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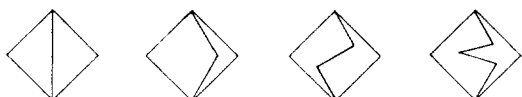
Bicyclo[2.1.1]hexane Derivatives¹

BY KENNETH B. WIBERG, BETTY R. LOWRY AND THOMAS H. COLBY

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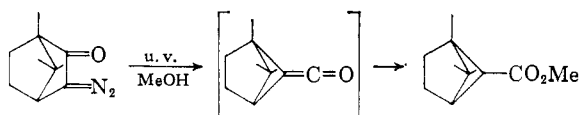
The syntheses of bicyclo[2.1.1]hexane, 1-chlorobicyclo[2.1.1]hexane and some of their derivatives are described. A convenient method of decarboxylating aliphatic acids *via* the decomposition of the *t*-butyl peresters in cymene has been developed. The reactions of bicyclo[2.1.1]hexanol-5 leading to unrearranged, partially rearranged or completely rearranged products depending on the reagents present are described.

Our interest in the effects of bond angle deformation on the properties of organic compounds has led us to try to obtain some suitably substituted derivatives of the ring systems



These compounds, particularly when the substituent is at the bridgehead position, would provide a graded series in which the bond angle deformation is decreased. This should lead to more detailed information than is available simply by the comparison of cyclopropane and cyclobutane derivatives. A derivative of the first member of the series, ethyl bicyclo[1.1.0]butane-2-carboxylate, was described recently² and this paper is concerned with the synthesis of derivatives of the third member of the series, bicyclo[2.1.1]hexane.

Although a compound having this ring system was first obtained by the degradation of carvone-camphor,³ the first synthetic method for the preparation of these compounds was developed by Horner and Spietschka⁴ in their study of the photolysis of diazocamphor. The reaction presumably proceeds by the loss of nitrogen and ring contraction to a ketene which then reacts with the solvent to give

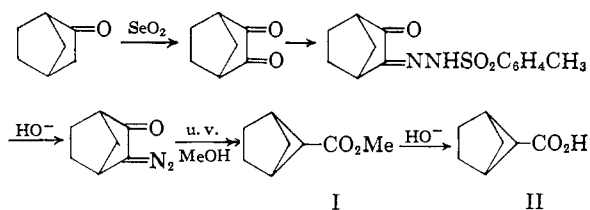


the observed products. Meinwald and Gassman⁵ have reported the preparation of a related compound by this method.

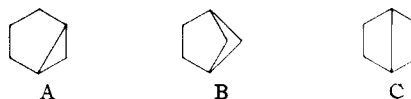
The previously reported compounds have the disadvantage of having extraneous methyl substituents which may affect the reactivity of compounds in the series. Thus, methods for the ring contraction of norcamphor were examined. In view of the recent conversion of cyclopentanone to cyclobutanecarboxylic acid by its reaction with hydrogen peroxide and selenium dioxide,⁶ norcamphor was treated with these reagents. The product was a lactone, and no ring contracted material was ob-

tained. The Favorskii and benzylic acid type rearrangements were also tried without success.

A number of the common methods for the conversion of ketones to diazoketones were employed with norcamphor. However, the only method which proved satisfactory was that developed by Cava and Little⁷ in which the ketone is first converted to the diketone. The latter is converted to the monotosylhydrazone which on treatment with base gives the diazoketone. Diazonorcamphor was irradiated in methanol solution using a Hanovia 500 w. immersion quartz lamp and a Corex filter giving 54% of methyl bicyclo[2.1.1]hexane-5-carboxylate (I). The ester was hydrolyzed with base to bicyclo[2.1.1]hexane-5-carboxylic acid (II). A small neutral fraction was obtained in the hydrolysis which proved to be nortricyclanone. This was obtained even when starting with distilled diazoketone and it therefore presumably is formed in the photolysis by internal rearrangement of the carbene first formed.



Although the method of preparation strongly suggests that the assigned structure is correct, an attempt was made to obtain other evidence. In view of the observation that the acid is saturated, it must be derived from one of the three ring systems



Since the n.m.r. spectra of II and also of bicyclo[2.1.1]hexane-5-methanol (III), formed by the reduction of I with lithium aluminum hydride, did not have bands above $\tau = 9.5$, the ring system A, unless substituted in the 6-position, is eliminated. Cyclopropane and its alkyl substituted derivatives invariably have methylene n.m.r. bands above $\tau = 9.5$.⁸ It will be evident from the reactions described below that I is not a 6-substituted bicyclo[3.1.0]hexane.

(7) M. P. Cava and R. L. Little, *Chemistry & Industry*, 367 (1957).

(8) For example, cyclopropane has its band at 9.78, norcarane has its cyclopropane methylene band at 9.98, and bicyclo[3.1.0]hexane has its corresponding band at 9.91 τ .

(1) This work was supported by the Office of Ordnance Research, U. S. Army. Taken in part from the Ph.D. thesis of T.H.C., 1957.

(2) K. B. Wiberg and R. P. Ciula, *J. Am. Chem. Soc.*, **81**, 5261 (1959).

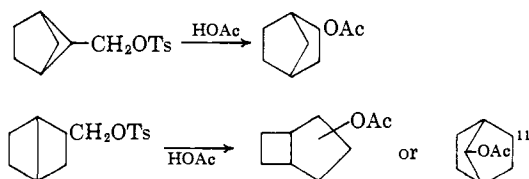
(3) E. Sernagiotto, *Gazz. chim. ital.*, **47**, 153 (1917); **48**, 52 (1918); G. Büchi and I. M. Goldman, *J. Am. Chem. Soc.*, **79**, 4741 (1957).

(4) L. Horner and E. Spietschka, *Ber.*, **88**, 934 (1955).

(5) J. Meinwald and P. G. Gassman, *J. Am. Chem. Soc.*, **82**, 2857 (1960); **82**, 5445 (1960).

(6) G. B. Payne and C. W. Smith, *J. Org. Chem.*, **22**, 1680 (1957).

One way in which to decide between the ring systems B and C is to investigate the rearrangement of the alcohol III. Reactions of this type of alcohol almost invariably lead to ring expansion. For example, cyclobutylmethanol on treatment with aqueous hydrogen bromide gave cyclopentyl bromide,⁹ and cyclopentylmethanol on treatment with this reagent gave cyclohexyl bromide.¹⁰ The expected products of the rearrangement of the tosylates formed from the derivatives of B and C are



The alcohol III was converted to the tosylate and the latter was solvolyzed in glacial acetic acid. The product was bicyclo[2.1.1]hexane-5-methyl acetate contaminated with a small amount of another acetate which appeared to be *exo*-norbornyl acetate.

In view of the difficulty with which the tosylate of III rearranged, some further experiments were performed. The alcohol III, on treatment with hydrobromic acid, gave bicyclo[2.1.1]hexane-5-methyl bromide. The latter did not rearrange on treatment with anhydrous zinc bromide, but rapidly rearranged in the presence of anhydrous aluminum bromide to give *exo*-norbornyl bromide. Apparently, the reaction has a higher than normal free energy of activation. It would seem probable that the geometry of the molecule is in some way responsible for the decreased reactivity, but this one case is not sufficient to indicate the exact nature of the effect. The rearrangement to norbornyl derivatives does, however, provide support for the proposed structure.

The configuration of the carboxyl group in II is of some importance in considering its reactions. Since it would be reasonable to expect the isomer which is formed to be the less stable one, corresponding to the addition of methanol from the less hindered side of the intermediate ketene,¹² attempts were made to effect isomerization of the acid and of the ester. The acid formed by the basic hydrolysis of I was converted to the acid chloride, and the latter was converted back to the ester with methanol and pyridine. Although both the basic hydrolysis step and the reaction forming the acid chloride are potentially capable of effecting isomerization to the more stable isomer, the resultant ester was found to be identical with that obtained directly from the photolysis, indicating either that the acid was the equilibrium mixture of the two isomers, or that isomerization is not facile.

The acid II was heated at 100° with acetic anhydride and sodium acetate for 48 hr.¹³ The result-

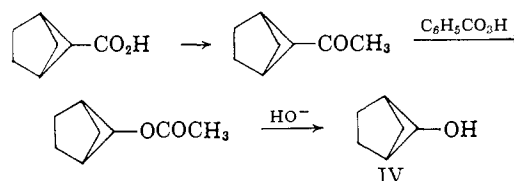
(9) N. J. Demjanov, *Ber.*, **40**, 4959 (1907).
 (10) S. Nametkin and O. Morosowa, *J. Russ. Phys.-Chem. Soc.*, **47**, 1607 (1915).

(11) S. Winstein, F. Gadiant, E. T. Stafford and P. E. Klinedinst, Jr., *J. Am. Chem. Soc.*, **80**, 5895 (1958), showed that the bicyclo[3.2.0]heptyl-2 cation rearranges to the 7-norcamphyl cation.

