

why the plot in Figure 1 for the mercaptide base is so much steeper than for the alkoxide base. Is it because the E2 rate coefficient for the sulfur base is very much greater? Or is it because  $\text{NaSC}_2\text{H}_5$  has a very favorable salt effect on ionization, whereas  $\text{NaOCH}_3$  has a rather unfavorable one? We do not feel that a firm decision can be made because of the unsatisfactoriness of the various models. On the whole, however, it appears that the data are better explained in terms of a distinctly higher E2 rate coefficient for the sulfur base. Thus, the rate of change of olefin fraction in Table I is greater for  $\text{NaSC}_2\text{H}_5$  than for  $\text{NaOCH}_3$ , and the former is less than half the concentration of the latter.

If this judgment is correct, it is noteworthy that the higher E2 reactivity of  $\text{C}_2\text{H}_5\text{S}^-$  than of  $\text{CH}_3\text{O}^-$  persists even when the substrate is highly hindered about  $\text{C}_\alpha$ ; the carbon to which chlorine is attached in **1a** is both tertiary and neopentyl. Such an out-

come is not compatible with the "E2C" mechanism which has been proposed by other workers for certain eliminations induced by reagents of relatively low basicity.<sup>17</sup> We have earlier reported that **1b** undergoes E2 elimination with chloride ion in acetone or dioxane faster than with its less hindered analog, *tert*-butyl bromide,<sup>18</sup> and we have made similar observations with respect to secondary alkyl halides and tosylates.<sup>19</sup> These studies provide no support for the E2C mechanism. Reasons for the surprisingly high E2 reactivity of mercaptide ions in certain eliminations have been discussed elsewhere.<sup>6</sup>

**Registry No.**—**1a**, 918-07-0; **1b**, 16468-75-0; **1c**, 27705-19-7; **2**, 594-56-9; **3**, 27705-21-1.

(17) A. J. Parker, M. Ruane, G. Biale, and S. Winstein, *Tetrahedron Lett.*, 2113 (1968); G. Biale, A. J. Parker, S. G. Smith, I. D. R. Stevens, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 115 (1970).

(18) D. Eck and J. F. Bunnett, *ibid.*, **91**, 3099 (1969).

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## Reactions of Bicyclo[2.1.0]pentane and Bicyclo[4.1.0]heptane with Hydrogen Chloride. Cleavage of Cyclopropane Rings<sup>1a</sup>

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The products of the reaction of bicyclo[2.1.0]pentane (I) and bicyclo[4.1.0]heptane (II) with HCl in the vapor phase and with concentrated hydrochloric acid in a two-phase system have been studied. In the case of I, both cyclopentene and cyclopentyl chloride were obtained. In the case of II, nonthermodynamic mixtures of six-membered and seven-membered olefins and chlorides were obtained. It is proposed that the olefins arise primarily *via* quasiheterolytic six-membered cyclic transition states and that the chlorides arise *via* pathways of somewhat greater heterolytic character. Relief of strain in the ground state and nonbonded interactions and strain in the transition state are invoked to explain the relative amounts of internal and external cleavage of the three-membered ring as well as product distributions.

In connection with our work on the chlorination of bicyclo[*n*.1.0]alkanes,<sup>1c,2</sup> we have also investigated the reaction of hydrogen chloride with bicyclo[2.1.0]pentane (I) and bicyclo[4.1.0]heptane (II). We wish to report our results since they are divergent from previously reported ones in at least one important respect, and since they serve to further elucidate the behavior of cyclopropanes in ring-opening reactions.

Cleavages of cyclopropyl compounds by acids or other electrophiles have been extensively studied.<sup>3-9</sup> Where rationales have been advanced,<sup>4,6a</sup> the course of the re-

action has been discussed in terms of polarization of the three-membered ring by the incoming electrophile. More recently<sup>9</sup> anti-Markovnikov ring opening of the cyclopropane in a tricyclo[3.2.2.0<sup>2,4</sup>]nonyl system has been interpreted in terms of steric inhibition to normal collapse of a protonated cyclopropyl intermediate.

We have studied the reactions of I and II with HCl under conditions which are not conducive to normal ionic modes of reaction. Nevertheless, the results parallel those obtained under more ionic conditions<sup>4</sup> in many ways.

