Classical Carbonium Ions. Part VIII.[1] Deamination of *cis*- and *trans*-4-t-Butylcyclohexylamines

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Using several different procedures *cis*- and *trans*-4-t-butylcyclohexylamines have been deaminated in acetic acid containing potassium acetate. Particular importance is attached to the acetolysis of the *N*-butyryl-*N*-nitroso derivatives in which the internal nucleophile X(butyrate) and the external nucleophile Y (acetate) give product mixtures which were separately analysed into unrearranged and rearranged esters of retained and inverted configurations. The product analyses define the effective intermediate in the deamination process as an ion-pair comprising a carbonium ion well separated from a hydrogen-bonded, complex anion $[X \cdots H \cdots Y]^-$. These ion-pairs are short lived compared with the rate of stereomutation; diazonium ions, if formed at all, live too briefly to have observable properties. The products of acetolysis of 1-diazo-4-t-butylcyclohexane are also reported and compared with those of the deamination reactions.

DEAMINATIONS have long been used as a means of functional group modification and were among the first reactions to be investigated mechanistically. The reaction between nitrous acid and primary aliphatic amines (nitrous deamination) is, however, complex and still only incompletely understood. Nitrosation of the amine is the rate-determining step and later, faster steps are product determining.[2] The mechanistic interpretation of the complex mixture of products is difficult, partly because nitrous acid reacts with olefins and alcohols,[3] the major products when the reaction is done in aqueous solution, and the recovery is usually low.

Modifications of the deamination procedure,[4] in which the alkylamine is initially converted into either an *N*-alkyl-*N*-nitrosoamide or a 1-alkyl-3-aryltriazene, are cleaner and more useful preparatively. Mechanistically these reactions are complementary to solvolyses of the corresponding alkyl arenesulphonates which have been more extensively investigated. Together these two groups of reactions provide information about short lived, electron-deficient intermediates, generated in particular environments under controlled conditions.[5]

Because cyclohexyl derivatives are widespread in nature and have interesting stereochemical features, they have attracted special attention. The solvolyses of 4-t-butylcyclohexyl arenesulphonates,[6a,b] picrates,[6c] and trifluoromethanesulphonates,[6d] lead tetra-acetate and anodic decarboxylations of 4-t-butylcyclohexanecarboxylic acids,[7] acid-catalysed cleavage of 4-t-butylcyclohexyl methyl ethers,[8] and silver-induced solvolyses of 4-t-butylcyclohexyl chloroformates[9] have recently been reported. We now report the results of an investigation of the products of the deaminations of *cis*- and *trans*-4-t-butylcyclohexylamines by various methods, using analytical procedures reported previously.[6b,10]

Earlier investigations of cyclohexylamine deaminations have been summarised and interpreted by Mills[11] and Streitwieser;[12] equatorial amino-groups give retained (equatorial) substitution and little elimination; axial amino-groups give extensive elimination and a small yield of predominantly inverted (equatorial) substitution product. Later investigations of nitrous deaminations of 4-t-butylcyclohexylamines[13-15] have refined the conclusions of Mills. Some inverted sub-

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[7] S. D. Elakovich and J. G. Traynham, *J. Org. Chem.*, 1973, **38**, 873; *Tetrahedron Letters*, 1971, 1435.
[8] S. Coffi-Nketsia and A. Kergomard, *Bull. Soc. chim. France*, 1973, 2115.
[9] P. Beak, J. T. Adams, and J. A. Barron, *J. Amer. Chem. Soc.*, 1974, **96**, 2494.
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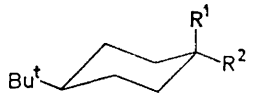
[11] J. A. Mills, *J. Chem. Soc.*, 1953, 260; see also A. K. Bose, *Experienta*, 1953, **9**, 256.
[12] A. Streitwieser, *Chem. Rev.*, 1957, **22**, 861.
[13] W. Hückel and K. Heyder, *Chem. Ber.*, 1963, **96**, 220.
[14] G. Lamaty, C. Tapiero, and R. Wylde, *Bull. Soc. chim. France*, 1968, 2039.
[15] C. W. Shoppee, C. Culshaw, and R. E. Lack, *J. Chem. Soc.* (*C*), 1969, 506.

stitution product was obtained from the *trans*-isomer, and the *cis*-isomer was reported to give substitution with low stereospecificity.

