acetone. The combined organic layers were distilled to remove solvent. The residue was distilled through a short Vigreux column to give 370 g, 2.76 mol (90%), of 5,6-dihydro-*endo*-dicyclopentadiene (**3**), bp 178–180°, mp 48–50°. Recrystallization from methanol gave mp 50° (lit.[27] mp 48.5–50°); nmr (CCl_4, TMS) δ 1.25 (s, 3.8 H), 1.45 (s, 2.2 H), 2.0–3.2 (m, broad, 6.2 H), 5.70 (s, broad, 2.0 H). Product was free from starting material by glpc.

(27) K. Alder and G. Stein, *Justus Liebigs Ann., Chem.*, **485**, 241 (1931).

Registry No.—Nickelous acetate, 373-02-4; sodium borohydride, 16940-66-2.

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Studies on Heterocage Compounds. V.[1] Reaction of 5-Hydroxymethyl-2-norbornene with Dihalocarbene. Novel Synthesis of Some Oxa-Modified Adamantane Analogs

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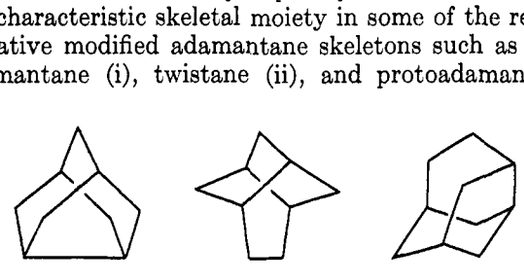
Reaction of *endo*-5-hydroxymethyl-2-norbornene (**1**) with dichloro- and dibromocarbene afforded oxahomobrendene derivatives, 3-chloro- (**2**) and 3-bromo-5-oxatricyclo[5.2.1.$0^{4,8}$]dec-2-ene (**10**), in good yields. Catalytic hydrogenation of **2** and **10** gave 5-oxahomobrendane (**6**). The Birch reduction of **2** afforded *endo*-6-hydroxymethylbicyclo[3.2.1]oct-2-ene (**7**), which was shown to be an excellent precursor to 5-oxaprotoadamantane (**12**) and its 10-acetoxy derivative (**13**). The mechanism for the reaction of **1** with dihalocarbene was discussed from the product distributions under various conditions.

Much attention has been paid recently to adamantane and its related cage compounds since the discovery of an efficient synthetic route to the adamantyl ring system by Schleyer and Donaldson, and the subsequent findings of the biological activities of a number of compounds with these ring systems.[2] However, studies on the heteroanalogs of the related cage compounds seem to be not extensively investigated compared to the carbocyclic analogs; this might be due to the lack of a very efficient synthetic route to heteroanalogs such as carbonium ion rearrangements.[3] In a continuation of our studies on heterocage compounds,[4] this paper describes a novel and facile synthetic route to 5-oxahomobrendane and 5-oxaprotoadamantane.

endo-6-Substituted bicyclo[3.2.1]octane is involved as the characteristic skeletal moiety in some of the representative modified adamantane skeletons such as noradamantane (i), twistane (ii), and protoadamantane (iii).



i ii iii

On the other hand, dihalocarbene addition to norbornene is known to afford bicyclo[3.2.1]octane derivatives.[5] Furthermore, dihalocarbene in a surfactant-catalyzed emulsion has been found recently to react with substrates very effectively.[6-8] Taking into consideration these facts, we employed readily accessible *endo*-5-hydroxymethyl-2-norbornene (**1**) as one of the most promising starting materials for synthesis of some oxa-modified adamantane analogs and examined the reactions of **1** with dihalocarbene.

Results and Discussion

Reaction of *endo*-5-Hydroxymethyl-2-norbornene (1) with Dichlorocarbene.—Dichlorocarbene addition to **1**[9] in 50% aqueous sodium hydroxide–benzene emulsion catalyzed with benzyltriethylammonium chloride at 20° afforded a mixture of 3-chloro-5-oxatricyclo[5.2.1.$0^{4,8}$]dec-2-ene (**2**), 3,3,6-trichlorotricyclo[3.3.1.$0^{2,4}$]nonane (**3**), 3,4,6-trichlorobicyclo[3.3.1]non-2-ene (**4**), and 3,3,7,8-tetrachlorotricyclo[4.3.1.$0^{2,4}$]dec-8-ene (**5**) (Table I, Scheme I). Both **3** and **5** were isolated by chromatography on basic alumina in 8.4 and 3.2% yields, respectively. Oily products **2** and **4** were purified on preparative glpc. Structural assignment of these products was based on the analytical and physical data, and some chemical conversions. The major product **2** had a formula $C_9H_{11}OCl$ from analysis and characteristic mass spectrum, *m/e* 170 (M^+) and 172 (M + 2) in 3:1 ratio. In the nmr ($CDCl_3$) spectrum, **2** had signals at τ 3.87 (d, 1, $J_{1,2}$ = 7.5 Hz, H_2), 5.58 (d, 1, $J_{4,8}$ = 6.5 Hz, H_4), 5.89 (t, 1, $J_{6,6}$ = $J_{6,7}$ = 8.8 Hz,

(1) Part IV of this series: T. Sasaki, S. Eguchi, T. Kiriyama, and Y. Sakito, *J. Org. Chem.*, **38**, 1648 (1973).

