composition of the highest occupied orbitals on passing from a [3.1.1]propellane derivative to its dihydro counterpart. The measured PE spectra differ considerably (see Table I). The lowest two, partially resolved, ionization bands of 3 appear at 9.3 and 9.7 eV, respectively, being thus considerably higher than the lowest ionization band of 2. The compositions of the corresponding MO's, as revealed by the calculated MNDO and HAM/3 wave functions, are quite different. For 2, as mentioned above, a strong localization of the HOMO between two inverted carbons is observed. In contrast, the two top occupied orbitals of 3 encompass the entire carbon skeleton and get the highest contributions from the carbon atoms forming the cyclobutane unit. Therefore, it is not surprising that the split between the first two bands in 3 roughly corresponds to that found in other alkyl-substituted cyclobutane derivatives.[22] For the third and fourth MO's of 3, which appear as shoulders to the second and third band respectively, the calculations also predict a high localization at the cyclobutane subunit. In fact, they bear a strong resemblance to the 4a$_1$ and 1b$_1$ MO of cyclobutane[22,23] (assuming D_{2h} symmetry for the cyclobutane moiety). The higher energy region of the PE spectrum of 3 is characterized by highly overlapping bands starting from ca. 10.3 eV. Their assignment, proposed in Table I, is tentative. More accurate geometries, provided by experiment or advanced ab initio calculations, and additional PE data for structurally related compounds are necessary for a more reliable assignment.

To summarize, the present study indicates that the HOMO of the [3.1.1]propellane 2 has a bonding character. This is evidenced by the Gaussian shape of the first band in the measured PE spectrum and supported by the MNDO calculations of the changes in HOMO energies upon elongation of the distance between inverted carbon atoms. The rather low first ionization energy of 2 is in line with the negligible[21] 2s orbital population at the inverted carbons in the HOMO and the inductive influence of the large σ molecular skeleton of adamantane in which [3.1.1]propellane unit is embedded. It appears that the stability of the HOMO in small propellanes may be significantly influenced by the enlargement of the molecular frame, affecting their reactivity in frontier orbital controlled reactions.[24]

Experimental Section

The [3.1.1]propellane 2 and its dihydro congener 3 were prepared following the procedures described in ref 7. Propellane 2 was trapped into a liquid nitrogen cooled trap and used for the PE measurements immediately after preparation. Prior and during measurements, 2 was kept in this trap at −10 °C in a dry nitrogen atmosphere or in vacuo.

The PE spectra of 2 and 3 were recorded on a Vacuum Generators UV-G 3 instrument using the He I line for excitation. The spectra were recorded at room temperature and were calibrated with xenon.

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Amide Activation for Cyclopropane Ortho Lithiation

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We recently found that the well-known[1] activation by amides for ortho lithiation of aromatics and other unsaturated systems could be extended to the "saturated" cubane system.[2] As cubane (31% s) and cyclopropane (33% s) have similar C–H bonding parameters,[3] we looked to see whether the chemistry we were developing for cubanes also applied to cyclopropanes.[4] Our preliminary results, detailed here, are encouraging.

Reaction of 1-methyl-1-(*N*,*N*-diisopropylcarbamoyl)cyclopropane (1)[5] with 8 equiv of lithium tetramethylpiperidide (LiTMP) in THF at 0 °C gives partial conversion to the ortho-lithiated derivative 2. On quenching with CH$_3$OD, the starting material is substantially recovered with approximately 60% monodeuterium incorporation as determined by mass spectral analysis (CI, isobutane[6]). NMR analysis places the deuterium atom on the cyclopropane ring, necessarily β to the amide group. It is predominately, perhaps exclusively, cis to the amide.

Following the lead provided by our cubane work, we treated compound 1 with excess LiTMP/HgCl$_2$. Complete conversion to the organomercury occurs quickly via transmetalation of the intermediate ortho-lithiated compound 2. The equilibrium lies well to the right. The organomercury 3 (X = Cl) can be isolated easily as its chloride.

Reaction of 3 with iodine in CHCl$_3$ gives the *cis*-iodoamide 4, pure and crystalline, in 81% yield. The cis geometry was inferred (albeit arguably) from NOE experiments[7] and then confirmed definitively by single-crystal X-ray analysis. Interestingly, and unexpectedly,[8] iodination of 3 in pyridine gives both cis and trans iodoamides, favoring 4 by 2:1, each configurationally stable in the reaction medium.

