Acknowledgment.—The authors thank Dr. R. G. Cooks for determining the mass spectrum and the National Science Foundation (GP-7818) for support of this research.

Condensation of Cyclic Olefins with Paraformaldehyde and Hydrogen Chloride

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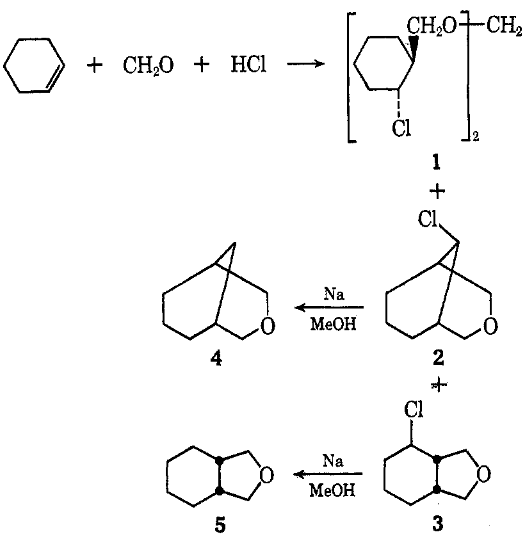
Condensation of cyclohexene with paraformaldehyde and hydrogen chloride at −60 to −70° gave a good yield of a mixture of two bicyclic chlorinated ethers along with a small amount of the formal of *trans*-2-chlorocyclohexanemethanol (**1**). The structure of the principal component (80% of the mixture) was established by chemical degradation, synthesis, and nmr as *trans*-9-chloro-*cis*-3-oxabicyclo[3.3.1]nonane (**2**), and the minor component was identified as *trans*-6-chloro-*cis*-3-oxabicyclo[4.3.0]nonane (**3**). Under similar conditions, cyclopentene gave 2-chlorocyclopentanemethanol (**7**) (60% yield) and a mixture of two isomeric bicyclic chlorinated ethers (32%) in a ratio of 2:1. These were separated and identified as 6-chloro-*cis*-3-oxabicyclo[3.3.0]octane (**8**) and 8-chloro-3-oxabicyclo[3.2.1]octane (**9**), respectively. Calculated nmr spectra were obtained which were useful in establishing the stereochemistry and nature of ring fusion in both the 3-oxabicyclononanes and 3-oxabicyclooctanes.

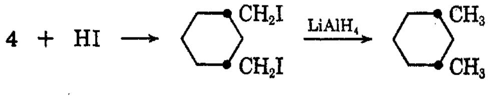
A number of investigators have studied the sulfuric acid catalyzed reaction of cyclohexene and formaldehyde in acetic acid solution.[1-3] The reaction leads to a complex mixture of products, but the major constituents are derivatives of *trans*-2-hydroxymethylcyclohexanol and none of the *cis* isomer is found. Blomquist[1] identified *trans*-9-hydroxy-*cis*-3-oxabicyclo[3.3.1]nonane as a minor by-product and Dolby[3] later isolated and identified small quantities of *trans*-6-hydroxy-*cis*-3-oxabicyclo[4.3.0]nonane from a similar reaction. In a related study of the reaction of cyclohexene, paraformaldehyde, and hydrochloric acid, Volynskii[4] identified the formal of *trans*-2-chlorocyclohexanemethanol (**1**) as the major product and found 5% each of *trans*-9-chloro-*cis*-3-oxabicyclo[3.3.1]nonane (**2**) and *trans*-6-chloro-*cis*-3-oxabicyclo[4.3.0]nonane (**3**).[5] The stereochemistry of **2** and **3** was elucidated by conversion to the known hydroxy compounds.

In previous articles[6-8] we described a novel modification of the Prins reaction in which various olefin types were treated with paraformaldehyde and hydrogen halides at low temperatures. Extension of this modified Prins reaction to include the condensation of cyclohexene and cyclopentene with paraformaldehyde is considered in this report. As a number of bicyclic compounds became available during the course of this work, an opportunity was afforded to consider some aspects of theoretical calculations of the nmr spectra of these bicyclic systems.

Introduction of hydrogen chloride into a paraformaldehyde–cyclohexene mixture (1.5:1 mol ratio) in methylene chloride at −60 to −70° gave, in addition to a substantial quantity of cyclohexyl chloride and a small amount of **1**, 65–75% yields of a mixture of two bicyclic chlorinated ethers. The structure of the principal component (80% of the mixture) was established by elemental analysis, chemical degradation, and its nmr spectrum as *trans*-9-chloro-*cis*-3-oxabicyclo[3.3.1]nonane (**2**) and the minor component was assigned the structure of *trans*-6-chloro-*cis*-3-oxabicyclo[4.3.0]nonane (**3**) (Scheme I). The structures of the basic ring systems were established by removal of the chlorine from the mixture of bicyclics with sodium and methanol to give *cis*-3-oxabicyclo[3.3.1]nonane (**4**) and *cis*-3-oxabicyclo[4.3.0]nonane (**5**) in the same 4:1 ratio. These were separated by preparative glpc; elemental analyses, mass spectra, and nmr spectra were in complete agreement with the assigned structures. Chemical confirmation of **4** as *cis*-3-oxabicyclo[3.3.1]nonane

SCHEME I





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[1] A. T. Blomquist and J. Wolinsky, *J. Amer. Chem. Soc.*, **79**, 6025 (1957).

[2] E. Smissman and R. A. Mode, *ibid.*, **79**, 3447 (1957).

[3] L. J. Dolby, *J. Org. Chem.*, **25**, 2971 (1962).

[4] N. P. Volynskii, G. D. Gal'pern, and A. B. Urin, *Zh. Org. Khim.*, **2**, 1043 (1966); *Chem. Abstr.*, **65**, 15306 (1966).

[5] In naming **2** as *trans*-9-chloro-*cis*-3-oxabicyclo[3.3.1]nonane, Volynskii[4] differs from earlier investigators by designating the ring fusion as *cis*. We are not aware of any derivatives of *trans*-3-oxabicyclo[3.3.1]nonane; hence it might appear that this is unnecessary. Inspection of molecular models of 3-oxabicyclo[3.3.1]nonane suggests that a *trans* fusion is possible, though strained, and to avoid possible ambiguity we will use the nomenclature of Volynskii.

