Table V. Crystallographic Data and Intensity Collections of $[WHClBr(\leftarrow N{=}N(\rightarrow BPh_3)H)(PMe_2Ph)_3]\cdot CH_2Cl_2$

a, Å	12.095 (5)
b, Å	18.148 (8)
c, Å	10.975 (5)
α, deg	101.03 (1)
β, deg	90.59 (1)
γ, deg	100.52 (1)
V, Å^3	2322.2 (18)
Z	2
d(calcd), g cm^{-3}	1.507
d(found), g cm^{-3}	1.497
systematic absences	none
space group	$P\bar{1}$
F(000)	1068
cryst dimens, mm	0.23 × 0.31 × 0.33
μ, cm^{-1}	37.9
scan	2θ–ω
2θ limits, deg	$0° < 2\theta < 50°$

parameters, and agreement indexes in successful refinements; (b) the clear and distinct location of 51 unique hydrogen atoms in a difference Fourier synthesis. The unit cell dimensions were obtained by least-squares refinement of 12 high-angle reflections in diverse regions of reciprocal space. The pertinent crystal information and details of data are shown in Table V. With $Z = 2$ and the molecular weight of this complex, the calculated density is 1.507 g cm^{-3} compared with a measured density of 1.497 g cm^{-3} obtained by flotation in a $ZnCl_2$ aqueous solution.

Data collection was carried out by using a Rigaku four-circle diffractometer. Background counts were measured in both ends of the scan range with both the counter and crystal stationary. The intensities of four standard reflections were measured every 50 reflections and were found to decrease uniformly and linearly about 4% during the course of data collection. The observed intensities were modified to correct for this apparent isotropic crystal decomposition.

All possible reflections with $2\theta \geq 50°$ were collected by using Mo Kα radiation (0.7107 Å) monochromatized by graphite. Of the 8667 reflections collected, 6895 reflections had $F_o > 3\sigma(F_o)$, were considered observed, and were used in subsequent calculations. Lorentz and polarization corrections were applied.

Solution and Refinement of the Structure.[19] The structure was solved using a Patterson synthesis to locate the tungsten atom. Subsequent refinements and difference Fourier syntheses were used to locate the remaining atoms, including 51 hydrogen atoms. The structure was refined by using block-diagonal least-squares techniques. The isotropic model converged to R indexes of $R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.094$ and $R_w = [w(|F_o| - |F_c|)^2/w|F_o|^2]^{1/2} = 0.111$. During the refinements, the quantity minimized was $\sum w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure amplitudes and the weights, w, are taken as $w = 1$ for $|F_o| > 30$. Atomic scattering factors were taken from Cromer and Waber's tabulation.[20a] The anomalous dispersion terms for W, P, Br, and Cl were included in Fc.[20b]

The position indicated by X1 was shown to be occupied by Cl (70%) and Br (30%), and the position X(2) by Cl (30%) and Br (70%), respectively, on the basis of the following results: (a) the distinction of X(1) and X(2) from Br or Cl in a difference Fourier synthesis; (b) the minimized R index in this ratio of Cl and Br in refinements. At this stage, the structure was refined by block-diagonal least-squares by using anisotropic thermal factors for nonhydrogen atoms. A difference Fourier synthesis was computed to reveal clear peaks of hydrogen atoms. The final cycle was then carried out including the positional parameters of the above hydrogen atoms, the isotropic temperature parameters of which were fixed at 6.0 Å^2. The final refinement resulted in final values of 0.044 and 0.059 for R and R_w, respectively.

Acknowledgment. This work was kindly supported by the Grant-in-Aid for a special research project (No. 411106) from the Ministry of Education. We thank Professor T. Miyazawa for recording the 270-MHz ^{1}H NMR spectra.

Supplementary Material Available: A listing of structure factor amplitudes of $[WHClBr(\leftarrow N{=}N(\rightarrow BPh_3)H)(PMe_2Ph)_3]\cdot CH_2Cl_2$ (31 pages). Ordering information is given on any current masthead page.

(19) The UNICS program for the HITAC 8700/8800 computers was employed at Tokyo University Computer Center: Sakurai's RSLC-3 lattice constants program, Ueda's PAM1 Patterson and minimum function program, Iwasaki's ANSFR-2 Fourier synthesis program, Ashida's HBLS-4 block-diagonal least-squares and Fourier program, Ashida's DAPH distance, angle, etc. program, and modified Johnson's ORTEP thermal ellipsoid plot program.

(20) (a) Cromer, D. T.; Waber, J. T. "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2a. (b) Cromer, D. T.; Liberman, D. *Ibid.*, Table 2.3.1.

Tricyclo[4.2.0.0^{1,4}]octane

Kenneth B. Wiberg,* Larry K. Olli, Nancy Golembeski, and Richard D. Adams*

Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06520. *Received June 12, 1980*

Abstract: The synthesis of tricyclo[4.2.0.0^{1,4}]octane-3-carboxylic acid (**15**) was effected via a diazoketone ring contraction of tricyclo[5.2.0.0^{1,5}]nonan-4-one. The structure was determined by X-ray crystallographic analysis of the *p*-bromoanilide derived from **15**. The parent hydrocarbon (**2**) may be formed via conversion of **15** to the 3-acetoxy compound and photolysis of the acetate in HMPA–water. Thermolysis of **2** occurs at 140–180 °C with an E_a = 36.5 kcal/mol and forms a mixture of products which could be derived from initial cleavage of one of the internal C–C bonds. The solvolyses of the 3-*endo*- and -*exo*-3,5-dinitrobenzoates derived from **2** strongly resemble those of the corresponding bicyclo[2.2.0]hexyl-2 dinitrobenzoates with regard both to rates and products. The energies of **2** and of some related hydrocarbons have been estimated by using molecular mechanics.

Planar tetravalent carbon has been the subject of several recent investigations.[1] In the absence of stabilizing substituents, planar methane has been calculated to be 150 kcal/mol less stable than tetrahedral methane.[2] Although this large destabilization makes it clear that such a simple planar carbon species will not be achieved, it is still of interest to have information concerning the potential function for flattening the bonds about a carbon.[2a] One experimental approach would be to synthesize and examine the tetracyclic hydrocarbon, **1**, which has been called "windowpane" or "fenestrane"[3] and which is properly named tetracyclo-[5.1.1.0^{3,8}.0^{5,8}]nonane. On the basis of models and the calculations on methane,[2a] we estimate that the angle C_1–C_8–C_5 should be

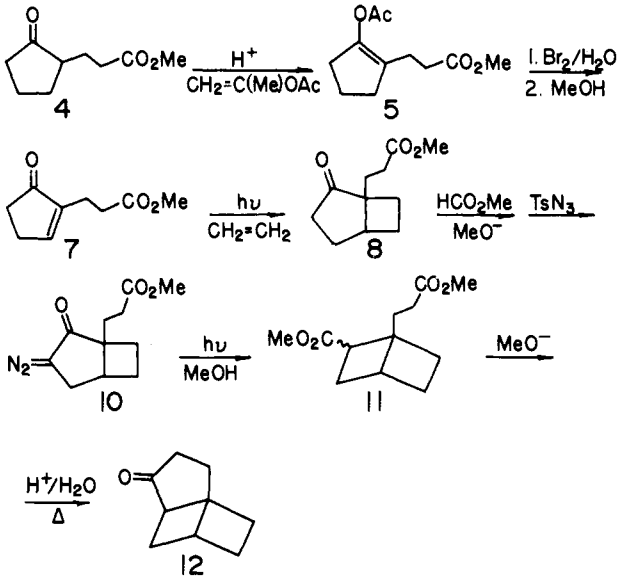
(1) (a) Hoffmann, R.; Alder, R. G.; Wilcox, C. F., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 4992. (b) Collins, J. B.; Dill, J. D.; Jemmis, E. D.; Apeloig, Y.; Schleyer, P. v. R.; Seeger, R.; Pople, J. A. *Ibid.* **1976**, *98*, 5419.

(2) (a) Wiberg, K. B.; Ellison, G. B.; Wendoloski, J. J. *J. Am. Chem. Soc.* **1976**, *98*, 1212. (b) Shavitt, I., footnote 6b in ref 1b. (c) Minkin, V. I.; Minyaev, R. M.; Zakharov, I. I.; Avdeev, V. I. *J. Org. Chem. USSR (Engl. Transl.)* **1978**, *14*, 3.

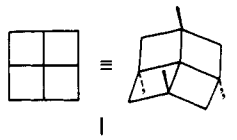
(3) Georgian, V.; Saltzman, M. *Tetrahedron Lett.* **1972**, 4315.

0002-7863/80/1502-7467$01.00/0

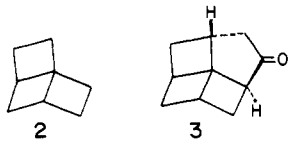
Scheme I



about 140°, and the strain at the central carbon should be on the order of 40 kcal/mol.



In view of the thermal reactivity of some bicyclo[2.2.0]hexanes and related compounds,[4] our first synthetic goal was the preparation of the related tricyclo[4.2.0.0^{1,4}]octane (**2**). We wished

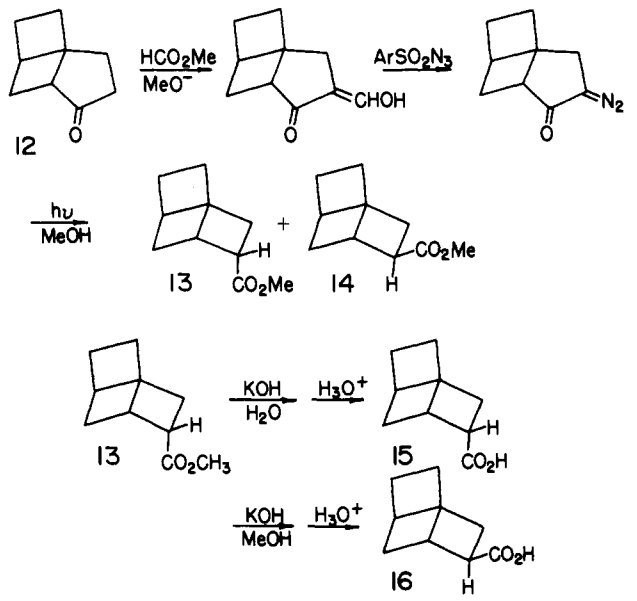


to determine its stability and geometry. The latter is important in indicating whether or not the tetracyclic ketone, **3**, would have a relatively unstrained five-membered ring. If this were the case, its synthesis would appear feasible, and it might reasonably be expected to undergo a diazoketone ring contraction to a derivative of **1**. We shall now describe the preparation of **2** and record some of its properties.

