459. *Deamination of the Four Epimeric 4-t-Butyl-2-aminocyclohexanols and Comments on the Course of the Deamination of* cis-*2-Aminocyclohexanol and* cis-*2-Aminocycloheptanol* *

By M. Chérest, H. Felkin, J. Sicher, F. Šipoš, and M. Tichý

The deamination of the four conformationally homogeneous 2-amino-4-t-butylcyclohexanols in aqueous perchloric acid is highly (97—100%) stereoselective, leading in every case to the expected product. Under the same conditions, the conformationally mobile *cis*-2-aminocyclohexanol and 2-aminocycloheptanol afford mixtures (53 : 47 and 40 : 60, respectively) of ring-contracted aldehyde and cycloalkanone, and these product ratios do not reflect the estimated position of the conformational equilibrium in the initial amino-alcohols.

It follows that deamination of the mobile compounds must involve conformational re-equilibration at some intermediate stage, and it is suggested that this is the diazo-hydroxide.

The reaction between nitrous acid and its derivatives and primary, non-aromatic, amino-compounds is known to be a multistage process involving, in its latter stages, the formation of a carbonium ion.[1,2] The products of deamination are, however, often very different

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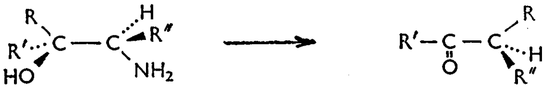
* This Paper is regarded as Part XXXIII of the series Stereochemical Studies of the Prague group; Part XXXII, J. Závada and J. Sicher, *Coll. Czech. Chem. Comm.*, in the press.

[1] F. C. Whitmore and D. P. Langlois, *J. Amer. Chem. Soc.*, 1932, **54**, 3441.

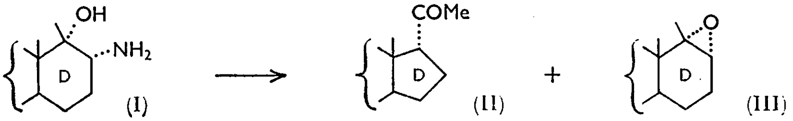
[2] J. H. Ridd, *Quart. Rev.*, 1961, **15**, 418.

from those of solvolyses, proceeding through what formally is the same carbonium ion.[2,3] These differences have been attributed to the ease, and probable exothermicity,[4] of C–N heterolysis; the carbonium ion formed in deamination is thought to be " hot " (*i.e.*, unsolvated and/or chemically activated), and, as a result, the products of deamination are determined by the conformation of the ground state rather than by electronic factors in the transition state.[2] Thus, with open-chain diastereoisomeric 2-amino-alcohols, the major deamination product arises from reaction between the cationic centre and the bond (on the hydroxyl-bearing carbon atom) which is antiperiplanar to the nitrogen in the conformation of the molecule which is assumed to be the most stable [2,5] (Scheme 1).



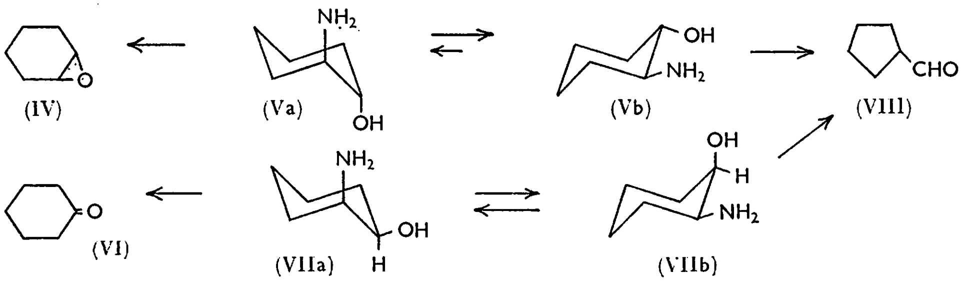
Scheme 1

Conformations of acyclic molecules are generally not known with any degree of certainty, and cyclohexane derivatives would be expected to represent a much simpler case.[6] This, however, is not always so: for instance, the deamination of 17α-amino-3β,17aα-dihydroxy-17a-methyl-D-homoandrost-5-ene (I) is said [7] to yield only a small proportion of the expected ketone (II), and a relatively large amount of epoxide (III) with retention of configuration at C_{17}.



