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Dimerization of Cubene. 1-Iodoadamantane as a Probe for Radical Intermediates

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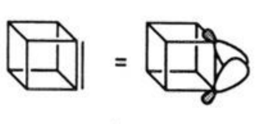
Abstract: Fluoride ion induced elimination from 1-bromo- and 1-iodo-2-(trimethylsilyl)cubanes is shown to produce cubene (**1**) in excellent yield and at high enough concentration for its dimerization to propellane **16**. This highly strained compound is unstable; the ultimate reaction products are characterized as the isomeric bis(tricyclo[4.2.0.0^{2,5}]octa-3,7-diene-3,8-diyl)s **11a,b**. These are believed to form via a set of radical ring openings of **16**. 1-Iodoadamantane is introduced as an iodine atom donor useful for probing the intermediacy of radicals in the chemistry of highly reactive, strained ring systems such as **16**.

Ab initio calculations indicate that sufficient overlap exists between the p-orbitals of 1,2-dehydrocubane for it to behave as an olefin (**1**, cubene) rather than a biradical (**1′**, cuba-1,2-diyl).[1] Recently,[2] the thermodynamic properties of cubene have been determined by way of an ICR study of its radical anion: $\Delta H_f = +238 \pm 4$ kcal mol^{-1}; SE = 227 ± 4 kcal mol^{-1}; OSE = 63 ± 4 kcal mol^{-1}; heat of hydrogenation = 90 ± 4 kcal mol^{-1}. These values are in good agreement with theory.[1a] The chemical reactivity of the double bond in cubene,[3] the most pyramidalized olefin known,[4] is intriguing. However, this aspect of cubene chemistry is largely unexplored.



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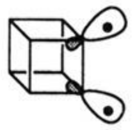
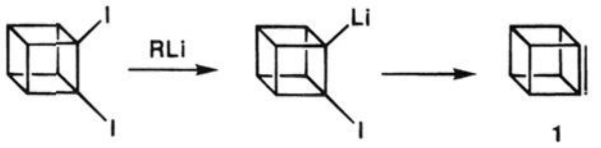


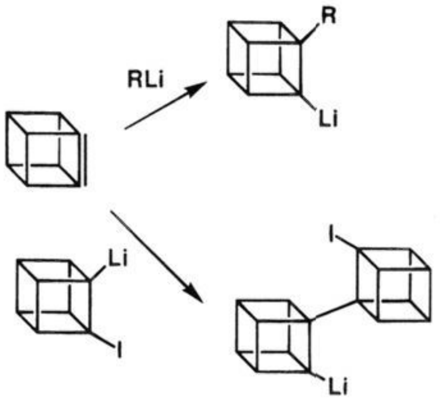
1′

In the original experimental work cubene was generated by reaction of 1,2-diiodocubane with an organolithium.[3] The reaction proceeds by a rapid halogen/metal exchange to 2-iodocubyllithium, then elimination of lithium iodide (eq 1).



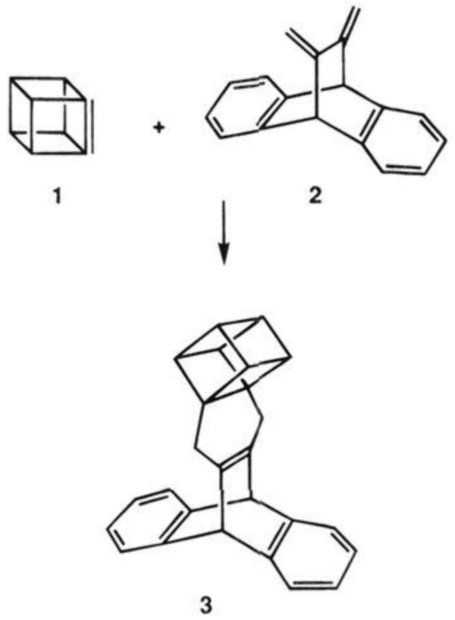
(1)

Unfortunately, cubene so formed is elusive, as it reacts very rapidly with one or another of the organolithiums present at its generation (eq 2).[3]



(2)

Although the addition products of such reactions are interesting in themselves,[5] the rapidity of the addition and the promiscuous reactivity of organolithium reagents severely restricts study of the behavior of cubene toward other reagent probes. So far, only diene **2** has been found to be an organolithium-compatible[6] trap that can compete with the organolithium addition process. Cubene and diene **2** react readily to give in good yield the easily isolable Diels−Alder adduct **3**.[3]



Further studies of the chemical properties of the unique double bond in cubene require development of a new method for the formation of cubene. We report here good synthetic procedures for the preparation of 1-halo-2-(trimethylsilyl)cubanes and our finding that cubene can be generated successfully by fluoride ion induced elimination from certain of these compounds.[7] Under the conditions of reaction, we find no evidence for additions of fluoride ion to cubene; indeed, the concentration

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[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1995.

[1] (a) Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1988**, *110*, 4710. (b) Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1990**, *112*, 875.

