(s), 1500 (s) cm^{-1}; NMR ($CDCl_3$) δ 1.5 (d, 3H, J = 6 Hz), 2.23 (s, 3H), 2.65 (d, 2H, J = 7 Hz), 4.1 (m, 1H), 6.72 (d, 1H, J = 8 Hz), 7.15 (br d, 1H, J = 7 Hz), 7.60 (br s, 1H).

Sodium Methoxide Catalyzed Cyclization of 32a. Compound **32a** (0.150, g, 0.85 mmol) and 0.100 g (1.85 mmol) of commercial sodium methoxide was dissolved in 5 mL of anhydrous methanol under nitrogen. The solution was allowed to stand for 4 h at room temperature and was then neutralized to pH 5 with 1 N hydrochloric acid. The solution was concentrated and the residue was extracted into ether, which was subsequently washed twice with water, once with brine, then dried ($MgSO_4$) and concentrated to give 0.140 g (93%) of tan crystals which were recrystallized from petroleum ether to give a product identical with that from closure in aqueous sodium hydroxide.

Sodium Methoxide Catalyzed Cyclization of 32b. A solution of 0.150 g (0.78 mmol) of **32b** and 0.100 g (1.85 mmol) of sodium methoxide in 5 mL of anhydrous methanol was treated exactly as above to yield 0.100 g (65%) light yellow oil, indistinguishable from the product obtained from the closure in aqueous sodium hydroxide.

Acknowledgments. We thank the National Science Foundation and the National Institutes of Health for financial support.

Registry No.—**1**, 63677-96-3; **2**, 1123-27-9; **3a**, 61541-23-9; **3b**, 20099-78-9; **4**, 63677-97-4; **5**, 63677-98-5; **8**, 23230-52-6; **9**, 63677-99-6; **10**, 63678-00-2; **11a**, 61541-24-0; **11b**, 61541-25-1; **13**, 63678-01-3; **15**, 63678-02-4; **17**, 119-67-5; **18** (R = t-Bu), 75-97-8; **21** (R = t-Bu), 63678-03-5; **22**, 63678-04-6; **23**, 63678-05-7; **24**, 63678,06-8; **25**, 63678-07-9; **25** DNP, 63678-08-0; **26**, 15495-23-5; **27**, 63678-09-1; **28**, 63678-10-4; **29** isomer A, 63678-11-5; **29** isomer B, 63678-12-6; **30**, 63678-13-7; **31**, 493-71-0; **32a**, 5631-63-0; **32b**, 24114-55-4; **33a**, 51423-95-1; **33b**, 63678-14-8; 3-hydroxy-3-methyl-2-butanone, 115-22-0; benzaldehyde, 100-52-7; p-methoxybenzaldehyde, 123-11-5; methanol-O-d, 1455-13-6; 4-hydroxybenzaldehyde, 123-08-0; acetone cyanohydrin, 75-86-5; dihydropyran, 110-87-2; phenylacetylene, 536-74-3; p-methyl anisole, 104-93-8; crotonyl chloride, 10487-71-5; dimethylacryloyl chloride, 3350-78-5.

References and Notes

(1) (a) National Cancer Institute Postdoctoral Trainee, Grant No. T32 CA09112, Sept 1, 1976–Mar 31, 1977; National Cancer Institute Postdoctoral Fellow, Grant No. F32 CA05968-01, Apr 1, 1977 to present; (b) National Science Foundation Predoctoral Fellow, 1977.

(2) J. E. Baldwin, *J. Chem. Soc., Chem. Commun.*, 734 (1976).

(3) (a) J. E. Baldwin, J. Cutting, W. Dupont, L. Kruse, L. Silberman, and R. C. Thomas, *J. Chem. Soc., Chem. Commun.*, 736 (1976); (b) J. E. Baldwin, *ibid.*, 738 (1976); (c) J. E. Baldwin and J. A. Reiss, *ibid.*, 77 (1977); (d) J. E. Baldwin and L. I. Kruse, *ibid.*, 233 (1977).

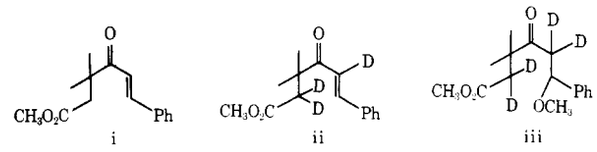
(4) The adjectives *favored* and *disfavored* were deliberately chosen to describe ring closures of acyclic molecules, which after suitable rotations around single bonds (conformations), can or cannot attain the necessary geometry for bond formation, dictated by the stereoelectronic requirements of the reaction. For example, reactions of tetrahedral systems by displacements require the collinear arrangement of reacting atoms, characteristic of the S_N2 transition state. If by rotation around single bonds in the acyclic precursor this geometry cannot be reached, e.g., in endo-tetrahedral processes, then these are disfavored and vice versa.

(5) References to these and other favored closures may be found in ref 2.

(6) I. N. Nazarov and A. N. Elizarova, *Bull. Acad. Sci. USSR Cl. Sci. Chem.*, 107 (1948); *Chem. Abstr.*, **42**, 7737 (1948).

(7) J. E. Baldwin, G. Hofle, and O. W. Lever, Jr., *J. Am. Chem. Soc.*, **96**, 7126 (1974).

(8) We have observed a similar reaction in the all-carbon system i which gave ii on treatment with sodium methoxide in methanol-O-d. In this case NMR and mass spectral evidence for trace amounts of the corresponding methanol adduct iii was obtained. J. E. Baldwin and R. C. Thomas, unpublished results.



(9) E. N. Marvell and J. L. Stephenson, *J. Am. Chem. Soc.*, **77**, 5177 (1955).

(10) E. W. Bousquet, M. D. Moran, J. Harmon, A. L. Johnson, and J. C. Summers, *J. Org. Chem.*, **40**, 2208 (1975).

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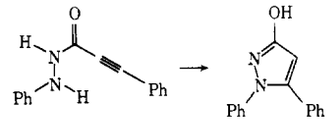
(12) H. C. Brown and C. P. Garg, *J. Am. Chem. Soc.*, **86**, 1085 (1964).

(13) Heating in a protic solvent is sufficient to cause cyclization of acetylenic hydrazides.[14] We have conducted a careful investigation of this reaction to establish that it is truly a 5-endo-digonal closure and not the result of prior addition of solvent to the triple bond followed by cyclization. J. E. Baldwin and R. C. Thomas, unpublished results.



(14) (a) H. N. Al-Jallo, *Tetrahedron Lett.*, 875 (1970); (b) N. Nakamura, Y. Kishida, and N. Ishida, *Chem. Pharm.*, **19**, 1389 (1971); (c) P. Bouchet, J. Elguero, and J. M. Periello, *Bull. Soc. Chem. Fr.*, 2482 (1973).