2-(2-Carbomethoxyethyl)cyclopentanone (**4**) was readily prepared by the reaction of *N*-(1-cyclopenten-1-yl)pyrrolidine with methyl acrylate.[5] The conversion of **4** to its enol acetate (**5**) was effected by treatment with isopropenyl acetate (Scheme I). Addition of bromine in a chloroform–water mixture gave the bromoketone (**6**). Elimination of hydrogen bromide from **6** proceeded readily in methanol solution, giving 2-(2-carbomethoxyethyl)-2-cyclopentenone (**7**). The elimination was acid catalyzed and did not occur when a small amount of base was added to the solvent. The photochemical addition of ethylene to **7** gave 1-(2-carbomethoxyethyl)bicyclo[3.2.0]heptan-2-one (**8**) in a 51% yield from the enol acetate (**5**).

The reaction of **8** with methyl formate gave the formyl derivative (**9**) which on treatment with tosyl azide gave the diazoketone (**10**). The photochemical Wolff rearrangement in methanol solution led to the formation of the diester (**11**) in an 83% yield based on **8**. This was a mixture of epimers as indicated by the NMR spectrum. Although it was likely that the major isomer had the

Scheme II



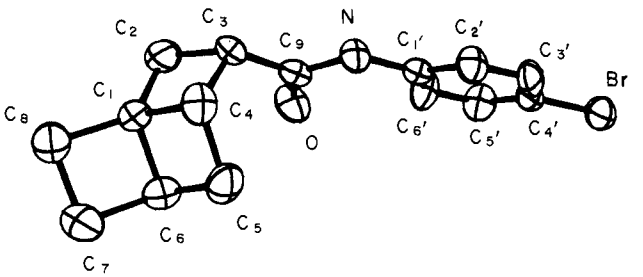
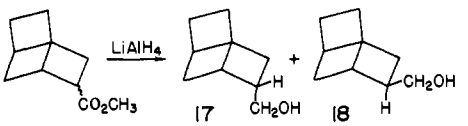


Figure 1. ORTEP diagram of the *p*-bromoanilide of *endo*-tricyclo-[4.2.0.0^{1,4}]octane-3-carboxylic acid showing 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity.

two ester functions trans to each other, epimerization occurred in base since **11** underwent a Dieckmann condensation to give a keto ester which was directly subjected to acid-catalyzed hydrolysis giving the tricyclic ketone, **12**.

The ketone, **12**, was converted to the diazoketone which was subjected to the photochemical Wolff rearrangement in methanol to give the tricyclic esters **13** and **14** in a 3:1 ratio (Scheme II) Hydrolysis in aqueous potassium hydroxide solution gave the acid, **15**, corresponding to the predominant ester as a solid, mp 79 °C. Hydrolysis in methanolic potassium hydroxide led mainly to the acid, **16**, corresponding to the minor ester component. It appears that epimerization is more rapid than hydrolysis in the homogeneous methanolic solution, whereas epimerization did not occur when aqueous base was used.

The esters, **13** and **14**, could not readily be separated by gas chromatography. However, a mixture containing mainly **14** was formed by treatment of **16** with diazomethane. The ^{1}H NMR spectra of the two esters could be obtained by subtracting the spectrum of one mixture from the other. Lithium aluminum hydride reduction of the esters gave the primary alcohols **17** and **18** which could be separated by GC (eq 1). Their ^{13}C NMR spectra indicated only saturated carbons, and H–^{13}C coupling constants in the range 133–140 Hz. This suggests that all of the ring carbons are part of cyclobutane rings[6] and provides strong evidence for the assigned structures.



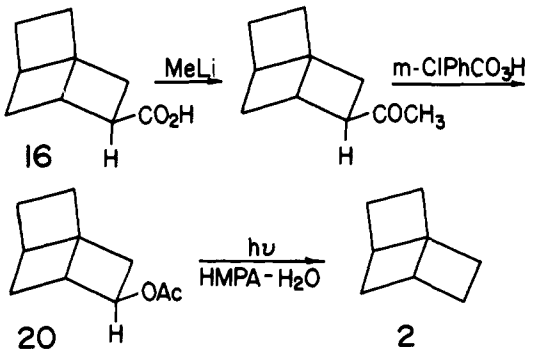
(1)

(4) Methyl 4-chlorobicyclo[2.2.0]hexane-1-carboxylate undergoes thermolysis at 100 °C (Scherer, K. V. *Tetrahedron Lett.* **1966**, 5685) and dimethyl bicyclo[2.2.0]hexane-1,4-dicarboxylate undergoes thermolysis at 75 °C (Bloomfield, J. J.; Owsley, D. C. *J. Org. Chem.* **1971**, *36*, 3768).

(5) Stork, G.; Landesman, H. K. *J. Am. Chem. Soc.* **1956**, *78*, 5128.

(6) Foote, C. S. *Tetrahedron Lett.* **1963**, 579. Hill, E. A.; Roberts, J. D. *J. Am. Chem. Soc.* **1967**, *89*, 2047.

Scheme III



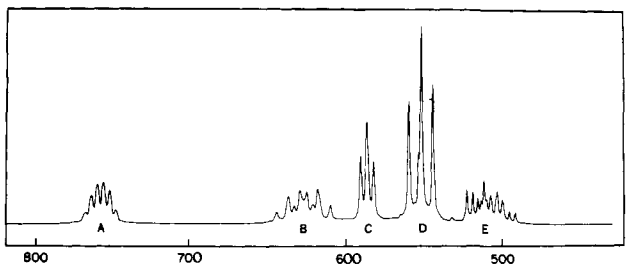
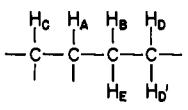


Figure 2. NMR spectrum (270 MHz) of tricyclo[4.2.0.0^{1,4}]octane. The frequencies are in hertz, downfield from internal Me_4Si.

In order to establish the structure definitively, we converted the acid **15** to the *p*-bromoanilide, **15a**, and the latter was subjected to an X-ray crystallographic analysis. The result is shown in Figure 1. The assigned structure is confirmed, and the solid acid **15** is shown to have the endo configuration. A detailed discussion of the structural parameters will be postponed until a later section where they will be considered in the context of the strain energies expected for **1** and **3**.

The conversion of the acids **15** and **16** to the parent hydrocarbon, **2**, made use of the photochemical reduction of acetates in hexamethylphosphoramide–water.[7] The exo acid, **16**, was converted to the methyl ketone via methyllithium and then to the acetate, **20**, with *m*-chloroperbenzoic acid (Scheme III). When the endo acid, **15**, was used, epimerization occurred, leading to a mixture of the *endo*-(**19**) and *exo*-(**20**) acetates. Photolysis in HMPA–water led to the formation of **2** as the only product. Both the exo and endo acetates could be used in the reduction.

The hydrocarbon, **2**, had a remarkably simple high-field NMR spectrum (Figure 2). Integration of the five bands (labeled A–E) gave area ratios of 1:1:1:2:1, respectively. Decoupling experriments indicated that protons leading to band C were coupled only to the A protons. The A protons were coupled to the B and E protons in addition to C. The B protons were coupled to A, D, and E, whereas the D protons were coupled to only B and E. This requires the structural unit I. This structure accounts for only half of



I

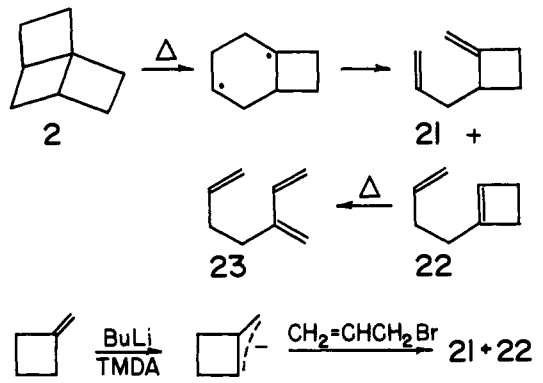
the protons, and therefore it must be doubled in a symmetrical fashion. Since there are no olefinic protons, this allows only two structures, A and B. The former structure is ruled out by the observed chemical shifts.[8] Thus, in this case, the structure of the hydrocarbon could be determined by using the NMR spectral data.[9,10]

Table I. NMR Parameters (Hz) for Tricyclo[4.2.0.0^{1,4}]octane (2)

Chemical Shifts		
$\nu_A = 760.3$	$\nu_D = 553.1^a$	
$\nu_B = 628.5$	$\nu_{D'} = 551.1^a$	
$\nu_C = 588.0$	$\nu_E = 507.8$	
Coupling Constants		
$J_{AB} = 7.94$	$J_{AC} = 4.22$	$J_{AD} = -0.06$
	$J_{AD'} = -0.11$	$J_{AE} = 3.93$
$J_{BC} = 0.0$	$J_{BD} = 8.32$	$J_{BD'} = 7.43$
	$J_{BE} = -12.02$	
$J_{CD} = 0.0$	$J_{CD'} = 0.0$	$J_{CE} = 0.0$
$J_{DD'} = -10.0^b$	$J_{DE} = 6.83$	$J_{D'E} = 9.71$

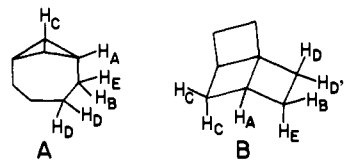
[a] The difference in chemical shift between D and D' is not well determined by the analysis and is a function of the value chosen for $J_{DD'}$. [b] Fixed at −10.0 which is a typical value for a gem coupling constant for a cyclobutane ring.[11]

Scheme IV



Computer simulation of the five-spin spectrum obtained by decoupling the C protons led to the parameters in Table I. Here, 53 calculated lines were assigned to the 23 observed frequencies, and a final root-mean-square error of 0.17 Hz was found. This is quite satisfactory since many of the observed bands resulted from several calculated lines, all of which were assigned to the center of the observed band. The coupling constant between H_D and $H_{D'}$[11] as well as the chemical shift difference between these protons have relatively high uncertainty since the spectrum is not sensitive to these values.

The ^{13}C spectrum also is in accord with the assigned structure. Only five lines were observed in the proton decoupled spectrum. The low-field line (51.4 ppm) was found to arise from a quaternary carbon. The undecoupled spectrum indicated three methylene



(7) Deshayes, H.; Pête, J. P.; Portella, C.; Scholler, D. *Chem. Commun.* **1975**, 439. Ernst, B.; Ganter, C. *Helv. Chim. Acta* **1978**, *61*, 1107.

