2-Substituted Bicyclo[1.1.1]pentanes

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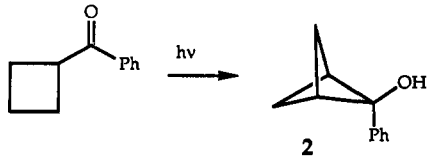
Received September 22, 1992

A simple procedure has been developed for the conversion of 2-phenylbicyclo[1.1.1]pentan-2-ol to 2-phenyl-bicyclo[1.1.1]pentane. Oxidation gives bicyclo[1.1.1]pentane-2-carboxylic acid which may be converted to the amine, the nitro derivative, and the phenyl ketone. The pK_a values for the carboxylic acid and related acids were determined, and the pK_a's of the amine hydrochloride and related compounds also were studied. The pK_a's of the amines were approximately linearly related to the percent s character determined from the ^1H–C NMR coupling constants. The pK_a of the nitro derivative was determined, and the kinetic acidity of the phenyl ketone also was measured. The relationship of the differences in energy to the changes in strain energy is discussed. In an effort to prepare a compound with substituents at both the 1- and 2-positions, the reaction of 1,3-dinitrobicyclo[1.1.1]pentane with oxalyl chloride was examined. The reaction had a surprising course, leading to 2,2-dichloro-1,3-dinitrobicyclo[1.1.1]pentane.

The bicyclo[1.1.1]pentane (1) ring system is of special interest with regard to substituent effects. The short bridgehead–bridgehead distance (1.85 Å)[1] and the short distance between methylene groups (2.14 Å) should lead to unusually large nonbonded interactions. Some of these effects have been studied by Applequist for 3-substituted bicyclo[1.1.1]pentane-1-carboxylic acids.[2] We[3] and others[4] have developed efficient procedures for preparing a variety of 1,3-disubstituted bicyclo[1.1.1]pentanes via free-radical additions to [1.1.1]propellane, allowing a detailed examination of these compounds.[5]

The 2-substituted derivatives are not so easily obtained. Although free radical substitution reactions on 1 will give some 2-substituted compounds,[6] the only effective method of placing a substituent at this position is the photolysis of cyclobutyl phenyl ketone to give 2-phenylbicyclo[1.1.1]-hexan-2-ol (2).[7] The hydroxy group in 2 has been removed



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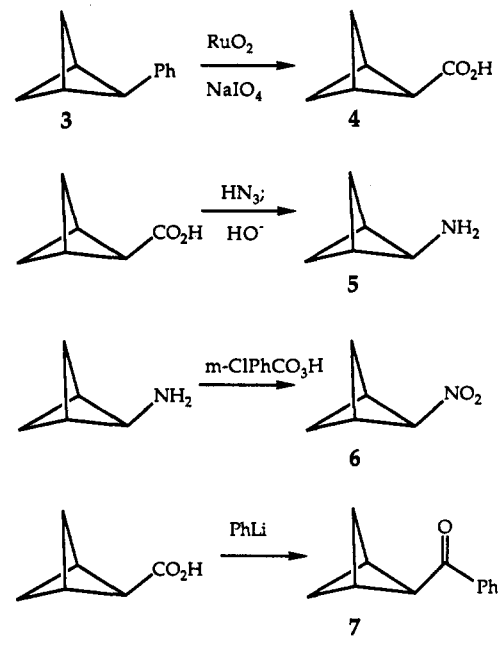
via a long series of reactions involving formation of the mandelic acid ester, photolysis, oxidation, and a Haller–Bauer cleavage.[8] Direct oxidation has given bicyclo[1.1.1]-pentan-2-one in low yield.[9]

Phenyl is not an ideal substituent because it is relatively difficult to convert it to other groups. Several other substituents were examined for the photolysis reaction including *o*-, *m*-, and *p*-anisyl, 2-furyl, and vinyl, but they did not yield a significant amount of the cyclized product. One major problem is that these substituents lead to a red shift of the π-π^* transition, and makes the relatively weak n-π^* photochemically ineffective.