(15) The correct structure and a total synthesis of Bullatenone was reported by W. Parker, R. A. Raphael, and D. I. Wilkinson, *J. Chem. Soc.*, 3871 (1958).

(16) K. von Auwers and E. Lämmerhirt, *Justus Liebigs Ann. Chem.*, **421**, 1 (1920).

(17) The nitrile stretch is absent in this compound owing to the effect of the neighboring oxygen atom. See P. E. Sonnet, *J. Org. Chem.*, **33**, 3662 (1968), and ref 8 therein.

Syntheses and Relative Stability of (D_3)-Trishomocubane (Pentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane), the Pentacycloundecane Stabilomer[1]

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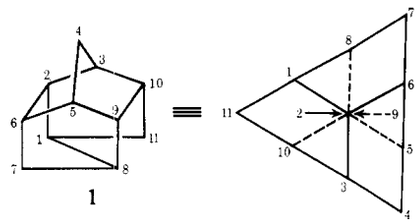
(D_3)-Trishomocubane (**1**) can be synthesized easily by aluminum bromide catalyzed isomerization of the "one-winged" bird-cage hydrocarbon **2** or by skeletal rearrangement during aqueous HI iodination of corresponding diol **11**, followed by dehalogenation. Syntheses of several derivatives of **1** and **2** including trishomocubanone (**14**) are also described. The isomerization results are in good agreement with predictions based on empirical force-field calculations on various $C_{11}H_{14}$ isomers which show that **1** is the pentacycloundecane stabilomer.

The trishomocubane (**1**) has two noteworthy features not explicitly mentioned by Underwood and Ramamoorthy in their account of the synthesis of this molecule.[3] First, **1** is one of the rare rigid organic molecules belonging to chiral point group D_3.[4] Second, **1** is the only structure possessing neither three- or four-membered rings nor other strained features among the large number of possible $C_{11}H_{14}$ pentacyclic isomers, and is thus likely to be the pentacycloundecane "sta-

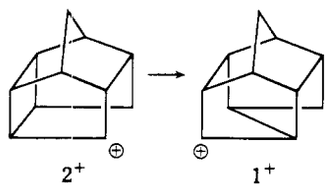
bilomer".[10] We have taken advantage of this expected thermodynamic stability to devise syntheses of 1 based on skeletal rearrangements which were improvements over the original methods.[3,11a] Subsequent to the preliminary publication of our work,[1] additional reports of syntheses of this ring system have appeared,[11b,12-14] including a preparation of enantiomerically pure 1.[14c]



1

Generation and Stability Evaluation of Pentacycloundecane Isomers. The structure generation program JAL-30XA[15] predicts 15 358 possibilities of constitution $C_{11}H_{14}$, excluding isomers with alkyl substituents. Based on the systematic method we have devised for predicting the stabilomer of a given constitution,[10] the thermodynamically most stable saturated $C_{11}H_{14}$ structure can be deduced. Isomers containing one or more tetrasubstituted carbon atoms should have relatively high strain,[16] and can be excluded from consideration with confidence. This leaves 482 candidates, of which only seven do not have three- or four-membered rings. Of these seven, six have intertwined structures and have no reasonable chance of existing. The only isomer left, 1, is the best candidate for the $C_{11}H_{14}$ stabilomer. In order to compare the stability of 1 with the next most stable structures, those isomers which have only one cyclobutane ring were sought. Among the 24 such structures given by the JAL-30XA program,[15] five of them are not intertwined and thus are possibilities. We also generated the 14 isomeric "trishomocubanes" manually; of these, four already appeared in the earlier selection process.

All 16 $C_{11}H_{14}$ structures thus selected were subjected to empirical force-field calculations using both Engler–Schleyer[17a] and Allinger[17b] force fields (Table I). The expected greater stability of 1 over all other pentacyclic isomers was confirmed. The enthalpy difference between 1 and all other tricycloundecanes (e.g., 2) was calculated to be 10 kcal/mol or more. This large energy difference and the possibility that 1 could be produced from 2 by a simple 1,2-alkyl shift of the intermediate secondary cation ($2^+ \rightarrow 1^+$, eq 1) suggests 2 as an excellent synthetic starting material.

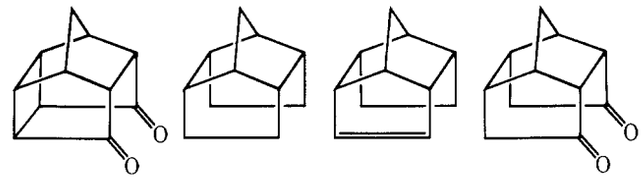


(1)

2^+ 1^+

Syntheses of (D_3)-Trishomocubane (1)[18] and Its Derivatives. We developed two simple routes for the preparation of 1 as well as several of its derivatives. The first route is the straightforward execution of eq 1.

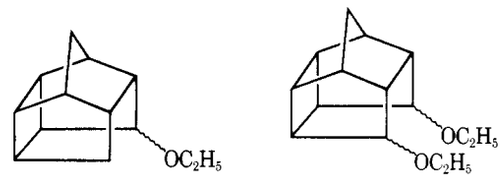
Modified Wolff–Kishner reduction of the easily accessible pentacyclic diketone 3[19] using sodium and diethylene glycol[20] gave in 75% yield a mixture of the desired hydrocarbon 2[21] (60%) as well as 4 (32%), 5 (4.3%), and two additional, yet unidentified, olefinic products of m/e 146 (1.8 and 1.4%). The saturated hydrocarbon 2 was identified by its distinctive ^1H NMR spectrum;[16,21a] 5 was found to be identical with the Wolff–Kishner reduction product of the known diketone 6.[22] The identity of 4 was established by its hydrogenation to 5. Separation of the saturated and unsaturated fractions was



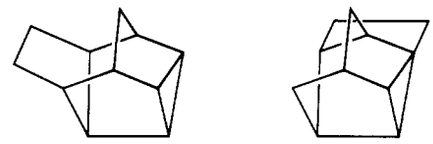
3 4 5 6

achieved easily by chromatography on a 10% $AgNO_3$ silica gel column.

Reduction under milder conditions appeared desirable because of the strain present in 3. Modified Clemmensen reduction with zinc and hydrochloric acid in ether at 0 °C[23] proceeded rapidly, but the product (an oil) was a mixture of at least six components. The predominant product (ca. 60%) was tentatively assigned an ethoxylated one-winged bird-cage structure 7 based on spectroscopic data. The second most abundant product (ca. 20%) is believed to be the bisethoxylated analogue 8.

