In deaerated 3-methylpentane solutions,[16] it was found that $\phi_{-\mathrm{PhN}_3}$ was dependent upon the concentration of phenyl azide ($[\mathrm{PhN}_3]$) whereby $\phi_{-\mathrm{PhN}_3}$ increased with increasing $[\mathrm{PhN}_3]$. At $[\mathrm{PhN}_3] = 1.8 \times 10^{-4}$, 2.1×10^{-3}, and 1.8×10^{-2} M, $\phi_{-\mathrm{PhN}_3} = 1.0 \pm 0.08$, 1.4, and 2.8, respectively. Quantum yield values of greater than unit efficiency are indicative of a chain reaction, thus further studies were made in a solvent that might promote such a reaction. Acetonitrile was selected, and notably high $\phi_{-\mathrm{PhN}_3}$ values were obtained.

Upon irradiation of a room temperature, aerated solution of phenyl azide in acetonitrile, it was observed that the $\phi_{-\mathrm{PhN}_3}$ *is quite sensitive to the exact experimental conditions.* For example, $\phi_{-\mathrm{PhN}_3} = 0.7$ at $[\mathrm{PhN}_3] = 3 \times 10^{-4}$ M but is notably larger at higher $[\mathrm{PhN}_3]$ or when $\phi_{-\mathrm{PhN}_3}$ is determined in deaerated solutions.[16] Indeed, *quantum yields of photodecomposition greater than unit efficiency can consistently be measured.* Under optimum experimental conditons, $\phi_{-\mathrm{PhN}_3} = 300$! Table I is a summary. Note that the high values of $\phi_{-\mathrm{PhN}_3}$ are substantially decreased (a) when $[\mathrm{PhN}_3]$ is decreased, (b) upon introduction of molecular oxygen to the solution at constant $[\mathrm{PhN}_3]$, or (c) upon addition of an equimolar amount of 2,3-dimethylbutene or tetracyanoethene. At $[\mathrm{PhN}_3] = 2 \times 10^{-4}$ M, $\phi_{-\mathrm{PhN}_3}$ is independent (±9%) of temperature in the 24 to −35 °C range.

Quantum yields of photodecomposition greater than unit efficiency were also measured for four phenyl azide derivatives that were examined. In a deaerated acetonitrile solution, $\phi_{-\mathrm{PhN}_3} = 210$ for 2-methylphenyl azide (6.9×10^{-2} M) and $\phi_{-\mathrm{PhN}_3} = 60$ for 4-methylphenyl azide (6.6×10^{-2} M). In addition, $\phi_{-\mathrm{PhN}_3} = 2.6$ and 2.1 for aerated acetonitrile solutions of 2-nitrophenyl azide (1.5×10^{-1} M) and 2-ethylphenyl azide (1.6×10^{-1} M), respectively. That these latter two aryl azides have $\phi_{-\mathrm{PhN}_3}$ values greater than unity is quite interesting since each nitrene can undergo an intramolecular reaction affording a bicyclic product.[14,17-19]

Acetonitrile is not a significant participant in the photochemical decomposition of phenyl azide. Analysis of ^{15}N NMR and mass spectral data obtained for irradiated solutions or for the isolated photoproducts of phenyl azide reveal that *cis*- and *trans*-azobenzene and the polymeric material are the primary products.[20] No products derived from reaction with acetonitrile (unless incorporated into the as yet uncharacterized polymeric material) or from hydrogen abstraction processes (i.e., anilines) are detected. High-pressure liquid chromatography would have allowed for their separation from the photochemical reaction mixture.

The notably high quantum yields of disappearance of phenyl azide upon irradiation in concentrated acetonitrile solutions can be rationalized based upon the suggestion of Smith[12] whereby a chain reaction occurs as a result of reaction of phenyl nitrene with phenyl azide to form 1,4-diphenyltetraazadiene (eq 3), which then decomposes into *two* phenyl nitrene intermediates (eq 5) which react further. Experimental evidence of the existence of 1,4-diphenyltetraazadiene is derived from the reaction of organometallics with aryl azides, which yield stable cobalt,[21] nickel, and platinum[22] complexes of 1,4-diaryltetraazadiene. Also, McDonald and Chowdhury[23] have employed quadrupole mass spectroscopic techniques to study the gas-phase reaction of phenyl nitrene anion radical with phenyl azide. The results suggest that the anion radical of 1,4-diphenyltetraazadiene is formed.