### Results

Reaction between HCl and bicyclo[2.1.0]pentane (I) and bicyclo[4.1.0]heptane (II) was brought about in several ways. In one approach, HCl vapor was added slowly to an excess of refluxing hydrocarbon and the two vapors were mixed, under anhydrous conditions, in a glass reaction chamber heated by sun lamps. These reactions were performed in a modification<sup>1c</sup> of a vapor phase chlorination apparatus designed by Roberts and Mazur.<sup>10</sup> In another approach, equimolar amounts of 12 *M* hydrochloric acid and I at 10° or II at 25° were shaken vigorously for 6 hr. In addition II was reacted with a twofold excess of anhydrous HCl in a glass ampoule, filled on a vacuum line, sealed, and heated

(1) (a) This research was supported in part by a grant from The Research Council of Rutgers University and by AFOSR (SRC) OAR, USAF, Grant No. 837-67. (b) To whom correspondence should be addressed at Douglass College, New Brunswick, N. J. (c) Abstracted, in part, from the thesis of M. M. submitted in partial fulfillment of the requirements for the M.S. Degree, State University of New York at Stony Brook, 1966.

(2) (a) R. Boikess and M. Mackay, *Tetrahedron Lett.*, 5991 (1968); (b) R. Boikess and M. Mackay, unpublished results.

(3) (a) C. J. Collins, *Chem. Rev.*, **69**, 543 (1969); (b) E. E. Royals, "Advanced Organic Chemistry," Prentice-Hall, Englewood Cliffs, N. J., 1954, pp 210-218.

(4) R. T. LaLonde and L. S. Forney, *J. Amer. Chem. Soc.*, **85**, 3767 (1963).

(5) (a) R. T. LaLonde, J. Ping, and M. A. Tobias, *ibid.*, **89**, 6651 (1967), and earlier papers; (b) A. C. Cope and G. L. Woo, *ibid.*, **85**, 3601 (1963).

(6) (a) R. J. Ouellette, A. South, Jr., and D. L. Shaw, *ibid.*, **87**, 2602 (1965); (b) S. Moon, *J. Org. Chem.*, **29**, 3456 (1964).

(7) R. Criegee and A. Rimmelin, *Chem. Ber.*, **90**, 414 (1957).

(8) R. C. Cookson, D. P. G. Hamon, and J. Hudec, *J. Chem. Soc.*, 5782 (1963).

(9) J. B. Hendrickson and R. K. Boeckman, Jr., *J. Amer. Chem. Soc.*, **91**, 3269 (1969).

(10) J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 2509, (1957).

TABLE I  
PER CENT DISTRIBUTION OF OLEFIN PRODUCTS FROM HYDROCHLORINATION REACTIONS

Reaction	Reactants	Reaction, %	Olefin, %	Cyclopentene	1-Methylcyclohexene	3-Methylcyclohexene	Cycloheptene
A	HCl (g) + I	98	40	100			
B	HCl (12 M) + I	86	46	100			
C	HCl (g) + II	68	21		3.8	90	6.6
C	HCl (g) + II <sup>a</sup>	87	13		3.7	90	6.7
D	HCl (12 M) + II	87	24 <sup>b</sup>		5.3	87	7.7
E	HCl (g) + II (sealed tube)	99	39		5.4	85	9.3

<sup>a</sup> Same reaction run in the dark. <sup>b</sup> An additional component here is toluene which accounts for 13% of the olefin fraction. The relative percentages of the three olefins are calculated after toluene is subtracted out and represent 87% of the olefin fraction.

at 160° for 24 hr. In all cases the reaction mixtures were worked up in standard ways and analyzed by vapor phase chromatography.

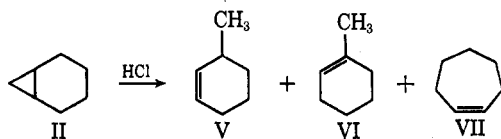
All the products obtained were known compounds, and identifications were made by comparisons of vpc retention times, infrared spectra, and nmr spectra with those of independently synthesized authentic compounds. Control experiments, using cycloheptyl chloride as an internal standard, showed that 99% of the products were accounted for by the vpc analyses. The products do not react or react much more slowly with HCl under the reaction conditions and survive unchanged through the work-up procedure. Both I and II could be recovered unchanged when subjected to the reaction conditions in the absence of HCl. Neither the starting materials nor the products decomposed under the vpc conditions.