Scheme I



It was important to find a simple way in which to remove the hydroxy group. The reaction of 2 with mild halogenating agents such as triphenylphosphine and bromine or triphenylphosphine and *N*-bromosuccinimide[10] led to rearrangement and the formation of olefinic products. Similarly, an attempted direct reduction to the hydrocarbon using triethylsilane and boron trifluoride etherate[11] again led to rearranged products. It was clear that reactions which might proceed via a carbocation were not suitable. The acid-catalyzed rearrangement of 2 to 3-phenyl-3-cyclopenten-2-ol has previously been reported.[7]

It is known that benzyl alcohols undergo hydrogenolysis

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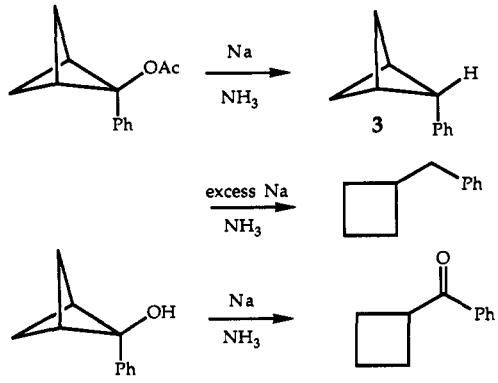
Table I. Acidities of Cycloalkanecarboxylic Acids

R	pK_a	% s[a]
CH_3	4.85	25
cyclohexyl	4.84	25
cyclopentyl	4.87	26
cyclobutyl	4.66	27
cyclopropyl	4.65	33
1-bicyclo[2.1.1]hexyl	4.46	31
2-bicyclo[1.1.1]pentyl	4.27	29
1-bicyclo[1.1.1]pentyl	4.09	33

[a] The percent s values were derived from the ^{13}C–H NMR coupling constants (ref 13).

under Birch reduction conditions.[12] The reaction of **2** with sodium and ammonia led only to reversion to the ketone, presumably via a base-catalyzed process. However, the acetate derived from **2** did undergo reduction under these conditions (−78 °C) giving 2-phenylbicyclo[1.1.1]pentane (**3**) in 80% yield. The reaction must be controlled because an excess of reducing agent causes cleavage of the bicyclic ring giving benzylcyclobutane. Some of this product also was obtained using 1 equiv of sodium at −33 °C (the boiling point of ammonia). It is interesting that the bicyclopentane ring is more easily reduced than the benzene ring.



The ready availability of **3** allowed a number of transformations to be effected (Scheme I). Oxidation using ruthenium tetroxide gave the carboxylic acid (**4**). The use of the Schmidt reaction led to the conversion of **4** to bicyclo[1.1.1]pentyl-2-amine (**5**). Oxidation of **5** with *m*-chloroperbenzoic acid gave the 2-nitro derivative **6**. The acid **4** also was converted to the phenyl ketone with phenyllithium.

The oxidation of the amine **5** presented some difficulties. Oxidation with *m*-chloroperbenzoic acid in methylene chloride at reflux gave no reaction. The use of chloroform at reflux gave a 25–40% yield of **6** as determined by analytical GC. However, the isolated yield was lower. If the oxidation were carried out in 1,2-dichloroethane as the solvent, loss of the bicyclic ring was noted. The use of peracetic acid was not successful.

We have previously reported the effect of some small ring structures on the acidity of carboxylic acids in order to examine the effect of hybridization on changes in acidity.[6] As an extension of the previous study, the pK_a values for **4** and several related acids were determined and are given in Table I. The first four acids have been studied previously[6] but were redetermined so that any systematic error should cancel. The pK values follow