(12) J. Meinwald, A. Lewis and P. G. Gassman, *ibid.*, **82**, 2649 (1960).

ant acid was identical with the original acid. Also, when the methyl ester was heated at 100° with potassium *t*-butoxide in *t*-butyl alcohol-*d* no change was observed other than deuterium exchange. It must therefore be concluded that the ester obtained from the photolysis is probably the equilibrium mixture of the *exo* and *endo* isomers.

Bicyclo[2.1.1]hexan-5-ol (IV) is of interest both with regard to developing a method for the removal of the carboxyl group from II, and in connection with the large difference in solvolytic reactivity between the *endo*- and *exo*-norbornyl derivatives and the 7-norcamphyl derivatives.^{11,14} The alcohol IV was prepared by converting II to the corresponding methyl ketone, and then treating with perbenzoic acid and hydrolyzing.



The alcohol IV could be oxidized to bicyclo[2.1.1]hexan-5-one (V) using benzoquinone and aluminum *t*-butoxide. The ketone had an n.m.r. spectrum characteristic of 5-substituted bicyclo[2.1.1]hexane derivatives,¹⁵ and had an infrared carbonyl band at 5.56 μ . This value may be compared with 5.63 μ for 7-ketonorcamphane derivatives,¹⁶ 5.59 μ for cyclobutanone and 5.51 μ for cyclopropanone.¹⁷ It is therefore in accord with one's expectation based on the amount of bond angle deformation at the carbonyl group.

Since IV was formed from the more stable isomer of the acid II by steps in which the configuration is retained,¹⁸ it should be possible to obtain its epimer by the reduction of V with lithium aluminum hydride at -78°. These reaction conditions give high stereospecificity in the reduction of norcamphor,¹⁹ and gives predominantly the less stable epimer corresponding to attack by the complex hydride from the less hindered side of the molecule.

The reduction of V gave a mixture of two alcohols in an 82:18 ratio (determined gas chromatographically). The minor constituent was IV, and the major isomer was a new alcohol, VI. The latter was shown to be the epimer of IV by its oxidation back to the ketone V.

The tosylate of IV could be prepared by the reaction of the alcohol with *p*-toluenesulfonyl chloride in a suspension of potassium hydroxide in

(13) This combination of reagents effected the isomerization of Feist's acid in 15 min.: M. G. Ettlinger and F. Kennedy, *Chemistry & Industry*, 891 (1957).

(14) S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **74**, 1147, 1154 (1952); S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, *ibid.*, **77**, 4183 (1955).

(15) A detailed discussion of the n.m.r. spectra of these compounds will be published subsequently.

(16) P. Wilder, Jr., and A. Winston, *J. Am. Chem. Soc.*, **78**, 868 (1956).

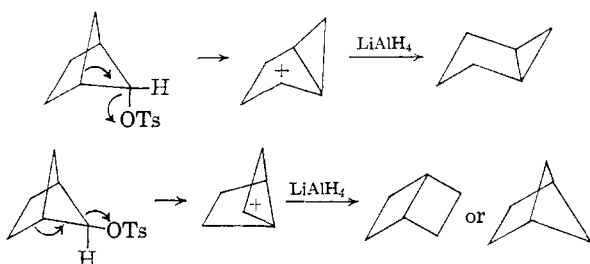
(17) The product of the reaction of ketene with methylene in a solid matrix at low temperature, which is presumably cyclopropanone, has an infrared band at 5.51 μ (gas phase spectrum): W. B. DeMore, H. O. Pritchard and N. Davidson, *ibid.*, **81**, 5878 (1959).

(18) R. B. Turner, *ibid.*, **72**, 878 (1950).

(19) P. Hirsjarvi, *Ann. Acad. Sci. Fennicae*, **AIII**, 81 (1957).

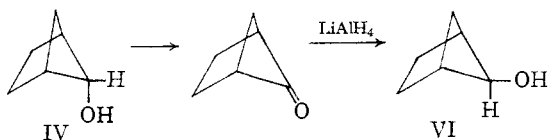
ether. The tosylate was quite unstable. After standing for a day, it became insoluble in most common solvents, and a few days later it again became soluble. The material thus obtained was shown to be cyclohexyl 4-tosylate by comparison with an authentic sample of the latter. It appears that ionization to an ion-pair occurred in the solid phase, followed by internal return giving the rearranged product. In this way it resembles bicyclo[3.2.0]heptyl 2-brosylate which on solvolysis gave largely internal return leading to 7-norcamphyl brosylate.¹¹ The latter reaction has, however, only been reported in solution.

The reduction of IV-tosylate with lithium aluminum hydride gave as the only product bicyclo[3.1.0]hexane (55%). The latter observation indicates that IV probably has the *endo* configuration since the *exo* isomer would be expected to give bicyclo[2.2.0]hexane or unrearranged material rather than the compound formed.



The epimeric alcohol VI was also converted to the tosylate. Qualitatively, the tosylate appeared to be much less reactive than that derived from IV. The lithium aluminum hydride reduction of VI-tosylate gave only the amount of bicyclo[3.1.0]hexane corresponding to the amount of IV present as an impurity, and no other hydrocarbon.

The oxidation reduction sequence then may be formulated as



The stereochemistry of VI is reasonable since one might expect the methylene bridge in V to be the major factor in controlling the steric effects about the carbonyl group.

The tosylate of IV was allowed to react with a high concentration of tetra-*n*-butylammonium chloride in acetone solution at 5° for 28 hours. The major product was a chloride having an n.m.r. spectrum very similar to that of IV, and thus having an unrearranged structure and the same configuration as the reactant. Similarly, the reaction of IV with phosphorus tribromide in the presence of pyridine gave primarily unrearranged bromide, whereas in the absence of pyridine, the product was 4-bromocyclohexene. Thus, in the presence of a nucleophilic species such as a halide ion, external return to the relatively stable halide occurs. In the absence of such a species, the reaction gives either half-rearranged material such as formed in the lithium aluminum hydride reduction, or

completely rearranged material, such as formed in the reaction with phosphorus tribromide. It might be noted that the rearranged ion first formed from IV easily can rearrange further to the 4-cyclohexenyl cation.

The isolation of the two epimeric alcohols in a state of high purity is in progress and this will be followed by a kinetic study of the solvolysis of suitable derivatives in order to determine the extent of alkyl participation in the ionization step. It appears likely that such participation occurs with the *endo* isomer in view of the qualitatively determined reactivity of IV-tosylate, and the observation of retention of configuration in the conversion of the tosylate to the chloride.

Although it may be possible to prepare bicyclo[2.1.1]hexane by the reduction of the ketone V, the low over-all yield in its formation from II made this route appear impractical, and therefore other methods were studied. One method was the decarbonylation of bicyclo[2.1.1]hexane-5-carboxaldehyde. The aldehyde was prepared by the reduction of *N,N*-dimethylbicyclo[2.1.1]hexane-5-carboxamide with lithium diethoxyaluminumhydride.²⁰ The decarbonylation was attempted using di-*t*-butyl peroxide as the catalyst. Carbon monoxide was obtained at first, but after a brief period no further gas was evolved. The aldehyde trimerized easily, and the trimerization may have been competitive with the decarbonylation reaction. A small amount of hydrocarbon was obtained from this reaction and was shown to be bicyclo[2.1.1]hexane (see below).

Bicyclo[2.1.1]hexane-5-carboxylic acid was converted to the acid chloride, and then to the *t*-butyl perester by reaction with *t*-butyl hydroperoxide in pyridine.²¹ The decomposition of the perester in *cymene* at 115–130° gave 58% carbon dioxide, and 45% of a saturated hydrocarbon. The hydrocarbon was shown not to be bicyclo[3.1.0]hexane or bicyclo[2.2.0]hexane by comparison of the n.m.r. spectra of these compounds.²² The n.m.r. spectrum of the hydrocarbon was very similar to that of the other bicyclo[2.1.1]derivatives, and thus must be the parent hydrocarbon of this series.

The compounds of primary interest are those having bridgehead substituents. In order to use the same route for the preparation of such compounds, it would be necessary to prepare a suitably substituted norcamphor. Of the several routes which were tried, the one which was successful consisted of the chromic acid oxidation of 1-chloronorcamphane to 4-chloronorcamphor (VII). The chloronorcamphane was obtained by the conversion of norcamphor to its dichloride with phosphorus pentachloride, followed by treatment with aluminum chloride and isopentane which leads to rearrangement and hydride transfer.²³

The structure of the ketone VII was demonstrated as follows: A Wolff-Kishner reduction led to

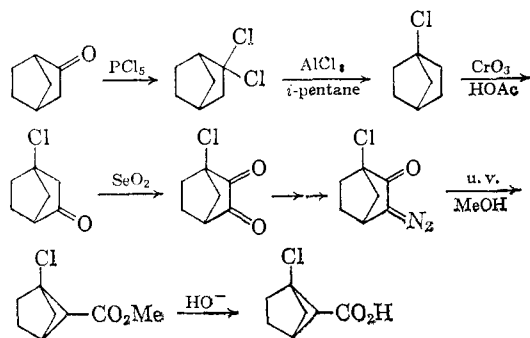
(20) H. C. Brown and A. Tsukamoto, *J. Am. Chem. Soc.*, **81**, 502 (1959).

