[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILL., AND THE CONVERSE MEMORIAL LABORATORY, HARVARD UNIVERSITY, CAMBRIDGE 38, MASS.]

The Deamination of *cis*- and *trans*-3-Bicyclo[3.1.0]hexylamines in Aqueous Solution

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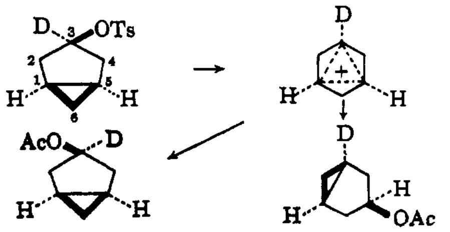
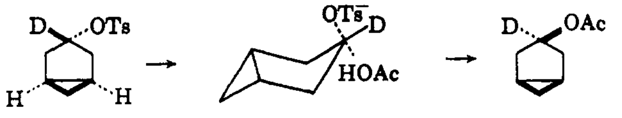
The isomeric 3-bicyclo[3.1.0]hexylamines are converted by deamination into a mixture of both 3- and 2-bicyclo-[3.1.0]hexanols. It has been shown by deuterium labeling that 1,3-valence rearrangement in the initially formed cation is not an important part of these reactions. The results cannot, therefore, be accommodated by an intermediate "tris-homocyclopropenyl" cation.

About five years ago we became interested in the investigation of some aspects of the chemistry of bicyclo[3.1.0]hexane derivatives including the possibility of unusual behavior of the 3-bicyclo[3.1.0]hexyl cation(s) due to transannular 1,3-interactions. In the meantime, Winstein and co-workers[2] reported results of an independent study of this cation as generated by arenesulfonate solvolysis which covered partly the same ground as our early program. This paper reports a portion of our investigation which has not previously been dealt with and which bears directly on the chemistry of the 3-bicyclo[3.1.0]hexyl cation system. In certain respects the work is complimentary to the published studies of solvolysis.[2] Specifically, we are concerned here with the deamination of *cis*- and *trans*-3-bicyclo[3.1.0]hexylamines and their 3-deuteriated counterparts. The investigation of amine deamination in this system was of special interest to us in connection with the question of whether bridged carbonium ions are ever produced directly in amine deamination and the recent evidence for the classical norbornyl cation from deamination reactions.[3-5]

It is appropriate first to summarize the previous work[2] on the acetolysis of *cis*- and *trans*-3-bicyclo-[3.1.0]hexyl toluenesulfonates. Both *cis*- and *trans*-toluenesulfonates afforded essentially a single acetate, the *cis*-3-acetate with a maximum contamination by the *trans*-3-acetate of 1.5%. The yield of acetate from the *cis*-toluenesulfonate was quantitative, but the *trans*-sulfonate produced only 67% of the theoretical acetate together with a volatile material, presumably olefinic. The measured first-order rate constant for acetolysis at 50° was 9.2 times greater for the *cis*-toluenesulfonate than for the *trans* isomer and both rate constants fell between the values for cyclopentyl and cyclohexyl toluenesulfonates. The acetolysis of the *cis*-toluenesulfonate showed a small "special salt effect,"[6] but that of the *trans* isomer did not. Finally, the acetolysis of the 3-deuteriated-3-bicyclo-[3.1.0]hexyl toluenesulfonates was reported to give acetate with equal distribution of deuterium over carbons 1, 3 and 5 in the case of the *cis* isomer and without redistribution in the case of the *trans* isomer. These results were interpreted in terms of a unique nonclassical ion, the "tris-homocyclopropenyl" cation, for acetolysis of the *cis*-sulfonate. The acetolysis of the *trans*-sulfonate was considered as being essentially a nucleophilic displacement by solvent.

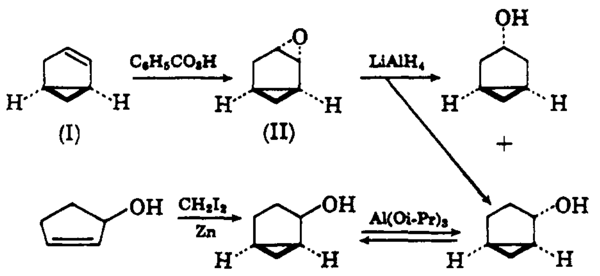




Results

The results from our experiments on amine deamination contrast strikingly with those just reviewed for sulfonate acetolysis. Amine deamination of either *cis*- or *trans*-3-amine produces a mixture consisting of the epimeric 3-alcohols and, in addition, the epimeric 2-alcohols. Because of the complexity of these reactions it is desirable to consider first some of the details of stereochemical and structural identification.

Stereochemistry of the 2- and 3-Hydroxybicyclo-[3.1.0]hexanes.—Although the stereochemical assignments made for the epimeric 3-alcohols in the previous work[2] seem reasonable, they are certainly not beyond reasonable doubt. Unequivocal evidence as to these configurations is now adduced on the basis of the present studies. Bicyclo[3.1.0]hexene-2 (I), prepared from interaction of the Simmons–Smith reagent[7] with excess cyclopentadiene, when treated with perbenzoic acid formed a single epoxide (stereospecificity checked by gas chromatography) which must be the *trans* isomer II because of the marked steric shielding by the cyclopropane ring. Reduction of this epoxide with lithium aluminum hydride afforded a mixture of *trans*-3-ol and *trans*-2-ol (46 and 54%, respectively, by gas chromatographic analysis). These were different from the alcohols prepared by the addition of methylene[7] to Δ^3-cyclopentenol and Δ^2-cyclopentenol, respectively, but identical with the corresponding epimers. This evidence shows conclusively that the reaction of Δ^3- and Δ^2-cyclopentenol with the Simmons–Smith reagent[7] produces the *cis*-alcohols, in agreement with the previous supposition.[2] In the present work it was noted that the equilibration of *cis*- and *trans*-bicyclo[3.1.0]hexane-2-ols with alumi-



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[1] National Science Foundation predoctoral fellow, 1958–1961.

[2] (a) S. Winstein, J. Sonnenberg and L. DeVries, *J. Am. Chem. Soc.*, **81**, 6523 (1959); (b) S. Winstein, *ibid.*, **81**, 6524 (1959); (c) S. Winstein and J. Sonnenberg, *ibid.*, **83**, 3235 (1961); (d) *ibid.*, **83**, 3244 (1961).

[3] E. J. Corey, J. Casanova, Jr., P. A. Vatakencherry and R. Winter, *ibid.*, **85**, 169 (1963).

[4] H. Zollinger, "Diazo and Azo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961, pp. 93–101, 123–136.

[5] J. H. Ridd, *Quart. Rev.*, **15**, 418 (1961).

[6] S. Winstein, *et al.*, *J. Am. Chem. Soc.*, **80**, 169 (1958).