(8) The spectrum would be expected to be similar to that of tricyclo[4.1.0.0^{2,7}]heptane: Moore, W. R.; Ward, H. R.; Merritt, R. E. *J. Am. Chem. Soc.* **1961**, *83*, 2019. Here, the chemical shifts were δ 1.45, 1.67, and 2.42 which are at higher field than those for **2**. It is known that cyclobutyl protons are downfield from normal aliphatic protons.[6,11]

(9) It may be noted that whereas the chemical shift difference between H_D and $H_{D'}$ is quite small, that between H_B and H_E is much larger (120 Hz, 0.44 ppm). This is probably due to anisotropic effects associated with the C_2–C_3 and C_5–C_6 bonds (ApSimon, J. W.; Craig, W. G.; Demarco, P. V.; Mathieson, D. W.; Saunders, L.; Whalley, W. B. *Tetrahedron* **1967**, *23*, 2339). The β,γ C–C bonds are symmetrically located with respect to H_D and $H_{D'}$ and should lead to no net difference in chemical shift. On the other hand, this is not the case with H_B and H_E and one might expect a chemical shift difference on the order of that between axial and equatorial protons in cyclohexane ($\Delta\delta = 0.5$ ppm: Jensen, F. R.; Noyce, D. S.; Sederholm, C. H.; Berlin, A. J. *J. Am. Chem. Soc.* **1960**, *82*, 1256; **1962**, *84*, 386).

(10) The endo isomer leads to a larger chemical shift for the proton at the substitution site (i.e., an exo proton) than the exo isomer, and the shapes of the bands are characteristic (Table VIII).

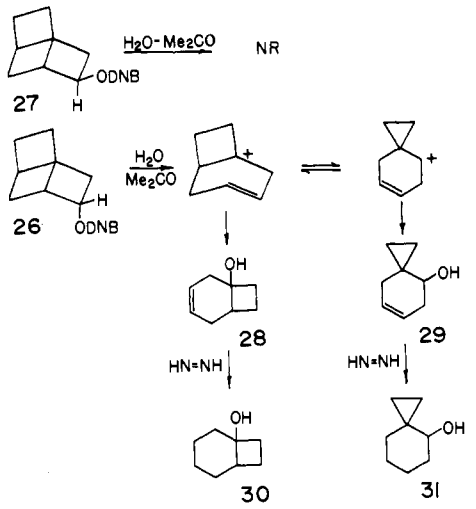
(11) Fleming, I.; Williams, D. H. *Tetrahedron* **1967**, *23*, 2747. Wiberg, K. B.; Barth, D. E.; Pratt, W. E. *J. Am. Chem. Soc.* **1977**, *99*, 4286 (reported values in the range −10 to −13 Hz).

Table II. Thermolysis of Tricyclo[4.2.0.0^{1,4}]octane

compd	medium	temp, °C	k, s^{-1}	E_a, kcal/mol	log A	ref
tricyclo[4.2.0.0^{1,4}]octane	*o*-dichlorobenzene	140	7.53×10^{-6}	36.3[a]	14.1	
		150	2.25×10^{-5}			
		160	6.25×10^{-5}			
		170	1.50×10^{-4}			
bicyclo[2.2.0]hexane	gas phase	170[b]	4.37×10^{-5}	36.0	13.4	13
cyclobutane	gas phase	170[b]	1.54×10^{-16}	65.5	16.5	15

[a] $\Delta H^{\ddagger} = 35.5$ kcal/mol; $\Delta S^{\ddagger} = 3.3$ eu. [b] Calculated from the reported activation parameters.

Scheme V



groups and one methine group. The proton ^{13}C coupling constants were between 131 and 137 Hz which is typical for cyclobutane rings.[6]

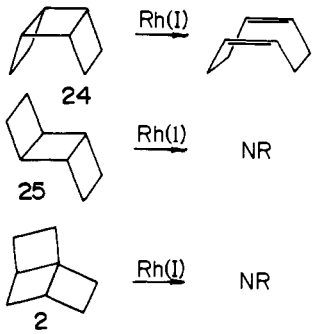
One of the reasons for preparing **2** was to determine its thermal stability. In *o*-dichlorobenzene solution, it was found to undergo thermolysis at temperatures around 180 °C and led to two products, **21** and **23**. The NMR spectra suggested the structures given in Scheme IV. Both could be formed via initial cleavage to a 1,4 diradical which could undergo ring opening in two ways leading to **21** and **22**. Cyclobutenes undergo ring cleavage under these conditions, and **22** would be expected to give **23**. A mixture of **21** and **22** could be formed by alkylating the anion derived from methylenecyclobutene[12] with allyl bromide. Thermolysis of **22** was found to give a triene identical with the second product derived from the thermolysis of **2**.

The rate constants for the thermolysis were determined at several temperatures, giving the data in Table II. The activation energy was found to be 36.5 kcal/mol, which is essentially the same as that for bicyclo[2.2.0]hexane.[13] It appears that the third cyclobutane ring has essentially no effect on the reactivity of the other two rings. This suggests that the third ring does not affect the strain energy of the first two rings or of the diradical formed by cleaving the central bond. It is also possible that it affects the energies of these species by an equal amount.

We have been able to determine the strain energies of some small ring compounds via reaction calorimetry.[14] It was hoped that a catalytic process could be found which would effect the isomerization of **2** to a simpler substance quickly and in quantitative yield. Previous studies of bicyclo[2.2.0]hexane suggest that only rhodium(I) derivatives have promise for this reaction.[16]

The reaction of **2** with the rhodium norbornadiene chloride dimer was examined. However, no reaction was observed at 50 °C after 32 h.

The low reactivity of **2** may be related to the difference in reactivity of *syn*- and *anti*-tricyclo[4.2.0.0^{2,5}]octanes (**24** and **25**).[17] Here, the syn isomer is reactive whereas the anti compound is not. One explanation for the difference in reactivity is steric hindrance to oxidative insertion into a bridging bond in **25**. The reaction of **2** would involve a similar steric interaction, and this may account for its low reactivity (eq 2–4).



The solvolytic reactions of derivatives *exo*- and *endo*-bicyclo[2.2.0]hexan-2-ols are of some interest.[18] The latter is more reactive than the former by a factor of about 10^7, and this results from the participation of the central bridge in the reaction of the endo isomer.[19] In order to see if an additional cyclobutane ring might affect the reaction, we converted the acetates **19** and **20** to the corresponding alcohols and then to the 3,5-dinitrobenzoates (**26** and **27**). The exo derivative, **27**, was inert to heating in 80% acetone. On the other hand, the endo derivative, **26**, underwent reaction and gave a rate constant of 4.7×10^{-5} s^{-1} at 70 °C. In order to be able to compare this constant with that for *endo*-bicyclo[2.2.0]hexyl-2 3,5-dinitrobenzoate which was studied in 60% acetone ($k = 2.0 \times 10^{-3}$ s^{-1} at 70 °C), we multiplied it by the conversion factor 29,[20] giving 1.4×10^{-3} s^{-1}. Thus, the rate constants are essentially the same.

The solvolysis led to two products which could be separated by GC. Both had olefinic protons, and one had high-field protons which are usually associated with a cyclopropane ring. A reasonable course for the reaction is indicated in Scheme V, and the spectra of the products are in accord with structures **28** and **29**. In order to establish the structures, we reduced the compounds by using diimide, giving **30** and **31** which were identified by comparison with authentic samples.[21]

(12) Wilson, S. R.; Phillips, L. R. *Tetrahedron Lett.* **1975**, 3047.
(13) Steel, C.; Zand, R.; Hurwtiz, P.; Cohen, S. G. *J. Am. Chem. Soc.* **1964**, *86*, 679.
(14) Wiberg, K. B.; Connon, H. A.; Pratt, W. E. *J. Am. Chem. Soc.* **1979**, *101*, 6970. Wiberg, K. B.; Connon, H. A. *Ibid.* **1976**, *98*, 5411. Wiberg, K. B.; Burgmaier, G. J.; Lupton, E. C., *Jr. Ibid.* **1969**, *91*, 3372. Wiberg, K. B.; Fenoglio, R. A. *J. Am. Chem. Soc.* **1968**, *90*, 3395.
(15) Beadle, P. C.; Golden, D. M.; King, K. D.; Benson, S. W. *J. Am. Chem. Soc.* **1972**, *94*, 2943.
(16) Sohn, M.; Blum, J.; Halpern, J. *J. Am. Chem. Soc.* **1979**, *101*, 2694. Lockman, B., unpublished results, this laboratory.
(17) Wristers, J.; Brener, L.; Petitt, R. *J. Am. Chem. Soc.* **1970**, *92*, 7499. Cf.: Gleiter, R.; Heilbronner, E.; Hekman, M.; Martin, H. D. *Chem. Ber.* **1973**, *106*, 28 for an mo explanation for the difference in reactivity between **24** and **25**.
(18) McDonald, R. N.; Reineke, C. E. *J. Org. Chem.* **1967**, *32*, 1878; *J. Am. Chem. Soc.* **1965**, *87*, 3020. McDonald, R. N.; Davis, G. E. *J. Am. Chem. Soc.* **1972**, *94*, 5078.
(19) For other examples of exo/endo rate differences caused by orbital participation see: Wiberg, K. B.; Hess, B. A., Jr.; Ashe, A. J. III In "Carbonium Ions"; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1972; Vol. III.
(20) This estimate is based on the Y values of the solvents: Grunwald, E.; Winstein, S. *J. Am. Chem. Soc.* **1948**, *70*, 846.
(21) Wiberg, K. B.; Hiatt, J. E.; Hsieh, K. *J. Am. Chem. Soc.* **1970**, *92*, 544.