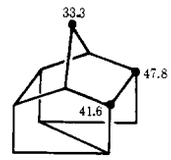


7 8



9 10

$AlBr_3$-catalyzed isomerization of the saturated fraction (2, 94%, 5, 6%) obtained from the Wolff–Kishner reduction of 3 gave in 2 h at room temperature in 86% yield a mixture consisting of three components: (D_3)-trishomocubane (1) (93%), as well as 2,4- and 2,8-ethanonoradamantane (9, 5%; 10, 2%). The two minor products were identified by comparison with authentic samples;[10a] both are believed to arise from tetracyclic 5. Treatment of pure 5 under the same condition affords a similar mixture of the ethanonoradamantanes.[10a,24] The composition of the product mixture from the saturated fraction (2 + 5) remained invariant under more vigorous conditions (higher temperatures, longer reaction times, and a large excess of catalyst). Preparative gas chromatography afforded a pure sample of 1, mp 150–152 °C. The IR and mass spectrum of 1 are identical with those reported by Underwood and Ramamoorthy.[3] At 60 MHz, there are only two ^1H NMR signals at δ 1.96 (8 H) and 1.34 (6 H).[3] The ^{13}C NMR spectrum (^1H decoupled) of 1 consists of three peaks, δ 47.8 (6 C), 41.6 (2 C), and 33.3 (3 C) ppm, as expected from the symmetry of 1; this data uniquely identifies 1 among all the possible saturated $C_{11}H_{14}$ isomers.[10b]



^{13}C chemical shifts

1

The second route to (D_3)-trishomocubane (1) also started from the pentacyclic diketone 3.[19] Reduction of 3 readily gave diol mixture 11a and 11b. Various reducing agents were investigated: lithium aluminum hydride in tetrahydrofuran (75% yield of the diol mixture, mp 260 °C),[13,19] aluminum 2-propoxide in 2-propanol (almost quantitative yield, mp 262

Table I. Empirical Force Field Calculations of Selected $C_{11}H_{14}$ Isomers and (D_3)-Trishomocubyl Cations $C_{11}H_{13}^+$

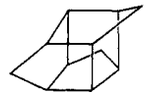
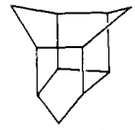
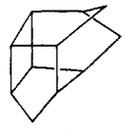
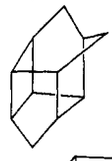
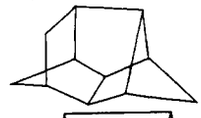
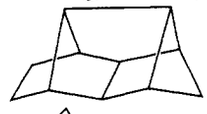
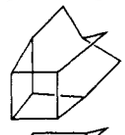
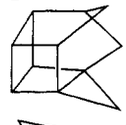
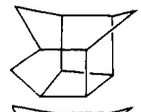
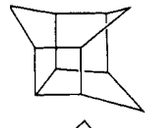
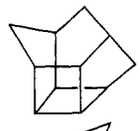
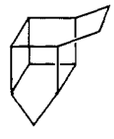
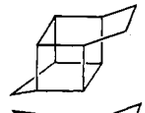
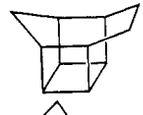
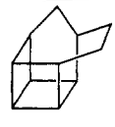
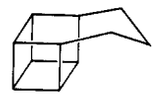
Registry no.	Structure		ΔH°_f, kcal/mol		Strain energy, kcal/mol	
			E^a	A^b	E^a	A^b
30114-56-8	Pentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (D_3)-Trishomocubane (**1**)^{c,d}		9.38^e	11.32	42.05	44.13
4421-32-3	Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (**2**)^{c,f}		19.62	21.93	52.29	54.74
63221-03-8	Pentacyclo[5.4.0.0^{2,5}.0^{3,10}.0^{4,8}]undecane (**21**)^c		18.82	22.00	51.49	54.81
63231-04-9	Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{4,8}]undecane^c		23.88	26.58	56.55	59.39
63231-05-0	Pentacyclo[6.3.0.0^{2,5}.0^{3,7}.0^{6,10}]undecane^c		32.46	37.18	65.13	69.99
63231-06-1	Pentacyclo[5.4.0.0^{2,5}.0^{4,11}.0^{6,10}]undecane		30.80	39.90	63.47	72.71
63231-07-2	Pentacyclo[5.3.1.0^{2,5}.0^{3,10}.0^{4,9}]undecane^c		47.49	53.12	80.16	85.93
63231-08-3	Pentacyclo[5.4.0.0^{3,10}.0^{5,9}.0^{8,11}]undecane^c		33.17	40.84	65.84	73.65
63231-09-4	Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,8}]undecane^c		33.92	37.74	66.59	70.55
63231-10-7	Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{4,9}]undecane^c		31.81	36.08	64.48	68.89
63231-11-8	Pentacyclo[5.4.0.0^{2,5}.0^{3,11}.0^{4,9}]undecane^c		43.36	46.22	76.03	79.03
62415-12-7	Pentacyclo[5.4.0.0^{2,5}.0^{3,11}.0^{4,8}]undecane (**22**)^{c,g}		40.99	43.82	73.66	76.63
63231-12-9	Pentacyclo[6.2.1.0^{2,7}.0^{3,10}.0^{6,9}]undecane^c		48.24	53.35	80.91	86.16
63231-13-0	Pentacyclo[5.4.0.0^{2,10}.0^{3,9}.0^{5,7}]undecane^c		53.91	60.79	86.58	93.60
63231-07-2	Pentacyclo[5.4.0.0^{2,10}.0^{5,9}.0^{8,11}]undecane^c		58.05	62.46	90.72	95.27

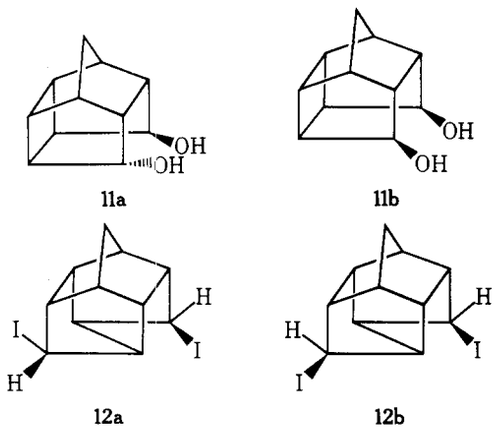
Table I (continued)

Registry no.	Structure		ΔH°_f, kcal/mol E^a	ΔH°_f, kcal/mol A^b	Strain energy, kcal/mol E^a	Strain energy, kcal/mol A^b
61304-39-0	Pentacyclo[5.4.0.0^{2,10}.0^{6,9}.0^{8,11}]undecane^c		85.34	90.14	118.01	122.95
63231-14-1	(D_3)-Trishomocubyl-1-cation^h		47.44		78.28	
63231-15-2	(D_3)-Trishomocubyl-2-cation^h		63.90		94.41	

^{a} Engler force field, ref 17a. ^{b} Allinger force field, ref 17b. ^{c} Trishomocubane isomer. ^{d} Present work; also see refs 3, 11, 13, and 14. ^{e} This was given incorrectly as 3.38 in ref 1. ^{f} Present work; also see ref 19. ^{g} Ref 24a. ^{h} For parameterization, see footnote 27.

