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Rearrangement of a Trishomocubane Derivative to a Tetracyclo[6.3.0.0^{2,6}.0^{3,10}]undec-4-ene

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Reaction of 8,8,11,11-tetrafluoropentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane with idio trimethylsilane leads to the expected D_3-trishomocubane derivative, but reaction with the more electrophilic boron tribromide yields a tetracyclo[6.3.0.0^{2,6}.0^{3,10}]undec-4-ene derivative which was characterized by X-ray diffraction. The most easily visualized pathway for this transformation would be an initial rearrangement of the starting material to a D_3-trishomocubane followed by additional bond breaking to form the undec-4-ene compound. Molecular mechanics calculations indicate the brominated D_3-trishomocubane is about 4 kcal/mol more stable than the brominated undec-4-ene molecule and the associated carbonium ions show the same ordering. These data would indicate an alternate reaction pathway must be operative; however, semiempirical calculations predict the reverse ordering of the above energies.

KEY WORDS: Tetracycloundecane; D_3-trishomocubane; tetracycloundec-4-ene; molecular mechanics; semiempirical calculations; X-ray analysis; carbonium ion rearrangements.

INTRODUCTION

Skeletal rearrangements of polysubstituted derivatives of pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (PCU) have not been investigated as thoroughly as those involving the mono and disubstituted derivatives [1, 2]. These polysubstituted compounds are of interest because of through-bond and/or through-space interactions which may lead to changes in reaction pathways. Normally, PCU and its derivatives rearrange under electrophilic conditions (Lewis acid catalysis) to the stabilomer D_3-trishomocubane. The effects of multiple substitutions upon this rearrangement are of current interest to our research groups. In an earlier study an indirect method of halogen displacement with concomitant framework isomerization was investigated [3]. The reaction of iodotrimethylsilane with 8,8,11,11-tetrafluoro-PCU (**1**) produced readily triiodofluoro-D_3-trishomocubane (**2**). However, the reaction of 8,8,11,11-tetrafluoro-PCU with the more electrophilic boron tribromide led to the replacement of all fluorine atoms but with an additional rearrangement of the cage to form the isomeric 4,6,7,9-tetrabromotetracyclo[6.3.0.0^{2,6}.0^{3,10}]-undec-4-ene (**3**). The structure of this compound was determined by X-ray diffraction techniques.

EXPERIMENTAL

To 10 mL of boron tribromide 2.18 g (0.01 mol) of 8,8,11,11-tetrafluoropentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]-undecane was added in small portions. After addition was complete the solution was stirred at rt for 3 h. The excess boron tribromide was evaporated at 20 mmHg and 50°C, and the residue was treated carefully with 50 mL of water, extracted with 50 mL of CH_2Cl_2 and the organic layer washed with water (3 × 50 mL). The or-

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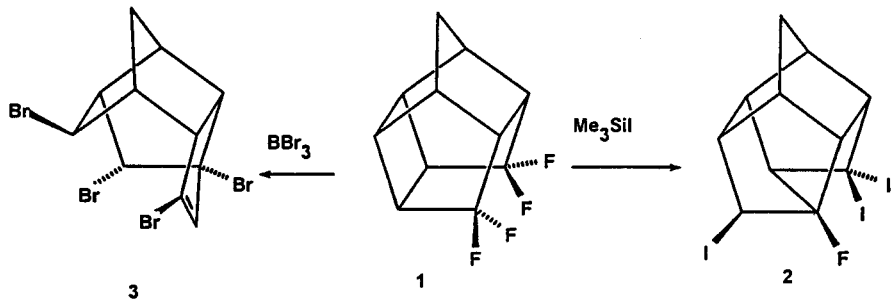


3 1 2

Scheme 1

ganic layer was dried over Na_2SO_4 and discolored by passing through charcoal. Yield 3.65 g (79%), m.p. 142–143°C. ^{13}C NMR ($CDCl_3$): δ, 46.51(1), 61.65(2), 59.58(3), 124.22(4), 136.97(5), 75.59(6), 59.24(7), 64.36(8), 50.59(9), 47.86(10), 37.98(11) [4].