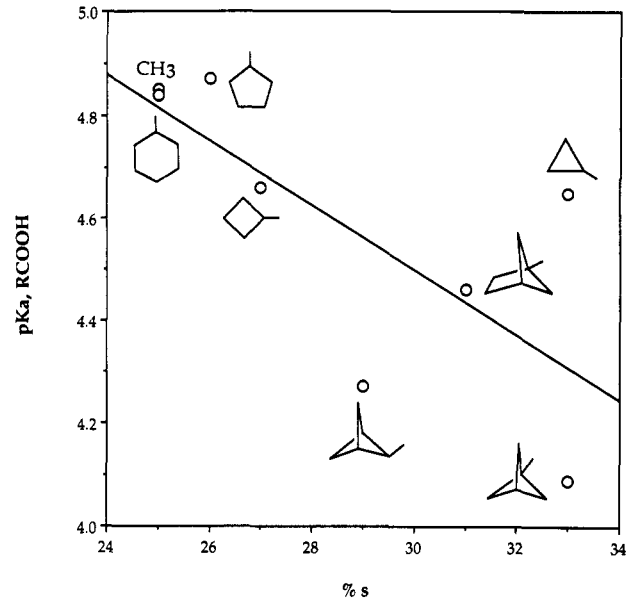


Figure 1. Relationship between the pK_a values for cycloalkanecarboxylic acids and the percent s character as determined from the ^{13}C–H NMR coupling constants.

Table II. Acidities of Cycloalkylamine Hydrochlorides

R	pK_a, 50% EtOH	pK_a, H_2O[a]
cyclohexyl	10.05	
cyclopentyl	10.16	
cyclobutyl	9.61	10.04
cyclopropyl	8.76	
1-bicyclo[2.1.1]hexyl	[8.9][b]	9.30
2-bicyclo[1.1.1]pentyl	8.90	
1-bicyclo[1.1.1]pentyl	[8.2][b]	8.58

[a] Reference 6. [b] Estimated values based on the pK_a in water.

roughly the trend expected from the percent s character determined from the ^1H–C NMR coupling constants.[13] However, the range of pK is quite small, and cyclopropanecarboxylic acid was considerably less acidic than expected. One problem with interpreting the acidity of acids is that in aqueous solution they have maximum pK_a values near 25 °C.[14] Thus, it is possible that the relative acidities of a pair of acids may invert on changing temperature.

The acidities of the corresponding amine hydrochlorides are of more interest because the charge is developed at an atom closer to the cyclic rings, and larger effects should be found. The pK_a values were determined for several hydrochlorides in 50% ethanol–water giving the data in Table II. Here, there was a much better relationship between the pK_a values and the percent s character (Figure 2).

2-Nitrobicyclo[1.1.1]pentane was interesting in that it would not dissolve in 1 M sodium hydroxide solution, whereas nitrocyclohexane is readily soluble.[15] This indicates that the pK_a has been significantly increased as a result of the angle strain at the 2-position. A similar observation has been reported for nitrocyclopropane.[16] In order to obtain more quantitative data, we have determined the pK_a values for some nitrocycloalkanes,[17] and they are

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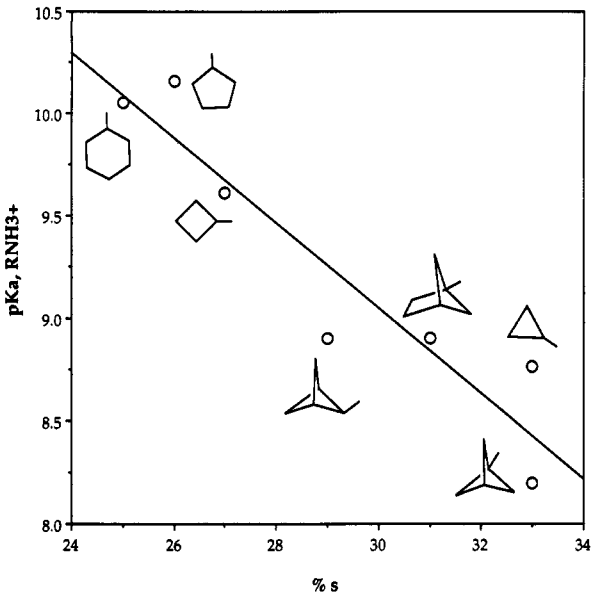

Figure 2. Relationship between the pK_a values for cycloalkylammonium ions and the percent s character.