[7] H. E. Simmons and R. D. Smith, *ibid.*, **81**, 4256 (1959).

num isopropoxide in isopropyl alcohol at reflux produced an equilibrium mixture containing 70% of the *cis* and 30% of the *trans* isomer. The transfer of methylene[7] to Δ^2-cyclopentenol appeared to be stereospecific.[7a]

Synthesis and Stereochemistry of the 3-Bicyclo[3.1.0]hexylamines.—The reaction of *trans*-3-bicyclo[3.1.0]hexyl toluenesulfonate with sodium azide in dimethyl sulfoxide and subsequent reduction of the azide so formed with lithium aluminum hydride produced a 3-bicyclo[3.1.0]hexylamine (over 94% stereospecificity) to which we assign the *cis* configuration since this is the expected product from either SN1 or SN2 pathways (the latter is the more likely, however). Similarly, *cis*-3-bicyclo[3.1.0]hexyl toluenesulfonate afforded the epimeric amine (*ca.* 96% stereospecificity), which is assigned the *trans* configuration. The epimeric amines were separated cleanly by gas chromatography using an alkali-treated Carbowax 20M column. Reduction of the oxime of bicyclo[3.1.0]hexan-3-one with lithium aluminum hydride gave a mixture of the *cis* (77%) and *trans* (23%) amines.[8] Pure *cis*-amine could be obtained from this mixture by recrystallization of the hydrogen oxalate salts. In this way, starting from the oxime and lithium aluminum deuteride, a sample of 3-deuterio-*cis*-bicyclo[3.1.0]hexylamine was prepared with purification by preparative gas chromatography. Reduction of the 3-oxime with sodium–ethanol mixture gave 43% of the *cis*-amine and 57% of the *trans*-amine. A sample of 3-deuterio-*trans*-bicyclo[3.1.0]hexylamine was prepared by sodium–ethanol-O-*d* reduction of the oxime and subsequent recrystallization of the amine hydrochloride.

Deamination Experiments.—The deamination of either *cis*- or *trans*-bicyclo[3.1.0]hexylamines produced a mixture of alcohols with four major components evident from vapor phase chromatographic analysis. These were[9]

cis-3-amine ⟶	*cis*-3-ol (5%)	*cis*-2-ol (27.5%)
	trans-3-ol (30.5%)	*trans*-2 ol (37%)
trans-3-amine ⟶	*cis*-3-ol (41%)	*cis*-2-ol (9%)
	trans-3-ol (14%)	*trans*-2-ol (36%)

In the chromatographic analysis the *cis*-3-ol and *trans*-2-ol were separated cleanly and could be determined directly. The *trans*-3-ol and *cis*-2-ol were not separated from one another, however, and had to be determined by collection and oxidation to a mixture of the corresponding ketones which was resolved cleanly by gas chromatography.

The *cis*-3-bicyclo[3.1.0]hexanol produced by deamination of 3-deuterio-*cis*-3-bicyclo[3.1.0]hexylamine contained two-thirds of its deuterium at carbon 3 with the remaining one-third probably at carbons 1 and 5 (*cf.* ref. 2d). The *trans*-3-ol produced in the same reaction contained essentially all the deuterium label at carbon 3, however. The *cis*-3-bicyclo[3.1.0]hexanol formed in the deamination of 3-deuterio-*trans*-bicyclo[3.1.0]hexylamine also contained essentially all of the deuterium label at carbon 3. The analyses for the fraction of deuterium remaining at carbon 3 in the 3-ol were performed by oxidation of the 3-alcohol to bicyclo[3.1.0]hexane-3-one and assay for deuterium by mass spectrometry (see Experimental for details).

Discussion

Perhaps the salient and most evocative feature of our results is the clear disparity between the products from deamination of *cis*- and *trans*-3-bicyclo[3.1.0]hexylamines and those from acetolysis of *cis*- and *trans*-3-bicyclo[3.1.0]hexyl toluenesulfonates. In contrast to acetolysis, which gives only one acetate, the *cis*-3-acetate, from either 3-toluenesulfonate deamination of either 3-amine in water leads to *both* epimeric 3-alcohols and, *moreover, to the pair of isomeric 2-alcohols* by rearrangement. The *cis*-3-amine in fact affords only a minor proportion of *cis*-3-alcohol (*ca.* 5% of total alcohols), the tris-homocyclopropenyl cation postulated by Winstein as the sole intermediate in acetolysis of the *cis*-3-toluenesulfonate cannot, under any assumptions, account for more than 7% of the total 3-alcohols from the deamination reaction of the *cis*-3-amine. Furthermore, at least 50% of the *cis*-3-alcohol cannot have been formed *via* the tris-homocyclopropenyl cation in this case. In the deamination of the *trans*-3-amine there is no evidence to suggest that the Winstein cation is involved in the slightest degree. Thus, the rationale advanced for the behavior of the 3-bicyclo[3.1.0]hexyl system in solvolysis and the concepts that have influenced general proposals of "homoaromaticity" can be seen to fail when applied to the case of amine deamination in the ring system for which these ideas were adduced. The possibility that cationic intermediates are not involved in the amine deamination seems exceedingly remote on general grounds and more specifically because of the nature of the admixture of alcohols, unrearranged and rearranged, produced from either epimeric amine. Clearly, the observations relating to amine deamination do not contradict the view that the tris-homocyclopropenyl structure is a correct formulation of the cationic intermediate in acetolysis of the *cis*-3-toluenesulfonate. They do, however, raise questions regarding the general chemical significance of such "homoaromatic" structures and, even more broadly, they weaken further the argument, commonly assumed as a sort of canon, that the mechanistic response of a carbon structure in sulfonate or halide solvolysis, will, in the absence of conformational complications,[10] be a valid guide to behavior in other reactions of the system which involve carbonium ion intermediates.

Evidence has recently been provided[3] that the deamination of either *exo*- or *endo*-norbornylamine in acetic acid as solvent produces the classical norbornyl cation rather than the bridged ion which has been implicated as an intermediate in solvolysis.[11] This is possibly a result of the very low[12] free energy of decomposition of the norbornyl diazonium ion which imposes a severe limit on the time available for the acquisition of vibrational energy in those modes which produce motion in the direction of the bridged or non-classical ion structure. The same hypothesis can be applied to the deamination of the isomeric 3-bicyclo[3.1.0]hexylamines. The decomposition of the diazonium ion III to the tris-homocyclopropenyl structure requires a rather complex displacement of nuclei, including stretching of the C_3–N bond and the C_1–C_5 bond and hence there is a probability factor (or negative entropy demand) which is detrimental to

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[7a] NOTE ADDED IN PROOF.—Similar findings have been reported recently by W. G. Dauben and G. H. Berezin, *J. Am. Chem. Soc.*, **85**, 468 (1963).

