Hz. In addition, Table I shows that the $^{3}J_{^{15}N-H_6}$ and $^{3}J_{^{15}N-H_7}$ coupling constants for 3 look like those for DNBF rather than those for the adducts 5.

Experimental Section

General. All melting points were determined on a Reichert Kofler block and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Brucker AM-250 spectrometer equipped with an ASPECT 3000 Computer. Chemical shifts are reported in parts per million (δ, J in hertz) relative to internal Me_4Si, and UV-visible spectra were recorded on a Beckman Acta III spectrophotometer. Electron-impact mass spectra were recorded on a Nermag R10-10C instrument. Elemental analyses were performed by the INSCIR Microanalytical Laboratory, Mont-Saint-Aignan, France.

Materials. 4-Nitrobenzofuroxan and 4,6-dinitrobenzofuroxan were prepared according to previously reported methods. 4-Nitrobenzofuroxan: mp 143 °C (lit.[11,12] mp 143 °C); DNBF, mp 173 °C (lit.[3b,c,11] mp 172–174.5 °C). Indene (Aldrich) was freshly distilled prior to use.

[6-^{15}N]-4,6-Dinitrobenzofuroxan. A solution of 1 mL of $H^{15}NO_3$, 40% (Aldrich, 98% ^{15}N), in 4 mL of sulfuric acid (d = 1.84) was added dropwise to a stirred solution of 1.1 g of 4-nitrobenzofuroxan (6.1 mmol) in 8 mL of sulfuric acid (d = 1.84) at 0 °C. The resulting mixture was kept at 0 °C for 30 min, heated at 50–60 °C for 3 h, and then allowed to return to room temperature. After the mixture was poured onto cracked ice, the resulting orange crystals were filtered, washed with water, and vacuum dried over P_2O_5 to yield 1.1 g of [6-^{15}N]DNBF (80%): mp 173 °C; mass spectrum (obsd), m/e 227, 211, 197, 151, 121, 87; for comparison, DNBF mass spectrum (obsd), m/e 226, 210, 196, 150, 120, 87.

Preparation of 3. The oxazine N-oxide 3 was prepared by the addition of DNBF (226 mg, 1 mmol) to a stirred solution of indene (128 mg, 1.1 mmol) in methylene chloride (2 mL) at room temperature. The solution turned orange and some precipitate was formed after 2 h. After 24 h at room temperature, the resulting yellow crystals were filtered, washed with diethyl ether, and vacuum dried over P_2O_5: mp 165 °C dec. Anal. Calcd for $C_{15}H_{10}N_4O_6$: C, 52.64; H, 2.94; N, 16.37. Found: C, 52.18; H, 2.76; N, 16.18. The same method was used to prepare 3 from ^{15}N-labeled DNBF.

Acknowledgment. We are indebted to the Consejo Nacional de Investigaciones Cientificas y Tecnicas de la Republica Argentina for a fellowship to P.M.C.

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Reinvestigation of the Metalation of Phenylcyclopropane: Does the Phenylcyclopropyl Anion Undergo Ring-Opening?

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There are several examples of ring-opening reactions of cyclopropanes with base that give allyl anions.[1-7] In the light of orbital-symmetry considerations,[8] these were thought to be examples of pericyclic reactions[1-3] with thermally allowed conrotatory ring-opening. Since acyclic allyl anions are not configurationally stable, the stereochemistry of the product and the sense of the ring-opening were uncertain. Later examples were shown to give symmetry-forbidden products in a tricyclic system.[4-7] It was then proposed that the reaction proceeds through a single electron transfer process from the base to the tricyclic carbon acid.[5] This reaction has since been shown to proceed by initial deprotonation of the acid rather than initial electron transfer from the metalating agent to the acceptor.[7] A universal requirement for the ring-opening to occur is that the incipient allyl anion must have at least one group on the allyl termini which is capable of stabilizing the charge.[1] Both symmetry-allowed and symmetry-forbidden ring-openings are observed; the mechanistic pathway is uncertain.

