was also obtained by preparative chromatography on the 1.5-ft 5% GE-SE 30 column at 150°, 15 psi of helium.

Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.46; H, 9.86.

Reactions of Dicyclopropyl Ketone and Cyclopropyl Methyl Ketone with 2-Butanol and DTBP at 130°.—A procedure similar to that used for cyclopropyl phenyl ketone was employed. Analysis was accomplished by the methods described earlier.[1]

Relative Reactivities of Ketones with DTBP and 2-Butanol.—A procedure like that employed earlier was employed.[1] Vpc analysis for residual ketone against an appropriate standard was employed.

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Research Corporation for support of this work. The research was greatly assisted by an institutional grant from the Research Corporation which provided A. P. Schaap with a summer stipend.

Reactive Intermediates in the Bicyclo[3.1.0]hexyl and Bicyclo[3.1.0]hexylidene Systems. III. The Addition of Hydrogen Chloride and Deuterium Chloride to Bicyclo[3.1.0]hexene-2[1,2]

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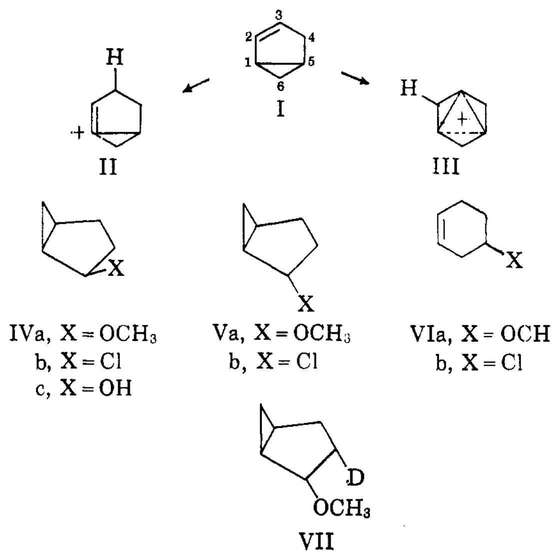
The addition of hydrogen chloride to bicyclo[3.1.0]hexene-2 results in *cis*-2-chlorobicyclo[3.1.0.]hexane and *trans*-2-chlorobicyclo[3.1.0]hexane, as the major products, accompanied by a small amount of 4-chlorocyclohexene. The addition of deuterium chloride to bicyclo[3.1.0]hexene-2 produces *cis*-2-chloro-*cis*-3-deuteriobicyclo[3.1.0]hexane and *trans*-2-chloro-*trans*-3-deuteriobicyclo[3.1.0]hexane, with a minor amount of deuterated 4-chlorocyclohexene.

Our recent investigation[4] of the reaction alternatives for electrophilic addition to bicyclo[3.1.0]hexene-2 utilized the acid-catalyzed additions of methanol and methanol-*d*. Using mild reaction conditions, the addition of methanol resulted in *cis*-2-methoxy- and *trans*-2-methoxybicyclo[3.1.0]hexane (IVa and Va) and small amounts of 4-methoxycyclohexene (VIa). Since no 3-methoxybicyclo[3.1.0]hexanes were detected using reaction conditions under which the 3 ethers would have survived if formed, it was concluded that the trishomocyclopropenyl carbonium ion (III) (or a classical relative) was not a product-determining intermediate. Formation of IVa, Va, and VIa can be accounted for as a result of generation of a 2-bicyclo[3.1.0]hexyl carbonium ion (II). The addition of methanol-*d* leading to *trans*-2 ether was investigated and found to be completely *cis*, producing *trans*-2-methoxy-*trans*-3-deuteriobicyclo[3.1.0]hexane (VII). (See Scheme I.)

SCHEME I



Interpretation of the *cis* polar addition of the elements of CH_3OD to I is complicated by the unknown degree to which the stereochemistry is controlled by the position of the cyclopropane methylene. Similar difficulties are encountered in interpreting the *cis* addition of methanol-*d* to *endo*-trimethylenenorbornene,[5] *cis* polar addition of deuterium bromide to norbornene,[6] *cis* oxymercuration of norbornadiene, norbornene, and norbornene derivatives,[7-10] *cis* oxythallation of norbornadiene and norbornene,[7,11] and *cis* addition of nitrosyl chloride and bromide to norbornadiene, norbornene, and norbornene derivatives.[12] In these cases one can argue that *cis* addition is not the result of the intrinsic requirements of the double bond but is the result of effective steric shielding by methano, ethano, or etheno bridge elements.[13] Clarification of the importance of such steric shielding

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[1] Part II: P. K. Freeman and D. G. Kuper, *J. Org. Chem.*, **30**, 1047 (1965).

[2] Presented at the Northwest Regional Meeting of the American Chemical Society, Corvallis, Ore., June 1965, Abstracts, p 40.

[3] National Defense Education Act Fellow, 1961–1964.

[4] P. K. Freeman, M. F. Grostic, and F. A. Raymond, *J. Org. Chem.*, **30**, 771 (1965).