Alternatively, it is possible that phenyl nitrene reacts with phenyl azide to form molecular nitrogen and a second phenyl nitrene without formation of a 1,4-tetraazadiene intermediate (eq 6).

$$\mathrm{PhN} + \mathrm{PhN_3} \longrightarrow 2\mathrm{PhN} + \mathrm{N_2} \qquad (6)$$

Were reaction 6 to occur, it would also account for the high $\phi_{-\mathrm{PhN}_3}$ values that are measured since it would act as the chain propagation step (instead of reactions 3 and 5) via continued formation of phenyl nitrene.[24]

Dimerization (eq 2) or polymerization reactions would compete with reaction 6 or reactions 3 and 5 to limit the chain. In 3-methylpentane, it is possible that hydrogen atom abstraction reactions also limit the chain, thus accounting for the lower $\phi_{-\mathrm{PhN}_3}$ values measured in that solvent at corresponding $[\mathrm{PhN}_3]$. We are continuing to investigate the photochemically initiated chain decomposition reaction of phenyl azide in order to elucidate mechanistic details of this reaction.

Acknowledgment. We acknowledge the technical assistance of Dr. Kohji Chihara during the initial stages of this project. This research was supported by the Center for the Joining of Materials, Carnegie-Mellon University, through the National Science Foundation, Materials Research Section (Grant DMR76-81561).

Registry No. Phenyl azide, 622-37-7; 2-methylphenyl azide, 31656-92-5; 4-methylphenyl azide, 2101-86-2; 2-ethylphenyl azide, 35774-47-1; 2-nitrophenyl azide, 1516-58-1.

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[16] Phenyl azide solutions were deaerated either by using a multiple freeze/pump/thaw vacuum line cycle or by bubbling with dry nitrogen gas (West-Penn Laco) for 3 min at 0 °C.

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[18] Smolinsky, G.; Feuer, B. I. *J. Org. Chem.* **1964**, *29*, 3097.

[19] Smith, P. A. S.; Brown, B. B. *J. Am. Chem. Soc.* **1951**, *73*, 2435.

[20] Upon prolonged irradiation nitrobenzene and azoxybenzene are formed but are not primary photoproducts.

[21] Otsuka, S.; Nakamura, A. *Inorg. Chem.* **1968**, *7*, 2542.

[22] Overbosch, P.; van Koten, G.; Overbeek, O. *J. Am. Chem. Soc.* **1980**, *102*, 2091.

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[24] Neither reaction mechanism attempts to clarify the multiplicity of phenyl nitrene, which can exist as a singlet or triplet,[9] or to address the question of whether phenyl nitrene undergoes intramolecular rearrangement to form 7-azabicyclo[4.1.0]hepta-2,4,6-triene[8] or 1-aza-1,2,4,6-cycloheptatetraene.[25,26]

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Synthetic Studies on Arene–Olefin Cycloadditions. 4.[1] Total Synthesis of (±)-Modhephene[†]

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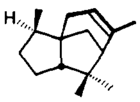
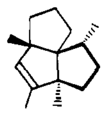
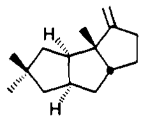
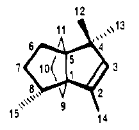
Received June 21, 1982

The arene–olefin meta cycloaddition[3] was shown in our previously described syntheses of (±)-α-cedrene (**1**),[1a] (±)-isocomene (**2**),[1b] and (±)-hirsutene (**3**)[1c] to offer a fundamentally new and particularly efficient approach to three distinct tricycloundecane skeletons.[4] We report herein its extension to a fourth structural


1
α-Cedrene


2
Isocomene


3
Hirsutene



4
Modhephene

[†] Dedicated to Professor Gilbert Stork on the occasion of his 60th birthday.

