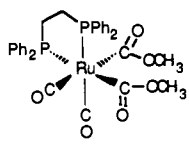
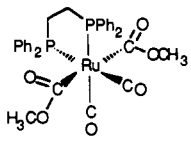
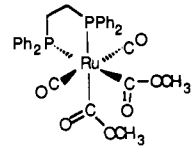
traces of carbamate were formed. Mass spectrometric data indicated that the formula of the new complex was $Ru[C(O)OCH_3]_2(dppe)(CO)_2$, and spectroscopic data were consistent with the structure shown in **2a**.[18] The ^{31}P NMR spectrum displayed a pair of doublets at 46.20 and 52.42 ppm (J_{P-P} = 12.5 Hz), which is typical for an octahedral Ru^{2+} complex having inequivalent cis phosphorus atoms. The resonances of the two methoxy groups were found at 3.03 and 3.76 ppm in the ^1H NMR spectrum, and two metal carbonyl absorptions in the infrared spectrum were located at 2048 and 1998 cm^{-1}. A broad, medium-intensity absorption was found at 1622 cm^{-1} characteristic of the carbomethoxy ligand. Although the ^{13}C NMR spectrum was consistent with this structure, all of the metal-coordinated carbons were found in the same region, and no specific assignments could be made. In all of the NMR studies, evidence was found for a second isomer having a symmetric structure, **2b** or **2c**. The ratio **2a**/**2b**(**2c**) remained constant at 5/1 in all experiments.



2a



2b



2c

Complex **2** *was found to react quantitatively with o-toluidine at 95 °C over 6 h in the presence or absence of CO to form* $Ru(dppe)(CO)_3$, CH_3OH, *and* $o\text{-}CH_3C_6H_4NHC(O)OCH_3$. These results along with our earlier studies allow us to piece together a catalytic cycle for eq 1 (Scheme I). The species isolated may or may not prove to be the actual productive intermediates in the catalytic cycle. Additional work is in progress to address this question. The individual events occurring during phase 1 suggest the involvement of a single electron transfer from the Ru(0) complex to the nitroaromatic followed by CO_2 expulsion and CO absorption to produce **1**.[8] Phase 2 remains the "black box" of this catalytic cycle. There must be several individual chemical events operative to cleave the second N–O bond and hydrogenate the NAr group. The previously suggested intermediates (nitrene complexes, amido complexes, etc.)[8] are among the species that could be invoked to explain phase 2, but experimental evidence supporting this or any other mechanism is still needed. Whatever the nature of these reactions, the selectivity (typically 70–85%) of the catalysis {defined as [carbamate]/([aniline] + [carbamate])} may be controlled by the events in phase 2. If **2** would have been formed quantitatively from **1**, then all of the aniline produced in phase 2 would have been converted to carbamate in phase 3. As stated above, 40% of $Ru(dppe)(CO)_3$ was regenerated in the stoichiometric reaction of **1** with methanol without formation of carbamate. Combining the knowledge of the selectivity of phase 2 with the higher activation barrier of phase 3 allowed us to design a high-yield synthesis of **2**. Three equivalents of *o*-nitrotoluene reacted with $Ru(dppe)(CO)_3$ in a methanol/toluene solution (1/9) under CO (2 atm) at 60–70 °C for 2 h, producing **2** in 95% yield. In phase 3, the formation of carbamate probably occurs via the nucleophilic attack of aniline on **2**. Expulsion of carbamate and methanol to regenerate $Ru(dppe)(CO)_3$ could occur by a few straightforward chemical reactions.

While Scheme I explains the qualitative features observed in the catalysis, additional research is required to elucidate the individual steps, especially in phase 2, and to put the entire mechanism on a more quantitative foundation.

Acknowledgment. This research was supported by a grant from the National Science Foundation (CHE-8714326). We gratefully acknowledge valuable discussions with John Grate and David Hamm.

Supplementary Material Available: Tables of crystallographic data, atomic positional and thermal parameters, and bond distances and angles for $RuC_{35}H_{28}P_2O_4NCl$ (14 pages); listing of observed and calculated structure factors for $RuC_{35}H_{28}P_2O_4NCl$ (33 pages). Ordering information is given on any current masthead page.