"Reverse transmetalation", as defined elsewhere,[2b] occurs cleanly on treatment of 3 with CH$_3$Li. This makes available stoichiometrically the organolithium 2, free of interfering reagents.[9] The transmetalation equilibrium

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(1) For reviews see: (a) Gschwend, H. W.; Rodrigues, H. R. *Org. React.* (*N.Y.*) **1979**, *26*, 1. (b) Beak, P.; Snieckus, V. *Acc. Chem. Res.* **1982**, *15*, 306. (c) Klumpp, G. W. *Recl. Trav. Chim. Pays-Bas* **1986**, *105*, 1.

(2) (a) Eaton, P. E.; Castaldi, G. *J. Am. Chem. Soc.* **1985**, *107*, 724. (b) Eaton, P. E.; Cunkle, G. T.; Marchioro, G.; Martin, R. M. *J. Am. Chem. Soc.* **1987**, *109*, 948. (c) Eaton, P. E.; Higuchi, H.; Millikan, R. *Tetrahedron Lett.* **1987**, *28*, 1055.

(3) Cf.: Luh, T.-Y.; Stock, L. M. *J. Am. Chem. Soc.* **1974**, *96*, 3712.

(4) It is very difficult to lithiate cyclopropanes by reaction with alkyllithiums. Certain examples of remote activation are known; cf. Section 2.2.2 in ref 1c.

(5) Prepared in standard fashion via the acid chloride (SOCl$_2$) from the commercially available acid (Aldrich): 1, mp 57–58 °C, from hexane.

(6) Chemical ionization was used for under electron impact conditions self-CI of *N*,*N*-diisopropylamides is a complication to quantitative MS analysis.

(7) These experiments were done in collaboration with Dr. J. S. Witzeman.

(8) Jensen, F. R.; Rickborn, B. *Electrophilic Substitution of Organomercurials*; McGraw-Hill: New York, 1968; p 86 ff.

(9) The organic byproduct is (CH$_3$)$_2$Hg, which is toxic and volatile. Due caution is called for. We used reaction with iodine at the end of our reaction sequences to obviate the problem. Butyllithium used instead of CH$_3$Li in the reverse transmetalation gives the less hazardous dibutylmercury.

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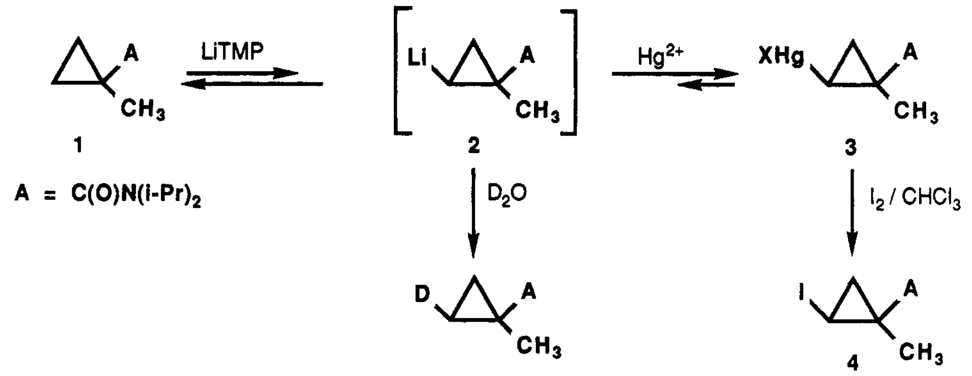
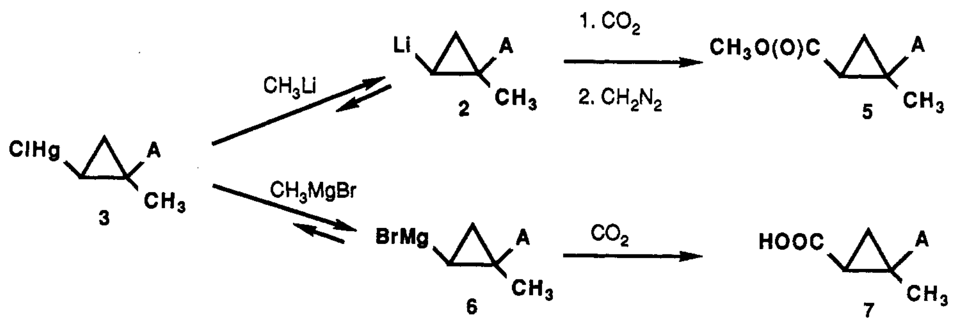
Scheme I