[1] For previous work in this series, see: (a) Wender, P. A.; Howbert, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 688. (b) Wender, P. A.; Dreyer, G. B. *Tetrahedron* **1981**, *37*, 4445. (c) Wender, P. A.; Howbert, J. J., submitted for publication in *Tetrahedron Lett.*

[2] A. P. Sloan Foundation Fellow; Camille and Henry Dreyfus Teacher–Scholar Award Recipient. Address correspondence to this author at Stanford University.

[3] Reviews: (a) Gilbert, A.; Yianni, P. *Tetrahedron* **1981**, *37*, 3275. (b) Gilbert, A. *Pure. Appl. Chem.* **1980**, *52*, 2669. (c) Bryce-Smith, D.; Gilbert, A. *Tetrahedron* **1977**, *33*, 2459.

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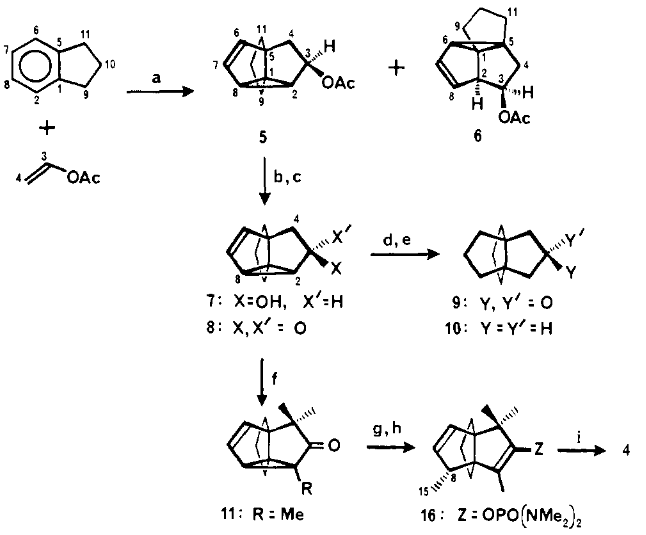
Scheme I

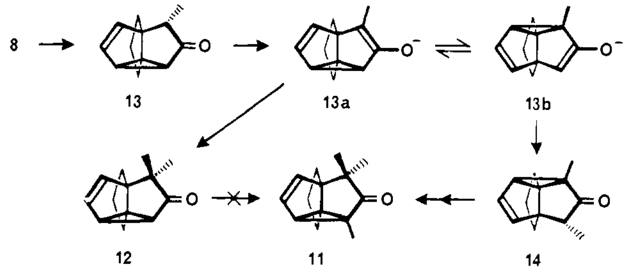


[a] $h\nu$, Vycor, cyclohexane, 35 h; **5**, 21%; **6**, 2%. [b] KOH, MeOH; 86%. [c] $BaMnO_4$; 95%. [d] H_2 (1 atm), 5% Pd/C; 100%. [e] KOH, H_2NNH_2, $(HOCH_2)_2$, heat; 54%. [f] *t*-BuOK (15 equiv), MeI (10 equiv), THF, 5 min, room temperature; **11**, 68%; **12**, 17%. [e] Me_2CuLi (5 equiv), THF, −78 °C, $Cl_2PO(NMe_2)$; Me_2NH; 76%. [h] Li^0, $EtNH_2$, THF, 0 °C; 93%. [i] H_2, PtO_2; 100%.

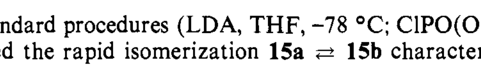
class, [3.3.3]propellanes,[5] which has led to the shortest synthesis of the unusual sesquiterpene modhephene (**4**)[6,7] report thus far. This study additionally establishes a new route to semibullvalenes, a novel alkylation based on the semibullvalene rearrangement, and an unprecedented example of exclusive 1,5-addition of a cuprate reagent to a vinylcyclopropyl ketone.