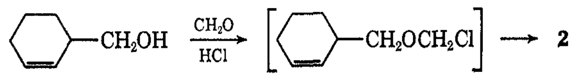
[6] P. R. Stapp, *J. Org. Chem.*, **34**, 479 (1969).

[7] P. R. Stapp, *ibid.*, **34**, 1143 (1969).

[8] P. R. Stapp and D. S. Weinberg, *ibid.*, **34**, 3592 (1969).

was provided by conversion to *cis*-1,3-dimethylcyclohexane *via* cleavage with hydriodic acid and lithium aluminum hydride reduction. Capillary gas chromatography of the product showed that the retention time eliminated all isomers except 1,1-, *cis*-1,3-, and *trans*-1,4-dimethylcyclohexane from consideration; final confirmation as *cis*-1,3-dimethylcyclohexane was furnished by dehydrogenation to *m*-xylene.[9]

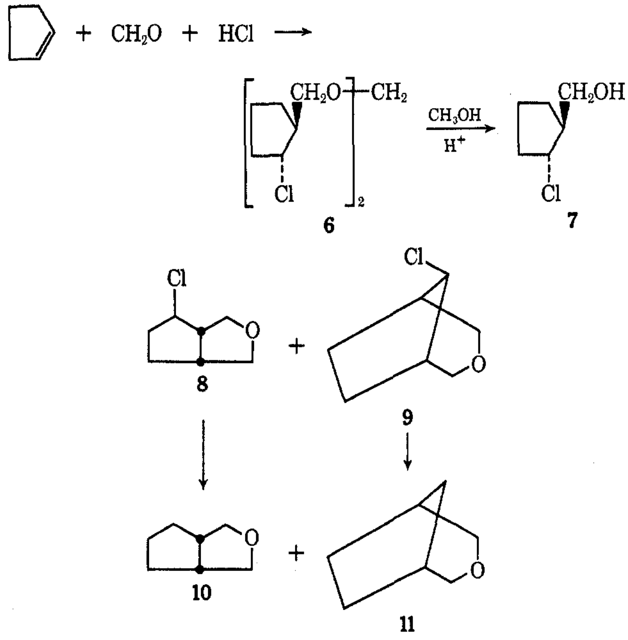
Low-temperature crystallization of the bicyclic chloride fraction from methanol readily gave pure **2** on a preparatively useful scale. Chemical evidence for assignment of the chlorine atom to the unreactive 9 position was supported by its inertness to nucleophilic reagents; **2** was recovered unchanged after a 6-hr treatment with excess potassium hydroxide in refluxing 2-propanol or heating with ammonia (18 mol) at 2000 psig and 200°. Earlier work[6,10] has shown that 4-chlorotetrahydropyrans are produced from homoallylic alcohols by treatment with paraformaldehyde and hydrogen chloride, presumably *via* an intermediate unstable chloromethyl ether. A similar condensation of 2-cyclohexenemethanol[11] gave synthetic **2** identical with that obtained from the cyclohexene reaction.



Pure **3** was obtained by preparative glpc of the enriched mother liquors from crystallization of **2**. Formulation of **3** as the *trans*-6-chloro isomer was based on the mode of formation and the nmr spectrum which showed a chemical shift for the proton α to the chlorine in the region of −235–240 Hz. The chemical shift of the proton α to the chlorine atom in **2** was observed downfield at −265–270 Hz. Since the conformation of the *cis*-3-oxabicyclo[3.3.1]nonane system has been established as chair–chair,[12] it is of interest that the proton chemical shift observed corresponds so closely to the shift of an equatorial hydrogen α to a chlorine atom.[13] A proton equatorial to the cyclohexane ring is expected for the *trans*-9-chloro configuration.

Cyclopentene gave a somewhat different distribution of products than did cyclohexene under the same reaction conditions (Scheme II).

SCHEME II



Only a small quantity of cyclopentyl chloride was formed, and the major product (60% yield) was characterized as the formal of 2-chlorocyclopentanemethanol (**6**) by elemental analysis and the infrared spectrum. Methanolysis gave 2-chlorocyclopentanemethanol (**7**) which yielded a sharply melting 3,5-dinitrobenzoate. Attempts to determine the stereochemistry of both the free alcohol and the ester were inconclusive. The complexity of the nmr spectrum of **7** indicated that a mixture of isomers was present, with the principal constituent comprising an estimated 75–85% of the total. This is in agreement with earlier work[8] which established that 2-butenes condensed with paraformaldehyde and hydrogen chloride with 70–80% stereoselectivity. In view of the well-documented formation of *trans* derivatives from cyclohexene, it appears logical to assign the *trans* configuration to the major component. A mixture of two bicyclic chlorinated ethers was also formed (32% yield) in a ratio of 2:1. These were separated by preparative glpc and assigned the structures 6-chloro-*cis*-3-oxabicyclo-[3.3.0]octane (**8**) and 8-chloro-3-oxabicyclo[3.2.1]octane (**9**) by elemental analysis and their nmr spectra. Reduction of **8** and **9** with sodium and methanol provided, respectively, *cis*-3-oxabicyclo-[3.3.0]octane (**10**) and 3-oxabicyclo[3.2.1]octane (**11**), a crystalline solid. The *cis* fusion in **10** was established by cleavage with hydriodic acid and reduction to *cis*-1,2-dimethylcyclopentane and by comparison with the nmr spectrum of an authentic sample.[14]

The nmr spectra of the bicyclics were uniformly consistent with the proposed structures in terms of chemical shifts and relative areas of the different proton types; however, some distinctive features were noted in the resonances from the methylene protons α to the oxygen atom, hereafter referred to as α methylene resonances. The complexity of these α methylene resonances varied significantly among the various bicyclic ethers; for example, the 3-oxabicyclooctanes gave more complex α methylene spectra when a chemical bond existed directly between bridgehead carbon atoms. A similar condition did not prevail among the 3-oxabicyclononanes, which gave spectra that were deceptively simple. Since the structure of the bicyclics had been reasonably established with the exception of **9** and **11**, which were assigned by analogy, the nmr spectra of the α methylene resonances were then closely examined for criteria that could support the proposed structures and for information that would prove constructive in later analyses.