The deamination of *cis*- and *trans*-2-aminocyclohexanol has been investigated by a number of workers [8-10] and, as expected, the *trans*-isomer (V), in which the diequatorial conformer (Vb) prevails, affords the ring-contracted aldehyde (VIII), the C_6 carbon atom migrating; [8,9] the formation of some epoxide (IV) has also been reported.[10]

The *cis*-isomer (VII) has been reported [8] to yield a mixture of ketone (VI) and aldehyde (VIII) " apparently richer in the latter," and it has been suggested [8,11] that this result must reflect the position of the equilibrium between the two conformers (VIIa and VIIb) of the amino-alcohol (Scheme 2). Since nitrosation, the first stage of the deamination reaction,



Scheme 2

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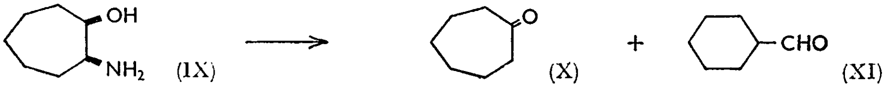
[3] D. J. Cram and M. R. Sahyun, *J. Amer. Chem. Soc.*, 1963, **85**, 1257.
[4] R. Huisgen and C. Rüchardt, *Annalen*, 1956, **601**, 1.
[5] B. M. Benjamin, H. J. Schaeffer, and C. J. Collins, *J. Amer. Chem. Soc.*, 1957, **79**, 6160.
[6] D. Y. Curtin and S. Schmukler, *J. Amer. Chem. Soc.*, 1955, **77**, 1105.
[7] R. J. W. Cremlyn, D. L. Garmaise, and C. W. Shoppee, *J.*, 1953, 1847.
[8] G. E. McCasland, *J. Amer. Chem. Soc.*, 1951, **73**, 2293.
[9] M. Godchot and M. Mousseron, *Compt. rend.*, 1934, **198**, 2000.
[10] N. A. B. Wilson and J. Read, *J.*, 1935, 1269.
[11] J. W. Huffman and J. E. Engle, *J. Org. Chem.*, 1959, **24**, 1844.

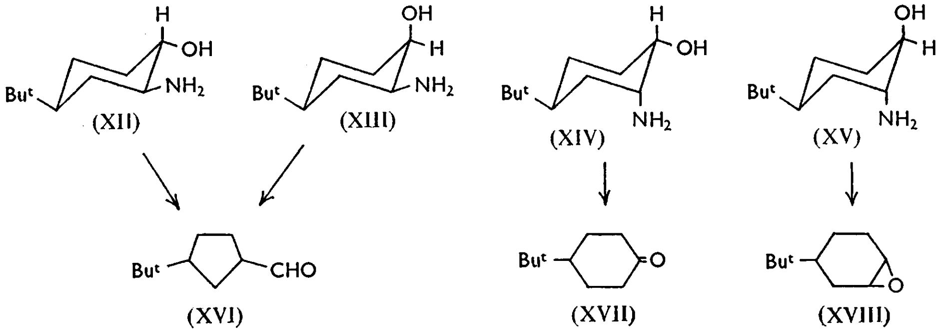
is rate-determining,[2] this implies that nitrosation of axial and equatorial amino groups must have the same specific rate.

cis-2-Aminocycloheptanol (IX), on the other hand, has been reported [11] to afford a 4 : 1 mixture of ketone (X) and aldehyde (XI) (Scheme 3). It is doubtful whether, in this case, there is any simple relationship between the preferred conformation of the amino-alcohol and the deamination products, and it has in fact been suggested [11] that the loss of nitrogen from the intermediate diazonium ion is slow enough to allow a change of conformation at this stage, and that the product ratio is determined by " the ratio of rates of proton loss to group migration."