[2] Staneke, P. O.; Ingemann, S.; Eaton, P. E.; Nibbering, N. M. M.; Kass, S. R. *J. Am. Chem. Soc.* **1994**, *116*, 6445.

[3] Eaton, P. E.; Maggini, M. *J. Am. Chem. Soc.* **1988**, *110*, 7230.

[4] For a review of olefins with distorted geometry see: Leuf, W.; Keese, R. Strained Olefins: Structure and Reactivity of Nonpolar Carbon−Carbon Double Bonds. In *Top. Stereochem.* **1991**, *20*, 231.

[5] Eaton, P. E. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1421.

[6] Diene **2** is not entirely stable to organolithiums; *tert*-butyllithium adds to it slowly even at −78 °C.

[7] For some earlier uses of fluoride ion induced eliminations from *vic*-halosilanes for the generation of strained olefins, see: (a) Chan, T.-H.; Masuda, D. *Tetrahedron Lett.* **1975**, *39*, 3383. (b) Cunico, R. F.; Dexheimer, E. M. *J. Organomet. Chem.* **1973**, *59*, 153. (c) Billups, W. E.; Lin, L.-J. *Tetrahedron* **1986**, *42*, 1575. (d) Szeimies, G. *Chimia* **1981**, *35*, 243. To the best of our knowledge, fluoride anion has not been reported to add to any strained olefin; see also: Chan, T.-H. *Acc. Chem. Res.* **1977**, *10*, 422.

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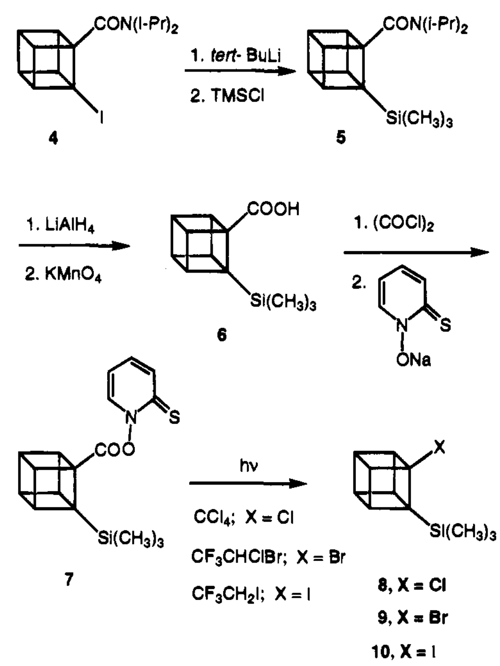
Scheme 1

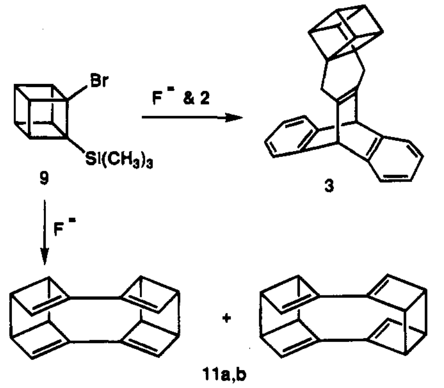


of cubene builds sufficiently so that the major reaction path is the result of cubene dimerization.

Our synthesis of 1-halo-2-(trimethylsilyl)cubanes is outlined in Scheme 1. Metalation of the readily available 1-[(diisopropylamino)carbonyl]-2-iodocubane (**4**)[3,8] with *tert*-butyllithium followed by quenching with chlorotrimethylsilane gave amide-silane **5** in 85% yield. The amide group in **5**, like the diisopropylcarboxamide groups in other molecules, is extremely resistant to any kind of hydrolysis. However, it could be converted efficiently to the carboxylic acid **6** in 65% yield by the useful reduction–oxidation sequence shown.[9] Barton decarboxylation[10] of **6** via photolysis of its PTOC ester **7** in the presence of appropriate halogen atom donors[11] gave the desired vicinial halo(trimethylsilyl)cubanes **8**–**10** in an average 70% yield. These are all stable liquids. Their structures were confirmed by elemental analysis and ^{1}H- and ^{13}C-NMR.

Treatment of 1-chloro-2-(trimethylsilyl)cubane (**8**) with either "anhydrous" tetrabutylammonium fluoride[12] or hexakis(dimethylamino)phosphazenium fluoride[13] in the presence of diene **2** resulted in exclusive formation of chlorocubane, identified by comparison to a reference sample.[14] 2-Chlorocubyl anion must be an intermediate in this reduction; this anion being eventually quenched with adventitious water. Apparently, there is not enough to be gained in elimination of chloride ion to balance formation of the highly strained cubene.[15] On the other hand, when the cubyl-to-halogen bond is weaker, the elimination occurs readily. Reaction of 1-bromo-2-(trimethylsilyl)cubane (**9**) in THF for 5 min at 0–5 °C with active fluoride[16] in the presence of diene **2** nicely afforded Diels–Alder adduct **3** in 75% isolated yield (eq 3a).