Under both sets of conditions, bicyclo[2.1.0]pentane (I) yielded approximately equal amounts of cyclopentene (III) and cyclopentyl chloride (IV) in contrast to

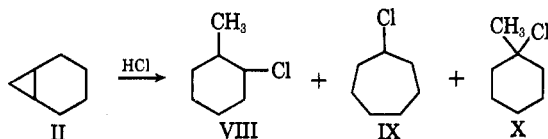


the report<sup>4</sup> that only cyclopentyl acetate was obtained on treating I with *p*-toluenesulfonic acid in acetic acid.

Similarly, under all three sets of conditions bicyclo[4.1.0]heptane (II) yielded both olefin products and chloride products. The same products were obtained in all cases with the exception that a small amount of toluene was formed when conditions were not anhydrous. The fraction of olefin in the total product varied but in all cases consisted of a major product, 3-methylcyclohexene (V), and two minor products, 1-methylcyclohexene (VI) and cycloheptene (VII). The chloride



fraction consisted in all cases of three compounds, which were, in order of relative abundance, *trans*-2-methylcyclohexyl chloride (VIII), the major product, cycloheptyl chloride (IX), and 1-methylcyclohexyl chloride (X).



The relative percentages of the products are summarized in Tables I and II.

TABLE II  
PER CENT DISTRIBUTION OF CHLORIDE PRODUCTS FROM HYDROCHLORINATION REACTIONS

Reaction	Chloride, %	Cyclopentyl chloride	<i>trans</i> -2-Methylcyclohexyl chloride	1-Methylcyclohexyl chloride	Cycloheptyl chloride
A	60	100			
B	54	100			
C	79		63	15	22
C	87		55	15	30
D	76		72	7	21
E	61		62	15	23

## Discussion

The conditions of the vapor phase reaction (slow addition of HCl to maintain an excess of hydrocarbon, absence of a proton source, and relatively low temperatures<sup>11</sup>) support an explanation for the course of the reaction in terms of quasiheterolytic processes involving only one molecule of HCl. The fact that the same products, in similar proportions, are obtained from the two-phase reactions with hydrochloric acid is not totally unexpected given the negligible solubility of hydrocarbons in water and the small solubility<sup>12</sup> of HCl in hydrocarbons. The formation of a small amount of toluene is puzzling but may be due to some ionic interfacial side reaction.

In contrast with our observation of almost equal amounts of cyclopentene (III) and cyclopentyl chloride (IV) from the reaction of HCl and I, Criegee and Rimmelin<sup>7</sup> reported only cyclopentyl bromide from treatment of I with hydrobromic acid, and LaLonde and Forney<sup>4</sup> reported only cyclopentyl acetate from treatment of I with *p*-toluenesulfonic acid in acetic acid. One possible explanation for this discrepancy is a changeover in mechanism under nonionic conditions. We postulate a six-membered cyclic transition state similar to those postulated for the HCl-catalyzed gas phase decompositions of 1,1-dimethylcyclopropane<sup>13</sup> and a variety of oxygenated compounds.<sup>14</sup> This transi-

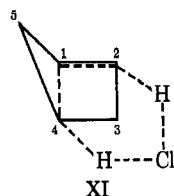
(11) The reaction temperatures must be close to the boiling point of I, 45°, and the boiling point of II, 116°.

(12) R. P. Bell, *J. Chem. Soc.*, 1371 (1931).

(13) J. Bullivant, J. S. Shapiro, and E. S. Swinbourne, *J. Amer. Chem. Soc.*, **91**, 7703 (1969).