Scheme 3

In these circumstances, we felt that a quantitative study of the deamination of 2-aminocyclohexanols in which the respective conformations of the amino and hydroxyl group are fixed and known would be highly desirable. Compounds in which these requirements are met were available to us in the four isomeric 4-t-butyl-2-aminocyclohexanols (XII—XV), the synthesis of which was described recently.[12] The configuration and conformational homogeneity of these compounds have been established with certainty,[12,13] and their application to studies of conformational features of reactions has been discussed at some length.[13]



Scheme 4

The outcome of the deamination of these compounds which, on simple conformational grounds, is expected to be as outlined in Scheme 4, should reveal whether the deamination of 2-amino-alcohols is in fact stereospecific or not. Furthermore, a comparison of the outcome of the deamination of the " fixed " t-butyl compounds with that of the conformationally " mobile " *cis*- and *trans*-2-aminocyclohexanols (V) and (VII) should show whether the latter reflects the conformational equilibrium in the starting amino-alcohols, as assumed by previous authors.[8,11] Since the yields previously reported for these reactions were quite low,[8,10,11] we have also quantitatively re-examined the deamination, under the same experimental conditions, of the " mobile " compounds (V), (VII), and (IX).

RESULTS

The deaminations were carried out at 0° in a mixture of aqueous perchloric acid and pentane,[14] with stirring. This has the advantage of removing acid-labile products (epoxides

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[12] J. Sicher, F. Šipoš, and M. Tichý, *Coll. Czech. Chem. Comm.*, 1961, **26**, 847.
[13] M. Tichý, F. Šipoš, and J. Sicher, *Coll. Czech. Chem. Comm.*, 1962, **27**, 2907.
[14] W. Hückel and P. Rieckmann, *Annalen*, 1959, **625**, 1.

in particular) from the aqueous layer as soon as they are formed. Analyses were by gas chromatography, with *trans*-decalin or methylcyclohexane as internal standards, and identifications and calculations were made by comparison with mixtures of known composition. Furthermore, the major product (or products) was in all cases collected and compared (infrared) with an authentic sample.

Pentane-extractable deamination products

Amino-alcohol	Total yield (%)	Percentage composition: Aldehyde *	Ketone *	Epoxide *
(V)	89	99	trace	0
(VII)	66	51—55	45—49	0
(IX)	75	38—42	58—62	—
(XII)	90	100	0	0
(XIII)	98	100	0	0
(XIV)	76	2—3	97—98	0
(XV)	77	1—2	trace	98—99 (" *cis* ")

* See Schemes 2, 3, and 4.

Only the pentane-soluble fraction of the deamination product was analysed and the results are shown in the Table (the yields indicated are the average of at least two runs).

The aldehyde (XVI) formed from the equatorial amino-compounds (XII) and (XIII) is expected to be *cis*, and indeed gave a single peak in gas chromatography on various columns. This, however, cannot be regarded as evidence for isomeric purity, since the aldehyde from the deamination reaction, a synthetic sample of (XVI) (see Experimental section), and the aldehyde recovered from treatment with hydrogen chloride in chloroform at 80° for one week, all showed identical infrared spectra and gas-chromatographic behaviour.

After completion of the reaction, the composition of the pentane layer, unseparated from the aqueous layer, remained unchanged for at least 24 hours; furthermore, it was demonstrated that the epoxide *trans*-(XVIII) was stable under the deamination conditions. This shows that the aldehyde (XVI), formed in small amount from the axial amino-alcohols (XIV) and (XV), is not an artefact, and the same applies to the trace of ketone (XVII) formed in the deamination of (XV). 1,2-Epoxycyclohexane, however, the partition coefficient of which is no doubt less in favour of pentane than that of the epoxides (XVIII), was found to undergo slow hydrolysis under the reaction conditions, but it would have been detected had it been formed in $>5\%$ yield in the deamination of the amino-alcohols (V) or (VII).