The most serious limitations of all the previous work are the use of analytical methods which are incapable of resolving the complex mixtures of products which are unquestionably obtained,[5] and, in most cases, the use of aqueous solvents. In nitrous deaminations this makes it impossible to distinguish between substitution product derived from the solvent (external substitution) and that from the diazohydroxide (internal substitution). It is now also known [16] that rates and stereochemical results of nitrous deaminations in aqueous media may be subject to micellar modification. The use of triazenes and nitrosoamides in acetic acid allows the separate analysis of internal and external substitution products, and is a system more obviously comparable with solvolytic reactions of arenesulphonates, free from complications due to micelles.

METHODS

The preparations of *cis*- and *trans*-4-t-butylcyclohexylamines (1) and (2), from which the other derivatives (except 1-diazo-4-t-butylcyclohexane) were made, were based upon



(1) $R^1 = NH_2, R^2 = H$
(2) $R^1 = H, R^2 = NH_2$
(3) a; $R^1 = NHN_2C_6H_5, R^2 = H$
b; $R^1 = NHN_2C_6H_4\text{-}p\text{-}NO_2, R^2 = H$
(4) a; $R^1 = H, R^2 = NHN_2C_6H_5$
b; $R^1 = H, R^2 = NHN_2C_6H_4\text{-}p\text{-}NO_2$
(5) $R^1 = N(NO)COCH_3, R^2 = H$
(6) a; $R^1 = H, R^2 = N(NO)COCH_3$
b; $R^1 = H, R^2 = N(NO)COC_3H_7$
(7) $R^1, R^2 = N_2$

literature methods.[13] Both amines react rapidly with atmospheric carbon dioxide and were stored as the hydrochloride salts. For comparison with earlier work, nitrous deaminations of both amines were carried out in acetic acid buffered with potassium acetate. Both were done in duplicate and each product mixture was analysed twice. As in all this work, internal g.l.c. standards were used so absolute yields were obtained. Averages from four analyses were normalised. One nitrous deamination of (1) was done under nitrogen [17] and this doubled the recovery (from 18 to 37%) without affecting any product ratios, so this is a recommended procedure.

The triazenes were made by established methods [18] and (3a), (3b), and (4a) were recrystallised. Compound (4b) was obtained as a powdery crystalline solid which was not successfully recrystallised, but the elemental analysis and recovery of products upon acetolysis suggested that it was not seriously impure. Two or three analyses of hydrocarbons and acetates were obtained from each of duplicate solvolyses of all four triazenes. Only the total yield of secondary amines (the internal substitution products) was obtained, by u.v. spectroscopy, once from each triazene. The extinction coefficients of the aryl-(t-butylcyclohexyl)-amines were presumed to be the same as the values for the *N*-methyl analogues.[19] The single determination of the secondary amine yield was included with the average hydrocarbon and ester yields and the results were normalised to 100%.

Compound (4a) was also acetolysed on a larger scale to facilitate the isolation of a low yield product which chromatographed with the olefinic products. Hydrocarbons were separated from other products by column chromatography and subjected to Lemieux [20] oxidation. The unknown compound was stable to these conditions, which strengthened the view that it was a cyclopropane derivative (*cf.* the reported production of bicyclo[3.1.0]hexane from the deamination of cyclohexylamine [21]). The n.m.r. spectrum of the compound included multiplets at τ 9.6—9.7 and 10.1 which are characteristic of *cis*-1,2-dialkylcyclopropanes.[22] The compound is believed to be a 2-t-butylbicyclo[3.1.0]hexane, and has recently been reported as a probable low yield product of the silver hexafluoroantimonate-induced acetolysis of *trans*-4-t-butylcyclohexyl chloroformate.[9]