(2) For recent reviews, see (a) R. D. Bingham and P. v. R. Schleyer, "Chemistry of Adamantane," Springer-Verlag, New York, New York, N. Y., 1971; (b) P. v. R. Schleyer, *Fortschr. Chem. Forsch.*, **18**, 1 (1971); (c) Z. Weidenhoffer and S. Hala, *Sb. Vys. Sk. Chem.-Technol. Praze, Technol. Paliv*, **22**, 5 (1971).

(3) For a recent review on heteroadamantane, see G. Gelbard, *Ann. Chim. (Paris)*, 331 (1969).

(4) For example, see (a) T. Sasaki, S. Eguchi, and T. Kiriyama, *J. Amer. Chem. Soc.*, **91**, 212 (1969); (b) T. Sasaki, S. Eguchi, and T. Kiriyama, *Tetrahedron*, **27**, 893 (1971).

(5) C. W. Jefford, S. Mahajan, J. Weslyn, and B. Waegell, *J. Amer. Chem. Soc.*, **87**, 2183 (1965), and references cited therein.

(6) For addition reactions of carbene to olefin, see (a) M. Makosza and M. Warzyniez, *Tetrahedron Lett.*, 4659 (1969); (b) M. Makosza and E. Biakecka, *ibid.*, 4517 (1971).

(7) (a) For insertion reaction of dihalocarbene, see I. Tabushi, Z. Yoshida, and N. Takahashi, *J. Amer. Chem. Soc.*, **92**, 6670 (1970); (b) for reaction of alcohol with dichlorocarbene, see I. Tabushi, Z. Yoshida, and N. Takahashi, *ibid.*, **93**, 1820 (1971).

(8) For the reaction site and the reaction mechanism, see (a) C. M. Starks, *J. Amer. Chem. Soc.*, **93**, 195 (1971); (b) G. C. Joshi, N. Singh, and L. M. Pande, *Tetrahedron Lett.*, 1461 (1972); (c) A. W. Herriott and D. Picker, *ibid.*, 4521 (1972).

(9) An exo–endo mixture (1:4) was used as a practical starting material because a 1:19 mixture gave a similar result (see Table I).