The complexity of the α methylene resonances in the various bicyclic ethers is undoubtedly a result of so-called virtual coupling;[15] however, such an oversim-

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[9] W. J. Hines and D. E. Smith, *Anal. Chem.*, **36**, 2250 (1964).

[10] J. Colonge and P. Boisde, *Bull. Soc. Chim. Fr.*, **23**, 824 (1956).

[11] A. T. Blomquist, J. Verdol, C. L. Adami, J. Wolinsky, and D. D. Phillips, *J. Amer. Chem. Soc.*, **79**, 4976 (1957).

[12] R. J. Bishop, L. E. Sutton, M. J. T. Robinson, and N. W. J. Pumphrey, *Tetrahedron*, **25**, 1417 (1969).

[13] R. V. Lemieux, R. K. Kullnig, H. J. Bernstein, and W. G. Schneider, *J. Amer. Chem. Soc.*, **80**, 6098 (1958).

[14] L. N. Owen, Imperial College of Science and Technology, personal communication, 1969.

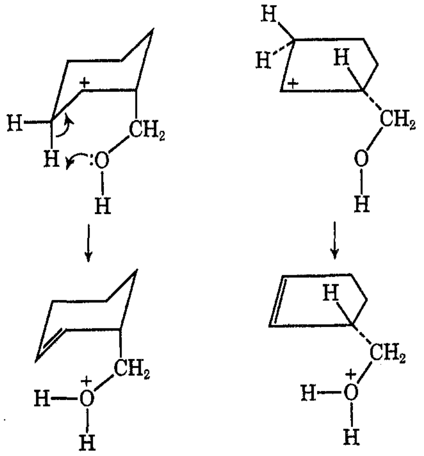
[15] J. I. Musher, and E. J. Corey, *Tetrahedron*, **18**, 791 (1962).

plification without qualification can lead to a loss of information, particularly with regard to the present compounds, which give obvious virtual coupling in only one of two analogous situations. The α methylene multiplets from **2**, **4**, **9**, and **11** can be treated approximately as AB portions of equivalent ABX systems if we choose temporarily to ignore the perturbations introduced from vicinal bridgehead (H_X) coupling with other hydrogen nuclei.[16] The AB portion of an ABX system can be easily recognized by a characteristic set of eight lines;[17] thus the α methylene resonances of **10** are clearly too complex for an ABX approximation, although the analogous compound, **5**, apparently fits neatly into the realm of ABX possibilities with eight distinctly recognizable transitions. Since the possibility exists for substantial vicinal coupling between the bridgehead hydrogens in **5** and 10, the α methylene resonances were considered as AB components of AA'BB'XX' systems. (With zero values for $J_{AA'}$ and $J_{BB'}$ the AA'BB'XX' system reduces to the ABX case when $J_{XX'}$ is also zero.) The nmr spectra of the isomeric pairs of bicyclic ethers **4**, **5**, **10**, and **11** are reproduced in Figures 1 and 2 with expanded α methylene multiplets shown in the insets. Calculated spectra (using computer program NMRIT) for **4** and **11** which were obtained from ABX analyses that adequately represent the observed multiplets are also included. The calculated spectra shown for **5** and **10** were obtained after identifying the eight-line ABX portion of the multiplet and obtaining the ABX parameters. The ABX case was then expanded to an AA'BB'XX' analysis with the introduction of only $J_{XX'}$. A systematic variation of $J_{XX'}$, while holding the remaining parameters constant, permits a determination of the effect of bridgehead coupling on the incipient spectra of the α methylene protons. The effect of such coupling is shown in Figure 3. The calculated spectra for **5** and **10**, included in the insets of Figures 1 and 2, respectively, are the best representations of the observed multiplets. The bridgehead coupling constant, $J_{XX'}$, is in the range 7–10 Hz for **10** and 0–2 Hz for **5**. The valleys between the eight-line spectrum of **5** are somewhat filled suggesting a finite XX' coupling constant. The relatively high bridgehead coupling constant for **10** is in the range generally found for *cis* coupling in five-membered rings.[18] The *trans* bridgehead coupling, by analogy, should be quite small. A 100-HMz spectrum of *trans*-3-oxabicyclo[3.3.0]octane[19] contained an eight-line multiplet with no unusual broadening or splitting. The opposite relationship, found in the bicyclics containing fused cyclohexane rings, is supported by the fact that J_{trans} has been noted to be larger than J_{cis} in six-membered-ring systems.[20] The relatively unobscured eight-line multiplet for **5** is therefore consistent with the structure *cis*-3-oxabicyclo[4.3.0]nonane. Likewise the structure of **10** as *cis*-3-oxabicyclo[3.3.0]octane is strongly supported by the nmr spectrum.

The identification of more than the expected eight lines for an α methylene multiplet can be used to establish the existence of a chemical bond directly between the bridgehead carbon atoms if the possibility of such an effect arising from perturbations from strong vicinal coupling with other nuclei is precluded. An extension of the ABX treatment for **2** and **9** to the ABXCYZ case, which includes all possible vicinal bridgehead coupling constants, gives only a slight splitting of the AB portion (0.01–0.03 Hz) for vicinal coupling constants up to 10 Hz. The splitting observed in **10** must, therefore, result predominantly from vicinal coupling directly between the bridgehead hydrogens. The complexity or broadness of the α methylene multiplets thus offers a means for determining the stereochemistry of ring fusion and the existence of a methylene or higher order bridge in these bicyclic ethers.