Illustrative of the ring-forming capability and the consequent increase in complexity[8] obtainable with the key cycloaddition, the propellane skeleton of **4** was conveniently assembled in one step and in multigram quantities from simple, inexpensive precursors (Scheme I). Thus, irradiation of indan (82 g) and vinyl acetate (103 g) in cyclohexane (100 mL) for 35 h with Vycor-filtered light from a 450-W Hanovia lamp produced a complex mixture from which the [3.3.3]propellane cycloadduct **5**[9] (4.2 g; 21% yield based on indan consumed) and [3.3.1]propellane cycloadduct **6**[9] (2–3% yield based on indan consumed) were isolated by flash chromatography. The formation of these products was expected on the basis of the known directing influence of arene alkyl substituents on the regiochemical course of the cycloaddition and the trend toward 3-endo-substituted cycloadducts (numbering as in Scheme I) found in related intermolecular cases.[3,10,11] The relationship of **5** and **6** as vinylcyclopropane isomers was confirmed when photolysis of pure **5** produced **6**, in analogy with a similar photochemical vinylcyclopropane rearrangement observed in the course of our isocomene synthesis.[1b] Finally, the structural assignment of the major cycloadduct **5**, and, therefore, also that of **6**, was verified by its conversion to [3.3.3]propellane (**10**)[12,13] as follows. Saponification of **5** (86% yield) gave alcohol **7** (mp 28.5–30 °C), which was oxidized with barium manganate[14] to vinylcyclopropyl ketone **8** in 95% yield. Simultaneous hydrogenation and hydrogenolysis of **8** (1 atm of H_2, 10% Pd/C, EtOAc) quantitatively afforded **9** (mp 148–150 °C), which upon Wolff–Kishner reduction provided the known [3.3.3]propellane **10**,[12,13] in 9% overall yield from indan.

Scheme II



Proceeding from vinylcyclopropyl ketone **8**, whose propellane nucleus was now firmly established, the synthesis of modhephene was seen to require the introduction of four methyl groups: two at C4 and one each at C2 and C8 (cf. **8** and **4**). While it is readily recognized that two of these methyl groups (at C4) could be easily introduced through alkylation of ketone **8**, we expected this reaction would result in the formation of the trimethylated ketone **11**. As outlined in Scheme II, this seemingly unlikely event could occur if the enolates of **8** and its mono- and dimethyl derivatives **13** and **14** exhibited the dynamic behavior of semibullvalenes.[15] Thus, methylation of the enolate of **8** would produce **13**, which, upon deprotonation, would generate enolate **13a** and, consequently, its Cope isomer **13b**. Methylation of the former would likely stop at the dialkylated stage, **12**, whereas if alkylation of **13b** were favored, ketone **14** would result. Further reaction of **14** would then produce trimethylated ketone **11**. Support for this prediction was found when enol phosphate **15**,[9] obtained in 90% yield from **8** by standard procedures (LDA, THF, −78 °C; $ClPO(OPh)_2$),[16] exhibited the rapid isomerization **15a** ⇄ **15b** characteristic of semibullvalene derivatives[19] even at temperatures as low as −100



15a **15b**

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(4) Tricyclo[5.3.1.0^{1,5}]undecanes, tricyclo[6.3.0.0^{1,5}]undecanes, and tricyclo[6.3.0.0^{2,6}]undecanes, respectively.

(5) A previous report appeared describing synthesis of the [4.3.3]propellane skeleton by meta photoaddition of olefins to Tetralin: Angadiyavar, C. S.; Cornelisse, J.; Merrit, V. Y.; Srinivasan, R. *Tetrahedron Lett.* **1973**, 4407.

(6) Isolation and Structure: (a) Zalkow, L. H.; Harris, R. N., III; Van Derveer, D. *J. Chem. Soc., Chem. Commun.* **1978**, 420. (b) Bohlmann, F.; Van, N. L.; Pham, T.; Jacupovic, J.; Schuster, A.; Zabel, V.; Watson, W. H. *Phytochemistry* **1979**, *18*, 1831.