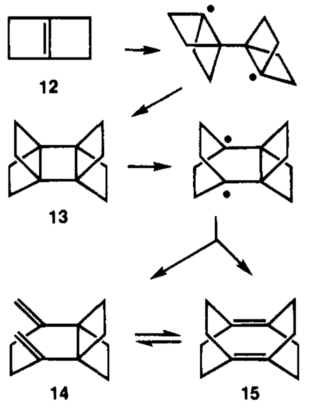
When the diene was left out (eq 3b), the same reaction gave two isomeric olefins in a 60:40 ratio as observed by ^{1}H-NMR. These products are unstable thermally and are sensitive to air oxidation as well. Quick column chromatography on silica gel under nitrogen allowed their separation from the reaction mixture in 15% isolated yield,[17] but during the course of isolation the ratio changed to 90:10. Both compounds showed molecular ions at *m/e* 204, corresponding to the mass of a cubene dimer. Combining this, mechanistic reasoning, and information from their NMR spectra (see Experimental Section)—chemical shifts like those of known tricyclo[4.2.0.$0^{2,5}$]-octadienes,[18] integration, and high symmetry—the compounds were assigned the structures of the isomeric bis(tricyclo-[4.2.0.$0^{2,5}$]octa-3,7-diene-3,8-diyl)s **11a,b**.[19]



(3a)

(3b)

Dimerization of highly strained olefins is not an uncommon event; the dimerization of bicyclo[2.2.0]hexene (**12**) reported by Wiberg *et al.* is the most relevant example.[20] This olefin was stable enough under the reaction conditions to be seen (NMR). Its second-order dimerization was assumed to proceed via a diradical intermediate to the highly strained propellane **13**. This dimer (unseen) then apparently underwent ring opening quickly to the observed dienes **14** and **15**.



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(8) Eaton, P. E.; Xiong, Y.; Lee, C. H. *J. Am. Chem. Soc.* **1989**, *111*, 8016.

(9) Bashir-Hashemi, A.; Yang, C.-X.; Eaton, P. E. Unpublished but see ref 8 and footnote 27 in ref 5.

(10) (a) Barton, D. H. R.; Crich, D.; Motherwell, W. B. *J. Chem. Soc., Chem. Commun.* **1983**, 939. (b) Barton, D. H. R.; Crich, D.; Motherwell, W. B. *Tetrahedron* **1985**, *41*, 3901. (c) For applications of the Barton reaction to the cubane system see: Eaton, P. E.; Nodari, N.; Tsanaktsidis, J.; Upadhyaya, S. *Synthesis* **1995**, 501.

(11) Tsanaktsidis, J.; Eaton, P. E. *Tetrahedron Lett.* **1989**, *30*, 6967.

(12) Cox, D. P.; Terpinski, J.; Lawryonowicz, W. *J. Org. Chem.* **1984**, *49*, 3216.

(13) Schwesinger, R.; Link, R.; Thiele, G.; Rotter, H.; Honert, D.; Limbach, H.-H.; Maunle, F. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1372.

(14) Luh, T.-Y.; Stock, L. M. *J. Org. Chem.* **1978**, *43*, 3271.

(15) *Cf.* the formation of cyclopropenes from fluoride ion induced elimination from 1-chloro-2-(trimethylsilyl)cyclopropanes.[7c]

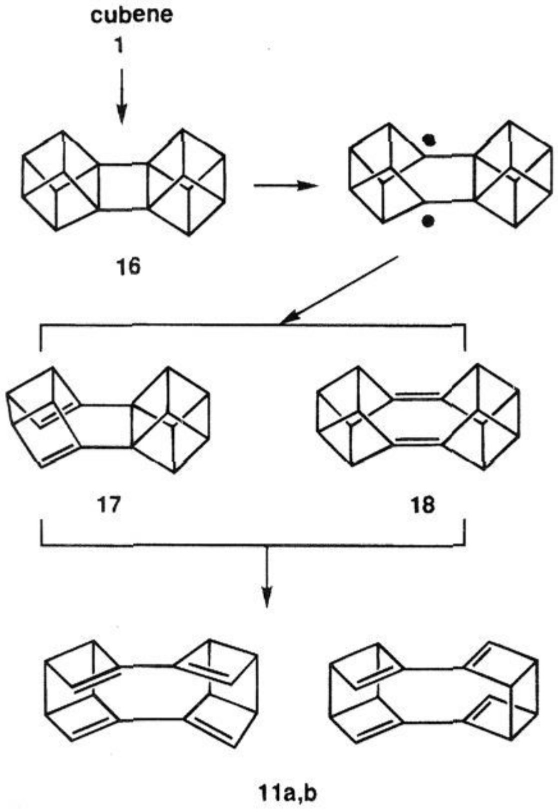
(16) "Anhydrous" tetrabutylammonium fluoride and hexakis(dimethylamino)phosphazenium fluoride gave identical results in all our experiments. We refer to them as "active fluoride".

(17) Bromocubane and bicubyl were isolated from the reaction mixture each in 2–4% yield.