[5] S. J. Cristol, L. K. Gaston, and D. W. Johnson, *Tetrahedron Letters*, **No. 4**, 185 (1963).

[6] H. Kwart and J. L. Nyce, *J. Am. Chem. Soc.*, **86**, 2601 (1964).

[7] K. C. Pande and S. Winstein, *Tetrahedron Letters*, **No. 46**, 3393 (1964).

[8] J. K. Stille and S. C. Stinson, *Tetrahedron*, **20**, 1387 (1964).

[9] T. G. Traylor and A. W. Baker, *J. Am. Chem. Soc.*, **85**, 2746 (1963); T. G. Traylor and A. W. Baker, *Tetrahedron Letters*, **No. 19**, 14 (1959).

[10] M. M. Anderson and P. M. Henry, *Chem. Ind.* (London), 2053 (1961).

[11] F. A. L. Anet, *Tetrahedron Letters*, **No. 46**, 3399 (1964).

[12] J. Meinwald, Y. C. Meinwald, and T. N. Baker, III, *J. Am. Chem. Soc.*, **86**, 4074 (1964).

[13] When both faces of the double bond are sterically shielded to the same degree, as in bicyclo[2.2.2]octene, oxymercuration in aqueous acetone yields both *cis* and *trans* addition products: T. G. Traylor, *ibid.*, **86**, 244 (1964). In comparing oxymercuration of norbornene and bicyclo[2.2.2]octene, Professor Traylor emphasizes the importance of the rigidity of the starting olefin. The greater flexibility of the bicyclo[2.2.2]octene mercurinium ion complex would permit backside attack with less torsional strain than in the corresponding process with the norbornene complex.

by cyclopropane methylene seemed possible through study of the stereochemistry of polar addition to I leading to *cis*-2-bicyclo[3.1.0]hexane derivatives.

Initial attempts to determine the spatial arrangement of the elements of CH_3OD in the *cis*-2 ether formed in the acid-catalyzed addition of methanol-*d* to I were frustrated owing to the fact that IVa and VIa had identical retention times on all vapor phase chromatographic columns investigated. Thus, in order to avoid this experimental difficulty and to determine if the product composition of the acid-catalyzed addition of methanol to I provides an accurate characterization of the intermediate(s), a study of the addition of hydrogen chloride and deuterium chloride to bicyclo[3.1.0]hexene-2 was undertaken.

Results

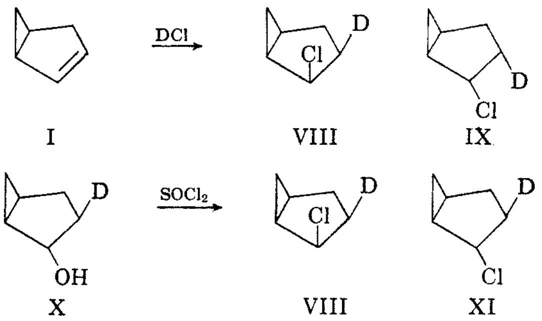
Treatment of bicyclo[3.1.0]hexene-2 (I) with a solution of hydrogen chloride in chloroform for 9 days at room temperature produced a 58% yield of monochlorides. Vapor phase chromatographic analysis indicated a two-component mixture with a ratio of 69:31. Infrared and nmr spectral comparison, using standard samples of *cis*- and *trans*-2-chlorobicyclo[3.1.0]hexane (IVb and Vb), prepared as described below, demonstrated that the 31% component is IVb, and the 69% component is a binary mixture of Vb and VIb in a ratio of 66:3.

The *cis*- and *trans*-2 chlorides were synthesized independently by the reaction of thionyl chloride with *cis*-2-bicyclo[3.1.0]hexanol (IVc) with and without pyridine as a catalyst. When pyridine was used as a catalyst the ratio of *cis*/*trans* chloride was 69:31, and when no pyridine was used the ratio of *cis*/*trans* increased to 89:11 owing to the decreased amount of SN2 attack by the chloride ion. This increased ratio supports the structural assignment of the *cis*-2 and *trans*-2 isomers and is consistent with the expectation that an SNi reaction would predominate giving retention of configuration.[14] Typical bicyclo[3.1.0]hexyl absorption bands[4] were observed for *cis*-2 chloride IVb (ν_{max} 3070, 3040, 3000, and 1025 cm^{-1}) and for the *trans*-2 chloride Vb (ν_{max} 3060, 3035, 3000, and 1025 cm^{-1}). In addition, the absorption at 3040 cm^{-1} in the *cis*-2 chloride is enhanced relative to the absorption at 3035 cm^{-1} in the *trans* epimer, which is consistent with the pattern found for all 2- and 3-bicyclo[3.1.0]hexane epimeric pairs investigated so far.[15] The nmr spectral data are also in agreement with the structural assignment for the chlorides obtained from the thionyl chloride–*cis*-2 alcohol reaction. The chloride assigned the *trans*-2 structure exhibits the expected doublet at τ 5.71 (J = 4.3 cps) for the *cis*-C-2 hydrogen α to the chlorine, which is due to splitting by the *cis*-C-3 hydrogen.[4] The *trans*-2 chloride exhibits a cyclopropane methylene absorption band at τ 9.34–10.00, while the corresponding band for the *cis*-2 chloride appears at 9.35–9.67. This downfield shift for the high-field proton of the cyclopropane methylene band of the *cis* isomer, relative to the *trans* isomer, is characteristic of *cis*- and *trans*-2- and -3-bicyclo[3.1.0]hexyl epimeric pairs containing electronegative substituents.[15] The downfield shift is caused by deshielding of the *syn*-C-6 proton by the *cis* substituent.[16,17]