(21) P. D. Bartlett and D. M. Simons, *ibid.*, **82**, 1753 (1960).

(22) We wish to thank Dr. R. Srinivasan for supplying us with the n.m.r. spectrum of the latter compound. Cf. S. Cremer and R. Srinivasan, *Tetrahedron Letters*, **21**, 24 (1960).

(23) W. v. E. Doering and W. P. Whelan, Jr., unpublished work; cf. W. P. Whelan, Ph.D. Thesis, Columbia University, 1953.

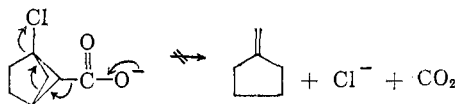
1-chloronorcamphane showing the chloride was still at the bridgehead position. Deuterium exchange with deuterium oxide and sodium deuterioxide led to the introduction of two deuteriums indicating that there was a methylene group adjacent to the carbonyl. The dipole moment of the chloroketone was found to be 2.14 D., whereas the calculated values for the 1- and 4-chloronorcamphors were 4.1 and 2.1 D., respectively. The assigned structure is also in agreement with the observation of only a small shift in the infrared carbonyl frequency (5.73μ as compared to 5.75μ in norcamphor). A larger shift would be expected if the chlorine were adjacent to the carbonyl.²⁴



The chloroketone VII was converted to the diazoketone by the same route as described for norcamphor. Irradiation of the diazoketone in methanol solution gave an ester containing a considerable amount of unsaturated impurity. After the removal of the latter with aqueous permanganate, there was obtained 25% of the theoretical amount of methyl 1-chlorobicyclo[2.1.1]hexane-5-carboxylate.

The ester was hydrolyzed with base to 1-chlorobicyclo[2.1.1]hexane-5-carboxylic acid (VIII). The acid had an n.m.r. spectrum which was quite similar to that of II except for the downfield shifts expected for chlorine substitution. The stability of VIII in basic solution is of interest since it has the possibility of rearranging with elimination of both carbon dioxide and chloride ion in a fashion similar to that of *trans*-bromocamphoric acid.²⁵

Apparently, this type of reaction does not occur readily in base since the acid was obtained from a basic hydrolysis. In order to see if it might occur if a "pull" were exerted on the chlorine, samples of the acid, 1-chloronorcamphane and 4-chloronorcamphor were mixed with portions of alcoholic silver nitrate solution and were heated to 100°. The rates of reaction appeared comparable, and all were quite slow. Thus, this type of cleavage is not particularly facile, although it may occur at a very slow rate.



(24) E. J. Corey, *J. Am. Chem. Soc.*, **75**, 2301 (1953).

(25) O. Aschan, *Ber.*, **27**, 2113, 3504 (1894); G. Stork and R. Breslow, *J. Am. Chem. Soc.*, **75**, 3292 (1953), have, however, suggested that the bromine and carboxyl groups are lost from the same carbon.

The acid VIII was converted to the *t*-butyl perester as with II, and the ester was decomposed in cymene at 130° giving 62% of carbon dioxide and 26% of 1-chlorobicyclo[2.1.1]hexane. The structure of the latter was indicated by the fact that it was saturated, and that its n.m.r. spectrum correlated well with that of bicyclo[2.1.1]hexane.

The conversion of the bridgehead chloride to other derivatives, and the reactions of these compounds will be reported subsequently.

Experimental²⁶

Norbornyl Formate.—A mixture of 452 g. (4.8 moles) of norbornene and 905 g. (19.3 moles) of 98% formic acid was heated in a flask equipped with a reflux condenser. When the temperature reached 100°, a vigorous reaction occurred. Heating was continued until the mixture became homogeneous. The formic acid was distilled under reduced pressure using a 12" glass helix packed column. Distillation gave 597 g. of norbornyl formate (89%), b.p. 67–69° at 14 mm., n_D^{20} 1.4610.²⁷ The forerun, b.p. 51–67° at 14 mm., also contained mainly norbornyl formate, the total yield being 95% of the theoretical amount. The formate was converted to norborneol (largely *exo*) and the latter was oxidized to norcamphor using the procedure of Winstein and Trifan.¹⁴

Norcamphorquinone Monotosylhydrazone.—A solution of 143 g. (0.77 mole) of tosylhydrazine in 220 ml. of hot glacial acetic acid was added with swirling to a solution of 95 g. (0.77 mole) of norcamphorquinone²⁸ in 100 ml. of glacial acetic acid with ice cooling. The product began to precipitate before the addition was completed. After standing overnight in a refrigerator, the solution was filtered, and the solid was washed with water giving 197 g. (88%) of material m.p. 150° dec.

The crude material could be recrystallized from acetonitrile or methanol giving the tosylhydrazone, m.p. 160.0–160.4° dec., with a 65% recovery.

Anal. Calcd. for $C_{14}H_{16}O_4N_2S$: C, 57.5; H, 5.5. Found: C, 57.4; H, 5.3.

Diazonorcamphor.—A solution of 160 g. (0.55 mole) of pure norcamphorquinone monotosylhydrazone and 26.5 g. (0.66 mole) of sodium hydroxide in 1250 ml. of water was stirred at room temperature with 1500-ml. portions of pentane. The pentane was decanted and replaced as it became yellow. A total of 18 l. of pentane was used. After 12 hours, the reaction appeared to have ceased. The combined pentane solutions were dried over anhydrous sodium sulfate and evaporated on a steam-bath. The remaining solvent was removed under reduced pressure giving crude diazonorcamphor as an orange syrup (71 g., 95%). Distillation gave pure material, b.p. 73–75° at 1–2 mm., n_D^{20} 1.5558, having strong infrared bands at 4.80μ (C=O), and ultraviolet absorption, λ_{max} 250 m μ (ϵ 11,200) with a shoulder at 302 m μ (ϵ 3300).

Anal. Calcd. for $C_7H_8ON_2$: C, 61.8; H, 5.9. Found: C, 61.8; H, 6.2.

Methyl Bicyclo[2.1.1]hexane-5-carboxylate.—A solution of 73.6 g. (0.54 mole) of crude diazonorcamphor in 4500 ml. of anhydrous methanol was irradiated with a water-cooled Hanovia 500 w. immersion quartz lamp using a Corex filter. After 24 hr., 95% of the diazo compound had reacted. Most of the solvent (4 l.) was removed by distillation through a 30" column packed with Heli-Pak. To the residue was added 1 l. of water and chopped ice, and the mixture was extracted with four 1-l. portions of pentane. The pentane solution was dried over anhydrous sodium sulfate and the solvent was removed by distillation through the above-mentioned column. Distillation of the residue gave 41 g. (54%) of methyl bicyclo[2.1.1]hexane-5-carboxylate, b.p. 67–71° at 17–18 mm., n_D^{20} 1.4568. The material thus

(26) Melting points were determined using calibrated total immersion thermometers; boiling points were not corrected. Microanalyses were performed by Drs. Straus and Weiler, Oxford, Eng., and A. Bernhardt, Max Planck Institute, Mulheim, Ger.

(27) L. Schermerling, J. P. Luvisi and R. W. Welch, *J. Am. Chem. Soc.*, **78**, 2819 (1956), reported b.p. 76–77° at 20 mm., n_D^{20} 1.4641.

(28) K. Alder, H. K. Schafer, H. Esser, H. Krieger and R. Reubke, *Ann.*, **593**, 23 (1955).

obtained contained a small amount of ketonic impurity. A pure sample was obtained by vapor phase chromatography and had n_D^{25} 1.4539.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.6; H, 8.6. Found: C, 68.6; H, 8.4.

Bicyclo[2.1.1]hexane-5-carboxylic Acid.—A solution of 37.5 (0.27 mole) of methyl bicyclo[2.1.1]hexane-5-carboxylate and 30 g. (0.54 mole) of potassium hydroxide in 175 ml. of methanol was heated for 2.25 hr., and then 75 ml. of methanol was removed by distillation. The residue was diluted with 300 ml. of water and extracted with 300-ml. portions of pentane to remove neutral material. The aqueous solution was cooled, acidified with hydrochloric acid and extracted with five 500-ml. portions of pentane. The solvent was removed by distillation through a 30" packed column and the residue was distilled giving 29.3 g. (88%) of bicyclo[2.1.1]hexane-5-carboxylic acid, b.p. 105–111° at 7–8 mm. On standing, the acid solidified, m.p. 45–52°.

Anal. Calcd. for $C_7H_{10}O_2$: C, 66.6; H, 8.0. Found: C, 66.4; H, 7.9.

The acid was converted back to the ester with diazomethane. The latter had n_D^{25} 1.4536 and had infrared and n.m.r. spectra identical with those of the purified ester from the irradiation.

β -Phenethylammonium Bicyclo[2.1.1]hexane-5-carboxylate.— β -Phenethylamine (6.5 g., 0.054 mole) was added dropwise to a solution of 5.0 g. (0.040 mole) of bicyclo[2.1.1]hexane-5-carboxylate in 50 ml. of pentane. The precipitate was filtered, washed with a small amount of pentane and dried giving 10.0 g. of the amine salt. The crude salt was fractionally crystallized from ethyl acetate. After one recrystallization it had m.p. 131–135°; after five recrystallizations the head fraction had m.p. 136.3–139.2°. The acid recovered from the latter material had m.p. 50.3–55.5°. The infrared and n.m.r. spectra were not significantly changed from that of the starting acid.