SCHEME I

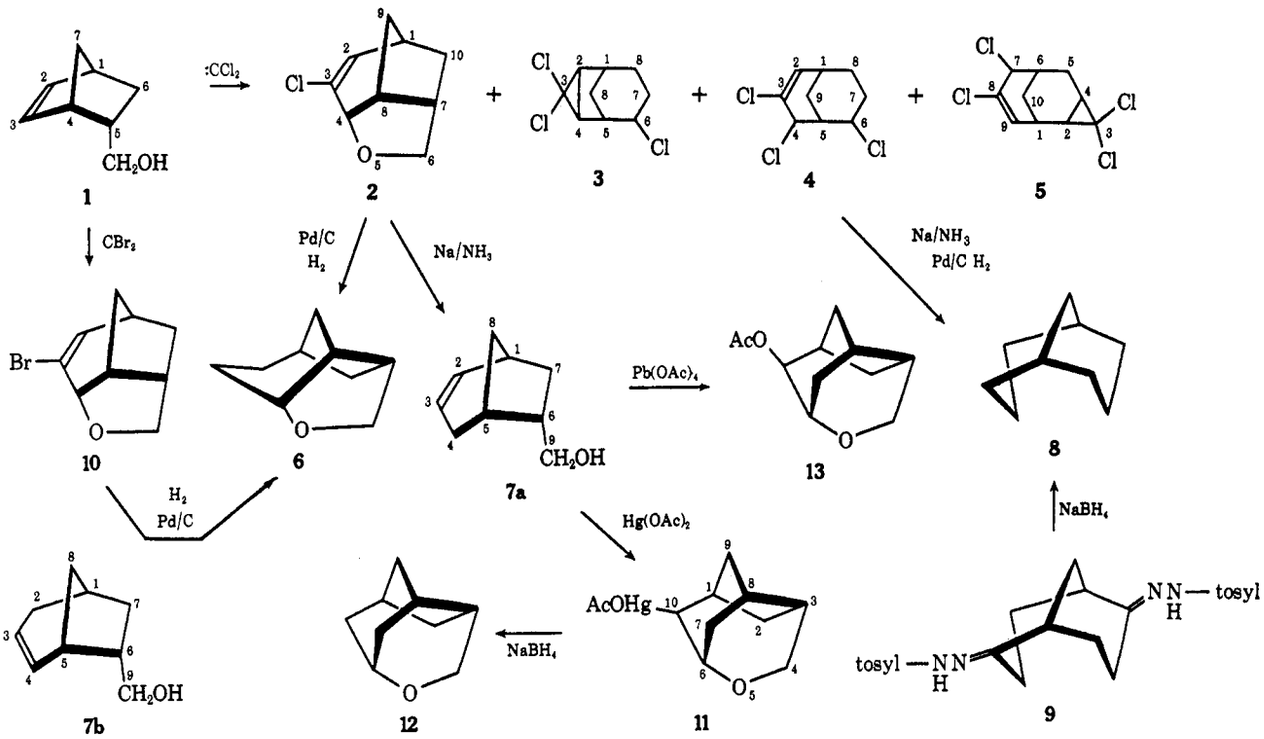


TABLE I

PRODUCT DISTRIBUTION RATIO AT 20°

Alkali metal	Total yield, %	Relative product ratio (on glpc), % 2	3	4	5	Unidentified
NaOH	40[a]	62	21	6	8	Trace
KOH	80[a]	81	9	6	4	Trace
KOH	*b*	67	15	14	4	Trace
KOH	*c*	19	7	26	5	43

[a] An exo–endo mixture (1:4) was used in 50-mmol scale; see ref 9. [b] An exo–endo mixture (1:19) was used in 1-mmol scale. [c] An exo–endo mixture (15:6) was used in 1-mmol scale.

H_{6x}), 6.68 (d of d, 1, $J_{6,6}$ = 8.8, $J_{6,7}$ = 3.8 Hz, H_{6n}), 7.00–7.70 (m, 3, H_1, H_7, and H_8), and 7.83–8.90 (m, 4, 2 H_9 and 2 H_{10}). The appearance of only one vinyl proton signal as well as an ir (neat) absorption at 1635 cm^{-1} supported the assigned structure. The coupling constants of H_2, H_4, H_{6x}, and H_{6n} were in good accordance with those predicted from the Karplus equation[10] and dihedral angles on a Dreiding stereomodel. The observed values were inconsistent with the predicted coupling constants for another possible structure of 3-chloro-5-oxatricyclo[5.3.0.$0^{4,9}$]dec-2-ene. Catalytic hydrogenation (Pd/C) of **2** in the presence of sodium hydroxide afforded 5-oxatricyclo[5.2.1.$0^{4,8}$]decane (**6**) (5-oxahomobrendane)[11] in 74% yield, which had a mass spectral molecular ion peak at *m/e* 138 (M^+), and nmr signals at τ 5.87 (d, 1, $J_{4,8}$ = 7.5 Hz, H_4), 6.41 (s with small split, 2, 2 H_6), 7.50 (m, 2, H_7 and H_8), and 7.8–9.1 (m, 9, other protons). The Birch reduction of **2** with sodium metal in liquid ammonia afforded *endo*-6-hydroxymethylbicyclo[3.2.1]oct-2-ene (**7a**) in 89% yield, which revealed ir (neat) absorptions at 3400 and 1638 cm^{-1} and a molecular ion peak at *m/e* 138 in the mass spectrum. In the nmr ($CDCl_3$) spectrum, **7a** had signals at τ 4.23 and 4.68 (m, each 1, H_3 and H_2), 6.52 (d, 2, J = 6.2 Hz, CH_2OH), 6.98 (s, 1, OH, disappeared on shaking with D_2O), and 7.40–9.33 (m, 9, other ring protons). The position of the double bond in **7a** was supported by the similarity of the relative europium shift values obtained for H_2 and H_3 (Table II): the *S* values

TABLE II

EUROPIUM SHIFT VALUES OF **7** IN $CDCl_3$

Obsd τ	Obsd *S*	Obsd S/S_{H_9}	Calcd **7a** S/S_{H_9}	Calcd **7b** S/S_{H_9}
4.68	5.2	0.297	0.231 (H_2)	0.247 (H_3)
4.23	5.3	0.303	0.298 (H_3)	0.458 (H_4)
6.52 (H_9)	17.5			

and their ratios to that of H_9 were quite close for both vinyl protons, indicating that the distances between these hydrogens and the complexed europium atom are similar. A study on a Dreiding stereomodel revealed clearly that the assigned structure **7a** is favored over another possible structure **7b**; the estimated relative shift values of the vinyl protons against H_9 by using Cockerill and Rackham's method are also very close for **7a** but not for **7b**.[12,13] All of these conversions of **2** and transannular cyclization of **7a** described below supported the assigned structure of **2**.

The mass spectrum of the second product **3** showed characteristic ion peaks due to the presence of three chlorine atoms at *m/e* (rel intensity) 224 (100), 226 (96), 228 (36), and 230 (4), and analysis indicated a formula $C_9H_{11}Cl_3$. In the nmr spectrum, a multiplet at τ 5.90 (H_6) and a broad singlet at τ 7.40 (H_5), as well as a multiplet at τ 7.55–9.30 (9 H, other protons), were observed but no vinyl proton signals. Taking into consideration

(10) M. J. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).
(11) We prefer this trivial name for **6** in this paper.
(12) A. F. Cockerill and D. M. Rackham, *Tetrahedron Lett.*, 5149 (1970).
(13) For more detailed discussion on paramagnetic shift reagents, see J. K. M. Sanders, S. W. Hanson, and D. H. Williams, *J. Amer. Chem. Soc.*, **94**, 5325 (1972), and references cited therein.

