

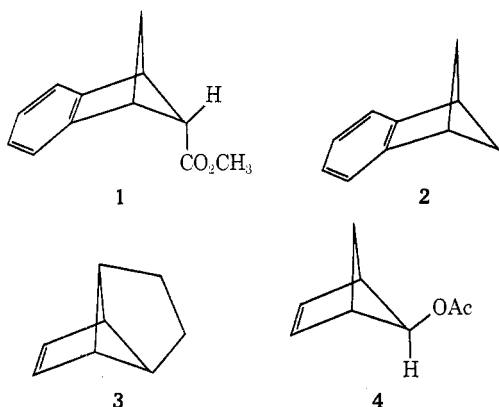
5-Substituted Bicyclo[2.1.1]hexenes¹KENNETH B. WIBERG* AND RICHARD W. UBERSAX²

Department of Chemistry, Yale University, New Haven, Connecticut 06520

Received March 27, 1972

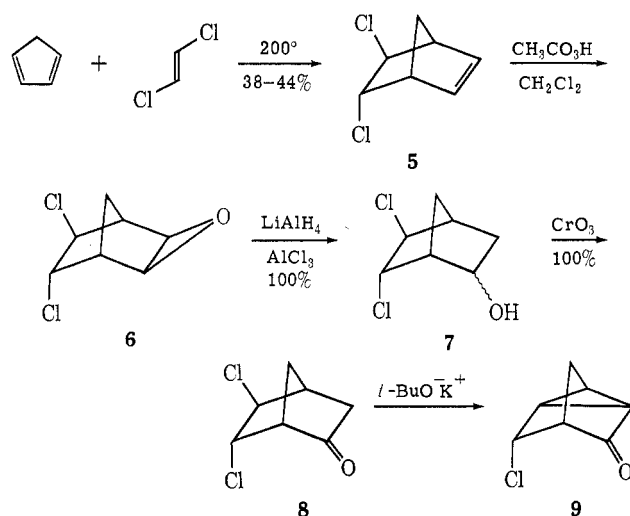
The synthesis of 5-substituted bicyclo[2.1.1]hexenes *via* the dehalogenation of 2,3-dichlorobicyclo[2.1.1]hexanes is described. The reaction was successful when the 5 substituent was carboethoxy, hydroxymethyl, or 2-hydroxyethyl. However, it failed when the substituent was acetoxy, and only benzene, derived from rearrangement and elimination of acetic acid, was obtained. The nmr spectra of the bicyclo[2.1.1]hexenes and of the 2,3-dichlorobicyclo[2.1.1]hexanes are discussed.

Bicyclo[2.1.1]hexene derivatives are of interest in connection with studies of double bond participation and of thermal rearrangements. The preparation of some of these compounds has been difficult,³ although methyl benzobicyclo[2.1.1]hexene-1-carboxylate (1),⁴ benzobicyclo[2.1.1]hexene (2),⁵ tricyclo[3.3.0.0^{2,6}]oct-3-ene (3),⁶ *exo*-bicyclo[2.1.1]hex-2-en-5-yl acetate (4),⁷ and the parent hydrocarbon⁸ have been reported. The



synthetic methods employed for these compounds were not suited to the preparation of the 5-substituted derivatives of particular interest to us. The following will report convenient preparations for some of these compounds.

The Diels-Alder reaction of *trans*-1,2-dichloroethylene with cyclopentadiene gave *trans*-5,6-dichloronorbornene (5).⁹ Epoxidation with peracetic acid afforded *exo*-2,3-epoxy-*trans*-5,6-dichloronorbornane (6).¹⁰ Reduction with lithium aluminum hydride-aluminum chloride to the alcohol 7 followed by oxidation with chromic acid gave the ketone 8. The arrangement of the chlorines in 8 was indicated by its facile reaction with potassium *tert*-butoxide to give *endo*-5-chlorotricyclo[2.2.1.0^{2,6}]heptan-3-one (9). Only an *exo* chlorine would be expected to be displaced under the reaction conditions.



Selenium dioxide oxidation of 8 gave the diketone 10, which was converted to its monotosylhydrazone. The latter, when passed over basic alumina,¹¹ gave the yellow crystalline diazo ketone 11. Photolysis of 11 in methanol gave a mixture of methyl *endo*- and *exo*-*trans*-2,3-dichlorobicyclo[2.1.1]hexane-5-carboxylates in an 85:15 ratio. Saponification with methanolic potassium hydroxide gave a 50:50 mixture of the epimeric acids 13 and 14, which could be separated by recrystallization from carbon tetrachloride.

The esters 12 were readily reduced to the corresponding carbinols 15 and 16 with lithium aluminum hydride. Elimination of halogen from 12, 15, and 16 proved difficult. Magnesium turnings in ether both with and without magnesium iodide, zinc dust in ethanol, the zinc-copper couple, and chromous sulfate in aqueous dimethylformamide¹² all failed to give any significant eliminations. Magnesium amalgam in glyme led to a slow elimination of halogen. However, the disodium phenanthrene¹³ was found to effect dehalogenation very effectively at low temperature. Catalytic hydrogenation of 17 and 18 gave the corresponding bicyclo[2.1.1]hexane derivatives, as shown by comparison of nmr and ir spectra with those of authentic samples.¹⁴

The acid 13 was subjected to the Arndt-Eistert reaction followed by reduction and dehalogenation to give 2-(bicyclo[2.1.1]hexen-*endo*-5-yl)ethanol (19). The acetate derived from 19 reacted with diazomethane

(1) This investigation was supported by Public Health Service Grant No. 12800 from the National Institutes of General Medical Science. A preliminary report of part of this work has appeared: K. B. Wiberg and R. W. Ubersax, *Tetrahedron Lett.*, 3063 (1968).

(2) Taken in part from the Ph.D. thesis of R. W. U., 1969.

(3) J. Meinwald and J. K. Crandall, *J. Amer. Chem. Soc.*, **88**, 1292 (1966).

(4) H. Tanida and Y. Hata, *ibid.*, **88**, 4289 (1966).

(5) M. Pomerantz, *ibid.*, **88**, 5349 (1966).

(6) J. Meinwald and B. E. Kaplan, *ibid.*, **89**, 2611 (1967).

(7) S. Masamune, E. N. Cain, R. Vukov, S. Takada, and N. Nakatsuka, *Chem. Commun.*, 243 (1969).

(8) J. Meinwald and F. Uno, *J. Amer. Chem. Soc.*, **90**, 800 (1968); F. T. Bond and L. Scerbo, *Tetrahedron Lett.*, 2789 (1968).

(9) L. Scherling, J. P. Luvisi, and R. W. Welch, *J. Amer. Chem. Soc.*, **78**, 2819 (1956).

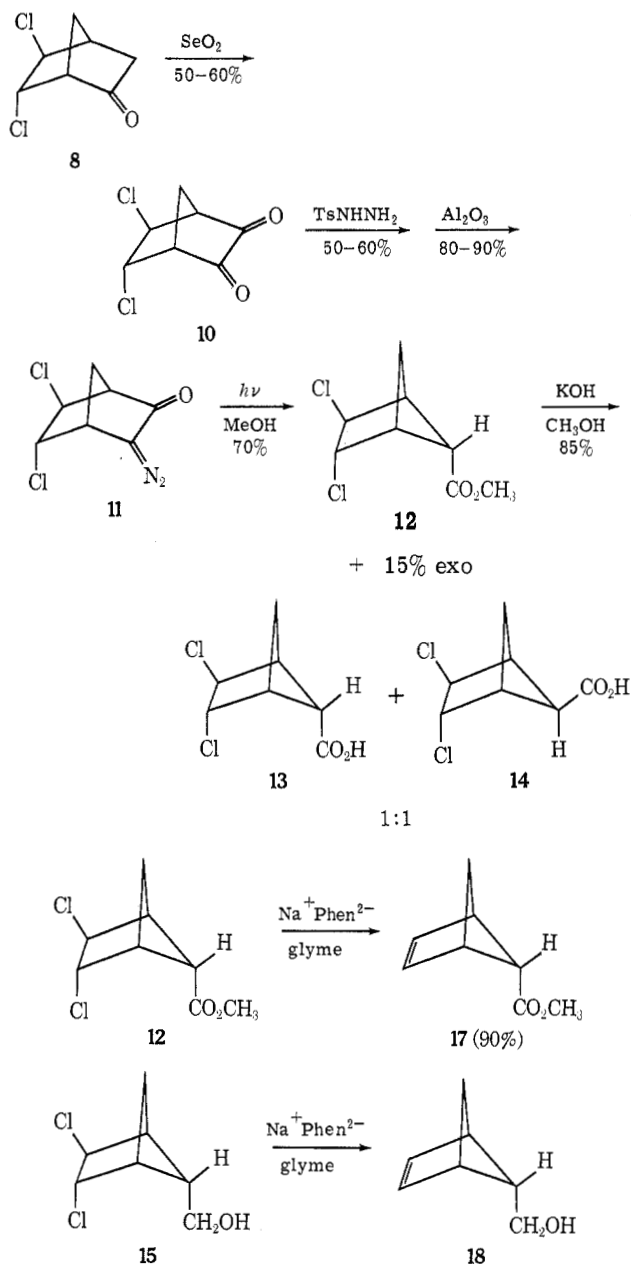
(10) V. Mark, U. S. Patent 2,771,470 (Nov 20, 1956); *Chem. Abstr.*, **51**, 6686 (1957).