Table III. Final Fractional Atomic Coordinates with Estimated Standard Deviations for *p*-$BrC_6H_4N(H)COC_8H_{11}$ (15a)

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
Br	0.19849 (7)	0.05047 (2)	0.12346 (5)	C(9)	1.0525 (5)	0.2444 (1)	0.1577 (3)
O	1.0227 (4)	0.2416 (1)	0.0320 (2)	H(2a)	1.365 (4)	0.291 (1)	0.050 (3)
N	0.9376 (4)	0.2136 (1)	0.2447 (3)	H(2b)	1.500 (4)	0.303 (1)	0.184 (3)
C(1)	1.2976 (5)	0.3783 (1)	0.1573 (3)	H(3)	1.254 (3)	0.262 (1)	0.314 (2)
C(2)	1.3727 (5)	0.3098 (2)	0.1431 (4)	H(4)	1.169 (4)	0.366 (1)	0.356 (2)
C(3)	1.2145 (5)	0.2843 (1)	0.2310 (3)	H(5a)	0.876 (4)	0.357 (1)	0.148 (3)
C(4)	1.1572 (5)	0.3555 (2)	0.2635 (3)	H(5b)	0.912 (4)	0.416 (1)	0.213 (2)
C(5)	0.9805 (5)	0.3847 (2)	0.1758 (4)	H(6)	1.070 (4)	0.393 (1)	−0.032 (3)
C(6)	1.1140 (6)	0.4073 (2)	0.0686 (4)	H(7a)	1.142 (6)	0.499 (2)	0.167 (3)
C(7)	1.2064 (6)	0.4756 (2)	0.0946 (4)	H(7b)	1.221 (5)	0.499 (2)	−0.002 (4)
C(8)	1.3991 (6)	0.4440 (2)	0.1601 (4)	H(8a)	1.503 (4)	0.447 (1)	0.108 (3)
C(1')	0.7674 (5)	0.1759 (1)	0.2107 (3)	H(8b)	1.460 (4)	0.461 (1)	0.249 (3)
C(2')	0.6457 (5)	0.1644 (2)	0.3125 (3)	H(N)	0.971 (4)	0.224 (1)	0.328 (3)
C(3')	0.4770 (6)	0.1271 (2)	0.2873 (4)	H(2')	0.675 (4)	0.184 (1)	0.398 (3)
C(4')	0.4321 (5)	0.1015 (2)	0.1584 (3)	H(3')	0.393 (5)	0.124 (1)	0.355 (3)
C(5')	0.5516 (5)	0.1116 (2)	0.0558 (4)	H(5')	0.526 (4)	0.093 (1)	−0.028 (3)
C(6')	0.7205 (5)	0.1487 (2)	0.0814 (3)	H(6')	0.800 (4)	0.155 (1)	0.014 (3)

Table IV. Intramolecular Bond Distances with Estimated Standard Deviations for *p*-$BrC_6H_4N(H)COC_8H_{11}$ (15a) in Angstroms

	(a) To Nonhydrogen Atoms		
C(1)-C(2)	1.515 (3)	C(9)-N	1.368 (3)
C(1)-C(4)	1.552 (3)	C(9)-O	1.223 (2)
C(1)-C(6)	1.571 (3)	N-C(1')	1.412 (3)
C(1)-C(8)	1.524 (4)	C(1')-C(2')	1.376 (3)
C(2)-C(3)	1.536 (4)	C(2')-C(3')	1.388 (3)
C(3)-C(4)	1.559 (3)	C(3')-C(4')	1.369 (3)
C(4)-C(5)	1.534 (4)	C(4')-C(5')	1.367 (4)
C(5)-C(6)	1.525 (4)	C(5')-C(6')	1.388 (3)
C(6)-C(7)	1.555 (4)	C(1')-C(6')	1.387 (3)
C(7)-C(8)	1.550 (4)	C(4')-Br	1.916 (2)
C(3)-C(9)	1.504 (3)	C-C(ring mean)	1.379 (4)
	(b) To Hydrogen Atoms		
C(2)-H(2a)	0.98 (2)	C(7)-H(7b)	1.07 (3)
C(2)-H(2b)	0.93 (2)	C(8)-H(8a)	0.91 (2)
C(3)-H(3)	0.94 (2)	C(8)-H(8b)	0.99 (2)
C(4)-H(4)	0.92 (2)	N-H	0.85 (2)
C(5)-H(5a)	0.93 (2)	C(2')-H(2')	0.93 (2)
C(5)-H(5b)	0.89 (2)	C(3')-H(3')	0.92 (2)
C(6)-H(6)	1.04 (2)	C(5')-H(5')	0.91 (2)
C(7)-H(7a)	0.99 (3)	C(6')-H(6')	0.90 (2)

Table V. Intramolecular Bond Angles with Estimated Standard Deviations for *p*-$BrC_6H_4N(H)COC_8H_{11}$ (15a) in Degrees

	(a) Involving Nonhydrogen Atoms		
C(1)-C(2)-C(3)	90.3 (2)	C(6)-C(1)-C(4)	88.2 (1)
C(1)-C(4)-C(3)	88.0 (2)	C(6)-C(1)-C(8)	90.5 (2)
C(1)-C(4)-C(5)	90.8 (2)	C(3)-C(9)-O	123.0 (2)
C(1)-C(6)-C(5)	90.5 (2)	C(3)-C(9)-N	113.7 (2)
C(1)-C(6)-C(7)	88.1 (2)	N-C(9)-O	123.3 (2)
C(1)-C(8)-C(7)	90.0 (2)	C(9)-N-C(1')	128.4 (2)
C(2)-C(1)-C(4)	90.9 (2)	N-C(1')-C(2')	118.0 (2)
C(2)-C(1)-C(6)	124.4 (2)	N-C(1')-C(6')	123.2 (3)
C(2)-C(1)-C(8)	132.5 (2)	C(1')-C(2')-C(3')	121.3 (3)
C(2)-C(3)-C(4)	89.8 (2)	C(2')-C(3')-C(4')	118.9 (3)
C(2)-C(3)-C(9)	116.7 (2)	C(3')-C(4')-C(5')	121.0 (3)
C(3)-C(4)-C(5)	117.2 (2)	C(4')-C(5')-C(6')	119.9 (3)
C(4)-C(1)-C(8)	124.7 (2)	C(5')-C(6')-C(1')	120.0 (3)
C(4)-C(3)-C(9)	115.1 (2)	C(6')-C(1')-C(2')	118.9 (3)
C(4)-C(5)-C(6)	90.5 (2)	C(3')-C(4')-Br	118.9 (2)
C(5)-C(6)-C(7)	115.2 (3)	C(5')-C(4')-Br	120.1 (2)
C(6)-C(7)-C(8)	90.1 (2)		
	(b) Involving Hydrogen Atoms		
C(1)-C(2)-H(2a)	118 (1)	C(6)-C(7)-H(7b)	110 (1)
C(1)-C(2)-H(2b)	114 (1)	C(9)-C(7)-H(7a)	109 (2)
C(3)-C(2)-H(2a)	114 (1)	C(9)-C(7)-H(7b)	114 (1)
C(3)-C(2)-H(2b)	113 (1)	H(7a)-C(7)-H(7b)	120 (2)
H(2a)-C(2)-H(2b)	107 (2)	C(1)-C(8)-H(8a)	116 (2)
C(2)-C(3)-H(3)	119 (1)	C(1)-C(8)-H(8b)	119 (1)
C(4)-C(3)-H(3)	110 (1)	C(7)-C(8)-H(8a)	114 (2)
C(9)-C(3)-H(3)	106 (1)	C(7)-H(8)-H(8b)	119 (1)
C(1)-C(4)-H(4)	126 (1)	H(8a)-C(7)-H(8b)	110 (2)
C(3)-C(4)-H(4)	114 (1)	C(9)-N-H(N)	110 (2)
C(5)-C(4)-H(4)	116 (1)	C(1')-N-H(N)	121 (2)
C(4)-C(5)-H(5a)	117 (1)	C(1')-C(2')-H(2')	118 (1)
C(4)-C(5)-H(5b)	118 (1)	C(3')-C(2')-H(2')	120 (1)
H(5a)-C(5)-H(5b)	98 (2)	C(2')-C(3')-H(3')	119 (2)
C(1)-C(6)-H(6)	123 (1)	C(4')-C(3')-H(3')	122 (2)
C(5)-C(6)-H(6)	115 (1)	C(4')-C(5')-H(5')	122 (2)
C(7)-C(6)-H(6)	115 (1)	C(6')-C(5')-H(5')	119 (2)
C(6)-C(7)-H(7a)	110 (2)	C(5')-C(6')-H(6')	120 (1)
		C(1')-C(6')-H(6')	120 (1)

It is clear that the reaction proceeds via a course similar to that for the corresponding bicyclo[2.2.0]hexyl derivative and that the third ring has little effect on the course or rate of the reaction. The results obtained both in the thermolysis and solvolysis suggest that the third ring has little effect on the energy of the parent bicyclo[2.2.0]hexane ring system.

Structural Studies

The molecular structure of the *p*-bromoanilide of tricyclo-[4.2.0.0^{1,4}]octane-3-carboxylic acid (**15a**) as determined by X-ray crystallography is shown in Figure 1. The values of fractional atomic coordinates which were obtained are listed in Table III. Bond distances and angles are listed in Tables IV and V.

The internal cyclobutane ring, C_1–C_4–C_5–C_6, is rigorously planar with no atom deviating from the least-squares plane by more than 0.003 (3) Å. The external rings, C_1–C_2–C_3–C_4 and C_1–C_6–C_7–C_8, are slightly puckered with dihedral angles of 10.8 and 12.6°, respectively. Simple substituted cyclobutane rings are generally puckered and exhibit dihedral angles of approximately 23–33°.[22] However, in fused ring systems, the amount of puckering may be substantially reduced. For cis-fused rings, the puckering is generally smaller and dependent on the tendency of the fusion to maintain a cis arrangement.[22] Dihedral angles of 8–9° have been reported for bicyclo[2.2.0]hexane[23] and the *syn*- and *anti*-tricyclo[4.2.0.0^{2,5}]octanes.[24]

Although all C–C bond distances compare favorably with the average value (1.550 (2) Å) found for cyclobutanes by X-ray crystallographic methods,[22] it may be significant that the two shortest distances, C_1–C_2 = 1.515 (3) Å and C_1–C_8 = 1.524 (4) Å, are both associated with the quaternary carbon, C_1. These bonds also define the edges of the angle C_2–C_1–C_8 which at 132.5° is the largest in the molecule. Indeed, all six bond angles around C_1 at 132.5°, 124.7, 124.4, 90.9, 90.5, and 88.2° differ substantially from the tetrahedral value.

The amido and aromatic groups appear to be normal in all respects. The amido group exists in the endo conformation with

(22) Cotton, F. A.; Frenz, B. A. *Tetrahedron* **1974**, *30*, 1587. Moriarty, R. M. *Top. Stereochem.* **1974**, *8*, 271.

(23) Anderson, B.; Srinivasan, R. *Acta Chem. Scand.* **1972**, *26*, 3468.

(24) Anderson, B.; Fernolt, L. *Acta Chem. Scand.* **1970**, *24*, 445.

