2-Bromo-2,4-dimethyl-3-methoxycyclobutenone (XIV).—The bromo compound IX (0.2 g., 1 mmole) suspended in dry ether (15 ml.) was treated with a slight excess of diazomethane in ethereal solution. Evaporation of the solvent left a yellow oil which was purified by distillation on a "molecular still" at 47–50° (0.05 mm.). On exposure of the oil to the atmosphere for a short while, crystals of IX were deposited. Erratic analytical results were obtained for this compound, evidently as a result of its facile hydrolysis; infrared: λ_{max} (neat) 5.63 (s), 6.15 (s), 7.2 (s), 7.4 (s), 8.0 (s), 10.3 (s), 13.1 (m), 14.65 (m) μ.

# Small Ring Bicyclic Azo Compounds and Bicyclic Hydrocarbons. Isomerization of Bicyclo[2.1.0]pentane and Bicyclo[2.2.0]hexane

BY COLIN STEEL, ROBERT ZAND, PETER HURWITZ, AND SAUL G. COHEN

The first-order homogeneous thermal isomerizations bicyclo[2.1.0]pentane → cyclopentene, bicyclo[2.1.0]-pentane → 1,4-pentadiene, and bicyclo[2.2.0]hexane → 1,5-pentadiene have been studied in the temperature ranges 223–294°, 232–315°, and 130–210°. The frequency factors are $10^{14.1}$, $10^{14.4}$, and $10^{13.4}$ sec.$^{-1}$, respectively, while the activation energies are 45.6, 52.3, and 36.0 kcal. mole^{-1}. In all cases the reaction pressure was about 40 cm. The energetics of these reactions are compared with those of other small-ring hydrocarbons and with thermodynamic data. Estimates have been made of the activation energies for the various elementary reactions from which the over-all reactions may be regarded as compounded to see whether the mechanisms can better be approximated by stepwise or by concerted processes.

Introduction

In our study[1,2] of the kinetics of the thermal decomposition of the bridged bicyclic azo compounds, 2,3-diazabicyclo[2.2.1]-2-heptene (I) and 2,3-diazabicyclo[2.2.2]-2-octene (II), pyrolysis of I in the temperature range 130 to 180° led to bicyclo[2.1.0]pentane (III), as had been reported,[3] and pyrolysis of II in the range 199 to 259° gave 1,5-hexadiene (IV). The bicyclic
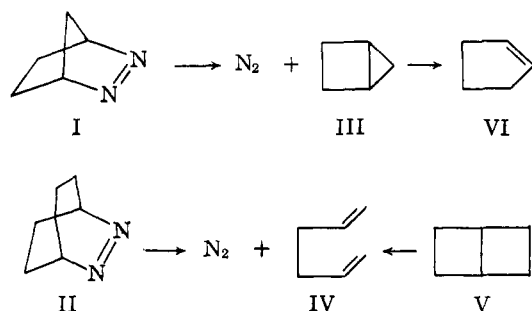
hydrocarbon III has been reported to be stable at 230° and to isomerize at 330° to cyclopentene (VI),[3] whereas V, which was obtained in low yield from the photolysis of bicyclo[3.2.0]heptanone-2, has been reported to isomerize to IV at 230°.[4] The absence of V as a product in the pyrolysis of II under the above experimental conditions is consistent with this latter isomerization. It seemed, therefore, of interest to examine the kinetics of the isomerization of III to cyclopentene, and to attempt the preparation of V and to examine its isomerization. While this work was in progress a study of the isomerization of III to cyclopentene was reported.[5] Our experiments were carried out over a wider temperature range, 223–294° as compared with 288–310°, and using a different technique. Although our results agree with and amplify those reported, our interpretations differ.

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(4) S. Cremer and R. Srinivasan, Tetrahedron Letters, No. **21**, 24 (1960).

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Experimental

Bicyclo[2.1.0]pentane (III).—The preparation of III was effected by pyrolysis of I for 15 hr. at 170°. From our earlier work[1] we know that this corresponds to 22 half-lives for the first-order decomposition of I. The infrared spectrum of III agreed exactly with that given by Criegee and Rimmelin,[3] while gas chromatographic analysis showed that this procedure gave less than 0.3% of VI as an impurity. The most satisfactory gas chromatographic column consisted of a series of two packings, 1 ft. of 20% (by weight) silicone oil Dow 710 on Chromosorb W followed by 3 ft. of 30% silver nitrate–ethylene glycol on Chromosorb W.[6] The nuclear magnetic resonance spectrum of III agreed exactly with that reported by Chesick.[7]