In all cases, except in the deamination of the amino-alcohol (VII), the products in the aqueous fraction represent less than 25% of the starting amino-alcohol, and no attempt was made to analyse them. It will be noted that the yields of pentane-soluble material were consistently higher (89—98%) from the amino-alcohols with an equatorial amino-group than from the others (66—77%); deamination of the latter may well afford a certain amount of glycol, which would remain in the aqueous layer along with a small quantity of unchanged amino-alcohol.

DISCUSSION

Let us first consider the deamination of the 4-t-butyl-2-aminocyclohexanols (XII—XV). With the two amino-alcohols (XII) and (XIII) with an equatorial amino-group, the reactions lead in high yield ($>90\%$) to the expected aldehyde (XVI) as the sole pentane-extractable product. No epoxide could be detected in the product from the amino-alcohol (XII), in contrast to the reported[7] course of the reaction in the D-homosteroid series (I). The yields of pentane-extractable products from the two amino-alcohols (XIV) and (XV) with an axial amino group are lower (*ca.* 75%), but here again the expected compounds, the ketone (XVII) from the amino-alcohol (XIV), and the epoxide *cis*-(XVIII) from the amino-alcohol (XV) are practically the sole products ($>97\%$).

There can be no doubt as to the purity of the starting materials, and there is independent evidence that the compounds are conformationally homogeneous;[13] moreover, we have shown that the aldehyde (XVI) and ketone (XVII) formed in $<3\%$ yield from the amino-alcohols (XIV) and (XV) are not artefacts. The formation of these compounds therefore indicates that some stereochemical leakage is occurring at the carbonium ion stage in the deamination of the amino-alcohols with an axial amino-group. This may be due to easier access by solvent (water) to the rear (equatorial) side of the developing cationic centre; the resulting equatorially solvated carbonium ion would be expected to rearrange to the aldehyde (XVI) and also to lead to glycol, and this probably explains why the yields of pentane-extractable products are significantly lower in these deaminations.

A suitably situated (antiperiplanar) group or atom on the adjacent carbon atom should obviously be much more readily " sucked in " by the cationic centre when this carbon atom carries a group with unshared electrons (*e.g.*, OH) than when it does not. Stereochemical leakage (*via* a solvated carbonium ion) is therefore expected to be more severe with simple amines than with amino-alcohols, and this is borne out by the fact that the deamination of the t-butyl-amino-alcohols is far more stereoselective than that of *cis*- and *trans*-4-t-butylcyclohexylamine, which both afford a mixture of 4-t-butylcyclohexene and *cis*- and *trans*-4-t-butylcyclohexanol (77 : 10 : 13 and 10 : 13 : 77, respectively).[15]

With all four rigid compounds, therefore, involving all four possible conformations of the amino- and hydroxyl groups, the practical outcome of deamination is essentially determined simply by which group is antiperiplanar to the amino-group (Scheme 4). This result is in complete agreement with current theory regarding the importance of conformational factors in the deamination of open-chain amino-alcohols.[2,5]

Turning now to the mobile systems (V), (VII) and (IX), we note first that our results in the cyclohexane series are in substantial agreement with those of McCasland,[8] even though the experimental conditions employed in the two investigations were different, but, as regards the *cis*-amino-alcohols (VII) and (IX), in substantial disagreement with those of Huffman and Engle,[11] who reported an aldehyde : ketone ratio of 70 : 30 from the amino-alcohol (VII) and 20 : 80 from the amino-alcohol (IX).

Secondly, we note that the difference in the course of deamination between the *cis*-isomers in the cyclohexane (VII) and cycloheptane (IX) series is small in terms of free energy (*ca.* 0·3 kcal. mole^{-1}), even though the aldehyde : ketone ratio is reversed on going from one series to the other. Although the conformational features of seven-membered rings are less well understood, it is reasonable to assume that they bear some resemblance to those of cyclohexane compounds,[16] and it may therefore be concluded that analogous factors are operating in determining the outcome of deamination in both *cis*-amino-alcohols (VII) and (IX).