Bicyclo[2.1.1]hexane-5-carbonyl Chloride.—A mixture of 56 g. (0.47 mole) of thionyl chloride and 29.3 g. (0.24 mole) of bicyclo[2.1.1]hexane-5-carboxylic acid was allowed to stand at room temperature for 1 hour, and then was heated on a steam-bath for 4 hours. The excess thionyl chloride was distilled at atmospheric pressure, and the residue was distilled giving 32.4 g. (95%) of the acid chloride, b.p. 68–70° at 19 mm., n_D^{25} 1.4808.

The acid chloride was converted back to the ester by treatment with methanol and pyridine. The ester obtained in this way had n_D^{25} 1.4538 and had an infrared spectrum identical with the purified ester obtained from the irradiation.

Attempted Equilibration of Bicyclo[2.1.1]hexane-5-carboxylic Acid and Ester.—A mixture of 3.07 g. of bicyclo[2.1.1]hexane-5-carboxylic acid, 0.1 g. of potassium acetate and 100 ml. of acetic anhydride was heated to reflux for 48 hr. The reaction mixture was added to 300 ml. of water and was neutralized with sodium hydroxide. The solution was made somewhat acidic with concentrated hydrochloric acid and was extracted with three 500-ml. portions of pentane. The pentane extract was washed with water and dried over anhydrous sodium sulfate. Distillation gave 2.3 g. (75%) of the acid, b.p. 91° at 3 mm., having an n.m.r. spectrum identical with that of the reactant.

A mixture of 2.02 g. of methyl bicyclo[2.1.1]hexane-5-carboxylate and 3.0 g. of sodium methoxide was heated in a sealed tube at 100° for 71 hr. The contents of the tube was dissolved in a mixture of 30 ml. of acetic acid, 40 ml. of water and 100 g. of ice. The cooled mixture was extracted with 150 ml. of pentane. The pentane solution was washed with cold 5% sodium hydroxide solution and with water, and was dried over anhydrous sodium sulfate. Distillation gave 0.3 g. of the ester, b.p. 77–78° at 25 mm., having an n.m.r. spectrum identical with that of the starting ester, n_D^{25} 1.4531.

A solution of potassium *t*-butoxide was prepared from 3.4 g. of potassium and 40 g. of 74% deuterated *t*-butyl alcohol. To this solution was added 1.46 g. of methyl bicyclo[2.1.1]hexane-5-carboxylate, and the mixture was sealed in a tube. After 15 days at 100°, the tube was cooled and opened. The solution was added to a mixture of 10 ml. of acetic acid and 50 g. of ice, and then was extracted with a total of 150 ml. of pentane. The pentane solution was washed with water, cold 5% sodium hydroxide solution,

and water. After drying over anhydrous sodium sulfate, the pentane was distilled leaving a small amount of material which appeared (n.m.r.) to be a *t*-butyl ester.

Acidification of the basic extract, and extraction with pentane gave 0.9 g. of bicyclo[2.1.1]hexane-5-carboxylic acid which had an n.m.r. spectrum identical with that of the starting acid, except for deuteration. The mass spectrum indicated 55% deuteration.

Bicyclo[2.1.1]hexane-5-methanol.—A solution of 10.0 g. (0.08 mole) of bicyclo[2.1.1]hexane-5-carboxylic acid in 50 ml. of anhydrous ether was added to a slurry of 3.2 g. of lithium aluminum hydride in 100 ml. of ether with stirring over a period of 30 minutes. The mixture was heated and stirred for an additional 30 minutes, and then 35 ml. of 30% Rochelle salt solution was added cautiously with ice cooling. The ether layer was decanted and the solid was washed with two 50-ml. portions of ether. The combined ether extracts were dried over anhydrous sodium sulfate. Distillation gave 7.8 g. (87%) of bicyclo[2.1.1]hexane-5-methanol, b.p. 65–69° at 5 mm., n_D^{25} 1.4809.

Anal. Calcd. for $C_7H_{12}O$: C, 75.0; H, 10.8. Found: C, 74.9, 74.9; H, 10.6, 10.5.

Bicyclo[2.1.1]hexane-5-methyl Tosylate.—A solution of 3.0 g. (0.027 mole) of bicyclo[2.1.1]hexane-5-methanol in 30 ml. of dry pyridine was cooled in an ice-salt-bath, and 5.66 g. (0.030 mole) of *p*-toluenesulfonyl chloride was added. The mixture was cooled and swirled until all of the *p*-toluenesulfonyl chloride had dissolved. The reaction mixture was stoppered and left in a refrigerator. After 21 hr., 20 g. of cracked ice was added, and then 30 ml. of water. The mixture was extracted with three 100-ml. portions of ether. The ether solution was washed twice with 1 *N* sulfuric acid, with water and with sodium bicarbonate solution. It was then dried over anhydrous sodium sulfate. Evaporation of the ether gave 6.1 g. (86%) of an oil which solidified after some time. The crude tosylate had m.p. 29.0–32.8° and after recrystallization from pentane it had m.p. 38.8–40.4°.

Anal. Calcd. for $C_{14}H_{18}O_2S$: C, 63.1; H, 6.8. Found: C, 63.3, 63.6; H, 6.9, 7.0.

Acetolysis of Bicyclo[2.1.1]hexane-5-methyl Tosylate.—A solution of 4.2 g. of the tosylate in 300 ml. of glacial acetic acid (containing 1% acetic anhydride) was heated to reflux for 36 hr. The mixture was cooled, diluted with 400 ml. of water, and extracted with four 250-ml. portions of pentane. The pentane solution was washed three times with 2.5% sodium bicarbonate solution, once with water and then dried over anhydrous sodium sulfate. Distillation gave 2.2 g. (91%) of an acetate, b.p. 69–71° at 9 mm., n_D^{25} 1.4556. This acetate had infrared and n.m.r. spectra which were essentially identical with those of bicyclo[2.1.1]hexane-5-methyl acetate, except that there were several extra weak bands which corresponded to those of *exo*-norbornyl acetate.

Bicyclo[2.1.1]hexane-5-methyl Acetate.—To a cold solution of 0.80 g. of bicyclo[2.1.1]hexane-5-methanol in 10 ml. of pyridine was added dropwise 5 g. of acetyl chloride. The solution was diluted with 10 ml. of water and extracted with three 50-ml. portions of pentane. The pentane solution was washed with water, 3 *N* hydrochloric acid, water, and 5% sodium bicarbonate solution. After drying over anhydrous sodium sulfate, distillation gave 0.84 g. of the acetate, b.p. 73–74° at 10 mm., n_D^{25} 1.4553.

Bicyclo[2.1.1]hexane-5-methyl Bromide.—To an ice-cooled mixture of 7.1 ml. of 48% hydrobromic acid and 3.0 ml. of concentrated sulfuric acid was added 2.0 g. of bicyclo[2.1.1]hexane-5-methanol. The solution was heated on a steam-bath overnight. After cooling, 30 ml. of pentane was added and the aqueous layer was discarded. The pentane solution was washed with sodium bicarbonate solution and water. After drying over anhydrous sodium sulfate, distillation gave 2.4 g. (77%) of bicyclo[2.1.1]hexane-5-methyl bromide, b.p. 72–74° at 19 mm., n_D^{25} 1.5080. The infrared and n.m.r. spectra were different from those of norbornyl bromide. The n.m.r. spectrum was very similar to that of the starting alcohol except for the shift in the position of the H–C–X resonance band due to a change in substituent from hydroxyl to bromine.

Rearrangement of Bicyclo[2.1.1]hexane-5-methyl Bromide. A. Zinc Bromide.—To 2.3 g. of the bromide was added 1.0 g. of anhydrous zinc bromide. The mixture was allowed to stand for 1 week at room temperature in a stoppered flask. The liquid was removed and distilled giving

1.6 g. of a bromide, b.p. 71–72° at 18 mm., n_D^{25} 1.5078. The infrared spectrum was identical with that of the starting material.

B. Aluminum Bromide.—Bicyclo[2.1.1]hexane-5-methyl bromide (1.5 g.) was treated with a small amount of anhydrous aluminum bromide. A vigorous reaction occurred. The organic material was taken up in pentane and the pentane solution was washed with water and dried over anhydrous sodium sulfate. Distillation gave 0.5 g. of a bromide, b.p. 72–74° at 17 mm., n_D^{25} 1.5116. The infrared spectrum was identical with that of *exo*-norbornyl bromide (b.p. 74–76° at 20 mm., n_D^{25} 1.5131).

Methyl Bicyclo[2.1.1]hexyl-5 Ketone.—A solution of dimethylcadmium in benzene was prepared from 2.5 moles of methylmagnesium bromide in the usual fashion.²⁹ A solution of 32.4 g. (0.224 mole) of bicyclo[2.1.1]hexane-5-carbonyl chloride in 50 ml. of dry benzene was added dropwise with stirring at such a rate which would permit the reaction mixture to become hot, but not to reflux. The mixture was stirred at room temperature for 2 hours, and then allowed to stand overnight.