Bicyclo[2.2.0]hexane (V).—Small amounts of V (ca. 3 mg.) were prepared by the photolysis of carefully degassed samples of II (ca. 0.1 g.) using light from an Osram 100-w. high-pressure mercury arc which had been passed through a Corning 7-54 filter. Prolonged exposure (ca. 5 days) was necessary because of the strong fluorescence of II. The photolysis yielded a high boiling tarry product and a volatile liquid fraction. This liquid was analyzed by gas chromatography using the above-mentioned column and one consisting simply of 30% silver nitrate–ethylene glycol on Chromosorb W. In both cases three fractions in the ratio 0.16:0.11:0.73 were obtained. The short gas chromatographic retention time (r.t.) of the first fraction on the latter column indicated the absence of unsaturation. This was confirmed by the infrared spectrum, taken in the region 2–13 μ, which showed no absorption at 6.1 μ. Peaks were obtained at 3.44 (s), 3.53 (shoulder), 6.96 (w), 8.06 (w), and 10.96 (w) μ. With the exception of the weak absorption at 8.06 μ this agrees well with the spectrum for bicyclo[2.2.0]hexane reported by Cremer and Srinivasan[4]; viz., 3.46 (s), 3.52 (shoulder), 6.98, (w) and 11.0 (w) μ. It does not agree with the spectrum reported for bicyclo-[2.1.1]hexane.[8] Mass spectrometry (Bendix, ionizing voltage 70 e.v., trap current 0.2 μa.) showed that the mol. wt. was 82. The major peaks occurred at masses 27, 39, 41, 54, and 67, with relative intensities 55.5, 75.9, 92.6, 83.3, and 100. These data, together with the fact that the material isomerized readily to 1,5-hexadiene at temperatures above 130°, confirm that the product is indeed bicyclo[2.2.0]hexane. The major component of the liquid fraction from the photolysis (73%) was biallyl. It was characterized by its r.t. and infrared spectrum. The minor product had the same r.t. as cyclohexene.

Isomerization of Bicyclo[2.1.0]pentane (III) to Cyclopentene (VI).—The isomerization was carried out in two ways. (a) A sample of III (ca. 1 μl.) which had been purified by gas chromatography was transferred from the gas chromatographic fraction collector into a small thin-walled ampoule (0.25 cc.). The ampoule was then sealed under a vacuum of 10^{-5} mm. and placed in a rapidly stirred salt bath, the temperature of which was kept constant to ±0.05°. The temperature was read on an N.B.S.

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CHART I
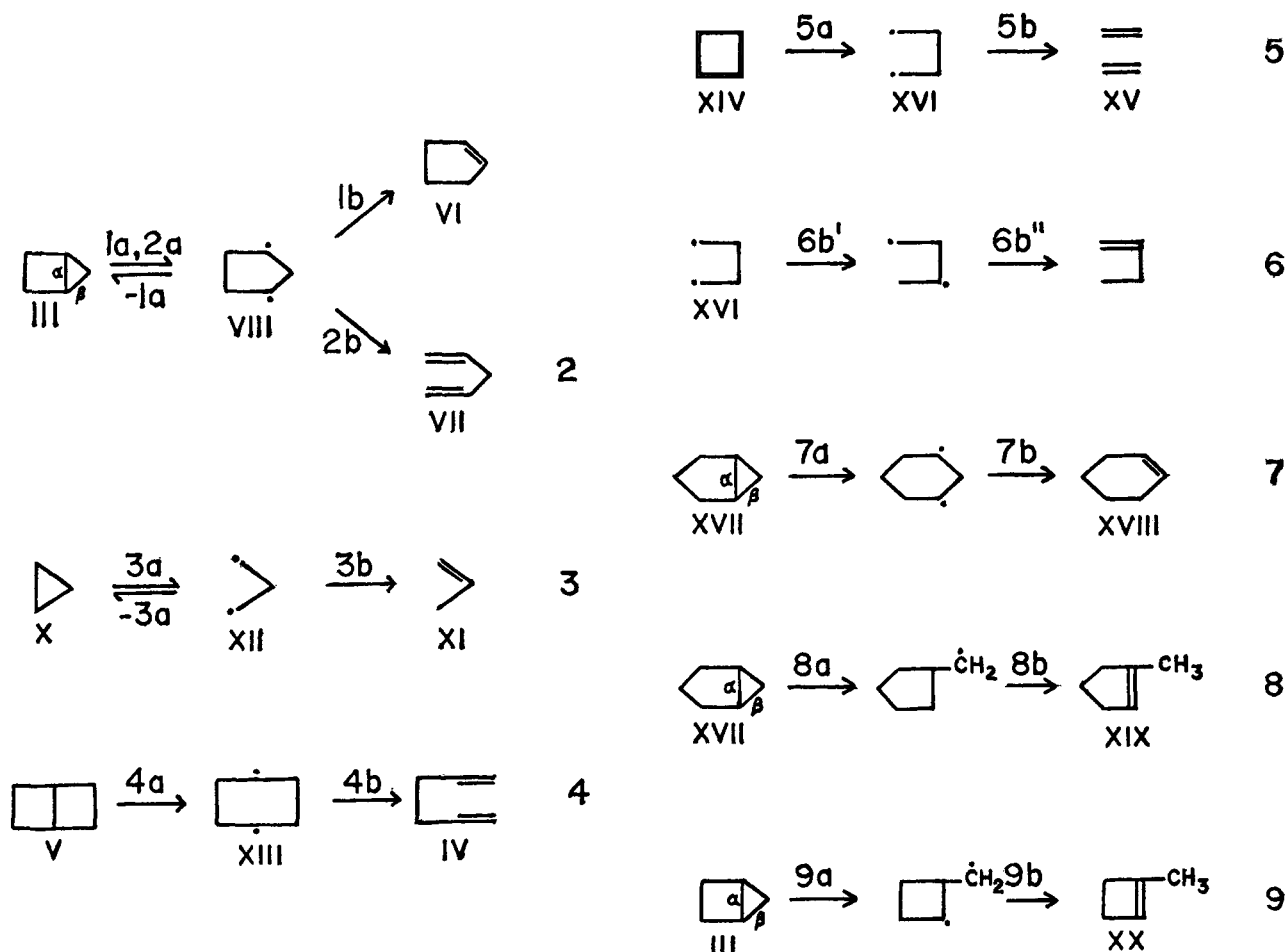
calibrated thermometer. After a given time the reaction was stopped by quenching the ampoule in ice water and the total contents of the ampoule were analyzed using a gas chromatograph fitted with an ampoule crusher at the entrance port. The analysis column was the silver nitrate–ethylene glycol–silicone oil column mentioned above. Peak areas were determined by means of an electronic integrator. Calibration with known mixtures of III and VI showed that both materials had the same sensitivity per mole with respect to the thermal conductivity detector. Thus experimental first-order rate constants could be determined directly from the ratio of the peak areas.

