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Photolysis of acetone has been used as a source of methyl radicals to study the abstraction of hydrogen atoms from bicyclo[2.1.1]hexane by methyl radicals. The reaction was found to have an activation energy of 10.3 kcal/mole and a pre-exponential factor that is typical of other abstraction reactions. The absolute rate of abstraction of hydrogen atoms from bicyclo[2.1.1]hexane by chlorine atoms at room temperature was measured to be 8.1×10^{10} l mole⁻¹ s⁻¹. The photochlorination of 1-methylbicyclo-[2.1.1]hexane in solution gave both the 1-chloromethyl and 2- or 3-chloro-1-methylbicyclohexanes. The relative rates of attack at the methyl and the 2- or 3-position were determined to be 1:2.1. It is pointed out that the rate parameters for the abstraction of an H atom from bicyclo[2.1.1]hexane by a methyl radical are slower than for cyclopentane, as would be expected for a highly strained hydrocarbon, whereas the abstraction by chlorine is slightly faster than the rate for cyclopentane.

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Introduction

The study of the chemistry of strained smallring compounds is of considerable interest in understanding the nature of chemical bonding. Quantitative data, on the basis of which correlations between strain and reactivity may be made, are not extensive. In this work we have obtained quantitative data on the abstraction of a hydrogen atom from bicyclo[2.1.1]hexane (1) by a chlorine atom or a methyl radical, and



competitive rates of chlorination of 1-methylbicyclo[2.1.1]hexane (2).

Experimental

Bicyclo [2.1.1] hexane was prepared by the photoisomerization of 1,5-hexadiene (1). Following distillation, it was partially chlorinated in order to remove all the unsaturated impurities, and finally purified by vapor phase chromatography. Its m.p. was 26.5°. 1-Methylbicyclo-[2.1.1] hexane was prepared by the photoisomerization of 2-methyl-1,5-hexadiene (2). It was purified in the same way as the bicyclo [2.1.1] hexane. Acetone (Mallinckrodt TR grade) was dried over Drierite and distilled *in vacuo* before use. Chlorine gas (Matheson Co.) was used as obtained in the solution phase experiments.

Apparatus

Materials

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> The photolysis of acetone vapor at 3130 Å was used as the source of methyl radicals. The light source was a Hanovia S-100 medium pressure mercury arc which was energized through a Sola constant voltage transformer.

The light beam was collimated, filtered with Pyrex glass (2 mm thickness), and admitted to the cylindrical quartz reaction cell of 9.3 cm length and 186.3 cc volume. The cell was placed in a furnace which was heated electrically. The temperature of the furnace was constant to $\pm 1^{\circ}$ during a run.

Procedure

Samples of acetone and bicyclo[2.1.1]hexane were measured in a calibrated part of the vacuum line and mixed together by condensation. The two compounds had boiling points which differed by only 15°. After photolysis, the mixture was separated into fractions by distillation. The fraction that was removed at liquid nitrogen temperature was found to consist of methane and CO. It was analyzed quantitatively by mass spectrometry. A second fraction which was removed at -156° was ethane only. The residue was analyzed by vapor phase chromatography. Three product peaks were invariably present in the C₇ region and were identified as C₇H₁₂ compounds by mass spectrometry. Attempts to prepare them in substantial quantity for further identification proved fruitless.

Reaction of Cl(3/2) with Bicyclo[2.1.1]hexane

These experiments were carried out by Davis and Braun¹ by the technique which has been described in detail elsewhere². The method involves the direct measurement of the concentration of chlorine atoms in the reaction system made up of chlorine gas and bicyclo-[2.1.1]hexane vapor by the change in the intensity of chlorine resonance fluorescence.

Photochlorination of 1-Methylbicyclo[2.1.1]hexane in Solution

The apparatus and procedure were exactly the same as in the earlier study (1) of the photochlorination of bicyclo[2.1.1]hexane in solution.

¹National Bureau of Standards. U.S. Department of Commerce, Washington, D.C.

²D. Davis and W. Braun, to be published.