Water (300 ml.) was added cautiously to the ice-cooled mixture, and then 400 ml. of 6 *N* hydrochloric acid. The layers were separated and the aqueous solution was washed with 1 l. of pentane in several portions. The combined organic solutions were washed with water, with 5% sodium bicarbonate solution, and again with water. After drying over anhydrous sodium sulfate, the pentane and benzene were distilled through an 11-plate bubble-cap column. Distillation of the residue gave 24.4 g. (88%) of the ketone, b.p. 75–77° at 28 mm., n_D^{25} 1.4612.

Anal. Calcd. for $C_8H_{12}O$: C, 77.4; H, 9.7. Found: C, 77.3; H, 10.0.

The 2,4-dinitrophenylhydrazone, m.p. 140.2–143.2° (from ethanol), and the semicarbazone, m.p. 184.2–184.8° (from ethanol-water), were prepared.

Anal. Calcd. for $C_{14}H_{16}O_4N_4$ (dinitrophenylhydrazone): C, 55.3; H, 5.3. Found: C, 55.0; H, 5.5. Calcd. for $C_9H_{13}ON_3$ (semicarbazone): C, 59.6; H, 8.3. Found: C, 59.8; H, 8.0.

Bicyclo[2.1.1]hexyl-5 Acetate.—To a solution of 17.9 g. (0.144 mole) of methyl bicyclo[2.1.1]hexyl-5 ketone in 10 ml. of methylene chloride was added 195 ml. of 1.47 *M* perbenzoic acid in methylene chloride. After standing for 13 days, the cold solution was extracted with several portions of cold 10% sodium hydroxide solution. The methylene chloride solution was then washed with 10% sodium bisulfite solution and with water. After drying over anhydrous sodium sulfate, most of the solvent was removed by distillation through a 30" packed column.

The residue was heated to reflux with a mixture of 20 g. of Girard reagent P, 120 g. of 95% ethanol and 12 g. of glacial acetic acid for 1 hour. To the mixture was added 50 ml. of water and enough sodium carbonate to bring the pH to 6. The mixture was then diluted with 150 ml. of water and 600 g. of ice, and extracted with 3 l. of pentane in several portions. The pentane solution was dried over anhydrous sodium sulfate, and the pentane was distilled through a 30" packed column. Distillation of the residue gave 15.3 g. (76%) of the ester, b.p. 75–79° at 30–31 mm., n_D^{25} 1.4483.

Anal. Calcd. for $C_9H_{12}O_2$: C, 68.5; H, 8.6. Found: C, 68.9, 69.3; H, 8.7, 8.9.

***endo*-Bicyclo[2.1.1]hexan-5-ol.**—A solution of 7.3 g. (0.052 mole) of bicyclo[2.1.1]hexyl-5 acetate and 3.6 g. of potassium hydroxide in 30 ml. of methanol was heated to reflux for 3 hr. The cooled solution was diluted with 50 ml. of water and extracted with 450 ml. of purified pentane in several portions. The pentane solution was dried over anhydrous sodium sulfate, and the pentane was distilled through a 30" packed column. Sublimation of the residue at 70° and atm. pressure gave 4.3 g. (85%) of *endo*-bicyclo[2.1.1]hexan-5-ol, m.p. 71–84°. Gas chromatographic analysis indicated that the material thus prepared contained 85% of the *endo* isomer.

Anal. Calcd. for $C_8H_{10}O$: C, 73.4; H, 10.3. Found: C, 73.8, 73.5; H, 10.3, 10.3.

***endo*-Bicyclo[2.1.1]hexyl-5 Tosylate.**—A solution of 1.50 g. (15.3 mmoles) of bicyclo[2.1.1]hexan-5-ol in 100 ml. of absolute ether was cooled to 0° in an ice-salt-bath, then 2.93 g. (15.3 mmoles) of tosyl chloride was added with stir-

ring. Powdered potassium hydroxide was added in portions (total 2.46 g., 0.044 mole) so that the temperature did not rise above –5°. Stirring and cooling was continued for 3 hours.

The mixture was poured onto 50 g. of ice. The aqueous layer was re-extracted with two 50-ml. portions of ether. The combined ether extract was washed with three 20-ml. portions of ice-water and dried over anhydrous potassium carbonate. After removal of the ether under reduced pressure, 3.5 g. (90%) of colorless crystalline product was obtained. The crude material had m.p. 36.5–41°. At 41° the almost colorless melt turned bright purple and then dark blue. A sample was recrystallized in the cold from an ether-pentane mixture and had m.p. 39.8–42.5°. It also underwent color change.

On standing overnight at 5° the crude tosylate became quite insoluble and dark blue in color. After standing for several days it became essentially colorless again. This material had the same n.m.r. spectrum as cyclohexenyl-4-tosylate.

The unrearranged tosylate had an n.m.r. spectrum quite similar to that of the starting alcohol, indicating an unrearranged structure.

Anal. Calcd. for $C_{12}H_{16}O_2S$: C, 61.9; H, 6.4. Found: C, 61.3; H, 6.4.

Lithium Aluminum Hydride Reduction of *endo*-Bicyclo[2.1.1]hexyl 5-Tosylate.—To a stirred slurry of 2.00 g. (53 mmoles) of lithium aluminum hydride in 40 ml. of diglyme at room temperature was added 2.8 g. (11 mmoles) of bicyclo[2.1.1]hexyl 5-tosylate over 20 minutes. Stirring was continued for 36 hours. The receiver was cooled to –70° and approximately 5 ml. of distillate (mainly diglyme) was collected at 1–2 mm. The hydrocarbon fraction, isolated by gas chromatography of the distillate, weighed 0.50 g. (55%), and had n_D^{25} 1.4358. The infrared spectrum (CH 3.32, 3.37, 9.80 μ) and the n.m.r. spectrum ($\tau = 9.91$) indicated the presence of a cyclopropane ring. Redistillation of the material from sodium yielded material with b.p. 78–81°, n_D^{25} 1.4376. The n.m.r. and infrared spectra were identical with that of an authentic sample of bicyclo[3.1.0]hexane, prepared by the reaction of iodozinc-methyl iodide with cyclopentene (b.p. 80.5–81°, n_D^{25} 1.4357).³⁰

Bicyclo[2.1.1]hexan-5-one.—A solution of 1.96 g. (20 mmoles) of bicyclo[2.1.1]hexan-5-ol, 8.64 g. (80 mmoles) of *p*-benzoquinone, and 4.92 g. (20 mmoles) of aluminum *t*-butoxide in 250 ml. of anhydrous ether was heated to reflux for 12.5 hours. The ether was distilled using an 8" jacketed Vigreux column. The residue was evacuated to about 2 mm. and the remaining volatile products trapped in Dry Ice-acetone-cooled traps. The ketone was isolated by gas phase chromatography on a silicone column, giving 0.60 g., (31%) of bicyclo[2.1.1]hexan-5-one. The infrared carbonyl absorption appeared at 5.56 μ . A sample of the ketone, distilled from Drierite, boiled at 140–141° and had n_D^{25} 1.4553. It solidified somewhat below room temperature.

Anal. Calcd. for C_8H_8O : C, 75.0; H, 8.4. Found: C, 74.5, 74.3; H, 8.5, 8.6.

The 2,4-dinitrophenylhydrazone, m.p. 151.8–152.4° (from ethanol-water), and the semicarbazone, m.p. 185.8–187.2° (from methanol), were prepared.

Anal. Calcd. for $C_{12}H_{12}O_4N_4$: C, 52.2; H, 4.4; N, 20.3. Found: C, 52.1, 52.2; H, 4.5, 4.4; N, 19.9, 20.2. Calcd. for $C_7H_{11}ON_3$: C, 54.9; H, 7.2; N, 27.4. Found: C, 54.8, 54.9; H, 7.2, 7.1; N, 27.4, 27.2.

***exo*-Bicyclo[2.1.1]hexan-5-ol.**—To a mixture of 0.50 g. of lithium aluminum hydride and 50 ml. of anhydrous ether at –78° was added dropwise a solution of 0.97 g. of bicyclo[2.1.1]hexan-5-one in 10 ml. of ether over a period of 45 min. The solution was stirred at –78° for 4 hr., and then allowed to warm to room temperature. The solution was treated with 6 ml. of 40% Rochelle salt solution. The ether solution was decanted and the solid was washed with 100 ml. of anhydrous ether in portions. After drying over anhydrous sodium sulfate, the ether was distilled through a 76-cm. Helipak packed column. A small amount of isopentane was added, and removed by distillation through the column. The residue was sublimed at 50° giving 0.80 g. (80%) of *exo*-bicyclo[2.1.1]hexan-5-ol, m.p. 51–60°.

(29) J. Cason, *J. Am. Chem. Soc.*, **68**, 2078 (1946).

(30) H. E. Simmons and R. D. Smith, *ibid.*, **81**, 4256 (1959).

Anal. Calcd. for $C_6H_{10}O$: C, 73.4; H, 10.3. Found: C, 72.9, 72.7; H, 10.1, 10.1.