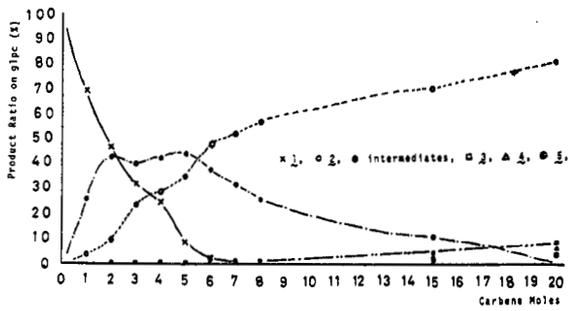


Figure 1.—Change of product distribution by molar ratio of carbene in 50% aqueous KOH–benzene emulsion at 20°.

that 2 mol of dichlorocarbene were trapped by both olefin and hydroxy group in **1**, we assigned **3** as 3,3,6-trichlorotricyclo[3.3.1.$0^{2,4}$]nonane.[14]

Compound **4** was an isomer of **3** from analysis and mass spectrum, but an ir absorption at 1640 cm^{-1} and nmr signals at τ 3.94 and 4.14 for one proton (d, J = 7.8 Hz) suggested the presence of an olefinic moiety in **4**.[15] The Birch reduction of **4**, followed by catalytic hydrogenation (Pd/C) afforded known bicyclo[3.3.1]-nonane (**8**).[16] Hence, **4** was determined as 3,4,6-trichlorobicyclo[3.3.1]non-2-ene, a doubly ring expanded product.

Compound **5** had a formula $C_{10}H_{10}Cl$ from analysis and characteristic mass spectral ion peaks, m/e (rel intensity) 270 (100), 272 (145), 274 (70), 276 (18), 278 (1). The presence of an olefinic moiety was supported by an ir (KBr) absorption at 1641 cm^{-1} and nmr signals at τ 3.85 (d, 1, $J_{1,9}$ = 6.5 Hz, H_9) and 5.82 (s, 1, H_7), which allowed us to assign **5** as 3,3,7,8-tetrachlorotricyclo[4.3.1.$0^{2,4}$]dec-8-ene.

The Carbene Addition Reactions under Various Conditions and Reaction Mechanisms Thereof.—A change of alkali metal from sodium to potassium in aqueous medium improved the overall yield of the adducts and also the relative yield of **2**. Dichlorocarbene generated in the emulsion of 50% aqueous potassium hydroxide and benzene afforded 64.8% of **2**, 7.2% of **3**, 4.8% of **4**, and 3.2% of **5** (Table I). A large excess amount of dichlorocarbene (20-mol excess) was required in order to obtain a better yield of **2**. The reaction with several moles of excess dichlorocarbene resulted only in the formation of the formyl derivative of **1**, which showed a strong ir absorption at 1725 cm^{-1}. The change of the product distribution was followed on glpc by using various molar ratios of dichlorocarbene (Figure 1). The starting material **1** did not disappear for longer reaction time despite the consumption of excess dichlorocarbene; the major product **2** increased very slowly as the intermediate decreased.

The temperature effect on the product distribution was examined at 0, 20, and 60° by using 20 mol of excess dichlorocarbene (Table III). Obviously a considerable temperature effect was observed. Interestingly, the formation of a transannular cyclized product **2** decreased and the formation of the ring-expanded products **3** and **4** increased at 60°. On the basis of these observations, dichlorocarbene addition to **1** could be explained by the reaction mechanism illustrated in Scheme II. The long life of **1** may demonstrate the predominant role of a cycling sequence of the reactions, in which an electrophilic attack of CCl_2 on the hydroxy group affords a dichloromethyl ether b *via* an ylide intermediate a, and b can be hydrolyzed to **1** *via* a formate derivative c. On the other hand, the Wagner–Meerwein rearrangement of b followed by a nucleophilic attack of chloride anion leads to **3** with additional equimolar dichlorocarbene. The major product **2** is formed from dichlorocyclopropane derivatives d and f *via* their thermally allowed disrotatory ring openings (e)[17] accompanied by an intramolecular nucleophilic cyclization. The disrotatory ring opening of dichlorocyclopropyl formate intermediate f can afford **4** and **5** *via* h and i followed by the Wagner–Meerwein rearrangement and nucleophilic substitution or elimination as depicted in Scheme II.