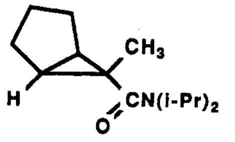


Scheme II

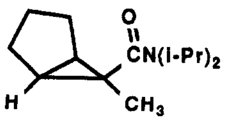


position is far to the right as the higher s character, exo cubyl orbital can better accommodate the more polar metal bond than can the simple sp^3 orbital of a methyl group. Formation of **2** at −70 °C followed by carboxylation and diazomethane esterification gives the cis-1-amide-2-ester **5** in 90% overall yield. The assignment of stereochemistry is based on NMR and mechanistic consideraions. If the reverse transmetalation is run at higher temperatures (above about −20 °C), some polymerization occurs as the amide group of **2** is susceptible to nucleophilic attack by a sister organolithium. This problem does not occur, even at 0 °C, if the transmetalation is done with CH_3MgBr for the Grignard **6** is much less reactive. Carboxylation gives the cis-1-amide-2-acid **7** in 75% yield without complication. Certainly, there is ample precedent to expect that other electrophiles will react with **2** and **6** and that these organometallics and their relatives will prove useful in more complex synthesis schemes.

We had thought to use the relative reactivities of isomer pairs like **8a,b** to separate the amide solvation effect from the amide inductive effect on ortho lithiation. Unfortunately, neither isomer is mercurated under the conditions described. This seems more than a simple steric problem and probably reflects the decreased acidity of alkyl-substituted cyclopropanes. Clearly, the use of bases stronger than LiTMP may overcome this problem. We shall report in due course on our work along these lines.



8a



8b

Experimental Section

NMR spectra were taken in FT mode: for ^1H NMR at 500 MHz on solutions in $CDCl_3$ containing Me_4Si as internal standard; for ^{13}C NMR at 100 MHz on solutions in $CDCl_3$ using the center line of the solvent (77.30 ppm) as internal standard. Chemical shifts and coupling constants are reported to a precision of ±0.02 and ±1 Hz, respectively, sufficient for the purposes here.

Preparation of LiTMP. Substantial care must be taken in the preparation of LiTMP in THF to avoid the formation of α-lithio-THF.[2c] Careful temperature control is essential. The thermometer must be in contact with the reaction mixture; control of the bath temperature is necessary, but not sufficient. A magnetically stirred solution of dry 2,2,6,6-tetramethylpiperidine (3.1 g, 22 mmol) in 20 mL of dry THF (distilled from sodium benzophenone ketyl) under argon was cooled to −70 °C. Butyllithium in hexanes solution (Aldrich; 13.7 mL, 1.6 M, 22 mmol) was added dropwise at a rate such that the temperature of the reaction mixture could be kept below −45 °C. After the addition was completed, the mixture was allowed to warm to 0 °C and stirred at this temperature for 30 min. The LiTMP solution can be stored at 0 °C for some time, but it is best if it is used within a few hours.

Mercuration of 1. A solution of $HgCl_2$ (1.35 g, 5.00 mmol) and the amide **1**[5] (0.50 g, 2.7 mmol) in 7 mL of dry THF was added to the above solution of LiTMP dropwise at a rate such that the temperature of the reaction solution never went above 5 °C. Afterward, the solution was stirred at 0 °C for 90 min, then the mixture was poured into 75 mL of 10% aqueous HCl, and the whole was extracted with $CHCl_3$ (4 × 30 mL). The extract was filtered through a plug of Celite, dried over $MgSO_4$, and evaporated to dryness in vacuo, leaving 2 g of a white solid containing mercury salts. This was taken up in a minimum volume of $CHCl_3$. Filtration through silica gel, eluting with 15 vol % ethyl acetate in hexanes followed by crystallization from 15 vol % benzene in hexanes gave 0.86 g (76%) of **3** as long white needles: mp 118–119.5 °C; IR ($CHCl_3$) ν 2971, 2935, 1600, 1371, 1348 cm^{-1}; ^1H NMR 4.56, (br s, 1 H), 3.34 (br s, 1 H), 1.38 (s, 3 H), 1.35–1.17 (3 br s, 12 H), 1.11 (dd, J = 10, 4.5 Hz, 1 H), 1.05 (dd, J = 7.5, 4.5 Hz, 1 H), 0.86 ppm (dd, J = 10, 7.5 Hz, 1 H); ^{13}C NMR δ 174.8 (CO), 48.4 (CH), 46.0 (CH), 32.1 (CH), 26.3 (C), 20.6 (CH_3), 20.5 (CH_3), 20.4 (CH_3), 19.9 (CH_3), 19.2 ppm (CH_2). Anal. Calcd for $C_{11}H_{20}ClHgNO$: C, 31.58; H, 4.82. Found: C, 31.65; H, 5.00.