Table III. Equilibrium Acidities of Nitrocycloalkanes

R	pK_a, 50% MeOH
cyclobutyl	10.05 ± 0.03
cyclopentyl	8.19 ± 0.04
cyclohexyl	10.02 ± 0.05
2-bicyclo[1.1.1]pentyl	11.20 ± 0.11

Table IV. Heats of Reduction of Cycloalkanones and Strain Energy Changes

compound	ΔH_{redn}, kcal/mol[a]	ΔSE (tet → trig), kcal/mol
acetone	−13.0	0.0
cyclopropanone	−31[b]	+18
cyclobutanone	−12.7	−0.3
cyclopentanone	−10.9	−2.1
cyclohexanone	−14.1	1.1
2-bicyclo[1.1.1]pentane	−18[b]	5

[a] Wiberg, K. B.; Crocker, L. S.; Morgan, K. M. *J. Am. Chem. Soc.* **1991**, *113*, 3447. [b] Estimated from ab initio calculations at the RHF/6-31G* level.

recorded in Table III. The data for the nitrocycloalkanes were in good agreement with those reported by Bordwell et al.[16] Nitrocyclopentane was the most acidic, and here, conversion to the anion will relieve some of the eclipsing strain in the cyclopentane ring. Nitrocyclobutane and nitrocyclohexane were significantly less acidic, and in both cases the formation of the anion with its larger normal bond angles will lead to some increase in strain. The least acidic of the nitro compounds was 2-nitrobicyclo[1.1.1]-pentane. Here, the formation of an anion stabilized by the nitro group will be very difficult since the bond angle is so small. The extreme of this behavior is, of course, nitrocyclopropane.

It might be expected that the free energy change on ionization would be related to the difference in strain energy between the parent ring system and one in which a trigonal center has been introduced. The best comparison might be with the heats of reduction of ketones, and the available data are summarized in Table IV. Taking the strain energy change for acetone as zero, the strain energy changes for the other compounds may be obtained. It can be seen that nitrocyclopentane has the largest acidity and a negative change in strain energy, whereas bicyclo-[1.1.1]pentan-2-one has the lowest acidity and the largest increase in strain. The other compounds have intermediate values. Thus, there is a rough correlation with the change in strain energy.

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Table V. Rates of Deuterium Exchange for Cycloalkyl Phenyl Ketones, 25 °C, Methanol-d_4

ring	k, min^{-1}
cyclopropane	1.63×10^{-4}
cyclobutane	2.11
cyclopentane	1.06
2-bicyclo[1.1.1]pentane	2.91×10^{-3}

We have attempted to convert **6** to 2,2-dinitrobicyclo-[1.1.1]pentane via a procedure which is quite effective for converting nitrocyclopentane to its dinitro derivative.[15] Whereas the latter is formed in good yield, only traces of the dinitro compound was found with **6**. The low acidity is presumably a major factor causing the difficulty in this reaction.

The kinetic acidity also was of interest, but with the difference in behavior of the nitro compounds, it was not convenient to study them. Therefore, we have examined the kinetic acidity of the corresponding phenyl ketones via the measurement of the rate of deuterium exchange in the presence of base. The results are shown in Table V. Here, cyclobutyl phenyl ketone and cyclopentyl phenyl ketone had comparable reactivities. Phenyl bicyclo[1.1.1]-pent-2-yl ketone was less reactive by a factor of 10^3 and less than 10 times more reactive than cyclopropyl phenyl ketone. The relative rates are roughly correlated with the change in strain energy on going from a tetrahedral to a trigonal center (Table IV). Here, cyclobutane and cyclopentane have a small change in strain energy, bicyclo-[1.1.1]pentane has an intermediate value, and cyclopropane has the largest increase in strain.