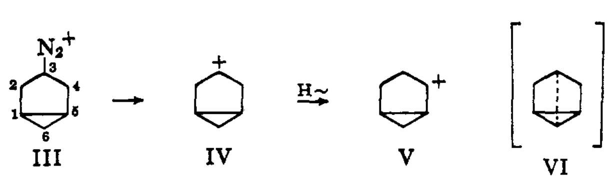
[8] Reduction of bicyclo[3.1.0]hexan-3-one with lithium aluminum hydride affords a mixture of *cis* (89%) and *trans* (11%) alcohols with a similar preponderance of the *cis* isomer (ref. 2c).

[9] The values shown have been corrected to compensate for the fact that the sample of starting *cis*-amine contained 7% of the *trans*-amine and the sample of *trans*-amine contained 6% of the *cis*-amine.

[10] For discussions of conformational effects in acyclic systems during amine deamination see (a) D. J. Cram and J. E. McCarthy, *J. Am. Chem. Soc.*, **79**, 2866 (1957); (b) J. C. Martin and W. G. Bentrude, *J. Org. Chem.*, **24**, 1902 (1959); (c) B. M. Benjamin, H. S. Schaeffer and D. J. Collins, *J. Am. Chem. Soc.*, **79**, 6160 (1957); (d) D. Semenow, C-H. Shih and W. G. Young, *ibid.*, **80**, 5472 (1958).

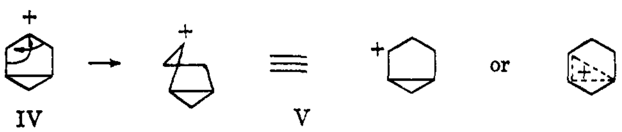
[11] S. Winstein and D. Trifan, *ibid.*, **74**, 1147, 1154 (1952).

[12] D. Y. Curtin and M. Wilhelm, *Helv. Chim. Acta*, **40**, 2129 (1957).



reaction by this pathway. In contrast, simple dissociation to the classical ion IV, a reaction of low activation enthalpy, is not so impeded by entropy requirements. We are inclined to accept this argument for the present as the most tenable rationale given the available data.

The intervention of the classical ion IV serves to explain the non-stereospecific formation of the 3-alcohols with an additional proviso, *viz.*, that the reaction with nucleophilic solvent be sufficiently fast so that the shielding effect of the detached nitrogen molecule is of some consequence (and sufficiently fast to compete with rearrangement). The occurrence of rearrangement to the 2-carbonium ion V may also be taken as consistent with the prior formation of the cation IV. Such a rearrangement can be regarded in principle as a 2 → 3-rearrangement of hydrogen or as a rearrangement of carbon, *e.g.*

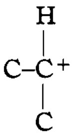


Although a decision between these pathways has not yet been made, experimentally the former, hydrogen rearrangement, seems preferable. There is good evidence to indicate that the 2-cation is far more stable than the 3-cation[13] and, hence, that there is abundant driving force for the interconversion. The striking aspect of this rearrangement to the 2-cation is that this mode of reaction of the classical ion IV competes so successfully with the isomerization to the tris-homocyclopropenyl ion or some other non-classical ion such as VI. (Expression VI is intended to convey an ion with essentially unchanged C_1–C_5 distance and weak cross-ring interaction between the vacent p-orbital at C_3 and the "loose" electrons of the cyclopropyl system.) This is somewhat unexpected if the tris-homocyclopropenyl cation is so stable as to provide driving force for the ionization of the *cis*-3-toluenesulfonate and, indeed, so stable as to justify emphasis on the "homoaromatic" concept in this case. From our data it can be argued that the interpretation which Winstein, *et al.*, attach to their experimental results is not above doubt. An alternative to their view which cannot be excluded at present and which seems quite plausible is that the ion VI is initially formed in the acetolysis of the *cis*-3-toluenesulfonate and that rearrangement occurs subsequently *via* the tris-homocyclopropenyl cation or possibly even interconverting ions of lower symmetry, in particular C_s symmetry as illustrated by VII.

VII

(In VII two 1,3- cross-ring interactions are accentuated to some degree at the expense of the third.[14])

It should be pointed out that the recognition of appreciable 1,3-interaction in the 3-bicyclo[3.1.0]hexyl system logically leads to several alternatives of which the possible stability of the tris-homocyclopropenyl cation is but *one;* another is the expectation that the isotope position rearrangement of more classical (charge-localized) structures such as IV, VI or VII would entail sharply lowered activation energies. In summary, it would seem that the experimental data *do* expose significant 1,3- or trans-annular interaction in the 3-bicyclo[3.1.0]hexyl cationic system. The evidence from solvolysis rates and the deamination studies tends to indicate that such effects are not universally large, and certainly their detailed interpretation must be subject to serious question at present.

In an earlier discussion[3] of the diversity of carbonium ions produced by amine deamination and solvolysis in the same, conformationally fixed system, the formation of vibrationally excited cations in deamination has been viewed as a possibility and, indeed, this is currently being studied experimentally in our laboratory. It is both relevant and essential then to examine the findings in the 3-bicyclo[3.1.0]hexyl system in full awareness of this potential complication. In general, it is not possible to predict whether excess vibrational energy, gained during exothermic decomposition, would be lost to surrounding molecules before rearrangement can occur. That energy must be concentrated, in some measure, in the vibrational mode leading to rearrangement (time interval unknown) and then an additional increment of time corresponding to the period of that vibration is required to complete the migration. This latter interval is comparable to the average time between collisions of a solvent molecule with a solute molecule of approximately the same size (*ca.* 10^{-13} sec.). We may, nonetheless, assume for the moment that the deamination of the 3-bicyclo[3.1.0]hexylamines produces a vibrationally excited cation and then proceed to examine the resulting argument. Clearly the isomeric 2-bicyclo[3.1.0]hexanols might be derived from the excited cation by hydrogen migration; it seems plausible that the energy released by C–N fission might quickly find its way into the  $\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{C{-}C^+} \\ | \\ \mathrm{C} \end{array}$ bending modes and thence into the bending modes of the adjacent C–H groups. On the other hand, direct extension of our supposition leads to the conclusion that the internal interconversion of 3-bicyclo[3.1.0]hexyl cations or their transformation to the "homoaromatic" tris-homocyclopropenyl cation must not be so accelerated and must, in fact, be unfavorable relative to bimolecular interaction with water. It is not obvious why the excess vibrational energy might not concentrate in the modes leading to the latter rearrangement and hence the assumption of an excited cation does not explain the absence of appreciable rearrangement of the type observed in acetolysis of the *cis*-3-toluenesulfonate.[15]

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[13] Personal communication from Prof. S. Winstein, who has examined recently the rates of solvolysis of the *cis*- and *trans*-2-arenesulfonates. These solvolyses produced derivatives of *cis*- and *trans*-2-alcohols, Δ^3-cyclohexenol and hydrocarbon. We were not able to detect Δ^3-cyclohexenol in our deamination products.