Iodination of 3. (A) In $CHCl_3$. Elemental iodine (0.30 g, 1.2 mmol) was added to a solution of **3** (0.199 g, 0.48 mmol) in 6 mL of $CHCl_3$. After 24 h open to air and room light, the mixture was diluted with 30 mL of CH_2Cl_2 and washed successively with 10% aqueous Na_2SO_3, 10% aqueous KI, and then H_2O. Standard workup left a damp, white solid that on sublimation at 60 °C (3 torr) gave 0.12 g (81%) of **4**: mp 71.5–73 °C; IR (CCl_4) ν 2999, 2967, 1640, 1435, 1369 cm^{-1}; ^{1}H NMR 4.25 and 3.36 (heptets, J = 6 Hz, 1 H each), 2.57 (dd, J = 7.6, 5.2 Hz, 1 H), 1.56 (dd, J = 6.3, 5.2 Hz, 1 H), 1.45–1.25 (4 br d, 12 H), 1.40 (s, 3 H), 1.22 ppm (dd, J = 7.6, 6.3 Hz, 1 H); MS (EI) calcd for $C_{11}H_{20}NOI$, m/e 310, found 310.

(B) In Pyridine. Iodine (0.063 g, 0.12 mmol) was added to a solution of 3 (0.050 g, 0.12 mmol) in dry pyridine (0.5 mL) at room temperature. The mixture was stirred for 20 h open to the air and unprotected from light. Much of the iodine color disappeared. The mixture was diluted with CH_2Cl_2 (15 mL) and then washed with 10% aqueous Na_2SO_3, 3% aqueous HCl, and H_2O. The organic layer was dried ($MgSO_4$) and the solvent removed in vacuo, leaving 0.038 g of a slightly orange oil. By ^{1}H NMR this contained approximately a 2:1 mixture of 4 and its trans isomer. These were separated by simple chromatography on silica gel, eluting with 15 vol % EtOAc in $CHCl_3$; the trans compound is the more mobile and was obtained as a slightly yellow oil that was not purified further: IR (CCl_4) ν 2968, 1645, 1436, 1370, 1338 cm^{-1}; ^{1}H NMR 4.16 (br 1 H), 3.29 (br, 1 H), 2.80 (dd, J = 8.5, 5.5 Hz, 1 H), 1.82 (dd, J = 8.5, 6.5 Hz, 1 H), 1.38 (s, 3 H), 1.4–1.1 (m, 12 H), 0.78 ppm (dd, J = 6.5, 5.5 Hz, 1 H); MS (EI) calcd for $C_{11}H_{20}NOI$, m/e 310, found 310.

Carboxylation of 1. (A) Via Cyclopropyllithium 2. Reverse transmetalation of 3 to 2 was accomplished by adding methyllithium in diethyl ether (Aldrich; 2.8 M, 0.70 mL, 2.0 mmol) to a stirred solution of 3 (0.30 g, 0.72 mmol) in dry THF (15 mL) at –70 °C under an argon atmosphere. The mixture was stirred for 30 min at this temperature, and then CO_2 was bubbled through for 10 min. The cooling bath was removed; CO_2 addition was continued for an additional 30 min as the solution warmed to room temperature. The mixture was acidified to pH 1 with 10% aqueous HCl and then treated with an excess of ethereal CH_2N_2. A crystal of iodine was added.[9] After 30 min, the solution was diluted with CH_2Cl_2 (50 mL) and then washed with aqueous Na_2HSO_3. The organic layer was dried ($MgSO_4$) and then evaporated in vacuo. The residue was chromatographed on silica gel, eluting with 1:2:8 $CHCl_3$/EtOAc/hexane to yield 0.158 g (90%) of 5 as an oil. This was not purified further: ^{1}H NMR 4.33 and 3.27 (heptets, J = 7 Hz, 1 H each), 3.64 (s, 3 H), 1.80–1.75 (m, 2 H), 1.38, 1.36, 1.22, 1.11 (d, J = 7 Hz, 3 H each), 1.34 (s, 3 H), 1.04 ppm (m, 1 H).