Table I. Product Distribution from Eq 1 under Various Conditions

entry no.	equiv of base	temp, °C	time	1:2
1	1.1	20	4 h	>100:1
2	1.1	70	4 h	5:1[a]
3	4.0	70	4 h	2:1
4	4.0	70	1 day	1:1
5	4.0	20	2 days	30:1
6	4.0	20	14 days	14:1
7	4.0	20	25 days	11:1
8	4.0	20	60 days	8:1

[a] Deuterium oxide quench of this was analyzed by electron-impact mass spectroscopy. As calculated by using the program HEAVY, **1b** had from 0.2 to 1.0 deuteriums per molecule and **2b** had from 1.6 to 1.8 deuteriums per molecule.

We are interested in cyclopropyl anion ring-openings as a synthetic route to cross-conjugated carbanions. The ring-opening of 1-vinylcyclopropyl carbanion[9] and spiropentyl carbanion[10] would lead to the simplest carbanion of this type, the as yet unknown isoprenyl carbanion.[11] As a model for the ring-opening of the conjugated cyclopropyl carbanions, we selected the 1-phenylcyclopropyl carbanion, which is readily prepared from commercially available cyclopropylbenzene.[12] We report herein the results of a study of the 1-phenylcyclopropyl anion and the subsequent ring-opening of a cyclopropyl anion species.

Results and Discussion

The results of the metalation studies of cyclopropylbenzene (**1a**) with Lochmann's base (n-butyllithium/potassium *tert*-butoxide in hexane)[13] are shown in Table I. Metalation at room temperature followed by quenching with D_2O gives rise to **1b** with an average of 0.8 deuterium

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[†] University of North Carolina at Charlotte.

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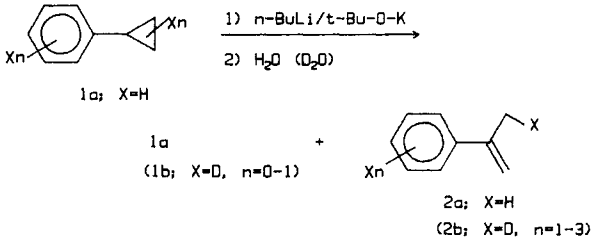
per molecule by mass spectroscopy[14] (entry 1, Table I). When the reaction temperature was increased to 70 °C before quenching, the ring-opened product 2-phenylpropene (17%) (**2a**) and the starting material, **1a**, were the sole products, eq 1. Deuterium oxide quenching of this

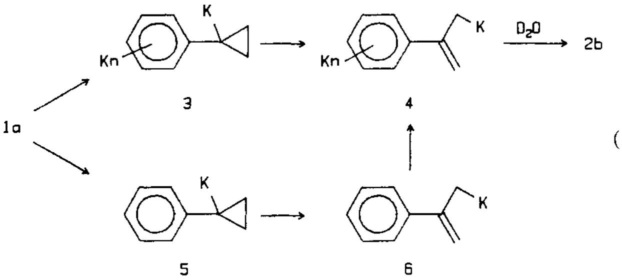


(1)

reaction was found, by mass spectroscopy, to give **1b** with a low percentage of deuterium incorporated into it. The opened product, **2b**, was found to have the P + 2 peak (*m/e* 120) as the largest peak in the mass spectrum (entry 2, Table I). When the amount of metalating agent was increased, the yield of compound **2a** increased correspondingly (entries 3 and 4, Table I). These results suggest that polymetalated species[2,16] are undergoing the ring-opening.

The deuterium distribution in the products (entry 2 of Table I) was investigated by deuterium NMR. Compound **1b** incorporates deuterium at all positions except the ortho, in a ratio of 1:0.66:0.66 for α:β:(meta + para). In **2b** it was found that deuterium is incorporated into all sites except the vinylic sites in a ratio of 1:2.5 for allylic:aromatic. A comparison by proton NMR of the integral for the allylic protons vs the vinylic protons of **2b** (entry 2, Table I) revealed a ratio of 1:1, indicating that each allylic methyl was substituted with one deuterium. From the ^{2}H and ^{1}H NMR results, there are approximately 3.5 deuteriums per molecule of **2b**.