(14) D. A. Kairaitis and V. R. Stimson, *Aust. J. Chem.*, **21**, 1711 (1968), and earlier papers.

tion state must have some heterolytic character<sup>15, 16</sup> but can be represented as the extreme form, XI. Although



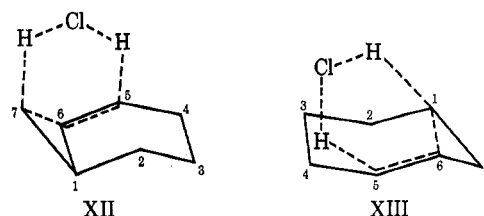
the hydrogen of the HCl is drawn as attacking a corner of the three-membered ring in XI and other related transition states, *vide infra*, this need not be required. Consistent with the well-known formation of bridged protonated cyclopropane intermediates,<sup>8a</sup> it is possible to conceive that the initial overlap between the partially bound hydrogen of HCl and the three-membered ring is along an edge. Its exact location would be determined by the balance between better overlap, nonbonded repulsions, and angle strain in the transition state. An alternative cyclic transition state is possible involving removal of H-5, but we prefer XI on steric grounds.

Cyclopentyl chloride (IV) can be envisaged to form by two possible pathways: a four-center concerted 1,3 addition of HCl across the very strained central bond or 1,2 addition of HCl between C-1 and C-5 with a simultaneous hydride shift from C-5 to C-4. Although both types of processes seem reasonable, the former possibility seems preferable for I since it leads to greater relief of strain in the transition state and requires less drastic reorganizations.

The absence of any methyl cyclobutyl products is consistent with previous work<sup>4, 7</sup> as well as with the tremendous relief of strain which occurs on cleavage of the very weak<sup>17</sup> bond between C-1 and C-4.

As has been previously observed,<sup>4</sup> but not fully accounted for, the addition of electrophiles to bicyclo[4.1.0]heptane (II) leads to a distribution of olefin products which does not reflect their relative thermodynamic stabilities. Under our conditions this discrepancy is even more pronounced. From available thermodynamic data,<sup>18</sup> it is possible to calculate approximate heats of formation for 3-methylcyclohexene (V), 1-methylcyclohexene (VI), and cycloheptene (VII) which are  $-9.6$  kcal/mol,  $-11.6$  kcal/mol, and  $-5.2$  kcal/mol, respectively. Although the preponderance of six-membered olefins, from external cleavage, over seven-membered olefin, from internal cleavage, is expected on the basis of relative stabilities and favorable statistics, we believe, as have previous workers,<sup>4</sup> that this is to a large extent fortuitous. However, rather than rationalizing the relative amounts of internal and external cleavage by an argument involving the most

favorable direction for polarization of a three-membered ring by a perturbing electrophile,<sup>4, 6a</sup> we suggest that, at least under the present conditions, simple steric arguments serve to account for not only the relative amounts of internal and external cleavage but also the preponderance of V, the less stable six-membered olefin, in the products. Reasonable quasiheterolytic cyclic six-membered transition states which lead to V and VII can be visualized and are represented in one extreme form as XII and XIII, respectively.



It can be readily seen that XII, which leads to the major product, is the less strained transition state, since the attacking HCl lies near the edge of the cyclohexane ring, thus minimizing nonbonded repulsions with hydrogens on C-2, C-3, and C-4, while at the same time the HCl easily spans the distance between C-7 and the hydrogen to be eliminated at C-5. On the other hand in XIII, which leads to cycloheptene (VII) by internal cleavage, the HCl must lie across the face of the cyclohexane ring leading to more serious interactions with hydrogens on C-2, C-3, and C-4, although here too the HCl easily spans the distance between C-2 and the hydrogen to be eliminated at C-5. It is not easy to visualize the formation of VI, the most stable and least abundant olefin, through a similar process since no reasonable cyclic transition state of the type shown above can be formulated which leads to this olefin. A six-center transition state leading to this product would involve a solid bridge between C-7 and C-1, making it unlikely. More reasonably, formation of VI occurs through a competing process of greater heterolytic character<sup>19</sup> rather than through direct collapse of a cyclic transition state. This hypothesis leads to the expectation that under more ionic conditions greater amounts of VI relative to VII should be formed. It has been found that in acetic acid the relative amounts of VI and VII are reversed, more than twice as much of the former being formed than the latter.<sup>4</sup>

