1677 (s, $C{=}O$), 1655 (m, $C{=}C$), 1365 (s, CH_3 bend of $COCH_3$), and 822 cm^{-1} (s, CH bend on a trisubstituted double bond); uv λ_{max}^{EtOH} 305 (w, R band) and 228 mμ (s, K band); mass spectrum *m/e* (rel intensity) 98 (33) (parent peak), 83 (25), 55 (100), 43 (55), 39 (22), 29 (29), 27 (32), and 15 (21). The compound gave a positive iodoform test.

4-Methyl-4-hepten-3-one (22).—This compound was prepared by condensation of propionaldehyde and 3-pentanone in a manner similar to the preparation of **23**.

Spectral data of compound **22** follow: nmr $\delta_{TMS}^{CCl_4}$ 6.46 (t, fine splitting, 1 H, $CH_3C{=}CHCH_2$), 2.59 (q, 2 H, $COCH_2CH_3$), 2.24 (quintet, broad, 2 H, CH_3CH_2CH, *trans* to carbonyl), 1.72 (s, fine splitting, 3 H, $CH{=}CCH_3$, α methyl), and 1.08 and 1.04 (2 t, 6 H, CH_2CH_3); ir (neat) ν_{max}^{NaCl} 3045 (w, vinyl H), 1670 (s, $C{=}O$), 1642 (w, $C{=}C$), and 802 cm^{-1} (s, CH bend on a trisubstituted double bond); uv λ_{max}^{EtOH} 305 (w, R band) and 224 mμ (s, K band); mass spectrum *m/e* (rel intensity) 126 (15) (parent peak), 97 (80), 69 (77), 57 (13), 41 (100), 39 (27), 29 (38), 28 (12), and 27 (38).

5-Ethyl-4-methyl-4-hepten-3-one (16).—Analogous to the condensations described above, 172 g (2 mol) of 3-pentanone was condensed by means of 108 g (0.66 mol) of phosphorus oxychloride. Twenty grams of zinc chloride was used as a catalyst in this reaction. The usual work-up procedure gave 145 g of crude product. Distillation under reduced pressure gave 85 g of colorless product, bp 75–104° (5 mm). Analysis of the product shows the presence of 7.0% **16** and 93.0% 5-ethyl-4-methyl-5-hepten-3-one (**33**). Separation was accomplished by means of a 20 ft × 0.375 in., 30% FFAP column.

Spectral data of compound **16** follow: nmr $\delta_{TMS}^{CCl_4}$ 2.44 (q, 2 H, $COCH_2CH_3$), 2.10 and 2.08 (pair of quartets, 4 H, CH_3CH_2), 1.79 (s, 3 H, α methyl), and 1.02 (overlapping t, 9 H, CH_2CH_3); ir (neat) ν_{max}^{NaCl} 1689 (s, $C{=}O$) and 1615 cm^{-1} (w, $C{=}C$); uv λ_{max}^{EtOH} 305 (w, R band) and 247 mμ (s, K band).

4,5-Dimethyl-4-hexen-3-one (15).[20,21]—Propionyl chloride (186 g, 2 mol) was mixed with 210 g (3 mol) of Eastman technical-grade pentene (*ca.* 2:1 ratio of 2-methyl-2-butene and 2-pentene) in a round-bttomed flask fitted with a reflux condenser. Twenty grams of stannic chloride was added slowly through the condenser, causing the temperature to rise to *ca.* 50°. The flask was heated gently for 30 min, at which time the temperature of the reaction mixture had reached *ca.* 100°. The resulting liquid was cooled and then poured into dilute hydrochloric acid prepared with 160 ml of concentrated hydrochloric acid and 600 ml of water. The top ketonic layer was washed with saturated sodium bicarbonate and dried over sodium sulfate. After low-boiling material had been removed, 305 g of crude chloro ketone was refluxed for 2 hr with 90 g of potassium hydroxide dissolved in 405 g of 95% ethanol. Treatment with a large volume of water separated 117 g of olefinic ketone. Although some unidentified products were present, most of the material was a mixture of the condensation products of propionyl chloride and 2-methyl-2-butene. Isolation of the olefinic ketone mixture by preparative gc and subsequent characterization showed the mixture to consist of 84.7% **15** and 15.3% 4,5-dimethyl-5-hexen-3-one (**34**). The two ketones were separated on an 8.5 ft × 0.375 in., 20% TCEP column at 123°.

Spectral data of compound **15** follow: nmr $\delta_{TMS}^{CCl_4}$ 2.42 (q, 2 H, $COCH_2CH_3$), 1.74 (s, 6 H, β methyls), 1.72 (s, 3 H, α methyl), and 0.99 (t, 3 H, CH_2CH_3); ir (neat) ν_{max}^{NaCl} 1695 (s, $C{=}O$), 1626 (m, $C{=}C$), and 1418 cm^{-1} (w, CH_2 bend of $COCH_2$); λ_{max}^{EtOH} 300–305 (w, R band) and 244 mμ (s, K band); mass spectrum *m/e* (rel intensity) 126 (20) (parent peak), 97 (88), 69 (92), 57 (18), 53 (13), 41 (100), 39 (28), 29 (36), and 27 (34).