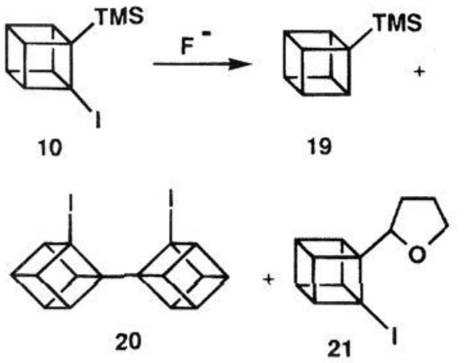
(18) (a) Yip, Y. Ph.D. Thesis, The University of Chicago, 1992. (b) Eaton, P. E.; Yip, Y. C. *J. Am. Chem. Soc.* **1991**, *113*, 7692.

(19) The *s-cis* 1,3-conjugated diene sub-systems in **11a** are each coplanar and thus potential Diels–Alder dienes. Nonetheless, all our attempts to effect addition to maleic anhydride or PTAD were unsuccessful. MM2 calculations reveal that the products of such addition would have severely distorted double bonds.

In the cubene case were the extremely strained dimer **16** formed it would certainly be even less stable than propellane **13**. Ring opening to **11a,b** could occur in a variety of ways via **17** and/or **18**, all accompanied by substantial release of strain.



A determined effort was made to find conditions under which one or another of the putative intermediates **16**−**18** would form and last long enough for NMR characterization. Unfortunately, reaction of 1-bromo-2-(trimethylsilyl)cubane with "anhydrous" tetrabutylammonium fluoride proved to be too slow to be useful at temperatures below 0 °C. We then turned to its iodo analog **10** as it was expected to be much more reactive. Indeed, fluoride ion induced elimination occurred at temperatures as low as −35 °C. However, and quite unexpectedly, only traces of tetraenes **11a,b** were formed. Instead, a mixture of compounds with the cubane skeleton intact was formed (eq 4). The major products, (trimethylsilyl)cubane (**19**),[21] 2,2′-diiodobicubyl (**20**), and 1-iodo-2-(α-tetrahydrofuryl)cubane (**21**) were identified by NMR spectral analysis/comparison. The isolated yields of the three together accounted for more than 55% of the starting material.[22]

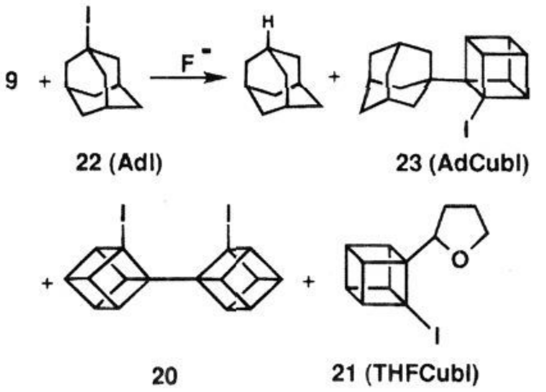


(4)

We proved unambiguously that cubene is a key intermediate in the formation of these products. When the reaction of **10** with active fluoride was repeated under the same conditions but in the presence of diene **2** Diels−Alder adduct **3** was formed cleanly; we were able to isolate it in 70% yield. Compounds **19**−**21** were not produced in identifiable amounts. Thus, whatever happens in eq 4, it occurs after cubene is formed and is intrinsically part of cubene chemistry, exactly what we set out to probe.

As the difference in behavior of iodide **10** and bromide **9** might relate to the suscepitibility of the carbon−iodine bond to homolytic fragmentation, we wanted to repeat the reaction of **9** with fluoride anion in the presence of an iodine atom donor. We needed to be certain that the donor was appropriate, namely, easily capable of iodine atom transfer, but quite unreactive toward fluoride anion. 1-Iodoadamantane (**22**) was selected. Ohno *et al.* had already demonstrated that **22** undergoes homolytic cleavage of the adamantyl−iodine bond under very mild conditions,[23] and we found that heterolytic cleavage, on the other hand, is quite slow. 1-Iodoadamantane and active fluoride ion barely react in THF at the concentrations used in our experiments with **10**, even at higher temperature; only 4% reduction to adamantane was observed (GC) after 1 h at room temperature.

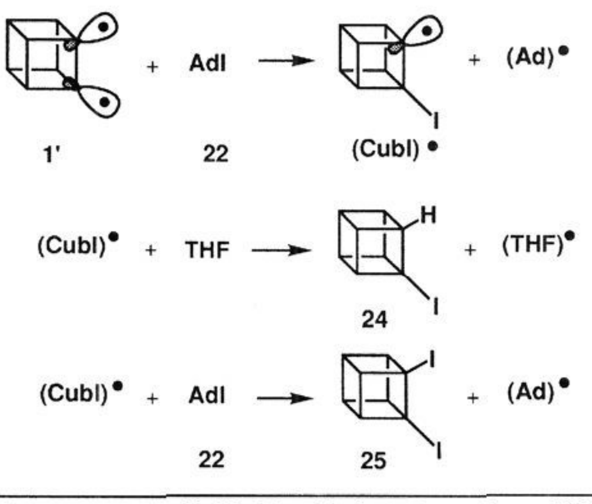
The presence of 1-iodoadamantane (2 equiv) during the reaction of **9** with active fluoride had a dramatic effect on the reaction products. None of the tetraenes **11a,b** was found. Instead (eq 5), the major product was 1-adamantyl-2-iodocubane (**23**), isolated by column chromatography in 50% yield, along with 2,2′-diiodobicubyl (**20**, 8% yield), and 1-iodo-2-(α-tetrahydrofuryl)cubane (**21**, 25% yield). In addition, a substantial amount of adamantane was formed.