[14] The order of stability of C_s and C_{3v} structures lies beyond our ken until such time that the calculation of *total* energies is possible or until this subtlety can be bared by experiment.

[15] (a) It can be argued that the classical 3-cation in aqueous medium would suffer reaction with water at a rate which is faster than the rate for coordination with acetic acid solvent. Clearly, this would probably hold for *both* normal and excited classical ions. Evidence is presented in the Experimental section, however, that deamination of the 3-bicyclo[3.1.0]hexylamines in acetic acid gives a product distribution similar to that from deamination in water and is in sharp contrast to the acetolysis of the corresponding 3-toluenesulfonates. (b) For a recent review of reactions of vibrationally excited species and the question of rates of randomization of internal energy in small molecules see H. M. Frey, *Ann. Rept. Chem. Soc.*, **57**, 38 (1960).

Experimental[16]

3-Bicyclo[3.1.0]hexanone.—The preparation used in this work was somewhat different from that given in the literature[3c] and proceeds in higher yield, so it is given here in detail. Ice-cold solutions of 9.55 g. (0.032 mole) of sodium dichromate dihydrate in 16 ml. of acetic acid and 9.39 g. (0.096 mole) of *cis*-3-bicyclo-[3.1.0]hexanol[3c] in 6 ml. of acetic acid were mixed in a 125-ml. erlenmeyer flask. The reaction flask was cooled in ice as needed to keep the original exothermic reaction under control and maintain the reaction temperature in the range 45–50°. After the temperature of the reaction mixture had returned to room temperature (about 1 hr.), the reaction mixture was diluted with 70 ml. of water and extracted continuously for 8 hr. with 50 ml. of pentane. The pentane extract was washed with saturated sodium bicarbonate solution and saturated salt solution, then dried over magnesium sulfate. The dried pentane solution was fractionally distilled at atmospheric pressure to give 5.8 g. of product (63%), b.p. 149–150°.

3-Bicyclo[3.1.0]hexanone Oxime.—To a solution of 6.5 g. of hydroxylamine hydrochloride in 39 ml. of water were added successively 26 ml. of 10% aqueous sodium hydroxide and 2.6 g. of 3-bicyclo[3.1.0]hexanone. Sufficient methanol was then added to bring the ketone into solution. The reaction mixture was heated for 15 min. on a steam-bath, cooled to 0°, and extracted with ether (3 × 50 ml.). The ether extract was washed with 1 *N* hydrochloric acid and saturated salt solution and dried over sodium sulfate. The ether was evaporated under reduced pressure leaving 2.5 g. (83%) of a colorless oil which solidified on cooling in the freezer to a white solid, m.p. 38–40°. The average yield of a dozen runs using 0.20–5.0 g. of ketone was 84%. The analytical sample was recrystallized to constant melting point from *n*-hexane, m.p. 40.0–41.5°.

Anal. Calcd. for C_6H_9NO: C, 64.84; H, 8.16; N, 12.60. Found: C, 64.42; H, 7.92; N, 12.43.

cis-**3-Bicyclo[3.1.0]hexylamine.** A.—To a clear solution of 3.3 g. of lithium aluminum hydride in 150 ml. of dry ether a solution of 4.9 g. of 3-bicyclo[3.1.0]hexanone oxime in 50 ml. of dry ether was added dropwise with stirring. The reaction was then refluxed for 48 hr. The excess reagent was decomposed by careful addition of water. Sufficient excess water was then added to give a granular precipitate, and the resulting suspension was filtered. The precipitate was washed thoroughly with ether. The solvent was removed from the combined ether solutions by distillation through a 2-ft. Vigreux column. The residue was distilled at atmospheric pressure to give 3.15 g. (74%) of a color-oil, b.p. 129–130°. The v.p.c. of the product showed a *cis*:*trans*-amine ratio of 77:23.

The hydrogen oxalate salt of the product was prepared in 99% yield by mixing ether solutions of the amine and oxalic acid and collecting the precipitated product by filtration; m.p. 197–199°. The crude hydrogen oxalate was recrystallized to constant melting point from ethanol with 33% recovery; m.p. 202.5–203.0°.

Anal. Calcd. for $C_8H_{13}NO_4$: C, 51.33; H, 7.00; N, 7.48. Found: C, 51.17; H, 6.96; N, 7.41.

The hydrogen oxalate was reconverted to the free amine by treatment with a 50% excess of 10% aqueous sodium hydroxide, extraction of the amine with ether, and distillation as in the previous work-up; recovery 95%. The amine so obtained showed a *cis*:*trans* ratio of 93:7 (v.p.c.).

B.—A solution of 0.636 g. (2.37 mmoles) of *trans*-3-bicyclo-[3.1.0]hexyl tosylate[3c] in 3 ml. of dimethyl sulfoxide was added to a solution of 0.65 g. (10 mmoles) of sodium azide in 10 ml. of dimethyl sulfoxide and 2 ml. of water preheated to 70°. The reaction was kept at the same temperature for 1 hr., cooled to room temperature, diluted with 17 ml. of water, and extracted with ether (3 × 6 ml.). The ether extract was washed with saturated salt solution and dried over calcium chloride.

The dried ether extract was added dropwise with stirring to a slurry of 0.91 g. of lithium aluminum hydride in 4 ml. of dry ether. After the addition was completed the reaction was refluxed for 1 hour. Excess reagent was decomposed by dropwise addition of water. Sufficient excess water was added to give a granular precipitate. The resulting suspension was filtered, and the precipitate was washed thoroughly with ether. The combined ether solutions were treated with an excess of a solution of oxalic acid in ether and the amine hydrogen oxalate so formed collected by filtration. There was obtained 0.305 g. of product (69%), m.p. 203–204°. The v.p.c. analysis of the amine obtained in the usual way from this salt showed two peaks in the ratio 94:6 (*cis*:*tras*).

trans-**3-Bicyclo[3.1.0]hexylamine.** A.—To a refluxing solution of 1.0 g. of 3-bicyclo[3.1.0]hexanone oxime in 20 ml. of ethanol dried over magnesium ethoxide was added 2.0 g. of sodium in small pieces as rapidly as possible. After the sodium had completely dissolved, the reaction mixture was cooled in ice and acidified with 20 ml. of 6 *N* hydrochloric acid. The resulting suspension was evaporated to dryness under reduced pressure. The residue was treated with 8 ml. of 10% aqueous sodium hydroxide and extracted with ether (3 × 8 ml.). The ether extract was dried over potassium carbonate, and the ether was removed by distillation through a 2-ft. Vigreux column. The residue was distilled at atmospheric pressure to give 0.46 g. (53%) of product, b.p. 129–130°. The v.p.c. of the product showed a ratio of *cis*:*trans*-amine of 43:57.