5-Ethyl-2,4-dimethyl-4-hepten-3-one (17).—Isobutyryl chloride (7.5 g) and 10.3 g (0.105 mol) of 3-ethyl-2-pentene were condensed in the presence of stannic chloride. The reaction and work-up procedure were similar to that described above. A mixture of **17** and 5-ethyl-2,4-dimethyl-5-hepten-3-one (**35**) was obtained. Separation was accomplished using a 6 ft × 0.375 in., 20% Carbowax column at 155°.

Spectral data of compound **17** follow: nmr $\delta_{TMS}^{CCl_4}$ 2.75 [m, 1 H, $COCH(CH_3)_2$], 2.04 (q, 2 H, $CH_3CH_2C{=}C$, *cis* to carbonyl), 1.95 (q, 2 H, $CH_3CH_2C{=}C$, *trans* to carbonyl), 1.76 (s, 3 H, α methyl), 1.02 [d, 6 H, $CH(CH_3)_2$], and 0.99 (t, 6 H, CH_2CH_3); ir (neat) ν_{max}^{NaCl} 1678 (s, $C{=}O$) and 1616 cm^{-1} (w, $C{=}C$); uv λ_{max}^{EtOH} 302 (w, R band) and 247 mμ (s, K band); mass spectrum *m/e* (rel intensity) 168 (7) (parent peak), 125 (56), 69 (21), 55 (100), 43 (28), 41 (36), 39 (16), 29 (15), and 27 (25).

Registry No.—**2**, 141-79-7; **5**, 13905-10-7; **6**, 20685-43-2; **7**, 20685-44-3; **8**, 22319-24-0; **9**, 22319-25-1; **10**, 22287-10-1; **11**, 22319-26-2; **12**, 22287-11-2; **13**, 22287-12-3; **14**, 22287-13-4; **15**, 17325-90-5; **16**, 22319-28-4; **17**, 22319-29-5; **18**, 684-94-6; **19**, 20685-45-4; **20**, 20685-46-5; **21**, 22319-31-9; **22**, 565-62-8; **23**, 78-94-4; **24**, 814-78-8.

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(20) J. Colonge and K. Mostafavi, *Bull. Soc. Chim. Fr.*, **6**, 335 (1939).

(21) J. Colonge and D. Joly, *Ann. Chem.*, **18**, 286 (1943).

Bicyclo[1.1.1]pentane Derivatives[1]

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The synthesis of a variety of 1- and 2-substituted bicyclo[1.1.1]pentanes is described. Free-radical substitution occurs primarily at the bridgehead, and both types of hydrogens are markedly deactivated toward free-radical attack. The bridgehead radical opens to the methylenecyclobutyl radical at an appreciable rate. The K_a of the bridgehead acid is higher than that for any other simple saturated carboxylic acid, and the K_b of the bridgehead amine is lower than that of any other simple aliphatic amine. The nmr spectra of the compounds are discussed and the coupling constants and chemical shifts are given.

In the case of bicyclo[1.1.1]pentane, the parent hydrocarbon is more easily obtained than its simple derivatives.[3] Bicyclopentane was originally prepared by the reaction of 3-bromomethylcyclobutyl bromide with lithium amalgam.[4] It has also been obtained by the photolysis of bicyclo[2.1.1]hexan-2-one[5] and of 1,4-pentadiene.[6] The Wurtz reaction has been improved using the naphthalene radical anion as the halogen abstractor to give a 6.5% yield of the hydrocarbon. Recently, Rifi has found that the electrochemical dehalogenation[7] also is successful with 3-bromomethylcyclobutyl bromide and gives over twice the yield obtained using the chemical reagents.[8] This

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

[2] Taken from part of the Ph.D. thesis of V. Z. Williams, 1968. Proctor and Gamble Fellow, 1966–1967; Heyl Fellow, 1967–1968.

[3] The only functional bicyclo[1.1.1]pentane derivative which has been obtained from a compound other than the parent hydrocarbon is the 2-phenyl-2-hydroxy compound formed *via* the irradiation of phenyl cyclobutyl ketone [A. Padwa and E. Alexander, *J. Amer. Chem. Soc.*, **89**, 6376 (1967)].

[4] K. B. Wiberg and D. S. Connor, *ibid.*, **88**, 4437 (1966).

[5] J. Meinwald, W. Szkrybalo, and D. R. Dimmel, *Tetrahedron Lett.*, 731 (1967).

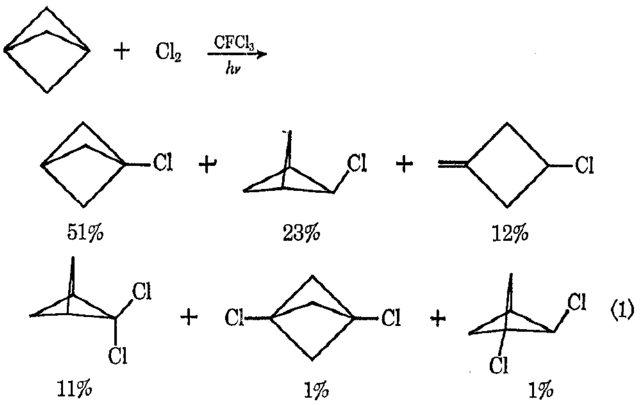
[6] R. Srinivasan and K. H. Carlough, *J. Amer. Chem. Soc.*, **89**, 4932 (1967).

