Bicyclo[2.1.1]hexane. Preparation and Photochlorination

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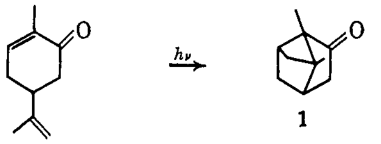
Abstract: A simple method for the preparation of bicyclo[2.1.1]hexane, which is based on the mercury ($^3P_1$) sensitized isomerization of 1,5-hexadiene, is described. Photochlorination of bicyclo[2.1.1]hexane in the gas phase, in solution in carbon tetrachloride or trifluorotrichloroethane, or as pure liquid, led to more than 95% of a single monochloride in good yield. Evidence to show that this compound is 2-chlorobicyclo[2.1.1]hexane is presented. Further chlorination gave 2,2-dichlorobicyclo[2.1.1]hexane and *trans*-2,3-dichlorobicyclo[2.1.1]hexane as products.

The earliest report of the synthesis of a bicyclo[2.1.1]hexane derivative (**1**) can be found in the literature in 1909[1] although the structure of the product was established as such only in 1957 by Büchi and Goldmann.[2] The reaction is an internal photocycloaddition of one double bond to another in a 1,5-hexadiene (eq 1). The possibility of preparing bicyclo[2.1.1]hexane (**2**) itself by this method was demonstrated in 1963.[3] Recently, Charlton, de Mayo, and Skattebol,[4] as well as Bond, Jones, and Scerbo,[5] have further shown the utility of this method by preparing **4** and **6** from the corresponding 1,5-hexadiene derivatives **3** and **5**.



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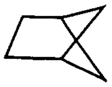
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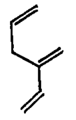
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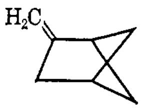

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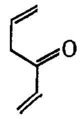

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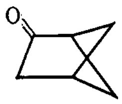

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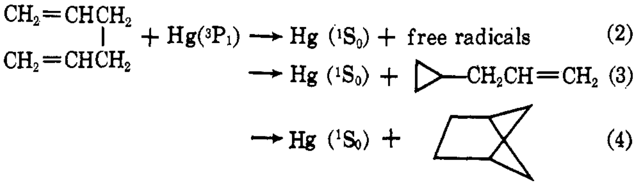
In studies on the chemistry of bicyclo[2.1.1]hexane and its derivatives, the synthetic method that has invariably been used is the photochemical ring contraction of α-diazo ketones derived from bicyclo[2.2.1]heptane and bicyclo[3.1.1]heptane by the Wolff rearrangement, a method that was first demonstrated by Horner and Spiestchka.[6] The statement has been made that this is the "only method of demonstrated general utility."[7] In the examples that have been reported, the photochemical ring contraction itself proceeds in 50% yield at best, but, since the diazo ketone that is the reactant is not generally available, it has to be made from readily available starting materials in two more steps of 50% over-all yield. It would appear that there is considerable need for additional synthetic methods to the bicyclo[2.1.1]hexane system from commercial starting materials and by procedures which can be operated on a reasonable scale. In this article, procedures for the preparation of bicyclo[2.1.1]hexane and some of its chloro derivatives are described. In subsequent articles, the introduction of other functional groups in the ring system will be described.

Results

Synthesis of Bicyclo[2.1.1]hexane. Earlier work[3] had shown that the mercury ($^3P_1$) sensitized isomerization of 1,5-hexadiene gives rise to three processes, the relative yields of which are strongly pressure dependent. These processes can be represented by eq 2, 3, and 4. Since