In another experiment, after the sodium had dissolved, 100 ml. of water was added to the reaction mixture, and the amine, along with ethanol, was steam distilled into 5 ml. of 6 *N* hydrochloric acid. The distillate was evaporated to dryness under reduced pressure, leaving 0.70 g. (66%) of crude amine hydrochloride, m.p. 192–195°. The hydrochloride was recrystallized to constant melting point from methanol–acetone giving 0.27 g. of material, m.p. 245–246°.

Anal. Calcd. for $C_6H_{12}NCl$: C, 53.93; H, 9.05; N, 10.48. Found: C, 54.08; H, 8.58; N, 10.60.

The hydrochloride was converted to the free amine by treatment with 10% aqueous sodium hydroxide, ether extraction, and distillation as before, giving the amine in 80% recovery. This material showed a *cis*:*trans* ratio of 6:94 on v.p.c.

B.—*cis*-3-Bicyclo[3.1.0]hexyl tosylate[3c] (1.80 g.) was converted to the amine hydrogen oxalate (1.02 g., 81%) in the manner previously described for the synthesis of the *cis*-amine from the *trans*-tosylate. The product had m.p. 204–206° and gave an amine mixture which showed a *cis*:*trans* ratio of 4:96 on v.p.c. A similar experiment using methanol–water in place of dimethyl sulfoxide gave a product having a *cis*:*trans* ratio of 63:37.

trans-**3-Bicyclo[3.1.0]hexylamine-3-*d*.**—To a refluxing solution of 1.91 g. of 3-bicyclo[3.1.0]hexanone oxime in 35 ml. of ethanol-O-*d* was added 4.15 g. of sodium in small pieces as rapidly as possible. After all the sodium had dissolved, the reaction mixture was diluted with 100 ml. of water and the amine, along with ethanol, was steam distilled into a mixture of 5 ml. of concd. hydrochloric acid and 5 ml. of water. The distillate was evaporated to dryness under reduced pressure and the residue was recrystallized from methanol–acetone to give 0.64 g. of amine hydrochloride, m.p. 234–235°. The v.p.c. of the amine obtained from this material showed a *cis*:*trans* ratio of 11:89. Deuterium combustion analysis of the hydrochloride gave 9.40 atom % excess deuterium, equivalent to 1.128 deuterium atoms per molecule. Evidently some deuterium has been introduced at other positions, doubtless alpha to the oximino group before reduction.

cis-**3-Bicyclo[3.1.0]hexylamine-3-*d*.**—The reduction of 5.32 g. of 3-bicyclo[3.1.0]hexanone oxime with 4.0 g. of lithium aluminum deuteride in ether was carried out in the same manner as the previously described lithium aluminum hydride reduction of the oxime. There was obtained 2.95 g. of amine shown by v.p.c. to have a *cis*:*trans* ratio of 81:19.

The purified hydrogen oxalate derivative was analyzed for deuterium by combustion analysis (performed by Mr. J. Nemeth).

Anal. Calcd. for $C_8H_{12}DNO_4$: 7.69 atom % excess deuterium. Found: 7.68 atom % excess deuterium.

The *cis*-amine was obtained over 99% pure in 70% recovery from the product mixture by preparative v.p.c.

Vapor Phase Chromatography of the Amines.—The chromatographic column used for both the analytical and preparative work was a 12-ft. column 0.25 in. in diameter packed with firebrick on which had been deposited in turn 20% by weight of potassium hydroxide and 1% of Carbowax 20 M. Helium was used as carrier gas.

The analytical chromatograms were run using 1-μl. samples of neat amine at a starting temperature of 50° and a programmed temperature rise of 3.3°/min., with a helium flow rate of *ca.* 50 ml./min. Under these conditions typical retention times are 12 min. 44 sec. and 15 min. 47 sec. for the *cis*- and *trans*-amines, respectively. The peak areas were determined by weighing pieces of paper cut to the shape of the peak. Peak ratios determined in this way were found to be reproducible to 0.5–0.9%.

The preparative chromatography was done using 20-μl. samples of neat amine at a constant temperature of 80° with the same helium flow rate. Under these conditions the amines showed retention times of approximately 8 and 11 min. for *cis*- and *trans*-amines, respectively. The eluted material was collected in a trap cooled with liquid nitrogen. Chromatography of the collected amine under analytical conditions showed the amine to be 99+% pure *cis* isomer.

Reaction of Nitrous Acid with 3-Bicyclo[3.1.0]hexylamine.—The deamination of *trans*-3-bicyclo[3.1.0]hexylamine is described as an example of the method used for all the deamination reactions.

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[16] Elemental analyses were performed by the Scandinavian Microanalytical Service, Copenhagen. Infrared spectra of most of the compounds reported herein were measured using a Perkin–Elmer Infracord with individual calibration and these are recorded in the Ph.D. thesis of R. L. D. (Harvard University). Vapor phase chromatographic work was carried out with an F and M model 300 instrument.

A solution of 0.224 g. (3.25 mmoles) of sodium nitrite in 0.3 ml. of water was added to a solution of 0.315 g. (3.25 mmoles) of *trans*-3-bicyclo[3.1.0]hexylamine and 0.375 g. (3.25 mmoles) of 85% phosphoric acid in 3.5 ml. of water cooled in an ice-bath. The reaction mixture was kept in an ice-bath for 2 hr., then at room temperature for 42 hr. The reaction mixture was then saturated with salt and extracted with ether (3 × 3 ml.). The ether extract was washed with saturated sodium bicarbonate solution, saturated salt solution, and dried over anhydrous sodium sulfate. The ether was removed from the dried extract by distillation through a 1-foot spiral wire column. The residue was distilled in a short path distillation apparatus at atmospheric pressure giving 0.140 g. of product which was analyzed by v.p.c. Infrared spectra of the alcohols are recorded in the Ph.D. thesis of R. L. D., Fig. 5–9.

Oxidation of the Mixed Alcohols.—The control experiment performed for these oxidations is described; all these oxidations were performed in the same manner.