TABLE III
TEMPERATURE EFFECT (REACTIONS OF 20 EXCESS MOL OF CARBENE IN 50% AQUEOUS KOH–BENZENE EMULSION)

	Yield, %			
Temp, °C	2	3	4	5
0	75	10	8	6
20	81	9	6	4
60	24	30	22	6

Reaction of 1 with Dibromocarbene.—Dibromocarbene addition to **1** in the emulsion of 50% aqueous potassium hydroxide–benzene afforded 3-bromo-5-oxatricyclo[5.2.1.$0^{4,8}$]dec-2-ene (**10**) as a major product. Compound **10** had characteristic mass spectral ion peaks at m/e (rel intensity) 214 (M^+, 100) and 216 (M + 2, 98), and an ir (neat) absorption at 1620 cm^{-1}; its nmr spectrum was very similar to that of **2**. Catalytic hydrogenation (Pd/C) in methanolic sodium hydroxide afforded **6** quantitatively, supporting the assigned structure (Scheme I).

Transannular Cyclizations of 7a.—Compound **7a**, obtained from **2** by the Birch reduction, has a suitable alignment of double bond and hydroxy group for a transannular cyclization. Treatment of **7a** with mercuric acetate in a buffered solution of sodium acetate afforded a mercuric acetate derivative **11** which, on reduction with sodium borohydride, gave 5-oxaprotoadamantane (**12**) in 83% yield. The assigned structure was evidenced by analytical and spectral data. The more symmetrical structure of **12** compared to **6** was reflected in the higher melting point of **12** (175–178°) compared with **6** (92–96°) and also in the nmr spectrum ($CDCl_3$) in which bridgehead methine protons such as H_1,H_3, and H_8 appeared at τ 7.25–8.00 and bridge methylene protons such as H_2, H_7, H_9, and H_{10} at τ 8.00–8.90, similar to those of adamantane,[2] while in the nmr spectrum of **6**, methine and methylene protons appeared in more complex patterns as described above.

Treatment of **7a** with lead tetraacetate afforded also a cyclized product **13** which was characterized as 10-acetoxy-5-oxaprotoadamantane on the basis of analysis and spectral data (Scheme I).

In summary, 5-oxahomobrendane (**6**) and 5-oxaprotoadamantane (**12**) were obtained in good yields from

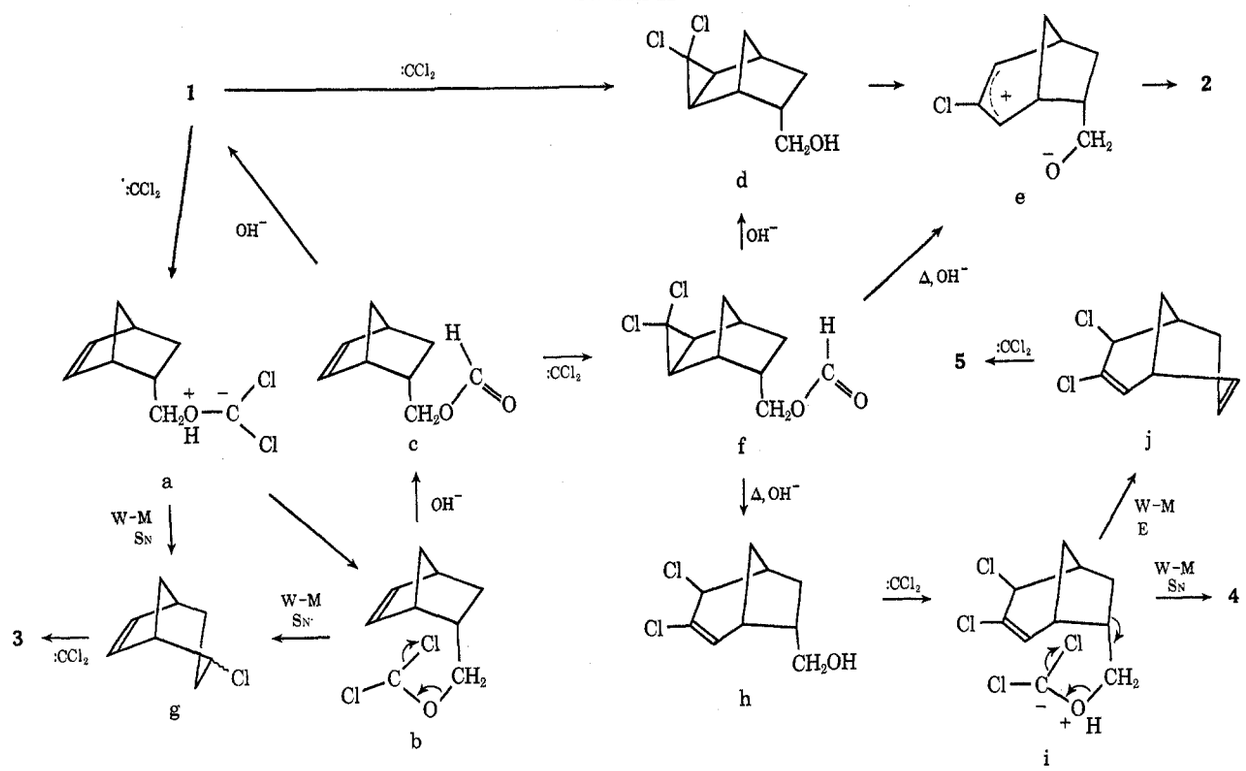
(14) The stereochemistry of dichlorocyclopropane and C_8Cl is uncertain. *Cf.* R. C. De Selms and C. M. Combs, *J. Org. Chem.*, **28**, 2206 (1963).