In order to do a complete analysis of the stereochemistry of addition, bicyclo[3.1.0]hexene-2 (I) was allowed to react with a chloroform solution of deuterium chloride at room temperature over a period of 8 days. A 45% yield of monochlorides was obtained. Vapor phase chromatographic analysis showed two peaks in the ratio of 67:33 for *trans*-2 chloride and *cis*-2 chloride. The infrared and nmr spectra of the deuterated *cis*-2 chloride were virtually identical with the corresponding spectra of *cis*-2-chloro-*cis*-3-deuterio-bicyclo[3.1.0]hexane (VIII), synthesized independently as described below.[18]

The nmr spectrum of the deuterated *trans*-2 chloride exhibited a doublet at τ 5.71 (J = 4.3 cps) for the *cis*-2 proton, while the analogous proton of the *trans*-2-chloro-*cis*-3-deuteriobicyclo[3.1.0]hexane (XI), synthesized as described below, appeared as a singlet at τ 5.71. Thus, it is clear that the deuterated *trans*-2 chloride is *trans*-2-chloro-*trans*-3-deuteriobicyclo[3.1.0]hexane (IX). The infrared spectrum of *cis*-3-deuterio-*trans*-2-chloride shows a strong absorption at 870 cm^{-1}; the absence of absorption at this frequency in the spectrum of the deuterium chloride addition product IX demonstrates that less than 1% *trans* addition product was present as a contaminant in the *cis* adduct IX. The nmr spectrum of *cis* adduct IX indicates that deuterated 4-chlorocyclohexene was present to an extent of 2%. No epimerization during the reaction of *cis* adducts VIII or IX was detected. (See Scheme II.)

SCHEME II



The *cis*-3-deuterio-*cis*-2 chloride VIII and *cis*-3-deuterio-*trans*-2 chloride XI were prepared starting with *cis*-3-deuterio-*trans*-2-bicyclo[3.1.0]hexanol, which was prepared by lithium aluminum deuteride reduction of *trans*-2,3-epoxybicyclo[3.1.0]hexane followed by vapor phase chromatographic separation of the *trans*-2 alcohol.[4,19] Treatment of X with thionyl chloride in the presence of pyridine as a catalyst

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[14] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart, and Winston, New York, N. Y., 1959, p 294.

[15] Reference 4; F. A. Raymond, Ph.D. Thesis, University of Idaho, 1965.

[16] For examples of a similar effect in similar systems, see P. Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1171 (1964); W. R. Moore, W. R. Moser, and J. E. LaPrade, *J. Org. Chem.*, **28**, 2200 (1963).

[17] For additional evidence indicating that the high-field proton absorption in the cyclopropane methylene band is due to the *syn*-C-6 proton, see P. G. Gassman and F. V. Zalar, *Tetrahedron Letters*, 3251 (1964).

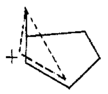
[18] The spectrum of the *cis*-2 chloride obtained from the deuterium chloride addition reaction exhibited a peak at 830 cm^{-1} which was not present in the *cis*-2-chloro-*cis*-3-deuterio standard. The correspondence of the remaining peaks at ν_{max} 3075, 3040, 3005, 2940, 2870, 2190, 1440, 1325, 1320, 1303, 1273, 1215, 1160, 1100, 1063, 1020, 963, 940, 910, 880, 815, 760, and 737 cm^{-1} suggests strongly that the absorption at 830 cm^{-1} is due to a minor amount of *trans* addition product or else a small amount of impurity.

[19] E. J. Corey and R. L. Dawson, *J. Am. Chem. Soc.*, **85**, 1782 (1963).

yielded *cis*-3-deuterio-*cis*-2 chloride (VIII), *cis*-3-deuterio-*trans*-2 chloride (XI), and deuterated 4-chlorocyclohexene in a ratio of 56:37:7. The nmr spectrum of VIII showed a complex splitting pattern (τ 5.38–5.73) for the proton α to the chlorine substituent, a complex splitting pattern (τ 7.50–8.80) for the two tertiary and three methylene protons, and a band for the two methylene protons on the cyclopropane ring in the region τ 9.32–9.70. The nmr spectrum of XI showed a singlet at τ 5.71 for the proton α to the chlorine atom, as mentioned above, a complex absorption region at 7.40–8.70 (5 H), and cyclopropane methylene absorption at 9.60–10.00 (2 H).