(11) The procedure of Meinwald and Crandall¹ was used.

(12) W. C. Kray and C. E. Castro, *J. Amer. Chem. Soc.*, **86**, 4603 (1964).

(13) E. Vogel, H. Kiefer, and W. R. Roth, *Angew. Chem., Int. Ed. Engl.*, **3**, 442 (1964). Cf. R. N. McDonald and D. G. Frickey, *J. Amer. Chem. Soc.*, **90**, 5316 (1968); L. A. Paquette and J. C. Stowell, *Tetrahedron Lett.*, 4159 (1969).

(14) K. B. Wiberg, B. R. Lowry, and T. H. Colby, *J. Amer. Chem. Soc.*, **83**, 3998 (1961).



and cuprous bromide to give 2-(*anti*-tricyclo[3.1.1.0^{2,4}]-hept-*endo*-6-yl)ethyl acetate, which was reduced to the corresponding alcohol **20** with lithium aluminum hydride. The configuration of the cyclopropane group is that expected for addition to the least hindered side of the double bond.¹⁵ It is shown to occupy the assigned position by its nmr spectrum (Table I). The chemical shifts of protons a and b are unaffected by the cyclopropane ring, whereas protons e and f show large diamagnetic shifts, indicating that they lie over the cyclopropane ring.¹⁶

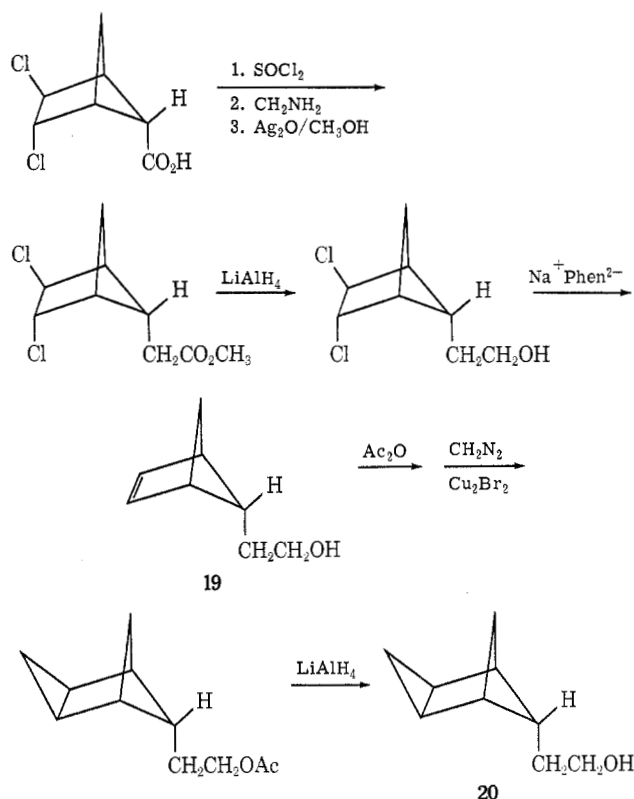
The preparation of *endo*-bicyclo[2.1.1]hexen-5-ol also was attempted. The *endo* acid **13** was converted to the methyl ketone **21** via the acid chloride and treatment with dimethylzinc in pentane. Treatment of **21** with either *m*-chloroperbenzoic acid or buffered trifluoroacetic acid was unsuccessful, only unreacted ketone being recovered. However, the reaction did

(15) A. C. Cope, S. Moon, and P. E. Peterson, *J. Amer. Chem. Soc.*, **84**, 1935 (1962).

(16) Cf. C. D. Poulter, R. S. Boikess, J. I. Brauman, and S. Winstein, *ibid.*, **94**, 2291 (1972).

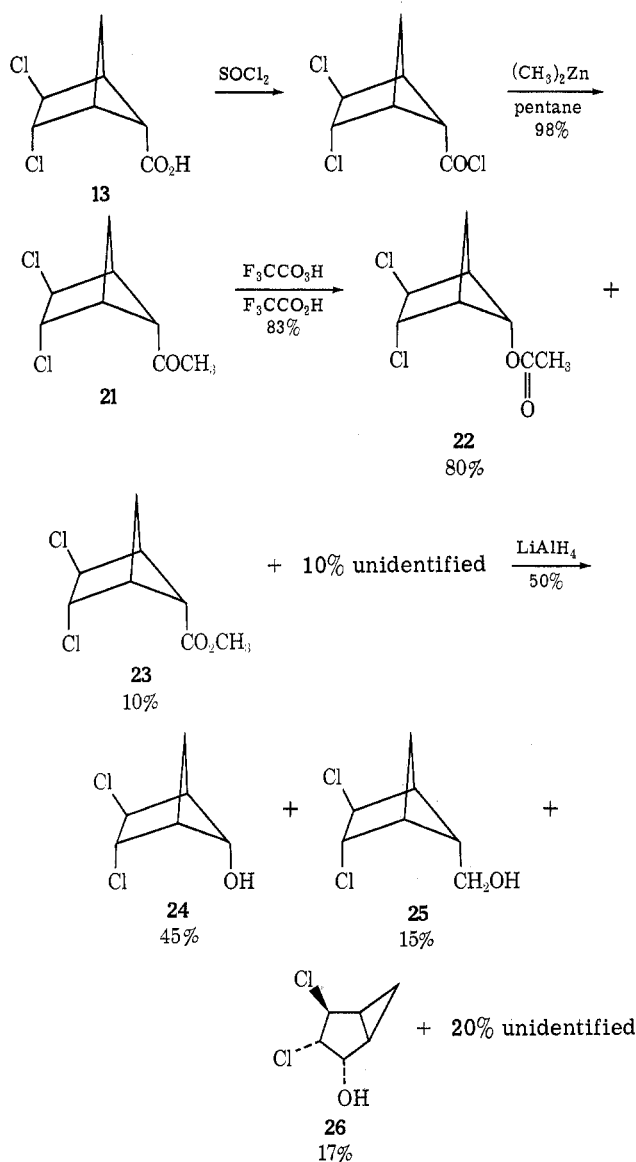
TABLE I
NMR SPECTRA OF
2-(BICYCLO[2.1.1]HEXEN-*endo*-5-YL)ETHANOL (**19**) AND
2-(*anti*-TRICYCLO[3.1.1.0^{2,4}]HEPT-*endo*-6-YL)ETHANOL (**20**)

Proton	Chemical shift, ppm	
	19	20
a	6.57	6.54
b	8.42	8.40
c	6.78	7.62
d	7.50	7.79
e	7.68	8.42
f	7.68	9.00

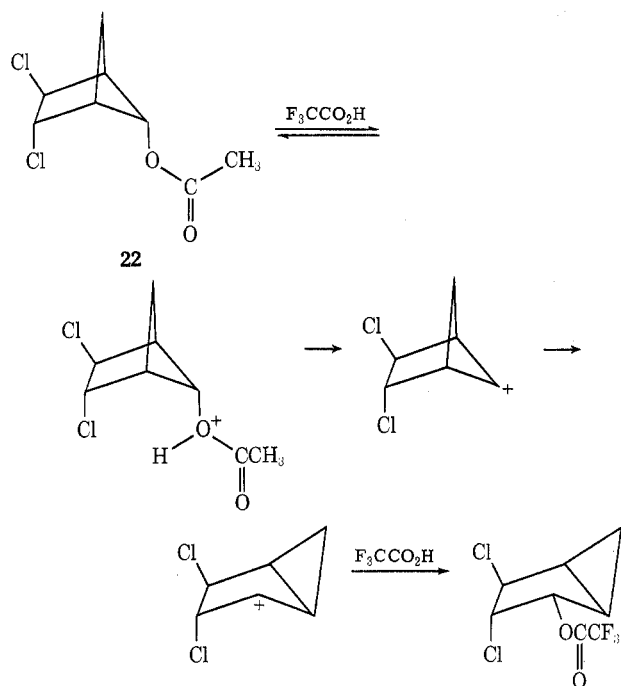


proceed using unbuffered trifluoroacetic acid in the presence of trifluoroacetic acid as a catalyst, giving the acetate along with some methyl *trans*-2,3-dichlorobicyclo[2.1.1]hexane-*endo*-5-carboxylate formed by methyl migration, and some unidentified material. Reduction of the above mixture with lithium aluminum hydride gave a mixture of alcohols in 50% yield. The products were *trans*-2,3-dichlorobicyclo[2.1.1]hexane-*endo*-5-ol (**24**) (45%), *trans*-2,3-dichlorobicyclo[2.1.1]hexane-*endo*-5-methanol (**25**) (15%), *cis*-2-chloro-*trans*-3-chloro-*trans*-4-hydroxybicyclo[3.1.0]hexane (**26**) (17%), and an unidentified product (20%) which had a vpc retention time about twice that of the other compounds.