(b) About 1 mg. of I was placed in an ampoule which was then degassed and sealed. This sample was pyrolyzed for 15 hr. at 170° to produce nitrogen and III. The ampoule was then placed in the constant temperature bath to effect the isomerization of III to VI. Both methods gave identical results within experimental error. Subsequent work was done using method (b) since it was more direct. The nature of the product of isomerization, namely cyclopentene, was established by its retention time on various gas chromatographic columns and by its infrared spectrum.

Isomerization of Bicyclo[2.1.0]pentane (III) to 1,4-Pentadiene (VII).—Careful analysis indicated that the isomerization of III always yielded small amounts of VII. After several trials it was determined that the silicone oil–silver nitrate–ethylene glycol gas chromatographic column gave the best separation of traces of VII in the presence of excess III and VI. It was established that the pyrolysis of the azo compound I at temperatures below 200° produced no VII and that in the temperature range used VI did not isomerize to VII; therefore VII must be formed from III. Bicyclo[2.1.0]pentane (III), prepared by method (b) above, was isomerized in the temperature range 232 to 315° and the products analyzed by gas chromatography. The relative rates of formation of VI and VII were determined by integration of their respective peak areas. The product VII was characterized by its r.t. on the above-mentioned column and on an Apiezon J column. Furthermore, its infrared spectrum agreed exactly with an authentic sample of 1,4-pentadiene.

Isomerization of Bicyclo[2.2.0]hexane (V) to 1,5-Hexadiene (IV).—To carry out a kinetic run a given pressure of V, 1 cm., was vaporized from the storage vessel into a 10-cc. calibrated volume. The material was then transferred from this volume into a 0.25-cc. thin-walled ampoule and the ampoule sealed. The subse-

quent procedure and method of analysis were similar to those used in the isomerization of III. The nature of the product of isomerization, namely 1,5-hexadiene, was first reported by Cremer and Srinivasan.[4] This we confirmed by observing its characteristic r.t. on a variety of gas chromatographic columns.

Results and Discussion

The reactions to be considered are given in Chart I.

The Isomerization Reactions of Bicyclo[2.1.0]pentane (III).—Although the main isomerization of III is to VI (reaction 1), we were also able to detect a small amount (ca. 0.4%) of 1,4-pentadiene (VII) in the products (reaction 2). The formation of VII was not reported by Halberstadt and Chesick[5] presumably because this minor product was not separated from cyclopentene under their experimental conditions. The formation of VII may be expected since the pyrolysis of cyclobutane yields two molecules of ethylene while the isomerization of V yields IV; see reactions 5 and 4. Reaction 2 was too minor to affect the simple first-order nature of reaction 1. This was shown by the invariance of the experimental first-order rate constants obtained from runs in which the percentage decomposition was varied from 10 to 90% (Table I). Furthermore, packing the reaction ampoules with Pyrex glass wool so as to effect a 20-fold increase in the surface-to-volume ratio did not affect the rate, indicating the absence of surface reaction (Table II). The experimental data which were obtained over the temperature range 223 to 294° are summarized in Fig. 1. Each point represents the average of 6–9 runs at the given temperature. In all cases the substrate pressure was in excess of 40 cm. so that the data refer to the high-pressure region. The size of the open circles gives the standard deviation in log k_1, where k_1 is the experimental
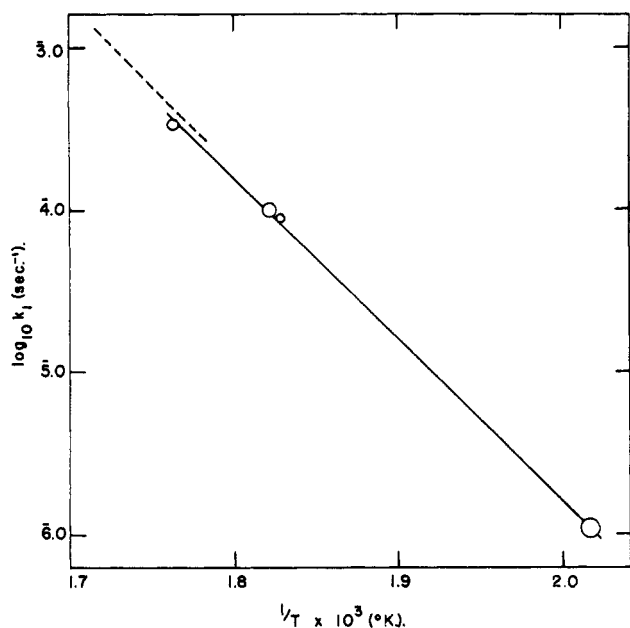
Fig. 1.—Arrhenius plots for the isomerization of bicyclo-[2.1.0]pentane (III) to cyclopentene (VI): O—O, this work; --------, Halberstadt and Chesick.[5]