(18) Data for **2**: ^1H NMR (ppm, C_6D_6) 2.22 (m, CH_2), 2.90 (m, CH_2), 3.71 [s, OCH_3 of **2b**(**2c**)]; ^{13}C NMR (ppm, C_6D_6) 27.0 (dd, J_{CP1} = 12.9 Hz, J_{CP2} = 25.1 Hz, CH_2), 48.94 (s, CH_3), 50.17 (s, CH_3), 120.2–134.6 (Ph), 195.4 (dd, J_{CP1} = 12.11 Hz, J_{CP2} = 89.5 Hz, CO), 197.8 (dd, J_{CP1} = 9.11 Hz, J_{CP2} = 89.3 Hz, CO), 197.77 (J_{CP1} = 10.58 Hz, J_{CP2} = 6.4 Hz, CO), 199.64 (t, $J_{CP1,CP2}$ = 12.5 Hz, CO); ^{31}P NMR [ppm, C_6D_6, referenced to 85% H_3PO_4) 43.7 (s, **2b**(**2c**)]; FABMS, P (*m/e*) 678.

Ring Opening Induced by Iminyl Radicals Derived from Cyclobutanones: New Aspects of Tin Hydride Cleavage of *S*-Phenyl Sulphenylimines

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Received September 17, 1990

Despite the dramatic surge in the application of radical reactions to organic synthesis,[1] the synthetic potential of iminyl radicals has hardly been exploited. The main limiting factor has been the lack of a convenient and general method for generating these species.[2] We have recently described[3] a mild and practical process for producing iminyls from *S*-aryl sulphenylimines using tributylstannane, which we applied to the synthesis of various Δ^1-pyrrolines derivatives. We have now found that this reaction could be used to induce ring opening of cyclobutanones via the corresponding cyclobutylimino radical.

The few kinetic studies of the β-scission of iminyl radicals[4] as well as scattered examples involving fragmentation of cycloalkyliminyl intermediates[2a,b,5] indicated that, for cyclobutyl derivatives, this process could be sufficiently rapid to compete favorably with premature quenching by the stannane. Indeed, slow addition (ca. 5 h) of n-Bu_3SnH in cyclohexane to a refluxing solution of sulphenylimine **3a**[6] in the same solvent (in the presence

(1) (a) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon–Carbon Bonds*; Pergamon Press: Oxford, 1986. (b) Curran, D. P. *Synthesis* **1988**, 417, 489. (c) Ramaiah, M. *Tetrahedron* **1987**, *43*, 3541. (d) Hart, D. J. *Science* **1984**, *223*, 883. (e) *Houben-Weyl Methoden der Organischen Chemie*; Regitz, M., Giese, B., Eds.; Georg Thieme Verlag: Stuttgart, 1989 (band E 19a). (f) Surzur, J.-M. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum: New York, 1982; Vol. 2, Chapter 2. (g) Stella, L. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 337.

(2) (a) Forrester, A. R. In *International Review of Science, Organic Chemistry Series Two: Free Radical Reactions*; Butterworths & Co.: London, 1975; Vol. 10, Chapter 5. (b) Nelsen, S. F. In *Radicals*; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. 2. (c) McNab, H. *J. Chem. Soc., Chem. Commun.* **1980**, 422. (d) McNab, H. *J. Chem. Soc., Perkin Trans. 1* **1982**, 1941. (e) Hudson, R. F.; Record, K. A. F. *J. Chem. Soc., Chem. Commun.* **1976**, 539. (f) Hasebe, M.; Hogawa, K.; Tsuchiya, T. *Tetrahedron Lett.* **1984**, *25*, 3887. (g) Poutsma, M. L.; Ibraria, P. A. *J. Org. Chem.* **1969**, *34*, 2848. (h) Forrester, A. R.; Gill, M.; Meyer, C. J.; Sadd, J. S.; Thomson, R. H. *J. Chem. Soc., Perkin Trans. 1* **1979**, 606.

(3) (a) Boivin, J.; Fouquet, E.; Zard, S. Z. *Tetrahedron Lett.* **1990**, *31*, 85. (b) Boivin, J.; Fouquet, E.; Zard, S. Z. *Tetrahedron Lett.* **1990**, *31*, 3545.

(4) The rate constant for the ring opening of the cyclobutylimino radical has been estimated to be greater than 10^3 s^{-1} at −73 °C: Roberts, B. P.; Winter, J. N. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1353. For other kinetic studies on iminyls, see: (a) Griller, D.; Mendenhall, G. D.; Van Hoof, W.; Ingold, K. U. *J. Am. Chem. Soc.* **1974**, *96*, 6068. (b) Lub, J.; Beekes, M. L.; de Boer, T. J. *J. Chem. Soc., Perkin Trans. 2* **1983**, 721, and references therein.