(7) For previous modhephene syntheses see: (a) Smith, A. B., III; Jerris, P. J. *J. Org. Chem.* **1982**, *47*, 1845. (b) Smith, A. B., III; Jerris, P. J. *J. Am. Chem. Soc.* **1981**, *103*, 194. (c) Karpf, M.; Dreiding, A. S. *Tetrahedron Lett.* **1980**, 4569. (d) Karpf, M.; Dreiding, A. S. *Helv. Chim. Acta* **1981**, *64*, 1123. (e) Schostarez, H.; Paquette, L. A. *Tetrahedron* **1981**, *37*, 4431. (f) Schostarez, H.; Paquette, L. A. *J. Am. Chem. Soc.* **1981**, *103*, 722. (g) Oppolzer, W.; Marazza, F. *Helv. Chim. Acta* **1981**, *64*, 1575. (h) Oppolzer, W.; Battig, K. *Helv. Chim. Acta* **1981**, *64*, 2489.

(8) Bertz, S. H. *J. Am. Chem. Soc.* **1981**, *103*, 3599.

(9) All new compounds gave satisfactory NMR, IR, and mass spectra and exact mass or combustion analyses. Selected spectral values are as follows. Photoadduct **5**: 300-MHz ^{1}H NMR ($CDCl_3$) δ 5.72 (1 H, dd, J = 5.2, 1.9 Hz), 5.53 (1 H, d, J = 5.2 Hz), 5.40 (1 H, dd, J = 5.9, 8.5 Hz), 2.16 (1 H, dd, J = 8.5, 13.1 Hz), 2.12 (1 H, dd, J = 5.9, 5.9 Hz; exact mass 204.11493 (calcd 204.11502). Photoadduct **6**: 300-MHz ^{1}H NMR ($CDCl_3$) δ 5.85 (1 H, dd, J = 5.5, 2.3 Hz), 5.63 (1 H, ddd, J = 5.5, 2.4, 0.7 Hz), 5.25 (1 H, ddd, J = 8.0, 9.4, 5.1 Hz), 3.26 (1 H, dd, J = 5.0, 2.4 Hz); exact mass 204.1148 (calcd 204.1150). Enol phosphate **15**: 300-MHz ^{1}H NMR ($CDCl_3$) δ 7.19 (10 H, m, Ar), 5.21 (1 H, t, H7), 4.20 (2 H, m, H2, H4), 3.99 (2 H, m, H6, H8), 1.56 (6 H); ^{13}C NMR ($CDCl_3$) δ 150.54, 129.84, 125.70, 125.52, 121.65, 120.26, 89.80, 77.65, 65.37, 31.26, 26.67; exact mass 392.11735 (calcd 392.11774).

(10) Gilbert, A.; Samsudin, M. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 552. See also ref 3a,b.

(11) For recent examples, see: (a) Jans, A. W. H.; van Dijk-Knepper, J. J.; Cornellisse, J. *Tetrahedron Lett.* **1982**, 1111. (b) Cornelisse, J.; Merritt, V. Y.; Srinivasan, R. *J. Am. Chem. Soc.* **1973**, *95*, 6197.

(12) Found for [3.3.3]propellane: mp 123–125 °C (lit. mp 130 °C (ref 13c), 116–117 °C (ref 13b)); ^{13}C NMR ($CDCl_3$) δ (relative height) 60.44 (2), 40.41 (6), 24.68 (3); exact mass: 150.14092 (calcd 150.14084).

(13) For other syntheses of [3.3.3]propellane see: (a) Takaichi, N.; Yoshiaki, I.; Kiyoshi, T.; Yashima, K.; Aigami, K. *J. Org. Chem.* **1975**, *40*, 2929. (b) Inamoto, Y.; Aigami, K.; Fujikura, Y.; Takaishi, N.; Tsuchihashi, K. *J. Org. Chem.* **1979**, *44*, 854. (c) Weber, R. W.; Cook, J. M. *Can. J. Chem.* **1978**, *56*, 189.