[7] M. R. Rifi, *ibid.*, **89**, 4442 (1967).

[8] Dr. M. R. Rifi, personal communication.

appears to be the best way in which to obtain bicyclo[1.1.1]pentane.

One of the simplest methods of obtaining a functional bicyclopentane derivative is free-radical halogenation. We have previously reported on the chlorination using *t*-butyl hypochlorite.[4] We have found it possible to effect direct, photochemically initiated chlorination in Freon 11 (trichlorofluoromethane) as a solvent. Using a limited concentration of chlorine, an 11% yield of a mixture of mono- and dichlorides was obtained with the following distribution (eq 1).



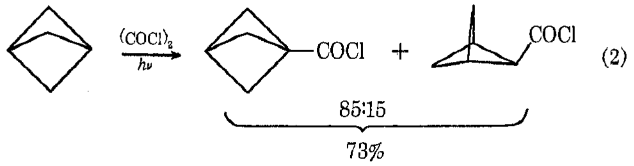
The products were easily identified by their nmr spectra. The majority of the products consisted of polyhalides, and at least part of this was derived from 3-methylenecyclobutyl chloride. It seems probable that the bridgehead radical was formed, and then opened to the 3-methylenecyclobutyl radical before reacting with chlorine. This hypothesis was tested by carrying out the reaction using a relatively high chlorine concentration. The mono- and dichlorides were now obtained in 50% yield and gave the products indicated above in the proportions 62, 15, 0, 14, 2, and 7%, respectively. The amount of ring opening was decreased markedly, suggesting that the 1-bicyclo[1.1.1]pentyl radical rearranges to the 3-methylenecyclobutyl radical with a significant activation energy.

The ratio of bridgehead to methylene substitution was 2.4:1 (assuming that the 1,2 dichloride was formed from the 1-chloro derivative), giving a relative reactivity per hydrogen of 7:1. The chlorination of other bicyclic hydrocarbons such as norbornane,[9] nortricyclane,[10] bicyclo[2.1.1]hexane,[11] and bicyclo[2.2.0]hexane[12] has also been studied. In each case, the majority of the products are derived from the unrearranged hydrocarbons, and only in the case of bicyclo[2.2.0]hexane was any bridgehead substitution (15%) found. In the case of bicyclo[2.1.1]hexane, all of the chlorides isolated were substituted at the two-carbon bridge.

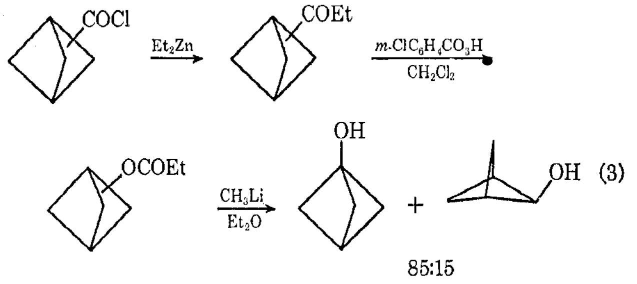
Srinivasan and Sonntag[11] found that the rate of chlorination of a methylene group in cyclohexane is only 1.25 times greater than that of the 2 position of bicyclo[2.1.1]hexane. An attempt was made to carry out a competitive chlorination of bicyclo[1.1.1]pentane and cyclohexane. However, cyclohexane reacted essentially instantaneously under conditions which led to a relatively slow reaction with bicyclopentane. It would appear that the relative reactivities must be on the order of 100:1 or greater.

Two factors may contribute to the low reactivity of bicyclo[1.1.1]pentane. First, both the bridgehead and methylene positions incorporate considerable strain, which should result in a marked decrease in reactivity. Second, the secondary hydrogens are sterically not so accessible so in cyclohexane. As a result, the tertiary bridgehead position becomes more reactive than the secondary methylene position.

In an effort to introduce conveniently a carbon-containing functional group, the little-used photochemical reaction between a hydrocarbon and oxalyl chloride[13] was tried. The reaction was found to give 73% of a mixture of acid chlorides (eq 2). Some disubstitution products also appear to have been formed. Again, bridgehead substitution predominates.

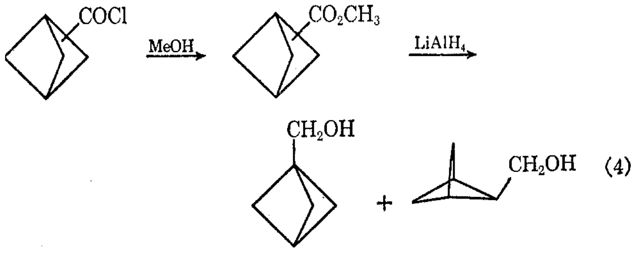


The acid chloride mixture could be converted into a mixture of the 1- and 2-hydroxy compounds by conversion into the ketone and peracid oxidation (eq 3).



The two alcohols could be separated by vpc, and were obtained in an 85:15 ratio corresponding to the acid chloride mixture. Bicyclo[1.1.1]pentan-1-ol was a solid, mp 61–62°.