(15) The appearance of one vinyl proton at τ 3.94 and 4.14 indicates that this product is a 3.5:1 mixture of 6- and 8-chloro isomers. The unsymmetrical peak of **4** on glpc analysis indicates also the presence of isomers.

(16) E. N. Marvell, R. S. Knutson, T. McEwen, D. Sturmer, W. Federici, and K. Salisbury, *J. Org. Chem.*, **35**, 391 (1970).

(17) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

SCHEME II



readily available *endo*-5-hydroxymethyl-2-norbornene (**1**) *via* dihalocarbene addition and successive reductions. This synthetic route might be useful for some other heteromodified adamantane analogs.

Experimental Section[18]

Dichlorocarbene Addition Reaction to *endo*-5-Hydroxymethyl-2-norbornene (1). A.—In a 1-l., three-necked flask fitted with a dropping funnel and a mechanical stirrer, a mixture of 50% (w/w) aqueous sodium hydroxide (500 g), benzene (40 ml), benzyltriethylammonium chloride (500 mg, 2.2 mmol), and **1**[9] (6.2 g, 50 mmol) was vigorously stirred at 20°. While the stirring was continued, chloroform (80 ml, 1.0 mol) was added slowly to the mixture for 10 hr. After the addition was completed, the mixture was stirred for a further 10 hr. The mixture was diluted with water (1.5 l.) and filtered on a Buchner funnel. The filtrate was extracted with chloroform (3 × 50 ml). The combined extracts were dried on anhydrous sodium sulfate and evaporated to give a dark brownish oil (8.45 g). A short-path chromatography on basic alumina eluting with methylene chloride afforded a mixture of products as an oil (3.41 g) which revealed four peaks on glpc analysis (Table I). Further purification on an alumina column eluting with *n*-hexane–benzene gave 3,3,6-trichlorotricyclo[3.3.1.$0^{2,4}$]nonane (**3**) as the first fraction, which crystallized on standing: mp 55–57°; ir (KBr) 800, 790, and 740 cm^{-1}.

Anal. Calcd for $C_9H_{11}Cl_3$: C, 47.93; H, 4.92. Found: C, 47.89; H, 4.96.

The second fraction gave a mixture of oily product and crystalline product, from which **3,3,7,8-tetrachlorotricyclo[4.3.1.$0^{2,4}$]-dec-8-ene** (**5**) was obtained, after washing with methanol, as colorless crystals: mp 157–159°; ir (KBr) 3050, 1641, 784, 768, and 716 cm^{-1}; nmr ($CDCl_3$) τ 3.85 (d, 1, H_9), 5.82 (s, 1, H_7), 7.12 (m, 1, H_1), and 7.50–9.0 (m, 7, other protons).

(18) Ir spectra were recorded on a JASCO IRA-1 grating infrared spectrophotometer. Nmr spectra were taken with a JEOL-C-60HL spectrometer using TMS as the internal standard at 60 MHz, and mass spectra with a JEOL-01SG spectrometer at 75 eV. Melting points were determined on a Yanagimoto hot-stage type melting point apparatus and are corrected. Microanalyses were performed with a Perkin-Elmer 240 elemental analyzer. Glpc analyses were performed with a NEVA gas chromatograph Model 1400 and preparative glpc with a Varian Aerograph Model 700.

Anal. Calcd for $C_{10}H_{10}Cl_4$: C, 44.16; H, 3.70. Found C, 44.20; H, 3.64.

The third fraction gave **3-chloro-5-oxatricyclo[5.2.1.$0^{4,8}$]dec-2-ene** (**2**). An analytical sample was purified by preparative glpc (30% silicone SE-30 on 45/60 mesh Chromosorb W at 180°): $n^{19.0}$D 1.5366; ir (neat) 1635, 755, and 738 cm^{-1}.

Anal. Calcd for $C_9H_{11}OCl$: C, 63.35; H, 6.50. Found: C, 63.36; H, 6.49.

Purification of the oily portion of the second fraction by preparative glpc afforded **3,4,6-trichlorobicyclo[3.3.1]non-2-ene** (**4**) as a colorless oil: $n^{22.5}$D 1.5574; ir (neat) 1640, 770, 760, and 745 cm^{-1}; mass spectrum *m/e* (rel intensity) 224 (M^+, 100), 226 (M + 2, 95), 228 (M + 4, 30), and 230 (M + 6, 5); nmr ($CDCl_3$) τ 3.94 and 4.14 (each d, 1, J = 7.8 Hz, ratio 3.5:1, C=CH), 5.68–6.22 (m, 2, H_4 and H_8), 7.00–7.50 (m, 2, H_1 and H_5), and 7.50–8.85 (m, 6, remaining protons).