an increase in pressure favored reaction 4 over 2 and 3, the best yield of bicyclo[2.1.1]hexane can obviously be obtained by operating at the maximum total pressure possible. In order to avoid the use of pressure equipment with quartz windows, which would have greatly reduced the appeal of this synthesis to an organic chemist, the operating pressure was chosen as 1 atm, and the system was held at the boiling point of 1,5-hexadiene, *i.e.*, 59°. By refluxing the 1,5-hexadiene through a quartz reactor, which was surrounded by mercury resonance lamps, it was possible to use as much as 2 moles of 1,5-hexadiene at one time. Under these conditions the relative importance of reactions 2, 3, and 4 were in the ratio of 0.3:1:1 while approximately one-tenth of the internal cycloaddition gave bicyclo[2.2.0]hexane. The yield of bicyclo[2.1.1]hexane was affected by the secondary attack of the radicals that were produced in reaction 2 on 1,5-hexadiene. From the photolyzate, the bicyclo[2.1.1]hexane (95% pure) could be readily isolated by two successive distillations. Its yield was 18–20% in several runs in which 0.5–2 moles of 1,5-hexadiene was used.

Photochlorination of Bicyclo[2.1.1]hexane. Reaction of bicyclo[2.1.1]hexane with chlorine in the presence of light was studied under a variety of conditions. The products that were isolable in these reactions were always the same monochloride and mixture of dichlorides. The monochloride appeared to be made up of at least 95% of one single compound on three different gas chromatographic columns. The formula C_6H_9Cl was indicated by analysis, and the molecular weight showed that the compound was monomeric.

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(1) G. Ciamician and P. Silber, *Chem. Ber.*, **41**, 1928 (1908).

(2) G. Büchi and I. M. Goldmann, *J. Am. Chem. Soc.*, **79**, 4741 (1957).

(3) R. Srinivasan, *J. Phys. Chem.*, **67**, 1367 (1963).

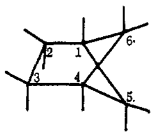
(4) J. L. Charlton, P. de Mayo, and L. Skattebol, *Tetrahedron Letters*, 4679 (1965).

(5) F. T. Bond, H. L. Jones, and L. Scerbo, *ibid.*, 4685 (1965).

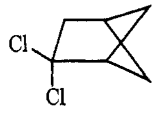
(6) L. Horner and E. Spietschka, *Chem. Ber.*, **88**, 934 (1955).

(7) J. Meinwald and J. K. Crandall, *J. Am. Chem. Soc.*, **88**, 1292 (1966).

It could be reduced to bicyclo[2.1.1]hexane in 47% yield with sodium and *n*-butyl alcohol, which indicated that the bicyclic ring system had not rearranged during chlorination. The nmr spectrum (in τ) consisted of a doublet at 5.61 (J = 6 cps, 1 proton), a complex pattern centered at 7.4 (2 protons), another doublet at 7.82 (1 proton), another complex pattern centered at 8.35 (4 protons), and a triplet at 9.0 (1 proton). The chlorine atom can be in the 1,2,5-*endo* or 5-*exo* positions. Since the absorption at τ 5.61 can only be ascribed to a proton on a carbon with chlorine attached to it, the tertiary position 1 is excluded. The choice among the remaining three positions can be made from the nmr spectra of the dichlorides.



Analysis of the two dichlorides that were observed to be derived from the monochloride indicated the molecular formula to be $C_6H_8Cl_2$; both showed no unsaturation. The first dichloride (mp 11.5°) had no absorption in its nmr spectrum at τ <6.8. There was a sextet at τ 7.0 (1 H), a broad absorption at τ 7.4 (3 H), and another complex pattern centered at τ 8.2 (4 H). Obviously, this dichloride has no H–C–Cl grouping which means that it must be 2,2-dichlorobicyclo- (**7**) or 5,5-dichlorobicyclo[2.1.1]hexane (**8**). The protons in bicyclo[2.1.1] hexane at the bridgehead positions (1 and 4) have usually been observed to occur at smaller τ values than protons in the 5-*exo* and 5-*endo* positions when the chemical shifts owing to substituent groups are taken into account. The odd proton at τ 7.0 is probably located on one bridgehead carbon, which requires that the $>CCl_2$ group not lie on a plane of symmetry between the two bridgeheads. This effectively rules out structure **8** and therefore the first dichloride is most probably **7**.