first-order rate constant for reaction 1. The data are best fitted by the Arrhenius equation

$$\log k_1 \ (\text{sec.}^{-1}) = (14.10 \pm 0.15) - (45,600 \pm 400/2.303RT)$$

This is to be compared with Halberstadt and Chesick's[5] high-pressure rates

$$\log k_1 \ (\text{sec.}^{-1}) = (14.6 \pm 0.4) - (46,600 \pm 1000/2.303RT)$$

Figure 2 shows the ratio of VII to VI formed as a function of temperature. In this case the circles represent individual runs. The ratio at a given temperature was independent of the time of reaction, con-
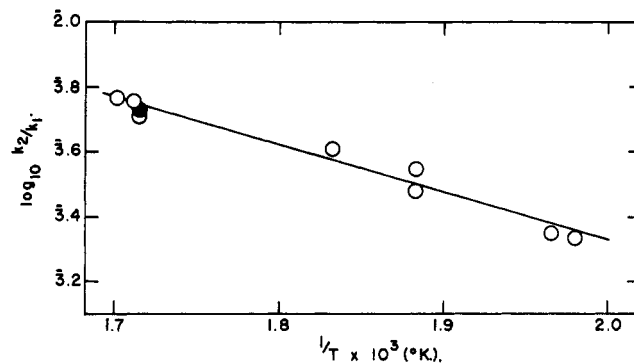
TABLE I

INVARIANCE OF RATE CONSTANT WITH PERCENTAGE DECOMPOSITION FOR THE ISOMERIZATION OF BICYCLO[2.1.0]PENTANE (III) TO CYCLOPENTENE (VI)

Run	T, °C.	k_1, sec.$^{-1}$	Decompn., %
82	274.2	9.1×10^{-5}	7
83	274.2	9.0×10^{-5}	22
84	274.2	8.5×10^{-5}	41
86	274.2	8.6×10^{-5}	50
87	274.2	8.8×10^{-5}	61
126	294.2	3.5×10^{-4}	19
127	294.2	3.2×10^{-4}	90

TABLE II

INVARIANCE OF RATE CONSTANT WITH SURFACE AREA FOR THE ISOMERIZATION OF BICYCLO[2.1.0]PENTANE (III) TO CYCLOPENTENE (VI)

Run	T, °C.	k_1, sec.$^{-1}$	Surface area/vol., cm.$^{-1}$
101	223.1	1.02×10^{-6}	250
102	223.1	1.25×10^{-6}	200
103–106	223.1	1.11×10^{-6a}	26
94	276.0	10.40×10^{-5}	1000
95	276.0	10.50×10^{-5}	450
92, 93			
96–100	276.0	10.24×10^{-5a}	30

^{a} Average rate constant.

firming that VII was being formed directly from III and not from VI. Furthermore, the ratio was not effected by packing the ampoule with Pyrex glass wool. Because both products are formed from a common substrate, we have log (VII/VI) = log k_2/k_1. Since

Fig. 2.—Arrhenius plot for the relative rates of formation of 1,4-pentadiene (VII) and cyclopentene (VI) from bicyclo[2.1.0]-pentane (III): O, unpacked ampoule; ●, packed ampoule, 20-fold increase in surface-to-volume ratio.

k_1 had been determined it was possible to obtain the following Arrhenius equation for k_2.

$$\log k_2 \ (\text{sec.}^{-1}) = (14.35 \pm 0.23) - (52,300 \pm 600/2.303RT)$$

The Isomerization of Cyclopropanes and the Reactions of 1,3-Biradicals.—The mechanism for the isomerization of cyclopropane and its derivatives, including III, is a matter of considerable speculation.[9-15] Halberstadt and Chesick estimate that if the isomerization of III could be represented by reaction 1, then the activation energy (E_1) would have the value 34 kcal. mole^{-1}. Since this does not agree with their experimental activation energy, 46.6 kcal. mole^{-1}, they suggest that the mechanism cannot be represented by reaction 1. They therefore favor a concerted process in which the C–C bond rupture and H-migration occur simultaneously.