(5) (a) Beckwith, A. L. J.; O'Shea, D. M.; Gerba, S.; Westwood, S. W. *J. Chem. Soc., Chem. Commun.* **1987**, 666. (b) Beckwith, A. L. J.; O'Shea, D. M.; Westwood, S. W. *J. Am. Chem. Soc.* **1988**, *110*, 2565. (c) Crow, W. D.; McNab, H.; Philip, J. M. *Aust. J. Chem.* **1976**, *29*, 2299. (d) Watt, D. S. *J. Am. Chem. Soc.* **1976**, *98*, 271. (e) Winters, L. J.; Fisher, J. F.; Ryan, E. R. *Tetrahedron Lett.* **1971**, 129.

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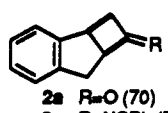
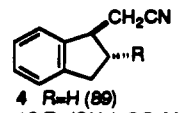
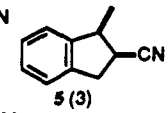
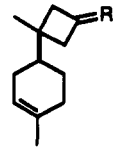
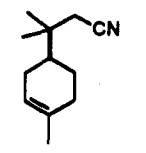
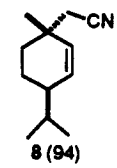
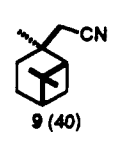
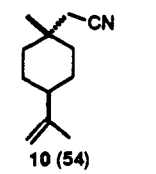
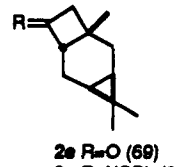
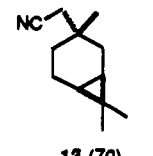
Table I. Tri-*n*-butylstannane-Induced Ring Opening of *S*-Phenyl Sulphenylimines Derived from Cyclobutanones[a]

entry	cyclobutanones[b] and *N*-phenyl sulphenylimines[c] (yield %)	products (yield %)
	 **2a** R=O (70) **3a** R=NSPh (77)	 **4** R=H (89) **16** R=$(CH_2)_2CO_2Me$
		 **5** (3)
	 **2b** R=O (50) **3b** R=NSPh (75)	 **7** (73)
		 **6** (20)
	 **2c** R=O (76) **3c** R=NSPh (94)	 **8** (94)
	 **2d** R=O (54) **3d** R=NSPh (79)	 **9** (40)
		 **10** (54)
	 **2e** R=O (69) **3e** R=NSPh (90)	 **13** (70)
		10 (19)

[a] Cyclobutanones **2a–e** were prepared from commercially available indene, (−)-limonene, Δ^2-(+)-carene, (−)-β-pinene, and Δ^3-(+)-carene, numbered **1a–e**, respectively. [b] Yield from olefins **1a–e**. [c] Yield from cyclobutanones.

of catalytic amounts of AIBN) resulted in the formation of nitrile **4** in high yield (89%) together with traces of compound **5** (3%), Under the same conditions, (−)-limonene derivative **3b** gave nitrile **6** but only as a minor product (20%). The major product was bicyclic compound **7** (73%, diastereomeric ratio 1,8:1), arising from the intramolecular addition of the intermediate carbon radical onto the endocyclic olefin, In the case of Δ^2-(+)-carene derivative **3c**, rupture of the cyclopropane ring[7] resulted in the formation of compound **8** in excellent yield (94%; entry 3, table).

More interestingly, reaction of (−)-β-pinene derivative **3d** under the same conditions led to nitrile **9** (minor product, 40%) as a *single isomer*, together with a major compound (54%) to which

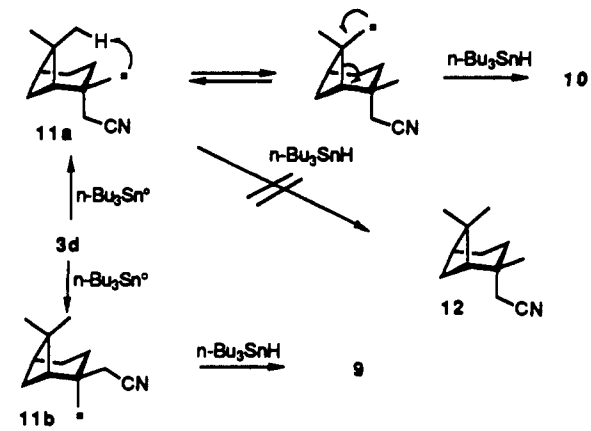


Figure 1.