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Results

 Reaction of CH₃· with Bicyclo[2.1.1]hexane The photolysis of acetone in the absence of addend yields methane and ethane by reactions
 and [2] only. Conditions for which this

[1]
$$CH_3 + CH_3COCH_3 \rightarrow CH_4 + CH_2COCH_3$$

$$[2] \qquad \qquad 2CH_3 \rightarrow C_2H_6$$

mechanism is valid are quite well established (3). The usual treatment (3) applied to data obtained in the interval 150 to 225° led to

$$\log k_1 / k_2^{\frac{1}{2}} = (4.2 \pm 0.9) - ((9200 \pm 500)/2.303RT)$$

in units of $1 \text{ mole}^{-1} \text{ s}^{-1}$. The Arrhenius parameters agree reasonably well with those recently obtained (4), even though the present data were taken at less than 20 mm pressure of acetone, and thus are near the low end of the "high pressure" region discussed by Shaw and Toby (4). This pressure was chosen to permit the slow abstraction from bicyclo[2.1.1]hexane to compete when the hydrocarbon was present. Under those conditions, methane is also formed in reaction [3]

$$[3] \qquad CH_3 + C_6H_{10} \rightarrow CH_4 + C_6H_9$$

The usual treatment of the data gives $k_3 [C_6 H_{10}]/k_2^{\frac{1}{2}}$. These values at various temperatures have been plotted in the usual way in Fig. 1. The best line through the points, which was determined by least-squares analysis, corresponded to a value for $E_3 - \frac{1}{2}E_2$ of 10.3 ± 0.5 kcal/mole. Using the expression $k_2 = 2 \times 10^9 T^{\frac{1}{2}}$ l mole⁻¹ s⁻¹ (4), the value of log A_3 can be calculated to be 8.7 in the same units.

2. Reaction of Cl(3/2) Atoms with Bicyclo-[2.1.1]hexane

This reaction was studied at room temperature at 2 different pressures of bicyclo [2.1.1] hexane. The bimolecular rate constant was 8.13×10^{10} l mole⁻¹ s⁻¹, with an uncertainty of $\pm 10\%$.

3. Photochlorination of 1-Methylbicyclo[2.1.1]hexane in Solution

In preparative experiments, it was found that photochlorination of 1-methylbicyclo[2.1.1]hexane gave 2 monochloro products in about 20% yield. The products were separated by



FIG. 1. Arrhenius plot for the abstraction of hydrogen atoms from bicyclo[2.1.1]hexane by methyl radicals. The ordinate should be multiplied by 8.00×10^{-5} to convert to units of l[±] mole^{-±} s^{-±}.

vapor phase chromatography. The first product, amounted to a third of the total monochloro compounds, was analyzed as follows.

Anal. Calcd. for $C_7H_{11}Cl$: C, 64.37; H, 8.49. Found: C, 64.61; H, 8.55.

It had an intense infrared absorption at 724 cm⁻¹ (C—Cl) and no strong absorption between 1350 and 1400 cm⁻¹, showing the absence of a CH₃ group. Its nuclear magnetic resonance (n.m.r.) spectrum consisted of a singlet 6.31 τ (2H), a broad absorption at 7.58 τ (1H), and a complex absorption from 8.1 to 9.0 τ which accounted for the remaining protons. The material could be reduced with sodium and ethanol to regenerate 1-methylbicyclo [2.1.1] hexane. This showed that the chloro compound had the same carbon skeleton as 1-methylbicyclo[2.1.1]hexane. The absence of a methyl absorption in the infrared, coupled with the unsplit absorption at 6.31 τ due to 2 protons, indicates that the chlorine was most probably in a CH₂Cl group adjacent to a carbon with no protons on it. The structure 3 would fit all of these observations. The remainder of the monochlorinated product is believed to be a mixture of possibly 2 com-

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SRINIVASAN AND SONNTAG: ABSTRACTION OF H ATOMS FROM BICYCLO[2.1.1]HEXANE

TABLE I

Ratio of rate of formation of (4+5) to 3 during photochlorination in solution*

Run no.	Temper- ature, °C	No. of determinations averaged	$\frac{R_{4+5}}{R_3}$	Remarks
$\frac{1}{2}$	5	5 7	2.1	Conversion at the end 14%
3	32	4	2.2	Rate of chlorocyclohexane formation/ $R_{(4+5)} \sim 2.3$

*Solvent: CCl₄; visible light (tungsten lamp).



pounds, although it could not be resolved into 2 peaks on a gas chromatograph.