The carbinol **25** is derived from **23**. The alcohol **26** could arise from an acetate formed in the Baeyer-Villiger reaction as shown in Scheme I.

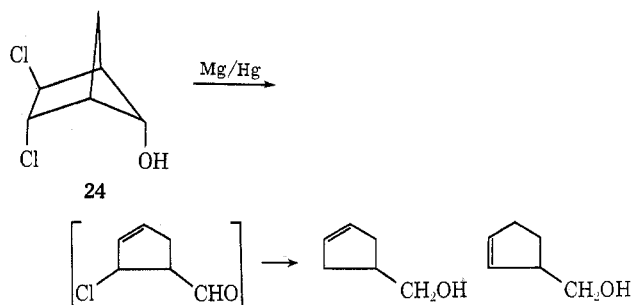


SCHEME I

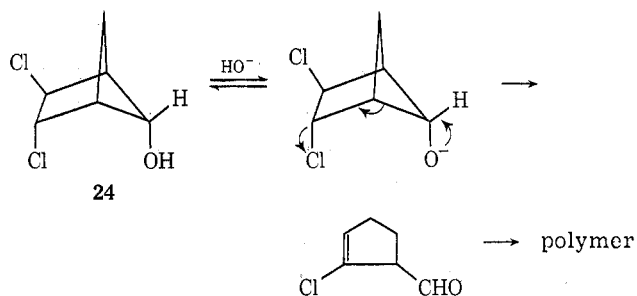


The use of methyllithium for the conversion of the acetates to alcohols raised the yield to 67%.

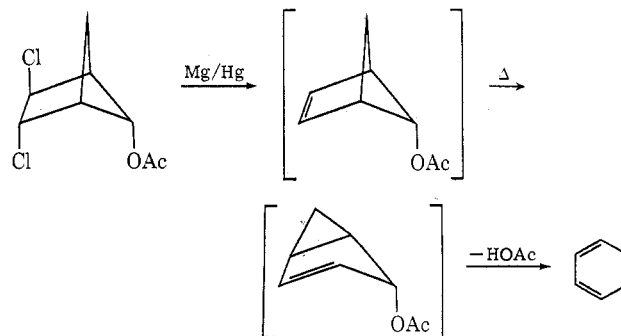
Conversion of *trans*-2,3-dichlorobicyclo[2.1.1]hexan-endo-5-ol to bicyclo[2.1.1]hexen-endo-5-ol with either magnesium amalgam or sodium phenanthrene was unsuccessful. The major product resulting from the magnesium amalgam reaction was Δ^3 -cyclopentenylmethanol along with a small amount of Δ^2 -cyclopentenylmethanol.



2-Chloro- Δ^3 -cyclopentenecarboxaldehyde is probably an intermediate in the reaction. The formation of this compound under basic conditions would be followed by dehydrohalogenation, giving cyclopentadienecarboxaldehyde, which could lead to the polymeric material found in the aqueous base hydrolysis of 22.

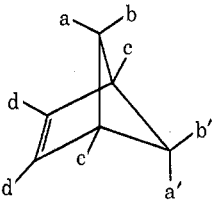


Dehalogenation of the acetate 22 would be expected to eliminate the undesirable cleavage reaction. However, the reaction of 22 with magnesium amalgam gave only benzene. This is not unexpected, since bicyclo[2.1.1]hexene rearranges thermally to bicyclo[3.1.0]hexene at 140° .¹⁷ The reaction conditions for the magnesium amalgam reaction (95°) could lead to a similar rearrangement.¹⁸ The bicyclo[3.1.0]hexenyl



(17) F. T. Bond and L. Scerbo, *Tetrahedron Lett.*, 2789 (1968).

(18) The rearrangement of *exo*-bicyclo[2.1.1]hex-2-en-5-yl acetate to *exo*-bicyclo[3.1.0]hex-2-en-6-yl acetate occurs readily at 85° : S. Masamune, S. Takada, N. Nakatsuka, R. Vukov, and E. N. Cain, *J. Amer. Chem. Soc.*, **91**, 4322 (1969).

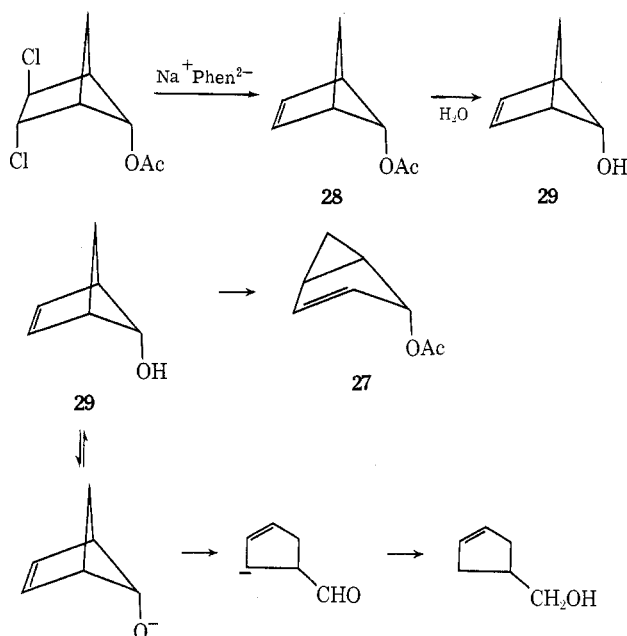
TABLE II
 NMR SPECTRA OF BICYCLO[2.1.1]HEXENE DERIVATIVES (τ)^a


Registry no.	Compd	a	b	a'(b')	c	d	Others
35672-56-1	<i>endo</i> -CO ₂ CH ₃	7.80 (d) (<i>J</i> = 6 Hz)	7.58 (dt)	6.40 (m)	7.12 (p) (<i>J</i> = 2 Hz)	3.18 (t) (<i>J</i> = 2 Hz)	CO ₂ CH ₃ 6.40 (s)
20441-30-9	<i>endo</i> -CH ₂ OH	7.70 (m)	7.70 (m)	6.75 (tt)	7.50 (m)	3.42 (<i>J</i> = 2 Hz)	CH ₂ O, 6.55 (m) OH, 7.21 (s)
35672-58-3	<i>endo</i> -CH ₂ OAc	7.65 (m)	7.65 (m)	6.78 (tt) (<i>J</i> = 7, 2 Hz)	7.45 (m)	3.35 (t) (<i>J</i> = 2 Hz)	CH ₂ O 6.04 (d) (<i>J</i> = 7 Hz) CH ₃ CO 8.08 (s)
35672-59-4	<i>endo</i> -CH ₂ CH ₂ OH	7.68 (m)	7.68 (m)	6.78 (tt)	7.50 (m)	3.30 (t) (<i>J</i> = 2 Hz)	CH ₂ O 6.57 (t) (<i>J</i> = 7 Hz) CH ₂ CH ₂ O 8.42 (t) (<i>J</i> = 7 Hz) OH 6.55 (s)
20441-31-0	<i>exo</i> -CH ₂ OH	7.78 (t)	7.10 (m)	7.10 (m)	7.57 (g)	3.10 (t) (<i>J</i> = 2 Hz)	CH ₂ O 6.16 (d) (<i>J</i> = 8 Hz) OH 6.82 (s)

^a The spectra were determined at 60 MHz using carbon tetrachloride as the solvent.

acetate would be expected readily to be converted to benzene by elimination of acetic acid.¹⁹

The sodium phenanthrene reaction carried out at -40° supports the formation of a bicyclo[3.1.0]hexene intermediate. The products were bicyclo[3.1.0]hex-2-en-3-ol (27) and Δ^3 -cyclopentenylmethanol. These products could be formed as follows.²⁰



The acetate 28 is probably formed, but may readily be hydrolyzed during work-up. Thermal rearrangement of the alcohol 29 would give the observed bicyclohexenol 27. Rearrangement of the anion derived from 29 would give the cyclohexenecarboxaldehyde, which could be reduced to cyclopentenylmethanol under the reaction conditions.