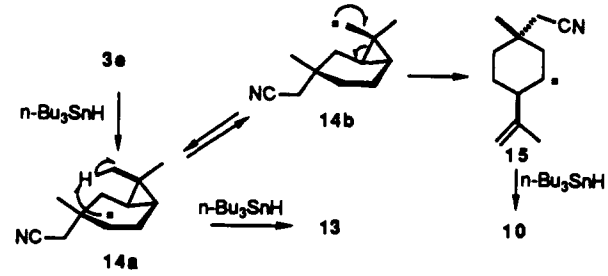


Figure 2.

structure **10** was attributed on the basis of ^1H and ^{13}C NMR data and the absence of optical rotation due to the presence of a plane of symmetry. The clean formation of the latter was unexpected at first as it implies a hydrogen atom transfer from a methyl group to a primary radical, followed by *regiospecific*[8] ring cleavage of the four-membered ring (Figure 1). The presumably reversible abstraction of hydrogen atom *must be fast* compared with quenching of intermediate radical **11a** by *n*-Bu_3SnH, None of isomer **12** is formed since the intramolecular hydrogen abstraction step is itself followed by a rapid[9,10] and essentially irreversible opening of the cyclobutane ring, Isomeric radical **11b** cannot undero a similar 1,5 hydrogen migration and therefore evolves simply into compound **9**. This efficient hydrogen atom transfer prompted us to examine the ring opening of Δ^3-(+)-carene derivative **3e**, Indeed, in addition to the "normal" product **13** (70%), a minor compound **10** (19%), identical with the one obtained previously,[11] was also isolated (table, entry 5), The yield of the latter could be easily raised to ~50% by simply adding the stannane more slowly (over ca. 12 h). In this instance, an a priori unfavorable 1,5 hydrogen exchange occurs between *secondary* radical **14a** and *primary* radical **14b**, followed again by a re-

(6) Cyclobutanones **2a–e** (table) were prepared by standard ketene chemistry from alkenes **1a–e**; see; (a) Mehta, G.; Rao, H. S. P. *Synth. Commun.* **1985**, 991. (b) Johnston, B. D.; Slessor, K. N.; Oehlschlager, A. C. *J. Org. Chem.* **1985**, *50*, 114. They were converted into the corresponding *S*-phenyl sulphenylimines **3a–e** by method of: Morimoto, T.; Nezu, T.; Achiwa, K.; Sekia, M. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1584.

(7) (a) Newcomb, M.; Glenn, A. G. *J. Am. Chem, Soc.* **1989**, *111*, 275. (b) Johnston, L. J.; Lusztyk, J.; Wayner, D. D. M.; Abeywickreyma, A. N.; Beckwith, A. L. J.; Scaiano, J. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1985**, *107*, 4594, (c) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am, Chem. Soc.* **1981**, *103*, 7739. (d) Maillard, B.; Forrest, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 7024. (e) Effio, O.; Griller, D.; Ingold, K. U.; Beckwith, A. L. J.; Seralio, A. K. *J. Am. Chem. Soc.* **1980**, *102*, 1734. (f) Mathew, L.; Warkentin, J. *J. Am. Chem. Soc.* **1986**, *108*, 7981. (g) Beckwith, A. L. J.; Bowry, V.; Moad, G. J. *J. Org. Chem.* **1988**, *53*, 1632.

(8) An explanation for the regiospecificity in the opening of cyclobutane or cyclopropane rings (in **9b** or **10b**, respectively) could be that steric repulsion causes a slight lengthening (and hence weakening) of the bond closest to the quaternary center. Small differences in bond lengths can have a large effect on the relative rates of bond breaking; see for example; Jones, P. G.; Kirby, A. J. *J. Am. Chem. Soc.* **1984**, *106*, 6207.

(9) Rates for cyclobutyl carbinyl radical opening range from 10^3 to 10^6 s^{-1} at 25 °C depending on substituents; see: (a) Beckwith, A. L. J.; Moad, G. J. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1083. (b) Ingold, K. U.; Maillard, B.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* **1981**, 970. (c) Maillard, B.; Walton, J. C. *J. Chem. Soc., Perkin Soc, 2* **1985**, 443. (d) Park, S.-U.; Varick, T. R.; Newcomb, M. *Tetrahedron Lett.* **1990**, *31*, 2975.