Anal. Calcd. for C₇H₁₁Cl: C, 64.37; H, 8.49; Cl, 27.14. Found: C, 64.34; H, 8.47; Cl, 27.37.

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Its infrared spectrum showed a medium absorption at 1365 cm^{-1} (CH₃—) and an intense one at 710 cm⁻¹ (C-Cl). There was no evidence of unsaturation. In the n.m.r. spectrum there was no absorption > 5.5τ . There was an absorption at about 5.7 τ which had 1/11 of the total intensity of the spectrum. The remaining absorptions formed a complex pattern from 7.3 to 9.1 τ. In 2-chlorobicyclo[2.1.1]hexane, the proton on the 2-carbon occurs at 5.7τ as a doublet with a splitting of 7 cycles (1). In the present case, the absorption at 5.7τ was made up of a pair of doublets 17 cycles apart, each of which had a separation of 7 cycles. This material was most probably a mixture that was made up of nearly equal amounts of 4 and 5, since extrapolation from earlier results on the photochlorination of bicyclo[2.1.1]hexane indicated that substitution in the ring in 2 would occur almost exclusively in the 2- and/or 3-positions (1).

The results of quantitative studies are given in Table I. The study was complicated by the fact that the $C_6H_{11}Cl$ compounds reacted much

more rapidly with chlorine than with hydrocarbon so that the conversion had to be kept low. At the same time, only 16-20% of the hydrocarbon that disappeared was observed to lead to **3**, **4**, and **5**. The ratio of **3** to **4** + **5** (*i*) could be consistently reproduced, (*ii*) held constant over conversions which ranged from 0 to 20%, and (*iii*) was the same at 5 and 32° . Owing to experimental problems in separating 1-methylbicyclo-[2.1.1]hexane from cyclohexane in the gas chromatograph, it was not possible to obtain accurate data on the relative rates of monochlorination of these two compounds. The result of only one run is included in Table I.

Discussion

In an earlier investigation on the photochlorination of bicyclo[2.1.1]hexane in solution (1), it was observed that (i) the chlorination was highly selective since better than 95% of the attack occurred at only one of 4 possible sites in the molecule, and (ii) the rate of monochlorination was comparable to the rate of monochlorination of cyclohexane, which meant that on a per atom basis, the C-H bond in the 2-position in bicyclo[2.1.1]hexane was slightly more reactive than a C-H bond in cyclohexane. Both these observations are considered unusual (5), in reference to what is known of the photochlorination of linear, aliphatic compounds. Bicyclo[2.1.1]hexane should, strictly speaking, be compared to other strained, bicyclic systems. It has already been noted (1) that the data on the photochlorination of bicyclo [2.2.1] heptane (6) also show the trends that are observed in bicyclo-[2.1.1]hexane.

The experiments undertaken in this study were intended to examine if

(*i*) The abstraction of a hydrogen atom from

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[4]

bicyclo[2.1.1]hexane by a radical other than chlorine (i.e. methyl) shows the trend that has been observed with the same radical and other strained hydrocarbons.

(*ii*) The absolute rate of reaction of chlorine atoms and bicyclo[2.1.1]hexane supports the contention that this rate is greater than that between chlorine atoms and a saturated, unstrained hydrocarbon.

(*iii*) In the photochlorination of 1-methylbicyclo[2.1.1]hexane, the chlorination in the 2- or 3-positions shows an acceleration in comparison to chlorination at the methyl group, which would serve as an internal reference for the reaction.

We shall analyze the present data in terms of these questions.