The composition of the mixture of chlorides is also somewhat unexpected. The preponderance of external over internal opening is not surprising, but here greater than 20% of the product comes from internal opening compared to less than 8% in the olefins. In addition, the relative amount of 1-methylcyclohexyl derivative has increased by a factor of between three and four. This suggests that the formation of the chlorides is less sterically controlled and proceeds by way of processes with more heterolytic character than those which lead to olefins. Formation of 1-methylcyclohexyl chloride (X) which formally requires a hydride shift is not anomalous; such shifts have been observed in quasiheterolytic reactions.<sup>15b</sup>

(15) (a) C. J. Harding, A. G. Loudon, A. Maccoll, P. G. Rodgers, R. A. Ross, S. K. Wong, J. S. Shapiro, E. S. Swinbourne, V. R. Stimson, and P. J. Thomas, *Chem. Commun.*, 1187 (1967); (b) A. Maccoll in "Advances in Physical Organic Chemistry," Vol. 3, V. Gold, Ed., Academic Press, New York, N. Y., 1965.

(16) S. W. Benson and A. N. Bose, *J. Chem. Phys.*, **39**, 3463 (1963).

(17) M. L. Halberstadt and J. P. Chesick, *J. Amer. Chem. Soc.*, **84**, 2688 (1962).

(18) (a) American Petroleum Institute, "Tables of Thermodynamic Properties," Project 44, Carnegie Institute of Technology, 1952; (b) J. Coops, H. Van Kamp, W. A. Lambregts, B. J. Visser, and H. Dekker, *Recl. Trav. Chim. Pays-Bas*, **79**, 1226 (1960); (c) R. B. Turner in "Kekule Symposium on Theoretical Organic Chemistry," Butterworths, London, 1959, p 67.

(19) Similarities between quasiheterolytic gas phase reactions and normal ionic processes in solution are well known.<sup>15b</sup>

The stereospecificity of the addition to give the trans isomer VIII as the only 1,2-disubstituted cyclohexyl product has also been noted under ionic conditions<sup>4</sup> and has been rationalized by comparison to the well-known preference for diaxial opening in epoxides.<sup>20</sup> However more recent work<sup>5</sup> indicates that cyclopropanes do not seem to have this same preference for diaxial opening, and the explanation must lie elsewhere. Inspection of models of a bicyclo[4.1.0]heptane in its preferred<sup>21</sup> half-chair conformation suggests that concerted attack of HCl, concurrent with conformational changes from the half-chair toward a chair, should lead to trans addition of HCl, although the argument is not overwhelming. Since the timing and extent of electrophile addition, bond breaking, and nucleophile addition in such a process is not understood, it is difficult to make convincing arguments to explain the stereospecificity.

### Experimental Section

Analytical and preparative vapor phase chromatography were carried out on an Aerograph A-90P fitted with 0.25 in.  $\times$  2 m columns. All infrared spectra were obtained on a Perkin-Elmer Model 21 spectrometer using a microcavity cell filled with neat liquids. Proton nmr spectra were recorded on a Varian Model A-60 spectrometer. The samples were either neat liquids or 20 vol % solutions in CCl<sub>4</sub>. Tetramethylsilane was used as the internal standard. All the products obtained were known compounds and identifications were made by comparison of vpc retention times, infrared spectra, and nmr spectra with those of independently synthesized compounds.

**Vapor Phase Hydrochlorinations. A. Bicyclo[2.1.0]pentane. Reaction A.**—The reaction assembly was a modification<sup>16</sup> of that of Roberts and Mazur.<sup>10</sup> A one-piece all-Pyrex apparatus consisted of a 50-ml round-bottom boiler fitted with a magnetic stirring bar, a rubber septum for withdrawing samples, and an inlet assembly fitted with two stopcocks for introducing the hydrocarbon. To the boiler was attached a vertical 4-in. Vigreux column. Atop this column was a reaction chamber fitted with a thermometer inlet. A gas inlet tube led directly into this chamber, which consisted of a 50-ml round bulb surmounted by three Pyrex loops 2 in. in diameter. Above the reaction chamber was a fitting for a condenser, arranged in such a way that condensate bypassed the reaction chamber and returned directly to the boiler at the bottom. To this one-piece assembly was fitted a spiral Dry Ice-acetone condenser. The top of the condenser was connected to a 1-l. flask, vented through a barium oxide-silica gel drying tube. All of the reaction chamber and its connections, except the spiral and the Vigreux column, were covered with asbestos paper. Gases (HCl or N<sub>2</sub>) introduced into the reaction chamber were first passed through a concentrated sulfuric acid drying tower, a Dry Ice-acetone cooled trap, and a calibrated gas flow meter, all connected by polyethylene tubing.