We were also interested in having bicyclo[1.1.1]pentane derivatives with functional groups at both the 1- and 2-positions. Some compounds of this type have been prepared by the direct chlorination of 1,3-disubstituted bicyclo[1.1.1]pentanes,[18] and here, the dichloro rather than monochloro derivative was obtained. The photochemically induced reaction of bicyclo[1.1.1]pentane with oxalyl chloride has been found to give substitution of a chlorocarbonyl group at both the 1- and 2-positions.[6] 1,3-Dinitrobicyclo[1.1.1]pentane may be prepared by the reaction of [1.1.1]propellane with N_2O_4,[3] and it appeared to be a promising substrate for functionalization at the 2-position. The procedure for the preparation of the dinitro derivative was developed for preparative use, and it was found that 1-nitrobicyclo[1.1.1]pentane was a major byproduct when the reaction was carried out in ether. The reaction of the dinitro derivative with oxalyl chloride was carried out in excess oxalyl chloride. On workup with methanol, the major product was found to be 2,2-dichloro-1,3-dinitrobicyclo[1.1.1]pentane, and only a trace (GCMS) of the methyl ester that would be formed from the expected acid chloride was found. The formation of the chloride rather than the acyl chloride is surprising, and it is interesting that here also the dichloro rather than monochloro derivative was obtained.

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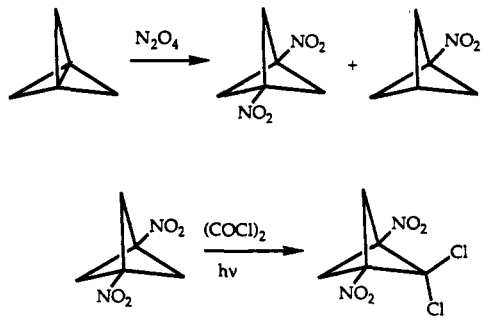

Conclusions

It is possible to prepare a variety of 2-substituted bicyclo[1.1.1]pentane from the photochemical closure product, 2. The properties of the 2-substituted bicyclo[1.1.1]pentanes appear to be largely determined by a combination of hybridization and angle strain. The acidities of a series of cycloalkylammonium halides were approximately related to the percent s character as determined from their ^{13}C–H NMR coupling constants. Both the equilibrium acidities of nitrocycloalkanes and the kinetic acidities of phenyl cycloalkyl ketones were found to be approximately related to the change in strain energy on going from a tetrahedral to a trigonal center.

Experimental Section

NMR spectra were determined in $CDCl_3$ solutions at 250 MHz for protons and 68 MHz for carbons and are reported in ppm downfield from TMS. Column chromatography made use of Kieselgel (230–400 mesh) as the solid support.

2-Phenylbicyclo[1.1.1]pentane. To a solution of 12.6 g (0.079 mol) of 2-phenylbicyclo[1.1.1]pentan-2-ol in 65 mL of pyridine at 0 °C was added dropwise with stirring 6.2 mL (0.087 mol) of acetyl chloride. The solution was stirred for 0.5 h at 0 °C and for 1 h at room temperature. The solution was added to ice and extracted with 300 mL of ether. The ether solution was washed with aqueous sodium bicarbonate solution and with saturated aqueous copper sulfate solution. After drying over $MgSO_4$ the solution was passed through a 6-in. florisil column and concentrated to give 13.0 g (82%) of the acetate. ^1H NMR (ppm): 7.26–7.47 (m, 5 H), 3.30 (s, 1 H), 2.42 (dd, J = 10.3, 2.7 Hz, 1 H), 1.94 (s, 3 H), 1.80 (d, J = 2.7 Hz, 1 H), 1.66 (d, J = 3.2 Hz, 1 H), 1.48 (dd, J = 10.4, 3.2 Hz, 1 H). ^{13}C NMR: 169.9, 138.0, 128.2, 127.7, 127.6, 95.4, 42.5, 41.6, 41.2, 21.0.

A solution of 27.2 g (0.135 mol) of the acetate in 500 mL of anhydrous ether was placed in a 5-L three-necked flask. The flask was cooled to −78 °C, and 1.5 L of liquid ammonia was added. Sodium (6.5 g, 0.28 mol) was added in small pieces over a period of 30 min. Stirring was continued until the blue color was discharged. The reaction was quenched by the addition of NH_4Cl, and the solvent was allowed to evaporate overnight. Pentane (200 mL) was added to the residue, and the solution was washed with NaCl solution, dried over $MgSO_4$, and concentrated. Purification via column chromatography (9:1 hexane–ether) gave 2-phenylbicyclo[1.1.1]pentane as a colorless liquid (15.5 g, 80%), bp 43 °C at 1 Torr. ^1H NMR: 7.27–7.40 (m, 5 H), 3.53 (d, J = 6.9 Hz, 1 H), 2.85 (s, 2 H), 2.26 (dd, J = 9.7, 2.6 Hz, 1 H), 2.00 (d, J = 1.9 Hz, 1 H), 1.90–1.94 (m, 2 H). ^{13}C NMR: 141.0, 128.1, 127.9, 125.7, 63.9, 47.7, 47.0, 36.2.