The two likely routes to **2a** are shown in eq 2. One route involves the metalation of **1a** to give the polyanion **3**, which ring-opens to give **4**. This would react with water or D_2O



(2)

to give **2a** or **2b**. An alternative to the ring-opening of **3** could be benzylic metalation of **1a** to give (1-phenylcyclopropyl)potassium (**5**). This could then undergo ring-opening to give (2-phenylallyl)potassium (**6**), which could subsequently be metalated to give **4**, eq 2. To exclude the latter route as a possibility, we independently prepared **5** and demonstrated its inability to ring-open in the following manner. 1-Phenylcyclopropanecarboxylic acid was chlorodecarboxylated with $Pb(OAc)_4$[17] to yield 1-phenylcyclopropyl chloride (**7**). The Grignard reagent

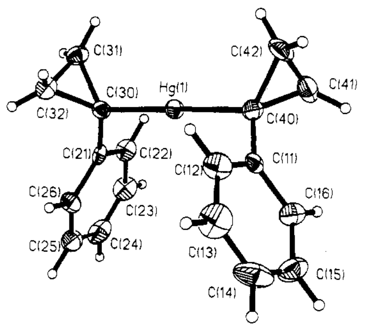
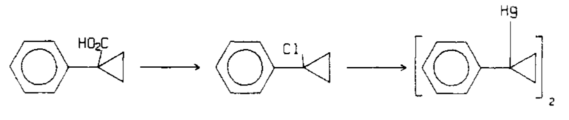


Figure 1. ORTEP perspective view of **8**. The non-hydrogen atoms are drawn as 30% thermal ellipsoids and hydrogens are drawn as spheres at standard C–H bond distances. Some noteworthy bond distances and bond angles are as follows:[18] C(40)–Hg(1), 2.124 (8) Å; C(30)–Hg(1), 2.104 (8) Å; ∠C(30)–Hg(1)–C(40), 178.0 (3)°; ∠Hg(1)–C(40)–C(11)–C(12), 75.6°; ∠Hg(1)–C(30)–C(21)–C(22), 84.5°.

of **7** was then prepared and allowed to react with $HgCl_2$, yielding bis(1-phenylcyclopropyl)mercury (**8**) (eq 3). The



(3)

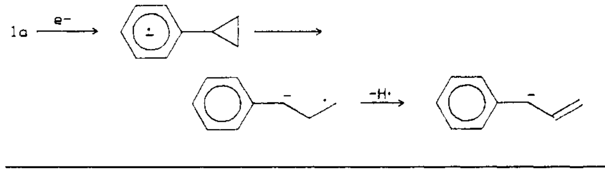
structure of **8** was determined by X-ray crystallography, Figure 1. Transmetalation of **8** with sodium/potassium alloy followed by treatment with water gave **1a**, demonstrating the presence of phenylcyclopropyl anion (**5**), eq 4. Attempts to persuade **5** to ring-open failed even at elevated temperatures and extended reaction times (120 °C and 24 h).

$$8 \xrightarrow{Na/K} 5 \xrightarrow{H_2O} 1a \qquad (4)$$

Furthermore, we found that with increased amounts of base and extended reaction times, very slow ring-opening of **1a** occurs even at room temperature (entries 5–8, Table I). This ring-opening reaction could probably be accelerated appreciably if it were carried out in an ethereal solvent, which would dissolve the reaction intermediates and products. Unfortunately, species like **3**–**6** react readily with THF above −40 °C to generate ethylene and the enolate anion.[12]

The ring-opening could likely occur via a radical or radical anion pathway. To check for this, the heterogeneous reaction mixture was observed with an EPR spectrometer at both room temperature and 70 °C and was found to give a broad signal. This was not surprising, since we have found that a suspension of Lochmann's base in hexane gives an EPR signal without the presence of substrate. Such a signal has also been observed previously with the similar system (2-ethylhexyl)lithium/potassium *tert*-amyloxide.[19]