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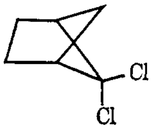

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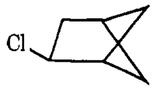
The monochloride which is the precursor for **7** must then be 2-chlorobicyclo[2.1.1]hexane (**9**). Other monofunctional bicyclo[2.1.1] hexanes with a substituent in the 2 position have been reported.[7] These are the alcohol **10** and two of its derivatives. The nmr spectrum of **10** also consisted of a 1-proton doublet at τ 5.68 (J = 6 cps), a broad 2-proton singlet at τ 7.58 (bridgehead protons), and a complex series of peaks between τ 7.8 and 9.3. The splitting of the single proton at *ca.* τ 5.6 agrees well with the monochloride **9** in the present instance.



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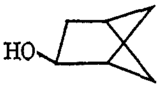

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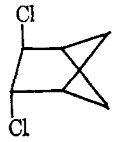
The 5-*endo* proton in the bicyclo[2.1.1]hexane structure is known to occur at *ca.* τ 9.0.[8] The fact that in 2-chlorobicyclo[2.1.1]hexane there is only one proton at τ 9.0 shows that a chlorine atom in the 2 position causes a chemical shift in one of the *endo* protons in the 5 or 6 positions. In the dichloride **7** both of the *endo* protons have been chemically shifted since absorption ceases at τ 8.45.

The second dichloride showed a singlet at τ 5.75 (2 H), a broad singlet at τ 7.3 (2 H), and a complex absorption centered at τ 8.2 (4 H). The first pair of protons indicated that the molecule has two Cl–C–H groups, while the second pair of protons showed that the chlorine atoms are symmetric to the bridgehead protons. The near identity of the four protons at *ca.* τ 8.2 in position and structure in both dichlorides indicates that the 5 and 6 positions of the two molecules are affected very similarly by the chlorine atoms. Thus, the second dichloride is most probably *trans*-2,3-dichlorobicyclo-[2.1.1]hexane (**11**). The *cis* structure would not leave the 5 and 6 positions equivalent and was therefore not favored. The sextet at τ 7.0 in the first dichloride deserves further comment. It was made up of two triplets which showed couplings of 8, 2, and 2 cycles. In 2,2-dichlorobicyclo[2.1.1]hexane (**7**), the only proton pair in an unsymmetrical position with respect to the chlorines is that at the bridgeheads. In this, the proton in the 1 position would couple to the two *exo* protons (J = 2 cps) on the 1-carbon bridges, as shown by Meinwald and Lewis.[8] However, the larger coupling of 8 cycles could come only from a coupling between the two bridgehead protons. This large coupling between protons across the cyclobutane ring is reminiscent of the coupling of 7 cps that exists between the *endo* protons which was also first described by Meinwald and Lewis.[8] The other bridgehead proton, which may be expected to show a more complex structure owing to the methylene group in the 3 position, is unfortunately masked by the two methylene protons.



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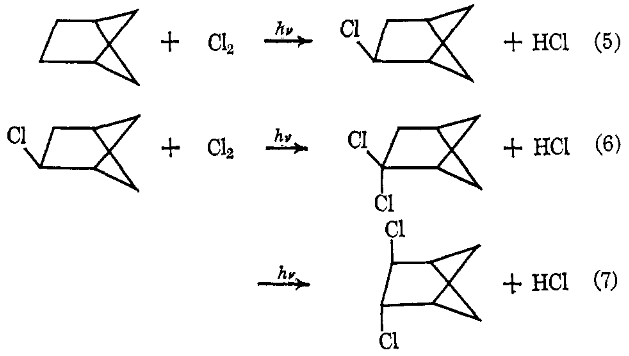
Rate Studies. From a study of the photochlorination of **9**, it was first established that photochlorination of bicyclo[2.1.1]hexane gave principally the monochloride **9**, and that the dichlorides **7** and **11** appeared on further chlorination of **9**. Considerable effort was