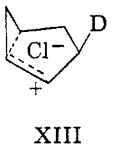
Discussion

The predominance of *cis*-2- and *trans*-2-chlorobicyclo[3.1.0]hexane over 4-chlorocyclohexene, with no detectable 3-chlorobicyclo[3.1.0]hexanes, resulting from the hydrogen chloride addition to I, is in close agreement with the results of the acid-catalyzed addition of methanol to bicyclo[3.1.0]hexene-2. Thus, again, there is no evidence for the formation of the trishomocyclopropenyl carbonium ion (III), and, since no nucleophilic attack on C-1 or C-6 of the carbonium ion was observed, there is also no evidence which requires an intermediate strictly analogous to a bicyclobutonium ion intermediate.[20] Furthermore, if the predominance of the 2-bicyclohexyl carbonium ion over the 3-bicyclohexyl carbonium ion were due to delocalization of cyclopropane electrons as pictured in bicyclobutonium ion XII, then attack by chloride ion would be expected to occur *trans* to the cyclopropane methylene group, with very little generation of *cis*-2 chloride.

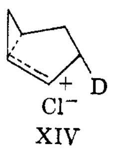


XII

cis addition of deuterium chloride to both faces of the bicyclo[3.1.0]hexene-2 double bond demonstrates that the *cis* addition is characteristic of the intrinsic requirements of the double bond and is not the result of steric control by the cyclopropane methylene. Clearly neither proton π complexes nor a carbonium ion π complex of the double bond (XII) controls the stereochemistry of addition, and one is tempted to postulate ion pairs XIII and XIV, analogous to those suggested by Dewar and Fahey,[21,22] to rationalize the *cis* addition. Since in nearly all previous cases of *cis*-polar addition the substrates were limited to the styrene family[21-28] (the addition of an electrophile to the double bond resulting in a stabilized benzyl-type carbonium ion) or the reaction was complicated by steric factors which cloud the interpretation,[4-12,29] the *cis* addition of deuterium chloride to bicyclo[3.1.0]hexene-2 would appear, at first impression, to extend the scope of *cis* addition. However, the direction of addition to I clearly indicates that the 2-bicyclohexyl carbonium ion is more stable than the 3-bicyclohexyl carbonium ion, and thus polar addition to I may be just another example of formation of a stabilized carbonium ion, actually quite similar, then, to the carbonium ions encountered in the acenaphthalene, indene, 1-phenylpropene series studied by Dewar.[21,22] In each case the scales are tipped against the π complex and in favor of the "classical" carbonium ion by delocalization of charge by an α-cyclopropyl or α-aryl substituent. If one narrows the view of analogous reactions to additions of proton acids, the recent example of *trans*-polar addition of hydrogen bromide to cyclohexene-2,6,6-d_3 reported by Fahey and Smith[30] stands out as an interesting case in which the substrate is not capable of forming a delocalized carbonium ion intermediate.[31]



XIII



XIV

If by analogy one can assume that the *cis* addition of methanol-*d* to I[4] is the result of the intrinsic requirements of the bicyclic double bond, then it is difficult to see how the mechanism discussed above for the addition of deuterium chloride can rationalize the *cis* addition of methanol-*d*. One would expect, owing to the different charge type of the electrophile, that, once the deuteron is transferred from the conjugate acid of methanol-*d* to the olefin, nucleophilic attack by methanol-*d* on the 2-bicyclohexyl carbonium ion should be independent of the *cis* or *trans* nature of deuteron transfer.[32] Thus, for the sake of illustration, if one assumes 33% *cis* transfer of a deuteron (as in the case of deuterium chloride addition), attack on the *cis*- and *trans*-3-deuterio-2-bicyclo[3.1.0]hexyl carbonium ions should generate a ratio of *cis*-3-deuterio-*trans*-2 methyl ether to *trans*-3-deuterio-*trans*-2 methyl ether of 1:2 (*trans*/*cis* addition) which would have been detected by nmr analysis. It thus appears possible that electrophilic addition of the conjugate acid of methanol may involve a transition state with some four-center character.

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[20] M. S. Silver, M. C. Caserio, H. E. Rice, and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 3671 (1961).

[21] M. J. S. Dewar and R. C. Fahey, *ibid.*, **85**, 2245, 2248, 3645 (1963).

[22] M. J. S. Dewar and R. C. Fahey, *Angew. Chem. Intern. Ed. Engl.*, **3**, 245 (1964).

[23] R. C. Fahey and C. Schubert, *J. Am. Chem. Soc.*, **87**, 5172 (1965).

[24] W. E. Rosen, L. Dorfman, and M. P. Linfield, *J. Org. Chem.*, **29**, 1723 (1964).

[25] L. Bernardi and A. Leone, *Tetrahedron Letters*, **No. 10**, 499 (1964).