However, if their estimate is correct, it is surprising that the reaction does not follow the path of lowest energy since there is no reason why this route should have an unfavorable entropy of activation as compared with a concerted process. In estimating the C–C bond dissociation energy, these authors use a value of 89 kcal. mole^{-1} for the bond dissociation energy of a secondary C–H bond. A more generally accepted value is 95 kcal. mole^{-1}.[16,17] By their method of calculation the latter value would give a total activation energy of 46 kcal. mole^{-1} for reaction 1, in agreement with the experimentally observed value. However, in their estimation of the activation energy of reaction 1b (E_{1b}) Halberstadt and Chesick compare the reaction to the methyl–methane exchange reaction which has an activation energy of 15 kcal. mole^{-1},[18] simply stating that the unfavorable orientation in the former case is likely to be offset by the gain in formation of the double bond. Reaction 1b might better be regarded as being formally similar to the disproportionation of two monoradicals to an alkane and to an alkene. Two mechanisms have been proposed for such reactions,[19-21] but for steric

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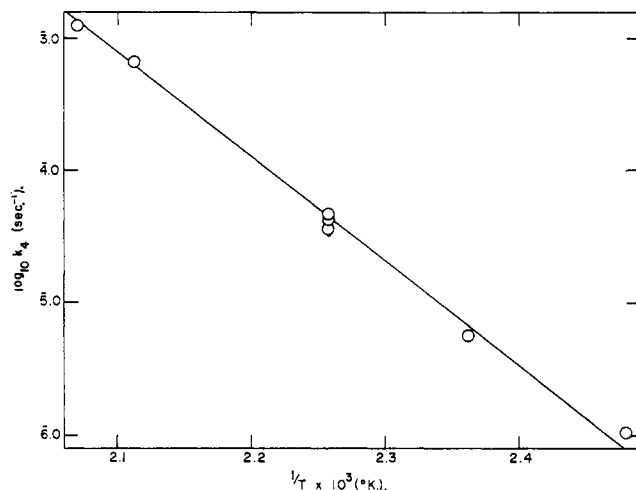(19) M. H. J. Wijnen and E. W. R. Steacie, Can. J. Chem., 29, 1092 (1951).

Fig. 3.—Arrhenius plot for the isomerization of bicyclo[2.2.0]-hexane (V) to 1,5-hexadiene (IV).

reasons neither can be exactly operative in reaction 1b, in which the transition state may be represented by structure IX. We cannot at this stage justify the employment of data from intermolecular hydrogen transfer in this intramolecular process.

IX

Benson has considered the mechanism of isomerization of cyclopropane (X). By extending the thermodynamic arguments of Seubold,[22,23] he obtained D-(C–C) for X, 56.0 kcal. mole^{-1} at 444°, and concluded that E_{3b} was 9.5 kcal. mole^{-1}, on the assumption that the isomerization of X proceeded via the biradical XII. It should be noted, however, that for this argument to be valid E_{3a} has to be less than the over-all activation energy, 65.5 kcal. mole^{-1}. In their most recent work Schlag and Rabinovich[15] have found that the activation energy for the geometrical isomerization of cyclopropane-d_2 is 65.1 kcal. mole^{-1}. Thus, when we remember that the experimental results are subject to an error of the order of 1 kcal. mole^{-1}, it is quite possible that E_{3a} is as large as the over-all activation energy so that the validity of Benson's estimate for E_{3b} appears doubtful. All that can be said is that if the reaction proceeds via the biradical, then $E_{3b} \leq 9.5$ kcal. mole^{-1}. If we accept the above thermodynamic value for D(C–C) in X and take the activation energy for the geometrical isomerization as a measure of E_{3a}, then E_{-3a} is equal to 9.1 kcal. mole^{-1}.

Since the heat of hydrogenation of III is known, we may use the Seubold–Benson method to determine D(C–C) for the bridgehead bond; the value obtained is 30.7 kcal. mole^{-1}. For comparison the bond dissociation energies of other cyclic alkanes are shown in Table III.

TABLE III

BOND DISSOCIATION ENERGIES FOR CYCLIC ALKANES[24]

Compound	Cyclo-C_3H_6	Cyclo-C_4H_8	Cyclo-C_5H_{10}	Cyclo-C_6H_{12}	Bicyclo-C_5H_8
D(C–C), kcal. mole^{-1}	54.4	56.1	75.3	81.2	30.7

Recently Chesick[7] has obtained the activation energy for the geometrical isomerization of 2-methylbicyclo-[2.1.0]pentane, 39.0 kcal. mole^{-1}. If we equate this with E_{1a}, then E_{-1a} would be 8.3 kcal. mole^{-1} while E_{1b} would have the value 14.9 kcal. mole^{-1} if the isomerization of III proceeded via the biradical VIII.