Table VI. Parameters Used in Molecular Mechanics Calculations[a]

(A) Cyclobutane Rings		
C-C bonds	$k = 4.20$[b]	$r_e = 1.55$ Å
C-H bonds	$k = 4.68$	$r_e = 1.09$ Å
C-C-C angle (ring)	$k = 2.20$	$\theta_e = 90.0°$
C-C-C angle (ext)	$k = 0.80$	$\theta_e = 114°$
C-C-H angle	$k = 0.50$	$\theta_e = 114°$
torsion	$k = 0.0130$	
(B) Other Rings		
C-C bonds	$k = 4.40$	$r_e = 1.53$ Å
C-H bonds	$k = 4.45$	$r_e = 1.09$ Å
C-C-C angles	$k = 0.80$	$\theta_e = 109.5°$
C-C-H angles	$k = 0.60$	$\theta_e = 109.5°$
torsion	$k = 0.0146$	

[a] Nonbonded interactions are those used by Boyd.[25] [b] k is in mdyn/Å^2.

respect to the C_1–C_4–C_5–C_6 ring. The plane of the aromatic ring is twisted 17.1° from that of the amido group. All of the hydrogen atoms have been located and refined. While the bond distances and angles for the hydrogen atoms of the tricyclooctyl unit show considerable scatter, those of the aromatic ring appear to be quite normal. In the crystal there is a weak intermolecular hydrogen bond between the hydrogen attached to nitrogen and a carbonyl oxygen at a neighboring molecule, H···O = 2.11 (2) Å. There were no other anomalously short intermolecular contacts.

We should like to use these data in order to make an estimate of the additional strain present in the tetracyclic compounds, **1** and **3**. We have done this by making use of molecular mechanics. For a normal cyclobutane ring, the C–C and C–H bond lengths were taken as 1.55 and 1.09 Å, respectively, and the C–C–C and H–C–C bond angles were taken as 90 and 113.3°, respectively.[25] Assigning the torsional function to the C–C–C–C angle with a barrier of 3 kcal/mol and using the force constants and nonbonded constants in Table VI, we found the equilibrium puckering angle to be 33° and the planar form to have the higher energy by 1.5 kcal/mol. These values are in good agreement with those obtained experimentally[26] and give a reasonable description of the forces acting upon the ring.

The parameters were used to estimate the geometries and energies of the compounds shown in Figure 3. The calculation leads to a puckered *cis*-bicyclo[2.2.0]hexane (B) with a torsional angle of 15° which may be compared with the observed 11°.[23] The calculated strain energy is twice that for cyclobutane as has been found in other molecular mechanics calculations.[27] The calculated geometry for tricyclo[4.1.0.0^{1,4}]octane (F) has slightly puckered cyclobutane rings (7°) and a C–C–C angle at the junction of the three rings of 130° as compared to the observed 132.5°. The smaller calculated angle suggests that the bond angle strain at this point is overestimated.[28] Thus, the strain energies for compounds D–I probably represent upper limits. The calculated energy for F is slightly greater than three times the strain energy of a cyclobutane ring, which appears reasonable.

A quantity of particular interest is the increase in strain on removing one methylene group. The increase in strain on going from cyclopentane to cyclobutane is 20 kcal/mol.[29] The calculated increase in strain on going from E to F or from G to H is only slightly higher than this value. The conversion of C to D is calculated to have a significantly greater increase in strain, although the strain in D is probably overestimated. A strikingly large increase in calculated strain is found for the conversion of H to I. The calculated structure of I is characterized by very large deviations from normal angles and very large angle strain. The strain energy is almost certainly considerably overestimated.[28]

The problem with molecular mechanics calculations for compounds such as D and I as well as other small ring hydrocarbons such as bicyclo[1.1.1]pentane and bicyclo[2.1.1]hexane is the lack of information on bond angle deformation potentials both for angles much less than tetrahedral (75–100°) and much larger than tetrahedral (115–140°). We are now trying to obtain information on these potential functions so that the energies of these and related compounds may be more satisfactorily estimated.

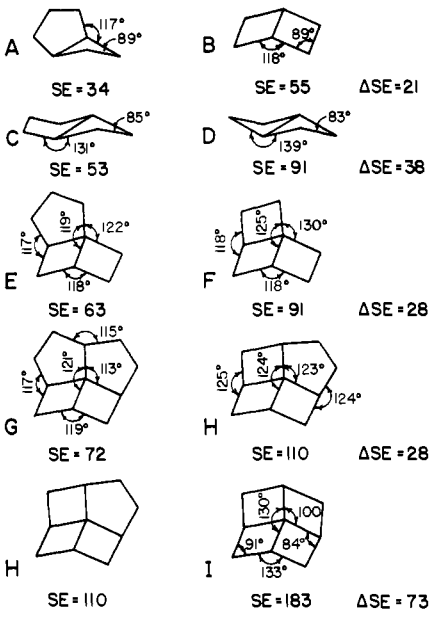


Figure 3. Strain energies and bond angles for some cyclic hydrocarbons.

Experimental Section

NMR spectra were obtained in $CDCl_3$ solution with internal Me_4Si as the reference. A Brucker HX270 spectrometer was used. The infrared spectra were obtained by using a Nicolet 7199 FT-IR spectrometer. Melting points were uncorrected.

2-(2-Carbomethoxyethyl)-2-cyclopentenone (7). In a 250-mL flask equipped with a magnetic stirrer and a 6 in. vacuum-jacketed distillation column packed with glass helices were placed 75 g (0.44 mol) of 2-(2-carbomethoxyethane)cyclopentanone (**4**), 90 g (0.90 mol) of isopropenyl acetate, and 2.0 mL of sulfuric acid. The solution was stirred and heated until slow distillation occurred. The reaction was monitored by GC (6 ft, 15% SE-30 on Anakrom ABS, 160 °C) and was continued until complete conversion had occurred. Distillation gave 73.4 g (79%) of the enol acetate (**5**), bp 110–112 °C (0.2mmHg). The IR spectrum (neat) had a band at 1740 cm^{-1}; the ^{1}H NMR spectrum ($CDCl_3$) had bands at δ 3.65 (s, 3 H), 2.75 (s, 6 H), 2.13 (s, 3 H), and 1.88 (m, 4 H).

A mixture of 36.7 g (0.13 mol) of **5**, 184 mL of chloroform, 321 mL of water, and 18.4 g of calcium carbonate was stirred while being cooled in an ice bath. A solution of 9.6 mL of bromine in 30 mL of chloroform was added dropwise until the bromine no longer was decolorized. After 1 h the layers were separated and the aqueous layer was washed with chloroform. The combined organic layers were washed with saturated sodium bisulfate solution, saturated sodium bicarbonate solution, and brine which was followed by drying and concentration. The resulting crude bromoketone (**6**) was immediately dissolved in 367 mL of methanol and heated under reflux. After 15–20 min, the solution became yellow. It was heated for another 10 min which led to an orange solution. The methanol solution was concentrated and the residue dissolved in methylene chloride. After being dried over magnesium sulfate, the solution was concentrated. The crude product was passed through neutral alumina

(25) Cyclobutane rings have been treated by molecular mechanics in two ways. One approach uses a normal equilibrium C–C–C bond angle, and adjusts the bending force constant so that it decreases with increasing angle (Allinger, N. L. *Adv. Phys. Org. Chem.* **1976**, *13*, 1). A second approach uses 90° as the equilibrium C–C–C bond angle in cyclobutanes along with the spectroscopically determined bending force constant and adds a constant destabilization factor for each cyclobutane ring (Chang, S.; McNally, D.; Shary-Tehrany, S.; Hickey, M. J.; Boyd, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 3109). The second approach is more successful in reproducing the observed torsional angles and has been used in this investigation.

(26) Stone, J. M. R.; Mills, I. M. *Mol. Phys.* **1970**, *18*, 631. Malloy, T. B., Jr.; Lafferty, W. J. *J. Mol. Spectrosc.* **1975**, *54*, 20.

(27) Baas, J. M. A.; van der Graaf, B.; van Rantwijk, F.; van Veen, A. *Tetrahedron* **1979**, *35*, 421.

(28) If the bending potential function for large angular deformations were somewhat weaker, the angle between the rings would increase, allowing the other angles to relax. This would lead to an overall decrease in energy.

(29) Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: London, 1970.

by using 3:7 methylene chloride–ether. The yellow fractions contained 28.4 g of crude **7** which decomposed on attempted distillation. The IR spectrum (CCl_4) had bands at 1740, 1705, and 1430 cm^{-1}, the ^{1}H NMR spectrum ($CDCl_3$) had bands at δ 7.35 (m, 1 H), 3.66 (s, 3 H), 2.52 (b s, 5 H), and 2.39 (m, 3 H).

1-(2-Carbomethoxyethyl)bicyclo[3.2.0]heptan-2-one (8). A solution of 28.4 g (0.17 mol) of crude **7** in 525 mL of acetone was placed in a vessel containing a vacuum-jacketed, water-cooled, Pyrex immersion well. The solution was cooled to −78 °C while ethylene was bubbled through it and then was irradiated by using a 450-W Hanovia mercury lamp. The reaction was monitored by GC (6 ft, 15% SE-30 on Anakrom ABS, 160 °C). Upon completion (42 h), the solution was concentrated and stirred with an excess of sodium bisulfite solution for 4 h to remove any aldehydic cleavage product and unreacted starting material. The mixture was extracted with ether, and the latter was washed with sodium bicarbonate solution and with brine, dried, and concentrated. The crude material was passed through a short alumina column with ether and distilled, giving 17.2 g (51% from **5**) of **8**, bp 85–87 °C (0.15mmHg). The IR carbonyl band (CCl_4) was at 1735 cm^{-1}. The ^{1}H NMR spectrum ($CDCl_3$) had bands at δ 3.66 (s, 3 H), 2.74 (m, 2 H), 2.26 (m, 4 H), and 1.98 (m, 7 H); the ^{13}C NMR spectrum ($CDCl_3$, ^{1}H decoupled) had bands at δ 173.0, 51.2, 50.9, 38.7, 36.5, 29.1, 28.7, 26.9, 26.0, and 21.1. Mass spectrum molecular ion: *m/e* 196. Anal. ($C_{11}H_{16}O_3$): C, H.

Methyl 1-(2-Carbomethoxyethyl)bicyclo[2.2.0]hexane-2-carboxylate (11). To a dry 100-mL three-necked flask equipped with a mechanical stirrer and addition funnel was added under nitrogen 30 mL of dry ether, 0.73 g (0.015 mol) of a 50% sodium hydride dispersion in oil, and 6 drops of methanol. The mixture was stirred in an ice bath and an ether solution of 3.0 g (0.015 mol) of **8** and 4.7 mL of methyl formate was added dropwise. The reaction mixture was stirred overnight as the ice in the bath melted. Methanol (2 mL) was added, and stirring was continued for 15 min. Water was added, and the layers were separated. The ether layer was washed with water, and the aqueous solutions were combined and washed with ether. The aqueous layer was acidified to pH 1 with 6 N hydrochloric acid and extracted with ether. The ether extract was washed with brine, dried, and concentrated, giving 3.8 g of the crude α-formyl ketone, **9**.