The *N*-(*trans*-4-t-butylcyclohexyl)-*N*-nitrosoamides (6) were reasonably stable at room temperature and were prepared by a literature method; [23] (6a) was recrystallised at low temperature. The rates of the acetolysis of (6b) and butyrolysis of (6a) were measured at 25° spectrophotometrically (k 4.0×10^{-4} and 7.7×10^{-5} s^{-1} respectively) so that the analytical solvolyses were known to have reacted for at least ten half-lives. Duplicate solvolyses of (6b) in buffered acetic acid and (6a) in both buffered butyric acid and buffered butyric [^{2}H]acid were carried out. In our hands the last solvent was best prepared by the uncatalysed reaction of butyryl chloride with deuterium oxide, as the acid-catalysed reaction of butyric anhydride with deuterium oxide [24] caused extensive exchange of α-CH_2 hydrogens. Two, three, or four analyses were made for each product mixture and, as usual, average results were normalised. *N*-(*cis*-4-t-Butylcyclohexyl)-*N*-nitrosoacetamide (5) was unstable and had to be prepared at low temperature [25] separately for each solvolysis. One butyrolysis mixture was analysed three times and two more reactions were analysed once only, as reproducibility between different solvolyses was worse than between different analyses of a single product mixture. This is

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[18] E. H. White and H. Scherrer, *Tetrahedron Letters*, 1961, 758.
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[21] O. E. Edwards and M. Lesage, *Canad. J. Chem.*, 1963, **41**, 1592.
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[23] E. H. White, *J. Amer. Chem. Soc.*, 1955, **77**, 6008, 6014; E. H. White and C. A. Aufdermarsh, *ibid.*, 1961, **83**, 1179.
[24] W. Weltner, *J. Amer. Chem. Soc.*, 1955, **77**, 3942.
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undoubtedly due to the difficulty in repeating exactly the preparation and solvolysis of an unstable compound. Again, the average results from the (three) solvolyses were normalised.

1-Diazo-4-t-butylcyclohexane (7) was prepared in low yield (judged largely by the low recovery of hydrocarbons and acetates upon acetolysis) from the ketone *via* the hydrazone by a literature method.[26] The crude, effervescing diazoalkane was solvolysed immediately and, as usual, duplicate analyses were made on the products of two separate solvolyses. They always included a substantial amount of 4-t-butylcyclohexanone and traces of *cis*- and *trans*-4-t-butylcyclohexanols which are probably not products of the acetolysis.

RESULTS AND DISCUSSION

The different deamination procedures from either *cis*- or *trans*-4-t-butylcyclohexylamines give analyses (shown in Tables 1 and 2) which, though generally similar,

TABLE 1

Combined analyses of deamination of *cis*-4-t-butylcyclohexylamine derivatives

	(3a) [c]	(3b) [c]	(5) [d]	(1) [e]
Elimination				
4-Ene	71.0	70.1	78.4	74.0
3-Ene	8.2	8.9	7.9	3.5
1-Ene	1.4	2.2	0.3	0.4
External substitution				
c-4-OAc (-OBt)	3.2	3.4	(0.7)	6.7
t-4-OAc (-OBt)	3.1	3.3	(1.0)	8.9
c-3-OAc (-OBt)	1.6	2.1	(0.3)	1.2
t-3-OAc (-OBt)	3.3	5.0	(0.8)	2.2
c-2-OAc		0.02		
Internal substitution				
c-4-X [a]	8.3	5.1	7.2	0.5
t-3-X [a]			0.1	
c-3-X [a]			2.7	2.6
t-4-X [a]			0.6	
Recovery (%)	99	93	55	18(37 [b])
Total hydride shift (%)	⩾29	⩾34	⩾26	⩾14

[a] From (3a) X = C_6H_5NH; from (3b) X = *p*-$NO_2C_6H_4NH$; from (5) X = AcO; from (1) X = HO. [b] When done under N_2. [c] In CH_3CO_2H–0.15M-CH_3CO_2K. [d] In $C_3H_7CO_2H$–0.15M-$C_3H_7CO_2K$. *n*-Ene = *n*-t-butylcyclohexene (*n* = 1, 3, or 4); cyclop. = 2-t-butylbicyclo[3.1.0]hexane; *c*-*n*-OAc(-OBt) = *cis*-*n*-t-butylcyclohexyl acetate (butyrate) (*n* = 2—4); *t*-*n*-OAc(-OBt) = *trans*-*n*-t-butylcyclohexyl acetate (butyrate) (*n* = 2—4).