Before the reaction was begun, all glass surfaces were flamed for 30 min, while maintaining a slow stream of nitrogen through the system. The bicyclo[2.1.0]pentane (0.1 mol), prepared by the method of Cohen, *et al.*,<sup>22</sup> and free of cyclopentene, was placed in a flask containing calcium hydride and allowed to stand overnight. The flask was connected to the boiler and the hydrocarbon distilled directly into it through the inlet assembly. During this transfer the entire system was closed by placing a glass stopper in the drying tube. After the transfer the stopper was removed and the entire assembly swept for a few minutes with a stream of dried nitrogen. The glass spiral was heated by two aluminum foil covered Sylvania 275-W sun lamps placed at a distance of 5 cm from the spiral. The Vigreux column was heated to 48° with a heating tape, whose temperature was mea-

sured with a chromel-alumel thermocouple. The boiler was heated to 70° with an oil bath. The hydrocarbon boiled vigorously, filling the apparatus with vapors which were condensed by the Dry Ice-acetone condenser and recycled back to the boiler. Dry hydrogen chloride gas was added at a rate of roughly 2–4 cm<sup>3</sup>/min. The reaction was stopped after 6.7 hr. The reaction mixture was poured into pyridine, washed with water and 5% sodium bicarbonate solution, and dried. Analysis was performed by vpc on a 20% squalane on a 60–40 mesh Chromosorb P column at 40° and on a 20% Apiezon L on a 60–80 mesh Chromosorb W column at 98°.

A small portion of the reaction mixture was mixed with an equal weight of cycloheptyl chloride as internal standard and analyzed by vpc under the same conditions. The calculated percentage of internal standard was within 0.0% of that measured. The products of the reaction were collected in the usual way in small test tubes fitted with side arms and compared with authentic samples. Reinjection of the collected products into the vapor phase chromatograph under the same conditions showed no detectable decomposition. When the reaction products were resubjected to the conditions of the work-up, they were recovered unchanged.

**B. Bicyclo[4.1.0]heptane. Reaction C.**—Following the above-described procedure, 5.8 g (0.06 mol) of bicyclo[4.1.0]heptane, prepared by the method of Simmons and Smith<sup>23</sup> and free of olefins, was allowed to react with an average hydrogen chloride flow of roughly 5 cm<sup>3</sup>/min for 3.7 hr. After work-up the reaction mixture was analyzed by vpc on a 20% Apiezon L on a 60–80 mesh Chromosorb W column at 98° and a 20% squalane on a 60–40 mesh Chromosorb P column at 60°.

A small portion of the reaction mixture was mixed with an equal weight of cycloheptyl chloride as internal standard and analyzed by vpc under the same conditions. The calculated percentage of internal standard was within 0.1% of that measured. The products of the reaction were collected as above and compared with authentic samples. Reinjection of the collected products into the vapor phase chromatograph under the same conditions showed no detectable decomposition.

In other runs the lights used to heat the reaction spiral were eliminated and the reaction was run in the dark. No significant change in products occurred.

**Liquid Phase Hydrochlorinations. A. Bicyclo[2.1.0]pentane. Reaction B.**—An equimolar mixture of I (1.1  $\times$  10<sup>-2</sup> mol) and 12 M hydrochloric acid was stirred for 1.5 hr at 10°. The organic layer was separated, worked up in the usual way, and analyzed by vpc, as above.

**B. Bicyclo[4.1.0]heptane. Reaction D.**—An equimolar mixture of II (0.1 mol) and 12 M hydrochloric acid was shaken for 6 hr at room temperature. The organic layer was separated, worked up in the usual way, and analyzed by vpc as above.

**C.**—Each of the product hydrocarbons was stirred with a large excess of 12 M hydrochloric acid for 24 hr. Analysis in the usual way showed that none of them showed greater than 5% decomposition.