(5)

As certainly the iodine transfers must involve homolytic C−I bond cleavages, eq 5 strongly supports the idea that radical processes are readily accessed during cubene chemistry. Might it be that cubene itself behaves as a 1,2-diradical (**1′**)? The products of eqs 4 and 5 speak against this. Were cubene to be responsible for the initiation of the radical reactions, a radical chain like that in Scheme 2 would develop, and iodocubane **24**

Scheme 2



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(20) Wiberg, K. B.; Matturo, M.; Okarma, P.; Jason, M. *J. Am. Chem. Soc.* **1984**, *106*, 2194. For another very recent example, see: Camps, R.; Mercè, F.-B.; Pérez, F.; Solans, X.; Vázquez *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 912.

(21) (a) Della, E. W.; Tsanaktsidis, J. *Organometallics* **1988**, *7*, 1178. (b) Nucleophilic attack of fluoride on the iodide of **10** to give 2-(trimethylsilyl)cubyl anion was ruled out as a source of (trimethylsilyl)cubane as no reaction at all between iodocubane itself and fluoride was observed in a control experiment. An adjacent silyl group would not be expected to stabilize a cubyl anion.

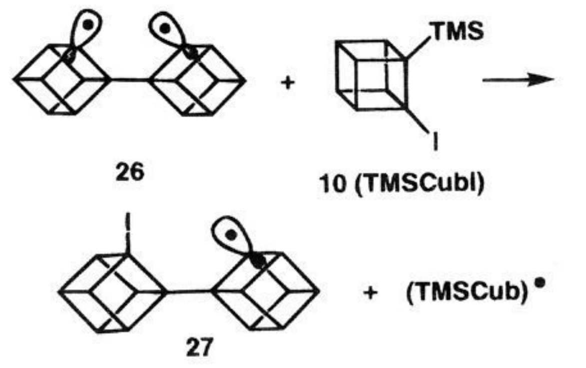
(22) Some of the minor products were identified (tentatively) as 2-iodobicubyl and (α-tetrahydrofuryl)cubane from the GC/MS trace of the reaction mixture. An even more complex mixture was obtained at 0−5 °C. In this case the formation of the above products became more important.

(23) (a) Ohno, M.; Ishizaki, K.; Egushi, S. *J. Org. Chem.* **1988**, *53*, 1285. (b) See also: Wieringa, J. H.; Strating, J.; Wynberg, H. *Synth. Communs.* **1972**, *2*, 191.

and/or 1,2-diiodocubane **25** would certainly be among the products of eq 5, but they are not. Those that are—**20**, **21**, and **23**—would be highly unlikely, as each could only arise in this scheme from radical–radical combinations.

A much more likely possibility is that biradical **26** is responsible for the observed radical processes, both in the absence of 1-iodoadamantane (Scheme 3) and in its presence (Scheme 4). As shown in these schemes the participation of biradical **26** nicely explains the formation of all products observed, as well as the absence of iodocubane and 1,2-diiodocubane. Whether or not **26** enters into Schemes 3 and 4 immediately after it is formed in the stepwise dimerization of cubene or later as a result of its being in equilibrium with cubene dimer **16** is a moot point at this time.

Scheme 3



$$\mathbf{27} + \text{TMSCubI} \longrightarrow \mathbf{20} + (\text{TMSCub})^\bullet$$

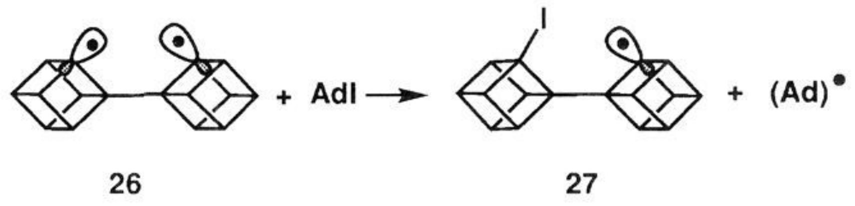
$$(\text{THF})^\bullet + \text{cubene} \longrightarrow (\text{THFCub})^\bullet$$

$$(\text{THFCub})^\bullet + \text{TMSCubI} \longrightarrow \mathbf{21} + (\text{TMSCub})^\bullet$$

$$(\text{TMSCub})^\bullet + \text{THF} \longrightarrow \mathbf{19} + (\text{THF})^\bullet$$

The intermediacy of biradicals has often been suggested to account for side products in the dimerizations of strained olefins.[6c,20] Here, with the use of 1-iodoadamantane as a probe, we have provided the first substantial demonstration that this is true.