differ to extents well outside possible experimental error. Clearly, the predominant deamination route in either diastereoisomeric series cannot be through a single, common intermediate. Furthermore, the amount of internal substitution in each reaction is comparable with the amount of external, solvent-derived substitution even though the external nucleophile is present in vast excess over the internal. These results agree with those reported for 1-propylpentylamine and differ from those reported for octylamine.[5,27] It follows that in the present cases, neither *cis*- nor *trans*-4-t-butylcyclohexyldiazonium ions are major, long lived intermediates. If either forms at all, it loses nitrogen before its initial counter-ion has diffused away, and gives a carbonium ion which also has a very short lifetime.

TABLE 2

Combined analyses of deamination of *trans*-4-t-butylcyclohexylamine derivatives

	(4a) [c]	(4b) [c]	(6a) [d]	(6a) [e]	(6b) [e]	(2) [e]
Elimination						
4-Ene	13.5	10.7	17.3	18.3	13.5	7.6
3-Ene	0.5	0.4	0.3	0.2	0.3	0.4
Cyclop.	1.4 [b]	1.5 [b]	6.0 [b]	6.7 [b]	3.1 [b]	3.5 [b]
External substitution						
c-4-OAc (-OBt)	7.0	8.2	(6.7)	(6.4)	5.4	16.2
t-4-OAc (-OBt)	52.1	55.6	(27.0)	(23.8)	38.0	55.7
c-3-OAc (-OBt)	0.3	0.3	(0.1)	(0.2)	0.2	0.4
t-3-OAc (-OBt)	0.5	0.5	(0.2)	(0.2)	0.4	0.4
c-2-OAc (-OBt)	0.05	0.04			0.02	0.04
t-2-OAc (-OBt)	0.1	0.2	(0.2)	(0.2)	0.1	0.3
Z [g]	0.5	0.3	(0.6)	(0.5)	0.4	0.4
Internal substitution						
c-4-X [a]	24.1	22.3	4.9	5.1	3.8	0.4
t-3-X [a]			0.1	0.1	1.2 [f]	
t-2-X [a]			0.1	0.1		
c-2-X [a]						
t-4-X [a]			33.9	35.7	32.2	14.7
c-3-X [a]			0.1	0.2	1.4 [f]	
W [g]			2.5	2.5		
Recovery (%)	85	77	84	84	75	14
Total hydride shift (%)	⩾2.2	⩾1.9	⩾1.3	1.3	⩾1.6	⩾1.9

[a] See Table 1. [b] May contain up to 0.1% of 1-ene. [c] In CH_3CO_2H–0.15M-CH_3CO_2K. [d] In $C_3H_7CO_2H$–0.15M-$C_3H_7CO_2K$. [e] In $C_3H_7CO_2^2H$–0.15M-$C_3H_7CO_2K$. [f] Overestimates due to unresolved unidentified contaminants. [g] See text.

See footnote to Table 1 for abbreviations.

However, when the results from the *cis*-compounds are compared with those from the *trans*-derivatives, it is clearly seen that the product ratios are much more grossly affected by the stereochemistry of the amine than by the mode of deamination. This is the result broadly expected from the earlier literature [11,12] as refined by others.[13-15] The two series of results are so different that there can be almost no crossover between the intermediates from the diastereoisomeric precursors; nor are the results diastereoisomerically related. This is in contrast to the results of the solvolysis of the corresponding arenesulphonates,[6b] both diastereoisomers of which gave predominantly elimination, and similar amounts of 1,2-hydride shift. The unrearranged substitution products from the arenesulphonates are approximately diastereoisomerically related, *i.e.* from both *cis*- and *trans*-precursors, the major products are formed by inversion. The product analyses [6b] and the β-deuterium kinetic isotope effects [28] require reaction of the *trans*-4-t-butylcyclohexyl arenesulphonate to be predominantly through a non-chair conformer. There is no reason to invoke a substantial amount of the deamination reactions through other than ground state, chair conformers.