Single-electron transfer from the base to **1a** is shown in eq 5. This would seem likely since Lochmann's base is extremely basic and has been demonstrated to have unpaired electrons. This can be quickly eliminated as a



(5)

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[14] Calculated by using the program HEAVY.[15] HEAVY works well when there is little or no P − 1 peak. In **1a** and **2a** the P − 1 peaks are large. HEAVY also assumes the same fragmentation for the enriched as for the unenriched. This seems unlikely for **1b** and **2b** since there are deuteriums substituted where they are likely lost, the allylic and benzylic positions.

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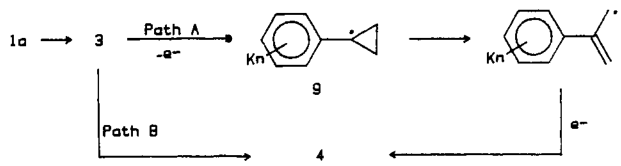
Scheme I



possibility since the radical anion formed by single-electron transfer would be expected to give ring-opening by scission of the α–β bond, giving the trimethylene radical anion.[20-22] This would yield linear products and dimers. Since no products from scission of the α–β bond were detected, we conclude that metalation occurs as a first step.

There are two probable pathways for the ring-opening to occur, which are represented in Scheme I. Paths A and B have metalation occurring first to yield **3**, which, in path A, expels an electron to give **9**, followed by ring-opening and reduction to give **4**. Expulsion of an electron from dianions to electron acceptors giving radical anions is known for dianions with the charges delocalized in the same π system.[23,24] In **3**, however, the anions are orthogonal to each other; one charge is localized in a σ orbital and the other charge is delocalized in the π system of the phenyl ring and the benzylic site. The ring-opening of cyclopropyl radicals and radical anions has been noted several times.[1,25] Since we were unable to detect any products from the coupling of radicals by GC/MS, we prefer path B, the direct opening of **3** to give **4**.

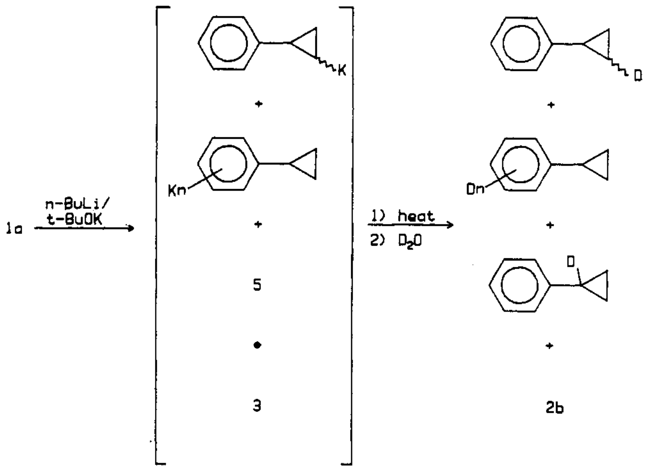
These results indicate that the species that ring-opens is α metalated. The observations of polydeuteriation in **2b** and the incorporation of deuterium at the allylic site of **2b** indicate that the species that gives rise to the ring-opened compound is metalated at the benzylic site and on the aromatic ring, compound **3**. From the above results, we propose the following reaction scheme, Scheme II. Scheme II shows the various metalated intermediates from the reaction of Lochmann's base with **1a**. We believe metalation first occurs to give the products in the brackets. The first three species are unchanged after heating and react in a straightforward manner with D_2O to give the corresponding deuteriated compound in which the deuterium has replaced the metal. Compound **3**, upon heating, ring-opens to give an allylic anion (**4**), which, after quenching with D_2O, gives rise to **2b**.

In conclusion, we believe the species that ring-open are metalated in the benzylic position and also on the aromatic ring. The ring-opening of these species yields a cross-conjugated system which is more stable due to relief of ring strain and a more stable charge distribution. The benzylic anion on opening becomes allylic and incapable of delocalizing charge onto the egregiously electron rich metalated aromatic ring. This is a rare example of a cyclopropyl anion ring-opening to give an allyl anion without the benefit of stabilizing substituents in the 1- and 3-positions.

