

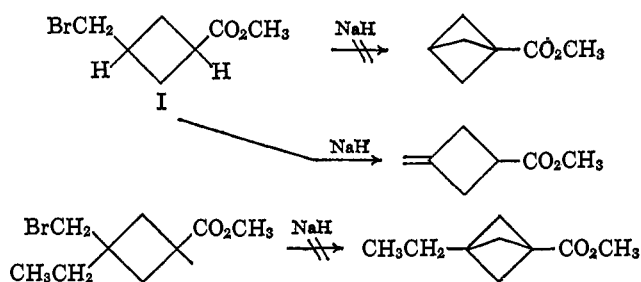
Bicyclo[1.1.1]pentane<sup>1</sup>Kenneth B. Wiberg and Daniel S. Connor<sup>2</sup>

Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut. Received June 6, 1966

**Abstract:** The synthesis of bicyclo[1.1.1]pentane and of its 1-methyl derivative is described. The physical properties (nmr, infrared, and mass spectra), the thermal rearrangement to 1,4-pentadiene, and halogenation reactions are reported.

Of the bicyclic small ring systems, bicyclo[1.1.1]pentane has been of particular interest to us. This ring system provides the possibility of examining the effect of placing two nonbonded atoms in close proximity (the nonbonded carbons, for example, should be about 1.9–2.2 Å apart), and of determining the effect of a cyclobutane ring on the reactivity at a bridgehead position. We now wish to report on the syntheses of bicyclo[1.1.1]pentanes<sup>3</sup> and on some of their properties and transformations.

Our original interest was with bridgehead-substituted derivatives, and in view of our success in preparing a bicyclo[1.1.0]butane derivative by an intramolecular halide displacement,<sup>4</sup> this method was tried with methyl 3-bromomethylcyclobutane-1-carboxylate (I) prepared by the anti-Markovnikov addition of hydrogen bromide to methyl 3-methylenecyclobutane-1-carboxylate.<sup>5</sup> Under conditions which lead to essentially complete bicyclobutane formation from methyl 3-bromocyclobutanecarboxylate,<sup>4</sup> no bicyclopentane derivative was formed and much of the starting ester was recovered. When more vigorous conditions were employed, less starting ester was recovered, but still no bicyclopentane derivative was formed. A major reaction was elimination of hydrogen bromide. When the 3 position was substituted with an ethyl group to block elimination, the results were no more satisfactory.



The availability of I made it attractive to attempt the preparation of bicyclo[1.1.1]pentane (III) *via* an intramolecular Wurtz reaction. This had proved very satisfactory in the synthesis of bicyclo[1.1.0]butane.<sup>4</sup> The reaction sequence is indicated below.

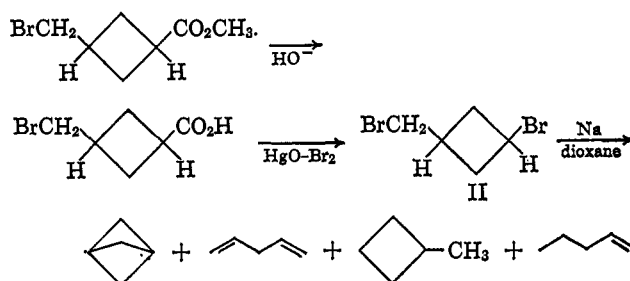
(1) This investigation was supported by the U. S. Army Research Office, Durham.

(2) Taken from part of the Ph.D. thesis of D. S. C., 1965.

(3) A preliminary account of the synthesis appeared in K. B. Wiberg and D. S. Connor, *Tetrahedron Letters*, 531 (1964).

(4) K. B. Wiberg and R. P. Ciula, *J. Am. Chem. Soc.*, **81**, 5261 (1959); K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, **21**, 2749 (1965).

(5) H. N. Cripps, J. K. Williams, and W. H. Sharkey, *J. Am. Chem. Soc.*, **81**, 2723 (1959).