**Hydrochlorination in a Sealed Ampoule. Reaction E.**—A 7-cm<sup>3</sup> ampoule covered with black tape was fitted to a vacuum line. It was filled with 1.22  $\times$  10<sup>-3</sup> mol of II and 2.30  $\times$  10<sup>-3</sup> mol of dry hydrogen chloride, sealed, and heated in an oven at 160° for 24 hr. At the end of this time the vial was cooled and opened, and the contents were poured into pyridine. The mixture was washed with water and 5% aqueous sodium bicarbonate solution, and the organic layer was separated, dried over anhydrous sodium sulfate, and analyzed by vpc as above.

**Authentic Samples.**—Samples of cyclopentene (III), *n*<sub>D</sub><sup>20</sup> 1.4220, cycloheptene (VII), *n*<sub>D</sub><sup>20</sup> 1.4565, and 3-methylcyclohexene (V), *n*<sub>D</sub><sup>20</sup> 1.4438, were all obtained from Aldrich Chemical Co., and were used without further purification. A sample of 1-methylcyclohexene (VI), *n*<sub>D</sub><sup>20</sup> 1.4506, was obtained from K and K Laboratories and used without further purification.

Cyclopentyl chloride (IV), *n*<sub>D</sub><sup>20</sup> 1.4511, was prepared by refluxing cyclopentene with an excess of 12 M hydrochloric acid and an excess of calcium chloride for 20 hr. Purification was effected by distillation. Cycloheptyl chloride (IX), *n*<sub>D</sub><sup>20</sup> 1.4752, was similarly prepared from cycloheptene and purified by distillation.

*trans*-2-Methylcyclohexyl chloride (VIII) was prepared from 2-methylcyclohexanol by the method of Botteron and Shulman.<sup>24</sup> Purification by preparative vpc on a 20% Apiezon L on a 60–80

(20) D. H. R. Barton in "Kekule Symposium on Theoretical Organic Chemistry," Butterworths, London, 1959, p 129.

(21) (a) W. G. Kumler, R. S. Boikess, P. Bruck, and S. Winstein, *J. Amer. Chem. Soc.*, **86**, 3126 (1964); (b) S. Winstein, R. S. Boikess, and J. I. Brauman, unpublished results.

(22) S. G. Cohen, R. Zand, and G. Steel, *J. Amer. Chem. Soc.*, **83**, 2895 (1961).

(23) R. O. Smith and H. E. Simmons, *Org. Syn.*, **41**, 72 (1961).

(24) D. G. Botteron and G. P. Shulman, *J. Org. Chem.*, **27**, 2007 (1962).

mesh Chromosorb W column yielded material,  $n_D^{20}$  1.4584 (lit.<sup>24</sup>  $n_D^{20}$  1.4588).

1-Methylcyclohexyl chloride (X) was prepared by the method of Russell<sup>25</sup> from 1-methylcyclohexanol and thionyl chloride.

(25) G. Russell, *J. Amer. Chem. Soc.*, **74**, 3882 (1952).

Purification was effected by distillation to yield material,  $n_D^{20}$  1.4580 (lit.<sup>25</sup>  $n_D^{20}$  1.4580).

Registry No.—I, 185-94-4; II, 286-08-8; HCl 7647-01-0.

## Reactive Intermediates in the Bicyclo[3.1.0]hexyl and Bicyclo[3.1.0]hexylidene Systems. VI.<sup>1</sup> The Free-Radical Addition of Methanethiol and Methanethiol-*d* to Bicyclo[3.1.0]hexene-2

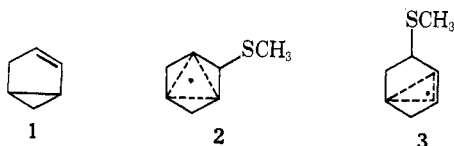
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Free-radical addition of methanethiol to bicyclo[3.1.0]hexene-2 results in a mixture of *cis*-3-methylthiobicyclo[3.1.0]hexane, *trans*-2-methylthiobicyclo[3.1.0]hexane, *trans*-3-methylthiobicyclo[3.1.0]hexane, and *cis*- and *trans*-3-methyl-5-methylthiocyclopentene. The dependence of product composition upon concentration of methanethiol suggests that an equilibrium of substituted 2-bicyclo[3.1.0]hexyl and  $\Delta^2$ -cyclopentylmethyl radicals are involved rather than the related delocalized intermediate. The stereochemistry of the radical addition of methanethiol-*d* leading to 3-deuterio-*trans*-2-methylthiobicyclo[3.1.0]hexane was investigated and found to be predominantly *trans* (81–91%).