Thirdly, we note that with *cis*-2-aminocyclohexanol (VII) the product ratio does not reflect the estimated position of the conformational equilibrium in the starting compound. The *A*-value of the amino-group has been determined recently in two independent investigations [17] and is approximately 1·8 (in protonic solvents), whereas the *A*-value of the hydroxyl group is [18] about 0·8. The conformational equilibrium would hence be expected to be in favour of the conformer (VIIb) with the amino-group equatorial, and the value of the conformational equilibrium constant for *cis*-2-aminocyclohexanol (NH_2-equatorial/NH_2-axial) has in fact been directly determined and found [19] to be about 3. On simple conformational grounds, the deamination would be expected to lead to an aldehyde : ketone ratio of about 3, rather than the ratio of 1·1 actually observed. Similar considerations apply to the reaction of *cis*-2-aminocycloheptanol (IX).

[15] W. Hückel and K. Heyder, *Chem. Ber.*, 1963, **96**, 220.

[16] W. Hückel and J. Wächter, *Annalen*, 1964, **672**, 62; J. Sicher, J. Jonáš, M. Svoboda, and O. Knessl, *Coll. Czech. Chem. Comm.*, 1958, **23**, 2141; J. Sicher, F. Šipoš and J. Jonáš, *ibid.*, 1961, **26**, 262; H. J. E. Loewenthal and P. Rona, *J.*, 1961, 1429; J. B. Hendrickson, *J. Amer. Chem. Soc.*, 1962, **84**, 3355.

[17] J. Sicher, J. Jonáš, and M. Tichý, *Tetrahedron Letters*, 1963, 825; E. L. Eliel, E. W. Della, and T. H. Williams, *ibid.*, p. 831.

[18] E. L. Eliel, " Stereochemistry of Carbon Compounds," McGraw-Hill, New York, 1962.

[19] J. Sicher and M. Tichý, unpublished data.

It should be pointed out that if the product ratios (aldehyde : ketone) from these compounds were determined by the conformational equilibrium constants (NH_2-equatorial/NH_2-axial) in the starting amino-alcohols, the former should in fact be greater than the latter by a factor of about 1·3, since, with the rigid amino-alcohols, the yields of aldehyde (XVI) from the amino-compounds (XII) and (XIII) with an equatorial amino-group are on the average about 1·3 times higher than the yield of ketone (XVII) from the amino-compound (XIV) with an axial amino-group. It will be noted that this correction, if applied, would still further increase the difference between what is expected on simple conformational grounds and what is in fact observed.

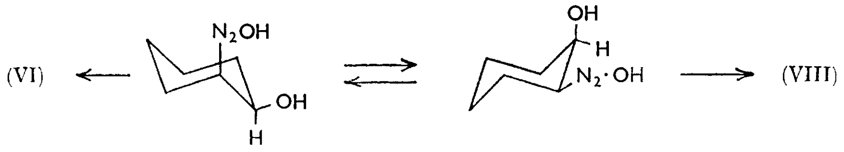
Since the product from the deamination of *cis*-2-aminocyclohexanol (VII) does not reflect the position of the conformational equilibrium in the starting material, and since we have shown that the deamination of the rigid models (XII—XV) is, on the contrary, highly stereoselective, it follows that some intermediate stage of the deamination reaction is slow enough to allow a conformational change to take place.

It has been suggested [11] that, with the *cis*-2-aminocycloheptanol (IX), this stage is the decomposition of the diazonium ion, and that the rate of decomposition of the axial diazonium ion is greater than that of the equatorial diazonium ion. The fact that *cis*-2-aminocyclohexanol and *cis*-2-aminocycloheptanol behave similarly on deamination shows that this assumption is untenable: the energy barrier for chair–chair interconversion in cyclohexane compounds [18] is about 10 kcal. mole^{-1}, and this is certainly not smaller than the activation energy for C–N heterolysis. The latter energy has been estimated [4] by rough calculation to be only 5—10 kcal. mole^{-1}, and, in view of the favourable entropy factor involved, the free energy of activation must be less than this. This is consistent with the results obtained in the deamination of open-chain amino-alcohols,[5,20] which show that the rate of nitrogen elimination cannot be much lower than the rate of internal rotation in these compounds.