The crude sample of **9** was dissolved in 25 mL of methylene chloride, and 3.0 g of triethylamine was added. The solution was cooled in an ice-salt bath while being stirred. A methylene chloride solution containing 15 mmol of tosyl azide was added dropwise. The solution was stirred for 2 h while the ice in the bath melted. Potassium hydroxide solution (12 mL, 6%) was added, and stirring was continued for 15 min. The layers were separated, and the aqueous layer was washed with methylene chloride. The combined organic solutions were washed twice with 1.5% potassium hydroxide solution and once with water and dried. The diazoketone (**10**) was purified via chromatography using activity I basic alumina and 1:1 pentane–ether, giving 3.05 g of **10**. The IR spectrum (neat) had bands at 2076, 1738, and 1650 cm^{-1}.

The diazoketone was dissolved in 85 mL of methanol, cooled in an ice bath, and irradiated with a 450-W Hanovia mercury lamp. The reaction was monitored by UV (255 nm) and was complete in 4 h. The reaction mixture was concentrated, and the mixture of esters (**11**) was isolated by molecular distillation, giving 2.87 g (83% yield based on **8**) of product. The IR spectrum (neat) had bands at 1735 and 1435 cm^{-1}; the ^{1}H NMR spectrum ($CDCl_3$) had bands at δ 3.69 (s, 6 H), 3.20 (m, 1 H), 2.15–2.65 (m, 7 H), and 1.70–2.10 (m, 4 H). Mass spectrum molecular ion: *m/e* 226. Anal. ($C_{12}H_{18}O_4$): C, H.

Tricyclo[5.2.0.0^{1,5}]nonan-4-one (12). To a 2-L three-necked flask equipped with a mechanical stirrer, addition funnel, and reflux condenser and swept with nitrogen was added 22 g (0.92 mol) of sodium hydride washed free of mineral oil with anhydrous ether, 600 mL of dry tetrahydrofuran, and 5 mL of methanol. To the stirred suspension was slowly added 200 mL of a tetrahydrofuran solution containing 51.8 g (0.23 mol) of methyl 1-(2-carbomethoxyethyl)bicyclo[2.2.0]hexane-2-carboxylate (**11**). The mixture was heated to 65 °C for 6 h and then stirred overnight at room temperature. While being cooled in an ice bath, the mixture was quenched by adding ether containing methanol to destroy excess sodium hydride, followed by water. The mixture was acidified to pH 2 with 6 N hydrochloric acid and extracted with ether. The ether solution was washed with saturated sodium bicarbonate solution and with brine, dried, and concentrated by using a rotary evaporator to give crude methyl tricyclo[5.2.0.0^{1,5}]nonan-4-one-3-carboxylate. The IR spectrum (neat) had bands at 1750, 1725, 1658, and 1610 cm^{-1}; the ^{1}H NMR spectrum ($CDCl_3$) had bands at δ 3.74 (s, 3 H), 3.28–3.48 (m, 1 H), 2.84–3.06 (m, 1 H), and 1.80–2.84 (m, 9 H). Mass spectrum molecular ion: *m/e* 194. Anal. ($C_{11}H_{14}O_3$): C, H.

The crude ester was stirred with 300 mL of 3 N hydrochloric acid and heated to 60 °C overnight. The solution was cooled and extracted with ether. The ether extract was washed with saturated sodium bicarbonate, dried, and concentrated with the use of a rotary evaporator. Distillation gave 23.0 g (74%) of tricyclo[5.2.0.0^{1,5}]nonan-4-one; bp 35 °C (0.4mmHg). The IR spectrum (neat) had a band at 1732 cm^{-1}; the ^{1}H NMR spectrum ($CDCl_3$) had bands at δ 2.70–2.81 (m, 1 H), 2.55–2.70 (m, 1 H), 2.39–2.55 (m, 1 H), 2.14–2.39 (m, 6 H), 2.02–2.14 (m, 1 H), 1.87–2.02 (m, 1 H), and 1.59–1.76 (m, 1 H). Mass spectrum molecular ion: *m/e* 136. Anal. ($C_9H_{12}O$): C, H.

Methyl Tricyclo[4.2.0.0^{1,4}]octane-3-carboxylates (13, 14). To a dry 100-mL three-necked flask equipped with a mechanical stirrer, addition funnel, and nitrogen inlet was added 50 mL of dry ether, 0.88 g (22 mmol) of a 61% sodium hydride dispersion in oil, and six drops of methanol. The mixture was stirred in an ice bath, and an ether solution of 3.0 g (22 mmol) of tricyclo[5.2.0.0^{1,5}]nonan-4-one (**12**) and 5 mL of methyl formate was added dropwise. The reaction mixture was stirred overnight as the ice in the ice bath melted. Methanol (2 mL) was added, and stirring was continued for 15 min. Water was added, and the layers were separated. The ether layer was acidified to pH 1 with 6 N hydrochloric acid and extracted with ether. The ether extract was washed with brine, dried, and concentrated, giving the crude α-formyl ketone. The IR spectrum (CCl_4) had bands at 1592 and 1673 cm^{-1}.

The crude α-formyl ketone was dissolved in 25 mL of methylene chloride and 4.4 g of triethylamine was added. The solution was cooled in an ice–salt bath and stirred while a methylene chloride solution containing 22.1 mmol of *p*-nitrobenzenesulfonyl azide was added dropwise. The solution was stirred for 2 h while the ice in the ice bath melted. The reaction mixture was concentrated by using a rotary evaporator, and the residue was washed repeatedly with ether until the washes were colorless. The ether solution was concentrated by using a rotary evaporator, and the solid residue was washed repeatedly with pentane. Concentration of the pentane solution gave 2.4 g (67%) of the crude diazoketone. The IR spectrum (neat) had bands at 2081, 1663, and 1321 cm^{-1}.

The diazoketone was dissolved in 70 mL of methanol, cooled in an ice bath, and irradiated with 450-W Hanovia mercury lamp. The reaction was monitored by IR and was complete in 5 h. The reaction mixture was concentrated, and the residue was distilled in a Kugelrohr (65 °C, 0.1mmHg) to give 1.52 g (42% yield based on **12**) of methyl tricyclo-[4.2.0.0^{1,4}]octane-3-carboxylates. The IR spectrum (neat) had a band at 1735 cm^{-1}. The ^{1}H NMR spectrum indicated the presence of two esters in a 3:1 ratio.

A sample of the exo isomer (**14**) was obtained by treating the exo acid (**16**) (see below) with diazomethane. The ^{1}H NMR spectra of the endo ester (**13**) was obtained by subtracting the spectrum of **14** from that of the mixture. The ^{1}H NMR spectrum of the endo ester (**13**) had bands at δ 3.72 (s, 3 H), 3.39–3.49 (m, 1 H), 3.15–3.23 (m, 1 H), 2.70–2.76 (m, 1 H), 2.51 (d, d, J = 13.2, 5.2 Hz, 1 H), 2.27–2.39 (m, 1 H), 2.05–2.22 (m, 5 H), 1.80–1.98 (m, 1 H), whereas that of the exo ester (**14**) had bands at δ 3.67 (s, 3 H), 2.98–3.08 (m, 1 H), 2.80–2.85 (m, 1 H), 2.26–2.39 (m, 5 H), 2.05–2.12 (m, 3 H), and 1.80–1.98 (m, 1 H). Mass spectrum molecular ion: *m/e* 166. Anal. ($C_{10}H_{14}O_2$): C, H.

***endo*-Tricyclo[4.2.0.0^{1,4}]octane-3-carboxylic Acid (15).** The hydrolysis of 0.77 g of the mixture of esters (**13** and **14**) was effected by heating a stirred suspension in 16 mL of 2% aqueous potassium hydroxide solution at 65 °C overnight. The cooled solution was extracted with methylene chloride, and the aqueous layer was acidified (pH 1) and extracted with methylene chloride. Concentration of the latter followed by distillation in a Kugelrohr (90 °C, 0.05mmHg) gave 0.57 g (81%) of a solid which was mainly the endo isomer. Recrystallization from hexane gave the pure acid, mp 78.5–79.5 °C. The IR spectrum had a band at 1703 cm^{-1}. The ^{1}H NMR spectrum had bands at δ 3.51 (t d, J = 9.0, 5.13 Hz, 1 H), 3.18–3.29 (m, 1 H), 2.70–2.80 (m, 1 H), 2.49 (d d, J = 13.0, 5.1 Hz, 1 H), 2.24–2.45 (m, 2 H), 2.03–2.24 (m, 4 H), and 1.84–2.03 (m, 1 H). Anal. ($C_9H_{12}O_2$): C, H.

***exo*-Tricyclo[4.2.0.0^{1,4}]octane-3-carboxylic Acid (16).** The hydrolysis of 0.2 g of the mixture of esters (**13**, **14**) with 5 mL of 2% methanolic potassium hydroxide solution was carried out at 60 °C overnight. Removal of the solvent followed by acidification, extraction with methylene chloride, and distillation in a Kugelrohr (90 °C, 0.05mmHg) gave 0.15 g (82%) of a liquid acid which was mainly **16**. The IR spectrum had a band at 1697 cm^{-1}. The ^{1}H NMR spectrum was obtained by subtracting that for the endo isomer impurity and had bands at δ 3.03–3.15 (m, 2 H), 2.80–2.90 (m, 1 H), 2.27–2.44 (m, 5 H), 2.07–2.16 (m, 2 H), and 1.86–2.00 (m, 1 H). Anal. ($C_6H_{12}O_2$): C, H.

Methyl 3-Tricyclo[4.2.0.0^{1,4}]octyl Ketones. A solution of 0.94 g (6.2 mmol) of tricyclo[4.2.0.0^{1,4}]octane-3-carboxylic acid in 25 mL of dry ether was cooled to 0 °C and a hexane solution of methyllithium (2.2 equiv) was added dropwise with stirring. After 1 h at room temperature, the reaction solution was added dropwise to 50 mL of 1 N hydrochloric acid at 0 °C with vigorous stirring. The ether layer was separated, and the aqueous layer was extracted three times with ether. The combined ether solutions were washed with 5% sodium carbonate solution, dried,

concentrated, and distilled by using a Kugelrohr (60 °C, 0.3mmHg), giving 0.85 g (92%) of the methyl ketones. The IR spectrum had a band at 1710 cm^{-1}. The ^1H NMR spectrum ($CDCl_3$) indicated a mixture of endo and exo isomers. When the reaction was carried out by using the thermodynamically more stable exo acid (**16**), the exo ketone was formed. It had ^1H NMR bands ($CDCl_3$) at δ 3.12–3.20 (m, 1 H), 2.93–2.99 (m, 1 H), 2.79–2.89 (m, 1 H), 2.14–2.43 (m, 5 H), 2.09 (s, 3 H), 2.00–2.14 (m, 2 H), and 1.83–2.00 (m, 1 H).