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(8) J. Meinwald and A. Lewis, *J. Am. Chem. Soc.*, **83**, 2769 (1961). It may be noted that the couplings between bridgehead protons in bicyclo[2.2.1]heptane and bicyclo[1.1.1]pentane are 1.5 and 18 cps, respectively. (R. W. King and P. E. Butler, Abstracts, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1962, p 84Q; K. B. Wiberg, *et al.*, *Tetrahedron*, **21**, 2749 (1965).)

made to establish if eq 5 is the *exclusive* reaction between bicyclo[2.1.1]hexane and chlorine in the presence of light. The problem was complicated by the rapidity with which monochlorobicyclo[2.1.1]hexane reacted with chlorine and the fact that **7** and **11** were *not* the major products of that reaction (see below). Only a lower limit of 0.8 can be placed on the fraction of bicyclo[2.1.1]hexane that appears as **9** relative to the disappearance of the hydrocarbon. The fraction can well be unity.

The dichlorides that appeared on the photochlorination of **9** accounted for only one-third of the monochloride that disappeared. In addition to **7** and **11** there was a third dichloride which was not identified. The relative amounts of the three were 2,2-dichloro:*trans*-2,3-dichloro:unknown::0.35:0.53:0.12. The ratio was not noticeably affected by a change in the reaction conditions as described in the Experimental Section.

The rates of photochlorination were determined relative to the formation of chlorocyclohexane from cyclohexane in the same solution. These ratios were $k_{\text{cyclohexane}}/k_{\text{bicyclohexane}} = 1.25$ and $k_{\text{cyclohexane}}/k_{\text{2-chlorobicyclohexane}} = 0.7$. Neither ratio has been "adjusted" for the actual number of reactive sites (*e.g.*, methylene groups in the first case) in each molecule. In the case of 2-chlorobicyclohexane, the rate of formation of the dichlorides alone is considered. The ratio

$$\frac{\text{rate of disappearance of 2-chlorobicyclohexane}}{\text{rate of disappearance of bicyclo[2.1.1]hexane}}$$

from these relations = $(3 \times 1.25)/0.7 = 5.3$. The value which could be calculated from the photochlorination of bicyclo[2.1.1]hexane alone to a conversion at which 2-chlorobicyclo[2.1.1]hexane had passed its maximum concentration agreed well with this figure.

Discussion

The details of the primary processes in the mercury-photosensitized reactions of 1,5-hexadiene have been pointed out before.[3] The present work shows that this method for the preparation of bicyclo[2.1.1]hexane is practical and competes favorably with the two other methods[9,10] that have been reported for the preparation of this compound.

Photochlorination of strained bicyclic systems has been shown to lead to substitution with retention of the bicyclic carbon skeleton in at least two instances. These are bicyclo[2.2.1]heptane (norbornane) which was investigated by Kooyman and Vegter,[11] and spiropentane which was studied by Applequist, Fanta, and Henrikson.[12] The case of bicyclo[2.2.1]heptane bears close resemblance to the present study of bicyclo[2.1.1]hexane. In both molecules, chlorine substitution occurs neither at the bridgehead nor at the shorter carbon bridge, but at the 2-carbon bridge by a preference better than 95%. In bicyclo[2.2.1]heptane this substitution can give rise to two monochlorides, but in bicyclo[2.1.1]hexane that possibility does not exist because the 2-carbon bridge lies on a plane of symmetry in the molecule. As suggested by Kooyman and Vegter,[11] for bicycloheptane, the strain at the site at which a free radical may be produced in the chlorination probably determines the selectivity of the substitution.