Nmr Spectra of 5-Substituted Bicyclo[2.1.1]hexenes.

(19) The bicyclo[3.1.0]hex-2-en-6-yl acetates are stable thermally¹⁸ but would not be expected to be stable in the presence of magnesium chloride under the reaction conditions.

(20) Masamune, *et al.*,¹⁸ have reported that the hydrolysis of *exo*-bicyclo[2.1.1]hex-2-en-5-yl acetate gives Δ^3 -cyclopentenecarboxaldehyde as one of the products.

The nmr spectra of the 5-substituted bicyclo[2.1.1]hexenes are somewhat simpler than those of the corresponding bicyclo[2.1.1]hexanes.²¹ Because of the similar geometries of the two ring systems, the coupling constants of the methylene protons are essentially the same.

The distinct feature of the spectra of the bicyclo[2.1.1]hexenes is the sharp triplet of the olefinic protons which are coupled to the adjacent bridgehead proton (*J* = 2 Hz) and are apparently coupled to the distant bridgehead proton (*J* = 1.5 Hz). This is similar to the coupling found for the other bicyclo[2.1.1]hexenes.²² The chemical shifts and description of the proton absorptions of selected bicyclo[2.1.1]hexenes are listed in Table II.

The carbonyl protons of bicyclo[2.1.1]hexene-*endo*-5-methanol appear as an unsymmetrical multiplet rather than as a sharp doublet as found with the *exo* isomer. However, in both the corresponding acetate and tosylate, the carbonyl protons do appear as a doublet. The unsymmetrical pattern found in the *endo* methanol appear to be related to the hydroxy group, but the details remain unclear.

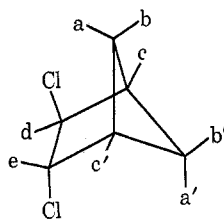
Nmr Spectra of *trans*-2,3-Dichlorobicyclo[2.1.1]hexanes.—The spectra of a group of *trans*-2,3-dichlorobicyclo[2.1.1]hexanes are summarized in Table III. In all of the *endo*-substituted derivatives, the C-6 methylene protons appear as a characteristic multiplet between τ 8.15 and 8.50. In addition, the *endo* C-3 proton always appears at lower field than the *exo* C-2 proton. One would expect these protons to have substantially different chemical shifts due to the magnetic anisotropy of the 5 substituent.

In the case of the *exo* 5-substituted derivatives, the C-2 and C-3 protons appear as a broad singlet between τ 5.65 and 5.75. These protons are expected to have about the same chemical shift, since the 5 substituent is now approximately equidistant from the protons in question.

The CH₃CH₂ protons of ethyl *trans*-2,3-dichloro-

(21) K. B. Wiberg and B. R. Lowry, *J. Amer. Chem. Soc.*, **84**, 1594 (1962).

(22) K. E. Wilzbach, J. S. Ritscher, and L. Kaplan, *ibid.*, **89**, 1031 (1967); J. Meinwald and B. E. Kaplan, *ibid.*, **89**, 2611 (1967).

TABLE III
 NMR SPECTRA OF *trans*-2,3-DICHLOROBICYCLO[2.1.1]HEXANE DERIVATIVES (τ)^a


Registry no.	Compd	a,b	a'(b')	c(c')	d	e	Other	
35672-61-8	CO ₂ CH ₃ ^b	8.05-8.50 (m)	6.75-7.15 (m)		5.15 (m)	5.68 (m)	OCH ₃	6.32 (s)
55672-62-9	CO ₂ H ^b	8.30 (m)	6.80 (m)	7.07 (m)	5.15 (m)	5.73 (m)	CO ₂ H	-1.55 (r)
35672-63-0	CH ₂ OH ^b	8.35 (m)	7.63 (t)	7.18 (m)	5.54 (m)	5.72 (m)	CH ₂ OH	6.30 (d)
35908-76-0	COCl ^b	8.23 (m)	6.75- 7.05 (m)	6.37- 6.75 (m)	5.22 (m)	5.60 (m)	OH	6.57 (s)
35672-64-1	COCHN ₂ ^b	8.33 (m)	6.67-7.13 (m)		5.05 (m)	5.80 (m)	CHN ₂	4.70 (s)
55672-65-2	CH ₂ CO ₂ CH ₃ ^b	8.30 (m)	7.42 (s)	7.20 (m)	5.57 (m)	5.72 (m)	OCH ₃	6.34 (s)
35672-66-3	CH ₂ CH ₂ OH ^b	8.42 (m)	7.75 (m)	7.25 (m)	5.50 (m)	5.72 (m)	CH ₂ CH ₂ O	8.28 (q)
							CH ₂ CH ₂ O	6.45 (t)
							OH	6.13 (s)
35672-68-5	COCH ₃ ^b	8.37	6.75 (m)	6.93- 7.35 (m)	5.35 (m)	5.80 (m)	COCH ₃	7.91 (s)
35672-67-4	COCH ₂ CH ₃ ^b	8.10-8.50 (m)	6.67 (m)	6.98- 7.30 (m)	5.24 (m)	5.72 (m)	CH ₃ CH ₂	5.72 (p)
							CH ₃	9.00 (t)
35672-69-6	OAc ^b	8.46 (m)	5.37 (q)	7.00 (m)	5.49 (m)	5.75 (m)	COCH ₃	7.98 (r)
35672-70-9	OH ^b	8.50-9.03 (m)	6.01 (q)	7.18 (t)	5.49 (m)	5.74 (m)	OH	7.87 (s)
35672-71-0	CO ₂ CH ₃ ^b	8.20 (t)	7.10 (d)	7.45 (m)	6.93- 7.10 (m)	5.66 (m)	OCH ₃	6.20 (s)
35672-72-0	CO ₂ H ^b	8.20 (t)	6.92- 7.13 (m)	7.44 (d)	6.92- 7.13 (m)	5.72 (m)	CO ₂ H	-1.50 (s)
35672-73-2	CH ₂ OH ^c	8.29 (t)	7.35-7.92 (m)			5.75 (m)	OH	6.45 (s)

^a The spectra were determined at 60 MHz using carbon tetrachloride as the solvent. ^b Endo isomer. ^c Exo isomer.

bicyclo[2.1.1]hexyl-*endo*-5 ketone appear as a symmetrical pentet centered at τ 7.52. Irradiation at the methyl frequency reduced the pattern to an AB quartet ($J = 7$ Hz, δ 13 Hz). The methylene hydrogens are diastereotopic, and as a result are magnetically nonequivalent.

Experimental Section

trans-5,6-Dichloro-*exo*-2-hydroxybicyclo[2.2.1]heptane.—Into a flask fitted with a mechanical stirrer, reflux condenser, and dropping funnel was placed 1 l. of ether. The ether was cooled in an ice water bath and 50 g (0.37 mol) of aluminum chloride was added cautiously. The mixture was stirred at ice temperature for 10 min and 50 g (1.31 mol) of lithium aluminum hydride was carefully added. The mixture was allowed to warm to room temperature and 330 g (1.84 mol) of *exo*-2,3-epoxy-*trans*-5,6-dichlorobicyclo[2.2.1]heptane in 1.8 l. of ether was added over a period of 1 hr. The mixture was heated at reflux for 72 hr and then was cooled in an ice water bath. After the cautious addition of 200 ml of water, the mixture was allowed to stir for 1.5 hr at room temperature. The solids were filtered and washed twice with 300 ml of ether. After drying over magnesium sulfate, the ether was removed by distillation. Traces of remaining ether were removed using a rotary evaporator, leaving 314 g (94%) of a clear liquid which solidified on standing. An analytical sample was prepared by two recrystallizations from hexane and sublimation at 50° (0.5 mm), mp 58–60°.

Anal. Calcd for C₇H₁₀Cl₂O: C, 46.4; H, 5.6; Cl, 39.2. Found: C, 46.5, 46.3; H, 5.6, 5.5; Cl, 39.0, 39.2.