The higher activation energy for reaction 1b (14.9 kcal. mole^{-1}) as compared to 3b (≤ 9.5 kcal. mole^{-1}) is to be expected because of the steric effects imposed by the ring. Firstly, the orbital of the migrating hydrogen does not overlap as effectively with that of the free electron on the adjacent carbon in the case of VIII as it does in the case of the acyclic biradical XII. Secondly, these steric requirements will also affect the ease with which the carbon atoms undergo changes in hybridization, from sp^3 to sp^2, as the olefinic bond is formed. Factors which may contribute to the small positive activation energy for reaction −3a have been discussed by Benson. The activation energy of reaction −1a can be understood in terms of eclipsing H–H interactions and distortions of the C–C bond angles as III is formed from VIII. It is to be realized that by the nature of the calculations the conformation of the biradical is the same as that of the corresponding hydrogenated alkane since in the determination of the heat of formation of the biradical the only process considered is the formation of two C–H bonds. The calculated bond dissociation energies and activation energies are therefore model activation energies in that they refer to particular, in general the most stable, conformations of the biradicals. Bond energies and activation energies involving biradicals in other conformations will be altered by the conformational energies involved which generally are in the range 3–7 kcal. mole^{-1}.[29]

The Isomerization of Bicyclo[2.2.0]hexane (V).—The isomerization of V to IV (reaction 4) was studied in the temperature range 130 to 210°, the pressure of reactant being 40 cm. No other products, in particular no cyclohexene, were observed. The number of kinetic runs was limited by the small amount of material available. The circles in Fig. 3 refer to individual runs. At 170° runs were performed in which the extent of isomerization was varied from 10 to 70%. There was no significant variation in the experimental first-order rate constant. The rate data are given by the Arrhenius equation

$$\log k_4 \text{ (sec.}^{-1}) = (13.4 \pm 0.3) - (36000 \pm 1000/2.303RT)$$

The Decomposition of Cyclobutanes and the Reactions of 1,4-Biradicals.—Walters and his co-workers have made an intensive study of the pyrolyses of cyclobutane (XIV) and its derivatives.[30–38] The possibility

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(22) F. H. Seubold, $J. Chem. Phys.$, **21**, 1616 (1953).

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(24) All values are calculated for 25°. Bond dissociation energies vary with temperature, but generally the variation is less than the sum of the errors involved in their computation. Where possible the heats of formation were taken from Circular 500, National Bureau of Standards (1952). The sources of the heats of formation of those compounds not given in the circular are to be found in ref. 25–28. The bond dissociation energy of H_2 was taken to have the value 104.2 kcal. mole^{-1}, while the bond dissociation energies of primary and secondary C–H bonds were assumed to have the same values for all the compounds under consideration and were assigned the values 98 and 95 kcal. mole^{-1}, respectively.[16,17]

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that in the case of cyclobutane the product ethylene (XV) is formed *via* a short-lived 1,4-butadiyl biradical (XVI), reaction 5, has been considered although it was not experimentally detected in the systems under investigation. For III and V the corresponding reactions are 2 and 4. On the assumption that cyclobutane decomposes to ethylene *via* the biradical, Benson[9] has calculated a value of 4 kcal. mole^{-1} for E_{5b}. From this and from the ease of formation of IV from V, we might expect that the formation of VII from III, reaction 2, would compete favorably with reaction 1. However, this argument neglects steric influences which are important. 1,3-Cyclopentadiyl (VIII) has a relatively rigid structure, and there is only poor overlap between the free electrons on C_1 and C_3 with those constituting the rupturing C_4-C_5 bond. On the other hand, 1,4-cyclohexadiyl (XIII) has considerable flexibility and good overlap can be obtained with little distortion from the tetrahedral angles.

Butene-1, which is thermodynamically more stable than two molecules of ethylene, is not formed in the pyrolysis of cyclobutane. The activation energy for the thermoneutral reaction 6b′ would be expected to be at least as high as that for the exchange reaction between methyl and methane (15 kcal. mole^{-1}). Indeed, the steric requirements in the former case might increase the value to above 15 kcal. mole^{-1}. The relatively high energy barrier of reaction 6b′ "blocks" the formation of 1-butene so that reaction 5b with its relatively low activation energy barrier becomes the favored pathway. This reasoning may also be applied to the failure of V to yield cyclohexene, although the latter is 28.5 kcal. mole^{-1} thermodynamically more stable than the isomeric 1,5-pentadiene (IV).

Ring Strain.—The various manifestations of ring strain have received extensive consideration in the literature.[9,22,29,39] The C–C bond dissociation energies of cyclic alkanes given in Table III reflect the strains associated with these rings. If we assume that cyclohexane has an unstrained structure, we might say that the strain energy associated with the cyclopentane ring is $(81.2 - 75.3)$ kcal. mole^{-1}; with the cyclobutane and cyclopropane the strains are 25.1 and 26.8 kcal. mole^{-1}, respectively.[9] This simple calculation does not distinguish between the various factors which contribute to ring strain, and if, for example, the strain caused by hydrogen–hydrogen interaction is relieved by the formation of the biradical, this will be included in the strain energy.