Scheme 4



$$\mathbf{27} + \text{AdI} \longrightarrow \mathbf{20} + (\text{Ad})^\bullet$$

$$(\text{Ad})^\bullet + \text{cubene} \longrightarrow (\text{AdCub})^\bullet$$

$$(\text{AdCub})^\bullet + \text{AdI} \longrightarrow \mathbf{23} + (\text{Ad})^\bullet$$

$$(\text{Ad})^\bullet + \text{THF} \longrightarrow \text{AdH} + (\text{THF})^\bullet$$

$$(\text{THF})^\bullet + \text{cubene} \longrightarrow (\text{THFCub})^\bullet$$

$$(\text{THFCub})^\bullet + \text{AdI} \longrightarrow \mathbf{21} + (\text{Ad})^\bullet$$

Experimental Section

General. Unless otherwise specified, NMR spectra were run in CDCl$_3$: ^{1}H-NMR spectra at 400 MHz and referenced to chloroform (δ 7.24 ppm); ^{13}C-NMR spectra at 100.6 MHz and referenced to the central line of CDCl$_3$. Proton chemical shifts are ±0.01 ppm; coupling constants are ±0.1 Hz. Carbon chemical shifts are ±0.1 ppm. EI low-resolution mass spectra were obtained at 70 eV using samples vaporized from a direct insertion probe. Merck silica gel 60 (230–400 mesh) was used for column chromatography. THF was distilled from sodium benzophenone ketyl. "Anhydrous" tetrabutylammonium fluoride was prepared fresh when needed by dehydration of commercial trihydrate (Aldrich) according to the literature procedure and used soon afterwards.[12] Hexakis(dimethylamino)phosphazenium fluoride was prepared as described by Schwesinger.[13] All reactions with these fluorides were carried out under argon in vacuum oven-dried glassware. "Removal of solvent *in vacuo*" and similar phrases generally refer to use of a rotary evaporator operated at house vacuum (*ca.* 50 Torr). The evaporator bath was not heated above room temperature.

1-[(Diisopropylamino)carbonyl]-2-(trimethylsilyl)cubane (5). A solution of iodoamide **4**[3] (1.37 g, 4 mmol) in diethyl ether (15 mL) was added dropwise to a solution of *tert*-butyllithium (9 mmol, 5.3 mL of 1.7 N solution in pentane) in ether (40 mL) cooled to −78 °C under nitrogen. The mixture was stirred for 20 min, then chlorotrimethylsilane (2 mL, excess) was added by syringe. The reaction mixture was stirred for an additional 30 min at −78 °C, allowed to warm to room temperature, then poured into water (25 mL). The organic phase was separated and dried over Na$_2$SO$_4$. The solvent was evaporated *in vacuo* leaving silylated amide **5** (0.92 g, 80%). An analytical sample of **5** was obtained by crystallization from hexane: ^{1}H NMR δ 0.02 (s, 9 H), 1.18 (d, $J = 8$ Hz, 6 H), 1.39 (d, $J = 8$ Hz, 6 H), 3.28 (m, 1 H), 3.55 (m, 1 H), 3.74 (m, 2 H), 3.93 (m, 1 H), 4.05 (m, 1 H), 4.16 ppm (m, 2 H); ^{13}C NMR δ −3.5 (3 C), 20.5 (2 C), 21.3 (2 C), 43.1 (2 C), 44.2, 45.6, 46.9, 47.8, 50.1 (C$_q$), 50.7 (2 C), 59.8 (C$_q$), 170.8 ppm (C=O). Anal. Calcd for C$_{18}$H$_{29}$NOSi: C, 71.23; H, 9.63; N, 4.61. Found: C, 71.00; H, 9.70; N, 4.63.

2-(Trimethylsilyl)cubanecarboxylic Acid (6). A solution of silyl amide **5** (1.3 g, 4.5 mmol) in THF (10 mL) was added dropwise to lithium aluminum hydride (340 mg, 9 mmol) suspended in THF (15 mL). The reaction mixture was stirred for 6 h at room temperature, then cooled in an ice-water bath. A saturated aqueous solution of Na$_2$SO$_4$ was added dropwise until a white gummy solid fully precipitated on the bottom of the flask. The ether layer was decanted, the residue was washed with ether (2 × 5 mL), and the combined organic phase was dried with Na$_2$SO$_4$. Evaporation of the solvent gave 1-[(diisopropylamino)methyl]-2-(trimethylsilyl)cubane (1.0 g, 80%) as a colorless oil: ^{1}H NMR δ (CD$_2$Cl$_2$) −0.02 (s, 9 H), 0.97 (d, $J = 7$ Hz, 12 H), 2.67 (s, 2 H), 2.95 (m, 2 H), 3.72 (m, 2 H), 3.90 (m, 3 H), 3.98 (m, 1 H).