(B) Via the Cyclopropyl Grignard 6. Methyl Grignard in diethyl ether (Aldrich; 2.7 M, 0.45 mL, 1.2 mmol) was added dropwise to a magnetically stirred solution of 3 (0.20 g, 0.48 mmol) in dry THF (7 mL) at 0 °C under nitrogen. The mixture was stirred for 5 min, and then dry CO_2 was bubbled through for 30 min during which time the reaction temperature was held near 0 °C. The mixture was diluted with ether (20 mL) and then extracted with 5% aqueous NaOH (3 × 10 mL). The combined basic extract was acidified slowly with concentrated aqueous HCl to pH 1 and then extracted with CH_2Cl_2 (3 × 20 mL). The extract was dried ($MgSO_4$) and the solvent removed in vacuo. The solid residue was crystallized from 2:1 hexane/benzene to afford 0.080 g (74%) of the fluffy, white solid 7: mp 142.5–144 °C; IR (CCl_4) ν 2969, 1703, 1439, 1370, 1277, 1175, 1038 cm^{-1}; ^{1}H NMR 4.34 and 3.28 (heptets, J = 7 Hz, 1 H), 1.81 (dd, J = 8, 5 Hz, 1 H), 1.77 (dd, J = 5, 4.5 Hz, 1 H), 1.36, 1.34, 1.21, 1.16 (d, J = 7 Hz, 3 H each), 1.35 (s, 3 H), 1.10 ppm (dd, J = 8, 4.5 Hz, 1 H); ^{13}C NMR δ 176.5 (CO), 169.2 (CO), 48.6 (CH), 46.0 (CH), 32.9 (C), 27.9 (CH), 22.4 (CH_3), 21.9 (CH_2), 20.9 (CH_3), 20.8 (CH_3), 20.2 (CH_3), 20.1 ppm (CH_3). Anal. Calcd for $C_{12}H_{21}NO_3$: C, 63.41; H, 9.31. Found: C, 63.26; H, 9.43.

X-ray Crystal Structure Analysis of 1-Methyl-1-(*N*,*N*-diisopropylcarbamoyl)-2-iodocyclopropane (4). A small, colorless crystal of 4 (0.1 × 0.1 × 0.1 mm) was cut from a larger crystal (larger samples did not show sharp diffraction spots). Preliminary Weissenberg photographs with Cu Kα radiation indicated that the crystals belong to the orthorhombic system. Systematic extinctions are $0kl$ ($k = 2n$), $h0l$ ($l = 2n$), and $hk0$ ($h = 2n$), thus defining the space group *Pbca*. Determination of the lattice parameters and intensity measurements were made with a Nonius CAD4 diffractometer, using graphite-monochromated Mo Kα radiation. Twenty-two reflections determined with the Nonius peak-hunting procedure in the range 9° < 2θ < 17° were carefully centered. Cell parameters were calculated by a least-squares procedure. All independent reflections in the range 2° ≤ 2θ ≤ 50° were measured at T = –85 (2) °C by the ω–2θ scan technique. Every 100 reflections the orientation of the crystal was controlled, and every 3.3 h the intensity of the $\bar{1}\bar{4}2$ reflection was checked. During the experiment a loss of intensity of 8% was observed. A total of 2522 reflections was measured. After multiple measurements were averaged, 2192 independent reflections remained, of which 797 were unobserved with $I < 2.58\sigma(I)$. The intensities were corrected for Lorentz and polarization effects, but no absorption correction was applied.

Crystal data (–85 °C; Mo K$\bar{\alpha}$, λ = 0.71069 Å, μ(Mo K$\bar{\alpha}$) = 24.382 cm^{-1}): orthorhombic *Pbca*; a = 12.617 (5), b = 12.713 (5), c = 16.016 (8) Å; V = 2569.0 Å^3; Z = 8; density = 1.60 g cm^{-3}; $C_{11}H_{20}NOI$, fw 309.2.

The structure was solved by Patterson methods. The light atoms were found with iodine-phased structure factors and successive Fourier calculations. The hydrogen atoms could not be seen. The structure was refined with block-diagonal least-squares calculations. In the last few cycles of refinement anisotropic temperature factors for the I, O, N, and C atoms were applied, the function minimized being $\sum w(|F_o| - |F_c|)^2$ and w = 1. The atomic and anomalous scattering factors were taken from tables.[10] The final agreement index was R = 0.10 for observed reflections. All calculations and drawings were done on the program system KRIPROG.[11] Additional details of the structure are available in the supplementary material.

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Supplementary Material Available: Tables of fractional coordinates and anisotropic thermal parameters for non-hydrogen and hydrogen atoms and bond distances and angles (7 pages). Ordering information is given on any current masthead page.

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Flash Vacuum Thermolysis of Alkyl Dicyanoethanoates

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Flash vacuum thermolysis of organic compounds has been of great utility in the synthesis of thermally labile compounds, in the spectroscopic characterization of short-lived intermediates, and in the investigation of thermolysis reactions.[1] The thermolysis of esters has been reviewed by Depuy and King,[2] Maccoll,[3] and Smith and Kelly.[4] For over a century it has been known that many esters decompose into an olefin and carboxylic acid when heated at 300–550 °C.[5] Evidence, such as stereochemistry

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