All X-ray data were collected on a Rigaku AFC-6S diffractometer using the ω-2θ mode at a fixed scan rate of 8°/min and all reflections with $I < 10.0\sigma(I)$ were rescanned a maximum of three times. Unit cell parameters were obtained by a least-squares refinement of 24 reflections. Lorentz-polarization corrections, a Ψ-scan empirical absorption correction, and an isotropic extinction correction were applied. The structure was solved by direct methods [5] and refined by a full-matrix least-squares technique with a weighting scheme based on the measured esd's. Hydrogen atom positions were found on a difference map and the coordinates were refined. Computer programs TEXSAN [6], SHELXS86 [5], and PLATON-94 [7] were used. Crystal and refinement data are given in Table I. Atomic positional parameters are given in Table II while bond lengths and valence angles are given in Table III. Figure 1 is a thermal ellipsoid plot of compound **3**, while a packing diagram is given in Fig. 2.

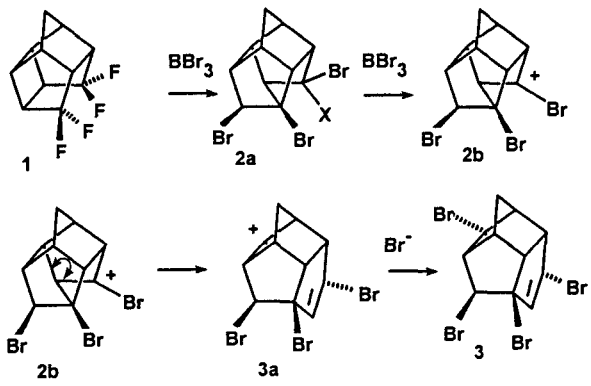
DISCUSSION

Compound **3** contains four five-membered rings fused into a partial cage structure (see Fig. 1). The two five-membered rings composing the norbornane moiety are slightly distorted away from the envelope conformation by unsymmetric fusion, ϕ = 136(1) and 319(1)° (ideal envelope $\phi = nx36°$) [7, 8]. The cyclopentene rig adopts a flattened envelope conformation (ϕ = 186(3)°) while the remaining five-membered ring is an envelope distorted toward half-chair, ϕ = 136(1)°. The C—C bond lengths around the molecule are normal for systems of this type [9]. The three C(sp^3)—Br bonds average 1.966(7) Å while the C(sp^2)—Br bond is shortened to 1.868(8) Å. There are only two intermolecular interactions closer than the sum of van der Waals contacts and these are shorter by less than 0.1 Å. A packing analysis indicates void areas of about 43 Å^3 (see

Table I. Crystal, Intensity Measurement, and Refinement Data for Compound 3.

Formula	$C_{11}H_{10}Br_4$	Formula weight	461.82
Color	colorless	Habit	prismatic
Space group	$P4_12_12^a$	a, Å	10.155(1)
c, Å	24.203(3)	cell volume, Å^3	2495.8(7)
Z	8	D_{calc}, g cm^{-3}	2.458
μ, cm^{-1}	156.6	Max. dimensions, mm	.15 × .15 × .25
Standard reflections	$(12\bar{5})(12\bar{4})(21\bar{4})$	2θ range, deg	3–158.4
Reflections measured	3241	Range of h, k, l	12;12;30
Observed [$I \geq 3\sigma(I)$]	2588	Transmission factors	0.72–1.00
Parameters	177	R; R_w	0.047; 0.043
S	2.32	$(\Delta/\sigma)_{max}$	0.005
ρ_{min}; ρ_{max} e/Å^3	−0.69; 0.78		

[a] Refinement in $P4_32_12$ gave R = 0.0487; R_w = 0.0444. Hamilton significance test [13] indicated a probability of less than 0.005 and the space group was rejected.



Scheme 2

Fig. 2) which is approximately the size of a water molecule; however, all crystallizations used anhydrous solvents.