The conversion of 3-bromomethylcyclobutane-1-carboxylic acid to the dibromide (II) using the Cristol-Firth modification<sup>6</sup> of the Hunsdiecker reaction proceeded satisfactorily provided water was removed *via* azeotropic distillation throughout the reaction. The reaction of II with sodium led to 40% of the theoretical amount of hydrocarbon containing 40% 1-pentene, 40% methylcyclobutane, 1% bicyclo[1.1.1]pentane, and 20% 1,4-pentadiene. The low yield of bicyclo[1.1.1]pentane led to an investigation of alternate metals, metal amalgams, and reaction conditions. The results are summarized in Table I. The metals

**Table I.** Reaction of Metals and Metal Amalgams with 3-Bromomethylcyclobutyl Bromide

Reagent	Solvent	% hydrocarbon	% 1-pentene	% methylcyclobutane	% bicyclopentane	% 1,4-pentadiene
Li	Dioxane	0				
Li(Hg) <sub>x</sub>	Dioxane	70	0	0	6	94
Na	Dioxane	40	40	40	1	20
Na(Hg) <sub>x</sub>	Dioxane	40	0	20	0	80
Na-K	Dioxane	10	0	0	0	0
Mg	<i>n</i> -Bu <sub>2</sub> O	10	(Some)	0	0	(Some)
Mg(Hg) <sub>x</sub>	Dioxane	85	0	0	0	100
Ca(Hg) <sub>x</sub>	Dioxane	84	0	6	2	90
Zn dust	Dioxane	Trace	0	0	Trace	0

were generally not very satisfactory, leading to relatively poor yields of hydrocarbon, and little, if any, bicyclo[1.1.1]pentane. The amalgams gave a higher yield of hydrocarbon with the main product being 1,4-pentadiene. For the formation of bicyclopentane, lithium amalgam was by far the most satisfactory reagent.

Since the amalgams were more satisfactory than the metals, it seemed of interest to try radical anions as the electron source. The results are summarized in

(6) S. J. Cristol and W. C. Firth, *J. Org. Chem.*, **26**, 280 (1961).

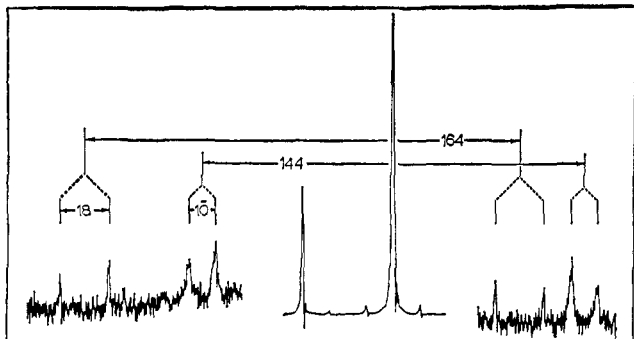


Figure 1. Nmr spectrum of bicyclo[1.1.1]pentane.

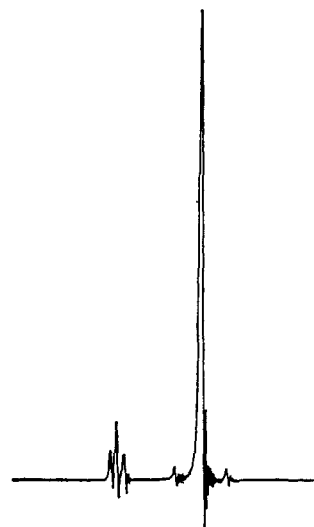
Table II. Although significant amounts of bicyclopentane could be obtained using the radical anion derived from naphthalene, the reaction was less convenient than that using lithium amalgam. The major part ( $\sim 90\%$ ) of the volatile material obtained in the former case was methyl vinyl ether, the cleavage product of 1,2-dimethoxyethane.

Table II. Reaction of Radical Anions with 3-Bromomethylcyclobutyl Bromide

Reagent	Solvent	Temp, °C	Result
Na-naphthalene	Dioxane	50 to 70	4% bicyclopentane
Na-naphthalene	1,2-Dimethoxyethane	-40 to +80	8% bicyclopentane
Na-anthracene	Dimethyl ether	-24	No bicyclopentane
Na-naphthalene	Dimethyl ether	-24	No bicyclopentane
Na-hexamethylphosphoramide	Hexamethylphosphoramide	110	No bicyclopentane

The bicyclo[1.1.1]pentane was easily identified because of its unique nmr spectrum having only two sharp bands at  $\tau$  8.16 and 7.55 in 3:1 ratio, coupled with the observation in the mass spectrum of a parent peak with  $m/e$  68. The compound must then have two different types of hydrogens in the ratio of 6:2, and these must be arranged so that spin-spin coupling is minimal. These structural features are provided in bicyclo[1.1.1]pentane which should have six hydrogens in an equatorial belt, and two bridgehead carbon-hydrogen bonds at right angles to the plane of the other hydrogens.