The corresponding chloro derivatives **2**, **3**, **8**, and **9** offered additional evidence for the structures of the parent bicyclic ring systems. The α methylene multiplets for **2** and **9** were not so collapsed as those in **4** and **11**, and ABX fits were easily obtained with the same sets of coupling constants calculated from the nmr spectra of the parents. The α methylene spectra for the chloro bicyclics are reproduced in Figure 4. Structurally equivalent sets of α methylene protons are indicated by the proposed structures for bicyclic pairs **2** and **4**, and **9** and **11**. The fact that satisfactory ABX fits were possible with only chemical shift changes supports the existence of equivalent sets of α methylene protons in each of the chlorine derivatives.

Complex α methylene multiplets could be anticipated for **3** and **8** because the α methylene protons are not structurally equivalent and the possibility for strong bridgehead coupling exists in each case. As expected, more than eight lines were observed for the α methylene resonances of **8**; unfortunately, overlap with the multiplet from proton α to the chlorine atom in **3** prevented an exact determination of the numbers of lines. The multiplet was complex in support of the proposed structure, as illustrated in Figure 4.



It has been previously suggested[6] that 4-chlorotetrahydropyrans are produced from 1 olefins, paraformaldehyde, and hydrogen chloride by cyclization of the unstable chloromethyl ether of an intermediate homoallylic alcohol. The proposal that the homoallylic

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(16) A. Alikhan, S. Rodmar, and R. A. Hoffman, *Acta Chem. Scand.*, **21**, 63 (1967).

(17) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York 1959, p 132.

(18) H. A. Sable, W. M. Ritchey, and J. E. Nordlander, *J. Org. Chem.*, **31**, 3771 (1966).

(19) We are indebted to Professor L. N. Owen for furnishing a copy of this spectrum.

(20) Reference 17, p 394.

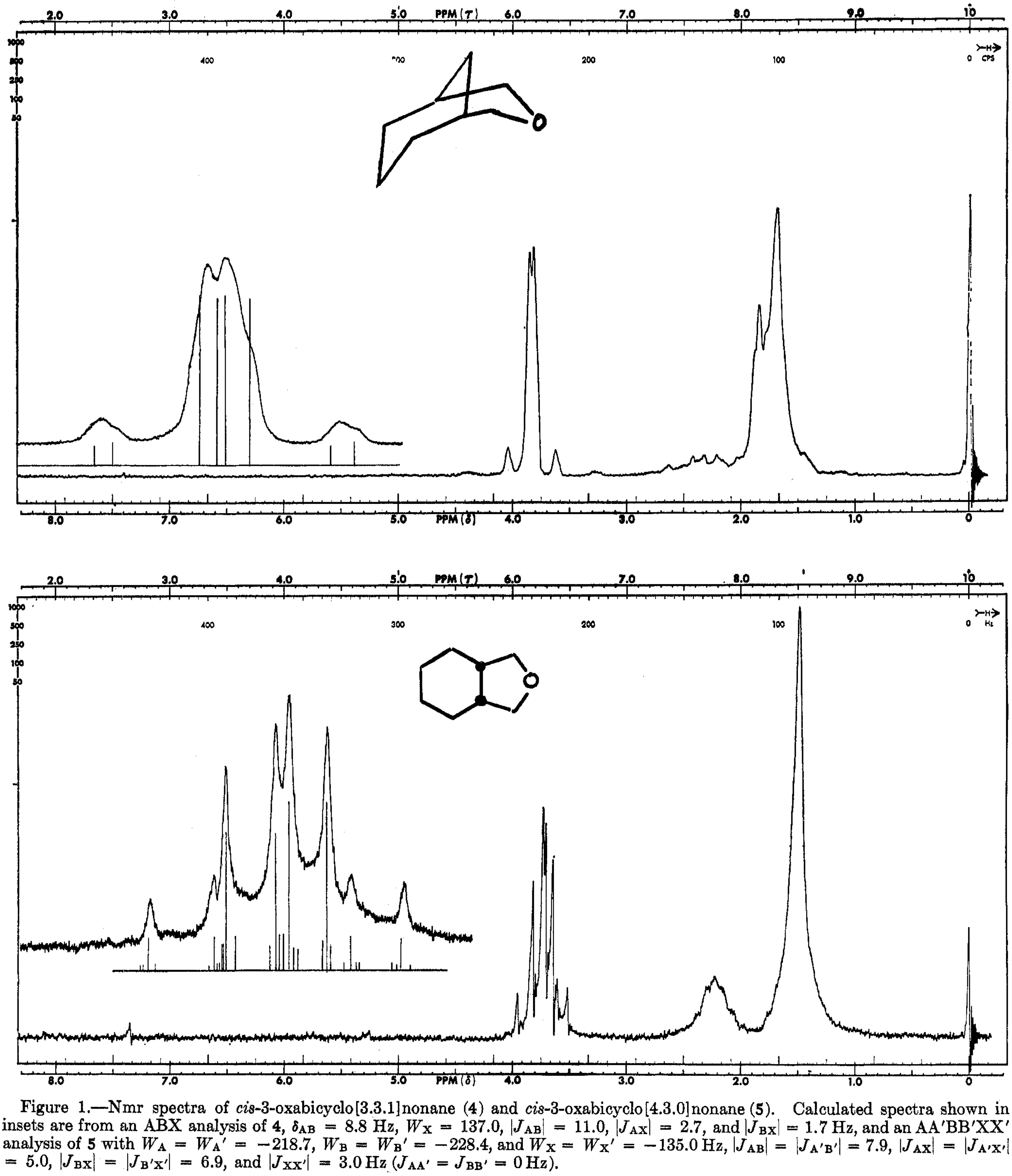

Figure 1.—Nmr spectra of *cis*-3-oxabicyclo[3.3.1]nonane (4) and *cis*-3-oxabicyclo[4.3.0]nonane (5). Calculated spectra shown in insets are from an ABX analysis of 4, $\delta_{AB} = 8.8$ Hz, $W_X = 137.0$, $|J_{AB}| = 11.0$, $|J_{AX}| = 2.7$, and $|J_{BX}| = 1.7$ Hz, and an AA'BB'XX' analysis of 5 with $W_A = W_{A'} = -218.7$, $W_B = W_{B'} = -228.4$, and $W_X = W_{X'} = -135.0$ Hz, $|J_{AB}| = |J_{A'B'}| = 7.9$, $|J_{AX}| = |J_{A'X'}| = 5.0$, $|J_{BX}| = |J_{B'X'}| = 6.9$, and $|J_{XX'}| = 3.0$ Hz ($J_{AA'} = J_{BB'} = 0$ Hz).