***endo*- and *exo*-3-Tricyclo[4.2.0.0^{1,4}]octyl Acetate (19, 20).** A solution of 1.45 g (8.4 mmol) of *m*-chloroperbenzoic acid in 25 mL of chloroform was cooled to 0 °C, and a solution of 0.85 g (5.1 mmol) of methyl 3-tricyclo[4.2.0.0^{1,4}]octyl ketones was added dropwise with stirring. After being stood overnight and warmed to room temperature, the reaction mixture was washed three times with 5% sodium carbonate solution and with brine and then dried. Distillation using a Kugelrohr (65 °C, 0.05mmHg) gave 0.81 g (86%) of tricyclo[4.2.0.0^{1,4}]octyl-3 acetate. Analysis by GC (20 ft 20% Carbowax on ABS, 148 °C) indicated two compounds, which were found to be the endo and exo acetates. The ^1H NMR spectrum ($CDCl_3$) of the first components identified it as the exo acetate (**20**) having bands at δ 4.94 (d of t, J = 6.23, 2.20 Hz, 1 H), 2.79–2.88 (m, 1 H), 2.68–2.79 (m, 1 H), 2.62 (d of d, J = 13.2, 6.2 Hz, 1 H), 2.27–2.44 (m, 2 H), 1.87–2.27 (m, 5 H), and 2.04 (s, 3 H). Mass spectrum molecular ion: m/e 166. The ^1H NMR spectrum of the second component identified it as the endo acetate (**19**) having bands at δ 5.14–5.23 (m, 1 H), 3.21–3.27 (m, 1 H), 2.64–2.76 (m, 1 H), 2.38–2.51 (m, 2 H), 2.27–2.38 (m, 1 H), 2.18–2.27 (m, 1 H), 1.91–2.18 (m, 4 H), and 2.11 (s, 3 H). Mass spectrum molecular ion: m/e 166. The IR spectrum (neat) had bands at 1739 and 1236 cm^{-1}. Anal. ($C_{10}H_{14}O_2$): C, H.

Tricyclo[4.2.0.0^{1,4}]octane (2). A solution of 0.81 g (4.9 mmol) of tricyclo[4.2.0.0^{1,4}]octyl-3 acetates in 30 mL of 8% water–92% hexamethylphosphoramide was placed in a 30 cm × 12 m quartz tube and irradiated in a Rayonet apparatus by using 254-nm low-pressure mercury lamps. The reaction was monitored by withdrawing aliquots, shaking with pentane–water, and analyzing the pentane solution by GC (1/4 in. × 14 in. Carbowax 20M on Anakrom ABS at 150 °C). After 56 h, 30 mL of water was added and the solution was extracted with pentane. The pentane solution was concentrated by distillation using a 12-in. vacuum-jacketed column packed with stainless steel helices. The residue was separated by GC (80 °C), and the hydrocarbon was trapped by using a dry ice–acetone bath, giving 120 mg (23%) of pure tricyclo[4.2.0.0^{1,4}]-octane (**2**). The ^1H NMR spectrum had bands at δ 2.77–2.85 (m, 2 H), 2.26–2.39 (m, 2 H), 2.18 (t, J = 4.2 Hz, 2 H), 2.01–2.08 (m, 4 H), and 1.81–1.93 (m, 2 H). The ^{13}C NMR spectrum had bands at δ 51.4 (s), 39.7 (d, J = 131 Hz), 37.2 (t, J = 131 Hz), 28.9 (t, J = 133 Hz), and 25.9 (t, J = 131 Hz). MS molecular ion: m/e 108. Anal. (C_8H_{12}): C, H.

Thermolysis of Tricyclo[4.2.0.0^{1,4}]octane (2). A solution of 15 mg of **2** in 0.5 mL of *o*-dichlorobenzene was sealed in an NMR tube. It was heated in an oil bath, and after 2 h at 180 °C the reaction had gone to completion. GC analysis (14 ft Carbowax 20M on Anakrom ABS) indicated two products which were separated by GC. The first fraction appeared to be 2-allyl-1-methylenecyclobutane (**21**) and had ^1H NMR bands at δ 5.74–5.90 (m, 1 H), 4.98–5.07 (m, 2 H), 4.74 (d of d, J = 16.1, 2.2 Hz, 2 H), 2.90–3.12 (m, 1 H), 2.48–2.70 (m, 2 H), 2.30–2.42 (m, 1 H), 1.99–2.25 (m, 2 H), 1.51–1.71 (m, 1 H). The second component appeared to be 3-methylene-1,6-heptadiene (**23**) and had ^1H NMR bands at δ 6.39 (d of d, J = 17.6, 10.3 Hz, 1 H), 5.79–5.99 (m, 1 H), 5.24 (d, J = 17.6 Hz, 1 H), 4.95–5.10 (m, 5 H), and 2.30 (m, 4 H). Both components had mass spectrum molecular ion at m/e 108.

A solution of 120 mg of **2** in 22 mL of *o*-dichlorobenzene was prepared, and 3–4 drops of benzene was added as an internal standard. Aliquots (0.5 mL) were sealed into vials and stored at 0 °C until used. Six vials were placed in a thermostated bath, removed separately at different times, and cooled to 0 °C until analyzed. Analysis was carried out by GC (14 ft, 18% OV-17 on Anaprep) by using an integrator to determine the ratio of **2** to benzene. The reaction was studied at four temperatures, and in each case good first-order kinetics was observed.

In order to identify the products, we prepared them as follows. Freshly distilled *N,N,N',N'*-tetramethylethylenediamine (3.28 mL, 22 mmol) was placed in a 50-mL round-bottomed flask flushed with argon and equipped with a stirrer and a rubber septum. Ten milliliters of pentane was added, and the solution was cooled to 0 °C. A hexane solution of *n*-butyllithium (22 mmol) was slowly added by syringe with stirring. The solution was warmed to room temperature for 1 h and cooled to 0 °C. A solution of 1.5 g (22 mmol) of methylenecyclobutane in pentane was added, and the solution was stirred overnight at room temperature. It was cooled to 0 °C, a pentane solution of 2.4 g (20 mmol) of allyl bromide was added, and the solution was stirred at room temperature for 1 h. The solution was poured into 50 mL of ice water. The pentane layer was washed with 0.1 N hydrochloric acid, saturated sodium bicarbonate solution, and brine. After being dried, the products were separated by GC. The first component was identical with the first (**21**) obtained in the thermolysis. The second was found to be 1-(3-butenyl)cyclobutene (**22**) and had ^1H NMR bands at δ 5.76–5.92 (m, 1 H), 5.69 (s, 1 H), 4.94–5.08 (m, 2 H), 2.42 (m, 2 H), 2.35 (m, 2 H), 2.14–2.22 (m, 2 H), and 2.09–2.14 (m, 2 H). Mass spectrum molecular ion: m/e 108. When this component was heated to 180 °C, it was converted to a triene identical with the second component (**23**) formed in the thermolysis.

***N*-(*p*-Bromophenyl)tricyclo[4.2.0.0^{1,4}]octane-3-carboxyamides (15a, 16a).** A mixture of 0.21 g of *endo*-tricyclo[4.2.0.0^{1,4}]octane-3-carboxylic acid (**15**) and 1.0 mL of thionyl chloride was heated at 75 °C for 30 min. To the cooled mixture was added a solution of 0.9 g of *p*-bromoaniline in 20 mL of benzene. After being heated for 2 min at 75 °C, it was extracted with 2 mL of water, 5 mL of 5% hydrochloric acid, 5 mL of 5% sodium hydroxide, and 2 mL of water. The solvent was removed, and the solid was washed with ether. Slow crystallization from acetonitrile at 6 °C over several weeks gave crystals of **15a**, mp 207–208 °C, which were suitable for X-ray crystallography. The ^1H NMR spectrum ($CDCl_3$) had bands at δ 7.44 (m, 4 H), 3.40–3.54 (m, 1 H), 2.73–2.83 (m, 1 H), 2.63 (d of d, J = 12.8, 5.1 Hz), 2.04–2.42 (m, 6 H), and 1.87–2.02 (m, 1 H).

The exo acid (**16**) containing some **15** was treated in the same fashion. The amide was soluble in ether and could not be satisfactorily purified by recrystallization. Purification was affeted by sublimation. The ^1H NMR spectrum indicated a mixture of isomers. Subtraction of the spectrum of the minor endo isomer gave the spectrum of **16a** ($CDCl_3$): δ 7.42 (s, 4 H), 2.99–3.13 (m, 2 H), 2.80–2.91 (m, 1 H), 2.26–2.53 (m, 5 H), 2.13 (t, J = 7.8 Hz, 2 H), 1.87–2.01 (m, 1 H).

Tricyclo[4.2.0.0^{1,4}]octyl-3-methanols (17, 18). To a suspension of 0.41 g of lithium aluminum hydride in 150 mL of anhydrous ether was added an ether solution of 0.9 g of the mixture of *endo*- and *exo*-methyl tricyclo[4.2.0.0^{1,4}]octane-3-carboxylates (**13, 14**). After being heated for 2.5 h, the reaction was quenched by dropwise addition of saturated sodium sulfate solution. The ether solution was dried over magnesium sulfate and concentrated to give 0.68 g (91%) of a mixture of **17** and **18**. The compounds were separated by GC ($^3/_8$ in. × 14 ft, 18% OV-17 on Anaprep). The first component was the *exo* isomer (**18**) which had ^1H NMR bands ($CDCl_3$) at δ 3.55 (d, J = 7.3 Hz, 2 H), 2.71–2.82 (m, 1 H), 2.48–2.56 (m, 1 H), 2.25–2.44 (m, 2 H), 2.11–2.25 (m, 2 H), 2.00–2.11 (m, 2 H), 1.78–2.00 (m, 2 H), and 1.64 (d of d, J = 12.5, 7.3 Hz, 1 H) and ^{13}C NMR bands at δ 67.2, 47.8, 42.3, 41.7, 39.7, 35.6, 32.1, 28.8, and 25.8. Mass spectrum molecular ion: m/e 138. Anal. ($C_9H_{14}O$): C, H.