Analysis by gas chromatography indicated that the material thus prepared consisted of 82% *exo*- and 18% *endo*-alcohols. Oxidation of the *exo*-alcohol by the procedure described above gave bicyclo[2.1.1]hexan-5-one (35%).

***exo*-Bicyclo[2.1.1]hexyl-5 Tosylate.**—To a solution of 1.07 g. (11 mmoles) of the *exo*-alcohol in 75 ml. of anhydrous ether at -10° was added 2.07 g. (11 mmoles) of tosyl chloride. After the latter had dissolved, 2.0 g. of powdered potassium hydroxide was added in portions at -8° . The mixture was stirred at -5 to -10° for 4 hr., and then was poured onto 50 g. of ice and water. The aqueous layer was washed with ether, and the combined ether solution was washed with water and dried over anhydrous potassium carbonate. Removal of the solvent gave 2.8 g. of the crude tosylate which did not solidify. The n.m.r. spectrum was similar to that of *exo*-bicyclo[2.1.1]hexan-5-ol, indicating that it had the correct structure.

Lithium Aluminum Hydride Reduction of *exo*-Bicyclo[2.1.1]hexyl-5 Tosylate.—To a slurry of 1.9 g. of lithium aluminum hydride in 35 ml. of diglyme at room temperature was added a solution of 2.7 g. of the tosylate in 15 ml. of diglyme. The mixture was stirred at room temperature for 29 hr., and then about 5 ml. of material was distilled into a Dry Ice-acetone cooled trap at about 2 mm. Gas chromatographic separation of the distillate gave only 0.1 g. of hydrocarbon, shown to be bicyclo[3.1.0]hexane by its n.m.r. spectrum. This is the amount expected from the *endo* impurity in the starting alcohol.

The solution was heated with an additional amount of lithium aluminum hydride at 80° for 24 hr., but no further amount of hydrocarbon was formed. The excess hydride was destroyed by water, and the mixture was diluted with water. The mixture was extracted with isopentane and with ether. Neither solution was found to contain the starting alcohol. The nature of the mixture formed made it impractical to attempt to isolate unreacted tosylate.

***endo*-Bicyclo[2.1.1]hexyl-5 Chloride.**—A solution of 2.0 g. of *endo*-bicyclo[2.1.1]hexane 5-tosylate (0.0079 mole) and 40 g. (0.106 mole) of tetra *n*-butylammonium chloride in 150 ml. of dry acetone was stoppered and allowed to stand at 5° for 29 hours; 100 ml. of acetone was distilled from the solution and the residue was poured onto 100 g. of ice and extracted with isopentane (one 150-ml. and three 50-ml. portions). The isopentane extract was washed with water and dried over anhydrous sodium sulfate. After distillation of the solvent, 0.40 g. (43%) of the chloride was obtained, b.p. $\sim 45^\circ$ at 20–25 mm. The chloride had an n.m.r. spectrum very similar to that of the *endo*-alcohol indicating that it was largely the unrearranged *endo*-chloride.

Reaction of *endo*-Bicyclo[2.1.1]hexan-5-ol with Phosphorus Tribromide.—To a solution of 1.96 g. of *endo*-bicyclo[2.1.1]hexan-5-ol in 10 ml. of pentane at -10° was added dropwise, with stirring, 1.98 g. of phosphorus tribromide over the course of 20 min. Stirring was continued for an additional 20 hr. while the solution warmed to room temperature. The reaction mixture was poured onto ice and the organic layer was separated. The latter was washed with sodium carbonate solution and with water, and then dried over anhydrous sodium sulfate. Distillation gave 2.3 g. (72%) of a bromide, b.p. 55 – 56° at 16 mm., n_D^{25} 1.5119.

Anal. Calcd. for C_6H_9Br : C, 44.7; H, 5.6; Br, 49.6. Found: C, 45.6; H, 5.7, 6.0; Br, 48.5, 48.8.

The infrared and n.m.r. spectra were identical with those of 4-bromocyclohexene.

The reaction was also carried out in the presence of pyridine. To a stirred mixture of 1.96 g. (20 mmoles) of *endo*-bicyclo[2.1.1]hexan-5-ol, 2.0 ml. of pyridine and 20 ml. of pentane at 0° was added 2.0 g. of phosphorus tribromide over 10 minutes. The mixture was stirred and allowed to come to room temperature overnight. Ice-water (50 ml.) was added and the aqueous phase was extracted with pentane. The combined pentane extract was washed with cold 1% hydrochloric acid (two 10-ml. portions), ice-water (20 ml.), cold 5% sodium bicarbonate solution (10 ml.), and more ice-water, then dried over anhydrous sodium sulfate. The solvent was distilled giving 0.56 g. (17%) of bromide, b.p. 58 – 59° at 15 mm., n_D^{25} 1.5051. A considerable residue remained. The n.m.r. spectrum indicated that the product

was largely bicyclo[2.1.1]hexyl 5-bromide contaminated with some 4-bromocyclohexene.

4-Bromocyclohexene.—The reaction of 1,4-cyclohexanediol with phosphorus tribromide at 80° gave a mixture of 1,4-dibromocyclohexane and 4-bromocyclohexene. The latter had b.p. 47 – 49° at 11 mm., n_D^{25} 1.5120.

Anal. Calcd. for C_6H_9Br : C, 44.7; H, 5.6; Br, 49.6. Found: C, 45.4, 45.5; H, 5.7, 5.8; Br, 48.9, 49.3.

N,N-Dimethylbicyclo[2.1.1]hexane-5-carboxamide.—To a solution of 30 g. (0.67 mole) of dimethylamine in 50 ml. of ether which was cooled in an ice-salt-bath was added 12.5 g. (0.086 mole) of bicyclo[2.1.1]hexane-5-carbonyl chloride with stirring over the course of 30 min. After the addition was completed, 100 ml. of water was added and the mixture was extracted with four 100-ml. portions of ether. The ether solution was dried over anhydrous sodium sulfate, and distilled giving 12.2 g. (92%) of the amide, b.p. 85 – 89° at 1–2 mm. A sample was redistilled, b.p. 105 – 105.5° at 8 mm., n_D^{25} 1.4908.

Anal. Calcd. for $C_9H_{15}NO$: C, 70.6; H, 9.9; N, 9.1. Found: C, 70.6, 70.7; H, 9.0, 9.1; N, 9.3, 9.3.

Bicyclo[2.1.1]hexane-5-carboxaldehyde.—To a solution of 12.2 g. (0.08 mole) of N,N-dimethylbicyclo[2.1.1]hexane-5-carboxamide in 50 ml. of anhydrous ether which had been cooled to 0° was added, with stirring, over a period of 30 min., a solution of lithium diethoxyaluminumhydride prepared by the addition of 4.7 g. of ethyl acetate in 40 ml. of anhydrous ether to 2.0 g. of lithium aluminum hydride in 50 ml. of anhydrous ether. After heating to reflux for 30 min., the mixture was hydrolyzed by the dropwise addition of 25 ml. of 30% Rochelle salt solution. The ether layer was decanted and the residue was washed with two 100-ml. portions of ether. The combined ether solution was washed with 1 *N* sulfuric acid, water, sodium bicarbonate solution and with water. After drying over anhydrous sodium sulfate, distillation gave 4.8 g. (55%) of the aldehyde, b.p. 62 – 65° at 28 mm. A sample was redistilled, b.p. 56 – 58° at 25 mm., n_D^{25} 1.4672.

Anal. Calcd. for $C_7H_{10}O$: C, 76.3; H, 9.2. Found: C, 75.9, 76.2; H, 9.3, 9.4.

The 2,4-dinitrophenylhydrazone, m.p. 153.3 – 153.3° (from ethanol), and the semicarbazone, m.p. 152 – 152.4° dec. (from methanol), m.p. 152.1 – 153.4° dec. (from acetonitrile), were prepared.

Anal. Calcd. for $C_{13}H_{14}O_4N_4$ (dinitrophenylhydrazone): C, 53.8; H, 4.9; N, 19.3. Found: C, 53.9, 54.0; H, 5.2, 5.2; N, 19.3, 19.5. Calcd. for $C_8H_{13}ON_3$ (semicarbazone): C, 57.5; H, 7.8; N, 25.1. Found: C, 57.5, 57.7; H, 7.2, 7.4; N, 25.2, 25.3.

***t*-Butyl Bicyclo[2.1.1]hexane-5-peroxycarboxylate.**—Over a period of 1 hr., 8.49 g. (58.8 mmoles) of bicyclo[2.1.1]hexane-5-carbonyl chloride was added to a stirred mixture of 8.0 g. (89 mmoles) of *t*-butyl hydroperoxide, 12 ml. of dry pyridine and 40 ml. of *p*-cymene cooled in an ice-salt-bath. Stirring and cooling was continued for an additional hour. The mixture was poured onto 50 g. of ice. The aqueous phase was separated and extracted with cymene (30 ml. total), then the combined cymene extract was washed with cold 10% sulfuric acid (two 20-ml. portions), ice-water (20 ml.), cold 10% sodium carbonate (10 ml.) and more ice-water (three 10-ml. portions). The cymene solution was dried over anhydrous magnesium sulfate. The perester was not isolated.