It is difficult to envision a mechanism by which compound **3** is formed directly from **1** via a carbonium ion rearrangement. It is easier to visualize **3** as arising from a D_3-trishomocubane derivative similar to **2a** where X might be Br or F (Scheme 2); however, this would be the first example of fragmentation of the D_3-trishomocubane skeleton under electrophilic conditions. A molecular mechanics (PCMODEL) [10] calculation gave ΔH_f values of 24.19, 10.87, and 17.14 kcal/mol for the parent hydrocarbons of **1**, **2**, and **3** while MM3 [11] calculations gave values of 26.35, 14.64, and 16.20 kcal/mol, respectively. These calculations predict the parent hydrocarbon of **3** to be less stable than D_3-trishomocubane by 6.27 and 1.56 kcal/mol, respectively, and the carbonium ion of the parent hydrocarbon **3a** to be less stable than the carbonium ion of the parent hydrocarbon of **2b** by 1.37 and 6.48 kcal/mol. This is consistent with the observed formation of the stable D_3-trishomocubane skeleton via carbonium ion rearrangement of other trishomocubane isomers [2]. PCMODEL predicts the fully brominated **2a** to be 3.77 kcal/mol more stable than **3** which also is not consistent with a thermodynamically controlled carbonium ion rearrangement of **2a** to **3**. These data would suggest the existence of an alternate kinetically controlled pathway to the observed product.

Contrary to the above calculations, MOPAC(PM3) [12] calculations predict the hydrocarbon of **3** to be more stable than the hydrocarbon of **2** by 4.68 kcal/mol, the brominated **3** more stable than **2a** by 13.36 kcal/mol, and the carbonium ion **3a** to be 10.33 kcal/mol more stable than the carbonium ion **2b**. The unsubstituted parent carbonium ions differ by 8.3 kcal/mol which is not

Table II. Atomic Positional Parameters and *B*(eq) Values for Compound 3.

Atom	*x*	*y*	*z*	*B*(eq)
Br(1)	−0.3589(1)	0.3677(1)	0.00032(6)	4.95(6)
Br(2)	0.0513(1)	0.08824(9)	0.08860(5)	4.48(6)
Br(3)	0.2813(1)	0.3189(1)	0.08504(5)	4.35(6)
Br(4)	−0.0218(1)	0.75407(8)	0.04703(4)	3.32(4)
C(1)	0.011(1)	0.4554(9)	0.1407(3)	2.6(4)
C(2)	−0.0709(9)	0.3342(8)	0.1239(4)	2.5(4)
C(3)	−0.1992(8)	0.3989(8)	0.0998(4)	2.8(4)
C(4)	−0.2128(8)	0.3347(8)	0.0451(4)	2.9(4)
C(5)	−0.107(1)	0.2660(8)	0.0290(4)	2.9(4)
C(6)	−0.0049(8)	0.2700(7)	0.0735(3)	2.6(4)
C(7)	0.1063(8)	0.3667(8)	0.0561(4)	2.3(4)
C(8)	0.0665(8)	0.4945(8)	0.0839(4)	2.2(3)
C(9)	−0.0521(8)	0.5648(7)	0.0570(4)	2.1(3)
C(10)	−0.1636(8)	0.5460(8)	0.0989(4)	2.6(4)
C(11)	−0.092(1)	0.562(1)	0.1530(4)	3.6(5)
H(1)	0.063(9)	0.436(9)	0.166(3)	4(2)
H(2)	−0.078(6)	0.265(6)	0.160(3)	1(1)
H(3)	−0.278(7)	0.378(7)	0.124(3)	2(1)
H(5)	−0.105(6)	0.213(6)	−0.006(3)	1(1)
H(7)	0.129(8)	0.362(8)	0.019(3)	3(2)
H(8)	0.135(7)	0.546(7)	0.083(3)	1(1)
H(9)	−0.070(7)	0.532(8)	0.022(3)	2(2)
H(10)	−0.228(7)	0.587(7)	0.094(3)	2(2)
H(11A)	−0.036(9)	0.652(9)	0.159(3)	4(2)
H(11B)	−0.140(9)	0.546(9)	0.189(3)	4(2)

Table III. Intramolecular Distances (Å) and Valence Angles (°) for Compound 3.