The second component was the endo isomer (**17**) which had ^1H NMR bands ($CDCl_3$) at δ 3.92–4.00 (m, 1 H), 3.72–3.80 (m, 1 H), 2.92–2.99 (m, 1 H), 2.60–2.78 (m, 2 H), 2.24–2.36 (m, 1 H), 1.87–2.17 (m, 4 H), and 1.71 (d of d, J = 12.8, 4.8 Hz, 2 H) and ^{13}C bands at δ 63.5, 48.3, 40.7, 39.5, 33.4, 31.2, 28.9, 28.5, and 26.4. Mass spectrum molecular ion: m/e 138. Anal. ($C_9H_{14}O$): C, H.

3-Tricyclo[4.1.0.0^{1,4}]octyl 3,5-Dinitrobenzoates (26, 27). To a suspension of 0.45 g of lithium aluminum hydride in 150 mL of anhydrous ether was added an ether solution of 0.9 g of a mixture of *endo*- and *exo*-3-tricyclo[4.2.0.0^{1,4}]octyl acetates (**19, 20**). The solution was heated to reflux for 4 h and then quenched by the slow addition of saturated sodium sulfate solution. The ether solution was dried over magnesium sulfate and concentrated, giving 0.6 g (89%) of a mixture of *endo*- and *exo*-tricyclo[4.2.0.0^{1,4}]octan-3-ols. It was not possible to separate them on a preparative scale by GC. Mass spectrum molecular ion: m/e = 124. Anal. ($C_8H_{12}O$): C, H.

The alcohol mixture obtained above was dissolved in 12 mL of anhydrous pyridine and 1.12 g of 3,5-dinitrobenzoyl chloride was added. After 1 h, the mixture was poured into water and extracted with ether. The ether solution was concentrated and then placed under vacuum to remove residual pyridine. The oil thus obtained was passed through a silica gel column (4 in., 10% ether–pentane), and the product was obtained as a solid on removal of the solvent.

The 3,5-dinitrobenzoates could be separated by high-pressure LC by using 5% ether–hexane. Three fractions were obtained. The first was an impurity. The second was the exo ester (**27**) which had ^1H NMR bands at δ 9.15–9.25 (m, 3 H), 5.30 (t of d, J = 6.23, 2.57 Hz, 1 H), 3.01–3.88 (m, 1 H), 2.81 (d of d, J = 13.20, 6.23 Hz, 2 H), 2.37–2.50 (m, 2 H), 2.14–2.37 (m, 4 H), and 1.92–2.08 (m, 1 H). The third fraction was the endo ester (**26**) which had ^1H NMR bands at δ 9.24–9.24 (m, 3 H), 5.49–5.57 (m, 1 H), 3.37–3.43 (m, 1 H), 2.74–2.86 (m, 1 H), 2.60–2.74 (m, 1 H), 2.30–2.55 (m, 3 H), and 1.99–2.30 (m, 4 H).

Solvolysis of *endo*-3-Tricyclo[4.2.0.0^{1,4}]octyl 3,5-Dinitrobenzoate (26). The 3,5-dinirobenzoate (10 mg) was dissolved in 3.5 mL of 80% acetone-d_6–20% D_2O (v/v) along with 20 μL of chloroform as an internal

Table VII. Experimental Data for X-ray Diffraction Study of *p*-$BrC_6H_4N(H)COC_8H_{11}$ (15a)

(A) Crystal Parameters at 20 °C

space group: $P2_1/c$, No. 14, $[C_{2h}^5]$	V = 1353.6 (7) Å^3
a = 6.838 (1) Å	Z = 4
b = 20.635 (3) Å	mol wt 306.2 g/mol
c = 9.740 (2) Å	ρ_{calcd} = 1.487 g/cm^3
β = 95.62 (2)°	

(B) Measurement of Intensity Data

radiatn: Mo Kα; λ = 0.710 73
monochromator: graphite
takeoff angle: 2.5°
detector aperture: horizontal, $A + B \tan\theta°$, A = 3.0 mm, B = 1.0 mm; vertical, 4.0 mm
crystal-detector dist: 330 mm
reflctns measured: $+h,+k,\pm l$
data range: 2θ(min) = 0.0°, 2θ(max) = 50.0°
scan type: moving crystal-stationary counter
scan speed: variable θ(max) = 10.0°/min; θ(min) = 1.25°/min
θ scan width: 0.70 + 0.347 tan θ° on each side of calcd position
background: $^1/_4$ additional scan at each end of scan
std reflctns: 3 measured after approx each 90 data reflections showed only random fluctuation of ±3%.
no. reflctns measd: 2657 including absences
data used ($F^2 > 3.0\sigma(F^2)$): 1322 reflctns

standard. Aliquots (0.5 mL) were sealed in NMR tubes and were placed in an oil bath maintained at 70.0 °C. Samples were removed at different times, quickly cooled to 0 °C, and analyzed by NMR spectroscopy. The rates of reaction were determined from the ratio of the integrated peak areas of the starting material and the internal standard.

The product studies were carried out by using a mixture of the two isomers since the exo isomer was found to be inert under the reaction conditions. A solution of 0.3 g of the dinitrobenzoates in 40 mL of 80% acetone was sealed in a tube and heated at 70 °C for 15 h. The reaction solution was concentrated by using a rotary evaporator, and the aqueous residue was extracted with ether. The ether solution was dried and concentrated, and the residue was shown by GC to consist of two compounds. They were separated by GC ($^1/_8$ in. × 12 ft, 10% Carbowax 20M on ABS 110–120). The first (**28**) had a ^{1}H NMR spectrum with bands at δ 5.87 (m, 2 H), 2.38–2.53 (m, 1 H), 2.20–2.38 (m, 2 H), 2.07–2.13 (m, 1 H), 1.82–2.05 (m, 3 H), 1.54–1.69 (m, 1 H), 1.04–1.26 (m, 2 H). Mass spectrum molecular ion: m/e 124. It was tentatively identified as bicyclo[4.2.0]oct-3-en-1-ol. The second (**29**) had ^{1}H NMR bands at δ 5.61–5.81 (m, 2H), 3.28 (s, 1 H), 2.48 (s, 1 H), 2.42 (s, 1 H), 2.19 (m, 1 H), 1.63 (s, 1 H), 1.26 (m, 1 H), 0.51–0.57 (m, 1 H), and 0.31–0.44 (m, 3 H). Mass spectrum molecular ion: m/e 124. It was tentatively identified as spiro[2.5]oct-6-en-4-ol.

Each of the compounds was separately reduced by using diimide and the following procedure. A solution of 1–3 mg of the compound in 20 mL of methanol was cooled to 0 °C under nitrogen and 10 mL of 85% hydrazine hydrate, and 0.1 mL of a 5% cupric sulfate solution was added. Diimide was generated by adding 30% hydrogen peroxide dropwise with stirring. After 4 mL had been added, an additional 10 mL of 85% hydrazine hydrate was introduced, and an additional 3 mL of hydrogen peroxide was added dropwise. The solution was extracted with four 20-mL portions of pentane. The latter was dried and concentrated by using a rotary evaporator. The product was analyzed by GC/MS via comparison with the MS of authentic samples. The first compound (**28**) gave on reduction bicyclo[4.2.0]octan-1-ol (**30**) whereas the second (**29**) gave on reduction spiro[2.5]octan-4-ol (**31**).

Table VIII. NMR Spectra of *endo*- and *exo*-Tricyclo[4.2.0.0^{1,4}]octane Derivatives

3-substituent	δ endo[a]	δ exo[b]
$-CO_2CH_3$	3.44	3.03
$-CO_2H$	3.51	3.09
$-CO_2NHC_6H_5Br$	3.47	3.06
$-CH_2OH$	2.95	2.52
-OAc	5.17	4.94
$-OCOC_6H_3(NO_2)_2$	5.52	5.30

[a] Endo substituent, exo proton. [b] Exo substituent, endo proton.

Crystal Data and Data Collection. Crystals of the *p*-bromoanilide, **15a**, were grown by slow concentration of an acetonitrile solution. A cuboidal crystal with dimensions 0.29 mm × 0.30 mm × 0.36 mm was selected and mounted in a thin-walled glass capillary. All diffraction measurements were performed by using an Enraf-Nonius CAD-4 fully automated four-circle diffractometer using graphite-monochromated Mo K$\bar{\alpha}$ radiation. The unit cell was determined and refined by using 25 randomly selected reflections and the CAD-4 automatic search, center, index, and least-squares routines. The space group, $P2_1/c$, was determined from systematic absences observed during data collection. The crystal faces were identified as 010, 0$\bar{1}$0, 110, $\bar{1}$10, 1$\bar{2}$0, 02$\bar{1}$, and 0$\bar{2}$1. ω-Scan peak widths at half height lay in the range 0.10–0.15°. A total of 2657 reflections were collected in the range 0.0° ≤ 2θ ≤ 50.0°. Of these, 1322 ($F^2 \geq 3.0\sigma(F^2)$) were used in the subsequent structure solution and refinement. The absorption coefficient for **15a** is 31.7 cm^{-1}. No correction for absorption effects was made. Crystal data and data collection parameters are listed in Table VII.

Structure Solution and Refinement. All calculations were carried out on a Digital PDP 11/45 computer using the Enraf-Nonius SDP program library. The structure was solved by a combination of Patterson and difference Fourier techniques. Scattering factors were calculated by standard procedures,[30] and anomalous dispersion corrections[30] were made for all nonhydrogen atoms. Least-squares refinements minimized the function $\sum_{hkl} w(F_o - F_c)^2$ where the weighting factor $w = 1/\sigma(F)^2$. Full-matrix least-squares refinement using anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for the hydrogen atoms produced the final residuals R_1 = 0.030 and R_2 = 0.025. The error in an observation of unit weight was 2.52. The largest value of shift–error parameter in the final cycle was 0.02. A final difference Fourier synthesis was featureless. The largest peaks were 0.33, 0.27, and 0.21 e/Å^3 and were clustered about the bromine atom. Final values of fractional atomic coordinates are listed in Table III. Bond distances and angles with estimated standard deviations determined from the inverse matrix obtained in the final cycle of least-squares refinement are listed in Tables IV and V. Tables of final structure factor amplitudes and thermal parameters are available (see supplementary material).

Acknowledgment. This investigation was supported by NSF Grant CHE-78-24880.

Supplementary Material Available: Tables of final anisotropic thermal parameters and structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

(30) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1975; Vol. IV: (a) Table 2.2B, pp 99–100; (b) Table 2.3.1, pp 149–150.