The relative rates for the substitution of cyclohexane and bicyclo[2.1.1]hexane seem to follow a surprising trend, indications of which are to be seen in bicyclo[2.2.1]heptane.[11] The value of $k_{\text{cyclohexane}}/k_{\text{bicyclohexane}}$ when multiplied by one-third to correct for the number of available methylene groups in each molecule yields a figure of 0.42 which may be compared with the value of 0.7 bicyclo[2.2.1]heptane near room temperature when chlorine gas and ultraviolet light are used.[13] Thus, the reactivity of the methylene group which undergoes substitution seems to increase with the strain in the system.

The relative rate of substitution of 2-chlorobicyclo[2.1.1]hexane also shows an acceleration for which no explanation can be offered at present. However, the pattern in the formation of the 2,2-dichloro and 2,3-dichloro compounds seems to follow conventional ideas of disubstitution in chlorinated compounds.[14]

Experimental Section[15]

Synthesis of Bicyclo[2.1.1]hexane. The irradiation apparatus consisted of a cylindrical quartz tube, 8 cm in diameter and 40 cm long, which was connected at one end to a reflux consenser and at the other end to a round-bottomed flask. In a typical experiment, 1,5-hexadiene (57 g, 0.7 mole) was placed in the flask along with mercury (4–5 g) and a few boiling chips. The flask was heated so that vapors of 1,5-hexadiene and mercury ascended the quartz tube and refluxed back from the condenser. The quartz tube was surrounded by 16 low-pressure mercury resonance lamps which had a combined output of 64 w of ultraviolet light.[16] After 115 hr of irradiation, the reaction was stopped, and the contents of the flask were distilled on a spinning-band column. The following cuts were collected: (i) bp <62°, 3.05 g; (ii) bp 62–68°, 10.05 g; (iii) bp 68–74°, 7.30 g; (iv) bp 74–84°, 1.75 g. The bicyclo[2.1.1]hexane was distributed among the second, third, and fourth fractions. These were refractionated to give bicyclo[2.1.1]hexane (bp 71°, 8.7 g, 18%) and bicyclo[2.2.0]hexane (bp 80°, 0.8 g, 2%). From fractions i, ii, and iii unreacted 1,5-hexadiene (6.7 g) can be recovered. The same fractions also contained allylcyclopropane which was not collected. Its amount can be estimated by difference to be about 6 g (12%).

Photochlorination of Bicyclo[2.1.1]hexane to the Monochloride. Bicyclo[2.1.1]hexane (3.8 g, 46 mmoles) dissolved in CCl_4 (5 ml) was kept in a 50-ml test tube fitted with an inlet tube that reached below the liquid level and a reflux condenser. A 75-w tungsten lamp was placed 16–18 cm from the solution. The flow of chlorine was regulated so that it did not accumulate in the solution and turn it yellow. The solution was sampled at 30-min intervals to watch for the buildup of the monochloro and the dichloro products. When the former started to level off (150 min), the reaction was stopped, and the contents were distilled. The fraction boiling between 70 and 80° contained all of the CCl_4 and unreacted bicyclohexane. This was chlorinated again until the formation of monochloro product flattened out again. A second distillation and a reirradiation of the first fraction were sufficient to carry the reaction to 75% completion. The combined photolyzate was distilled through a Vigreux column to give three cuts. The first, bp 70–80°, contained all of the unreacted bicyclo[2.1.1]hexane along with the CCl_4. It was fractionated on a spinning-band column to give unreacted bicyclo[2.1.1]hexane (0.95 g). The

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(9) R. Srinivasan, *J. Am. Chem. Soc.*, **83**, 2590 (1961).

(10) K. B. Wiberg, B. R. Lowry, and T. H. Colby, *ibid.*, **83**, 3998 (1961).

(11) E. C. Kooyman and G. C. Vegter, *Tetrahedron*, **4**, 382 (1958).

(12) D. E. Applequist, G. F. Fanta, and B. W. Henrikson, *J. Am. Chem. Soc.*, **82**, 2368 (1960).