Br(1)−C(4)	1.868(8)	C(3)−C(4)	1.48(1)
Br(2)−C(6)	1.966(7)	C(3)−C(10)	1.54(1)
Br(3)−C(7)	1.970(8)	C(4)−C(5)	1.34(1)
Br(4)−C(9)	1.962(7)	C(5)−C(6)	1.50(1)
C(1)−C(2)	1.54(1)	C(6)−C(7)	1.55(1)
C(1)−C(8)	1.54(1)	C(7)−C(8)	1.52(1)
C(1)−C(11)	1.54(1)	C(8)−C(9)	1.54(1)
C(2)−C(3)	1.57(1)	C(9)−C(10)	1.53(1)
C(2)−C(6)	1.54(1)	C(10)−C(11)	1.51(1)
C(2)−C(1)−C(8)	99.6(7)	C(2)−C(6)−C(5)	106.4(7)
C(2)−C(1)−C(11)	104.3(8)	C(2)−C(6)−C(7)	105.3(6)
C(8)−C(1)−C(11)	103.8(7)	C(5)−C(6)−C(7)	108.9(7)
C(1)−C(2)−C(3)	102.3(7)	Br(3)−C(7)−C(6)	113.8(6)
C(1)−C(2)−C(6)	108.3(7)	Br(3)−C(7)−C(8)	107.0(6)
C(3)−C(2)−C(6)	104.1(7)	C(6)−C(7)−C(8)	103.1(7)
C(2)−C(3)−C(4)	103.0(7)	C(1)−C(8)−C(7)	105.9(7)
C(2)−C(3)−C(10)	102.5(7)	C(1)−C(8)−C(9)	102.2(7)
C(4)−C(3)−C(10)	115.9(8)	C(7)−C(8)−C(9)	114.6(7)
Br(1)−C(4)−C(3)	120.9(6)	Br(4)−C(9)−C(8)	112.5(5)
Br(1)−C(4)−C(5)	124.2(8)	Br(4)−C(9)−C(10)	108.6(5)
C(3)−C(4)−C(5)	114.5(8)	C(8)−C(9)−C(10)	103.9(7)
C(4)−C(5)−C(6)	109.3(8)	C(3)−C(10)−C(9)	107.7(7)
Br(2)−C(6)−C(2)	112.2(6)	C(3)−C(10)−C(11)	102.0(8)
Br(2)−C(6)−C(5)	108.0(5)	C(9)−C(10)−C(11)	101.7(7)
Br(2)−C(6)−C(7)	115.6(6)	C(1)−C(11)−C(10)	94.9(7)