Experimental Section

All reagents were obtained from Aldrich Chemical Co. The potassium *tert*-butoxide was used without further purification.

Scheme II



Alkane solvents used in metalation reactions were washed with concentrated sulfuric acid and then distilled from calcium hydride. Tetrahydrofuran was distilled from sodium/benzophenone. Melting points are uncorrected. Elemental analyses were performed by Atlantic Microlab. NMR spectra were obtained with a 7.1 T broad-band QE300 NMR instrument operating at 300.2 MHz for proton, 75.4 MHz for ^{13}C, and 46.1 MHz for deuterium. Chemical shifts are reported relative to TMS except in the case of the deuterium NMR, where the samples were run in protic acetone and the shifts were obtained relative to acetone-d_6. Mass spectra were obtained with a Hewlett-Packard 5970 selective ion detector coupled with a Hewlett-Packard 5990 GC instrument equipped with a fused-silica capillary column coated with methyl silicone. ESR spectra were obtained with a JEOL JES-PE-1X spectrometer. All gas chromatographic analyses were carried out on a 10-ft column of 10% SP2100 on 80/100 Supelcoport.

X-ray Data. Clear colorless prisms of **8** ($C_{18}H_{18}Hg$, 434.9 aMU) were obtained by recrystallization from acetone/water. A crystal suitable for X-ray diffraction was obtained by cutting a needle to give a parallelepiped prism, 0.20 mm × 0.20 mm × 0.40 mm. X-ray diffraction data were collected with a Nicolet R3/V four-circle diffractometer [Mo Kα (λ = 0.71073 Å)] at room temperature. The data indicated the monoclinic space group $P2_1/a$ with $Z = 4$. Final cell parameters were a = 10.693 (2) Å, b = 11.118 (4) Å, c = 12.562 (4) Å, and β = 95.51 (2)° with volume of 1489 (1) Å^3. The calculated density, 1.94 g/cm^3, was in good agreement with the measured density of 1.96 g/cm^3. A $\theta/2\theta$ scan, with variable scan rate, over the range of $3° \leq 2\theta \leq 50°$, was used to collect 2636 independent reflections. Of these, 2226 having $I \geq 3\sigma(I)$ were used to solve and refine the structure. During data collection, two test reflections were made every 48 reflections. These check reflections showed a 3% decrease in intensity over the course of the data collection, indicating little decomposition of the crystal by the incident X-ray beam.

Direct methods were used to solve the structure, which was refined by full-matrix least-squares techniques.[26] Each hydrogen was located on a difference electron density map, set to a standard C–H bond length of 0.96 Å, and assigned the thermal parameters of the atom to which it is attached. The hydrogen parameters were not refined. The non-hydrogen atoms were refined anisotropically to convergence (R = 0.0461 and R_w = 0.0508). The largest residual peak in the final electron density difference map was 2.73 e/Å^3 (0.82 Å from the mercury atom). Empirical absorption correction of the ψ scan data did not significantly change the refinement.

Complete lists of final atomic positions, atomic thermal parameters, bond distances, and bond angles are available as supplementary material. Observed and calculated structure factors are available from J.L.H. or C.A.O.

Deuterium NMR of 1b and 2b. A mixture of **1b** and **2b** (1.1 g) was bulb-to-bulb distilled and placed as a mixture in acetone for the deuterium NMR studies. Chemical shifts were assigned from the proton NMR of the commercial materials in acetone-d_6.

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[26] Nicolet SHELXTL PLUS.

The deuterium NMR experiments were run with a spectral width of 500 Hz and an 8K block size giving an acquisition time of 8.19 s. The spectra were broad-band decoupled. The tip angle was set at 10°. On multipulse experiments, a delay of 5 s was sufficient to let the nuclei relax completely. This was shown by comparing the integration with the corresponding single-pulse experiment.