(13) From ref 11, the values for $k_{\text{cyclohexane}}$ and $k_{\text{norbornane}}$ are found to be 1.01×0.67 and 1.27×0.67, respectively. The value at 25° was estimated from these two figures.

(14) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 362.

(15) Infrared spectra were obtained on a Perkin-Elmer Infracord instrument. Nmr spectra were obtained on a Varian A 60-A spectrometer; solvent, $CDCl_3$; tetramethylsilane as internal standard. Microanalysis by Microtech Laboratories, Skokie, Ill.

(16) A commercial light source of this design with twice the output of ultraviolet light is available from the Southern New England Ultraviolet Co.

second fraction (bp 134–136°) was better than 95% monchloride (3.2 g, 80%). It could be used as such for further reaction. On vpc examination (Silicone oil column 20 ft, or Ucon-550 column 6 ft, or diisodecyl phthalate column 6 ft) the material was found to consist of three monochlorides which were in the ratio 2.5:95.0:2.5. The major component was separated by chromatography, The minor components were not identified. The purified monochloride, n^{25}D 1.4725, had strong infrared absorptions (μ, neat liquid) at 3.35, 7.78, 10.85, and 14.10; mol wt 116, 118 (mass spectrometry). (For the nmr spectrum, see Results.) *Anal.* Calcd for C_6H_9Cl: C, 61.79; H, 7.78; Cl, 30.40. Found: C, 61.83; H, 7.73; Cl, 30.28.

From the residue, two dichlorides could be separated by vapor phase chromatography.

2,2-Dichlorobicyclo[2.1.1]hexane gave the following data: mp 11.5°; $n^{25.5}$D 1.4885; infrared spectrum (μ, neat liquid) 3.33, 10.45, and 13.45. *Anal.* Calcd for $C_6H_8Cl_2$: C, 47.72; H, 5.34; Cl, 46.96. Found: C, 47.83; H, 5.33; Cl, 46.92.

***trans*-2,3-Dichlorobicyclo[2.1.1]hexane** showed bp 158–160°; infrared spectrum (μ, neat liquid) 3.30, 7.77, 12.10, and 13.20.

Anal. Calcd for $C_6H_8Cl_2$: C, 47.72; H, 5.34; Cl, 46.96. Found: C, 47.57; H, 5.47; Cl, 46.85.

Chlorination can also be carried out in neat bicyclo[2.1.1]hexane or in trichlorotrifluoroethane solution. The composition of the monochloride and the yields were comparable. The principal advantages in using a solvent are: (i) the loss of bicyclo[2.1.1]-hexane through vaporization is reduced; and (ii) in distilling the partially chlorinated material, the solidification of the bicyclo-[2.1.1]hexane does not cause difficulties. CCl_4 is a better solvent than $C_2Cl_3F_3$ since its boiling point is closer to that of bicyclo-[2.1.1]hexane.

Chlorination at the boiling point of CCl_4 did not give a different distribution of monochlorides. There was some indication that the bicyclo[2.1.1]hexane underwent decomposition.

Chlorination in the vapor phase was carried out in a 1-l. Pyrex flask which was filled successively with bicyclo[2.1.1]hexane vapor and chlorine gas. Oxygen was carefully excluded. On exposure to a source of 3130 A, the reaction was over in a few seconds when a 1:1 ratio of materials was used. When the chlorine ratio was increased to 2:1, the reaction produced a blue flame. Mixtures of mono- and dichlorides, and carbon were produced.

Reduction of 2-Chlorobicyclo[2.1.1]hexane. *n*-Butyl alcohol (20.0 g) and 2-chlorobicyclo[2.1.1]hexane (1.0 g, 8.6 mmoles) were heated under nitrogen in a 100-ml flask equipped with a condenser. To the boiling solution sodium (2.0 g, 87 g-atoms) cut into small pieces was added over a period of 30 min. Reflux was maintained for an additional hour. Most of the liquid was then removed by distillation. Due to the high solid content, the mixture had to be stirred during this operation. An additional quantity (5 ml) of butyl alcohol was added to the almost solid residue and distilled out. The combined distillates were fractionated through a 10-cm column packed with glass beads. The first fraction (bp 70–105°, 0.57 g) contained all of the bicyclo[2.1.1]hexane. A small portion of the hydrocarbon was separated by vpc. It was found to be identical with the authentic material in its melting point, retention time, and infrared spectrum, total yield (calculated by calibrating the vpc for bicyclo[2.1.1]hexane) 47%.