Bicyclo[1.1.1]pentane-2-carboxylic Acid. A mixture of 5.0 g (0.035 mol) of 2-phenylbicyclo[1.1.1]pentane, 0.2 g of ruthenium dioxide, 100 g (0.47 mol) of sodium periodate, 310 mL of water, 220 mL of carbon tetrachloride, and 220 mL of acetonitrile was stirred for 2 days during which time a gelatinous precipitate formed. Approximately 300 mL of CH_2Cl_2 was added to the mixture, and the solids were removed by filtration. The organic layer was separated, and the aqueous layer was washed with ether. The combined organic solution was concentrated. Ether (250 mL) was added to precipitate ruthenium salts. After standing overnight, the solution was filtered through Celite, dried over Na_2SO_4, and evaporated to dryness. The product was dissolved in aqueous NaOH and extracted with ether. Flash chromatography (9:1 pentane–ether followed by 4:1) and evaporation of the solvent gave the acid as a white solid (2.2 g, 56%). It could be further purified by sublimation at 50 °C and 0.2 Torr and had mp 40–41 °C. ^1H NMR: 2.92 (d, J = 7.3 Hz, 1 H), 2.77 (s, 2 H), 2.45 (dd, J = 10.4, 3.2 Hz, 1 H), 1.88 (dd, J = 7.3, 3.2 Hz, 1 H), 1.72–1.76 (m, 2 H). ^{13}C NMR: 178.8, 61.5, 48.2, 47.9, 36.7. Anal. Calcd for $C_6H_8O_2$: C, 64.3; H, 7.2. Found: C, 64.2; H, 7.2.

Bicyclo[1.1.1]pentyl-2-amine Hydrochloride. To a 500-mL three-necked flask equipped with a mechanical stirrer and reflux condenser was added 100 mL of chloroform, 1.04 g (9.7 mmol) of bicyclo[1.1.1]pentane-2-carboxylic acid, and 4.0 mL of concd sulfuric acid. Sodium azide (1.2 g, 18.5 mmol) was added in portions to minimize heating and bubbling due to release of nitrogen. The mixture was heated at 50 °C for 30 min, cooled, and diluted with ice. Slow addition of aqueous KOH to pH 12–13 gave the free amine. The amine, along with water and chloroform, was distilled into a cooled flask containing dilute hydrochloric acid. Concentration of the acidic solution gave the hydrochloride (83%) which could be purified by recrystallized from ether–1-propanol, mp 177–187 °C. ^1H NMR (D_2O): 3.38 (d, J = 6.6 Hz, 1 H), 2.54 (s, 2 H), 2.31 (dd, J = 10.3, 4.8 Hz, 1 H), 1.90 (dd, J = 6.4, 4.9 Hz, 1 H), 1.79 (d, J = 2.8 Hz, 1 H), 1.50 (dd, J = 10.3, 3.0 Hz, 1 H). ^{13}C NMR: 69.2, 44.5, 42.6, 39.3. Anal. Calcd for $C_5H_{10}NCl$: C, 50.2; H, 8.4. Found: C, 49.8; H, 8.6.