(14) Firouzabadi, H.; Ghaderi, E. *Tetrahedron Lett.* **1978**, 839.

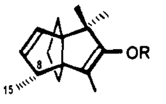
(15) Semibullvalene does not begin to show distinct valence isomers by ^{1}H NMR until cooled to −130 °C: (a) Zimmerman, H. E.; Grunwald, G. L. *J. Am. Chem. Soc.* **1966**, *88*, 183. (b) Cheng, A. K.; Anet, F. A. L.; Mioduski, J.; Meinwald, J. *Ibid.* **1974**, *96*, 2887.

(16) Ireland, R. E.; Muchmore, D. C.; Hengartner, U. *J. Am. Chem. Soc.* **1972**, *94*, 5098.

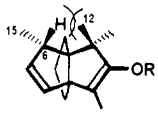
°C, as determined by ^{1}H and ^{13}C NMR spectroscopy.[9]

The foregoing predictions were borne out when treatment of ketone **8** with *t*-BuOK (15 equiv) and MeI (10 equiv) in THF at room temperature produced **11** (mp 88 °C) and **12** (mp 91 °C) in 68% and 17% yields, respectively, after flash chromatography. Furthermore, in accord with the previous analysis, when **12** was resubmitted to the alkylation conditions it was recovered unchanged.[17]

Introduction of the fourth methyl group (C15) required for modhephene was accomplished by reaction of vinylcyclopropyl ketone **11** with $LiMe_2Cu$ (5 equiv; THF, −78 °C), which proceeded with complete stereoselectivity and with exclusive 1,5-addition to provide, after in situ enolate trapping,[18,19] **16** in 76% yield.[20] The unusual regiochemical selectivity (1,5-addition favored over 1,7-addition[21,22]) observed in this reaction can be explained on the basis of product development control. Thus, in the transition state leading to **19** (R = metal cation) via either an S_N2' or a reductive elimination mechanism,[22] quaternization of C6 would be accompanied by development of a significant steric interaction between the C6 hydrogen and the C12 methyl group. This effect would be absent during quaternization of C8 in the event of 1,5-addition. This interpretation was supported by molecular mechanics calculations using Allinger's MM2 program,[23] which indicated that enol **19** (R = H)[24] has 4.7 kcal/mol more strain energy than enol **18** (R = H).



18



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Completion of the synthesis involved reduction (Li^0, $EtNH_2$, *t*-BuOH, THF, 0 °C)[16] of the now readily available (five steps) propellane phosphorodiamidate **16**, which furnished **17** in 93% yield. Finally, selective hydrogenation of **17** quantitatively provided (±)-modhephene (**4**), spectroscopically identical with authentic samples of natural and synthetic material kindly provided by Professors Zalkow and Smith.[25]

In summary, this synthesis, proceeding from indan and vinyl acetate in seven steps and in 8.2% overall yield, presents a concise solution to the modhephene problem and the basis for the extension of the arene–olefin cycloaddition to other problems in propellane synthesis. Further studies are in progress.

Acknowledgment. This work was supported by grants (CA21136 and CA31845) awarded by the National Cancer Institute, DHHS.

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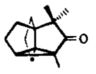
[17] Doering has tested the concept of a fluxional enolate by observing perdeuteration of bullvalone: Doering, W. von E.; Ferrier, B. M.; Fossel, E. T.; Hartenstein, J. H.; Jones, M., Jr.; Klump, G.; Rubin, R. M.; Saunders, M. *Tetrahedron* **1967**, *23*, 3943.

[18] Liu, H. J.; Lee, S. P.; Chan, W. H. *Can. J. Chem.* **1977**, *55*, 3797.

[19] Ireland, R. E.; Pfister, G. *Tetrahedron Lett.* **1969**, 2145.