°C), $NaAl(C_2H_5)_2H_2$ (almost quantitative yield, mp 269 °C), and sodium borohydride[19b] (quantitative yield, mp 240–250 °C). Common to all the reducing agents studied, the endo,endo isomer (**11a**) always predominates over the exo,endo isomer (**11b**) in the product mixtures.

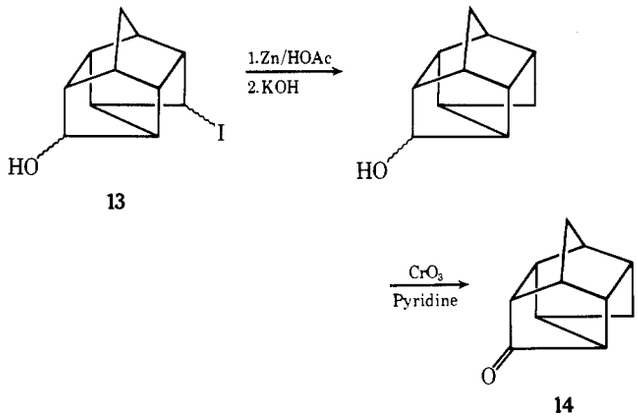
Treatment of this diol mixture **11** with aqueous HI at 160 °C for 20 h produced a mixture of *anti*- and *syn*-diiodotrishomocubane (**12a** and **12b**) in 93% yield. The skeletal rearrangement of **11** was first discovered by us by observing the conversion of the characteristic AB pattern of the methylene proton NMR signal of **11** into the broad singlet characteristic of the corresponding methylene protons in **12**.[1] The structure of diiodide **12a** has subsequently been established by x-ray analysis (see below).[14b] Deiodination of the iodide mixture **12**



11a **11b** **12a** **12b**

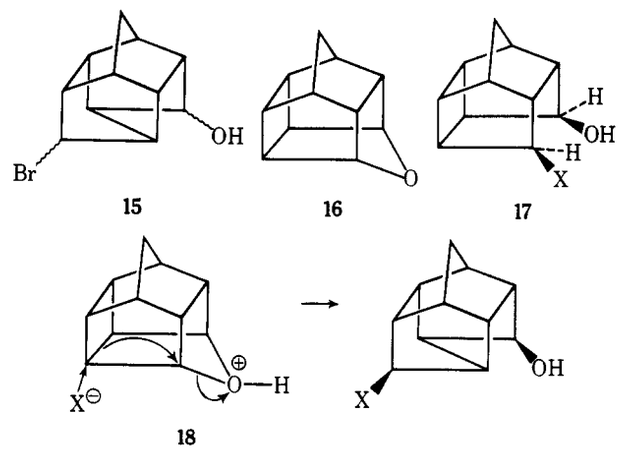
with zinc in acetic acid gave (D_3)-trishomocubane (**1**) in 93% yield. This second, three-step synthesis of **1** is more practicable than the first, but this would not be the case if methods could be found whereby the reduction **3** → **2** could be carried out more cleanly. The rearrangement of diol **11** into the (D_3)-trishomocubyl system can be effected with acid under milder conditions. At 100 °C for 2 h with aqueous HI, the diol mixture **11** is converted in excellent yield into iodotrishomocubyl alcohol (**13**).

A simple, three-step sequence converts **13** into trishomocubanone (**14**). This method is the third reported syntheses of **14**,[11a,12] but is more convenient in view of the readily available reagents required, the preparative simplicity and good overall yield. This route has been developed independently, and has been employed in the preparation of chiral (D_3)-trishomocubyl derivatives.[14c] Treatment of diol **11** in petroleum ether with hydrobromic acid at 100 °C gave bromo alcohol **15** together with the known hexacyclic ether **16**.[13,19a,d,25] Ether **16** gave diiodotrishomocubane **12** upon



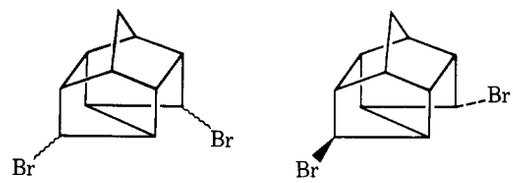
13 **14**

treatment with aqueous HI; **16** has been shown to be the primary product of the reaction of the diol **11** with strong aqueous acid.[13] Failure to observe unrearranged halo alcohol **17** from



15 **16** **17** **18**

the reaction mixture suggests the possibility of a concerted halide-displacement mechanism involving protonated ether **18**.[26] Prolonged treatment of diol **11** with refluxing hydrobromic acid gave dibromotrishomocubane **19**. The melting



19 **20**

point of this substance, 84.5 °C, is quite low compared to the reported value of 146–148 °C by Underwood and Rama-

Table II. Comparison of X-Ray with Empirical Force-Field Structures of (D_3)-Trishomocubane Derivatives (12a vs. 12c)[a]

Bond length, Å				Bond angle, deg			
Bond	Engler[b]	Allinger[c]	X-ray[d]	Angle	Engler[b]	Allinger[c]	X-ray[d]
C_3–C_4	1.516	1.522	1.52	$C_3C_4C_5$	91.9	92.7	93
C_5–C_9	1.540	1.543	1.56	$C_2C_3C_4$	107.4	106.7	106
C_5–C_6	1.527	1.530	1.51	$C_4C_3C_{10}$	103.0	102.3	103
C_6–C_7	1.518	1.521	1.53	$C_3C_{10}C_9$	99.0	99.0	99
C_7–C_8	1.522	1.525	1.53	$C_3C_2C_6$	103.0	103.4	103
C_1–C_8	1.528	1.527	1.53	$C_5C_6C_7$	102.0	102.0	100
C_7–C_{12}	1.532	1.531		$C_5C_9C_8$	102.7	103.9	104
C_8–C_9	1.542	1.544	1.57	$C_{10}C_{11}C_1$	91.3	92.9	96
				$C_8C_1C_{11}$	105.8	103.8	102
				$C_9C_8C_1$	98.3	98.6	100
				$C_6C_5C_9$	99.1	98.9	101
				$C_9C_{10}C_{11}$	108.3	106.6	106
				$C_2C_1C_{11}$	106.6	105.9	103
				$C_6C_2C_1$	103.7	104.4	104

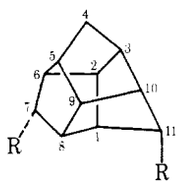
[a] X-ray structure of *syn*-4,7-diiodopentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (**12a**), ref 14b. Force-field calculations performed on *syn*-4,7-dimethylpentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (**12c**). For numbering, see figures in text. [b] Engler force field, ref 12a. [c] Allinger (1971) force field, ref 12b. The empirical force-field results are reproducible to 0.001 Å in bond lengths, and 0.1° in bond angles. [d] Ref 14b, bond lengths ±0.01 Å, bond angles ±1°.

moorthy.[3] However, Underwood's sample was prepared by bromine addition to homohypostrophene and is likely to be the anti isomer (**20**). In analogy with diiodo compound **12**, our material probably is a mixture of the syn and anti isomers. GLC analysis indicated two components (97:3). Concentrated hydrochloric acid gave essentially the same results as hydrobromic acid.