Our interests in carbonium ion<sup>4</sup> and carbene<sup>5</sup> intermediates in the bicyclo[3.1.0]hexyl and bicyclo[3.1.0]hexylidene systems provided the impetus to investigate the nature of analogous free-radical intermediates. We have recently discussed free-radical abstraction reactions of bicyclo[3.1.0]hexane,<sup>6</sup> and now report on a complementary study of radical addition of methanethiol to bicyclo[3.1.0]hexene-2 (1). In terms of orientation, there are two possible reaction pathways. Addition of the methylthio radical to C-2 might generate a delocalized radical (2) analogous to the tris-homocyclopropenyl carbonium ion<sup>7</sup> (or a related set of equilibrating classical radicals), while addition at C-3 might produce a delocalized radical analogous to either the bicyclobutonium ion<sup>8</sup> (3) or the closely



related symmetrical bisected cyclopropylcarbanyl carbonium ion<sup>9</sup> (or, alternatively, a related set of equilibrating classical radicals).

Radical addition of methanethiol to bicyclo[3.1.0]hexene-2 proceeded smoothly upon irradiation to give an 85–95% yield of 1:1 addition products. Vapor phase chromatography on a Carbowax 1500 column

showed that four components were present in a 1.5:33:59:6.5 composition. The 6.5% component was isolated by vapor phase chromatography and infrared analysis suggested a bicyclic structure (CH absorption at 3060, 3040, and 3000  $\text{cm}^{-1}$ , no C=C absorption, and cyclopropane at 1020  $\text{cm}^{-1}$ ). In particular, the 3040- $\text{cm}^{-1}$  CH absorption was enhanced, which indicates a *cis* isomer.<sup>4</sup> Consistent with this picture, the 6.5% component was identified as *cis*-3-methylthiobicyclo[3.1.0]hexane (4) by comparison of its infrared spectrum with that of an authentic standard. The 59% component was isolated by vapor phase chromatography and its infrared spectra also suggested a [3.1.0] ring system (CH at 3070, 3040, and 3005  $\text{cm}^{-1}$ , no C=C absorption, and cyclopropane absorption at 1020  $\text{cm}^{-1}$ ). The nmr spectrum exhibited two *S*-methyl peaks at  $\tau$  7.94 and 8.02 with a relative ratio of 80:20. With this accurate lead, the composition of the 59% component was determined to be a mixture of *trans*-2-methylthiobicyclo[3.1.0]hexane (5) and *trans*-3-methylthiobicyclo[3.1.0]hexane (6), with the *trans*-2 thio ether present as the major component, by preparation of authentic standards and infrared spectral comparison.

Infrared analysis of the 33% component, isolated by vapor phase chromatography, gives a clear indication of a cyclopentene ring (3050, 3045, 1600, and 750  $\text{cm}^{-1}$ ) with a *C*-methyl group (1375  $\text{cm}^{-1}$ ). The nmr spectrum exhibits absorption for olefinic protons at  $\tau$  4.30–4.58 (2 H), hydrogen  $\alpha$  to *S*-methyl at 6.08–6.48, hydrogen  $\alpha$  to *C*-methyl at 6.90–7.50, *S*-methyl at 8.02 and 8.07 (two singlets, 3 H), methylene hydrogens at 7.58–8.80 (2 H), and *C*-methyl at 8.90 and 8.97 (two doublets in a 20:80 ratio). That the hydrogens  $\alpha$  to *S*-methyl and  $\alpha$  to *C*-methyl are allylic is indicated by comparison with the analogous hydrogens in 3-methylthiocyclopentene,  $\tau$  6.08–6.46, and 3-methylcyclopentene, 7.02–7.48. Confirmation of the methylcyclopentene ring structure was achieved by the desulfurization of the methylthiomethylcyclopentenes with deactivated Raney nickel catalyst in 3-pentanone, which produced a mixture of 1-methyl-, 3-methyl-, and 4-methylcyclo-

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