Treatment of the acid chloride mixture with methanol gave the methyl esters, which could be reduced to the carbinols with lithium aluminum hydride (eq 4).



The carbinol mixture could be separated by vpc. Treatment of the acid chlorides with water gave the carboxylic acids, which could be separated by vpc. The bridgehead acid was a solid, mp 59–59.7°. The

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[9] E. C. Kooyman and G. C. Vegter, *Tetrahedron*, **4**, 382 (1958).

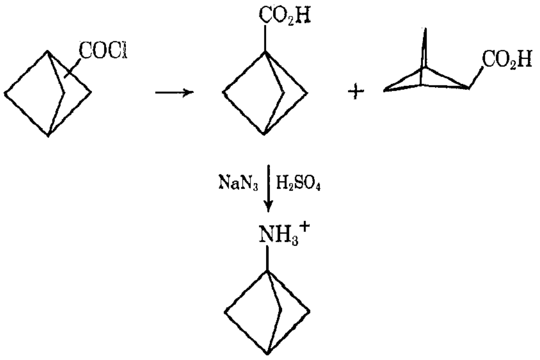
[10] M. L. Poutsma, *J. Amer. Chem. Soc.*, **87**, 4293 (1965).

[11] R. Srinivasan and F. I. Sonntag, *ibid.*, **89**, 407 (1967).

[12] R. Srinivasan and F. I. Sonntag, *Tetrahedron Lett.*, 603 (1967).

[13] M. S. Kharasch and H. C. Brown, *J. Amer. Chem. Soc.*, **64**, 329 (1942). This reaction has recently been applied to a bicyclic system by P. K. Freeman, F. A. Raymond, J. C. Sutton, and W. R. Kindley, *J. Org. Chem.*, **33**, 1448 (1968).

bridgehead acid was converted into the amine *via* the Schmidt reaction (eq 5).

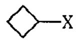
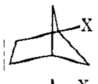


(5)

We have previously noted the effect of hybridization at the bridgehead position on the dissociation constant of carboxylic acids and on the basicity of amines.[14] In order to extend these observations, the compounds obtained in this series were studied. Bicyclo[1.1.1]pentane-1-carboxylic acid was found to have a K_a of 8.05×10^{-5} in water at 25°, which is the largest value so far noted for a simple saturated carboxylic acid. The corresponding amine was found to have a K_b of 3.8×10^{-6}, and thus is considerably less basic than even ammonia. A summary of some of the available data is recorded in Table I. The 1-bicyclo[1.1.1]pentanecarboxylic acid is nine times as acidic as pivalic acid, and over twice as acidic as the closely related 1-bicyclo[2.1.1]hexanecarboxylic acid. A similar trend is found with the amines, with 1-bicyclo[1.1.1]pentylamine being much less basic than even ammonia. The changes in acidity and basicity almost certainly arise primarily from the change in s character in the bridgehead–X bond as the bond angles at the bridgehead are distorted from their normal values.[14] In accord with this, the ^{13}C–H nmr coupling constant at the bridgehead position of bicyclo[1.1.1]pentane is 160 Hz.[4]

TABLE I

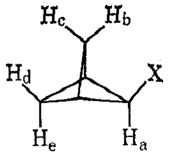
DISSOCIATION CONSTANTS OF CARBOXYLIC ACIDS AND AMINES IN WATER AT 25°

Compd	$K_a \times 10^5$, X = CO_2H^a	$K_b \times 10^5$, X = NH_2
H–X		1.98
CH_3–X	1.77	42
$(CH_3)_3C$–X	0.89	28
	1.64	11
	3.48	2.0^b
	8.05	0.38

^{a} Except for the bicyclic compounds, the data were taken from M. Kotake, "Constants of Organic Compounds," Asakura Publishing Co., Tokyo, 1963, pp 585 and 615. ^{b} Reference 14.

Finally, we may consider the nmr spectra of the bicyclo[1.1.1]pentane derivatives. The 1-substituted derivatives exhibit very simple spectra (two singlets), since there is no coupling between the bridgehead and methylene protons. The chemical shifts are summarized in Table II. The effect of the substituent is remarkably small at the C_3 hydrogen. A larger range of values is found for the C_2 hydrogens, and the difference in values for the two types of hydrogens varies from 0.32 to 0.78 ppm.

Considerably more data may be derived from the spectra of the 2-substituted derivatives (Table III). In each case, the two bridgehead hydrogens lead to a sharp singlet. The methylene protons are all nonequivalent, allowing the observation of both geminal and long-range coupling. The hydroxy and chloro compounds gave essentially first-order splitting patterns and the spectra were easily analyzed. With approximate values of the coupling constants, it was possible to analyze the spectra of the other compounds with the aid of the program LAOCN 3.[15] The designation of the protons is shown below. The long-range coupling constants were *ca.* 10 Hz for the unsubstituted position and *ca.* 7 Hz for the coupling involving H_a. This corresponds to the value found for the parent hydrocarbon.[4] The geminal coupling constants were *ca.* 3 Hz, which is reasonable for this structure.[16]



The magnitudes of the chemical shifts are of interest in connection with development of approaches to calculating these quantities, since the molecules have rigid, well-defined geometries. However, a detailed discussion of this problem will be postponed until other related data may be presented.