Two data of interest may be extracted from the carbon-13 proton nmr coupling; the  $C^{13}$ -H coupling constant and the H-H coupling constant between structurally similar hydrogens located on different carbons. The  $C^{13}$  satellites are shown in Figure 1, and indicate an 18-cps coupling between the bridgehead hydrogens and a 10-cps coupling between methylene hydrogens on adjacent carbons. The large bridgehead long-range coupling constant was confirmed by the preparation of bicyclo[1.1.1]pentane-1- $d$  via the use of deuterium bromide in the addition to methyl 3-methylencyclobutane-1-carboxylate followed by the other steps in the sequence. The spectrum (Figure 2) clearly shows the coupling between the deuterium and the bridgehead hydrogen, with a coupling constant of  $2.6 \pm 0.1$  cps. Deuterium-hydrogen coupling should be 0.154 times as great as hydrogen-hydrogen coupling,<sup>7</sup>

Figure 2. Nmr spectrum of bicyclo[1.1.1]pentane-1- $d$ .

and thus this value is in good agreement with the 18-cps H-H coupling.

The bridgehead-bridgehead long-range coupling constant is the largest thus far reported, although large values have been reported for other compounds.<sup>8</sup> It is clear that the coupling constant increases with a decrease in the distance between the carbons to which the hydrogens are attached, and it seems likely that the angle between the C-H bond orbitals is also of importance. A more quantitative correlation of coupling constant with geometry must await further structural data regarding the compounds. It is interesting to note that the methylene-methylene long-range coupling constant is the same as that for the *exo* hydrogens of bicyclobutane,<sup>4</sup> and the geometrical arrangement of the hydrogens should be essentially the same for both compounds.

The  $C^{13}$ -H coupling constants were 164 cps at the bridgehead and 144 cps at the methylene position. The bridgehead coupling is essentially that observed with cyclopropane (161 cps)<sup>8</sup> and that for the methylene hydrogens is somewhat larger than that for cyclobutane (134 cps). The results are in accord with one's qualitative expectation based on the bond angle deformation at each position. In view of our reservations concerning a quantitative relationship between s character and the coupling constant in compounds having considerable bond angle deformation,<sup>4</sup> no further conclusions will be drawn from these data at this time.

The infrared spectrum of bicyclo[1.1.1]pentane is particularly interesting. In the gas phase, each of the bands had clearly defined P, Q, and R branches. The selection rules governing the coupling of the rotation with vibration<sup>9</sup> predict that this should occur only with molecules which may be described as spherical tops. Using Wilcox's estimate<sup>10</sup> of the structure of bicyclopentane, the moments of inertia were calculated to be  $I_x = 13.0 \times 10^{-39}$  g cm<sup>2</sup> and  $I_y = I_z = 11.5 \times 10^{-39}$  g

(7) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 188.

(8) Cf. the summary in ref 4b.

(9) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p 36.

(10) C. F. Wilcox, Jr., *J. Am. Chem. Soc.*, **82**, 414 (1960).

cm<sup>2</sup>. The near-accidental degeneracy then permits the observed type of spectrum.<sup>11</sup>

The mass spectrum of bicyclopentane is also interesting. Under normal conditions, using 68-ev electrons, the principal peak had  $m/e$  67. Thus the process involving the loss of a hydrogen is a facile one. The nature of the fragmentation reactions occurring during ionization was investigated using the deuterium-labeled hydrocarbon. Using 15-ev electrons, the data in Table III were obtained.

Table III. Mass Spectrum of Bicyclo[1.1.1]pentane-d<sub>1</sub><sup>a</sup>

Peak <sup>b</sup> $m/e$	Rel intensity <sup>c</sup>	Probable structure	% D incor- porated
68	100.0		
67	22.6		79
53	38.5		59
42	39.2		62
41	43.5		48
40	59.7		42
39	49.6		25

<sup>a</sup> Using 15-ev electrons. <sup>b</sup>  $m/e$  ratio for unlabeled species. <sup>c</sup> Relative abundance for unlabeled species.