A solution of 53.8 mg. (0.18 mmole) of sodium dichromate dihydrate in 0.1 ml. of acetic acid was added to a mixture of 20.5 mg. (0.21 mmole) of 3-bicyclo[3.1.0]hexanol (from the reaction of methylene iodide and zinc–copper couple with Δ^3-cyclopentenol) and 31.3 mg. (0.32 mmole) of 2-bicyclo[3.1.0]hexanol (from the lithium aluminum hydride reduction of 2-bicyclo-[3.1.0]hexanone) cooled in ice. The reaction mixture was allowed to stand at room temperature for 0.5 hr., then heated in a water-bath at 75° for 5 min. The reaction mixture was then diluted with 3 ml. of saturated salt solution and extracted with pentane (3 × 5 ml.). The pentane extract was dried over Drierite and the pentane was removed by distillation through a spiral wire column. The residue was subjected directly to v.p.c. analysis on a 4-ft. commercial column of dinonyl phthalate on firebrick. Material collected under the two major peaks had infrared spectra identical with those of 3-bicyclo[3.1.0]-hexanone and 2-bicyclo[3.1.0]hexanone, respectively. The peak ratio was 40.7:59.4, while the ratio of starting alcohols was 39.8:60.3. The infrared spectrum of 2-bicyclo[3.1.0]hexanone is recorded in Fig. 7 of the aforementioned thesis.

***cis*- and *trans*-3-Bicyclo[3.1.0]hexanol. A. By Lithium Aluminum Hydride Reduction of 2-Bicyclo[3.1.0]hexanone.**—A solution of 2.88 g. (0.03 mole) of 2-bicyclo[3.1.0]hexanone in 10 ml. of dry ether was added with stirring to a suspension of 1.14 g. (0.03 mole) of lithium aluminum hydride in 40 ml. of dry ether at a rate sufficient to cause the reaction mixture to reflux gently. After the addition was completed the reaction was refluxed for 12 hr. Excess reagent was destroyed by dropwise addition of water, then sufficient excess water was added to cause the precipitated alumina to become granular. The solid was removed by filtration and washed with several portions of ether. The combined filtrate and washings were dried over anhydrous sodium sulfate. The ether was distilled off through a 2-ft. Vigreux column and the residue was fractionally distilled at reduced pressure to give 2.81 g. of product (95%), b.p. 70–71° (24 mm.). The v.p.c. of the product showed a *cis*:*trans* ratio of 87:13.

B. By Sodium and Alcohol Reduction of 2-Bicyclo[3.1.0]-hexanone.—A solution of 2.88 g. (0.03 mole) of 2-bicyclo[3.1.0]-hexanone in a mixture of 9 ml. of 95% ethanol and 3 ml. of water was cooled in ice while 1.6 g. of sodium was added to it in small pieces with stirring. After the sodium had completely dissolved, the reaction mixture was diluted with 30 ml. of water, saturated with salt, and extracted with ether (3 × 25 ml.). Water and alcohol were removed from the ether extract with a 4 Å. molecular sieve and the ether was distilled off through a 2-ft. Vigreux column. The residue was fractionally distilled at atmospheric pressure and a fraction taken, b.p. 162–166°, amounting to 1.34 g., which by its infrared spectrum appeared to be a mixture of the desired alcohols and the starting ketone. The v.p.c. of the product showed three peaks in addition to solvent peaks. The retention times of these peaks corresponded to those for *trans*- and *cis*-2-bicyclo[3.1.0]hexanol and 2-bicyclo[3.1.0]-hexanone, respectively. The two alcohols were in the ratio 9:91. Samples collected under the v.p.c. peaks corresponding to the *cis*-alcohol and the starting ketone gave infrared spectra identical with those of other samples of these compounds.

C. *From Δ^2-Cyclopentenol.*[17]—A catalytic amount of iodine and 53.5 g. (0.20 mole) of methylene iodide were added in that order to a stirred suspension of 19.4 g. (0.30 mole) of zinc–copper couple in 170 ml. of dry ether, and the mixture was refluxed with continued stirring for 0.5 hr. Heating was discontinued while a solution of 10 g. (0.119 mole) of Δ^2-cyclopentenol in 35 ml. of dry ether was added dropwise with stirring, during which time the reaction mixture continued to reflux. After the addition was complete, heating was resumed and the reaction was refluxed for 24 hr., then allowed to cool and filtered through Celite. The filter pad was washed thoroughly with ether. The combined filtrate and washings were washed with 5% hydrochloric acid (3 × 60 ml.), saturated sodium bicarbonate solution (3 × 60 ml.) and saturated salt solution. The combined aqueous wash solutions were extracted with two portions of ether. The combined ether solutions were dried over magnesium sulfate, and the ether was distilled through a 2-ft. Vigreux column. The residue was distilled under reduced pressure to give 6.95 g. (60%) of product boiling at 60–61° (10 mm.). The v.p.c. of the product showed it to be *ca.* 98% *cis*-2-bicyclo[3.1.0]hexanol.

D. By Meerwein–Ponndorf–Verley Reduction of 2-Bicyclo-[3.1.0]hexanone.—A solution of 0.96 g. (0.01 mole) of 2-bicyclo-[3.1.0]hexanone and 4.08 g. (0.02 mole) of freshly distilled aluminum isopropoxide in 20 ml. of isopropyl alcohol (dried over calcium oxide) was slowly distilled through a spiral wire column (distillation temperature 60–80°) until the distillate no longer gave a positive test with 2,4-dinitrophenylhydrazine reagent (about 3 hr.). The major portion of the isopropyl alcohol was then removed by distillation. The residue was decomposed with 10 ml. of 6 *N* hydrochloric acid. The aqueous solution was saturated with salt and extracted with ether (4 × 5 ml.). The ether extract was washed with saturated sodium bicarbonate solution and saturated salt solution and dried over sodium sulfate. The ether was removed by distillation through a 2-ft. Vigreux column, and the residue was fractionally distilled at reduced pressure to give 0.59 g. of product, b.p. 61–62° (12 mm.). The v.p.c. of the product showed a *trans*:*cis* ratio of 49:51.

The analytical samples of the two alcohols were prepared by collection of material from a small scale preparative v.p.c. separation of the product of this last reaction.

Anal. Calcd. for $C_6H_{10}O$: C, 73.43; H, 10.27. Found for the *trans*-alcohol: C, 73.55; H, 10.34. Found for the *cis*-alcohol: C, 73.14; H, 10.55.

Equilibration of the 2-Bicyclo[3.1.0]hexanols.—The method used was essentially that used by Winstein and Sonnenberg for the 3-alcohols.[2c] A solution of 0.24 g. of 2-bicyclo[3.1.0]hexanol (from the lithium aluminum hydride reduction of 2-bicyclo[3.1.0]-hexanone), 0.7 ml. of acetone and a small amount of aluminum isopropoxide in 40 ml. of isopropyl alcohol was refluxed, with exclusion of moisture, for 123 hr. During this time the reaction was followed by analyzing aliquots of the reaction mixture by v.p.c. At the end of this time there had been no change in the ratio of the alcohols for 24 hr., and only minor change for over 72 hr. The reaction mixture was diluted with 20 ml. of water, neutralized with concd. hydrochloric acid, and extracted with pentane (5 × 7 ml.). The pentane extract was washed with saturated salt solution and dried over sodium sulfate. The solvent was removed from the extract by distillation through a 2-ft. Vigreux column, and the residue was analyzed directly by v.p.c., *trans*:*cis* ratio, 31:69.