2-Nitrobicyclo[1.1.1]pentane (6). A solution of 7.3 g of *m*-chloroperbenzoic acid in 150 mL of chloroform was heated to reflux and 2-bicyclo[1.1.1]pentylamine from 1.0 g of the hydrochloride in 10 mL of chloroform was added. After being stirred for 16 h at reflux, the solution was cooled to room temperature and 2 mL of dimethyl sulfide was added to remove excess oxidant. The reaction mixture was separated by column chromatography with chloroform as the eluent. The nitro compound eluted immediately after dimethyl sulfide. The solvent was removed by distillation through a 4-in. glass bead column giving 0.23 g (24%) of 6. ^1H NMR: 4.48 (d, J = 7.0 Hz, 1 H), 3.01 (s, 2 H), 2.35 (dd, J = 10.2, 4.0 Hz, 1 H), 1.97 (dd, J = 7.0, 4.0 Hz), 1.77 (d, J = 3.1 Hz, 1 H), 1.55 (dd, J = 10.2, 3.1 Hz, 1 H). ^{13}C NMR: 91.8, 46.5, 39.4, 38.5. MS (CI): Calcd for $C_5H_8NO_2$ (p + 1) 114.0555, found 114.0546. EIMS: 54 (40), 67 (100), 82 (43).

2-Benzoylbicyclo[1.1.1]pentane. A solution of 210 mg (1.8 mmol) of bicyclo[1.1.1]pentane-2-carboxylic acid in 20 mL of dry ether was placed in a 100-mL flask with a reflux condenser. Phenyllithium (2.75 mL, 1.3 M, 3.6 mmol) was added dropwise, and the solution was heated at reflux for 30 min. The solution was treated with 2 mL of 10% sulfuric acid, and the layers were separated. The ether layer was washed with aqueous $NaHCO_3$, dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography (ether–pentane) to give the ketone as a colorless liquid (195 mg, 63%). ^1H NMR: 7.95–7.99 (m, 2 H), 7.41–7.56 (m, 3 H), 3.51 (d, J = 6.8 Hz, 1 H), 2.96 (s, 2 H), 2.27 (dd, J = 3.0, 9.8 Hz, 1 H), 1.90 (dd, J = 2.0, 9.8 Hz, 1 H), 1.82–1.86 (m, 2 H). ^{13}C NMR: 199.3, 136.9, 132.8, 128.4, 128.2, 67.4, 47.7, 46.7, 37.7. Anal. Calcd for $C_{12}H_{12}O$: C, 83.7; H, 7.0. Found: C, 84.0; H, 7.2.

Determination of Ionization Constants. The pK_a values for the carboxylic acids and the amine hydrochlorides were determined via potentiometric titration as previously described.[6] The pK_a values for the nitro compounds were determined using the procedure described by Bordwell et al.[16] The rate of base-catalyzed deuterium incorporation into the phenyl cycloalkyl ketones was measured in methanol-d_4 solution at 25 °C via NMR spectroscopy. They gave good pseudo-first-order kinetics. The rate constants were divided by the base concentration ($\sim 5 \times 10^{-3}$ M for the more reactive compounds and $\sim 4 \times 10^{-2}$ M for the less reactive compounds) to give the reported second order rate constants.

Addition of Nitrogen Dioxide (N_2O_4) to [1.1.1]Propellane: 1,3-Dinitrobicyclo[1.1.1]pentane and 1-Nitrobicyclo[1.1.1]pentane. The procedure reported here is based upon that reported by Wiberg and Waddell.[3] During a scaled up synthesis using the original procedure, a detonation of the concentrated reaction mixture occurred. We report a new procedure that safely decomposes the unstable compounds in the reaction mixture before purification.

To a three-necked flask equipped with magnetic stirring, cooled in an ice bath and purged under an argon atmosphere, was added 250 mL of dry diethyl ether. Nitrogen dioxide gas (50 mmol, approximately 4.6 g) was added to the ether through a bubbler. To this solution over 10 min was added 72 mL of a 0.28 M solution of [1.1.1]propellane (1.33 g, 20.2 mmol) in ether prepared as described previously.[19] The reaction mixture was then allowed to stir for an additional 15 min. Then the ice bath was removed, and 250 mL of an aqueous 5% NaCl solution was added to hydrolyze reactive compounds. The biphasic mixture was stirred for 5 min and was then decanted into a separatory funnel, and the layers were separated. The organic layer was washed five times with 125 mL of aqueous saturated sodium bicarbonate. The combined aqueous washes were extracted three times with 50 mL of ether. All the organic layers were combined and dried over sodium sulfate. The pale green ether solution was carefully concentrated to approximately one-fifth of the original volume. The resultant liquid was filtered to remove a yellow precipitate. The remaining solution was then concentrated to give 2.6 g of a semicrystalline liquid. This mixture was purified by column chromatography using a 1:1 mixture of hexanes and methylene chloride mixture as eluent. From this was collected 528 mg (3.34 mmol, 16.5% yield) of crystalline 1,3-dinitrobicyclo[1.1.1]pentane and 198 mg (1.75 mmol, 8.7% yield) of 1-nitrobicyclo[1.1.1]-pentane as a liquid.