Anal. Calcd for $C_9H_{11}Cl_3$: C, 47.93; H, 4.92. Found: C, 47.84; H, 4.91.

B.—Dichlorocarbene addition reaction in 50% potassium hydroxide was carried out similarly as above. Purification of crude product (6.83 g) gave **2–5** (Table I).

The reaction at 0° was carried out similarly by using a mixture of 50% potassium hydroxide (40 g), *n*-hexane (2.5 ml), benzene (2.5 ml), benzyltriethylammonium chloride (50 mg, 0.22 mmol), and **1** (0.12 g, 1.0 mmol). To the vigorously stirred mixture was added chloroform (2.4 g, 20 mmol) in 2 hr at 0°. The work-up gave 155 mg of crude product which was analyzed on glpc (Table III).

The reaction at 60° was carried out similarly but by using benzene (5 ml) instead of *n*-hexane–benzene in a flask fitted with a reflux condenser. Work-up gave crude product (190 mg) which was analyzed on glpc (Table III).

***endo*-6-Hydroxymethylbicyclo[3.2.1]oct-2-ene** (**7a**).—In a three-necked flask fitted with a sealed mechanical stirrer, a drying tube (soda lime), and a gas inlet was introduced anhydrous liquid ammonia (*ca.* 100 ml) at −78° under nitrogen. Clean metallic sodium (1.5 g, 65 g-atoms) was added into the flask with stirring. To the resulting dark blue solution was added **2** (500 mg, 2.94 mmol) in ethanol (1 ml) dropwise with stirring. After the stirring was continued for 4 hr at −78° and for 1 hr at −40°, ethanol was added at −78° until the color disappeared. The mixture was allowed to warm gradually to room temperature after further addition of ethanol (30 ml). The residual mixture was diluted with water (100 ml) and extracted with chloroform (3 × 50 ml). The combined extracts were dried (Na_2SO_4) and evaporated to

afford **7a** as an oil (360 mg, 89%). An analytical sample was obtained after chromatography on a silica gel column eluting with chloroform as a colorless oil, $n^{20}D$ 1.5163.

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.27; H, 10.15.

5-Oxahomobrendane (6).—Catalytic hydrogenation of **2** (1.70 g, 10.0 mmol) with 5% Pd/C (1.7 g) in 4% (w/v) methanolic sodium hydroxide solution (50 ml) at room temperature and under atmospheric pressure afforded a colorless oil (1.02 g, 74%) after work-up as usual. Sublimation of the oil at 80° gave **6** as colorless crystals: mp 92–96° (sealed tube); ir (KBr) 2925, 1456, 1085, 1056, 1038, and 1017 cm^{-1}.

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.40; H, 10.02.

Conversion of 4 to Bicyclo[3.3.1]nonane (8).—To a mixture of liquid ammonia (50 ml) and sodium metal (1.0 g, 43 g-atoms) was added an ethanol (0.1 ml) solution of **4** (0.30 g, 1.3 mmol). After the mixture was stirred for 8 hr at −78° and ammonia was removed, the work-up afforded a colorless syrup (40 mg) which revealed ir absorption at 1638 cm^{-1} ($CHCl_3$). Catalytic hydrogenation of this syrup with 5% Pd/C (50 mg) in ethanol afforded **8** as a major product on glpc analysis. An authentic sample of **8**[16] prepared from $NaBH_4$ reduction of bicyclo[3.3.1]nonane-2,6-dione bistosylhydrazone (**9**)[19] had the same retention time on two different columns (10% silicone SE-30 on Chromosorb W and 10% Apiezon on Chromosorb W).

3-Bromo-5-oxatricyclo[5.2.1.0^{4,8}]dec-2-ene (10).—To a vigorously stirred mixture of 50% potassium hydroxide (500 g), benzene (30 ml), benzyltriethylammonium chloride (500 mg, 2.2 mmol), and **1** (2.4 g, 20 mmol) was added bromoform (101 g, 0.40 mol) in 10 hr at 20°. After stirring was continued for a further 12 hr, work-up as above gave a dark brownish oil (4.13 g) which was purified on an alumina column eluting with methylene chloride to give an oily mixture (2.25 g) of **10** (relative yield 58%, total yield 31%) and five other minor products (*ca.* 42%) on glpc analysis. Further purification of this oil on an alumina column eluting with *n*-hexane–benzene afforded **10** as a colorless oil (865 mg, 20%): $n^{28.5}D$ 1.5552; ir (neat) 2930, 2855, 1620, 1032, 796, 765, and 692 cm^{-1}; nmr (CCl_4) τ 3.65 (d, 1, $J_{1,2}$ = 7.3 Hz, H_2), 5.53 (d, 1, $J_{4,5}$ = 6.6 Hz, H_4), 5.91 (t, 1, $J_{5,6}$ = $J_{6,7}$ = 8.8 Hz, H_{6x}), 6.70 (d of d, 1, $J_{6,6}$ = 8.8, $J_{6,7}$ = 3.8 Hz, H_{6n}), 7.00–7.72 (m, 3, H_1, H_7, and H_8), and 7.75–8.80 (m, 4, 2 H_9 and 2 H_{10}).