It is generally assumed that the intermediate stages in aliphatic deamination are the same as in aromatic diazotation: [21]

$$R{-}NH_2 \longrightarrow R{-}NH{-}NO \longrightarrow R{-}N{=}N{-}OH \longrightarrow R{-}N{=}N{-}\overset{+}{O}H_2 \longrightarrow R{-}\overset{+}{N}{\equiv}N + H_2O$$

Aromatic diazo-hydroxides are known to be stronger acids than the corresponding phenols,[21] and they are therefore unlikely to be stronger bases. If, as seems probable, the same relationship holds between their aliphatic counterparts and the corresponding alcohols (which are weaker bases than water), then aliphatic diazo-hydroxides must be extremely weak bases; it is therefore not inconceivable that their conversion, in weakly acid solution, to the corresponding diazo-hydroxonium ions is slower than the cyclohexane chair–chair interconversion.



Scheme 5

There is no reason to suppose that the rates of protonation of axial and equatorial diazo-hydroxides will differ significantly, and we suggest that the product ratio in the deamination of *cis*-2-aminocyclohexanol (VII) [and of the seven-membered analogue (IX)] is determined to a large extent by the position of the conformational equilibrium at the diazo-hydroxide stage (Scheme 5).

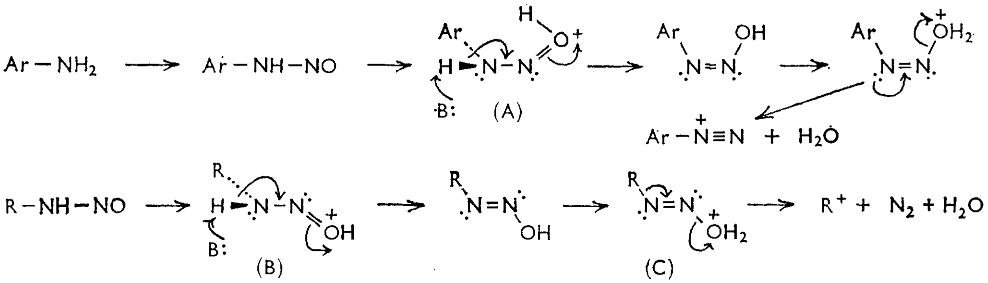
The *A*-value of the diazo-hydroxide group is certainly smaller than that of the amino group, just as the *A*-value of the carbethoxy-group, in which the carbon atom is trigonal,

[20] D. Y. Curtin and M. C. Crew, *J. Amer. Chem. Soc.*, 1954, **76**, 3719.

[21] H. Zollinger, " Azo and Diazo Chemistry," Interscience Publishers, New York, 1961.

is smaller than that of the methyl group,[18] and the expected position of the above equilibrium is, therefore, consistent with the observed (*ca.* 1 : 1) product ratio.

It has been assumed, in the above discussion, that the deamination of aliphatic amino-compounds involves the intermediate formation of a diazonium ion. There is no experimental proof of this, and there is one other possibility that should be mentioned, although it would obviously not affect the above argument: in aromatic diazotation, the diazonium ion must be formed from a *syn*-diazo-hydroxide, since *anti*-diazo-hydroxides can only be converted with difficulty to diazonium ions: [21]



The preferential formation of a *syn*-diazo-hydroxide in the aromatic case is understandable, since the aromatic group could well be held *syn* to the oxygen atom (cf. A) by electrostatic attraction and/or intramolecular hydrogen bonding, and these attractive forces may be sufficient to overcome the repulsion between the two free-electron pairs.

In the aliphatic case, however, no such attractive forces exist, and rearrangement of an aliphatic nitrosamine should lead to the *anti*-diazo-hydroxide (cf. B). This, on protonation, would be expected, on stereo-electronic grounds (cf. C), to lead not to the diazonium ion, but directly to the carbonium ion, nitrogen and water. It may well be, therefore, that a diazonium ion is never involved in aliphatic deamination.