Force-Field Calculations. Both Engler[12a] and Allinger[12b] force fields (Table I) predict (D_3)-trishomocubane (**1**) to be 10.4 ± 0.2 kcal/mol (ΔH) more stable than **2**. Structural details given by the two force fields are also in good agreement. The three C–C bond lengths are calculated to be significantly different: C_1C_2 = 1.541 ± 0.002 Å, C_1C_8 = 1.528 ± 0.002 Å, and C_1C_{11} = 1.521 ± 0.003 Å (average of the results from both force fields).

All C–C–C bond angles are significantly smaller than tetrahedral; those at the three equivalent diastereotopic methylene groups are particularly strained (e.g., ∠ $C_1C_{11}C_{10}$ = 92.5 ± 0.5 °C). All angles (e.g. ∠ $C_1C_2C_3$) at bridgeheads C_2 and C_9, which lie on the threefold axis, are 103.4 ± 0.4°, while the angles at the six other equivalent bridgeheads are, e.g.: ∠ $C_1C_8C_7$ = 102.7 ± 0.3°, ∠ $C_1C_8C_9$ = 99.1 ± 0.1°, and ∠ $C_7C_8C_9$ = 106.8 ± 0.4°.

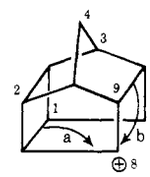
An x-ray structure of **12a** has been reported recently.[14b] A comparison of this x-ray structure and the calculated structure for dimethyltrishomocubane **12c** ($CH_3 \approx$ I in size) is given in



12a (R = I), **12c** (R = CH_3)

Table II. The structure calculated by the force fields is in good agreement. The largest deviations in C–C–C angles between the x-ray and calculated structures are naturally those in the close vicinity of the substituted sites, e.g.: ∠ $C_{10}C_{11}C_1$, ∠ $C_8C_1C_{11}$, and ∠ $C_2C_1C_{11}$. Cations at bridgehead positions C_1 and C_2 are expected to be highly strained. Force-field calculations for these cations are included in Table I.[27] Δ Strain values, as defined by ($\Delta H°_f$ cation − $\Delta H°_f$ hydrocarbon),[29] are 38 and 55 kcal/mol for 1- and 2-cation, respectively, both very high compared to familiar bridgehead cations,[29] and indicate that both bridgehead positions should be highly unreactive toward carbocation or free-radical formation. The same should be true of the methylene groups, which are 7-norbornane-like in character. Experimentally, we have found **1** to be particularly difficult to functionalize by a variety of substitution reactions which work well with adamantane.[30]

Mechanism of Aluminum Bromide Catalyzed Rearrangement of 2. The ease of rearrangement of **2** to (D_3)-trishomocubane (**1**) can be rationalized by considering the various cations derivable from **2**. Cations at C_3 and C_4 are



2$^+$

analogous to the 1- and 7-norbornyl cations, respectively, and should be quite unfavorable. Cations at C_1 and C_2 would appear to be even more unstable. A cation at C_9 may not be prohibitively strained, but all possible 1,2-alkyl shifts lead to products having four-membered rings (involving ca. 25 kcal/mol of strain increase). Thus, the most likely positively charged species to be involved is at C_8. Of the four possible 1,2-alkyl shifts from this cation, only paths a and b do not form new four-membered rings. The product from path b is **21** (Table I), whose carbon skeleton is, however, calculated to be 9 to 11 kcal/mol less stable than that of **1**; this path should not compete with path a which leads to (D_3)-trishomocubane (**1**) with considerable strain relief.

Experimental Section

Microanalyses were performed at the Combustion Analysis Center, Department of Pharmacy, Hokkaido University, and at Hoffmann-La Roche, Inc., Nutley, N.J. Mass spectra were taken on AEI MS-9 and Hitachi RMV-6D and -6E spectrometers. GC–MS analyses were performed on a DuPont 21-490 instrument. ^{1}H and ^{13}C NMR spectra were measured on Varian A-60A and CFT-20 spectrometers.

Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione (3). This compound was prepared according to literature methods,[19,21a] which involve Diels–Alder reaction of *p*-benzoquinone and cyclopentadiene to yield *endo*-tricyclo[6.2.1.0^{2,7}]undeca-4,9-dien-3,6-dione. Irradiation (sunlight) of the diene–dione gave **3** in 90% yield: mp 240.0–242.0 °C, lit.[19a] 245 °C; ^{1}H NMR δ 2.6–3.3 (br m, 8 H), 1.9–2.0 (2 H); IR 2980, 2930, 2870, 1775, 1730, 1460, 1200, and 1070 cm^{-1}; MS *m/e* 174 (M$^+$,

relative intensity 100%), 146 (26%), 145 (24%), 131 (15%), and 117 (55%).

Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (2). Freshly distilled diethylene glycol[20] (200 mL) was added to a 500-mL, one-neck, round-bottom flask equipped with a magnetic stirrer and an air condenser. The solution was heated to 80 °C and sodium metal (16.8 g, 0.73 g-atom) was carefully added in small pieces over 2 h. The pentacyclo diketone **3** (14.9 g, 0.086 mol) was then added with stirring followed by 35 mL of anhydrous hydrazine. The mixture was heated at 140 °C for 2 h and then the temperature was slowly raised to 210 °C over a 12-h period. During this time a clear white solid sublimed into the air condenser. The product was removed from the condenser with ether. The ether solution was washed twice with saturated aqueous NaCl solution and dried over anhydrous magnesium sulfate, and solvent was removed at reduced pressure to give 10.2 g of a white solid. Sublimation (50 °C, 0.01 Torr) gave 9.2 g of a mixture of **2** (60.2%), **4** (32.3%), **5** (4.3%), and two additional olefinic products of mass 146 (1.8 and 1.4%) as yet unidentified (analyses by GC–MS). The Wolff–Kishner reduction product was charged onto a 10% silver nitrate–silica gel column to separate the saturated (**2, 5**) and unsaturated fractions (**4** and the two olefins of mass 146). Elution with petroleum ether (1 L) gave the saturated compounds **2** and **5** (80% recovery). GLC analysis indicated a 94:6 ratio of **2:5**. The major fraction **2** was identified by its distinctive ^{1}H NMR, GC–MS and ^{13}C NMR (CD_3COCD_3):26.5, 33.2, 35.8, 41.8, 43.2, 46.2 ppm. GC–MS indicated **5** to have mass 148. Coinjection of **5** and the Wolff–Kishner reduction product of the known tetracyclic diketone (**6**)[22] (Silicone DC-550, 3 mm × 3 m, FFAP, 3 mm × 3 m) gave a single symmetrical peak.