Experimental Section

Bicyclo[1.1.1]pentane.—To a 3-l., three-necked flask equipped with an addition funnel with helium inlet, Trubore stirrer with Teflon paddle, and an Allihn condenser attached to a Dry Ice–acetone-cooled trap was added 23 g (1 g-atom) of sodium, 1500 ml of dry glyme, and 128 g (1 mol) of naphthalene. The mixture was stirred under helium at room temperature to allow the deep green radical anion solution to form. The flask was cooled to −30° using a Dry Ice–isopropyl alcohol bath, and a solution of 57 g (0.25 mol) of 3-bromomethylcyclobutyl bromide in 250 ml of dry glyme was added dropwise over a 3-hr period. The addition funnel was replaced by a helium inlet tube which extended below the surface of the solution and the flow of gas was increased to a moderate rate. The solution was allowed to warm slowly and then was heated to reflux for 1.5 hr to distil the products into the trap. The product was bulb-to-bulb distilled into a storage trap for subsequent purification. The excess radical anion in the reaction flask was destroyed with water and the solvent was recovered by centrifugation of the suspended solids and redistillation from sodium.

In a typical run, about 20 ml of volatile material was collected in the trap. Nmr analysis indicated 32% glyme, 55% methyl vinyl ether (from solvent cleavage), and 13% hydrocarbons. The combined crude product from several runs was fractionally distilled in a cold room at 2° using a 25 × 1 cm column with Helipak packing. The condenser was held at −10°. Methyl vinyl ether, bp 8°, was collected, followed by the hydrocarbon fraction, bp 25–45°.

The hydrocarbon fraction was cooled in an ice bath and stirred magnetically. Bromine was added dropwise until the color

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(14) K. B. Wiberg and B. R. Lowry, *J. Amer. Chem. Soc.*, **85**, 3188 (1963).

(15) A. A. Bothner-By and S. M. Castellano, "Computer Programs for Chemistry," D. F. DeTar, Ed., W. A. Benjamin, New York, N. Y., 1968, p 10.

(16) I. Fleming and D. H. Williams, *Tetrahedron*, **23**, 2747 (1967).

Table II

Chemical Shifts for 1-Substituted Bicyclo[1.1.1]pentanes

R	Registry no.	Chemical shift, δ		R	Registry no.	Chemical shift, δ	
		Bridgehead	Methylene			Bridgehead	Methylene
OH	22287-25-8	2.35	1.92	H	311-75-1	2.45	1.88
CH_3	10555-48-3	2.40	1.67	CH_2OH	22287-32-7	2.48	1.70
CO_2Et	22287-27-0	2.42	2.05	OCOEt	22287-33-8	2.49	2.10
CO_2H	22287-28-1	2.43	2.10	COCl	22287-34-9	2.50	2.18
CH_2OAc	22287-29-2	2.44	1.70	$NH_3^+Cl^-$	22287-35-0	2.61	2.06
COEt	22287-30-5	2.45	2.01	Cl	10555-50-7	2.77	2.27

Table III

Nmr Spectra of 2-Substituted Bicyclo[1.1.1]pentanes

Substituent	Registry no.	Chemical shift, δ						Coupling constant, Hz			
		H_a	H_b	H_c	H_d	H_e	Bridgehead	J_{ac}	J_{be}	J_{bc}	J_{de}
Cl	10555-49-4	4.19	2.78	1.91	2.07	1.61	2.62	7.4	10.1	−3.0	−3.0
OH	22287-38-3	4.21	2.81	1.85	1.66	1.25	2.52	6.3	10.1	−2.7	−3.0
$OCOC_2H_5$	22319-33-1	4.58	2.55	1.78	1.75	1.46	2.65	6.9	9.8	−2.7	−3.2
COC_2H_5	22319-34-2	2.85	2.20	1.80	1.74	1.70	2.77	6.7	9.8	−3.0	−2.3
CO_2CH_3	22287-39-4	2.81	2.38	1.85	1.73	1.72	2.73	7.2	9.6	−3.2	−1.9
CO_2H	22287-40-7	2.94	2.49	1.90	1.75	1.76	2.78	7.3	10.0	−3.2	−2.2
CH_2OH	22287-41-8	2.55	2.43	1.88	1.87	1.70	2.49	6.7	10.0	−3.5	−2.5

persisted. The volatile hydrocarbons were bulb-to-bulb distilled into a storage trap. The hydrocarbon mixture was separated by vpc using an 8 ft × 1 in. 30% isoquinoline on 50-60 mesh Anaprep U column. Bicyclo[1.1.1]pentane had a retention time of 15.5 min at room temperature and was isolated in 6.5% yield.

Chlorination of Bicyclo[1.1.1]pentane. A. Low Chlorine Concentration.—To a 25-ml, two-necked flask fitted with a capillary gas inlet tube extending almost to the bottom of the flask, a magnetic stirrer, and a reflux condenser fitted with a drying tube was added 1.5 g (22 mmol) of bicyclo[1.1.1]pentane in 15 ml of Freon 11. The condenser was cooled to −10 to −15° using a circulating bath and the reaction was carried out in a cold room at 2°. Chlorine was bubbled slowly into the stirred mixture while it was irradiated with a 75-W incandescent lamp at a distance of 10 cm. The rate of chlorine addition was such that the solution maintained a light yellow color. The reaction was followed by vpc, and after 8 hr it appeared complete.