1,3-Dinitrobicyclo[1.1.1]pentane. Mp: 65 °C (1.0 mmHg) sublimed. ^{1}H NMR: δ 3.01 (s, 6 H). ^{13}C NMR: δ 61.7 (C-NO_2), 57.1 (CH_2). FTIR: 1549 and 1380 cm^{-1} (NO_2 stretch). CIMS (isobutane): m/z 159 (M + 1). EIMS: m/z 82 (7), 66 (15), 65 (100), 54 (28), 39 (88). HRMS (CI, isobutane): Calcd for $C_5H_7N_2O_4$ (M + 1) 159.0406, found 159.0435.

1-Nitrobicyclo[1.1.1]pentane. ^{1}H NMR: δ 2.34 (s, 6 H), 2.61 (s, 1 H). ^{13}C NMR: δ 66.4 (C-NO_2), 53.1 (CH_2), 20.0 (C-H). FTIR: 1532 and 1384 cm^{-1} (NO_2 stretch). CIMS (isobutane): m/z 114 (M + 1). EIMS: m/z 67 (100), 65 (67), 41 (67). HRMS (CI, isobutane): Calcd for $C_5H_8NO_2$ (M + 1) 114.0555, found 114.0541.

2,2-Dichloro-1,3-dinitrobicyclo[1.1.1]pentane. Into a quartz tube was placed 90.0 mg (0.569 mmol) of 1,3-dinitrobicyclo[1.1.1]-pentane. The tube was sealed with a rubber septum and purged with argon. To this was added 10 mL of freshly distilled oxalyl chloride. The mixture was briefly degassed with argon and allowed to remain attached to a bubbler to prevent pressure build-up. The sample was irradiated in an ice bath with a 250-W Hanovia medium-pressure mercury vapor lamp equipped with a quartz filter for 5 days. After irradiation was complete, oxalyl chloride was removed under reduced pressure on a rotary evaporator. Excess methanol was then added to destroy any acid chlorides which remained. The methanol was removed, and the remaining crystalline sample was purified by column chromatography using 3:2 hexanes–methylene chloride was eluent. A total of 6.5 mg of starting material as well as 56.2 mg of 99.2% pure and 2.7 mg of 95% pure (total of 58.9 mg, 0.260 mmol, 49% yield based on recovered starting material) 2,2-dichloro-1,3-dinitrobicyclo[1.1.1]pentane was obtained. A white, crystalline, analytical sample was obtained by sublimation at 75 °C and 0.9 mmHg pressure. ^{1}H NMR: δ 3.20 (dd, J = 0.67 Hz, 2 H), 3.69 (dd, J = 0.67 Hz, 2 H). ^{13}C NMR: δ 71.07 (C-NO_2), 53.50 (CH_2), 91.35 (CCl_2). FTIR: 1556 and 1357 cm^{-1} (NO_2 stretch). CIMS (isobutane): m/z 227, 229 (M + 1). EIMS: m/z 134 (3), 122 (35), 120 (37), 99 (46), 87 (100), 73 (83), 63 (60). HRMS (CI, isobutane): Calcd for $C_5H_5Cl_2N_2O_4$ (M + 1) 226.9626, found 226.9620. Anal. Calcd for $C_5H_4Cl_2N_2O_4$: C, 26.46; H, 1.78. Found: C, 26.56; H, 1.81.

Acknowledgment. This investigation was supported by U.S. Army ARDEC via Geo-Centers, Inc. We thank Dr. Hortensia Sanchez-Martinez, U. C. Torrelaguna, Madrid, for a generous gift of cyclobutyl phenyl ketone.

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