Bicyclo[2.1.1]hexane.—The dry cymene-perester solution was placed in a reaction flask equipped with distillation-cooled trap, and two interchangeable tubes containing Ascarite (to measure carbon dioxide evolution). About 10 ml. of cymene was used to rinse the magnesium sulfate. The solution was heated in a wax-bath at 115 – 130° . Nitrogen was used occasionally to sweep the carbon dioxide into the Ascarite tubes. After 2 hours, carbon dioxide evolution ceased, 1.52 g. of carbon dioxide (58% based on the acid chloride) having been produced. The mixture was distilled until the head temperature reached 176° (*p*-cymene). Bicyclo[2.1.1]hexane was isolated by gas chromatography of the distillate using a silicone column at 70° , giving 2.17 g. of the hydrocarbon (45%). It was redistilled from potassium, b.p. 71.5 – 72.5° , n_D^{25} 1.4341, m.p. 20.4 – 24.2° .

Anal. Calcd. for C_6H_{10} : C, 87.7; H, 12.3. Found: C, 87.4; H, 12.3.

Norcamphor Dichloride.²²—To a solution of 204 g. (1.85 moles) of norcamphor in 131 ml. of phosphorus trichloride which was cooled in an ice-salt-bath was added, in portions, 435 g. (2.09 moles) of phosphorus pentachloride over the course of 1 hour. The mixture was allowed to warm slowly to room temperature, and was allowed to stand overnight. The mixture was poured onto ice (2–3 kg.) and extracted with three 1-l. portions of pentane. The pentane solution was washed with water and dried over anhydrous magnesium sulfate. After removal of the solvent, the residue was distilled under reduced pressure until solid distillate appeared. The solid fraction (b.p. 77–79° (19 mm.)) then was collected giving 245–260 g. (80–85%) of norcamphor dichloride; redistillation of the forerun gave a total yield of 92%.

1-Chloronorcamphane.²³—A solution of 315 g. (1.92 moles) of norcamphor dichloride was prepared in a mixture of 400 ml. of purified isopentane and 1330 ml. of purified *n*-pentane. Both solvents were purified by stirring with anhydrous aluminum chloride and then distilling. The solution was stirred and 123.5 g. (0.84 mole) of anhydrous aluminum chloride was added in small portions as rapidly as the hydrogen chloride evolution would permit. The stirring was continued for 6–8 hr. The pentane layer was decanted and the dark sludge which remained was washed with four 100-ml. portions of *n*-pentane. The combined pentane solution was washed with water, with sodium bicarbonate solution and again with water. After drying over anhydrous sodium sulfate, the mixture was distilled through an 8" glass helix packed column giving 124–137 g. (50–55%) of 1-chloronorcamphane, b.p. 148–154°, n_D^{20} 1.4648. Although this material was not pure, it was suitable for use in the subsequent reaction.

4-Chloronorcamphor.—To a cold solution of 41 g. of sodium dichromate in 400 ml. of glacial acetic acid was added a cold mixture of 21.3 g. of pure 1-chloronorcamphane, 60 ml. of concentrated sulfuric acid and 60 ml. of glacial acetic acid with thorough mixing. The solution was allowed to stand without external cooling for 15 minutes and then was diluted with 1 liter of water. The aqueous solution was extracted with three 300-ml. portions of pentane. The pentane solution was washed with water, dried over sodium sulfate and reduced in volume to 75 ml. by distillation. To the residue was added 25 ml. of methanol and a solution of 9 g. of sodium acetate and 6 g. of semicarbazide hydrochloride in 25 ml. of water. The mixture was shaken for 30 min. and then cooled in ice. Filtration gave 3.8–6.2 g. (13–21%) of 4-chloronorcamphor semicarbazone and a two-phase filtrate. The pentane layer was separated, washed with water, dried over anhydrous sodium sulfate and distilled giving 15 g. of pure 1-chloronorcamphane, b.p. 56–58° at 27 mm., m.p. 40.8–42.9°. The net yield of the semicarbazone was 39–41%. Recrystallization from methanol-water gave the pure semicarbazone, m.p. 220–222° dec.

Anal. Calcd. for $C_8H_{12}ON_3Cl$: C, 47.6; H, 6.0. Found: C, 47.5; H, 6.1.

To a solution of 8 g. of oxalic acid in 80 ml. of water was added 4.7 g. of the semicarbazone. Distillation gave crude 4-chloronorcamphor. The mixture was shaken with pentane (150 ml.) and the pentane layer was separated, dried over anhydrous sodium sulfate, and distilled. Sublimation of the residue gave 3.2 g. (97%) of pure 4-chloronorcamphor, m.p. 80.6–82.0°.

Anal. Calcd. for C_7H_9OCl : C, 58.1; H, 6.3; Cl, 24.5. Found: C, 58.0; H, 6.3; Cl, 24.7.

A 2,4-dinitrophenylhydrazone was prepared, and was purified by recrystallization from ethanol-water, and by chromatography over alumina using toluene as the eluent. It had m.p. 157–159°.

Anal. Calcd. for $C_{13}H_{13}N_4O_4Cl$: C, 48.1; H, 4.0. Found: C, 48.4; H, 3.9.

4-Chloronorcamphor was heated to reflux for 4 days with silver nitrate in 50% aqueous ethanol, and less than 3% silver chloride was obtained. The dipole moment was determined in the usual way using benzene solutions and a heterodyne beat apparatus, and was found to be 2.14 D. Using 2.08 D. as the C—Cl moment (from cyclopentyl chloride), 2.95 D. for the C=O moment (from camphor) and bond angles derived from molecular models, the calculated values for 1 and 4-chloronorcamphor were 4.1 and 2.1 D., respectively.

Wolff-Kishner Reduction of 4-Chloronorcamphor.—A mixture of 5.6 g. (0.028 mole) of 4-chloronorcamphor semicarbazone, 4.6 g. (0.08 mole) of potassium hydroxide and 35 ml. of triethylene glycol was heated cautiously and then distilled until no further material readily distilled. The partially solid distillate was treated with 30 ml. of water and was taken up in 100 ml. of pentane. The pentane solution was washed with 5% hydrochloric acid, and with water. After drying over anhydrous sodium sulfate, distillation gave 1.8 g. (50%) of 1-chloronorcamphane, b.p. 150–153°, m.p. 40.2–43.2°. The u.m.r. infrared spectra were identical with those of authentic material, and the melting point was not depressed on admixture with the latter.

1-Chloronorcamphorquinone.—A mixture of 4.6 g. (0.032 mole) of 4-chloronorcamphor, 10 ml. of xylene (distilled from sodium) and 3.6 g. of freshly prepared selenium dioxide was stirred and brought to reflux temperature. After 9.5 hr., the solution was cooled, the selenium was removed by filtration and was washed with 40 ml. of benzene. The solvents were removed under reduced pressure, and the residue was distilled giving 3.9 g. (77%) of the yellow-orange diketone, b.p. ~ 138° at 12 mm.

A sample of the diketone was crystallized from a benzene-petroleum ether mixture and repeatedly sublimed giving bright yellow needles, m.p. 94.8–96.6°. The compound decomposed rapidly on standing.

Anal. Calcd. for $C_7H_7O_2Cl$: C, 53.0; H, 4.5; Cl, 22.4. Found: C, 52.6, 52.7; H, 3.8, 4.6; Cl, 22.1, 22.2.

The quinoxaline was prepared, and after two recrystallizations from ethanol-water it had m.p. 139–139.6°.

Anal. Calcd. for $C_{13}H_{11}N_2Cl$: C, 67.7; H, 4.8, N, 12.2; Cl, 15.4. Found: C, 67.9, 67.7; H, 4.6, 4.7; N, 12.1, 12.0; Cl, 15.3, 15.3.

1-Chloronorcamphorquinone Monotosylhydrazone.—A solution of 81 g. (0.44 mole) of tosylhydrazine in 130 ml. of hot glacial acetic acid was added in portions with swirling to a solution of 69 g. (0.44 mole) of 1-chloronorcamphorquinone in 130 ml. of glacial acetic acid. The mixture was allowed to stand overnight in a refrigerator. The product was filtered, mixed with 400 ml. of water, refiltered, washed with water and air-dried giving 123 g. (86%) of the tosylhydrazone, m.p. 168.5° dec. Two recrystallizations from methanol gave the pure tosylhydrazone, m.p. 187.0° dec.

Anal. Calcd. for $C_{14}H_{15}O_3N_2S_2Cl$: C, 51.5; H, 4.6; N, 8.6. Found: C, 51.4, 51.4; H, 4.7, 4.6; N, 8.5, 8.4.

1-Chlorodiazonorcamphor.—1-Chloronorcamphorquinone monotosylhydrazone (4.6 g., 0.014 mole) was dissolved in a solution of 0.65 g. (0.016 mole) of sodium hydroxide in 25 ml. of water. The solution was stirred with *n*-pentane, the organic layer being decanted and dried over anhydrous sodium sulfate when it became bright yellow. At these times, fresh portions of pentane were added. When no further color was developed, the pentane solution was evaporated giving 1.4 g. (59%) of the yellow diazoketone, m.p. 77.0–79.2°. Recrystallization from benzene-heptane raised the m.p. to 77.8–79.0°.