(10) The remote functionalization of one of the *gem*-dimethyl groups in methylpinanol (via the Barton nitrite photolysis or by the action of lead tetraacetate–iodine and irradiation) has been reported to occur *without* opening of the cyclobutane ring: (a) Gibson, T. W.; Erman, W. F. *J. Am, Chem. Soc.* **1969**, *91*, 4771. (b) Hortmann, A. G.; Youngstrom, *J. Org. Chem*, **1979**, *34*, 3392.

(11) Compound **10** is arrived at by way of two different (isomeric) radical precursors, which are both *chiral*. This of course has various synthetic implications, which we have not yet exploited.

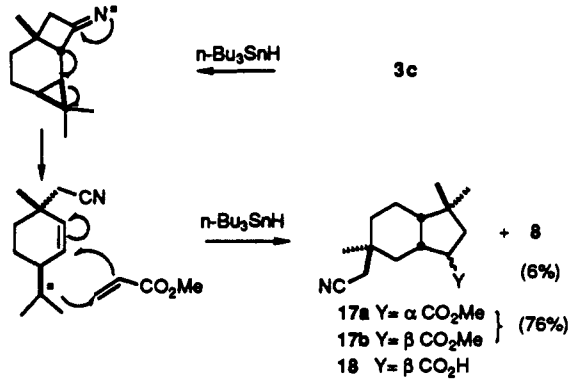


Figure 3.

markably *regiospecific*[9] cleavage of the cyclopropyl ring (Figure 2).[12] Absolute kinetic data on carbon to carbon 1,5-migration of a hydrogen atom are rather scanty,[13a] and those involving saturated carbons have generally been considered as too sluggish and unselective for synthetic purposes.[13,14] Evidently, in the light of the present results, these processes certainly embody a far greater synthetic potential than has hitherto been appreciated.

The intermediate carbon radical may be captured by an external electrophilic olefin. Thus, in the presence of methyl acrylate, the reaction of sulphenylimine **3a** with tributylstannane gives the *trans-substituted* compound **16** in 65–70% yield.[15] Under the same conditions, sulphenylimine **3c** afforded, via the sequence displayed in Figure 3, bicyclic compound **17** as a mixture of epimers (α/β 3;7) in 76% yield, and only a small amount of **8** (6%). Epimerization (K_2CO_3/MeOH, 20 °C, 48 h) and saponification furnished acid **18** (98%) as a sole isomer.

In view of the fact that cyclobutanones are readily available by a variety of methods, some of which are regio-, stereo-, and even enantioselective,[16] we feel that this novel methodology holds considerable synthetic promise.

Acknowledgment. We thank Prof. J.-Y. Lallemand for help and encouragement and Rhône-Poulenc Agrochimie for generous financial support (to E.F.).

Supplementary Material Available: Experimental procedure and spectral data for **6–10**, **13**, **16**, **17a**, **17b**, and **18** (2 pages). Ordering information is given on any current masthead page.

(12) The geometric disposition in the transition state of the atoms involved in the migration of the hydrogen is not favorable for a stabilizing interaction with the cyclopropyl ring which, in any case, is relatively small for radicals (3–4 kcal/mol); see: (a) de Meijere, A. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 809, and references therein. (b) Wong, H. N. C.; Hon, M.-Y.; Tse, C.-W.; Yip, Y.-C.; Tanko, J.; Hudlicky, T. *Chem. Rev.* **1989**, *89*, 169. (c) Wilcox, C. F.; Loew, L.; Hoffmann, R. *J. Am. Chem. Soc.* **1973**, *95*, 8192.

(13) (a) Beckwith, A. L. J.; Ingold, K. U. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1. (b) Choi, J. K.; Hart, D. J. *Tetrahedron* **1985**, *41*, 3959. (c) Chenera, B.; Chuang, C.-P.; Hart, D. J.; Hsu, L.-Y. *J. Org. Chem.* **1985**, *50*, 5409. (d) Winkler, J. D.; Sridar, V.; Rubo, L.; Hey, J. P.; Haddad, N. *J. Org. Chem.* **1989**, *54*, 3004, and references cited therein. (e) For a rare example of an efficient 1,5 hydrogen atom migration involving saturated carbons, see: Boivin, J.; Da Silva, E.; Ourisson, G., Zard, S. Z. *Tetrahedron Lett.* **1990**, *31*, 2501.