The nmr spectrum showed absorption at τ 5.75 (2 H, m), 6.42 (1 H, m), 7.42 (1 H, s), 7.60 (2 H, m), and 7.90–8.70 (4 H, m).

trans-5,6-Dichloro-2-norcamphor.—To a solution of 300 g (1.66 mol) of *trans*-5,6-dichloro-*exo*-2-hydroxybicyclo[2.2.1]heptane in 2 l. of ether was added a solution of 333 g (2.0 equiv) of sodium dichromate and 250 ml of concentrated sulfuric acid in 1.6 l. of

water. The cooled chromic acid solution was added at a rate to maintain moderate reflux (2 hr). The mixture was stirred for an additional 5 hr at room temperature. The aqueous layer was separated and extracted with four 250-ml portions of ether. The combined ether solutions were washed three times with 250 ml of 5% sodium carbonate solution, twice with 250 ml of water, and twice with 250 ml of saturated sodium chloride solution. After drying over magnesium sulfate, the ether was removed by distillation. The residual ether was removed using a rotary evaporator, leaving 279 g (93%) of a colorless liquid which solidified on standing. An analytical sample was prepared by two recrystallizations from hexane and sublimation at 60° (0.5 mm), mp 77.0–77.4°.

Anal. Calcd for C₇H₈Cl₂O: C, 47.0; H, 4.5; Cl, 39.6. Found: C, 46.9, 47.0; H, 4.3, 4.3; Cl, 39.5, 39.5.

The nmr spectrum showed absorption at τ 5.67 (1 H, pentet, $J = 2$ Hz), 5.98 (1 H, t, $J = 2$ Hz), 7.21 (2 H, m), and 7.40–8.32 (4 H, m). The ir spectrum showed absorption at 1772 cm⁻¹.

Reaction of *trans*-5,6-Dichloro-2-norcamphor with Potassium *tert*-Butoxide.—A slurry of potassium *tert*-butoxide formed from 5.5 g of potassium in 200 ml of toluene was treated with a solution of 17.9 g (0.1 mol) of *trans*-5,6-dichloro-2-norcamphor in 20 ml of toluene. The mixture was allowed to stir at room temperature for 20 hr. The mixture was shaken with 200 ml of ice water in a separatory funnel. An aqueous layer was drawn off and the toluene was washed with 100 ml of saturated sodium chloride solution. The solution was dried over sodium sulfate and the toluene was removed using a rotary evaporator, giving 13.3 g (93%) of a yellow oil. Analysis by vpc indicated that only one product was formed. The ir spectrum (1770 cm⁻¹) and nmr spectra are consistent with the product being *endo*-5-chlorotricyclo[2.2.1.0^{2,5}]heptan-3-one. The nmr spectrum (CCl₄) showed absorption at τ 5.58 (1 H, t, $J = 1$ Hz), 7.58 (2 H, pentet, $J = 6$ Hz, split further into multiplets), 8.00 (3 H, m), and 8.50 (1 H, t, $J = 6$ Hz).

Anal. Calcd for C₇H₇ClO: C, 59.0; H, 5.0; Cl, 24.9. Found: C, 58.8, 58.9; H, 5.1, 5.1; Cl, 24.8, 24.9.

trans-5,6-Dichloronorcamphorquinone.—Into a flask fitted with a mechanical stirrer and water separator were placed 626 g

(5.6 mol) of freshly sublimed selenium dioxide, 915 g (5.1 mol) of *trans*-5,6-dichloro-2-norcamphor, and 1.8 l. of xylene. The flask was heated in an oil bath at 165° for 8 hr, during which time 92 ml (100%) of water was collected. The mixture was stored in a refrigerator overnight and filtered. The solvent was removed under reduced pressure and the residue was divided into three equal portions. Each portion was bulb to bulb distilled at 1–2 mm using an oil bath at 150°, giving a total of 708 g (72%) of an orange, waxy solid, bp 110–130°. The crude diketone was converted immediately to the monotosylhydrazone.

The nmr spectrum (CCl₄) showed absorption at τ 5.40 (1 H, sextet, $J = 2$ Hz), 5.80 (1 H, t, $J = 2$ Hz), 6.57 (1 H, m), 6.75 (1 H, pentet, $J = 1$ Hz), 7.17 (1 H, d, $J = 12$ Hz, split further into triplets, $J = 1$ Hz), 7.74 (1 H, d, $J = 12$ Hz, split further into quartets, $J = 1$ Hz). The ir spectrum showed absorption at 1756 and 1790 cm⁻¹.

***trans*-5,6-Dichlorodiazonorcamphor.**—To a solution of 225 g (1.32 mol) of *trans*-5,6-dichloronorcamphorquinone and 350 ml of glacial acetic acid cooled in an ice water bath was added a boiling solution of 234 g (1.26 mol) of *p*-toluenesulfonylhydrazide in 300 ml of acetic acid at a rate to maintain the temperature below 15°. The stirring was continued until precipitation occurred. The mixture was stored in a refrigerator overnight and filtered. The solid was mixed with 1.5 l. of water and again filtered. After it was dried in the atmosphere for 24 hr and then under reduced pressure over phosphorus pentoxide, there was obtained 267 g (56%) of the cream colored monotosylhydrazone, mp 160–161° dec.

The tosylhydrazone (30.0 g, 83.2 mmol) was ground to a fine powder and mixed with 100 g of 80–200 mesh basic alumina in a 250-ml flask. Chloroform (70 ml) was added and the wetted mixture was stirred with a spatula until it was of a uniform consistency. The mixture was poured onto a column (65 mm diameter) containing 130 g of alumina and was eluted with chloroform until the eluent was colorless. The eluents from five runs were combined and the chloroform was distilled until the volume was 300 ml. The remaining solvent was removed using a rotary evaporator, giving 75.2 g (88%) of an orange oil which solidified on standing. The diazo ketone could be purified by recrystallization from *n*-hexane-cyclohexane and was obtained as needles, mp 88.4–89.2°.

Anal. Calcd for C₇H₆Cl₂N₂O: C, 41.0; H, 3.0; Cl, 34.6; N, 13.7. Found: C, 40.9, 41.0; H, 2.9, 3.0; Cl, 34.6, 34.6; N, 13.7, 13.8.

The nmr spectrum (CDCl₃) showed absorption at τ 5.62 (2 H, m), 6.40 (1 H, m), 7.04 (1 H, m), and 7.74 (2 H, m). The ir spectrum showed absorption at 1710 (C=O) and 2090 cm⁻¹ (C=N₂).

Methyl *trans*-2,3-Dichlorobicyclo[2.1.1]hexane-5-carboxylate.—A solution of 66.7 g (0.33 mol) of *trans*-5,6-dichlorodiazonorcamphor in 2.5 l. of absolute methanol was irradiated with a water-cooled Hanovia 450-W quartz immersion lamp using a Corex filter. After 72 hr, 6.6 l. (90%) of nitrogen was evolved. The solution was concentrated to 100 ml using a rotary evaporator. The residue was diluted with 250 ml of ether and the ether solution was washed with 100 ml of cold water, 100 ml of saturated sodium carbonate solution, and twice with 100 ml of saturated sodium chloride solution. The ether solution was dried over magnesium sulfate and the solvent was removed using a rotary evaporator. Distillation of the residue gave 44.4 g (66%) of methyl *trans*-2,3-dichlorobicyclo[2.1.1]hexane-5-carboxylate, bp 86–88° (0.5 mm). Vpc analysis on a 10 ft \times 0.375 in. 20% DEGS column at 160° showed that the product consisted of 85% of the endo epimer (18 min) and 15% of the exo epimer (13 min). Analytical samples were obtained by collection of the corresponding peaks.

Anal. Calcd for C₈H₁₀Cl₂O₂: C, 46.0; Cl, 33.9. Found: endo, C, 46.0, 45.7; H, 5.0, 5.0; Cl, 33.7, 33.8; exo, C, 46.1, 46.0; H, 4.9, 4.8; Cl, 33.9, 33.8.

endo- and exo-*trans*-2,3-dichlorobicyclo[2.1.1]hexane-5-carboxylic Acids.—A solution of 10.0 g (48 mmol) of methyl *trans*-2,3-dichlorobicyclo[2.1.1]hexane-5-carboxylate in 30 ml of methanol was added to a solution of 5.3 g (94 mmol) of potassium hydroxide in 65 ml of methanol at room temperature. The mixture was stirred at reflux for 2 hr and then poured into 500 ml of ice water. The aqueous layer was washed three times with 150 ml of ether and then acidified with hydrochloric acid. The solution was extracted three times with 150 ml of ether. After the solution was dried over magnesium sulfate and solvent was removed with a rotary evaporator, there was obtained 7.0 g (75%) of a yellow

oil which partially solidified on standing. An nmr analysis indicated a 1:1 mixture of exo and endo acids. The crude acids were dissolved in 50 ml of hot carbon tetrachloride and the solution was decolorized with charcoal. On cooling, 1.8 g of the endo acid precipitated, mp 83–85°. Removal of the solvent from the filtrate followed by recrystallization from hexane gave 4.8 g of a 3:1 mixture of the exo and endo acids. The pure endo acid could be obtained by further recrystallization from hexane, mp 151–152.6°.