Anal. Calcd for $C_9H_{11}OBr$: C, 50.26; H, 5.15. Found: C, 50.41; H, 5.00.

On catalytic hydrogenation with 5% Pd/C in methanolic sodium hydroxide solution at room temperature and under atmospheric pressure, **10** afforded **6** (97%).

5-Oxaprotoadamantane (12).—To a solution of mercuric acetate (1.152 g, 3.61 mmol) and sodium acetate (295 mg, 0.360 mmol) in water (10 ml) was added a solution of **7a** (414 mg, 3.00 mmol) in methanol (1.5 ml). After the mixture was stirred for 1 hr at room temperature, the mixture was diluted with water (30 ml) and extracted with chloroform (3 × 10 ml). The combined extracts were dried (Na_2SO_4) and evaporated to afford an oily product (**11**) (1.20 g, 100%), which was treated with sodium borohydride (150 mg, 3.95 mmol) in 3.4% aqueous sodium hydroxide (24 ml) for 6 hr at room temperature. Work-up in the usual way afforded **12** as crystals which were sublimed at 120° (25 mm) to give analytically pure **12** (355 mg, 83%): mp 175–178° (sealed tube); ir (KBr) 2925, 1184, and 1092 cm^{-1}.

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.36; H, 10.06.

10-Acetoxy-5-oxaprotoadamantane (13).—A mixture of **7a** (138 mg, 1.00 mmol) and lead tetraacetate (886 mg, 2.00 mmol) in chloroform (40 ml) was refluxed for 1 day. The cooled mixture was washed with 5% aqueous sodium hydroxide (2 × 10 ml) and water (10 ml) successively. The dried (Na_2SO_4) organic layer was evaporated to give **13** as an oil (175 mg, 89%). An analytical sample was obtained by preparative tlc (silica gel, 50% benzene–methylene chloride) as an oil: $n^{23.5}D$ 1.5035; ir (neat) 2940, 1730, 1240, and 1195 cm^{-1}; mass spectrum *m/e* 196 (M^+); nmr ($CDCl_3$) τ 5.24 (m, 1, H_{10}), 5.77–6.47 (m, 3, $2H_4$ and H_6), 7.17–9.06 (m, 9, other ring protons), and 7.95 (s, 3, $COCH_3$).

Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.31; H, 8.23.

Registry No.—*endo*-**1**, 15507-06-9; *exo*-**1**, 13360-81-1; **2**, 39833-55-1; **3**, 39833-56-2; **4**, 39833-57-3; **5**, 39833-58-4; **6**, 39837-56-4; **7a**, 39837-57-5; **10**, 39837-58-6; **11**, 39837-59-7; **12**, 39837-60-0; **13**, 39837-61-1; dichlorocarbene, 1605-72-7; dibromocarbene, 4371-77-1.

(19) H. Musso and U. Biethan, *Chem. Ber.*, **100**, 119 (1967).

Notes

Chemistry of Heterocyclic Compounds. 8. A One-Step Synthesis of 2-Hydroxy-4*H*-quinolizin-4-ones[1]

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In connection with a current project related to construction of heteromacrocycles, we needed large quantities of substituted ethyl 2-pyridylacetates. The simplest preparation of ethyl 2-pyridylacetate is the condensation[2] of 2-picolyllithium with diethyl carbonate under very mild conditions.[3] After prolonged extraction with petroleum ether (bp 30–60°), the major side product, 1,3-di(2-pyridyl)acetone, was recovered in trace amounts, as indicated by analysis of its dipicrate.[2]

Repetition of this procedure is easily accomplished. However, in an initial attempt to isolate increased yields of **1** and **5**, during the work-up procedure the strongly alkaline aqueous solution was neutralized to a pH of 7.5–8 by addition of dilute hydrochloric acid; extraction with chloroform afforded additional quantities of **1** and **5**, as well as the previously undetected 1-carboethoxy-2-hydroxy-3-(2-pyridyl)-4*H*-quinolizin-4-one (**4**). Structural assignment[4] of **4** was based

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(2) N. N. Goldberg, B. M. Perfetti, and R. Levine, *J. Amer. Chem. Soc.*, **75**, 3843 (1953).

(3) Alternate routes are known; see references in ref 2, as well as K. Winterfeld and K. Flick, *Arch. Pharm. (Weinheim)*, 448 (1956), and K. Winterfeld and K. Nonn, *Pharmazie*, **29**, 337 (1965).

(4) The infrared spectral data of related compounds have been previously assigned.