alcohol was formed by a cyclic deprotonation of the adduct of the olefin with protonated formaldehyde was supported by isolation of the intermediate under certain conditions. The isomeric 2-butene adducts did not deprotonate readily, and chloride ion capture occurred to give the chloro alcohols as the major products.[8] Consideration of the geometry of the protonated formaldehyde adducts with cyclopentene and cyclohexene suggests that deprotonation to the homoallylic alcohol would be far more facile with cyclohexene; thus, more bicyclic product is expected from cyclohexene, and trapping of the intermediate carbonium ion by chloride would result in preferential production of the chloro alcohol from cyclopentene. The isolation of significant quantities of tetrahydrofuran derivatives, *e.g.*, **3** and **8**, was somewhat unexpected since none was found in the earlier work with 1 olefins. In addition, allyl chloromethyl ethers are known to be very difficult to cyclize.[10] Examination of molecular models of the isomeric pairs of bicyclics qualitatively supports the assumption that the least strained bicyclic system is formed from both cyclohexene and cyclopentene.

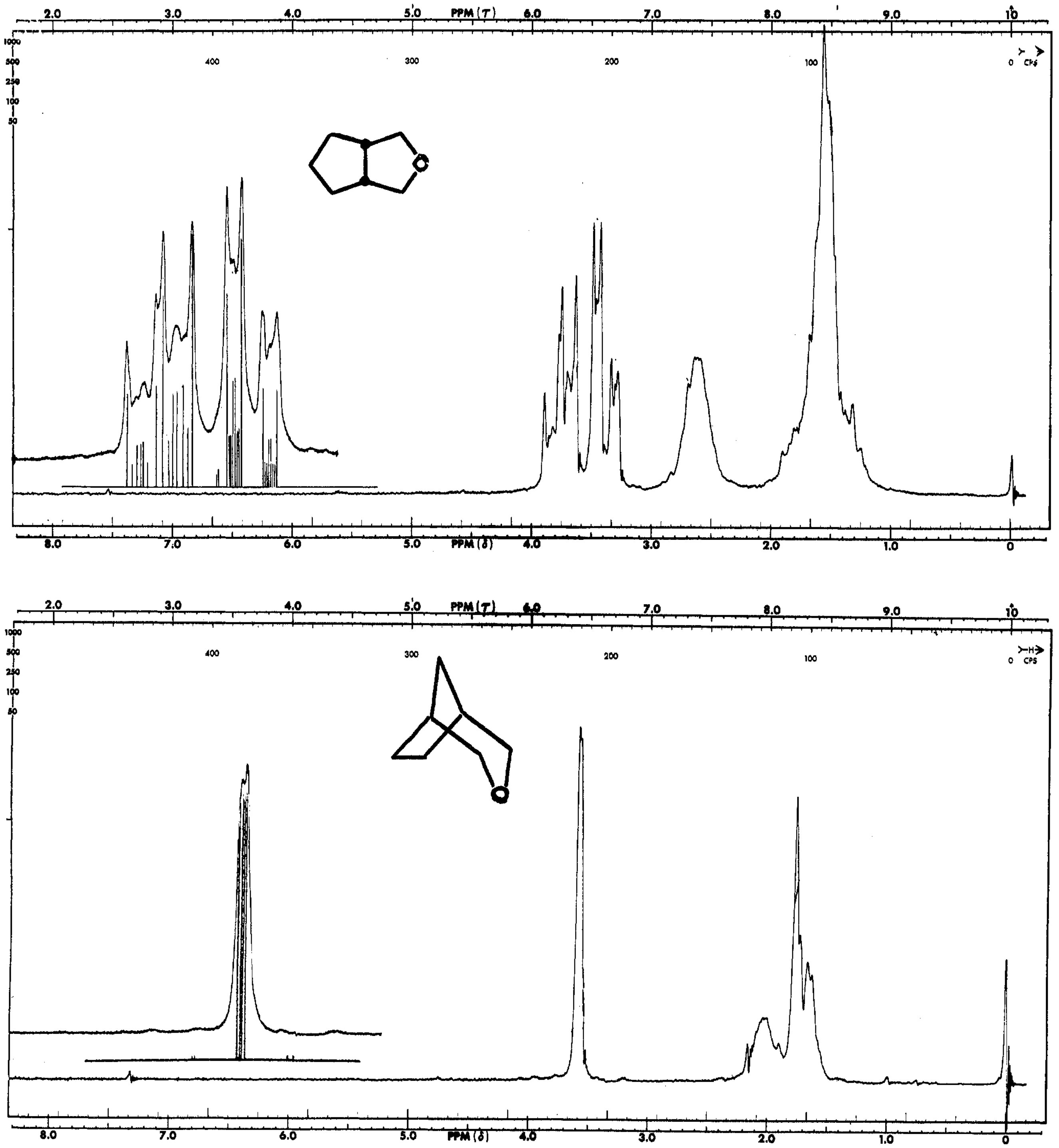

Figure 2.—Nmr spectra of *cis*-3-oxabicyclo[3.3.0]octane (10) and 3-oxabicyclo[3.2.1]octane (11). Calculated spectra shown in insets are from an AA'BB'XX' analysis of 10, $W_A = W_{A'} = -224.2$, $W_B = W_{B'} = -202.6$, and $W_X = W_{X'} = -158.0$ Hz, $|J_{AB}| = |J_{A'B'}| = 9.3$, $|J_{AX}| = |J_{A'X'}| = 7.6$, $|J_{BX}| = |J_{B'X'}| = 3.5$, and $|J_{XX'}| = 9.0$ Hz ($J_{AA'} = J_{BB'} = 0$ Hz), and an ABX analysis of 11, $\delta_{AB} = 4.0$ Hz, $W_X = -112.0$ Hz, $|J_{AB}| = 11.0$, $|J_{AX}| = 0.5$, and $|J_{BX}| = 2.7$ Hz.