The majority of the solvent was removed by cautious distillation through a short-path still. The products were isolated by vpc using a 10 ft × 0.375 in. 20% Carbowax column at 130°. Nine components were found, and six were in sufficient quantity to be isolated and identified. The first component (51% of the volatile material) was 1-chlorobicyclo[1.1.1]pentane, nmr δ 2.27 (s, 6 H) and 2.77 (s, 1 H).

Anal. Calcd for C_5H_7Cl: C, 58.6; H, 6.9; Cl, 34.6. Found: C, 58.5, 58.6; H, 6.7, 6.9; Cl, 34.7, 34.6.

The second component (12%) was shown to be 3-methylenecyclobutyl chloride by its nmr spectrum: δ 2.6–3.6 (m, 4 H), 4.42 (quintuplet, 1H, J = 7.0 Hz), and 4.8–5.0 (m, 2 H).

Anal. Calcd for C_5H_7Cl: C, 58.6; H, 6.7; Cl, 34.6. Found: C, 58.4, 58.4; H, 7.0, 7.0; Cl, 34.5.

The third component (23%) was found to be 2-chlorobicyclo[1.1.1]pentane by its nmr spectrum (Table III).

Anal. Calcd for C_5H_7Cl: C, 58.6; H, 6.9; Cl, 34.6. Found: C, 58.5, 58.4; H, 6.9, 6.9; Cl, 34.7, 34.5.

The fourth and fifth components were too small to be collected. The sixth component (1.4%) was 1,3-dichlorobicyclo[1.1.1]pentane, mp 72°, nmr δ 2.43 (s). The seventh component (11%) was 2,2-dichlorobicyclo[1.1.1]pentane: nmr δ 1.95 (d, 2H, J = 1.7 Hz), 2.61 (d, 2 H, J = 1.7 Hz), and 3.13 (s, 2 H).

Anal. Calcd for $C_5H_6Cl_2$: C, 43.8; H, 4.4; Cl, 51.8. Found: C, 43.9, 43.8; H, 4.5, 4.5; Cl, 51.7, 51.7.

The eighth component (1.4%) was 1,2-dichlorobicyclo[1.1.1]pentane. Its nmr spectrum was analogous to that of 2-chlorobicyclo[1.1.1]pentane, with the band for the bridgehead hydrogen integrating for only one proton: δ 1.93 (d of d, 1 H, J = 10.0 and 2.7 Hz), 2.18 (d of d, 1 H, J = 7.2 and 2.5 Hz), 2.37 (d, 1 H, J = 2.7 Hz), 2.94 (s, 1 H), 2.98 (d of d, 1 H, J = 10.0 and 2.5 Hz), and 4.19 (d, 1H, J = 7.2 Hz). The ninth component was not isolated. The total yield of purified mono- and dichlorides was 250 mg (11%).

B. High Chlorine Concentration.—A mixture of 1.0 g of bicyclo[1.1.1]pentane and 2.0 ml of Freon-11 was placed in a 10-ml flask attached to a −5° condenser. An excess of chlorine was bubbled in and the flask was then illuminated. After 3 hr, nitrogen was passed through the solution to sweep out hydrogen chloride. Analysis by vpc indicated the chloride composition to be 62% 1-chlorobicyclo[1.1.1]pentane, 15% 2-chlorobicyclo-[1.1.1]pentane, 2% 1,3-dichlorobicyclo[1.1.1]pentane, 14% 2,2-dichlorobicyclo[1.1.1]pentane, and 7% 1,2-dichlorobicyclo-[1.1.1]pentane. Isolation by preparative vpc gave 0.46 g (31%) of 1-chlorobicyclo[1.1.1]pentane. Some unreacted bicyclo-[1.1.1]pentane also was present.

Bicyclo[1.1.1]pentanecarbonyl Chloride.—A 20 × 1 cm (i.d.) quartz tube was fitted with a long, thin glass stirrer and an efficient condenser with drying tube. The condenser was held at −5° using a circulating bath. Into the reaction vessel was placed 3.0 g (44 mmol) of bicyclo[1.1.1]pentane, 7.6 g (60 mmol) of freshly distilled oxalyl chloride, and 4 ml of Freon 11 as a diluent. The area above the liquid level was covered with aluminum foil. The stirrer was started and the solution was irradiated with two Sylvania G15T8 low-pressure mercury lamps at a distance of 6 in. Irradiation was continued for 10 hr or until the volume of the solution had decreased by about 4 ml. The reaction mixture was transferred to a distillation flask with the aid of a little Freon 11. Distillation gave 4.2 g (73%) of a mixture of 1- and 2-bicyclo[1.1.1]pentanecarbonyl chlorides, bp 34–40° (10 mm). The ratio of the two components was affected by temperature. At 1–2°, the ratio of 1- to 2-substituted derivatives was 78:22 and at 25° it was 85:15.

The pot residue (1.3 g) was treated with methanol and analyzed by nmr and vpc. A complex mixture was found which contained diesters.