It may be noted that the  $p - 1$  peak ( $m/e$  67) is formed with the loss of 21% deuterium. Thus, it is not lost exclusively from the methylene position as might have been expected on the basis of studies of bridgehead carbonium ions.<sup>12</sup> If the loss of deuterium were statistical, and there were no isotope effects, only 12.5% deuterium should have been lost. Therefore, the bridgehead position appears to lose a hydrogen more readily than the methylene position. If only the bridgehead C-H bonds were involved, the result would require a kinetic isotope effect of  $k_H/k_D = 3.7$  which is somewhat larger than the values obtained in some cases.<sup>13</sup>

It is interesting that such a large proportion of deuterium was lost in the formation of the C<sub>4</sub> fragment. The result suggests that the carbon lost may be the bridgehead carbon, although it is difficult to see how this might come about. Further tracer work will be done in order to obtain more definitive evidence concerning the mode of fragmentation.

The appearance potentials for the  $m/e$  67 and 68 peaks were determined using krypton (AP = 14.00 ev) as the standard. The parent peak had an appearance potential (ev) of 9.65 and the  $p - 1$  peak had an appearance

(11) A vibrational analysis by bicyclo[1.1.1]pentane will be presented subsequently.

(12) W. von E. Doering, M. Levitz, A. Sayigh, M. Sprecher, and W. P. Whelan, Jr., *J. Am. Chem. Soc.*, **75**, 1008 (1953); P. von R. Schleyer and R. D. Nickolas, *ibid.*, **83**, 2700 (1961).

(13) M. W. Evans, N. Bauer, and J. Y. Beach, *J. Chem. Phys.*, **14**, 701 (1946).

Table IV. Appearance Potentials for Hydrocarbons<sup>a</sup>

<i>n</i> -Butane	10.80	1-Butene	9.72
<i>n</i> -Pentane	10.55	Isobutene	9.26
Isopentane	10.1	Isoprene	9.08
Cyclopentane	11.1	Dimethylacetylene	9.85
Cyclopropane	10.23	1,4-Pentadiene	9.58
Bicyclo[1.1.1]- pentane	9.65	Cubane	8.74 <sup>b</sup>

<sup>a</sup> See ref 15. <sup>b</sup> B. D. Kybett, S. Carroll, P. Natalis, D. W. Bonnell, J. L. Margrave and J. L. Franklin *J. Am. Chem. Soc.*, **88**, 626 (1966).

potential of 10.60. A comparison of the first datum with those for other hydrocarbons is recorded in Table IV.

The appearance potential for cyclopropane has been found to be lower than that for other saturated hydrocarbons—this is presumably a result in the change in the nature of bonding as a result of bond angle deformation. The value for bicyclopentane is significantly less—close to that of the alkenes. The recently reported appearance potential for the cubane molecular ion (8.74 ev) is also very low for a saturated compound. At first one might think that the decrease in appearance potential might result from a rearrangement to a less strained structure with a resultant decrease in energy of formation. However, the formation of the molecule ion is believed to be a vertical transition which occurs so rapidly that motion of the nuclei is insignificant.<sup>14</sup> Thus the structure cannot change during the ionization process.

The low appearance potential for the molecule ion has its counterpart in the potential for the  $p - 1$  ion. The appearance potential for the *t*-C<sub>4</sub>H<sub>9</sub> cation from isobutane is 11.6 ev. The value for bicyclo[1.1.1]pentane is less by about 1 ev and that for cubane (9.50 ev<sup>14</sup>) is less by about 2 ev. The formation of the  $p - 1$  ion need not be a vertical transition. The molecule ion may be formed with excess energy, and if the excess is sufficient, it may lose a hydrogen atom and give a possibly rearranged ion. It would not be surprising if the  $p - 1$  ion from bicyclo[1.1.1]pentane were the 3-methylenecyclobutyl cation. The thermochemical data needed for testing this hypothesis are not as yet available.















Finally, the thermal isomerization of bicyclopentane is of interest. The reaction occurs at about 300° giving 1,4-pentadiene as the product. The rate of rearrangement at 305° was determined giving  $k = 3 \times 10^{-5} \text{ sec}^{-1}$ . This value is compared with those for related hydrocarbons in Table V. A detailed comparison would require a knowledge of the activation energy for the reaction of bicyclo[1.1.1]pentane. This will be determined. It may be noted that the rates of reaction are not simply correlated with the over-all enthalpy changes since the  $\Delta H$  values for bicyclo[2.2.0]-hexane, the most reactive of the group, and for cyclopropane, the least reactive, are about the same. The reactions of bicyclo[1.1.0]butane and of bicyclo[2.1.0]pentane are considerably more exothermic.

Although bicyclo[1.1.1]pentane itself is of considerable interest, more information could be obtained if

(14) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press Inc., New York, N. Y., 1957, pp 258-267.