Experimental Section[21]

Reaction of Cyclohexene with Paraformaldehyde and Hydrogen Chloride.—Hydrogen chloride was passed into a stirred mixture of 139 g (4.5 mol) of 97% paraformaldehyde, 246 g (3.0 mol) of cyclohexene, and 500 ml of methylene chloride at −60 to −70° for 4 hr. After standing overnight, the reaction mixture was washed twice with water, then with saturated sodium carbonate solution, dried ($MgSO_4$), and filtered, and the solvent was removed. Fractionation gave 128 g (36%) of cyclohexyl chloride, bp 36–42° (17 mm), 202 g (65.5% crude yield) of bicyclic products, bp 85–120° (12 mm), and 41 g of residue containing the formal of the chloro alcohol. The residue was refluxed for 3 hr with 200 ml of methanol and 10 ml of concentrated hydrochloric acid; after distillation there was obtained 31 g (79%) of *trans*-2-chlorocyclohexanemethanol, bp 75–77° (0.8 mm), $n^{20}D$ 1.4897, lit.[4] bp 113° (15 mm), $n^{20}D$ 1.4910, lit.[22] bp 103–104° (14 mm), $n^{25}D$ 1.4771.

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[21] All melting and boiling points are uncorrected. Olefins used were Phillips Petroleum Company Pure Grade materials. Glpc analyses were carried out on a Perkin-Elmer Model 720 gas chromatograph using 5 ft and 10 ft × 0.25 in. columns of 20% Ucon LB-550-X on Chromosorb P. Nmr data were obtained on a Varian Model A-60 spectrometer in chloroform-*d* with tetramethylsilane as an internal standard. Calculated spectra were obtained with computer program NMRIT (IBM SHARE Library No. 3165).

[22] M. Mousseron, J. Jullien, and F. Winternitz, *Bull. Soc. Chim. Fr.* **15**, 878 (1948).

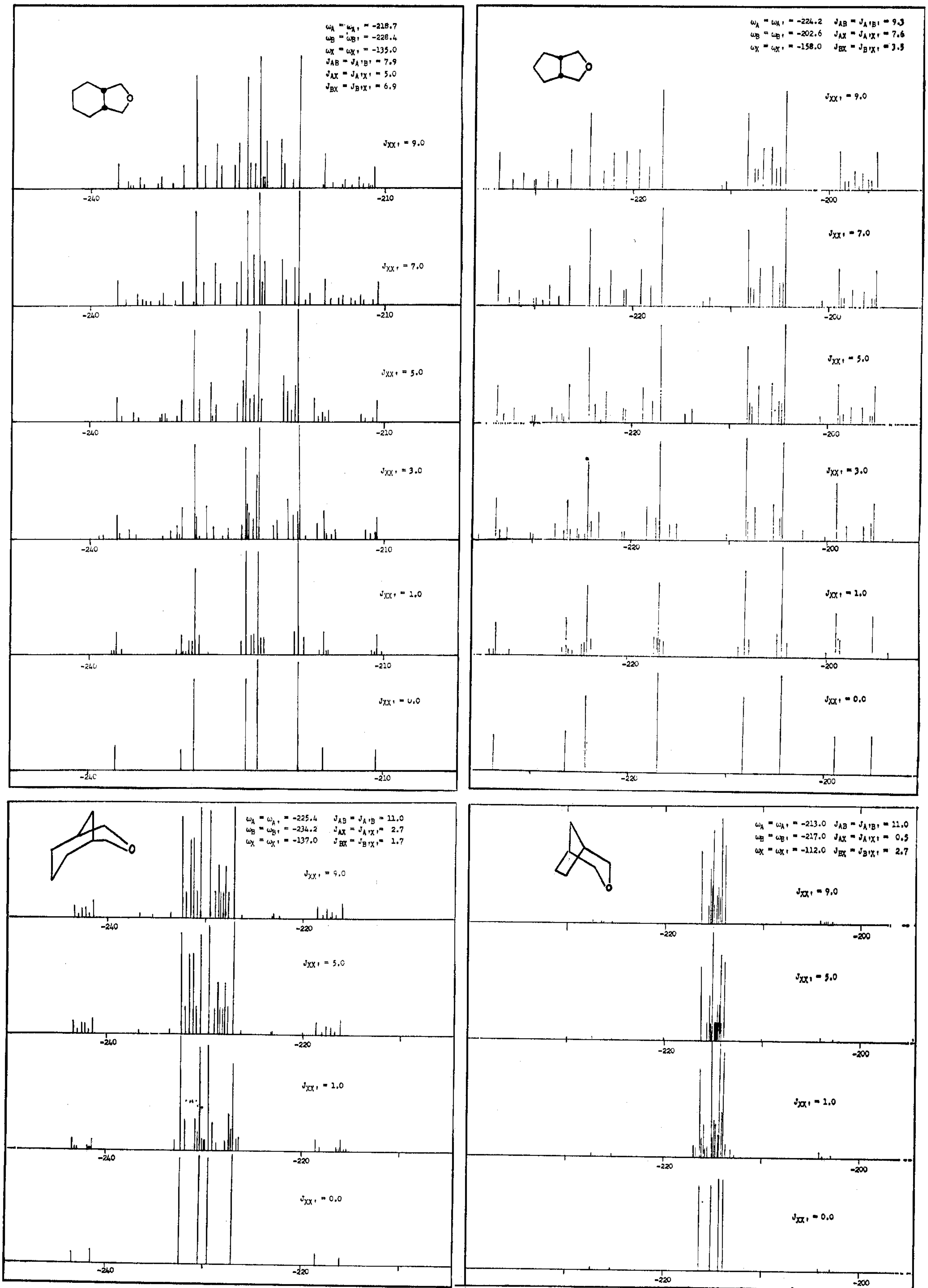

Figure 3.—Calculated line spectra from AA′BB′XX′ analyses of α-methylene resonances of 3-oxabicyclo[3.2.1]octane, *cis*-3-oxabicyclo[3.3.1]nonane, *cis*-3-oxabicyclo[4.3.0]nonane, and *cis*-3-oxabicyclo[3.3.0]octane with changes only in $J_{XX'}$, the bridgehead coupling constant.