Bicyclo[1.1.1]pentyl Ethyl Ketones.—To a 250-ml, three-necked flask fitted with a nitrogen inlet was added 100 ml of dry ether and 2.0 g (16 mmol) of diethylzinc. A nitrogen flow was maintained during the addition to prevent ignition of the diethylzinc. The flask was then equipped with a magnetic stirrer, a reflux condenser with a drying tube, and an addition funnel to which the nitrogen inlet was attached. Under a slow nitrogen flow, 4.08 g (31 mmol) of a mixture of 1- and 2-bicyclo[1.1.1]pentanecarbonyl chlorides in 25 ml of ether was added over 0.5 hr. The solution was stirred for 0.5 hr after addition and cooled in an ice-salt bath, and 20 ml of saturated ammonium chloride solution was added slowly followed by enough 2% hydrochloric acid to dissolve all the solids.

The mixture was transferred to a separatory funnel and the layers were separated. The aqueous layer was extracted with two 25-ml portions of ether. The combined ether solution was washed with 25-ml portions of saturated sodium bicarbonate solution, water, and saturated salt solution, and dried over magnesium sulfate. The solvent was removed by distillation. The ketones appeared to decompose on distillation and therefore were used in the following step without purification. The yield was estimated to be 55%.

A sample of the mixture was analyzed by vpc. On a 10 ft × 0.375 in. 20% DEGS column at 110°, the two isomers were separated cleanly. 1-Bicyclo[1.1.1]pentyl ethyl ketone (t_R 12.5 min) had the nmr spectrum summarized in Table II and had an ir carbonyl band at 1705 cm^{-1}. 2-Bicyclo[1.1.1]pentyl ethyl ketone (t_R 15 min) had the nmr spectrum summarized in Table III and had an ir carbonyl band at 1705 cm^{-1}.

Bicyclo[1.1.1]pentyl Propionates.—The crude mixture of bicyclo[1.1.1]pentyl ethyl ketones was mixed with 60 ml of methylene chloride and 5.6 g of *m*-chloroperbenzoic acid. The solution was stirred at room temperature for 4 days. The solution was filtered and then washed with 25 ml of 1.0 *M* sodium sulfate solution, two 25-ml portions of saturated sodium bicarbonate solution, 25 ml of water, and 25 ml of saturated salt solution. The organic layer was dried over sodium sulfate and the solvent was removed using a rotary evaporator. Distillation gave 1.92 g (91%) of a mixture of bicyclo[1.1.1]pentyl propionates, bp 65–67° (23 mm).

The mixture could be separated by vpc using a 20% DEGS column at 110°, giving 74% bridgehead ester (t_R 7.6 min) and 26% secondary ester (t_R 12.5 min).

Bicyclo[1.1.1]pentanols.—Methyllithium was formed from 0.44 g (63 mg-atom) of lithium wire and methyl bromide in 30 ml of dry ether. The flask was cooled in an ice bath and 1.92 g (13.7 mmol) of the mixture of 1- and 2-bicyclo[1.1.1]pentyl propionates in 20 ml of dry ether was added over 1 hr. The solution was allowed to warm at room temperature and was stirred for an additional 1 hr.

The flask was again cooled in an ice bath and a solution of 1.65 g (31.3 mmol) of ammonium chloride in 10 ml of water was added slowly. The solution was transferred to a separatory funnel and enough water was added to dissolve all the solids. The ethereal layer was washed with 20 ml of water and 20 ml of saturated salt solution and dried over sodium sulfate. The majority of the solvent was removed by distillation through a 25 × 1 cm column packed with Helipak. The products were isolated by preparative vpc using a 20% didecyl phthalate column at 110°. 1-Bicyclo[1.1.1]pentanol (t_R 3.4 min) was the first component.

Anal. Calcd for C_5H_8O: C, 71.4; H, 9.5. Found: C, 70.6; H, 9.4.

2-Bicyclo[1.1.1]pentanol (t_R 6.0 min) was the second component.

Anal. Calcd for C_5H_8O: C, 71.4; H, 9.5. Found: C, 70.7, 70.7; H, 9.4, 9.3.

The structures were easily shown from the nmr spectra (Tables II and III).

1-Bicyclo[1.1.1]pentanol was converted into its 3,5-dinitrobenzoate, mp 143.6–144.6° after recrystallization from hexane.

Anal. Calcd for $C_{12}H_{10}N_2O_8$: C, 51.8; H, 3.6; N, 10.1. Found: C, 51.8, 52.0; H, 3.7. 3.8; N, 10.1, 10.1.

2-Bicyclo[1.1.1]pentanol also was converted into its 3,5-dinitrobenzoate, mp 126.4–127.4° after recrystallization from hexane.

Methyl Bicyclo[1.1.1]pentanecarboxylates.—A solution of 2.0 ml of methanol in 25 ml of dry ether was cooled and stirred in an ice bath. A solution of 5.0 g of the 85:15 mixture of bicyclo[1.1.1]pentanecarbonyl chlorides in 15 ml of dry ether was added and the solution was allowed to warm to room temperature over 0.5 hr. The solution was treated with two 15-ml portions of water and two 15-ml portions of sodium bicarbonate solution and dried over magnesium sulfate. The solvent was removed through a short Vigreux column, giving 4.4 g (92%) of esters. The esters were separated by vpc using a 10 ft × 0.375 in. Carbowax column at 140°.