(14) Useful carbon to carbon translocations of radical centers are normally triggered by a highly energetic (vinylic or aromatic) initial carbon radical so that the migration becomes exothermic and irreversible: see: (a) Curran, D. P.; Kim, D.; Liu, H. T.; Shen, W. *J. Am. Chem. Soc.* **1988**, *110*, 5900. (b) Lathbury, D. C.; Parsons, P. J.; Pinto, I. J. *J. Chem. Soc., Chem. Commun.* **1988**, 81. (c) Bennett, S. M.; Clive, D. L. J. *J. Chem. Soc., Chem. Commun.* **1986**, 878. (d) See also refs 5a,b.

(15) It is worth noting that a base-catalyzed Dieckmann-type cyclization between the nitrile and ester-containing chains would lead to a six-membered ring *trans-fused* to the original cyclopentene unit in **1a**.

(16) See, inter alia: (a) Bellus, D.; Ernst, B. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 797, and references therein. (b) Snider, B. B. *Chem. Rev.* **1988**, *88*, 793. (c) Moore, H. W.; Gheorghiu, M. *Chem. Soc. Rev.* **1981**, *10*, 289. (d) Brady, W. T. *Tetrahedron* **1981**, *37*, 2949. (e) For a recent practical asymmetric synthesis of cyclobutanones, see: Chen, L.-Y.; Ghosez, L. *Tetrahedron Lett.* **1990**, *31*, 4467.

Synthesis of the Highly Oxygenated Ergostane Type Steroid (+)-Withanolide E

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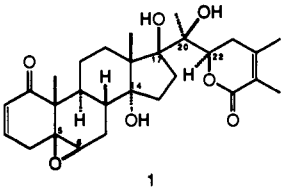
Received November 2, 1990

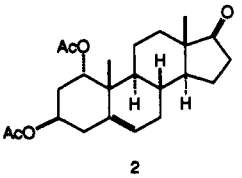
Withanolide E (**1**)[1] belongs to a group of highly oxygenated steroid-based δ lactones isolated from *Withania somnifera* Dun, chemotype III (Solaneceae) found in Israel and possesses a rich array of pharmacological properties including insect antifeedant, antifungal, and antitumor activity similar to the biological properties associated with cardenolides and bufadienolides.[2] It



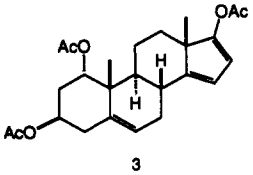
1

is interesting to note that withanolide E, which possesses 10 contiguous chiral centers of which six are oxygenated, differs from cardenolides and bufadienolides by (1) the unusual C(17) α arrangement of the side chain and (2) the CD trans ring fusion bearing an α hydroxyl group at C(14),[3] We detail below the synthesis of (+)-withanolide E, which constitutes the first reported synthesis of a withanolide of chemotype III,[4]

Our strategy for elaboration of (+)-withanolide E involves a hetero Diels–Alder reaction[6] between steroidal dienol acetate **3** and benzyl nitrosoformate which allows for the introduction of an α-hydroxyl group into the C(14) position. The requisite dienol



2



3

acetate **3** was prepared in straightforward fashion from the known steroidal diacetate **2**.[7] Conversion [TMSI, $(TMS)_2NH$, Et_3N, $ClCH_2CH_2Cl$, −23 °C, 45 min] of **2** into its corresponding silyl enol ether via a modification of the Miller procedure[8] followed by a Saegusa reaction [$Pd(OAc)_2$, K_2CO_3, CH_3CN, 12 h][9] and subsequent exposure to refluxing isopropenyl acetate containing *p*-toluenesulfonic acid gave rise to **3**, $[\alpha]_D$ +104,8° (*c* 3,88, $CHCl_3$) in 86% overall yield. Treatment (CH_2Cl_2, 0 °C, 20 min) of **3** with benzyl nitrosoformate, generated in situ by oxidation of benzyl *N*-hydroxycarbamate with tetrabutylammonium periodate, afforded in nearly quantitative yield the isomeric cycloadducts **4**

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(3) Note that the withanolides of chemotypes I and II possess the natural C(17) β orientation typical of cardenolides and bufadienolides. For a review on withanolides, see: Kirson, I.; Glotter, E. *J. Nat. Prod.* **1981**, *44*, 633.

(4) Withanolides of chemotypes I and II have been previously synthesized;[5] however, they lack the presence of hydroxyl groups at C(14), C(17), and, in some cases, C(20).

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