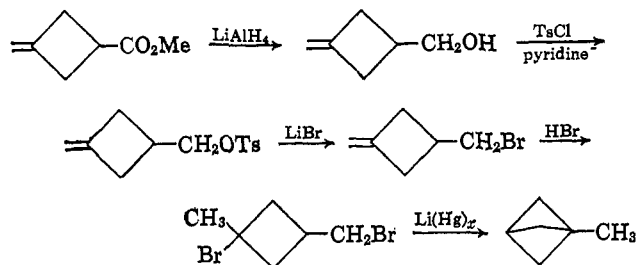
(15) R. I. Reed, "Ion Production by Electron Impact," Academic Press Inc., London, 1962, p 8.

Table V. Rates of Thermal Rearrangement of Hydrocarbons

Reactant	Product	$k_{30.5}$	Ref
		$6 \times 10^{-1}$	a
		$8 \times 10^{-2}$	b
		$1 \times 10^{-3}$	a, c
		$3 \times 10^{-6}$	
		$3 \times 10^{-6}$	
		$1 \times 10^{-8}$	e
		$5 \times 10^{-10}$	f

<sup>a</sup> C. Steel, R. Zand, P. Hurwitz, and S. G. Cohen, *J. Am. Chem. Soc.*, **86**, 679 (1964). <sup>b</sup> H. M. Frey and I. D. R. Stevens, *Trans. Faraday Soc.*, **61**, 90 (1965). <sup>c</sup> M. L. Halberstadt and J. P. Chesick, *J. Am. Chem. Soc.*, **84**, 2688 (1962). <sup>d</sup> R. Srinivasan and A. A. Levi, *ibid.*, **85**, 3363 (1963). <sup>e</sup> C. T. Genaux, F. Kern, and W. D. Walters, *ibid.*, **75**, 6196 (1953). <sup>f</sup> T. S. Chambers and G. B. Kistiakowsky, *ibid.*, **56**, 399 (1934).

bridgehead-substituted derivatives were available. Several attempts were made to obtain such compounds. The precursor for the preparation of the 1-methyl derivatives *via* a Wurtz reaction could be readily obtained *via* the reaction sequence



The reaction of the dibromide with lithium amalgam proceeded satisfactorily and gave 4% 1-methylbicyclo[1.1.1]pentane. The nmr spectrum of this compound had three sharp singlets at  $\tau$  8.89 ( $\text{CH}_3$ ), 8.33 ( $\text{CH}_2$ ), and 7.60 (CH) with relative areas of 3:6:1.

Chlorination of 1-methylbicyclo[1.1.1]pentane using *t*-butyl hypochlorite proceeded to give a modest yield (7%) of 1-chloromethylbicyclo[1.1.1]pentane having in the nmr spectrum three sharp singlets at  $\tau$  8.23 ( $\text{CH}_2$ ), 7.51 (CH), and 6.61 ( $\text{CH}_2\text{Cl}$ ) with relative areas of 6:1:2. The positions of the ring protons are not significantly affected by the chlorine.

The chlorination of bicyclo[1.1.1]pentane itself was also studied, again using *t*-butyl hypochlorite. This reaction proceeded quite well, and a typical run gave 45% recovered hydrocarbon, 45% 1-chlorobicyclo[1.1.1]pentane, and 6% 2-chlorobicyclo[1.1.1]pentane. The mixture could be separated by gas chromatography. The 1-chloro derivative was identified *via* its nmr spectrum ( $\tau$  7.89 and 7.24 singlets in a ratio of 6:1), mass spectrum (parent peaks at  $m/e$  102 and 104, resulting from the two chlorine isotopes), as well as elemental analysis. Here both types of hydrogens are shifted downfield by 0.3 ppm with respect to the parent hydrocarbon.

The 2-chloro derivative had a more complex nmr spectrum. The bridgehead protons gave a singlet at  $\tau$  7.37, and the proton on the carbon having the chlorine appeared as a doublet ( $J = 7$  cps) at  $\tau$  5.82. The remaining protons gave a series of bands from about  $\tau$  7.5–8.5. The mass spectrum had parent peaks at  $m/e$  102 and 104.