Elution of the silver nitrate–silica gel column with diethyl ether (400 mL) gave the unsaturated fraction. The major component **4** was isolated by preparative GLC (6 mm × 9 m, FFAP 10%): mp 159–161 °C; ^{1}H NMR δ 6.0 (2 H, m), 2.33, 2.74 (6 H, m), 1.53 (6 H, br s); MS *m/e* 146 (12.5%), 80 (100%).

Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.23; H, 9.65.

Hydrogenation of **4** in *n*-hexane–ethanol solution with a catalytic amount of 5% Pd-on-charcoal gave known tetracycloundecane **5**, identical (^{1}H NMR, GLC) with the Wolff–Kishner reduction product of tetracyclic diketone **6**.[22] This confirmed **4** as the structure for the major component of the unsaturated fraction.

Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-diol (11). The endo, endo (**11a**) and exo, endo (**11b**) mixture of diols was prepared by reduction of diketone **3** with sodium borohydride in ethanol according to the method of Cookson et al.[19b] In order to reduce the intermediate ketol, a large excess of $NaBH_4$ was used, portions being added over a 2-day period with warming. The product (quantitative yield) shows two TLC spots on Chromar 500 with C_6H_6/ethyl acetate (1:1) eluent R_f 0.61 (endo, endo), 0.34 (exo, endo). These isomeric alcohols show very distinctive patterns in the 1000–1100 cm^{-1} infrared spectral region. Although unnecessary for practical purposes, the mixture can be conveniently separated by recrystallization from ether–chloroform, in which the endo,endo isomer (mp 276 °C) is more soluble than the exo, endo isomer (mp 273 °C). The reduction of **11** can be carried out in up to 96% yield by using $LiAlH_4$ in refluxing tetrahydrofuran.[13,19,31] The endo, endo isomer strongly predominated: ^{1}H NMR δ 6.07 (s, 2 H), 4.3 (s, 2 H), 2.2–2.8 (br m, 8 H), 1.03 and 1.63 ($J_{AB} \approx 10$ Hz, 2 H); IR 3200, 2950, 2860, 1480, 1270, and 1110 cm^{-1}; MS *m/e* 178 (M$^+$, relative intensity 21%), 160 (94%), 145 (15%), 131 (27%), 117 (34%), 95 (100%), and 94 (29%); ^{13}C NMR δ 71.52, 45.51, 42.96, 39.88, 38.32, and 34.52 ppm.

Modified Clemmensen Reduction of Diketone 3. To 200 mL of ether cooled to −10 °C and saturated with hydrogen chloride gas was added 5.0 g (0.029 mol) of diketone **3** and to this solution at this temperature was added 22.5 g (0.34 g-atom) of activated zinc in small portions during 1 h. After stirring at 0 °C for an additional hour, the ethereal solution was washed twice with 5% sodium bicarbonate solution and twice with saturated sodium chloride, and dried over magnesium sulfate. The clear yellow oil obtained by evaporation of the ether could be distilled at 85–90 °C (0.2 Torr).

The resulting clear oil showed at least six GLC peaks (SE 30, 3 mm × 2 m). The first (ca. 60%) and second (ca. 20%) most predominant peaks were collected by preparative GLC (FFAP 6 mm × 9 m). The major product, a liquid eluting earlier than the second peak, was assigned the 6-ethoxypentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane structure (**7**), on the basis of the following data: ^{1}H NMR δ 3.34 (2 H, q, J = 8 Hz), 2.2–1.3 (13 H, complex m), 1.11 (3 H, triplet, J = 8 Hz); mass spectrum *m/e* 190 (M$^+$, relative intensity 13%), 124 (49%), 123 (43%), 105 (100%); IR (neat) 2970, 2885, 1318, 1117 cm^{-1}.

Anal. Calcd for $C_{13}H_{18}O$: C, 82.08; H, 9.53. Found: C, 81.55; H, 9.44.

The collected sample of the second most abundant product was only 80% pure, but its ^{1}H NMR and mass spectrum indicate a bisethoxy structure analogous to that of the predominant product 8,11-bisethoxypentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (**8**). No further purification was attempted; ^{1}H NMR, δ 3.7–3.1 (4 H, complex m), 3.0–1.2 (14 H, complex m), 1.2–0.96 (6 H, complex m); mass spectrum *m/e* 234 (M$^+$, relative intensity 15%), 124 (42%), 123 (63%), 111 (68%), 95 (100%), 82 (94%).

(D_3)-Trishomocubane Diiodide (12) (4,7-Diiodopentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane). The pentacyclic diol mixture **11** (19.0 g, 0.107 mol) and 175 mL of 47% aqueous hydroiodic acid were added to a 1-L, one-neck, round-bottom flask equipped with a reflux condenser and magnetic stirrer. The mixture was heated at 160 °C with stirring for 20 h, cooled in ice, and cautiously neutralized with cold 3 N aqueous NaOH. The aqueous solution was extracted four times with ether. The ether extracts were combined, washed twice with saturated aqueous sodium bisulfite and three times with saturated aqueous NaCl and dried over anhydrous magnesium sulfate, and the solvent was removed at reduced pressure to yield 36.9 g (93%) of a white solid, mp 73.5–75.0 °C. Recrystallization from ethanol–methylene chloride (1:1) raised the melting point to 84.3–85.3 °C, but the material was still a mixture of anti (**12a**) and syn (**12b**) isomers (compare ref 13 and 14b). The ring structure of **12** was determined by Zn–AcOH dehalogenation to **1** (see below) and is consistent with spectral data: ^{1}H NMR (CCl_4) δ 3.9 (2 H, s), 3.1 and 2.3 (8 H, br m), 1.5 (2 H, s).

(D_3)-Trishomocubane (Pentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane) (1). (a) By Aluminum Bromide Isomerization of 2. Aluminum bromide (two to three times the weight of the hydrocarbon) was added to a carbon disulfide solution of the saturated fraction (**2**, 94%; **5**, 6%) from the modified Wolff–Kishner reduction of diketone **3**. The reaction mixture was stirred at room temperature for 2 h and then poured onto ice. The organic phase was separated and dried over anhydrous magnesium sulfate, and the solvent was removed. Care must be taken in removing the solvent because **1** is very volatile. The white solid that was obtained (88% yield) consisted of 93% (D_3)-trishomocubane (**1**) and 5 and 2%, respectively, of 2,4- and 2,8-ethanonoradamantane (**9** and **10**). Preparative GLC (6 mm × 9 m, FFAP) afforded an analytical sample of **1**, mp 150–152 °C, lit. 147–149,[3] 149–151,[14a] 150.5–152 °C.[16] IR and MS of **1** are identical with those reported by Underwood and Ramamoorthy.[3] The composition of the product mixture did not change when the mixture was refluxed with fresh $AlBr_3$ for 8 h, and then heated in a sealed tube at 100 °C for 0.5 h.

Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.58; H, 9.85.