Anal. Calcd. for $C_7H_7ON_2Cl$: C, 49.3; H, 4.1; N, 16.4; Cl, 20.8. Found: C, 49.2, 49.5; H, 4.2, 4.1; N, 16.2, 16.3; Cl, 20.4, 20.4.

The infrared spectrum had bands at 5.81, 5.85 (C=O) and 4.8 μ (diazo). The ultraviolet spectrum had λ_{max} 249 $m\mu$ (ϵ 11,400), 295 $m\mu$ (ϵ 3900) in ethanol.

Methyl 1-Chlorobicyclo[2.1.1]hexane-5-carboxylate.—A solution of 38.2 g. (0.224 mole) of 1-chlorodiazonorcamphor in 4 l. of methanol was irradiated for 19.5 hr. with a 500 w. Hanovia immersion quartz lamp equipped with a Corex filter. The lamp was water cooled. The solution was distilled using a bubble-cap column, collecting 3 l. of methanol. The residue was diluted with 1 l. of ice-water and extracted with 6 l. of pentane in several portions. The pentane solution was dried over anhydrous sodium sulfate and distilled giving 20.4 g. (52%) of the crude ester, b.p. 86–93° at 7 mm.

The crude ester (19.4 g.) was dissolved in 200 ml. of pentane. The solution was cooled in an ice-bath, carbon dioxide was bubbled in, and potassium permanganate solution was added with stirring. When the permanganate was no longer decolorized, water was added, the pentane layer was removed, and the aqueous solution was extracted with pentane. The pentane solution was washed with dilute sodium bisulfite solution and with water, and was dried over

anhydrous sodium sulfate. Distillation gave 9.5 g. of the chloroester, b.p. 73–78° at 3–4 mm. The analytical sample had b.p. 81–82° at 7 mm., n_{D}^{25} 1.4735. The ester still contained a small amount of a ketone impurity.

Anal. Calcd. for $C_8H_{11}O_2Cl$: C, 55.0; H, 6.4; Cl, 20.3. Found: C, 54.4, 54.5; H, 6.3, 6.2; Cl, 20.6, 20.6.

1-Chlorobicyclo[2.1.1]hexane-5-carboxylic Acid.—A solution of 8.6 g. (0.049 mole) of methyl 1-chlorobicyclo[2.1.1]hexane-5-carboxylate in 60 ml. of methanol was treated with 5.6 g. (0.1 mole) of potassium hydroxide. The mixture was heated to reflux for 1.5 hr. and then 30 ml. of methanol was removed by distillation. The solution was diluted with 100 ml. of water and extracted with three 100-ml. portions of ether. The aqueous phase was cooled in an ice-bath, acidified with hydrochloric acid and extracted with six 100-ml. portions of ether. The ether solution was dried over anhydrous sodium sulfate and distilled giving 5.7 g. (72%) of the acid. Two recrystallizations from cyclohexane followed by sublimation at 90° and 10 mm. gave the pure acid, m.p. 101.1–103.9°.

Anal. Calcd. for $C_7H_9O_2Cl$: C, 52.4; H, 5.6; Cl, 22.1; neut. equiv., 160.5. Found: C, 52.3, 52.4; H, 5.4, 5.6; Cl, 21.8, 21.9; neut. equiv., 159.

1-Chlorobicyclo[2.1.1]hexane-5-carbonyl Chloride.—A mixture of 6.42 g. (40 mmoles) of 1-chlorobicyclo[2.1.1]hexane-5-carboxylic acid and 10.00 g. (84 mmoles) of thionyl chloride, protected with a drying tube, was heated on a steam-bath for 5 hours. The excess thionyl chloride was removed under reduced pressure. The residue was distilled,

giving 6.86 g. (96%), of the acid chloride, b.p. 78° at 7 mm., n_{D}^{25} 1.4965.

***t*-Butyl 1-Chlorobicyclo[2.1.1]hexane-5-peroxycarboxylate.**—A mixture of 6.0 g. (67 mmoles) of *t*-butyl hydroperoxide, 7.0 ml. pyridine and 40 ml. of cymene was stirred and cooled thoroughly in an ice-salt-bath. 1-Chlorobicyclo[2.1.1]hexane-5-carbonyl chloride (5.17 g., 28.9 mmoles) was added dropwise over a 1-hour period, and the solution was stirred for another hour. The mixture was poured onto 50 g. of ice, the aqueous phase extracted with 30 ml. of cymene (in two portions), the combined cymene extract was washed with two 20-ml. portions of cold 10% sulfuric acid, ice-water (10 ml.), cold 10% sodium carbonate (10 ml.) and ice-water (three 10-ml. portions). The solution was dried over magnesium sulfate.

1-Chlorobicyclo[2.1.1]hexane.—The same apparatus as described for the preparation of bicyclo[2.1.1]hexane preparation was used with the exception of addition of an 8" Vigreux column. The decomposition of the peroxyester was carried out at about 130°. Within 2 hours, carbon dioxide evolution ceased with the formation of 0.79 g. of carbon dioxide (62% based on the acid chloride). The solution was distilled until about 5 ml. of cymene had been collected. The product was isolated by gas phase chromatography using a silicone column at 130° giving 0.89 g. (26%) of 1-chlorobicyclo[2.1.1]hexane.

Redistillation of the chloride gave material having b.p. 122°, n_{D}^{25} 1.4629. A sample of the compound was heated in a sealed tube at 100° for a week with 2% ethanolic silver nitrate with negative results.

Anal. Calcd. for C_8H_9Cl : C, 61.8; H, 7.8; Cl, 30.4. Found: C, 61.8, 61.8; H, 7.8, 7.6; Cl, 30.2, 30.5.

[CONTRIBUTION FROM FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, PRINCETON, N. J.]

Stereochemistry of Hydroanthracenes¹

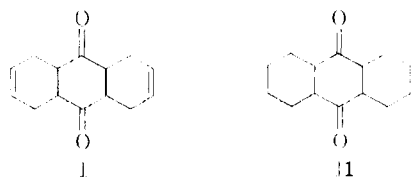
By RICHARD K. HILL, JAMES G. MARTIN² AND WILLIAM H. STOUCH

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Raney nickel reduction of the bis-thioacetal of the bis-butadiene-*p*-benzoquinone adduct (I) gave perhydroanthracene VIII. Several experiments proved that no epimerization occurred during this process, and I consequently has the *cis,anti,cis* configuration, in contrast to the earlier assignment of Alder and Stein. Reduction of the bis-thioacetal of the stereoisomeric diketone IV gave *trans,syn,trans*-perhydroanthracene (VII), proving the configuration of IV. The four diols corresponding to I and its saturated derivative were prepared and their stereochemistry determined by infrared spectroscopy. Huang-Minlon reduction of I, III or IV, followed by hydrogenation, or of II directly, led to a mixture of VIII and IX. The perhydroanthracenes were equilibrated by aluminum bromide to a mixture composed of 96% of VII and 4% of VI.

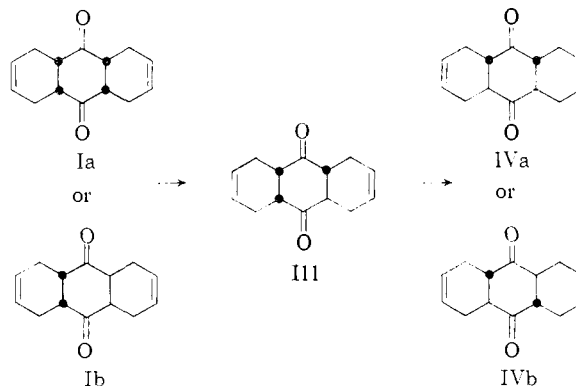
Introduction

In 1933, Alder and Stein³ prepared a bis-butadiene adduct (I) of *p*-benzoquinone, and showed, by oxidation of the tetrahydro derivative II to *cis*-cyclohexane-1,2-dicarboxylic acid, that only *cis* ring junctions were present in the adduct. Refluxing acetic anhydride epimerized I to a stereo-



isomer III, and either I or III could be further isomerized by heat, alkali or longer reflux with acetic anhydride to a third isomer IV. Both

III and IV were shown to possess at least one *trans* ring junction.



Compound III, as the primary isomerization product of the all-*cis* adduct, was assigned the *cis,trans* configuration, but two configurations were possible for each of the other stereoisomers. Alder and Stein did not provide evidence to permit a decision between the two *cis,cis* configurations

(1) Taken from theses presented to Princeton University by J. G. Martin for the Ph.D. degree, 1960, and by W. H. Stouch for the B.A. degree, 1957. Presented, in part, at the Delaware Valley Regional Meeting, American Chemical Society, Philadelphia, Pa., February, 1960.

(2) Danforth Foundation Fellow, 1957–1960.

(3) K. Alder and G. Stein, *Ann.*, **501**, 247 (1933).