The formation of the bridgehead chloride as the principal product is striking when this result is compared with that for other bicyclic hydrocarbons such as norbornane which gives essentially no substitution at the bridgehead.<sup>16</sup>

## Experimental Section

**Methyl 3-(Bromomethyl)cyclobutanecarboxylate.** Dry air was bubbled through a solution containing 210 g (1.67 moles) of methyl 3-methylenecyclobutanecarboxylate<sup>6</sup> and 6 g of benzoyl chloride in 1.5 l. of carbon tetrachloride for 15 min while a sunlamp was positioned directly outside the flask. Anhydrous hydrogen bromide was bubbled into the solution until the reaction was complete (about 3 hr). During this time the solution warmed to about 40–50°; no external heating was required. The extent of reaction was followed using the nmr spectrum.

Most of the carbon tetrachloride was removed by distillation from the stirred solution. The pot temperature must be kept under 130°. The residue was distilled under reduced pressure giving 350 g (92%) of the bromo ester, bp 65–70° at 0.2 mm. The nmr spectrum (in  $\tau$  units: cyclobutane ring, 6.9–8.3; methyl ester, "doublet" at 6.38;  $-\text{CH}_2\text{Br}$ , two overlapping doublets centered at 6.57; area ratios 6:2:3) suggested a 50:50 mixture of *cis* and *trans* isomers.

*Anal.* Calcd for  $\text{C}_7\text{H}_{11}\text{O}_2\text{Br}$ : C, 40.6; H, 5.4; Br, 38.6. Found: C, 40.7, 40.6; H, 5.2, 5.2; Br, 38.7, 38.6.

**3-(Bromomethyl)cyclobutanecarboxylic Acid.** Sodium hydroxide solution (1 l., 0.5 M) was cooled to 0° and 1035 g (5 moles) of methyl 3-(bromomethyl)cyclobutanecarboxylate was added with stirring, maintaining the temperature at 0°. Cold sodium hydroxide solution (1 l., 5.0 M) was added from an addition funnel as fast as possible without having the reaction temperature exceed 6°. This required about 0.5 hr. When the base had been added, the stirred mixture was allowed to warm to room temperature. When the reaction mixture became homogeneous (3–4 hr), the solution was cooled to 0°, and 475 ml (5.5 moles) of concentrated hydrochloric acid was added. The reaction mixture was extracted with two 2-l. and two 500-ml portions of ether. The combined ether extract was washed with saturated salt solution, dried over sodium sulfate, and concentrated using a rotary evaporator. Distillation gave 850 g (88%) of the bromo acid, bp 107–112° at 0.1 to 0.5 mm.

*Anal.* Calcd for  $\text{C}_6\text{H}_9\text{O}_2\text{Br}$ : C, 37.3; H, 4.7; Br, 41.4. Found: C, 37.4, 37.5; H, 4.8, 4.7; Br, 41.2, 41.2.

**3-(Bromomethyl)cyclobutyl Bromide.** The apparatus consisted of a 5-l. three-necked flask equipped with a Trubore stirrer with a Teflon paddle, a heating mantle, a 1-l. pressure-equalizing addition funnel, and a water separator to which an Allihn condenser had been fitted. The flask was covered with aluminum foil to exclude light. To the flask was added 216 g (1.0 mole) of red mercuric oxide and 2 l. of carbon tetrachloride. Stirring was started, and the solvent was heated to reflux to remove residual water. A solution of 193 g (1.0 mole) of 3-(bromomethyl)cyclobutanecarboxylic acid and 200 g (64 ml, 1.25 moles) of bromine in 700 ml of carbon tetrachloride was added over 2–3 hr with stirring at the reflux temperature. Heating was continued for 0.5 hr after the addition had been completed.

The solution was now cooled in cold water and filtered into a 4-l. separatory funnel. The solution was extracted twice with 1-l. portions of saturated sodium carbonate solution and once with 1 l. of saturated salt solution. After drying over anhydrous sodium sulfate, the carbon tetrachloride was removed by distillation at 35° and 120 mm. The residue was distilled giving 171–194 g (75–85%) of 3-(bromomethyl)cyclobutyl bromide, bp 60–65° at 0.5 mm. The nmr spectrum had the cyclobutane band at  $\tau$  6.7–8.0;  $-\text{CH}_2\text{Br}$ , doublet ( $J = 6.0$  cps),  $\tau$  6.55; and the hydrogen  $\alpha$  to the bromine at  $\tau$  5.60, pentuplet. The areas had a 5:2:1 ratio.

(16) E. C. Kooyman and G. C. Vegter, *Tetrahedron*, **4**, 382 (1958).

*Anal.* Calcd for  $C_5H_8Br_2$ : C, 26.3; H, 3.5; Br, 70.1. Found: C, 26.5, 26.5; H, 3.6, 3.5; Br, 70.0, 70.0.