The crude amine (0.96 g, 3.5 mmol) was dissolved in boiling acetone (30 mL). A solution of KMnO$_4$ (2.45 g) in water (14 mL) and acetone (70 mL) was added dropwise to the refluxing solution until the purple color of KMnO$_4$ was persistent. The mixture was cooled to room temperature. Solid sodium bisulfite was added until the color of the mixture turned dirty white. The solid was filtered and washed with acetone (30 mL). The filtrate and wash were combined, and the solvent was removed under vacuum. The residue was diluted with water (5 mL); 40% aqueous NaOH was added to adjust the pH to 10. The aqueous solution was extracted with ether (5 mL), then acidified to pH 1, and extracted with ether (3 × 10 mL). This extract was dried with Na$_2$SO$_4$. Evaporation of the solvent left acid **7** (578 mg, 75%): mp 83–84 °C; ^{1}H NMR δ (CD$_2$Cl$_2$) −0.01 (s, 9 H), 3.84 (m, 2 H), 3.96 (m, 1 H), 4.08 (m, 1 H), 4.28 ppm (m, 2 H); ^{13}C NMR δ −4.5 (3 C), 43.8 (2 C), 45.4, 48.1, 49.5 (2 C), 51.7 (C$_q$), 54.9 (C$_q$), 179.1 ppm (C=O). Anal. Calcd for C$_{12}$H$_{16}$O$_2$Si: C, 65.41; H, 7.32. Found: C, 65.45; H, 7.45.

1-Chloro-2-(trimethylsilyl)cubane (8). The procedure described below for the bromo analog was used except the crude acid chloride was dissolved in dry tetrachloromethane (1 mL). The same irradiation and workup gave chloride **8** in 75% yield: ^{1}H NMR δ 0.02 (s, 9 H), 3.83 (m, 2 H), 3.99 (m, 1 H), 4.05 (m, 1 H), 4.17 ppm (m, 2 H).

1-Bromo-2-(trimethylsilyl)cubane (9). Thionyl chloride (1.5 mL) was added to a solution of silyl acid **7** (220 mg, 1 mmol) in dichloromethane (2.5 mL). The resulting mixture was stirred for 1 h at room temperature. The solvent and excess thionyl chloride were removed *in vacuo*. The crude (trimethylsilyl)cubane carboxylic acid chloride so obtained was dissolved in 1-bromo-1-chloro-2,2,2-trifluoroethane (1.5 mL), and the solution was added dropwise to a stirred mixture of the anhydrous sodium salt of 2-thiopyridone *N*-oxide (200 mg, 1.3 mmol), 4-(dimethylamino)pyridine (5 mg), and 1-bromo-1-chloro-2,2,2-trifluoroethane (3 mL) at reflux irradiated with a 250-W tungsten lamp. After the addition, the reaction mixture was irradiated and refluxed for 1 h, then cooled to room temperature, washed with 1 N HCl, and dried with Na_2SO_4. Evaporation of the solvent followed by column chromatography with pentane as eluant gave bromide **9** (180 mg, 70%) as a colorless oil: ^{1}H NMR δ 0.03 (s, 9 H), 3.94 (m, 2 H), 4.06 (m, 1 H), 4.15 (m, 1 H), 4.31 ppm (m, 2 H); ^{13}C NMR δ −4.4 (3 C), 45.2 (2 C), 46.0, 48.3, 58.4 (C$_q$), 58.7 (2 C), 68.6 ppm (C$_q$). Anal. Calcd for $C_{11}H_{15}BrSi$: C, 51.76; H, 5.92. Found: C, 51.99; H, 5.98.

1-Iodo-2-(trimethylsilyl)cubane (10). The procedure described for the bromo analog was used except the crude acid chloride was dissolved in dry benzene (3 mL) and the other reactants in a mixture of 1-iodo-2,2,2-trifluoroethane (0.25 mL, 2.5 mmol) and benzene (5 mL). The same irradiation and workup gave iodide **10** (210 mg, 70%): ^{1}H NMR δ 0.03 (s, 9 H), 4.06 (m, 2 H), 4.19 (m, 1 H), 4.23 (m, 1 H), 4.42 ppm (m, 2 H); ^{13}C NMR δ −5.1 (3 C), 44.6 (C$_q$), 47.96, 47.98 (2 C), 48.6, 58.6 (C$_q$), 59.4 ppm (2 C). Anal. Calcd for $C_{11}H_{15}ISi$: C, 43.71; H, 5.00. Found: C, 43.26; H, 4.99.