[26] S. J. Cristol and R. S. Bly, *J. Am. Chem. Soc.*, **82**, 142 (1960).

[27] S. J. Cristol, F. R. Stermitz, and P. S. Ramey, *ibid.*, **78**, 4939 (1956).

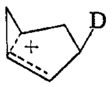
[28] P. B. D. de la Mare, N. V. Klassen, and R. Koenigsberger, *J. Chem. Soc.*, 5285 (1961).

[29] For two examples of *cis* addition outside the styrene family and uncomplicated by steric factors, see M. Ohno, M. Okamoto, and K. Nukuda, *Tetrahedron Letters*, **No. 45**, 4047 (1965), and ref 13.

[30] R. C. Fahey and R. A. Smith, *J. Am. Chem. Soc.*, **86**, 5035 (1964).

[31] The *trans* addition found by Fahey and Smith contrasts with the 26–74% *cis* addition of deuterium bromide to cyclohexene reported by J. V. Smirnov-Zamkov and G. A. Piskovitina, *Ukr. Khim. Zh.*, **28**, 531 (1962).

[32] A referee has suggested that stereospecific opening of a *cis*-deuteron π complex of I might lead to a *cis*-3-deuterio homoallylic cation involving delocalization of the C-1–C-5 bond (i), while stereospecific rearrangement of the *trans*-deuteron π complex would produce *trans*-3-deuterio XII. In each case it is postulated that the delocalized intermediates exhibit electronic memories and provide protection of opposite faces of the double bond. While this suggestion has some merit and would provide a single explanation for the *cis* addition of both deuterium chloride and methanol-*d*, we do not favor it, since it seems unlikely that homoallylic ion i would protect the *trans* face of the molecule near C-2 much more than the *cis* face.



i

Experimental Section[33]

Addition of Hydrogen Chloride to Bicyclo[3.1.0]hexene-2.—Bicyclo[3.1.0]hexene-2 was prepared as described previously.[4] To 90 ml of 0.110 *N* hydrogen chloride (9.9 mmoles) in chloroform was added 2.00 g (25.0 mmoles) of bicyclo[3.1.0]hexene-2. The flask was stoppered and shaken at room temperature for 9 days. The chloroform and unreacted starting materials were removed by evaporation at reduced pressure to yield 0.73 g (58%) of a mixture of chlorides. Analysis of this mixture on an 8-ft aluminum column of 13% tris(cyanoethoxy)propane (TCEP) on HMDS-treated Chromosorb W revealed two peaks in the ratio of 69:31, with retention times of 14.3 and 19.2 min, respectively, at a flow rate of 50 ml/min and a column temperature of 70°. The 31% peak had a retention time corresponding to that of *cis*-2-chlorobicyclo[3.1.0]hexane and was shown to be *cis*-2-chlorobicyclo[3.1.0]hexane by comparison of the infrared and nmr spectra with those of an authentic sample. The 69% peak had a retention time corresponding to those of *trans*-2-chlorobicyclo-[3.1.0]hexane and 4-chlorocyclohexene. The infrared and nmr spectra of the 69% peak were the same as those of *trans*-2-chlorobicyclo[3.1.0]hexane with minor differences due to 4-chlorocyclohexene, which was present to an extent of 3–4% of the total chlorides, based on calculations using the 1140-cm^{-1} band and the area of the olefinic protons at τ 4.42 in the infrared and nmr spectra. The presence of *cis*-3-chlorobicyclo[3.1.0]hexane was ruled out by the absence of its 747-cm^{-1} band in the infrared spectrum of the *trans*-2-chlorobicyclo[3.1.0]hexane fraction, since 1% or more could have been detected. There was also no evidence in the τ 9.07–9.34 region in the nmr spectrum to indicate the presence of any *cis*-3-chlorobicyclo[3.1.0]hexane. The presence of *trans*-3-chlorobicyclo[3.1.0]hexane was ruled out based upon the absence of any peak with a retention time of 10.0 min in the vpc analysis on the TCEP column.

Preparation of *cis*- and *trans*-2-Chlorobicyclo[3.1.0]hexane.—The *cis*- and *trans*-2-chlorobicyclo[3.1.0]hexanes were prepared by the reaction of thionyl chloride on *cis*-2-bicyclo[3.1.0]hexanol,[34] with and without pyridine as a catalyst. To a stirred solution of 2.00 g (20.2 mmoles) of *cis*-2-bicyclo[3.1.0]hexanol in 25 ml of dry ether, containing 3 drops of pyridine, was added dropwise 2.60 g (21.8 mmoles) of thionyl chloride. After the addition was complete, the ether solution was heated at reflux for 2 hr. The ether and excess thionyl chloride were removed by evaporation under reduced pressure yielding 1.93 g (81%) of *cis*- and *trans*-2-chlorobicyclo[3.1.0]hexane. The mixture of chlorides was analyzed on an 8-ft aluminum column of 13% tris(cyanoethoxy)propane (TCEP) on HMDS-treated Chromosorb W. The mixture showed two peaks in the ratio of 69:31 for *cis*- and *trans*-2-chlorobicyclo[3.1.0]hexane, respectively. When no pyridine was used the ratio of *cis*/*trans* increased to 89:11 owing to the decreased amount of SN2 attack by the chloride ion at the C-2 position. At a flow rate of 50 ml/min and a column temperature of 70° the retention times for *cis*- and *trans*-2-chlorobicyclo[3.1.0]hexane were 19.2 and 14.3 min, respectively. Analytical samples were separated by vapor phase chromatography.