The weakness of the bridgehead C–C bond of III is not surprising in that when this bond is ruptured both cyclopropane and cyclobutane strain are relieved since an essentially unstrained cyclopentane ring is formed. We might expect the strain associated with the bridgehead bond to be an approximately additive property. The estimated C–C bond dissociation energy would then be $D(C–C) = (81.2 - 26.8 - 25.1)$ kcal. mole^{-1} = 29.3 kcal. mole^{-1}. The value calculated by the thermodynamic method is 30.7 kcal. mole^{-1}. Although quantitative significance is not claimed, additivity of ring strain may be qualitatively useful in discussing the reactions of such bicyclic compounds where thermodynamic heats of formation have not yet been determined.

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Further evidence for the additivity of ring strain may be sought in the work of Frey and Smith[40] who recently studied reactions 7 and 8. That E_7 (57.4 kcal. mole^{-1}) is larger than E_1 (45.6 kcal. mole^{-1}) is consistent with the smaller strain associated with bond α in bicyclo[3.1.0]hexane (XVII) compared to the strain in bond α in III. Bond α in XVII has only cyclopropane and cyclopentane strain. Furthermore, the fact that XVII forms 1-methylcyclopentene (XIX) while III forms no 1-methylcyclobutene (XX) reflects the greater difference between the bond dissociation energies of bonds β and α in III compared with the difference between those bond energies in XVII. In the former $D(\beta)$ and $D(\alpha)$ differ by cyclobutane strain; in the latter they differ by only cyclopentane strain.

By the thermodynamic method we can show that for XVII

$$D(\beta) - D(\alpha) = \Delta H_f(\text{methylcyclopentane}) - \\ \Delta H_f(\text{cyclohexane}) + D(\text{C–H}_{prim}) - \\ D(\text{C–H}_{sec}) = 6.9 \text{ kcal. mole}^{-1}$$

The observed difference between the over-all activation energies of reactions 8 and 7 was 4 kcal. mole^{-1}.[40] Similarly, for III we have $D(\beta) - D(\alpha) = 17.2$ kcal. mole^{-1}. This difference in bond dissociation energy will be reflected in a much higher activation energy for reaction 9 compared with reaction 1. Thus the formation of XX is effectively blocked. Although the activation energy for reaction 9 is not known, it should be similar to that for reaction 8. The activation energy for the latter is 14.6 kcal. mole^{-1} higher than the activation energy of reaction 1. Under our experimental conditions XX would not be observed directly since it would rapidly isomerize to isoprene.[41,42] Careful gas chromatographic analysis showed that there was less than 0.005% of isoprene present when III was pyrolyzed at 320°. This indicates that the activation energy difference between reactions 9 and 1 is at least 14 kcal. mole^{-1}.

Unfortunately no thermodynamic data exist for V. On the basis of simple additivity of bond strains, we estimate a value of $(81.2 - 2 \times 25.1) = 31.0$ kcal. mole^{-1} for the C–C bridgehead bond dissociation energy. The activation energy of reaction 4 is 36.0 kcal. mole^{-1}, and the bridgehead bond dissociation energy will certainly not be greater than this unless the possible concerted character of the reaction acts to decrease the activation energy. The low value for the bridgehead dissociation energy indicated by this work should be reflected in a high heat of hydrogenation for V. On the other hand, from the above arguments we should expect that bicyclo[2.1.1]hexane which is isomeric with V should be thermally more stable and have a lower heat of hydrogenation.[43]

Extent of Concertion.—In the previous discussion we have considered the reactions of small ring compounds and have shown that the reactions can at least be approximated to by stepwise mechanisms. In particular, in no case is an activation energy obtained which is less than the bond dissociation energy of the rupturing C–C bond. The latter would be a sufficient condition to invalidate the stepwise mechanism. In the case of cyclobutane and its analogs, the symmetry of the reaction makes the concerted mechanism particularly

(40) H. M. Frey and R. C. Smith, *Trans. Faraday Soc.*, **58**, 697 (1962).

(41) H. M. Frey, *ibid.*, **57**, 957 (1961).

(42) W. Cooper and W. D. Walters, *J. Am. Chem. Soc.*, **80**, 4220 (1958).

(43) NOTE ADDED IN PROOF.—Very recently R. Srinivasan and A. A. Levi, *ibid.*, **85**, 3363 (1963), have reported on the thermal isomerization of bicyclo[2.1.1]hexane to IV. The activation energy is 19 kcal. mole^{-1} greater than the activation energy of reaction 4.

attractive. The very low activation energy for the isomerization of bicyclo[2.2.0]hexane may offer an indication of the concerted nature of this reaction. For this reason it would be extremely valuable to have a reliable thermodynamic determination of the bridge-head bond dissociation energy. The low activation energies for the isomerization of cyclobutene and its derivatives[41,42] is strong evidence in favor of concerted electronic rearrangement in these reactions.