Metalation of Phenylcyclopropane. In a typical metalation reaction, potassium *tert*-butoxide (1.25 g, 11.2 mmol), phenylcyclopropane (1.25 g, 10.6 mmol), *n*-butyllithium (6.9 mL of 1.6 M *n*-butyllithium, 11.0 mmol), and 20 mL of dry hexane were combined under nitrogen in a Schlenk flask equipped with a magnetic stirring bar. The heterogeneous reaction was stirred at room temperature under nitrogen before quenching with D_2O or H_2O. If the reaction mixture was heated, the stopper was replaced by a reflux condenser and gas tube. The flask was placed in an oil bath, and the solvent was allowed to reflux with stirring.

Preparation of 1-Phenylchlorocyclopropane (7). In a 250-mL three-neck round-bottom flask equipped with a reflux condenser and magnetic stirring bar, 100 mL of dry benzene, 1-phenylcyclopropanecarboxylic acid (5 g, 30.9 mmol; mp 80-81 °C),[27] and LiCl (1.3 g, 30.6 mmol) were combined and degassed. $Pb(OAc)_4$[28] (14 g, 31.6 mmol) was added, and then the mixture was stirred until it became nearly homogeneous. The flask was then placed in an oil bath at 100 °C and the mixture stirred until gas evolution ceased. The reaction mixture was filtered, the solids were washed with ether, and the combined organic phase was then washed three times with saturated aqueous $NaHCO_3$ and then dried over $MgSO_4$. After removal of the drying agent, the benzene and ether were then removed by rotary evaporation. The residue was then bulb-to-bulb distilled to give 2.8 g of 1-phenylchlorocyclopropane (7), pure by GLC analysis:[29] NMR ($CDCl_3$) δ 1.28 (m, 2 H), 1.49 (m, 2 H), 7.25 (m, 3 H), 7.48 (m, 2 H). Anal. Calcd for C_9H_9Cl: C, 70.83; H, 5.94. Found: C, 70.78; H, 5.96.

Preparation of Bis(1-phenylcyclopropyl)mercury (8). In a three-neck 100-mL round-bottom flask equipped with a reflux condenser, magnetic stirring bar, and dropping funnel, Mg (0.40 g, 17 mmol), 20 mL of the THF, and a crystal of iodine were combined under nitrogen. 1-Phenylchlorocyclopropane (2.5 g, 16 mmol) in 5 mL of THF was added dropwise with stirring. Upon completion of the addition, the mixture was heated at reflux for 1 h under nitrogen. After cooling to room temperature, the Grignard reagent was taken up by syringe and added slowly to $HgCl_2$ (1.7 g, 6.3 mmol) in 20 mL of THF under nitrogen. The reaction mixture was then heated at reflux for 1 h and then worked up as follows: saturated aqueous ammonium chloride (50 mL) and ether (50 mL) were added; the organic layer was separated, and the aqueous layer was washed twice with 25 mL of ether. The combined organic layers were dried over $MgSO_4$ and filtered, and the solvents were removed by rotary evaporation. The residue was recrystallized from acetone/water, giving 2.1 g of bis(1-phenylcyclopropyl)mercury (8) as clear colorless needles, mp 109-111 °C: ^1H NMR ($CDCl_3$) δ 0.98 (m, 4 H), 1.11 (m, 4 H), 7.00 (m, 4 H), 7.17 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 10.08 (t), 49.11 (s, $^1J_{^{13}C-^{199}Hg}$ = 532 Hz), 124.37 (d), 128.12 (d), 128.93 (d, $^3J_{^{13}C-^{199}Hg}$ = 19 Hz), 150.63 (s); MS (EI), *m/e* (relative intensity) 436 (9), 206 (15), 117 (100), 91 (53). Anal. Calcd for $C_{18}H_{18}Hg$: C, 49.71; H, 4.17. Found: C, 49.66; H, 4.17.