Rate Studies. Standard solutions (solvent, CCl_4) of bicyclo-[2.1.1]hexane and cyclohexane in equimolar ratio as well as 2-chloro-bicyclo[2.1.1]hexane and cyclohexane in equimolar ratio were prepared. Chlorinations were carried out with chlorine gas in the presence of a 75-w tungsten lamp. No special effort was made to degas the solution before irradiation, but the positive pressure of chlorine and HCl would have prevented additional oxygen from diffusing in.

Analyses were carried out by vpc (Ucon-550 X, 6-ft column) at several temperatures so that maximum resolution between the two reactants or products could be obtained. The rate of chlorination of bicyclo[2.1.1]hexane was followed both by the disappearance of the hydrocarbon (relative to C_6H_{12}) and the appearance of the monochloride (relative to $C_6H_{11}Cl$). The chlorination of C_6H_9Cl could be followed relative to the appearance of $C_6H_{11}Cl$. In a separate experiment the chlorination of C_6H_9Cl could be followed relative to its formation from C_6H_{10}. The three rates checked with each other within 25%.

Acknowledgment. The authors wish to express their gratitude to Dr M. Poutsma and Dr. E. B. Whipple of Union Carbide Research Institute, Tarrytown, N. Y., for much useful advice and many helpful discussions.

Anomalous Reductions of 7-Substituted Norbornadienes with Diimide[1a]

William C. Baird, Jr.,[1b] Boris Franzus, and John H. Surridge

Contribution from the Central Basic Research Laboratory, Esso Research and Engineering Company, Linden, New Jersey 07036. *Received September 6, 1966*

Abstract: The diimide reduction of several 7-substituted norbornadienes yields *anti*-7-substituted norbornenes rather than the corresponding *syn* isomers whose formation would be anticipated on the basis of theoretical and stereochemical considerations. Reductions utilizing deuteriodiimide yield deuterated *anti*-7-substituted norbornenes in which the deuterium atoms exhibit an *exo,exo* configuration. A similar reduction of the parent hydrocarbon, norbornadiene, also involves the introduction of *exo*-deuterium. Competitive diimide reductions show that this preferential reduction is characteristic of the *syn* double bond of 7-substituted norbornenes as well as that of 7-substituted norbornadienes.

As part of a study of the chemistry of 7-substituted norbornadienes and norbornenes, convenient syntheses for the *syn* and *anti* isomers of the latter compounds were desired. Reasonable routes to these structures appeared to be the specific reduction of either the *anti* or the *syn* double bond of the corresponding norbornadienes[2] (eq 1) by means of the properly selected catalytic[3] or chemical reducing system. The reducing agent, diimide (N_2H_2), suggested itself as a useful reagent which, for stereochemical reasons, would selectively attack the *anti* double bond of 7-

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[1] (a) Presented in part at the 148th National Meeting of the American Chemical Society, Aug 1964, p 91S. (b) Enjay Chemical Intermediates Laboratory, Linden, N. J. 07036.

[2] These compounds may be readily prepared according to published synthetic procedures: P. R. Story, *J. Org. Chem.*, **26**, 287 (1961).

[3] B. Franzus, E. I. Snyder, and W. C. Baird, Jr., "Reductions In the 7-Substituted Norbornyl System; A Convenient Synthesis of *Syn*- and *Anti*-7-Substituted Norbornenes," in preparation; presented in part at the Regional Metropolitan American Chemical Society Meeting, New York, N. Y., Feb 1965.