The ether extract of the basic solution was evaporated, giving 1.5 g of a 1:1 mixture of endo and exo carboxylic esters.

Anal. Calcd for C₈H₈Cl₂O₂: C, 43.1; H, 4.1; Cl, 36.4. Found: endo, C, 43.1, 43.0; H, 4.2, 4.2; Cl, 36.2, 36.3; exo, C, 43.3, 43.3; H, 4.2, 4.3; Cl, 36.3, 36.3.

The acids could also be obtained directly *via* the photolysis of the diazo ketone in aqueous dioxane. Using a solution of 49.0 g of the diazo ketone in 1600 ml of aqueous dioxane (75 ml of dioxane to 200 ml of water) and irradiating for 48 hr, 88% of the theoretical amount of nitrogen was evolved. The acid mixture was isolated as described above, giving 26.7 g (57%) of an 85:15 mixture of the endo and exo acids.

Methyl Bicyclo[2.1.1]hexene-endo-5-carboxylate.—A mixture of 1.5 g (62 g-atoms) of 20 mesh granular magnesium and 150 g of mercury was placed in a 3 \times 0.5 in. iron pipe which was then capped at both ends. The pipe was heated with a Bunsen burner for 3 hr and allowed to cool. The content was scraped into a 250-ml three-necked flask with a helium inlet, Herschberg stirrer, and reflux condenser with a drying tube. The amalgam was covered with 40 ml of glyme, and a solution of 3.0 g (14 mmol) of pure methyl *trans*-2,3-dichlorobicyclo[2.1.1]-endo-5-carboxylate in 40 ml of glyme was added with stirring. The mixture was heated at reflux for 9 days. The supernatant suspension was decanted into a 250-ml centrifuge bottle and the solids remaining in the flask were washed three times with 50 ml of ether and twice with 50 ml of pentane. The combined organic solution was centrifuged and then washed five times with 100 ml of water and twice with 100 ml of saturated salt solution. After the solution was dried over magnesium sulfate, the solvent was distilled through a 12-ft Vigreux column until a residue of 5 ml remained. This was separated by preparative vpc (10 ft \times 0.375 in. 20% DEGS at 155°) into two components with retention times of 2.5 and 25 min. The more volatile component (60% of the mixture) was methyl bicyclo[2.1.1]hexene-endo-5-carboxylate. The minor component was unreacted starting material.

Anal. Calcd for C₈H₁₀O₂: C, 69.5; H, 7.3. Found: C, 69.3, 69.4; H, 7.2, 7.4.

The ir spectrum had a carbonyl band at 1738 cm⁻¹.

The ester could also be prepared using the phenanthrene dianion. A mixture of 1.78 g (10 mmol) of phenanthrene, 0.46 g (20 g-atoms) of sodium, and 50 ml of glyme was stirred under a nitrogen atmosphere. After 0.5 hr, the mixture turned dark green. Stirring was continued for 2 hr at room temperature. The green solution was cooled to -40° in a Dry Ice-methanol bath and 1.0 g (4.8 mmol) of methyl *trans*-2,3-dichlorobicyclo[2.1.1]-hexene-endo-5-carboxylate in 10 ml of glyme was added over a period of 10 min. After stirring for 2 hr at -40°, the solution was poured into 100 ml of ether and 100 ml of ice water. The layers were separated and the aqueous layer was washed with 80 ml of ether. The combined ether solutions were washed with 60 ml of water and 60 ml of saturated salt solution, and dried over sodium sulfate. The ether was distilled through an 18-in. packed column and the residue (0.9 g) was separated by preparative vpc into three components with retention times of 7, 20, and 34 min. They were identified as methyl bicyclo[2.1.1]hexene-endo-5-carboxylate (35%), and *exo*- (35%) and *endo*- (30%) methyl *trans*-2,3-dichlorobicyclo[2.1.1]hexane-5-carboxylates.

Hydrogenation of Methyl Bicyclo[2.1.1]hexene-endo-5-carboxylate.—A mixture of 60 mg of the ester, 5 mg of 5% palladium on carbon catalyst, and 1 ml of dry methanol was treated with hydrogen for 2.5 hr at room temperature. The product was analyzed by vpc (10 ft \times 0.375 in. 20% DEGS at 135°) and found to be a single component. The product was collected and shown to be methyl bicyclo[2.1.1]hexene-endo-5-carboxylate by comparison of ir and nmr spectra with those of an authentic sample.¹⁴

***trans*-2,3-Dichlorobicyclo[2.1.1]hexane-endo-5-methanol.**—A solution of 10.0 g (48 mmol) of methyl *trans*-2,3-dichlorobicyclo[2.1.1]hexane-endo-5-carboxylate in 30 ml of ether was added to 5.0 g (130 mmol) of lithium aluminum hydride in 30 ml of ether. After stirring for 4 hr, the mixture was worked up in the usual

fashion, giving 7.6 g (87%) of *trans*-2,3-dichlorobicyclo[2.1.1]-hexane-*endo*-5-methanol, bp 79–80° (0.1 mm).

Anal. Calcd for C₇H₁₀Cl₂O: C, 46.4; H, 5.6; Cl, 39.2. Found: C, 46.4, 46.4; H, 5.7, 5.6; Cl, 39.0, 39.0.

Bicyclo[2.1.1]hexene-*endo*-5-methanol.—Magnesium amalgam prepared from 3.0 g of magnesium and 300 g of mercury was covered with 50 ml of glyme. A solution of 5.0 g (28 mmol) of *trans*-2,3-dichlorobicyclo[2.1.1]hexane-*endo*-5-methanol in 10 ml of glyme was added and the mixture was vigorously stirred at reflux for 48 hr. Ether (400 ml) was added and the mixture was cooled in an ice water bath. Water (200 ml) was cautiously added and the cold mixture was stirred for 1 hr. The solids were separated by centrifugation and washed with 600 ml of ether. The combined ether solution was washed with 100 ml of saturated salt solution, dried over potassium carbonate, and concentrated to 35 ml by distillation through a 12-in. Vigreux column. The solution was transferred to a small flask and the glyme was removed by distillation at 20° (0.1 mm). The product was collected by raising the bath temperature to 60°, giving 1.05 g of distillate. It was analyzed by preparative vpc (10 ft × 0.375 in. 5% Carbowax 20M at 100°), and 412 mg (14%) of bicyclo[2.1.1]hexene-*endo*-5-methanol was collected.

Anal. Calcd for C₇H₁₀O: C, 76.3; H, 9.2. Found: C, 76.2, 76.2; H, 9.1, 9.1.

The dehalogenation was also effected using sodium phenanthrene formed from 3.56 g (20 mmol) of phenanthrene, 1.5 g (65 mg-atoms) of sodium, and 60 ml of glyme. To a solution of 1.0 g (5.5 mmol) of *trans*-2,3-dichlorobicyclo[2.1.1]hexane-*endo*-5-methanol was added at –40° the sodium phenanthrene solution until the dark green color persisted. The mixture was poured into 300 ml of ice water and extracted twice with 150 ml of ether. The ether solution was washed with 100 ml of saturated salt solution, dried over sodium sulfate, and distilled through an 18-in. packed column to remove the solvent. Most of the glyme was removed by distillation (20 mm, 40°) and the residue was distilled at 0.5 mm (bath temperature 85°), giving 2 g of distillate. The latter was found by vpc to contain 0.5 g (80%) of bicyclo[2.1.1]hexene-*endo*-5-carboxylate along with glyme.

***trans*-2,3-Dichlorobicyclo[2.1.1]hexane-*exo*-5-methanol.**—2,3-Dichlorobicyclo[2.1.1]hexane-*exo*-5-carboxylic acid (25% *endo*) was converted to its methyl ester with diazomethane. A solution of 22.8 g (0.11 mol) of the ester in 50 ml of ether was added to 5.0 g (0.13 mol) of lithium aluminum hydride in 250 ml of ether. After the usual work-up there was obtained 17.0 g (86%) of *trans*-2,3-dichlorobicyclo[2.1.1]hexane-5-methanol, bp 58–72° (0.1 mm). Nmr analysis indicated it to be 77% *exo* and 23% *endo*.

