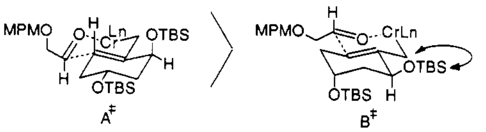
as the sole product in almost quantitative yield. One might rationalize the exclusive production of 18 by assuming a transition state resembling A‡ which is preferred over B‡ because of minimization of $A^{1,2}$ type of steric interactions.[19]



Having prepared the desired common intermediate 18, we then examined the stereo- and regioselective dehydration of 18 by several conventional methods in order to construct the requisite diene. However, unexpected difficulties were encountered in this transformation. For example, treatment of 18 with methanesulfonyl chloride in pyridine gave enol ether 20 as a major product instead of diene 19. These difficulties were eventually overcome by use of Mitsunobu's reagent.[20] Thus, reaction of alcohol 18 with triphenylphosphine and diethyl azodicarboxylate in tetrahydrofuran at room temperature gave the diene 19, $[\alpha]^{24}_D$ -9.6° (c 1.23, $CHCl_3$), and enol ether 20 in a ratio of 6:1. Oxidative deprotection[21] of 19 furnished dienol 21, mp 64–67 °C (lit.[4b] mp 69–71 °C), $[\alpha]^{25}_D$ +7.7° (c 0.73, EtOH) [lit.[4b] +7.9° (c 0.4, EtOH)], whose spectral data (^1H NMR, IR, MS) are identical with those reported.[4b] Since 21 has already been converted to phosphine oxide 2 in 82% yield by the Roche group,[4b] the present synthetic route should enable us to prepare 2 from (R)-(–)-carvone (10) in 25% overall yield (15 steps).

For the synthesis of A-ring synthons 3 and 4, alcohol 18 was converted to diol 22 by oxidative deprotection[21] followed by methanolysis of the resulting p-methoxybenzoates. Without purification, diol 22 was then successively subjected to oxidative cleavage and isomerization to furnish aldehyde 3, $[\alpha]^{29}_D$ -86.1° (c 0.32, EtOH) [lit.[4a] -91.1° (c 0.3, EtOH)], $[\alpha]^{28}_D$ -85.6° (c 1.08, $CHCl_3$) [lit.[4d] -86° (c 1.00, $CHCl_3$)], which exhibited spectral properties (^1H NMR, IR) in accord with those reported.[4a,d] Aldehyde 3 was thus obtained from (R)-(–)-carvone in 35% overall yield (14 steps). Since aldehyde 3 is a synthetic precursor of acetylene 4,[4f] the synthesis of 3 also means development of a new route to 4 from (R)-(–)-carvone (10).

Acknowledgment. We thank the Japan Society for the Promotion of Science for Japanese Junior Scientists for financial support (to Dr. Hirotoshi Numata).

Supplementary Material Available: Experimental procedures for preparation of 18, 19, 21, and 3 as well as spectral (^1H NMR, IR, MS) and analytical data for 12–16, 18, 19, 21, and 3 (4 pages). Ordering information is given on any current masthead page.

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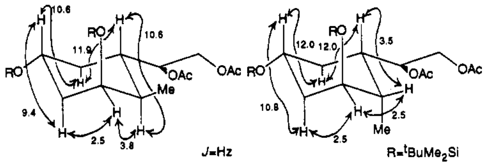
[17] The stereochemistry of 18 is tentatively assigned on the basis of mechanistic considerations in addition to the fact that dehydration of 18 gave the Z isomer 19 exclusively. Furthermore, on the basis of 500-MHz ^1H NMR spectral analysis of two diacetates derived from 18 (shown below) and MTPA ester derivatives of 18,[18] we empirically determined the configurations of C-5 and C-6 to be both S.



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Nickel(0)-Promoted Cyclization of 1,n-Diynes with Isocyanide: The First Practical Synthesis of Polycyclic Iminocyclopentadienes

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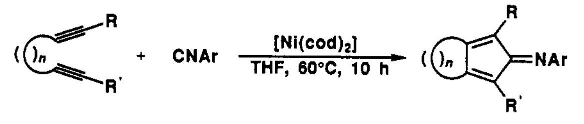
Received May 11, 1989

Summary: 1,n-Diynes having alkyl, aryl, and trimethylsilyl groups as the terminal substituents undergo cyclization with 2,6-dimethylphenyl isocyanide in the presence of a stoichiometric amount of bis(cyclooctadiene)nickel(0) to form polycyclic iminocyclopentadienes as red-orange crystals or oils, which show interesting spectral properties and chemical reactivities.