Anal. Calcd for C_6H_9Cl: C, 61.95; H, 7.80. Found (for *cis*-2 chloride): C, 62.02; H, 8.01. Found (for *trans*-2 chloride): C, 61.99; H, 7.90.

The infrared spectrum of *cis*-2-chlorobicyclo[3.1.0]hexane exhibits characteristic absorption bands at 3070, 3040, 3000, and 1025 cm^{-1}, while *trans*-2-chlorobicyclo[3.1.0]hexane shows similar bands at 3060, 3035, 3000, and 1025 cm^{-1}. The nmr spectra for the *cis* and *trans* isomers show a complex splitting pattern in the region τ 7.40 to 8.80 representing the two tertiary protons of the cyclopropane ring and the four methylene protons of the cyclopentane ring. The cyclopropane methylene protons at the C-6 position appear at τ 9.35–9.67 with the *cis*-2 epimer and at 9.34 to 10.00 with the *trans*-2 epimer. The tertiary proton α to the chlorine substituent appears at τ 5.71 (doublet, J = 4.3 cps) with the *trans*-2 chloride and at 5.65 (complex band) with the *cis*-2 chloride.

Preparation of *cis*- and *trans*-3-Chlorobicyclo[3.1.0]hexane.—To 6.00 g (61.2 mmoles) of *cis*-3-bicyclo[3.1.0]hexanol[35] in 25 ml of anhydrous ether, containing 8 drops of pyridine, was added dropwise with stirring 7.30 g (61.2 mmoles) of thionyl chloride. After completion of the addition, the reaction mixture was heated at reflux overnight. The ether solution was decanted from the pyridine hydrochloride and the ether was removed at reduced pressure, using a rotary evaporator, yielding 6.30 g (88%) of product. The product showed two peaks in the ratio of 71:29 for *cis*- and *trans*-3-chlorobicyclo[3.1.0]hexane on vpc analysis using an 8-ft TCEP column at 70°. The 29% component eluted from the TCEP column before the 71% component. Since the reaction conditions favored an SNi mechanism (as established in the case of the 2-chlorides), the 71% peak was assumed to be the *cis*-3 chloride. The order of elution (*trans* before *cis*) was consistent with the order of elution of the *cis*- and *trans*-2 chlorides from the same column.

The infrared spectra of the *trans*-3 chloride show the typical bicyclo[3.1.0]hexyl absorption bands at 3060, 3040, and 3000 cm^{-1} and the cyclopropane band at 1025 cm^{-1}. The C–Cl band appears at 770 cm^{-1} with other strong absorption bands at 1440, 1300, 1200, 920, and 817 cm^{-1}. The infrared spectra of the *cis*-3 chloride show the typical bicyclo[3.1.0]hexyl absorption bands at 3070, 3035, and 3000 cm^{-1} with the 3035-cm^{-1} band enhanced relative to the same band for *trans* epimer. The cyclopropane band appears at 1015 and the C–Cl band at 747 cm^{-1}. Other strong bands appear at 1440, 1338, 1300, 1265, 1175, 885, and 815 cm^{-1}.

The nmr spectrum of the *cis*-3 chloride shows the two cyclopropane methylene protons shifted downfield to τ 9.07–9.64; whereas, the spectrum of the *trans*-3 chloride shows a more normal absorption region at 9.44 to 10.00 (when compared with the cyclopropane methylene absorption region of bicyclo[3.1.0]hexane at τ 9.60–10.00). The spectrum for the *cis*-3 chloride also exhibits a complex absorption band at τ 5.63 for the tertiary proton α to the chlorine atom, a complex absorption in the region 7.26 to 8.20 for four methylene protons β to the chlorine atom, and a complex absorption in the region 8.46 to 8.82 for the two tertiary protons on the cyclopropane ring. The spectrum for the *trans*-3 chloride shows a quintuplet at τ 6.17 for the proton α to the chlorine atom, a complex absorption in the region 7.42 to 8.27 for the four protons β to the chlorine atom, and a complex absorption in the region 8.50 to 8.84 for the two tertiary protons on the cyclopropane ring.

Anal. Calcd for C_6H_9Cl: C, 61.95; H, 7.80. Found (for *trans*-3 chloride): C, 61.64; H, 7.92. Found (for *cis*-3 chloride): C, 61.77; H, 7.74.

