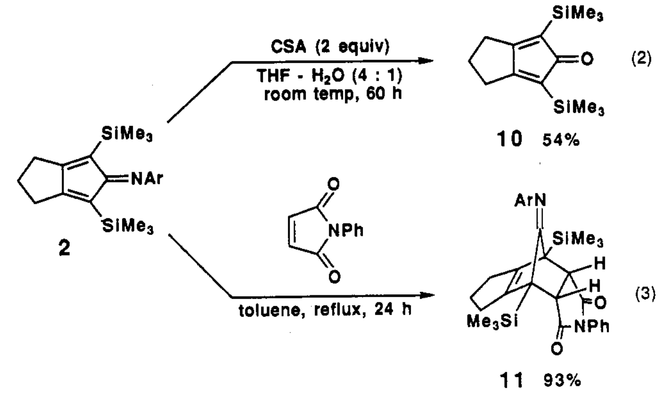
temperature, possibly owing to the bulky trimethylsilyl groups.

The electronic absorption spectra, $\pi-\pi^*$ (λ_1) and $n-\pi^*$ (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

Philip J. Chenier* and Dale A. Southard, Jr.

Department of Chemistry, University of Wisconsin—Eau Claire, Eau Claire, Wisconsin 54702-4004

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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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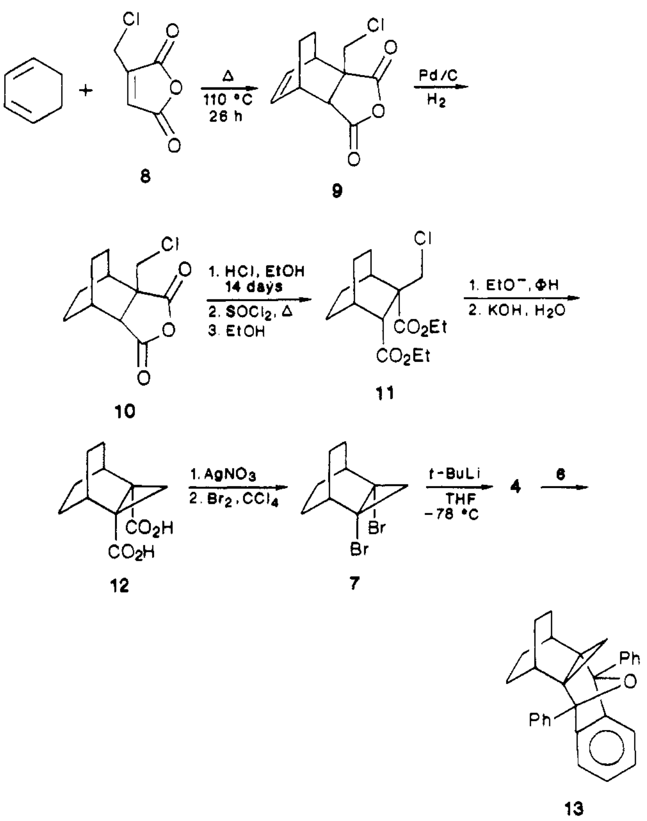
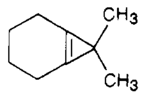
Scheme I



tures and chemistry for study. They would also serve as precursors to [*n.m.*1]propellanes via additions to the double bond, another area of active study.



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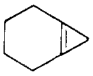

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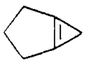

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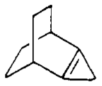

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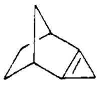
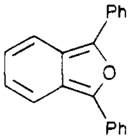


5



6

We report the successful synthesis of tricyclo[3.2.2.$0^{2,4}$]non-2(4)-ene (**4**) and its Diels–Alder adduct with diphenylisobenzofuran (**6**). After a number of unsuccessful syntheses, the choice of a precursor to **4** eventually settled on dibromide **7**. The synthesis of dibromide **7** and olefin **4** is somewhat analogous to the Wiberg route[9] for **2**, though substantial changes in experimental procedure were necessary for some steps. Scheme I outlines the present synthesis.[12]

Chloro anhydride **8** can be made in two steps from itaconic anhydride.[13] Cycloaddition of **8** with cyclohexadiene in refluxing toluene afforded **9**. Hydrogenation of the double bond with palladium in ethyl acetate proceeded smoothly to **10**. Anhydride **10** had to be refluxed for 2 weeks for complete ring opening to diester **11**. Refluxing benzene and sodium ethoxide resulted in elimination of HCl to form a cyclopropane; hydrolysis of the ester groups yielded diacid **12**. The Cristol–Firth modification[14] of the Hunsdiecker reaction failed to give a good yield of dibromide **7**, presumably because diacid **12** easily dehydrates to the cyclic anhydride, but the original Hunsdiecker reaction conditions[15] gave dibromide **7** in acceptable yield.

Treatment of dibromide **7** (560 mg, 2.00 mmol) in the presence of diphenylisobenzofuran (**6**, 540 mg, 2.00 mmol) in tetrahydrofuran (25 mL) at −78 °C with *tert*-butyllithium (3.40 mmol) in pentane (1.7 M, 2.0 mL), followed by stirring for 0.5 h, quenching with methanol (4.5 mL) at −78 °C, aqueous workup, and ether extraction gave a yellow solid (780 mg). TLC showed that no starting materials were present. Recrystallization from hexane–ether gave a white solid (140 mg), mp 205–209 °C, which showed two spots. Spectral properties were in accord with two possible isomers of adduct **13** (only one is shown in Scheme I), but a second recrystallization failed to separate the two compounds.

The residue from the recrystallizations was column chromatographed on silica gel and eluted with 80:20 hexane–ethyl acetate. A fraction of 300 mg was isolated and recrystallized twice from hexane to give a white solid, mp 207–209 °C, which showed one spot by TLC: ^{1}H NMR ($CDCl_3$, 80 MHz) δ 7.3–6.7 (m), 2.4–0.1 (m); ^{13}C NMR ($CDCl_3$, 20 MHz) δ 147.7, 137.7, 128.2, 127.0, 126.6, 126.4, 118.3, 93.0, 32.5, 26.6, 25.6, 24.8, 23.2; exact mass calcd for $C_{29}H_{26}O$ 390.1982, found 390.1982. Anal. Calcd for $C_{29}H_{26}O$: C, 89.19; H, 6.71. Found: C, 88.70; H, 6.86. The 13 different carbons and the parent (and base) peak with the anticipated exact mass are particularly conclusive for the structure of **13**. The estimated yield of **13** is 440 mg, 1.13 mmol, 57%.

Efforts are under way to study the chemistry of olefin **4** under a variety of conditions, with and without dienes present. The synthesis of strained olefin **5** will also be investigated.

Acknowledgment. This research was supported in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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(12) Intermediates in the synthesis of **4** had spectral properties in accord with their structures. Intermediates **10**, **12**, and **7** had acceptable elemental analyses. Details of the experimental procedure will be published in a forthcoming paper.

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