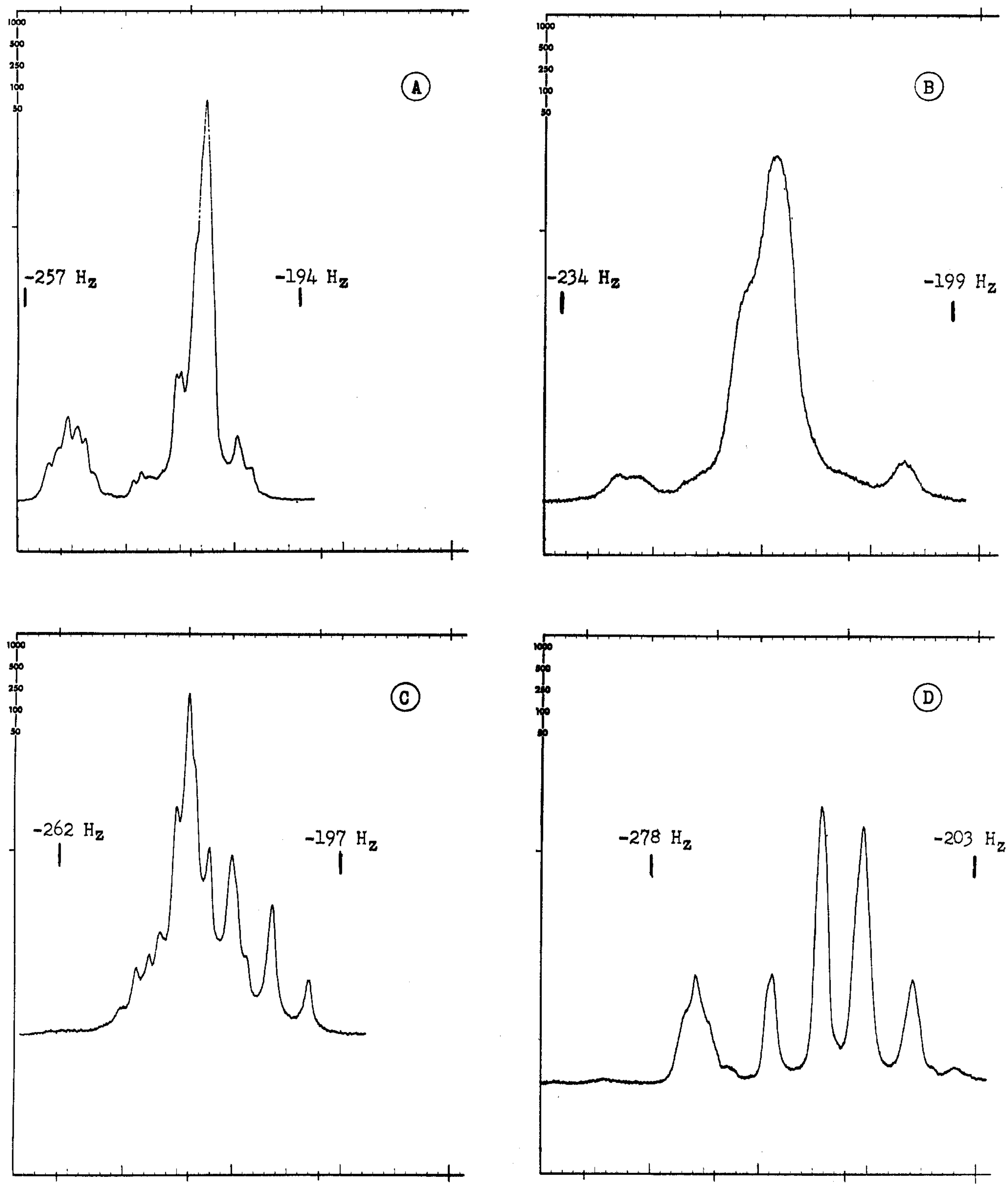

Figure 4.—α methylene resonance region for (A) 6-chloro-*cis*-3-oxabicyclo[3.3.0]octane (**8**), (B) 8-chloro-3-oxabicyclo-[3.2.1]octane (**9**), (C) *trans*-6-chloro-*cis*-3-oxabicyclo[4.3.0]nonane (**3**), and (D) *trans*-9-chloro-*cis*-3-oxabicyclo[3.3.1]nonane (**2**).

Anal. Calcd for $C_7H_{13}ClO$: C, 56.5; H, 8.8; Cl, 23.4. Found: C, 56.6; H, 9.0; Cl, 23.1.

The 3,5-dinitrobenzoate was obtained as colorless platelets, mp 85–86°, after two recrystallizations from 95% ethanol.

Anal. Calcd for $C_{13}H_{15}ClN_2O_6$: C, 47.2; H, 4.5; N, 8.5; Cl, 10.7. Found: C, 47.4; H, 4.4; N, 8.7; Cl, 10.5.

Reduction of Bicyclic Chlorides from Cyclohexene.—A solution of 32.1 g (0.2 mol) of the bicyclic chloride mixture (containing *ca.* 80% **2** and 20% **3** by glpc on the 5-ft Ucon column at 225°) in 300 ml of methanol was treated with 23 g (1.0 g-atom) of sodium cut into small pieces. After dilution with water, the product was extracted into ether and dried ($MgSO_4$); the ether was removed to give 20.8 g (83%) of a colorless, nearly solid product, which by glpc consisted of two isomers in a 4:1 ratio.

A portion of the product was separated by preparative gas chromatography on a 40 ft × $^3/_4$ in. Ucon column at 175°. The major component (**4**) eluted first and solidified; after purification by sublimation at 15 mm it melted at 141–143° (sealed tube), lit.[23] mp 135–138°, 120°.[1]

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[23] E. L. Wittbecker, H. K. Hall, Jr., and T. W. Campbell, *J. Amer. Chem. Soc.*, **82**, 1218 (1959).