Addition of Deuterium Chloride to Bicyclo[3.1.0]hexene-2.—The deuterium chloride was prepared by the method of Brown and Groot.[36] A 0.21 *N* solution of deuterium chloride in alcohol free chloroform[37] was obtained by bubbling 0.50 mole of deuterium chloride into 400 ml of purified chloroform. To 2.07 g (26.0 mmoles) of bicyclo[3.1.0]hexene-2 was added 24 mmoles (115 ml of 0.21 *M*) of deuterium chloride. The mixture was shaken at room temperature for 8 days. The chloroform and unreacted starting materials were removed at reduced pressure yielding 1.48 g (45%) of product. The mixture of chlorides was analyzed by vpc on an 8-ft TCEP column at 70°. The analysis showed peaks for *cis*- and *trans*-2 chlorides in the ratio of 33:67. The 67% component was found to contain 2% deuterated 4-chlorocyclohexene as determined from the olefinic proton absorption (τ 4.42) in the nmr spectrum.

The infrared and nmr spectra of the deuterated *cis*-2 chloride showed it to be *cis*-3-deuterio-*cis*-2-chlorobicyclo[3.1.0]hexane by comparison with the infrared and nmr spectra of an authentic sample. The extent of deuteration was obtained by comparing the relative area of the two tertiary and three methylene protons in the region τ 7.70 to 8.80 with the same region of an authentic sample containing 98–100% deuteration at the *cis*-3 position. This comparison showed a relative area of five protons indicating 95–100% deuteration, since this area would correspond to six protons if no deuterium were present. The infrared spectrum showed 95–100% deuteration by comparison of the optical den-

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[33] Infrared spectra were determined as pure liquids using Perkin-Elmer Model 137 and 237 spectrophotometers. Nmr spectra were run in carbon tetrachloride with tetramethylsilane as the internal reference using a Varian Associates A-60 nmr spectrometer. Gas chromatographic analyses were performed using either Aerograph Model A-700 or Model A-90-P chromatographs, and helium was used as the carrier gas. Elemental analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn., and by Max Bernhardt, Mikroanalytisches Laboratorium, Max-Planck Institute, Mülheim, Germany.

[34] W. G. Dauben and G. H. Berezin, *J. Am. Chem. Soc.*, **85**, 468 (1963).

[35] S. Winstein and J. Sonnenberg, *ibid.*, **83**, 3235 (1961).

[36] H. C. Brown and C. Groot, *ibid.*, **64**, 2223 (1942).

[37] K. B. Wiberg, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 250.

sity of the C–D stretching frequency at 2190 cm^{-1} with that of an authentic sample. Since the infrared and nmr spectra of the *cis*-3-deuterio-*cis*-2-chlorobicyclo[3.1.0]hexane were virtually identical with those of an authentic sample, it was concluded that the addition of deuterium chloride was predominately *cis*.

The nmr spectrum of the deuterated *trans*-2 chloride shows a doublet (J = 4.3 cps) at τ 5.71 for the tertiary proton α to the chlorine atom, and thus the *trans*-2 chloride must be *trans*-3-deuterio-*trans*-2-chlorbicyclo[3.1.0]hexane. The infrared spectra of the *cis*-3-deuterio-*trans*-2 chloride and *trans*-3-deuterio-*trans*-2 chloride were different, with the *trans*-3-deuterio chloride exhibiting two unique, strong bands at 990 and 928 cm^{-1} and the *cis*-3-deuterio chloride showing a unique, strong band at 870 cm^{-1}. The absence of a band at 870 cm^{-1} in the infrared spectrum of the *trans*-3-deuterio-*trans*-2-chlorobicyclo[3.1.0]hexane, from the deuterium chloride addition to bicyclo[3.1.0]hexene-2, demonstrates that less than 1% *trans* addition occurred. Nmr comparison of the deuterated *trans*-2 chloride addition product with undeuterated *trans*-2 chloride and with the *cis*-3-deuterio-*trans*-2 chloride demonstrated that the *trans*-3-deuterio-*trans*-2-chlorobicyclo[3.1.0]hexane obtained was 95–100% deuterated.

***cis*-3-Deuterio-*cis*-2- and *cis*-3-Deuterio-*trans*-2-chlorobicyclo-[3.1.0]hexane.**—To a stirred solution of 0.93 g (7.9 mmoles) of *cis*-3-deuterio-*trans*-2-bicyclo[3.1.0]hexanol[4] (98–100% deuterated) and 7 drops of pyridine in 13 ml of ether was added 1.25 g (10.5 mmoles) of thionyl chloride. After the addition was completed, the reaction mixture was heated at reflux for 3 hr. The ether solution was decanted from the reaction flask leaving behind the pyridine hydrochloride. The ether and excess thionyl chloride were removed at reduced pressure, using a rotary evaporator, to yield 1.02 g (93%) of product. The mixture was shown to consist of 7% deuterated 4-chlorocyclohexene, 37% *cis*-3-deuterio-*trans*-2-chlorobicyclo[3.1.0]hexane, and 56% *cis*-3-deuterio-*cis*-2-chlorobicyclo[3.1.0]hexane when analyzed as described in the hydrogen chloride addition to bicyclo[3.1.0]hexene-2.

