schaap and co-workers made similar observations and showed that this electron transfer could result in the enhancement of reactivity of the donor olefin.[5]

We now report that photooxygenation of tetraphenylethylene and other aromatic olefins of low-oxidation potential can be sensitized by an indirect mechanism involving this type of process. When TS (0.05 M) is photooxygenated with 9,10-dicyanoanthracene (DCA) in oxygenated acetonitrile containing 0.005 M TPE, production of benzophenone (from oxidation of TPE) is enhanced (compared to TPE oxidation without TS), and the formation of benzaldehyde (from TS) is suppressed[6] (Table I).

(1) (a) Paper 5: J. Eriksen and C. S. Foote, *J. Am. Chem. Soc.*, **102**, 6083 (1980); (b) work supported by National Science Foundation Grant CHE 77-21560.

(2) Reference 1a.

(3) K. A. Brown-Wensley, S. L. Mattes, and S. Farid, *J. Am. Chem. Soc.*, **100**, 4162 (1978).

(4) L. T. Spada and C. S. Foote, *J. Am. Chem. Soc.*, **102**, 391 (1980).

(5) A. P. Schaap, *J. Am. Chem. Soc.*, **102**, 389 (1980).

(6) Photooxygenations were carried out with a Hanovia 1200 W medium-pressure mercury vapor lamp in a water-cooled immersion well surrounded with a 1-cm filter solution consisting of 30.0 g of $NaNO_2$ in 1 L of H_2O. Solutions were contained in 15- × 125-mm Pyrex tubes fitted with septa which were oxygenated by bubbling for 1 min prior to irradiation. Solutions were irradiated 35 min while rotating around the light source on a merry-go-round. $E_{1/2}$ (ox) vs. SCE: TPE = 1.33 V; TS = 1.51 V.

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