Methyl bicyclo[1.1.1]pentane-1-carboxylate (t_R 4.5 min) formed 85% of the mixture.

Anal. Calcd for $C_7H_{10}O_2$: C, 66.7; H, 7.9. Found: C, 66.8; H, 7.8.

Methyl bicyclo[1.1.1]pentane-2-carboxylate formed 15% of the mixture. The nmr spectra of the compounds are summarized in Tables II and III.

Bicyclo[1.1.1]pentanemethanols.—A solution of 5.25 g (42 mmol) of a mixture of 15% methyl bicyclo[1.1.1]pentane-2-carboxylate and 85% methyl bicyclo[1.1.1]pentane-1-carboxylate in 25 ml of dry ether was added over a 1-hr period to 3.8 g of lithium aluminum hydride in 100 ml of ether at 0°. The solution was stirred for 1 hr and treated with 3.8 ml of water, 3.8 ml of 15% potassium hydroxide solution, and 11.4 ml of water. The solution was filtered and dried over magnesium sulfate. The ether was removed by distillation, and the products were isolated by preparative vpc using a 10 ft × 0.375 in. 20% DEGS column at 150°. There was obtained 0.86 g of bicyclo[1.1.1]pentane-1-methanol (t_R 3.0 min) and 0.33 g of bicyclo[1.1.1]pentane-2-methanol (t_R 5.2 min). The nmr spectra are summarized in Tables II and III.

Anal. Calcd for $C_6H_{10}O$: C, 73.4; H, 10.3. Found (1 isomer): C, 72.7, 72.8; H, 9.7, 9.7. Found (2 isomer): C, 73.2, 73.2; H, 10.1, 9.9.

Bicyclo[1.1.1]pentanecarboxylic Acids.—A mixture (1.0 g) of bicyclo[1.1.1]pentanecarbonyl chlorides was dissolved in 25 ml of ether and added dropwise to a stirred salt solution to which 1.0 ml of saturated sodium carbonate solution had been added. The solution was stirred for 3 hr, the aqueous layer was acidified with hydrochloric acid, and the layers were separated. The aqueous layer was extracted with three 25-ml portions of ether, and the combined ether solutions were washed with two 15-ml portions of saturated salt solution and dried over magnesium sulfate. The solvent was removed using a rotary evaporator, giving 0.95 g of crude acid. Separation was effected at 150° using a 10 ft × 0.375 in. 710 silicone column which had been treated with several 0.1-ml injections of acetic acid. The bridgehead isomer (t_R 6.0 min) could be collected in good purity, but, because of tailing, the secondary isomer (t_R 7.2 min) was contaminated with 8–10% bridgehead compound.

Bicyclo[1.1.1]pentane-1-carboxylic acid had a melting point of 59–59.7°.

Anal. Calcd for C_6H_6O: C, 64.1; H, 7.2. Found: C, 63.3, 63.2; H, 6.9, 7.0.

It was converted into a *p*-bromophenacyl ester, mp 104.3–104.6° after recrystallization from methanol.

Anal. Calcd for $C_{14}H_{13}O_3Br$: C, 54.4; H, 4.2; Br, 25.8. Found: C, 54.3, 54.4; H, 4.2, 4.6; Br, 26.0, 26.1.

1-Bicyclo[1.1.1]pentylamine Hydrochloride.—In a 50-ml flask equipped with a stirrer and reflux condenser were placed 13 ml of chloroform, 2.5 ml of concentrated sulfuric acid, and 0.8 g of bicyclo[1.1.1]pentane-1-carboxylic acid. The solution was heated to 35–40° in an oil bath, and 0.95 g (14.5 mmol) of sodium azide was added in small portions over a 1-hr period. The solution was stirred for 1 hr, cooled, made basic with 33% sodium hydroxide solution, and steam distilled into a well-cooled receiver containing 15 ml of 3 *N* hydrochloric acid. The chloroform and excess aqueous acid were removed using a rotary evaporator. The salt was purified by precipitation from 1-propanol, using three times the volume of dry ether. The nmr spectrum is summarized in Table II.

Anal. Calcd for $C_5H_{10}NCl$: C, 50.2; H, 8.4; Cl, 29.7. Found: C, 50.2, 50.3; H, 8.4, 8.3; Cl, 29.5.

Dissociation Constants.—The dissociation constants were determined potentiometrically in water solution, as described previously.[14]

Registry No.—1-Bicyclo[1.1.1]pentanol 3,5-dinitrobenzoate, 22319-35-3; 2-bicyclo[1.1.1]pentanol 3,5-dinitrobenzoate, 22319-36-4; bicyclo[1.1.1]pentane-1-carboxylic acid *p*-bromophenacyl ester, 22319-37-5; 2-bicyclo[1.1.1]pentanecarbonyl chloride, 22319-38-6; 3-methylenecyclobutyl chloride, 22287-42-9; 1,3-dichlorobicyclo[1.1.1]pentane, 22287-43-0; 2,2-dichlorobicyclo[1.1.1]pentane, 22287-44-1; 1,2-dichlorobicyclo[1.1.1]pentane, 22287-45-2.