Sir: We have recently reported a one-step synthesis of polycyclic iminocyclopentenes via nickel(0)-promoted cyclization of enynes with isocyanides.[1] Reported herein is a similar cyclization of diynes[2] to form polycyclic iminocyclopentadienes,[3] nitrogen analogues of cyclopentadienones (eq 1).



(1)

Cyclopentadienones have long been studied from both of the synthetic and theoretical points of view, but the substituents on the ring have been restricted only to the stabilizing groups such as aryl and tert-butyl.[4] In 1980, Vollhardt and his co-workers reported a cobalt-mediated

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[3] Transition metal promoted cyclization of diphenylacetylene or analogues with isocyanides has been reported. (a) Co: Yamazaki, H.; Wakatsuki, Y. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1239. (b) Rh: Mueller, E. *Synthesis* **1974**, 761. (c) Ni, Pd: Suzuki, Y.; Takizawa, T. *J. Chem. Soc., Chem. Commun.* **1972**, 837. (d) Ni: Eisch, J. J.; Aradi, A. A.; Han, K. I. *Tetrahedron Lett.* **1983**, *24*, 2073. Other iminocyclopentadiene chemistry: (e) Freeman, B. H.; Lloyd, D.; Singer, M. I. C. *Tetrahedron* **1972**, *28*, 343. (f) Atkinson, R. S.; Harger, M. J. P. *J. Chem. Soc., Perkin Trans. 1* **1974**, 2619.

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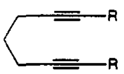
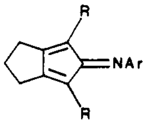
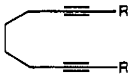
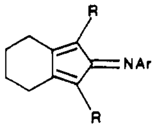
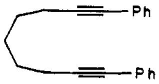
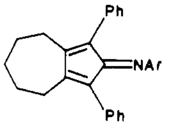
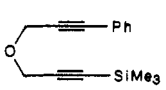
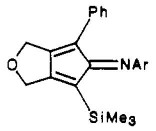
0022-3263/89/1954-3517$01.50/0

Table I. Nickel(0)-Promoted Cyclization of 1,*n*-Diynes with Isocyanide[a]

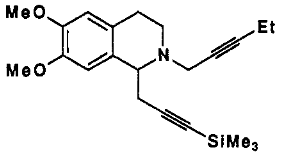
entry	substrate	product[b]	isolated yield, %	UV, nm (log ε)[c]	
				λ_1	λ_2
					
1	R = Ph	1, R = Ph[d]	87	248 (4.53)	454 (3.57)
2	R = SiMe_3	2, R = SiMe_3[e]	88	250 (4.33)	409 (3.18)
					
3	R = Ph	3, R = Ph[f]	76	247 (4.55)	453 (3.39)
4	R = SiMe_3	4, R = SiMe_3[g]	56	251 (4.30)	434 (3.29)
5	R = Et	5, R = Et[e]	94	244 (4.27)	415 (2.74)
6		 6[e]	47	242 (4.57)	439 (3.19)
7		 7[h]	82	238 (4.37)	419 (3.34)

[a] Diyne:ArNC:[Ni(cod)$_2$] = 1:2:1, THF, 60 °C, 10 h. [b] Ar = 2,6-dimethylphenyl. [c] In cyclohexane. [d] Mp 169–170 °C. [e] Red orange, viscous oil. [f] Mp 181–182 °C. [g] Mp 104–105 °C. [h] Mp 138–139 °C.

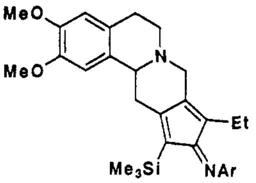
synthesis of new types of bicyclic cyclopentadienones which contained the trimethylsilyl group or no substituents on the 2,5-positions.[5] Iminocyclopentadienes have only been described in several scattered papers, mostly in the 1970s.[3] Our present development may, therefore, shed a new light on these still rather unexplored field.

Representative results on the one-step synthesis of bicyclic iminocyclopentadienes are summarized in Table I, which contains yields, melting points, and UV absorptions of the products.[6] A general experimental procedure is as follows. Under a nitrogen atmosphere, a mixture of a diyne (1 mmol), 2,6-dimethylphenyl isocyanide (2 mmol), bis(1,5-cyclooctadiene)nickel(0), [Ni(cod)$_2$], (1 mmol), and THF (4 mL) was heated at 60 °C for 10 h. The resulting mixture was stirred with CuCl (2 equiv) in air at room temperature for 2 h to remove the excess isocyanide. Filtration and column chromatography on silica gel gave the product as red-orange crystals or viscous oils.