Accurate rate parameters for a large number of abstraction reactions of methyl radicals are known (7, 8). In a series of saturated hydrocarbons, which serve as the donor molecules, the activation energies increase as the C-H bonds go from tertiary to secondary and primary, while for similarly substituted C-H bonds, the activation energies increase with increasing strain in the molecules. The activation energies for abstraction from cyclopentane, cyclobutane, and cyclopropane (all of which contain only secondary C-H bonds) are 9.1, 10.1, and 12.9 kcal/ mole, respectively (8). In bicyclo [2.1.1]hexane, it is reasonable to assume that abstraction of a hydrogen atom will occur only in the 2-position, since even such an unselective agent as a chlorine atom will abstract hydrogen from only that position 95% of the time. Although the 2-position is part of a cyclopentane ring, the fusion of a second ring should increase the strain in the 5-membered ring. One may expect the activation energy for the abstraction of a hydrogen atom to be considerably more than that for a cyclopentane ring (strain energy ~ 6 kcal/mole), and comparable to that for a cyclobutane (strain energy 26.1 kcal/ mole) or a cyclopropane (strain energy 27.5 kcal/ mole) (9). The experimental value of 10.3 kcal/ mole for [3] indicates the considerable influence of strain on the activation energy. The A factor for [3] when reduced to a per "active hydrogen" basis is comparable to those for similar abstractions from cyclopropane, cyclobutane, and cyclopentane (8). These data strongly suggest that the C-H bond in the 2-position in bicyclo-[2.1.1] hexane behaves predictably as far as the abstraction reaction by methyl radicals is concerned³.

The absolute rate of the abstraction reaction [4] in the gas phase when RH is cyclohexane is

$$Cl + RH \rightarrow HCl + R$$

not known, but the rate with RH = cyclopentane has been found to be 8.35×10^{10}] $mole^{-1} s^{-1}$ at 25 °C (10). The relative rates of abstraction of a hydrogen from cyclopentane and bicyclo [2.1.1] hexane would hence be 1:0.97. On an "active hydrogen" basis, this ratio would be cyclopentane: bicyclo[2.1.1] hexane = 1:2.4. From the rates of photochlorination of cyclopentane and cyclohexane in solution, it is known (11) that⁴ abstraction from cyclopentane is 0.85(relative to cyclohexane as 1.00) per hydrogen at 68° and 0.95 at 0°. If, at 25°, this value is taken to be 0.9, and assumed to be applicable to the gas phase reaction, the ratio cyclohexane: bicyclo[2.1.1]hexane (on a per "active hydrogen" basis) would be 1:2.2. This compares favorably with the value of 2.4 that was found (1)by competitive chlorination of cyclohexane and bicyclo [2.1.1] hexane in solution. There seems to be no doubt that on the basis of per "active hydrogen", bicyclo[2.1.1]hexane is more reactive towards chlorine atoms than cyclohexane.

The photochlorination of 1-methylbicyclo-[2.1.1]hexane is obviously not a simple reaction as the yield of monochlorinated products is poor. A check of the consistency of the present values on chlorination, at two competitive sites within the molecule, against the earlier values on competitive attack on bicyclo[2.1.1]hexane and cyclohexane (if methylcyclohexane is used as a reference compound to provide a correlation between the two ring systems), showed that the

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³The trend has been found to persist in the more highly strained bicyclic hydrocarbons. The activation energy for the abstraction of a hydrogen by methyl radicals from bicyclo[1.1.1]pentane has been measured to be 11.2 kcal/ mole. It is likely that in the case of bicyclo[1.1.0]butane and bicyclo[2.2.0]hexane, the hydrocarbon may not survive the temperatures at which such competitive abstraction reactions can be studied.

⁴The reactivity of cyclopentane relative to cyclohexane is so nearly the same that there are other studies in the literature (5) that place cyclopentane ahead of cyclohexane on the reactivity scale. However, it seems to be agreed that the difference is no more than $\pm 10\%$, so that this is the correction that has to be applied in this investigation to the bicyclo[2.1.1]hexane value to take it from cyclopentane scale to the cyclohexane scale.

present results were not in quantitative agreement with the earlier work (1).

In conclusion, it is relevent to speculate on the cause of the increased reactivity of the hydrogen in the 2-position in bicyclo[2.1.1]hexane relative to cyclohexane. Since the experiments with methyl radicals show that the activation energy for abstraction does increase as would be expected, the activation energy for the abstraction process [5] may be expected to be about 200 cal/



mole greater than the value of 600 cal/mole that has been measured for cyclopentane (10). There is a similar increase in going from cyclopentane to cyclobutane. The resultant value of $\log A_5 =$ 11.4 would be outside the observed range of 9.7–10.6 for the values of $\log A$ for such reactions (10). There is no doubt that more data on reaction [5] over a range of experimental conditions are needed before these unusual effects can be explained.

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