EXPERIMENTAL

The amino-alcohols were made by published procedures: (V); [8] (VII); [22] (IX); [23] (XII—XV).[12]

Authentic samples of the various possible pentane-soluble deamination products were all purified by gas chromatography before being made up into standard solutions. They were commercial products [(VI) (X) (XI)] or were made by published procedures [(IV); [24] (XVII); [12] *cis*- and *trans*-(XVIII) [12]], except for cyclopentylmethanal (VIII), which was a gift from Mrs. R. Wylde (Montpellier) and 3-t-butylcyclopentylmethanal (XVI), which was prepared as follows.

3-t-Butylcyclopentylmethanal.—A solution of 3-t-butylcyclopentanone [25] (20·0 g., 0·142 mole) and ethyl chloroacetate (20·9 g., 0·165 mole) in benzene (10 ml.), cooled and stirred, was treated with dry sodium ethoxide (15·8 g., 0·18 mole); the mixture was allowed to stand at room temperature for 12 hours and then heated for 4 hours on a bath kept at 135°. The cooled reaction mixture was decomposed with ice and the products taken up in ether. The ethereal extracts were dried (sodium sulphate), the solvent was evaporated and the residue fractionated. Two distillations afforded about 2·5 g. (12%) of the starting ketone and 17·8 g. (56%) of *3-t-butyl-6-oxa-7-ethoxycarbonylspiro*[4,2]*heptane*, b. p. 120—122°/1 mm., n_D^{20} 1·4575. (Found: C, 69·14; H, 9·77. $C_{13}H_{22}O_3$ requires C, 68·99; H, 9·80%.)

The above glycidic ester (9·8 g.) was gradually added to 50 ml. of 50% sulphuric acid, steam being simultaneously passed through the solution, and the distillate was collected. The steam-volatile fractions were taken up in ether and afforded 1·5 g. of crude 3-t-butylcyclopentylmethanal. Repeated distillation yielded 1·0 g. (15%) of *product*, b. p. 105°/40 mm., 120°/82 mm., n_D^{25} 1·4505. (Found: C, 77·39; H, 11·50. $C_{10}H_{18}O$ requires C, 77·86; H, 11·76%.)

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[22] G. E. McCasland and D. A. Smith, *J. Amer. Chem. Soc.*, 1950, **72**, 2190; W. S. Johnson and E. N. Schubert, *ibid.*, p. 2187.

[23] J. Sicher and M. Svoboda, *Coll. Czech. Chem. Comm.*, 1958, **23**, 1252.

[24] P. D. Bartlett, *J. Amer. Chem. Soc.*, 1935, **57**, 224.

[25] H. Pines and V. N. Ipatieff, *J. Amer. Chem. Soc.*, 1939, **61**, 2728.

The aldehyde behaved as a uniform compound on gas chromatography on polyethylene glycol adipate, silicone-quadrol (see below) and polypropylene glycol (50 m. capillary). It (15 µl.) was recovered unchanged after treatment with 0·2M-hydrochloric acid in chloroform (0·7 ml.) for one week at 80° (sealed tube, nitrogen atmosphere).

Samples for standard solutions were purified by gas chromatography and had n_D^{25} 1·4450; they had to be used at once.

Deamination Procedure.—The amino-alcohol (50·0 mg.) was treated with two drops of an aqueous solution of bromophenol blue and sufficient 0·9M-aqueous perchloric acid to produce a solution just acid to this indicator (pH 3); in some cases, the amino-alcohol perchlorate was insufficiently soluble, and up to 0·5 ml. of water was added to dissolve it, at least in part. Pentane (2 ml.) and *trans*-decalin (65 µl.) were added, and the mixture was treated, with stirring and cooling (0°), with sufficient 4M-aqueous sodium nitrite (about 0·1 ml.) to render it claret-coloured (pH *ca.* 4). Evolution of gas generally began almost at once and, when it slowed down, more perchloric acid and sodium nitrite were added, in such a way as to maintain the pH of the mixture approximately constant. When (after about 2 hours) further addition of these reagents produced no further evolution of gas, it was assumed that the reaction was completed, and samples of the pentane layer were analysed by gas chromatography.