Preparation of (1-Phenylcyclopropyl)potassium (5). In a Schlenk flask under nitrogen were combined Na/K alloy (0.10 mL), 8 (0.11 g, 0.25 mmol), and 10 mL of hexane. The flask was stoppered and the mixture stirred at room temperature for 1 h. The stopper was removed and replaced by a refulx condenser and gas tube. The reaction mixture was then heated to reflux in an oil bath. After heating for 4 h, the heterogeneous mixture was allowed to cool to room temperature and 2 mL of water was added. The sole product detected by GLC analysis was phenylcyclopropane (96% yield by the internal standard method).

Acknowledgment. We thank the Research Corporation (Grant 10693) and the UNCC Foundation for their partial support of this work. C.A.O. would also like to thank Dan Deadwyler for obtaining the ESR spectra and Tony Aldridge for obtaining the GC/MS data.

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(27) Sychkova, L. D.; Shabarov, Y. S. *Zh. Org. Khim.* **1980**, *16*, 2086-91; *Chem. Abstr.* **1981**, *94*, 156437z. Attempts to prepare 1-phenylbromocyclopropane by the procedure suggested here failed in our hands.

(28) When old $Pb(OAc)_4$ was used or the reaction was not thoroughly degassed, the major product was 1-phenylcyclopropyl acetate: ^1H NMR ($CDCl_3$) δ 1.24 (m, 2 H), 1.31 (m, 2 H), 2.06 (s, 3 H), 7.18-7.37 (m, 5 H); IR neat 1742 cm^{-1}.

(29) If the temperature of the injector port was greater than 150 °C or the injector port was dirty, 7 was observed to rearrange to give 2-phenylallyl chloride: ^1H NMR ($CDCl_3$) δ 4.51 (s, 2 H), 5.56 (s, 1 H), 5.74 (s, 1 H), 7.30-7.60 (m, 5 H).

Synthesis of Substituted Cyclopentenones via Boron Trifluoride Mediated Ring Cleavage in Polycyclic Ketones

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The use of the retrograde Diels-Alder reaction as a strategy in the synthesis of natural products is well documented.[1,2] Currently, there is intense interest in the use of substituted tricyclo[5.2.1.$0^{2,6}$]decenones and -decadienones as intermediates in the synthesis of cyclopentanoid natural products. These compounds have been found to undergo [4 + 2] cycloreversion under flash vacuum pyrolysis (FVP) conditions to afford substituted cyclopentenones.[3-5] We now report a procedure for effecting ring cleavage in these systems that employs a Lewis acid catalyst (i.e., boron trifluoride etherate) at low temperatures (-10 °C to room temperature).

Thus, *exo*-2-carbomethoxy-*exo*-3-methyltricyclo[5.2.1.$0^{2,6}$]dec-8-en-5-one (1)[6] was reacted with a slight molar excess of boron trifluoride etherate at room temperature. Workup of the reaction mixture afforded 3-carbomethoxy-4-methylcyclopent-2-en-1-one (2) in 95% yield along with dicyclopentadiene. Compound **2** could also be obtained in similar yield via reaction of $F_3B\cdot OEt_2$ with *exo*-2-carbomethoxy-*exo*-3,7-dimethyltricyclo[5.2.1.$0^{2,6}$]dec-8-en-5-one (**3**[6]) at -10 °C. In another set of experiments, the reaction of either **1** or **3** with $F_3B\cdot OEt_2$ was initiated at -78 °C and then allowed to warm slowly to 0 °C. In each case, the reaction mixture was stirred for 3 h at 0 °C, at which time ethanedithiol (1 equiv) was added. Workup of each reaction mixture afforded **4** (i.e., the dithioketal of keto ester **2**) in essentially quantitative yield. These results along with the results of other closely related reactions are summarized in Table I.

Other results that appear in Table I merit comment. First, the corresponding reaction of dimer ketone **5** (synthesized via $Fe(CO)_5$-promoted coupling of norbornadiene to carbon monoxide)[7] with boron trifluoride etherate at ambient temperature affords *exo*-tricyclo[5.2.1.$0^{2,6}$]deca-

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