[20] The necessity of the olefin in **11** was verified when cyclopropyl ketone **20** (mp 92 °C; prepared from **11** in 96% yield by the following sequence: $LiAlH_4$; H_2, Pd/C; Jones reagent) was found to be completely resistant to conjugate addition by Me_2CuLi both with (ref 7a) and without added BF_3.



20

[21] (a) Danishefsky, S. *Acc. Chem. Res.* **1979**, *12*, 66. (b) Miyaura, N.; Itoh, M.; Sasaki, N.; Suzuki, A. *Synthesis* **1977**, 317. (c) Grieco, P.; Finkelhor, R. *J. Org. Chem.* **1973**, *38*, 2100. (d) Daviaud, G.; Miginiac, P. *Tetrahedron Lett.* **1972**, 997.

[22] (a) House, H. O.; McDaniel, W. C.; Sieloff, R. F.; Vanderveer, D. *J. Org. Chem.* **1978**, *43*, 4316. (b) House, H. O.; Snoble, K. A. J. *J. Org. Chem.* **1976**, *41*, 3076. (c) Marshall, J. A.; Ruden, R. A. *Tetrahedron Lett.* **1977**, 2875.

[23] Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127.

[24] Enols **18** and **19** (R = H) were used as models for the corresponding enolates.

[25] We thank Professor A. B. Smith, III (University of Pennsylvania) for providing samples of natural (via Professor Zalkow; see ref 6a) and synthetic (see ref 7a,b) modhephene.

Registry No. (±)-**4**, 76739-64-5; (±)-**5**, 83060-51-9; (±)-**6**, 83060-52-0; (±)-**7**, 83043-45-2; (±)-**8**, 83043-46-3; **9**, 83043-47-4; **10**, 51027-89-5; (±)-**11**, 83043-48-5; (±)-**12**, 83043-49-6; (±)-**15a**, 83043-50-9; (±)-**16**, 83043-51-0; (±)-**17**, 83043-52-1; (±)-**18**, 83043-53-2; (±)-**19**, 83043-54-3; (±)-**20**, 83043-55-4; vinyl acetate, 108-05-4; indan, 496-11-7; lithium dimethylcuprate, 15681-48-8.

Titanium-Induced Reductive Elimination. Syntheses of 1,3-Dienes[1]

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van Tamelen and his co-workers Schwartz,[2] Hanzlik,[3] and Sharpless[3] showed that low-valent titanium can be used to effect reductive coupling of benzylic[2] and allylic alcohols.[3] Subsequently, low-valent titanium has been employed in the pinacolic coupling of carbonyls and in the reductive coupling of carbonyls to olefins.[4] Reductive elimination of 1,2-glycols to olefins[5] as well as the cyclization of 1,3-glycols to cyclopropanes[6] have also been reported. We now report that low-valent titanium reacts with 2-ene-1,4-diols and a 2-yne-1,4-diol to yield 1,3-dienes by a 1,4-reductive elimination reaction (Scheme I).

(*E*)- and (*Z*)-1,2-bis(1-hydroxycyclohexyl)ethylene were conveniently prepared from readily available 1,2-bis(1-hydroxycyclohexyl)acetylene. Catalytic hydrogenation over a Lindlar catalyst[7] produced the pure *Z* isomer and reduction of the acetylenic diol with lithium aluminum hydride[8] yielded the *E* isomer. Refluxing a tetrahydrofuran solution of either the *E* or the *Z* diol for 3 h with an excess of the low-valent titanium (2–4:1 molar ratio) yielded dicyclohexylideneethane in 75% and 70% yields, respectively. Since dicyclohexylideneethane is a key moiety of vitamin-D, this result suggests that this mode of generating 1,3-dienes might be effectively used in the syntheses of vitamin-D's and their analogues.[9,10]

Low-valent titanium reagents have been prepared by reduction of $TiCl_3$ or $TiCl_4$ with metals[4-6] such as magnesium, potassium, sodium, lithium, zinc–copper couple, or metal hydrides, particu-

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[1] The support of this work by a grant from the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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0002-7863/82/1504-5807$01.25/0