(b) By Dehalogenation of the Diiodide (12). Glacial acetic acid (100 mL) and 10.0 g (0.025 mol) of trishomocubane diiodide (**12**) were placed in a 500-mL, one-neck, round-bottom flask fitted with a magnetic stirrer and reflux condenser. Activated zinc[32] (20.0 g, 0.306 g-atom) was added and the mixture was heated at reflux under stirring for 2.5 h. The mixture was filtered hot into 400 mL of cold water and cooled in ice for 2 h and the solid that separated was filtered, washed with cold water, and air-dried to give 3.4 g of **1** (93%). The hydrocarbon obtained is identical in all respects with **1** produced by $AlBr_3$ isomerization.

Iodotrishomocubanol (4-Iodopentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-7-ol (13). To 70 mL of freshly distilled (over hypophosphorous acid) hydroiodic acid (55–58%) in a 250-mL one-neck flask equipped with a reflux condenser and magnetic stirrer was placed 10.5 g (0.059 mol) of pentacyclic mixed alcohols **11**. After heating with stirring at 100 °C for 2 h, the mixture was cooled in ice and neutralized with cold 3 N sodium hydroxide. The aqueous layer was extracted four times with ether; the combined ether extracts were washed twice with saturated sodium bisulfite solution and twice with saturated sodium chloride solution. After drying over magnesium sulfate, the solvent was removed at reduced pressure to give a white solid, 7.5 g (44%), mp 134.2 °C. Recrystallization from methylene chloride–hexane gave a pure sample, mp 134.8 °C. Two epimeric iodo alcohols, mp 132 and 94 °C, have recently been characterized from a similar reaction.[14c] An improved yield (86%) has been obtained in repeating this procedure:[31] ^{1}H NMR δ 4.2 (s, 1 H), 3.9 (s, 1 H), 2.8–3.1 (br, m 2 H), 1.9–2.6 (7 H, br m), 1.35 (s, 2 H); IR 3350, 3290, 2960, 2900, 2870, 1470, 1360, 1310, 1290, 1200, 1110, and 1085 cm^{-1}; MS *m/e* 288 (M$^+$, relative intensity 26%), 161 (100%), 143 (86%).

Anal. Calcd for $C_{11}H_{13}IO$: C, 45.85; H, 4.56; I, 44.04. Found: C, 45.69; H, 4.58; I, 44.13.

4-(D_3)-Trishomocubanol (4-Pentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecanol). Iodotrishomocubanol (**13**) (5.0 g, 0.017 mol) and 55 mL of glacial acetic acid were placed in a 250-mL one-neck round-bottom

flask equipped with a reflux condenser, drying tube, and magnetic stirrer. With stirring, activated zinc[32] (25 g, 0.38 g-atom) was added in portions; the mixture was heated at the reflux temperature for 2 h. While hot, the solution was filtered into 150 mL of water. The aqueous solution was extracted four times with ether and the ether extracts were washed twice with 5% sodium bicarbonate solution and twice with saturated sodium chloride solution, and were dried over magnesium sulfate. The solvent was removed at reduced pressure to give 3.35 g of a light yellow oil. Infrared analysis indicated the presence of an acetate. This oil was treated with a solution of 3.3 g of potassium hydroxide dissolved in 80 mL of 50% aqueous ethanol and heated under reflux for 3 h. The solution resulting was cooled to room temperature, neutralized with 1.5 N sulfuric acid, and extracted three times with chloroform. The combined chloroform extracts were washed three times with saturated sodium chloride solution. After drying, the solvent was removed under reduced pressure to give 2.2 g (78%) of a white solid, mp 168.5 °C. Recrystallization from hexane gave 4-(D_3)-trishomocubanol, mp 170.0 °C. A melting point of 166 °C has been reported for the enantiomerically pure alcohol:[14c] ^{1}H NMR δ 4.17 (s, 1 H), 2.60 (br m, 1 H), 2.38 (s, 1 H), 1.8–2.2 (br m, 7 H), 1.25–1.5 (br m, 4 H); IR 3300, 2950, 2870, 1460, 1350, 1300, 1280, 1070 cm^{-1}; MS m/e 162 (M$^+$, relative intensity 45%), 144 (100%), 129 (28%), 96 (70%), 95 (88%), 79 (70%).

Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.41; H, 8.72.

(D_3)-Trishomocubanone (4-Pentacyclo[6.3.0^{2,6}.0^{3,10}.0^{5,9}]-undecanone (14). Pyridine (20 mL) was placed in a 50-mL Erlenmeyer flask equipped with a magnetic stirrer. With stirring and cooling, chromium trioxide (1.5 g) was added in small portions. To this CrO_3–pyridine complex was added 1.0 g (6.2 mmol) of 4-(D_3)-trishomocubanol dissolved in 7 mL of pyridine. After stirring at about 25 °C for 14 h, ether was added, the solution filtered, and the precipitated chromium salts were washed well with ether. The ether filtrate was washed twice with dilute hydrochloric acid, twice with saturated sodium chloride solution, and then dried over magnesium sulfate. When the solvent was removed under reduced pressure, 810 mg (82%) of a white solid, mp 160 °C, resulted. Sublimation (90 °C, 0.5 Torr) gave pure (D_3)-trishomocubanone (14): mp 163.5 °C (lit. 163–164 °C[11a]); ^{1}H NMR δ 2.4 (6 H), 1.8 (2 H), 1.6 (2 H), 1.5 (2 H); IR 2960, 2870, 1770, 1750, 1465, 1290, 1280, 1220, 1160, 890 cm^{-1}; MS m/e 160 (M$^+$, relative intensity 100%), 132 (30%), 117 (22%), 95 (25%), 91 (26%), 66 (34%).

4-Oxahexacyclo[5.4.1.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}]dodecane (16) and Bromotrishomocubanol (4-Bromopentacyclo[6.3.0.0^{2,6}.-0^{3,10}.0^{5,9}]undecan-7-ol) (15). In a 500-mL, one-neck round-bottom flask equipped with a reflux condenser were placed 10.0 g (0.042 mol) of pentacyclic diol mixture 11 and 150 mL of petroleum ether. Hydrobromic acid (48%) (150 mL) was added, the mixture was heated at 100 °C for 14 h and cooled to room temperature, the petroleum ether layer was separated and the aqueous phase extracted four times with petroleum ether, the combined organic extracts were washed twice with 5% aqueous sodium bicarbonate and twice with saturated sodium chloride solution and dried over magnesium sulfate, and the solvent was removed under reduced pressure to give 4.7 g of hexacyclic ether **16**, mp 217.6 °C (lit. 228–230 °C,[13] 190–191 °C[3,19a,25]).

Anal. Calcd for $C_{11}H_{12}O$: C, 82.45; h, 7.55. Found, C, 82.24; H, 7.59.