With the amino-alcohol (XIV), only 32 µl. of *trans*-decalin were used, since the katharometer detector response to 4-t-butylcyclohexanone was particularly low.

With the amino-alcohols (V) and (VII), methylcyclohexane (40 µl.) was used as internal standard instead of *trans*-decalin.

cis-2-Aminocycloheptanol hydrochloride was used instead of the free amino-alcohol, and it was dissolved in water; only 20 µl. of *trans*-decalin were used.

The deamination mixtures could be kept at 0° for at least 24 hours with no significant change in the composition of the pentane layer.

The stability, under the deamination conditions, of the two epoxides that were never found in the deamination mixtures was also investigated. The concentration of a dilute (0·1%) pentane solution of the epoxide (IV) was reduced to about 0·05% after 2 hours' stirring with aqueous perchloric acid/sodium nitrite (pH 3), and no epoxide could be detected after 16 hours. The concentration (2·00%) of a pentane solution of " *trans* "-epoxide (XVIII) was almost unchanged (1·88%) after 4 hours under the same conditions.

Product Analysis.—Aliquots (40 µl.) of the pentane layer were analysed by gas chromatography. The column was provided with a katharometer detector and the carrier gas was nitrogen.

Some difficulty was experienced in finding a suitable stationary phase: the polar phases tried did not separate cyclopentylmethanal (VIII) from epoxycyclohexane (IV), and with non-polar phases (*e.g.*, silicone E 301) on firebrick, although the separation was satisfactory, the epoxide was partly isomerised. Finally, it was found that the addition of 10% of *NNN'N'*-tetrakis-(2-hydroxy-1-propyl) ethylenediamine (" Quadrol ") to the silicone E 301 prevented the isomerisation without impairing the separation, and a 160 cm. column of 4·5 mm. bore containing 20% of this mixed stationary phase on firebrick (80—100 mesh) was used for all the analyses.

Conditions and retention times (min.) were as follows: (*a*) 150°, inlet pressure 700 g./cm.^{2}: *trans*-decalin, 6; aldehyde (XVI), 8·5; *cis*- and *trans*-epoxide (XVIII) (not separated), 12; ketone (XVII), 14. (*b*) 105°, inlet pressure 400 g./cm.^{2}: methylcyclohexane, 5; aldehyde (VIII), 8; epoxide (IV), 9; ketone (VI), 11. (*c*) 100°, inlet pressure 600 g./cm.^{2}: aldehyde (XI), 22; ketone (X), 37; *trans*-decalin, 43.

The deamination products were identified by their retention times on the silicone-quadrol column and also on a 50 m. polypropylene glycol capillary column with a flame-ionisation detector. Furthermore, the major products were collected and their identification was confirmed by comparison of their infrared spectra with those of authentic samples.

The *cis*- and *trans*-epoxides (XVIII) could be separated on the capillary column (140°, inlet pressure 700 g./cm.^{2}; retention times 16 and 16·3 min., respectively), and it was thus possible to show that the product from the deamination of the amino-alcohol (XV) contained no *trans*-isomer.

The yield of each major deamination product was calculated by comparing the ratio of its peak height to the peak height of the internal standard with the ratio of peak heights given by a standard solution of similar composition.

The yields of the minor products were estimated from their peak areas.

It was found that the dilute standard solutions of the aldehydes in pentane were very unstable; for example, the concentration of a 2% solution of the aldehyde (XVI) in pentane dropped to 1·9% within about 30 minutes. Since the deamination mixtures containing this aldehyde were stable indefinitely, it was thought that the addition of amyl nitrite might serve to stabilise the standard solutions, and this met with limited success. The spread in the percentage composition values for the products from the amino alcohols (VII) and (IX) in the Table is due more to the instability of the standard solutions of the aldehydes than to any lack of reproducibility in the deamination reaction.

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