Anal. Calcd for $C_8H_{14}O$: C, 76.1; H, 11.1; mol wt, 126.1448. Found: C, 75.9; H, 11.3; mol wt, 126.1466 (high-resolution mass spectrometer).

The minor product (**5**), liquid, was submitted for elemental analysis.

Anal. Calcd for $C_8H_{14}O$: C, 76.1; H, 11.1. Found: C, 75.8; H, 11.0.

Purification of *trans*-9-Chloro-*cis*-3-oxabicyclo[3.3.1]nonane (2).—Fractionation of a 175-g sample of mixed bicyclic chlorides through an efficient column gave 121 g of a center cut, bp 90–96° (11 mm), which partly solidified. Two recrystallizations from a minimum amount of methanol at 0° provided pure **2** as a crystalline solid with a camphor-like odor, mp 115–117°, lit.[4] mp 116.5–118°, in about 60% recovery.

Anal. Calcd for $C_8H_{13}ClO$: C, 59.8; H, 8.1; Cl, 22.1. Found: C, 59.8; H, 8.3; Cl, 22.0.

Preparative separation of **3** from the mother liquors was accomplished on the 40-ft Ucon column at 175°.

Cleavage of *cis*-3-Oxabicyclo[3.3.1]nonane (4).—A mixture of 5.5 g of *cis*-3-oxabicyclo[3.3.1]nonane and 50 ml of 47% hydriodic acid was refluxed for 2 hr, diluted with water, and extracted into ether (25 ml). The ether solution was dried ($MgSO_4$) and added dropwise to 1.0 g of lithium aluminum hydride in 50 ml of tetrahydrofuran. The mixture was refluxed for 3 hr during which time the ether was distilled out. The excess hydride was decomposed with water and the solution was filtered. Fractionation gave 3.1 g of liquid, bp 118–125°, which by glpc on a 150-ft squalane capillary column was found to contain more than 90% of a single isomer, *cis*-1,3-, *trans*-1,4-, or 1,1-dimethylcyclohexane. Dehydrogenation over platinum on carbon at 305° gave *m*-xylene in greater than 85% purity by glpc on the same column.

Synthesis of *trans*-9-Chloro-*cis*-3-oxabicyclo[3.3.1]nonane (2) from 2-Cyclohexenemethanol—Hydrogen chloride was passed into 50 g of 2-cyclohexenemethanol[11] (*ca.* 80% isomeric purity) and 18 g of 97% paraformaldehyde in 200 ml of methylene chloride at −65° for 3 hr. Work-up and distillation gave 47.5 g of crude product, bp 74–88° (6 mm). Crystallization from methanol gave 24.6 g (45%) of colorless crystals, mp 112–116°, which was identical by infrared and nmr with the sample obtained from cyclohexene.

Reaction of Cyclopentene with Paraformaldehyde and Hydrogen Chloride.—Reaction of 272 g (4.0 mol) of cyclopentene and 186 g (6.0 mol) of 97% paraformaldehyde with hydrogen chloride in 500 ml of methylene chloride was carried out for 4 hr. Work-up and distillation gave 143.8 g of material, bp 81–96° (32 to 8 mm) and 247 g (66%) of crude formal, bp 127–154° (0.9 mm). A center cut of the formal fraction, bp 145–147° (0.5 mm), $n^{20}{}_D$ 1.4921, was submitted for elemental analysis.

Anal. Calcd for $C_{13}H_{22}Cl_2O_2$: C, 55.6; H, 7.8. Found: C, 55.8; H, 7.9.

Methanolysis of the formal gave *trans*-2-chlorocyclopentanemethanol, bp 74–76° (2.5 mm), $n^{20}{}_D$ 1.4875, in 70% yield.

Anal. Calcd for $C_6H_{11}ClO$: C, 53.5; H, 8.2. Found: C, 53.8; H, 8.3.

The 3,5-dinitrobenzoate was obtained as colorless platelets from absolute ethanol, mp 105–106°.

Anal. Calcd for $C_{13}H_{13}ClN_2O_6$: C, 47.5; H, 4.0; N, 8.5. Found: C, 47.4; H, 4.0; N, 8.3.

Purification of Bicyclic Chlorides from Cyclopentene.—The low-boiling material from the reaction was refractionated through an efficient column to give a center cut, bp 84–86° (15 mm), which was analyzed.

Anal. Calcd for $C_7H_{11}ClO$: C, 57.4; H, 7.5; Cl, 24.3. Found: C, 57.3; H, 7.5; Cl, 24.1.

Separation of **8** and **9** was accomplished on the 40-ft column at 125°.

Sodium and Methanol Reduction of Bicyclic Chlorides from Cyclopentene.—A solution of 50 g (0.34 mol) of the bicyclic chloride mixture in 300 ml of methanol was treated with 46 g (2.0 g-atom) of sodium. Ether extraction followed by distillation gave 23.1 g (61%) of colorless liquid, bp 62–64° (47 mm), which by glpc on a 10-ft Ucon column at 175° contained two compounds in the proportion of 1:2, respectively, in order of elution. The isomers were separated on a preparative scale on the 40-ft Ucon column at 125°.

The minor component, a solid, mp 109–110°, was identified as 3-oxabicyclo[3.2.1]octane.

Anal. Calcd for $C_7H_{12}O$: C, 75.0; H, 10.7. Found: C, 74.8; H, 10.6.

The major component, a liquid, was identified by nmr as *cis*-3-oxabicyclo[3.3.0]octane.

Anal. Calcd for $C_7H_{12}O$: C, 75.0; H, 10.7. Found: C, 74.9; H, 10.9.

Registry No.—**2**, 25236-89-9; **3**, 7639-11-4; **4**, 280-71-7; **5**, 13149-01-4, **6**, 25236-93-5; **7**, 25236-94-6; **7** (3,5-dinitrobenzoate), 25236-95-7; **8**, 25236-96-8; **9**, 25236-97-9; **10**, 5117-83-9; **11**, 279-83-4; hydrogen chloride, 7647-01-0; *trans*-2-chlorocyclohexane methanol (3,5-dinitrobenzoate), 25237-00-7.

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