Vpc collection (10 ft × 0.375 in., 5% Carbowax 20M at 175°) gave a pure sample of the *exo* isomer (*exo*, 22 min; *endo*, 31 min).

Anal. Calcd for C₇H₁₀Cl₂O: C, 46.4; H, 5.6; Cl, 39.2. Found: C, 46.2, 46.1; H, 5.9, 6.0; Cl, 38.9, 38.8.

Bicyclo[2.1.1]hexene-*exo*-5-methanol.—The dehalogenation of 4.0 g of *trans*-2,3-dichlorobicyclo[2.1.1]hexane-*exo*-5-methanol (23% *endo*) with magnesium amalgam was carried out as described above. There was obtained 522 mg (22%) of bicyclo[2.1.1]hexene-*exo*-5-methanol and 150 mg (6%) of bicyclo[2.2.1]hexene-*endo*-5-methanol.

Anal. Calcd for C₇H₁₀O: C, 76.3; H, 9.2. Found: C, 76.1, 76.2; H, 9.1, 9.0.

Methyl *trans*-2,3-Dichlorobicyclo[2.1.1]hexane-*endo*-5-acetate.—A mixture of 26.3 g of *trans*-2,3-dichlorobicyclo[2.1.1]hexane-*endo*-5-carboxylic acid and 50 g of thionyl chloride was heated at reflux for 3 hr and distilled, giving 23.2 g (84%) of *trans*-2,3-dichlorobicyclo[2.1.1]hexane-*endo*-5-carbonyl chloride, bp 91–92° (1.1 mm).

An ether solution of diazomethane was prepared by adding 28.0 g of *N*-methyl-*N*-nitrosourea to an ice-cooled mixture of 100 ml of 40% potassium hydroxide solution and 400 ml of ether. The ether layer was dried at 0° for 8 hr over potassium hydroxide pellets. The ether solution was transferred to a clean flask and triethylamine (9.5 g) was added. After the solution was cooled in an ice-salt bath, 20.0 g of the acid chloride in 100 ml of ether was added over 0.5 hr with vigorous stirring. The mixture was filtered and concentrated using a rotary evaporator, giving 21.3 g of a dark orange oil.

A solution of the diazo ketone in 60 ml of methanol was added to a boiling suspension of 0.5 g of silver oxide in 100 ml of methanol. The mixture was vigorously stirred at reflux for 5 hr with 0.5-g portions of silver oxide added hourly. The mixture was cooled in a ice bath and filtered. The solid was washed twice

with 50 ml of ether. The orange solution was concentrated to 30 ml using a rotary evaporator. The residue was diluted with 200 ml of ether, and the solution was washed with 100 ml of water and 100 ml of saturated salt solution. After drying over magnesium sulfate, the solvent was removed using a rotary evaporator. The residue was distilled, giving 17.7 g (82%) of methyl *trans*-2,3-dichlorobicyclo[2.1.1]hexane-*endo*-5-acetate, bp 77–78° (0.15 mm).

Anal. Calcd for C₉H₁₂Cl₂O₂: C, 48.5; H, 5.4; Cl, 31.8. Found: C, 48.4, 48.2; H, 5.3, 5.4; Cl, 31.7, 31.7.

2-(*trans*-2,3-Dichlorobicyclo[2.1.1]hex-*endo*-5-yl)ethanol.—A solution of 17.0 g (76 mmol) of methyl *trans*-2,3-dichlorobicyclo[2.1.1]hexane-*endo*-5-acetate in 40 ml of ether was added to 4.0 g (105 mmol) of lithium aluminum hydride in 100 ml of ether with stirring. After 2 hr the mixture was worked up in the usual fashion, giving 14.0 g (94%) of 2-(*trans*-2,3-dichlorobicyclo[2.1.1]hex-*endo*-5-yl)ethanol, bp 99–100° (0.4 mm). Vpc analysis indicated the materials to be homogeneous.

Anal. Calcd for C₈H₁₂Cl₂O: C, 49.3; H, 6.2; Cl, 36.4. Found: C, 49.1, 49.1; H, 6.3, 6.2; Cl, 36.3, 36.3.

2-(Bicyclo[2.1.1]hexen-*endo*-5-yl)ethanol.—A mixture of 4.0 g (21 mmol) of *trans*-2,3-dichlorobicyclo[2.1.1]hexane-*endo*-5-ethanol, magnesium amalgam (1.5 g of magnesium and 150 g of mercury), and 50 ml of glyme was vigorously stirred at reflux for 24 hr. The mixture was worked up as described above, giving 970 mg (38%) of 2-(bicyclo[2.1.1]hexen-*endo*-5-yl)ethanol (10 ft × 0.375 in., 5% Carbowax 20M column at 155°).

Anal. Calcd for C₈H₁₂O: C, 77.4; H, 9.7. Found: C, 77.3, 77.2; H, 10.2, 10.3.

The alcohol also was prepared using sodium phenanthrene prepared from 6.0 g (34 mmol) of phenanthrene and 2.5 g (110 mmol) of sodium in 80 ml of dimethyl ether at –40°. The solution was cooled to –60° and 6.0 g (31 mmol) of 2-(*trans*-2,3-dichlorobicyclo[2.1.1]hex-*endo*-5-yl)ethanol was slowly added with stirring. After an additional hour at –40°, 40 ml of diethyl ether and 2 ml of water were added. The mixture was allowed to warm to 0° to distil the dimethyl ether. It was poured into 300 ml of ice water and extracted twice with 150 ml of ether. The ether solution was cooled with saturated salt solution, dried over magnesium sulfate, and distilled, giving 3.8 g (99%) of 2-(bicyclo[2.1.1]hexen-*endo*-5-yl)ethanol, bp 50–55° (2 mm).

2-(*anti*-Tricyclo[3.1.1.0^{2,4}]hept-*endo*-6-yl)ethanol.—2-(Bicyclo[2.1.1]hexen-*endo*-5-yl)ethanol (3.8 g) was converted to the acetate (4.8 g, 95%) with pyridine and acetic anhydride. The acetate (3.0 g) was placed in a flask along with 7 ml of *n*-hexane and 200 mg of freshly prepared cuprous bromide. The mixture was treated with diazomethane prepared from 20 g of *N*-methyl-*N*-nitrosourea, 200 ml of 33% potassium hydroxide solution, and 50 ml of decalin as described previously.²³ The reaction was followed by vpc using a 10 ft × 0.375 in. 5% Carbowax 20M column at 135°. The reaction mixture was filtered and the solid was washed with dry ether. The ether solution was added to 2.0 g of lithium aluminum hydride in 50 ml of ether, and after stirring for 1 hr, the mixture was worked up in the usual fashion, giving 2.1 g (85%) of 2-(*anti*-tricyclo[3.1.1.0^{2,4}]hept-*endo*-6-yl)ethanol, bp 58–60° (2 mm).

Anal. Calcd for C₈H₁₄O: C, 78.2; H, 10.2. Found: C, 77.6, 77.6; H, 10.1, 10.2.

Methyl *trans*-2,3-Dichlorobicyclo[2.1.1]hexyl-*endo*-5 Ketone.—To a solution of 30 g (0.32 mol) of dimethylzinc in 600 ml of pentane was added 20.0 g (93 mmol) of *trans*-2,3-dichlorobicyclo[2.1.1]hexane-*endo*-5-carbonyl chloride in 150 ml of pentane. The solution was stirred to reflux for 6 hr, during which time an orange oil separated. The mixture was cooled in an ice water bath and 300 ml of saturated ammonium chloride solution was cautiously added. The pentane layer was washed with 100 ml of water, 100 ml of saturated sodium carbonate solution, and 100 ml of saturated salt solution. It was dried over sodium sulfate, the pentane was removed using a rotary evaporator, and the residue was distilled, giving 18.0 g (98%) of the ketone, bp 73–76° (0.2 mm).

Anal. Calcd for C₈H₁₀Cl₂O: C, 49.8; H, 5.2; Cl, 36.7. Found: C, 49.7, 49.9; H, 5.4, 5.4; Cl, 36.6, 36.7.