**Bicyclo[1.1.1]pentane.** Lithium amalgam was prepared from 2.5 g of lithium (0.35 g-atom) and 500 g of mercury. The amalgam and 150 ml of dioxane (distilled from the benzophenone ketyl) was placed in a 500-ml flask equipped with a stirrer, a condenser, an addition funnel, and a Dry Ice-acetone cooled trap. A solution of 22.8 g (0.1 mole) of 3-(bromomethyl)cyclobutyl bromide in 30 ml of purified dioxane was added over 3–5 hr to the amalgam-dioxane mixture which was stirred and heated to reflux. With the water in the condenser maintained at 60–80°, the hydrocarbons distilled into the trap. At the end of the addition, the remaining bicyclopentane was swept into the trap with helium.

A 500-ml flask containing 15 g of bromine was attached to a vacuum line and covered with aluminum foil. After freezing in liquid nitrogen, the flask was evacuated, and the hydrocarbon mixture was distilled into the flask. The coolant was removed and the flask allowed to warm slowly. When the pressure began to increase rapidly, the flask was quickly cooled (care must be exercised—the pressure rises very rapidly and could lead to a rupture of some part of the vacuum system). The process was repeated until no further reaction occurred. The more volatile contents of the flask were transferred to a storage trap.

The product from several runs was separated using a large vpc at room temperature. A silver nitrate-glycol column was used to separate bicyclo[1.1.1]pentane (0.75 min) and methylcyclobutane (0.75 min) from 1,4-pentadiene (12 min). A  $\beta,\beta'$ -oxydipropionitrile column was used to separate methylcyclobutane (4.6 min) from bicyclopentane (5.5 min). At this stage, the hydrocarbon appeared to be 98% pure. Further purification could be effected when necessary using a nitrobenzene column.

The vapor pressure of bicyclo[1.1.1]pentane was determined at 14 temperatures from  $-0.8$  to  $21.5^\circ$ . From these data, the normal boiling point was calculated to be  $36.0 \pm 0.05^\circ$  and the enthalpy of vaporization was found to be 6.36 kcal/mole. The complete mass spectrum and the infrared spectrum may be found in the thesis of D. S. C.

**Bicyclo[1.1.1]pentane-1-*d*<sub>1</sub>.** The procedures described above were used except that deuterium bromide (prepared by the reaction of phosphorus tribromide with deuterium oxide) was used instead of hydrogen bromide.

**3-Methylenecyclobutane-1-methanol.** A solution of 252 g (2.0 moles) of methyl 3-methylenecyclobutanecarboxylate in 1 l. of anhydrous ether was added with stirring over a 3-hr period to 76 g (2.0 moles) of lithium aluminum hydride in 3 l. of dry ether. The thick mixture was heated to reflux and stirred for 7 hr. Then 144 g of water was added as rapidly as possible. The ether solution was separated by decantation, and the solid residue was washed with ether by decantation. The combined ether solution was dried over anhydrous sodium sulfate and distilled giving 133 g (58%) of 3-methylenecyclobutane-1-methanol, bp  $80^\circ$  at 25 mm.

**3-Methylenecyclobutane-1-methyl Bromide.** A solution of 220 g (1.16 moles) of *p*-toluenesulfonyl chloride in 500 ml (6.3 moles) of dry pyridine was cooled in an ice-water bath. To this was added 113 g (1.15 moles) of 3-methylenecyclobutane-1-methanol. After standing overnight in a refrigerator the solution was allowed to come to room temperature. Water (10 ml) was added to hydrolyze any remaining *p*-toluenesulfonyl chloride. The solution was poured into a mixture of 500 g of ice and 500 ml of concentrated hydrochloric acid. The mixture was extracted with one 1-l. and two 500-ml portions of ether. The ether extract was washed with a mixture of 250 ml of concentrated hydrochloric acid and 200 g of ice, with 5% sodium hydroxide solution, with 5% sodium bicarbonate solution, and with saturated salt solution. The ether was

removed using a rotary evaporator to give 241 g (81%) of the tosylate.

The tosylate was added to 3 l. of dry acetone containing 435 g (5.0 moles) of dry lithium bromide, and the solution was heated to reflux overnight with stirring. The acetone was removed using a rotary evaporator. The residue was added to 1 l. of water, and the mixture was extracted with two 1-l. portions of ether. After drying over magnesium sulfate, the ether was removed using a rotary evaporator. Distillation of the residue gave 97 g (63%) of 3-methylenecyclobutane-1-methyl bromide, bp  $80^\circ$  at 80 mm.