Vapor Phase Chromatography of the Alcohols.—The chromatography was done on a 6-ft. column 0.25 in. in diameter packed with firebrick coated with 10% by weight of β,β^1-oxydipropionitrile. The column was run at a constant temperature of 90°, using helium as the carrier gas at a flow rate of *ca.* 70 ml./min. Samples of 1 μl. were used for the analytical determinations, while 10-μl. samples were used for the small scale preparative work. Under these conditions the alcohols had approximate retention times: *cis*- 3-ol, 24 min.; *trans*-2-ol, 28 min.; *trans*-3-ol and *cis*-2-ol, 33.5 min. The relative peak areas were determined by weighing pieces of paper cut to the shape of the peaks.

2-Bicyclo[3.1.0]hexene.—A catalytic amount of iodine and 268 g. of methylene iodide were added in that order to a stirred suspension of 82 g. of zinc–copper couple in 800 ml. of dry diglyme. The mixture was stirred and heated at *ca.* 50° for 2 hours, then allowed to cool to room temperature. To the reaction mixture was then added 200 g. of freshly distilled cyclopentadiene and stirring was continued at room temperature for 60 hr. The reaction mixture was then heated with an oil-bath and the volatile material which distilled was collected in an ice-cold receiver. Material was collected in a boiling point range of 35–55°. After the maximum temperature had been reached, the distillation temperature dropped to 42°, at which time distillation was discontinued. The distillate was redistilled through a spinning band column at atmospheric pressure using a reflux ratio of 10:1. The product was taken as a cut, b.p. 71–74°, weighing 3.72 g. The pot temperature was not allowed to rise above 140° during the distillation. A center cut was taken, b.p. 74°, as an analytical sample. This material showed one peak on v.p.c. on a 4 ft. by 0.25 in. column packed with 20% silicon rubber on firebrick run at 30°. The n.m.r. spectrum (CCl_4), shows six complex groups of peaks centered at 4.16 τ(1H), 4.68 τ(1H), 7.60 τ(2H), 8.46 τ(2H), 9.21 τ(1H) and 10.19 τ(1H)

Anal. Calcd. for C_6H_8: C, 89.94; H, 10.06. Found: C, 89.85; H, 10.12.

***trans*-2,3-Epoxybicyclo[3.1.0]hexane.**—To 2.00 g. (24.9 m-moles) of 2-bicyclo[3.1.0]hexene contained in a 100-ml. flask cooled in ice was added dropwise with stirring a solution of perbenzoic acid in methylene chloride (45.2 ml. of 0.555 *M* solution, 25.0 mmoles) during 0.5 hr. After the addition was completed, the reaction mixture was kept at 0° for 15 hr. The methylene chloride solution was then washed with saturated

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[17] K. Alder and F. H. Flock, *Ber.*, **89**, 1732 (1956).

sodium bicarbonate solution (2 × 15 ml.) and saturated salt solution, then dried over sodium sulfate. The methylene chloride was slowly distilled from the dried solution through a 2-ft. Vigreux column. The residue was fractionally distilled through a spiral wire column at atmospheric pressure to give 1.70 g. (72%), b.p. 128–130°.

The v.p.c. analysis of this material was done on a 4-ft. column of tricyanoethoxypropane on firebrick and showed only a single symmetrical peak for the epoxide. The analytical sample was collected from the v.p.c. The n.m.r. spectrum of this compound taken as the neat liquid showed the following sets of peaks: quartet centered at 9.83 τ(1H), a multiplet at *ca.* 9.2 τ(2H), a multiplet at *ca.* 8.2 τ(3H), and slightly resolved peaks at 6.93 τ(1H) and 6.52 τ(1H).

Anal. Calcd. for C_6H_8O: C, 74.97; H, 8.39. Found: C, 74.78; H, 8.44.

Reduction of *trans*-2,3-Epoxybicyclo[3.1.0]hexane.—To a solution of 0.38 g. (10.0 mmoles) of lithium aluminum hydride in 15 ml. of dry ether was added dropwise a solution of 10 g. (10.4 mmoles) of *trans*-2,3-epoxybicyclo[3.1.0]hexane in 5 ml. of dry ether. After the addition had been completed, the reaction was refluxed for 1 hour. The excess reagent was decomposed by dropwise addition of water, and sufficient excess water was added to give a granular precipitate. The resulting suspension was filtered, and the precipitate was washed thoroughly with ether. The ether was distilled from the combined filtrate and washings through a 2-ft. Vigreux column and the residue was distilled at atmospheric pressure without fractionation to give 0.50 g. (49%) of product, b.p. 155–160°. The v.p.c. of the product showed two peaks in the ratio 54:46. The infrared spectra of material collected under these peaks were identical respectively with those of the compounds described in this work as *trans*-2-bicyclo[3.1.0]hexanol and *trans*-3-bicyclo[3.1.0]hexanol. No evidence for the presence of either *cis*-alcohol was observed in either the v.p.c. or the infrared spectra.

Deamination of *trans*-3-Bicyclo[3.1.0]hexylamine-3-*d*.—To an ice-cold solution of 0.454 g. (3.40 mmoles) of *trans*-3-bicyclo[3.1.0]hexylamine-3-*d* hydrochloride and 0.463 g. (3.40 mmoles) of potassium dihydrogen phosphate in 4 ml. of water was added 0.235 g. (3.40 mmoles) of sodium nitrite. The solution so obtained was cooled in an ice-bath for 2 hr., then allowed to stand at room temperature for 40 hr. The reaction mixture was saturated with salt and extracted with ether (4 × 1 ml.). The ether extract was washed with saturated sodium bicarbonate solution and saturated salt solution, then dried over sodium sulfate. The ether was removed from the dried extract by distillation through a fractionating column. The residue, which weighed 0.219 g., was analyzed directly by v.p.c. Three peaks corresponding to the alcoholic products were observed in the ratio 36:31:33.

Oxidation of *cis*-Bicyclo[3.1.0]hexanol from the Above Experiment.—To 33.2 mg. (0.4 mmole) of *cis*-3-bicyclo[3.1.0]hexanol collected under the first peak of the v.p.c. of the deamination products of *trans*-3-bicyclo[3.1.0]hexylamine-3-*d* was added a solution of 34 mg. (0.11 mmole) of sodium dichromate dihydrate in 0.09 ml. of acetic acid. The reaction mixture was allowed to stand at room temperature for 1 hr., then heated in a water-bath at 70° for 5 min. The reaction mixture was diluted with 2 ml. of saturated salt solution and extracted with pentane (3 × 2 ml.). The pentane was distilled from the extract through a fractionating column and the residue of 3-ketone was purified directly by v.p.c. and analyzed for deuterium by mass spectrometer.