There are several significant features in the reaction. (1) The cyclization did not require phosphine ligand, which was the essential additive for the cyclization of enynes.[1] (2) Substituents (R or R′) on acetylenes may be alkyl, aryl, and silyl groups, but not hydrogen atom, a complex mixture of products being formed in the last case. (3) Bisacetylenes which are connected with tri- to pentamethylene groups (*n* = 3, 4, and 5) can afford the corresponding five- to seven-membered ring-fused iminocyclopentadienes. The yield decreases in the order *n* = 3 > 4 > 5 (entries 1, 3, and 6). (4) The reaction can be applied to an oxygen-containing substrate (entry 7). (5) Polycyclic iminocyclopentadienes can also be obtained under a similar condition, as exemplified by the synthesis of an alkaloid analogue **9**[7] from a nitrogen-containing diyne derivative **8**.



8



9 56%

Bicyclic iminocyclopentadienes exhibit interesting ^{1}H NMR spectral features. Thus, there are some broad signals due to the ring methylene and the 2,5-substituent protons, together with sharp signals due to the 2,6-dimethylphenyl group, the phenomena being dependent upon the structure. Thus, **3** shows two broad signals due to the ring α-methylene groups at room temperature;[8] the two signals coalesce in one broad signal at 50 °C. In **5**, the two ethyl groups are nonequivalent: one of them shows up-field shift because of the anisotropic effect of the 2,6-dimethylphenyl ring on the imino group.[8] The above results reveal that the imino group in these compounds is fixed on one side[9] even in solution at room temperature. On the other hand, **4** shows only one broad singlet due to the two trimethylsilyl groups at room temperature,[8] which sharpens at 50 °C, indicative of the flipping of the imino group even at room

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[5] Gesing, E. R. F.; Tane, J. P.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 1023.

[6] All new compounds showed consistent spectral and analytical data.

[7] **9**: red orange crystals; mp 174–175 °C; UV 243 (4.47), 426 (3.06).

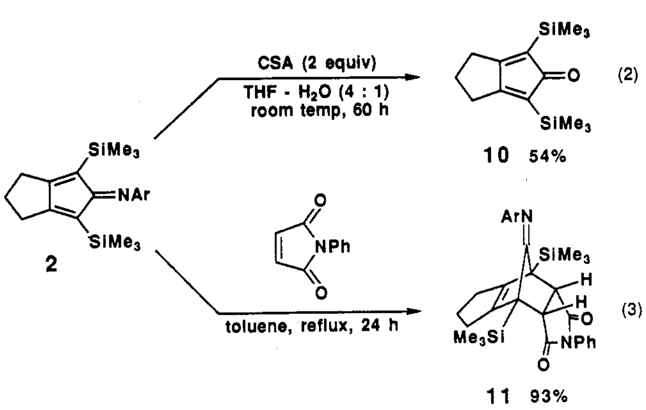
[8] 200-MHz ^{1}H NMR data (CDCl$_3$) at 20 °C. **3**: 1.61–1.74 (br m, 4 H), 1.99 (s, 6 H), 2.35–2.54 (br m, 2 H), 2.67–2.88 (br m, 2 H), 6.43–6.58 (sharp m, 3 H), 6.69–7.68 (br m, 10 H). **4**: –0.01 (br s, 18 H), 1.64 (quintet, *J* = 3.7 Hz, 4 H), 1.98 (s, 6 H), 2.65–2.72 (m, 4 H), 6.80–6.99 (sharp m, 3 H). **5**: 0.51 (br t, *J* = 7.3 Hz, 3 H), 1.11 (br t, *J* = 7.3 Hz, 3 H), 1.59–1.66 (sharp m, 6 H), 2.04 (s, 6 H), 2.26–2.55 (br m, 6 H), 6.82–6.99 (sharp m, 3 H).

[9] This point has been confirmed by an X-ray study of **3**. The result will be published in the full paper.

temperature, possibly owing to the bulky trimethylsilyl groups.