**3-Bromo-3-methylcyclobutane-1-methyl Bromide.** A mixture of 40 g (0.25 mole) of 3-methylenecyclobutane-1-methyl bromide, 1 g of hydroquinone, and 200 ml of pentane was placed in a flask equipped with a Dry Ice cooled condenser and wrapped with aluminum foil, and the system was purged with nitrogen. Hydrogen bromide was added rapidly for 2 hr, and the mixture was then allowed to stand overnight. Distillation gave 54 g (90%) of 3-bromo-3-methylcyclobutane-1-methyl bromide, bp  $55^\circ$  at 1 mm. The nmr spectrum showed a split methyl band (*cis* and *trans* isomers) centered about  $\tau$  8.10, a  $CH_2Br$  band at  $\tau$  6.54 (multiplet), and a cyclobutane band at  $\tau$  6.5–8.0 with area ratios of 3:2:5.

**1-Methylbicyclo[1.1.1]pentane.** The reaction of lithium amalgam (from 2.0 g of lithium and 500 ml of mercury) with 28 g of 3-bromo-3-methylcyclobutane-1-methyl bromide was carried out essentially as described for bicyclopentane, except that the gas trap was omitted, and the condenser was cooled with tap water. After the reaction was completed, the condenser was replaced by a  $10 \times 250$  mm vacuum-jacketed column packed with Helipak and a partial reflux head. The pot was heated to  $122^\circ$ , and the fraction with bp  $53$ – $85^\circ$  (0.52 g) was collected. Nmr analysis indicated 19% dioxane, 69% 2-methyl-1,4-pentadiene, and 12% 1-methylbicyclo[1.1.1]pentane. The mixture was cooled in an ice-water bath, and bromine was added slowly from a fine dropper until the bromine color persisted. The volatile material was separated and purified by vpc using a GE SF-96 silicone column at  $75^\circ$ . 1-Methylbicyclo[1.1.1]pentane had a retention time of 2.5 min, and its nmr spectrum had three sharp singlets at  $\tau$  8.89, 8.33, and 7.60 with area ratios of 3:6:1.

**Thermal Isomerization of Bicyclo[1.1.1]pentane.** After heating at  $305 \pm 2^\circ$  for 9.0 hr, a sample of bicyclo[1.1.1]pentane was converted to a 1:1 mixture of bicyclopentane and 1,4-pentadiene as indicated by the nmr spectrum of the mixture.

**Chlorination of Bicyclo[1.1.1]pentane.** Bicyclo[1.1.1]pentane was distilled into a thin-wall 5-mm nmr tube to a depth of 20 mm, and *t*-butyl hypochlorite was added dropwise to give a total depth of 100 mm. The tube was frozen in liquid nitrogen, degassed twice, and sealed. After warming to room temperature, the tube was placed along the inner wall of a 800-ml beaker filled with ice-water and was irradiated at a distance of 5 cm with a 100-w incandescent light bulb until the yellow color of the hypochlorite disappeared ( $\sim 3$  hr). The products were separated by vpc using a 0.25 in.  $\times 5$  ft GE SF-96 column at  $95^\circ$ . Besides *t*-butyl alcohol there was obtained recovered bicyclo[1.1.1]pentane (1.0 min, 45%) and 2-chlorobicyclo[1.1.1]pentane (6.2 min, 6%).

1-Chlorobicyclo[1.1.1]pentane had a characteristic nmr spectrum with two sharp singlets at  $\tau$  7.86 and 7.24 with an area ratio of 6:1. The mass spectrum had parent peaks at  $m/e$  102 and 104.

*Anal.* Calcd for  $C_5H_7Cl$ : C, 58.6; H, 6.8; Cl, 34.6. Found: C, 58.4, 58.5; H, 6.9, 6.9; Cl, 34.5.

The compound believed to be 2-chlorobicyclo[1.1.1]pentane had a more complex nmr spectrum with a singlet at  $\tau$  7.37 (area 2, bridgehead), a doublet ( $J = 7$  cps) at  $\tau$  5.82 corresponding to the proton  $\alpha$  to the chlorine, and a series of bands from  $\tau$  7.5 to 8.4 for the remaining protons. The mass spectrum had parent peaks at  $m/e$  102 and 104.