***trans*-2,3-Dichlorobicyclo[2.1.1]hexyl *endo*-5-Acetate.**—A solution of trifluoroacetic acid in methylene chloride was prepared from 2.8 ml of 90% hydrogen peroxide, 100 ml of methylene chloride, and 20.0 g of trifluoroacetic anhydride. To the solution was added 0.8 ml of trifluoroacetic acid and 9.1 g (47 mmol) of

(23) W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

methyl *trans*-2,3-dichlorobicyclo[2.1.1]hexyl-*endo*-5 ketone in 20 ml of methylene chloride. The solution was stirred for 1 hr at 0° and 24 hr at room temperature. It was poured into 100 g of ice water, the mixture was shaken vigorously, and the methylene chloride layer was separated. After the mixture was washed with 100 ml of 5% sodium carbonate solution and 100 ml of saturated salt solution and dried over magnesium sulfate, distillation gave 8.2 g (83%) of *trans*-2,3-dichlorobicyclo[2.1.1]hexyl-*endo*-5-acetate, bp 60–65° (0.1 mm). Vpc analysis indicated 80% purity, with 10% of methyl *trans*-2,3-dichlorobicyclo[2.1.1]hexane-*endo*-5-carboxylate and 10% of unidentified impurities. An analytical sample was collected by vpc.

Anal. Calcd for C₈H₁₀Cl₂O₂: C, 46.0; H, 4.8; Cl, 33.9. Found: C, 45.8, 45.7; H, 4.8, 4.8; Cl, 34.0, 34.0.

Attempted Dehalogenation of *trans*-2,3-Dichlorobicyclo[2.1.1]hexyl-*endo*-5-Acetate.—The dehalogenation with magnesium amalgam as described above was carried out for 7 days. The only products formed were methyl bicyclo[2.1.1]hexene-*endo*-5-carboxylate (formed from the 10% dichloro ester impurity) and benzene. The dehalogenation with sodium phenanthrene also was carried out as described above. The product was separated by vpc (10 ft × 0.375 in. 5% Carbowax 20M at 115°) into four components with retention times of 2, 6, 7.5, and 10 min. The first component appeared to be 1,2-di(Δ³-cyclopentenyl)ethane (10%). The second and third components were identified as *exo*-bicyclo[3.1.0]hex-3-en-2-ol (70%) (identified by hydrogenation to the known *exo*-bicyclo[3.1.0]hexanol-2)²⁴ and Δ³-cyclopentenylmethanol (10%). The fourth component (10%) appeared to be a mixture and was not identified.

***trans*-2,3-Dichlorobicyclo[2.1.1]hexan-*endo*-5-ol.**—An ether solution of methyl lithium was prepared from 2.0 g of lithium, 150 ml of anhydrous ether, and methyl bromide. A solution of 5.0 g (24 mmol) of *trans*-2,3-dichlorobicyclo[2.1.1]hexyl-*endo*-5-acetate (80% pure) in 75 ml of ether was cooled in an ice-salt bath and 72 ml (1.5 equiv) of the methyl lithium solution was added over a period of 10 min with stirring. After stirring for an additional 5 min, the solution was added dropwise to a rapidly stirred mixture of 100 ml of saturated ammonium chloride solution and 100 ml of chipped ice. The ether layer was washed twice with 100 ml of water, and twice with saturated salt solution. After the solution was dried over magnesium sulfate, the solvent was removed using a rotary evaporator, giving 4.5 g of a semi-solid. The residue was dissolved in 10 ml of carbon tetrachloride. Cooling afforded 1.5 g (37%) of long white needles. The filtrate contained an additional 30% of the alcohol. After recrystallization from hexane-cyclohexane it had mp 88.8–90.6°.

Anal. Calcd for C₈H₈Cl₂O: C, 43.1; H, 4.8; Cl, 42.5. Found: C, 43.0, 43.1; H, 5.2, 5.2; Cl, 42.4, 42.5.

(24) E. J. Corey and R. L. Dawson, *J. Amer. Chem. Soc.*, **85**, 1782 (1963).

Reduction of *trans*-2,3-Dichlorobicyclo[2.1.1]hexyl-*endo*-5-Acetate with Lithium Aluminum Hydride.—A solution of 0.5 g of *trans*-2,3-dichlorobicyclo[2.1.1]hexyl-*endo*-5-acetate (80% pure) in 10 ml of ether was added to 200 mg of lithium aluminum hydride in 30 ml of ether. After the usual work-up, the residue (0.2 g, 50%) was analyzed by vpc (10 ft × 0.375 in. 5% Carbowax 20M at 165°) and found to contain four components with retention times of 14, 16, 30, and 35 min. The first component (45%) was *trans*-2,3-dichlorobicyclo[2.1.1]hexan-*endo*-5-ol. The second (17%) was *trans*-3-chloro-*cis*-2-chloro-*trans*-4-hydroxybicyclo[3.1.0]hexane, and the third (15%) was *trans*-2,3-dichlorobicyclo[2.1.1]hexane-*endo*-5-methanol (from the methyl ester impurity). The fourth component (20%) was not identified.

Hydrolysis of *trans*-2,3-Dichlorobicyclo[2.1.1]hexyl-*endo*-5-Acetate.—A mixture of 1.0 g of the acetate, 10 ml of 1 *N* sodium hydroxide solution, and 20 ml of ether was stirred at room temperature for 8 hr. The ether layer was washed with saturated salt solution and dried over magnesium sulfate. Removal of the solvent using a rotary evaporator gave 0.5 g of a yellow oil. It was separated into five components with retention times of 5, 10, 13, 16, and 34 min by vpc. The ratios were 2:5:2:2:1. The major component was unchanged starting material. The first component appeared to be 2-chloro-*trans*-4-hydroxybicyclo[3.1.0]hex-2-ene. The third component was a 1:1 mixture of two compounds, one of which was methyl *trans*-2,3-dichlorobicyclo[2.1.1]hexane-*endo*-5-carboxylate (present in the reactant). The fourth was *cis*-2-chloro-*trans*-3-chloro-*trans*-4-hydroxybicyclo[3.1.0]hexane. The fifth was identical with the last component from the lithium aluminum hydride reduction.

Attempted Dehalogenation of *trans*-2,3-Dichlorobicyclo[2.1.1]hexan-*endo*-5-ol.—The reaction of 1.0 g of the alcohol with magnesium amalgam formed from 1.5 g of magnesium and 150 g of mercury was carried out as described above. Vpc analysis of the product (10 ft × 0.375 in. 5% Carbowax 20M at 120°) showed four components with retention times of 5, 6, 7.5, and 8.5 min. The major component (8.5 min, 85%) was identified as Δ³-cyclopentenylmethanol, and the third component was found to be Δ³-cyclopentenylmethanol. The remaining components were not identified because of their low concentration.

The reaction of 0.5 g of the alcohol with sodium phenanthrene in dimethyl ether was carried out using the procedure described above. The residue was analyzed by nmr and none of the desired olefinic alcohol was found. Vpc analysis was not successful because of the apparent thermal instability of the product.

Registry No.—*exo*-7, 35672-74-3; 8, 35672-75-4; 9, 823-71-2; 10, 35672-77-6; 10 monotosylhydrazone, 35655-59-5; 11, 35672-78-7; 20, 35672-79-8.

The Structures and Syntheses of Two Dihydropyridines Isolated from California Petroleum¹

S. A. MONTI,* ROBERT R. SCHMIDT, III, B. A. SHOULDERS, AND H. L. LOCHTE

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712

Received June 8, 1972

The structures of two nitrogen bases isolated from California petroleum have been assigned as *trans*-5,7-dimethyl-6,7-dihydro-5*H*-1-pyridine and 5,7,7-trimethyl-6,7-dihydro-5*H*-1-pyridine on the basis of spectral and synthetic studies. The *cis*-5,7-dimethyl and the 5,5,7-trimethyl analogs were prepared also. An improved synthesis of the 1-pyridone nucleus is described. The nmr spectra of various 6,7-dihydro-5*H*-1-pyridines are presented.

The occurrence of nitrogen bases as minor constituents of petroleum has led to numerous studies on the nature of these substances.² In general these bases are simple alkyl derivatives of pyridine, quinoline,

and related benzo analogs, although a few more complex compounds have been identified.^{2,3}

We wish to report the structure elucidations and syntheses of two new bases isolated from California

(1) Financial support of this research by the Robert A. Welch Foundation is gratefully acknowledged.

(2) (a) H. L. Lochte and E. R. Littman, "The Petroleum Acids and Bases," Chemical Publishing Co., New York, N. Y., 1955; (b) L. R. Snyder, *Accounts Chem. Res.*, **3**, 290 (1970).

(3) (a) L. R. Snyder, *Anal. Chem.*, **41**, 1084 (1969); (b) L. R. Snyder and B. E. Buell, *ibid.*, **40**, 1295 (1968); (c) E. J. Buell, *ibid.*, **39**, 756 (1967); (d) D. K. Albert, *ibid.*, **39**, 1113 (1967); (e) H. V. Drushel and A. J. Sommers, *ibid.*, **38**, 19 (1966); D. R. Latham and W. E. Haines, *ibid.*, **37**, 54 (1965).