The nmr spectrum of the *cis*-3-deuterio-*trans*-2-chlorobicyclo-[3.1.0]hexane shows a singlet (τ 5.71) for the proton α to the chlorine atom, a complex splitting pattern in the region τ 7.40 to 8.70 corresponding to two tertiary and three methylene protons, and a complex splitting pattern (τ 9.60 to 10.00) for the two methylene protons on the cyclopropane ring.

The nmr spectrum of the *cis*-3-deuterio-*cis*-2-chlorobicyclo-[3.1.0]hexane shows a complex splitting pattern (τ 5.38 to 5.73) for the proton α to the chlorine atom, a complex band (τ 7.50 to 8.80) for two tertiary and three methylene protons, and a complex pattern for the two methylene protons on the cyclopropane ring in the region τ 9.32 to 9.70.

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1,2-Diphenylcyclobutene

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Treatment of 1,4-dichloro-1,4-diphenylbutane (III) with sodium amide in liquid ammonia produced 1,2-diphenylcyclobutene (IV) in excellent yield. 1,2-Diphenylcyclobutene (IV) was easily reduced to *cis*-1,2-diphenylcyclobutane (V), which in turn was isomerized readily with potassium *t*-butoxide in dimethyl sulfoxide to *trans*-1,2-diphenylcyclobutane (VI). The stereochemistry of V and VI was assigned from their method of preparation and from their nmr spectra.

We have recently found that treatment of either *cis*- or *trans*-2,5-diphenyltetrahydrothiophene dioxide with ethylmagnesium bromide produced 1,2-diphenylcyclobutene (IV) in moderate yield. Consideration of the possible mechanisms of this reaction led us to believe that reaction of 1,4-dichloro-1,4-diphenylbutane (III) with sodium amide would also yield 1,2-diphenylcyclobutene (IV).[2] This seemed particularly probable in view of the synthesis of α,α'-dimethylstilbene from α-phenylethyl chloride and sodium amide by Hauser and co-workers.[3]

A mixture of *meso*- and *dl*-1,4-dichloro-1,4-diphenylbutane (III) was easily prepared from dibenzoylethane (I) by the reactions shown in the accompanying equations. Reduction of dibenzoylethane (I) with sodium borohydride gave, in excellent yield, only the low-melting isomer of 1,4-diphenyl-1,4-butanediol (II), mp 90.5–92°. This was converted into a mixture of *meso*- and *dl*-1,4-dichloro-1,4-diphenylbutane (III) with anhydrous hydrogen chloride in acetic acid. The mixture could be separated into the pure *meso* and *dl* isomers, mp 106–107.5 and 36.5–38.5°, respectively,[4] by crystallization from ethanol. However, for the preparation of 1,2-diphenylcyclobutene the crude mixture of isomers gave yields comparable with those from the pure isomers. (See Scheme I.)

Reaction of 1,4-dichloro-1,4-diphenylbutane (III) with sodium amide yielded 1,2-diphenylcyclobutene (IV) in 89% yield. The structure of IV was established by analysis, by comparison of its ultraviolet spectrum with that of related compounds,[5] from its nmr spectrum, and by oxidation to dibenzoylethane (I). The most intense peak in the mass spectrum of IV corresponded to the molecular ion (206) of IV or the molecular ion of 2,3-diphenylbutadiene. The physical properties of IV correspond very well with those subsequently reported for 1,2-diphenylcyclobutene synthesized by alternate methods.[2]

The formation of 1,2-diphenylcyclobutene (IV) from 1,4-dichloro-1,4-diphenylbutane (III) probably proceeds by an intramolecular S$_N$2 displacement reaction similar to that shown to occur during the for-

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(2) (a) A preliminary report of this work has been published: R. M. Dodson and A. G. Zielske, *Chem. Commun.*, 353 (1965). Since our report, publications describing three different syntheses of 1,2-diphenylcyclobutene have appeared: (b) M. S. Newman and G. Kaugers, *J. Org. Chem.*, **30**, 3295 (1965); (c) E. H. White and J. P. Anhalt, *Tetrahedron Letters*, 3937 (1965); (d) M. A. Battiste and M. E. Burns, *ibid.*, 523 (1966).

(3) W. R. Brasen, S. W. Kantor, P. S. Skell, and C. R. Hauser, *J. Am. Chem. Soc.*, **79**, 397 (1957).

(4) The stereochemistry of *meso*-1,4-dichloro-1,4-diphenylbutane, mp 106–107.5°, and *dl*-1,4-dichloro-1,4-diphenylbutane, mp 36.5–38.5°, was assigned from the stereochemistry of the respective *cis*- and *trans*-2,5-diphenyltetrahydrothiophenes obtained from them on treatment with Na$_2$S. This work will be reported in a future publication.

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