The Mechanistic Fate of the Anilino Moiety in the Rearrangement of α-Anilinoketones[1]

BY K. LEROI NELSON, JEROLD C. ROBERTSON,[2] AND JOHN J. DUVALL[2]

Mass spectrographic analysis of the product mixture obtained from the competitive rearrangement of 2-(4-bromoanilino)-1-(4-bromophenyl)-2-(4-methoxyphenyl)-1-ethanone and 2-(4-chloroanilino)-1-(4-chloro-phenyl)-2-(4-methoxyphenyl)-1-ethanone in the presence of γ-picoline hydrobromide clearly indicated the presence of fragments containing both bromine and chlorine in the same fragment. Analysis of a mechanical mixture of the two ketones showed no crossover fragments as indicated by the simple superposition of their respective mass spectra. These results substantiate the mechanism proposed by Nelson and Seefeld.[3] Thus, the migration of carbonyl oxygen is intramolecular while migration of the anilino moiety is clearly intermolecular. 2-(4-Chloroanilino)-1-(4-chlorophenyl)-2-propanone was rearranged to 1-(4-chloroanilino)-1-(4-chloro-phenyl)-2-propanone in the presence of p-chloroaniline hydrobromide but not with pyridine hydrobromide or γ-picoline hydrobromide. Reverse rearrangements were unsuccessful with 1-(4-chloroanilino)-1-(4-chloro-phenyl)-2-propanone, 1-(4-bromoanilino)-1-(4-bromophenyl)-2-propanone, and 1-(3-chloroanilino)-1-(3-chloro-phenyl)-2-propanone using γ-picoline hydrobromide.

In the first paper of this series[3] we enumerated several different mechanistic schemes which have been proposed for the rearrangements of α-arylaminoketones and reported experimental work which demonstrated the intramolecular migration of carbonyl oxygen. We then proposed a mechanism involving an amino-epoxide intermediate which would allow intramolecular migration of the carbonyl oxygen and require an intermolecular migration of the anilino moiety. This proposal was consistent with the report of Weygand and Richter[4] who treated phenacylaniline with aniline (C-14) or m-bromoaniline (Br-82) and the arylamine salt which is usually added as a catalyst. They found that the labeled aniline was equally distributed between the resulting indole and the aniline remaining.

Recently, Stevens and co-workers[5] reported that α-bromopropiophenone reacted with methylamine to form the rearranged α-aminoketone. In a procedure similar to that used by us[3] they utilized O-18 as a tracer to demonstrate that the migration of carbonyl oxygen was intramolecular. They similarly proposed an aminoepoxide intermediate. The reaction stops at the hydroxyimine stage with compounds which lack the necessary α-hydrogen to permit tautomeric conversion to the aminoketone. Under vigorous conditions (185–250°) α-aminoketones containing no α-hydrogens undergo skeletal rearrangement.[6]

The rearrangement appears to require a mild acid since it does not occur under strictly neutral or alkaline conditions.[7,8] The necessity of free amine is suggested

by the failure of the hydrochloride salt of the aminoketone to rearrange,[8] the great difference in reaction rates between aniline and pyridine,[3] and the failure to rearrange with N,N-dimethylaniline.[9] The finding that an α-C–N bond is easily cleaved under strong acid conditions might provide "free" amine[10] for rearrangements under acid conditions in the absence of added amine.[8,9]

Discussion of Results

We prepared several halogen-labeled α-aminoketones I and II for use in competitive rearrangement experi-
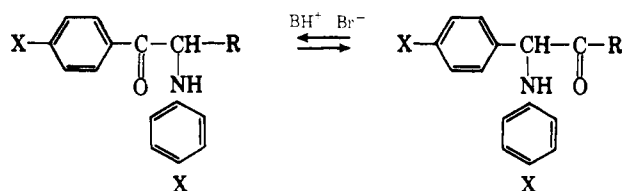
Ia, R = CH₃, X = Cl   IIa, R = CH₃, X = Cl
b, R = CH₃, X = Br   b, R = CH₃, X = Br
c, R = 4-CH₃OC₆H₄, X = Cl c, R = 4-CH₃OC₆H₄, X = Cl
d, R = 4-CH₃OC₆H₄, X = Br d, R = 4-CH₃OC₆H₄, X = Br

ments to check the claim of Cowper and Stevens[11] that the reaction involved intramolecular migration of the aniline moiety. This seemed unlikely to us when we had clearly demonstrated that the carbonyl oxygen migrates intramolecularly.[3]

Using pyridine hydrobromide or γ-picoline hydrobromide we were unable to convert any detectable amount of Ia to IIa. With the view that conjugation of the halogen with the carbonyl group was a stabilizing factor which effectively set the equilibrium position to the far left, we prepared IIa and IIb but found they also failed to rearrange to Ia and Ib, respectively. We

(1) The Mechanism of the Möhlau–Bischler Indole Synthesis. II.

(2) This paper is based in part upon work reported in dissertations submitted to the Graduate School of Brigham Young University in partial fulfillment of the requirements for the Ph.D. Degree. It was presented before the Organic Division, 139th National Meeting of the American Chemical Society, St. Louis, Mo., March 28, 1961.

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(6) C. L. Stevens, R. D. Elliot, B. L. Winch, and I. L. Klundt, J. Am. Chem. Soc., 84, 2272 (1962).

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(11) R. M. Cowper and T. S. Stevens, J. Chem. Soc., 1041 (1947).