The aqueous extract was cooled in ice, neutralized with cold 3 N sodium hydroxide solution, and then extracted four times with chloroform. The combined organic extracts were washed three times with saturated sodium chloride solution and dried over magnesium sulfate, and the solvent was removed under reduced pressure to give a white solid, mp 117.6 °C. Sublimation (90 °C, 0.1 Torr) gave pure bromotrishomocubanol (15): mp 131.4 °C, lit. mp 128–130 °C;[16] ^{1}H NMR δ 4.20 (1 H, s), 4.09 (1 H, s), 2.90 (2 H, br m), 2.33 (3 H, br m), 2.03 (3 H, br m), 1.72 (1 H, concentration dependent, s), 1.42 (2 H, s); mass spectrum m/e 243, 241 (M$^+$, relative intensity 0.2%), 161 (100%), 143 (78%).

TLC (Chromar 500 hexane–ether 2:1) of hexacyclic ether (16), bromotrishomocubanol (15), and dibromotrishomocubane (19) gave R_f values, respectively, 0.81, 0.45, and 0.95.

Anal. Calcd for $C_{11}H_{13}BrO$: C, 54.79; H, 5.43; Br, 33.14. Found: C, 54.61; H, 5.44; Br, 33.24.

Diiodotrishomocubane (12) from Ether 16. In a 25-mL, one-neck flask equipped with magnetic stirrer and reflux condenser were placed 10 mL of freshly distilled (over hypophosphorous acid) hydroiodic acid (55–58%) and 500 mg (3.12 mmol) of hexacyclic ether **16**. After heating with stirring at the reflux temperature for 20 h, the solution was cooled in ice and neutralized with cold 3 N sodium hydroxide. The aqueous layer was extracted three times with ether and the combined organic phase was washed three times with saturated sodium chloride solution. After drying over magnesium sulfate, solvent removal in vacuo gave a light orange solid which was recrystallized from ethanol–methylene chloride (1:1) to give **12**, mp 82 °C. Its infrared spectrum was identical with that of **12** prepared from the pentacyclic diol mixture **11**.

Dibromotrishomocubane (4,7-dibromopentacyclo[6.3.0.-0^{2,6}.0^{3,10}.0^{5,9}]undecane) (19). The pentacyclic diol mixture **11** (5.0 g, 0.028 mol) and 50 mL of 48% aqueous hydrobromic acid were combined in a 100-mL, one-neck, round-bottom flask equipped with reflux condenser and magnetic stirrer. This mixture was heated with stirring at the reflux temperature for 14 h. During this time, the solid which collected in the reflux condenser was returned to the flask by turning off the cooling water briefly. The dark mixture resulting was cooled in ice and neutralized with cold 3 N aqueous NaOH. The aqueous layer was extracted four times with ether. The ether extracts were combined, washed three times with saturated sodium chloride, and dried over anhydrous magnesium sulfate. Solvent removal at reduced pressure gave a dark gum. When this was dissolved in hot ethanol and treated with decolorizing charcoal (Darco G-60), white crystals of **19** were obtained by crystallization, mp 84.5 °C (sealed tube).

GLC analysis (SE 30, 3 mm × 2 m) revealed two barely resolved peaks (3:97): ^{1}H NMR δ 4.10 (2 H, s), 3.00 (2 H, br s), 2.3 (6 H, br m), 1.51 (2 H, s); MS m/e 306, 304, 302 (M$^+$, relative intensity 1.4, 2.7, 1.2%), 224, 222 (58, 60%), 143 (64%), 79 (100%).

Anal. Calcd for $C_{11}H_{12}Br_2$: C, 43.45; H, 3.98; Br, 52.57. Found: C, 43.34; H, 3.97; Br, 52.19.

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Registry No.—**3**, 2958-72-7; **4**, 56061-34-8; **5**, 59015-02-0; **7**, 63231-16-3; **8**, 63231-17-4; **11a**, 56143-86-3; **11b**, 56143-85-2; **12a**, 58383-17-8; **12c**, 56061-35-9; **13**, 63268-41-7; **14**, 56061-32-6; **15**, 63231-18-5; **16**, 4378-84-1; **19**, 30401-93-5; 4-(D_3)-trishomocubanol, 63268-42-8.

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Dimerizations of Electronegatively Substituted Dienes

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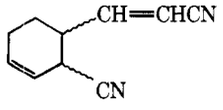
Structures have been assigned to four Diels–Alder dimers of 1-cyanobutadiene and two dimers of 2-fluorobutadiene by NMR techniques. Diradical stabilities can account for the structural change in the dimers of 2-fluorobutadiene and 2-cyanobutadiene. A new eight-membered ring dimer of 2-cyanobutadiene has been isolated, and some chemistry of the cyanobutadienes and their dimers is described.

The major product of the thermal dimerization of butadiene, 4-vinylcyclohexene, is derived from a 2 + 4 cycloaddition.[1] Minor amounts of the 2 + 2 product 1,2-divinylcyclobutane and its Cope rearrangement product 1,5-cyclooctadiene are also found.[1] 2-Methylbutadiene[2] and 2-chlorobutadiene[3] dimerizations have also been studied in detail. Before modern spectroscopic tools for structure identification were available, the dimerizations of 1-[4] and 2-cyanobutadienes[5] and 2-fluorobutadiene[6] were reported.

In this paper we present spectral evidence which revises the structures of the 1-cyanobutadiene and 2-fluorobutadiene dimers. A new 2-cyanobutadiene dimer has been isolated and characterized, and some chemistry of the cyanobutadiene dimers is presented.

1-Cyanobutadiene Dimerization. Heating 1-cyanobutadiene either neat or in *N*-methylpyrrolidinone solution at a pot temperature of 200 °C until no further reflux occurs followed by vacuum distillation gives a mixture of four major 1-cyanobutadiene dimers (**1a–d**). Gas chromatography on a 1,4-cyclohexane–dimethanol succinate column revealed many more minor peaks, all of which had the empirical formula of cyanobutadiene dimers by GC/MS. Only the four major products were characterized. Heating either pure *cis*- or pure *trans*-1-cyanobutadienes gives two major products from each with no crossover.



1a–d

Pure samples of two of the four isomers could be isolated. Isomer **1a**, the lowest boiling, could be purified by distillation. Isomer **1b** crystallized from the crude liquid on extended standing. Isomers **1c** and **1d** could be concentrated by preparative GC but not completely separated. By ^{1}H NMR isomers **1a** and **1b** have cis-substituted external double bonds while the other two are trans.

The ring configurations are inferred from the general pattern of the NMR spectrum of the aliphatic region. The cis isomers should be flexible and invert between two relatively equally populated twist chair conformations. The conformation of the trans isomers should be biased toward a diequatorial orientation. Isomers **1a** and **1d** show only two multiplets for the CH_2CH_2 protons while isomers **1b** and **1c** show three resonances in the ratio 2:1:1. The former are assigned to cis isomers and the latter two to trans. The four dimers are present in essentially equal amounts when formed from mixed *cis*- and *trans*-1-cyanobutadienes.

Palladium-catalyzed hydrogenation at room temperature