Bis(tricyclo[4.2.0.0^{2,5}]octa-3,7-diene-3,8diyl)s (11a,b). A solution of silyl bromide **9** (128 mg, 0.5 mmol) in THF (0.2 mL) was added to a mixture of "anhydrous" tetrabutylammonium fluoride (470 mg, 1.8 mmol) *or* phosphazenium fluoride (540 mg, 1.5 mmol) in THF (0.3 mL) at 0−5 °C *via* syringe. TLC analysis indicated that **9** had almost disappeared after 5−7 min. A 3:1 mixture of pentane and diethyl ether (4 mL) was added. The clear organic solution was decanted and the solvents removed *in vacuo*. The residue was chromatographed with pentane under nitrogen atmosphere to give tetraenes **11a,b** (7.5 mg, 15%): MS *m/e* 204 (M^+), 202 (100). Major isomer: ^{1}H NMR (δ, $CDCl_3$) 3.18 (m, 4 H); 3.38 (m, 4 H); 5.73 ppm (s, 4 H); ^{13}C NMR (δ, CD_2Cl_2, −30 °C) 40.3, 44.6, 132.0, 142.5 ppm. Minor isomer: ^{1}H NMR (δ, $CDCl_3$) 3.03 (m, 4 H); 3.22 (m, 4 H); 6.04 ppm (s, 4 H); ^{13}C NMR (δ, CD_2Cl_2, −30 °C) 39.2, 39.9, 131.7, 140.9 ppm.

Cubene Diels−Alder Adduct (3). The reaction described above of **9** (or iodide **10**) with fluoride anion was carried out in the presence of 1.5 equiv of [(bismethylene)ethano]anthracene[24] (**2**). A 3:1 mixture of pentane and diethyl ether (4 mL) was added. The clear organic solution was decanted and the solvent removed *in vacuo*. The residue was chromatographed with pentane to give adduct **3** in 70−75% yield. The properties of **3** were identical to those reported in literature.[3]

Reaction of 1-Iodo-2-(trimethylsilyl)cubane (10) with Fluoride Anion. A solution of silyl iodide **10** (75 mg, 0.25 mmol) in THF (0.2 mL) was added by syringe to a suspension of "anhydrous" tetrabutylammonium fluoride (208 mg, 0.8 mmol) in THF (0.3 mL) at −30 to −35 °C. TLC analysis indicated that starting iodide had almost disappeared after 10 min. A 3:1 mixture of pentane and diethyl ether (4 mL) was added. The clear organic solution was decanted and the solvents were removed. The products were separated by column chromatography. Elution with pentane gave (trimethylsilyl)cubane (**19**, 13 mg, 30%) and 2,2′-diiodobicubyl (**20**, 6 mg, 10%). Further elution but with 10:1 pentane−ether gave 1-iodo-2-(2-tetrahydrofuryl)cubane (**21**, 11 mg, 15%).

(Trimethylsilyl)cubane (19):[21] ^{1}H NMR δ −0.09 (s, 9 H), 3.86 (m, 3 H), 4.02 (m, 3 H), 4.09 ppm (m, 1 H).

2,2′-Diiodobicubyl (20): mp > 190 °C dec; ^{1}H NMR δ 4.07 (m, 2 H), 4.13 (m, 2 H), 4.23 (m, 4 H), 4.29 ppm (m, 4 H); ^{13}C NMR δ 39.1 (2 C), 45.0 (2 C), 48.0 (4 C), 49.2 (2 C), 55.3 (4 C), 63.9 ppm (2 C). Anal. Calcd for $C_{16}H_{12}I_2$: C, 41.95; H, 2.64. Found: C, 42.06; H, 2.66.

1-Iodo-2-(2-tetrahydrofuryl)cubane (21): ^{1}H NMR δ 1.60 (m, 1 H), 1.92 (m, 2 H), 2.04 (m, 1 H), 3.70−3.90 (m, 2 H), 3.98 (m, 1 H), 4.05 (m, 2 H), 4.10−4.25 ppm (m, 4 H); ^{13}C NMR δ 25.7 (CH_2), 26.2 (CH_2), 40.5, 44.5, 48.1, 48.5, 49.3, 54.9, 68.5 (CH_2O), 79.0 ppm (CHO).

Reaction of 1-Bromo-2-(trimethylsilyl)cubane (9) with Fluoride Anion in the Presence of 1-Iodoadamantane. The reaction of **10** with fluoride anion described above was carried out in the presence of 2 equiv of 1-iodoadamantane (Aldrich). The same workup was used. In addition to compounds **20** (8%) and **21** (25%), 1-(1-adamantyl)-2-iodocubane (**23**) was isolated in 50% yield by column chromatography: mp 142−143 °C; ^{1}H NMR δ 1.64 (m, 6 H), 1.70 (m, 6 H), 2.04 (m, 3 H), 3.90 (m, 1 H), 4.08 (m, 1 h), 4.13 ppm (m, 4 H); ^{13}C NMR δ 27.6 (3 C), 33.3, 33.6 (3 C), 37.2 (3 C), 40.3 (C$_q$), 43.4, 46.7 (2 C), 48.3, 54.6 (2 C), 71.8 ppm (C$_q$). Anal. Calcd for $C_{18}H_{21}I$: C, 59.35; H, 5.81. Found: C, 59.04; H, 5.91.

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[24] Hart, H.; Bashir-Hashemi, A.; Luo, J.; Meador, M. A. *Tetrahedron* **1986**, *42*, 1641.