The electronic absorption spectra, π–π^* (λ_1) and n–π^* (λ_2),[4] show interesting structure dependencies. Thus, both absorption maxima shift to longer wavelengths with the decrease of the ring size ($n = 5 < 4 < 3$) in the 2,5-diphenyl series (**6**, **3**, and **1**), but in the reverse order in the 2,5-disilyl series (**2** and **4**), the latter order being the same as that observed in the cyclopentadienone series.[5] The absorptions are also dependent upon the substituents on the 2,5-positions, as observed in the series of $n = 4$ (**3**, **4**, and **5**):λ_1 decreases in the order R = $SiMe_3$ > Ph > Et, while λ_2 decreases in the order R = Ph > $SiMe_3$ > Et.

Two representative transformations of bicyclic iminocyclopentadiene **2** are presented in eq 2 and 3. Thus, the imino group could be hydrolyzed to form the corresponding, known cyclopentadienone **10**,[5] the silyl groups being retained under a weakly acidic condition. The Diels–Alder reaction[3f] proceeded smoothly at the toluene reflux temperature to form the polycyclic adduct **11** as a single stereoisomer in almost quantitative yield. It should be noted here that the bicyclic iminocyclopentadiene showed no tendency to dimerization under the thermal condition.



We anticipate that further chemical and physical properties of a new class of compounds described herein might be disclosed by more detailed studies, which are now in progress in our laboratories.

Acknowledgment. We thank Dr. Motoo Shiro of Shionogi Research Laboratory, Osaka, for the X-ray study of compound **3**.

Supplementary Material Available: Experimental procedures for the synthesis of compounds **3**, **10**, and **11** and physical, spectral, and analytical data of compounds **1–7** and **9–11** (3 pages). Ordering information is given on any current masthead page.

Synthesis of a Highly Strained Cyclopropene: Tricyclo[3.2.2.0^{2,4}]non-2(4)-ene

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Received April 24, 1989

Summary: Tricyclo[3.2.2.0^{2,4}]non-2(4)-ene has been synthesized. This is one of the most highly strained cyclopropenes yet reported. It can be made by treatment of a vicinal dibromocyclopropane with *tert*-butyllithium in THF at −78 °C. It was identified by its reaction with diphenylisobenzofuran. The adduct is fully characterized by spectral and elemental analyses.

Sir: Recently there has been a rebirth of interest in strained olefin chemistry.[1] There is current work being reported on the synthesis of homocubene[2] and cubene.[3] For years there has been a fascination on the part of many organic chemists to synthesize and trap or isolate such unusually strained molecules. Cyclopropenes have been included in these studies. Simple cyclopropenes themselves are not without strain, and only a few good methods of synthesis have been developed.[4] Placing a cyclopropene in a small bicyclic structure increases the olefinic strain. The syntheses of bicyclic cyclopropenes **1**, **2**, and **3** have been reported. The dimethyl derivative **1** was observed by NMR at −60 °C,[5] and molecular orbital calculations indicate that **1–3** may prefer to be nonplanar.[6] Bicyclo[4.1.0]hept-1(6)-ene (**2**) has been proven as an intermediate in a reaction[7] and bicyclo[3.1.0]hex-1(5)-ene (**3**) has also been postulated as an intermediate.[8] Wiberg and Bonneville[9] reported the synthesis and trapping, via cycloadditions, of **2** and **3**. Originally, calculations by these workers predicted a nonplanar structure for **2**,[10a] but newer calculations[10b] show that **2** is planar. Finally **2** has been made and trapped with cyclopentadiene in the gas phase.[11]

In contrast to bicyclic cyclopropene-containing compounds, tricyclic cyclopropenes such as **4** and **5** have not been investigated. The tricyclic compounds of smaller size rings should be as strained as **1–3**, do present a fascinating synthetic challenge, and would possess interesting struc-

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[1] *Abstracts of Papers*, 196th National Meeting of the American Chemical Society, Los Angeles, CA, September, 1988; American Chemical Society: Washington, DC, 1988; a group of papers entitled "Symposium on Pyramidalized Alkenes", A. P. Marchand and P. Vogel presiding; ORGN 221-224 and 258-261.

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[9] (a) Wiberg, K.; Bonneville, G. *Tetrahedron Lett.* **1982**, *23*, 5385. (b) Bonneville, G. W. Ph.D. Dissertation, Yale University, 1983.

[10] (a) Wiberg, K. B.; Bonneville, G.; Dempsey, R. *Isr. J. Chem.* **1983**, *23*, 85. (b) Wiberg, K. B. *Abstracts of Papers*, 196th National Meeting of the American Chemical Society, Los Angeles, CA; American Chemical Society: Washington, DC, 1988; ORGN 261.

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