Deamination of *cis*-3-Bicyclo[3.1.0]hexylamine-3-*d* and Conversion of the *cis*- and *trans*-3-Alcohols to Ketone.—The general procedure outlined above was followed. The *cis*-3-ol was obtained directly by v.p.c. and oxidized to the 3-ketone which was also purified by v.p.c. The *trans*-3-ol was not isolated but was oxidized together with the *cis*-2-ol, from which it was not separated by v.p.c. The ketones which resulted from oxidation of this v.p.c. collected mixture were themselves easily separated by v.p.c. and the pure 3-ketone was collected in this way for mass spectral analysis.

Analytical Method for Deuterium in the 3-Bicyclo[3.1.0]-hexanols Produced by Deamination of *cis*- and *trans*-3-Bicyclo[3.1.0]hexylamines.—Samples of 3-bicyclo[3.1.0]hexanone were obtained separately from the *cis*- and *trans*-3-bicyclo[3.1.0]-hexanols produced in deamination using preparative v.p.c. as indicated above and these samples of 3-bicyclo[3.1.0]hexanone were subjected to mass spectral analysis to determine the amount of excess deuterium remaining in this material. A sample of undeuterated ketone was also run as a standard. The raw data obtained from the mass spectra of the ketone samples were the ratio of peak heights at mass numbers 96 and 97, and the fact that there is no measurable peak at mass number 95. This was used to calculate the excess deuterium content in the following manner: It is assumed that the peak heights at mass numbers 96 and 97 (and 98) are in the same ratio as the number of molecules of these approximate molecular weights in the ketone sample. The justification of this assumption is that the major mode of fragmentation, and presumably the parent ion formation of ketones, involves the carbonyl group[18] and since the excess deuterium would be on the cyclopropyl ring this isotopic substitution should have a minimal effect on the probability of parent ion formation. Let KH represent the mole fraction of molecular weight 96 in the ketone sample and K'H represent the mole fraction of undeuterated molecules of molecular weight 97 (substituted with C^{13}). Let KD and K'D be the mole fractions of the corresponding deuterated molecules. Let R_0 be the ratio of the peak height at mass number 97 to that at 96 for ketone with normal isotopic distribution and let R be the ratio of these peak heights measured for the sample under consideration. The number desired is the percentage of deuterated molecules in the sample (P_d). Then

$$P_d = \frac{\mathrm{KD} + \mathrm{K'D}}{\mathrm{KH} + \mathrm{K'H} + \mathrm{KD} + \mathrm{K'D}} \times 100$$

$$R_0 = \mathrm{K'H/KH} = \mathrm{K'D/KD}$$

$$R = (\mathrm{KD} + \mathrm{K'H})/\mathrm{KH} = \mathrm{KD/KH} + R_0$$

$$\mathrm{KD/KH} = R - R_0$$

$$P_d = \frac{\frac{\mathrm{KD}}{\mathrm{KH}} + R_0\frac{\mathrm{KD}}{\mathrm{KH}}}{1 + R_0 + \frac{\mathrm{KD}}{\mathrm{KH}} + R_0\frac{\mathrm{KD}}{\mathrm{KH}}} \times 100$$

$$P_d = \frac{R - R_0 + RR_0 - R_0^2}{1 + R + RR_0 - R_0^2} \times 100$$

$$P_d = \frac{R - R_0}{1 + R - R_0} \times 100$$

Six different determinations of R_0 were made at various times during the mass spectral analysis. The average of these values was 0.072 ± 0.006. The value given in the literature is 0.06651.[19] Three independent determinations of R were made on 3-bicyclo[3.1.0]hexanone obtained from *cis*-3-amine *via* the *cis*-3-alcohol, giving an average value of 0.605 ± 0.003. This gives a calculated value for P_d of 34.8 ± 0.8%, which is roughly half the value predicted for a symmetrical non-classical ion. The value of R found for the oxidation product of the *trans*-3-alcohol which was obtained from the *cis*-3-amine was 0.0712 ± 0.003, which gives a value for P_d of zero within the accuracy of the measurements.

The average value of P_d is 17.4 ± 0.1% for the *cis*-alcohol obtained from the deuteriated *trans*-3-amine. From these data it is evident that the *trans*-formation of *trans*-3-bicyclo[3.1.0]-hexylamine-3-*d* into 3-bicyclo[3.1.0]hexanone has been accompanied by the loss of 0.954 deuterium atom per molecule (*cf.* data above on deuteriated *trans*-3-amine). It therefore is concluded that (1) the 3-position of the starting amine was fully deuterated and (2) less than 5% of scrambling of deuterium from this position to the cyclopropane ring occurred in the deamination reaction. Using the product ratios found in the earlier deaminations, it is calculated that the *cis*-3-bicyclo[3.1.0]-hexylamine present in the starting amine would give only 1.5% of the *cis*-3-bicyclo[3.1.0]hexanol obtained, so that the deuterium scrambling which occurs in the deamination of the *cis*-amine is negligible in these experiments.

Detailed tabulations of the mass spectral data are contained in the aforementioned thesis.[16]

Deamination of *cis*- and *trans*-3-Bicyclo[3.1.0]hexylamines in Acetic Acid Solvent.—To a stirred solution of 450 mg. of a *cis*- and *trans*- 3-bicyclo[3.1.0]hexylamine mixture (43% *cis*, 57% *trans*) in 4 ml. of acetic acid was added over several hours 650 mg. of sodium nitrite. After storage at room temperature overnight the product was recovered by dilution with water and extraction in the usual way. The acetates so obtained were treated with lithium aluminum hydride in ether to form the corresponding bicyclic alcohols which were distilled to give 205 mg. of a mixture. This was found by v.p.c. to consist of 28% and 44%, respectively, of *cis*- and *trans*-3-bicyclo[3.1.0]hexanols and 28% of *trans*-2- bicyclo[3.1.0.] hexanol. Thus, even in acetic acid, deamination affords the *trans*-2- and 3-alcohols, products which are not obtained in toluenesulfonate acetolysis. The amounts of alcohols which were calculated to result from deamination of the particular mixture of amines used in this experiment if the reaction be carried out in water are: 26% *cis*-3-ol, 30% *trans*-3-ol, 8% *cis*-2-ol and 36% *trans*-2-ol.

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[18] A. G. Sharkey, Jr., J. L. Schultz and R. A. Friedel, *Anal. Chem.*, **28**, 934 (1956).

[19] J. H. Beynon, "Mass Spectrometry and its Applications to Organic Chemistry," Elsevier Publishing Co., New York, N. Y., 1960, p. 492.