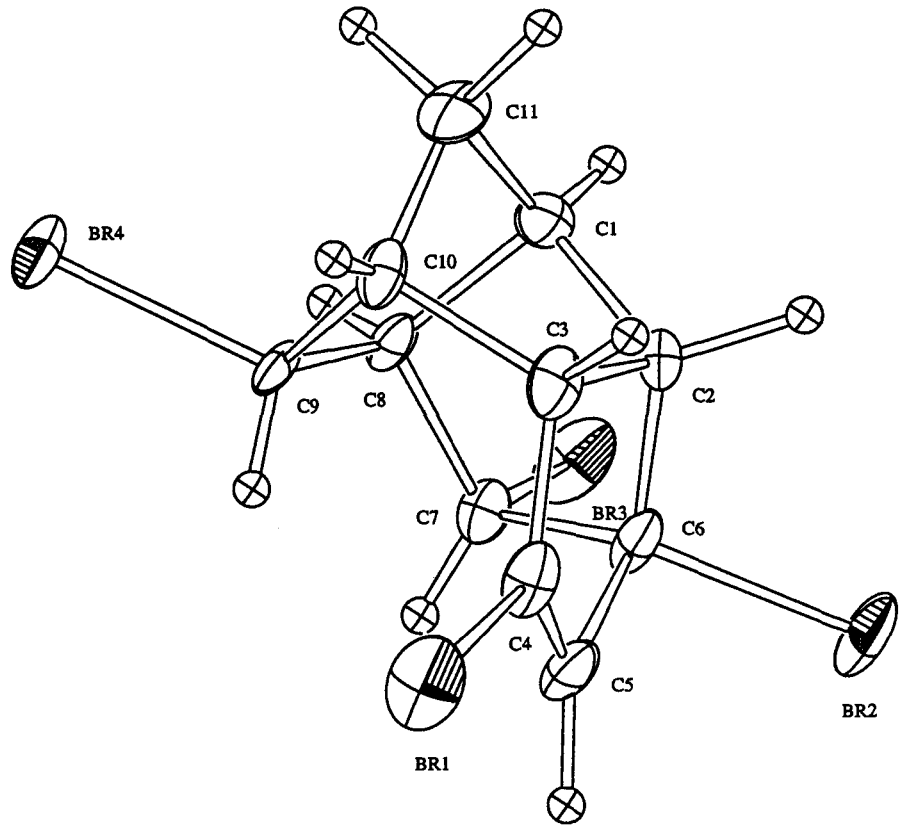


Fig. 1. Thermal ellipsoid drawing of compound 3. Heavy atoms are drawn at the 35% probability level while H atoms are an arbitrary size.

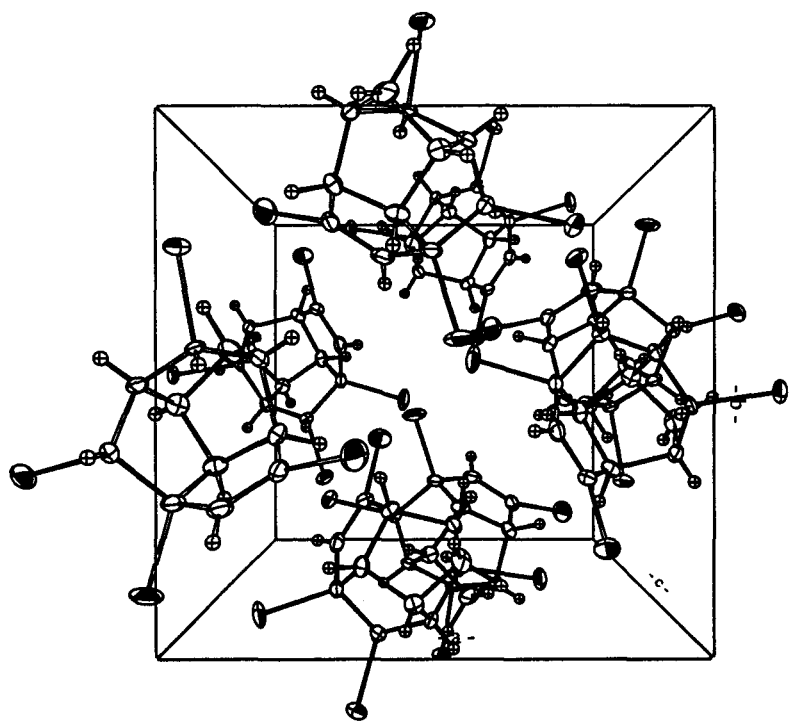


Fig. 2. Packing diagram for compound 3.

consistent with rearrangements reported for the homocubane system.

If MOPAC calculations are correct, **3** may arise from **2a** via a carbonium ion mechanism; however, if molecular mechanics calculations are correct an alternate mechanistic pathway has to be found which is possibly dependent upon the nature of the electrophilic agent. The experimental observations are more easily rationalized by the pathway shown in Scheme 2; however, one should be cognizant that different empirical calculation schemes may give conflicting answers when comparing skeletal rearrangements, and the prejudices of the investigator can be supported by a judicious choice.

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