[26] A. C. Day, P. Raymond, R. M. Southam, and M. C. Whiting, *J. Chem. Soc.* (*C*), 1966, 467.

[27] (*a*) H. Maskill, R. M. Southam, and M. C. Whiting, *Chem. Comm.*, 1965, 496; (*b*) R. M. Southam, D.Phil. Thesis, Oxford, 1965.

[28] V. J. Shiner and J. G. Jewett, *J. Amer. Chem. Soc.*, 1964, **86**, 945; 1965, **87**, 1382, 1383.

cis-4-*t*-Butylcyclohexylamine *Deaminations*.—The *cis*-compounds (1), (3), and (5) give no products which were not unambiguously synthesised, and the recoveries from the triazene reactions are very high. The unstable nitrosoamide (5) underwent extensive denitrosation,[29] in competition with the deamination, and this almost certainly accounts for the low recovery of esters and hydrocarbons. Independent of the deamination method used, the main products are formed by elimination. About 35% of the product mixture is formed *via* hydride shift; this allows for the fraction of the major product, 4-t-butylcyclohexene, attributable to the 3-t-butylcyclohexyl cation.[6b] This massive amount of rearrangement, which was undetected in earlier investigations [13-15] and which has no apparent enthalpic driving force, is in contrast to the very small amount (*ca.* 2%; see later) which occurs in the deamination of the *trans*-isomers. Clearly, a 1,2-hydride shift has stringent stereochemical requirements,[30] and this fact supports the view that the *trans*-β-hydrogen begins its migration before the carbon–nitrogen bond is completely broken. In other words, the rearrangement of the *trans*, axial, β-hydride is loosely concerted with the departure of the leaving group, even though the bond breaking and making processes may not be exactly synchronous. Further evidence is found by scrutiny of the products from the butyrolysis of (5). The ratio of internal to external substitution at the rearranged position (2.8 : 1.1) is not greatly reduced from the corresponding value at the unrearranged position (7.8 : 1.7). Moreover, the preference for retention of configuration at the rearranged position with the internal nucleophile is even higher (2.7 : 0.1) than at the unrearranged position (7.2 : 0.6). Clearly the internal nucleophile has neither diffused away nor greatly changed its geometrical relationship with the cation in the time required for the hydride atom to migrate.

The small yields of 1-t-butylcyclohexene (0.3—2.2%) probably implicate the 2-t-butylcyclohexyl cation. There is insufficient evidence to distinguish between its formation (*a*) from the 3-t-butylcyclohexyl cation by a second, discrete hydride shift,[31] (*b*) directly from the diazo compound RN_2–X by a concerted, double hydride shift, by-passing the 4- and 3-t-butylcyclohexyl cations, or (*c*) by a 1,3-hydride shift from the 4-t-butylcyclohexyl cation.[32]

The failure to appreciate that axial amines undergo deamination with such extensive rearrangement may account in part for the earlier, conflicting reports about the stereochemistry of the substitution products (Table 3). There are reports of predominant inversion,[11,33] and exclusive retention,[34] as well as of no high measure of selectivity.[13,14] A further cause of the lack of consensus is the failure to distinguish between internal and external substitution processes, each with its own different stereochemical consequences. White and Bachelor,[35] Cohen and Jankowski,[3] and Shoppee *et al.*[15,36] were able to resolve internal and external substitution (though not rearrangement) and, with the exception of some results on steroidal amines,[36a] reported predominant retention for internal substitution and non-stereospecific substitution for the external process. These are essentially our results concerning the unrearranged products (Table 1).

At the rearranged position, the external substitution shows a small preference for inversion, in contrast to the strong preference for retention by the internal nucleophile referred to above.

trans-4-*t*-Butylcyclohexylamine *Deaminations*.—These

TABLE 3

Nitrous deamination of axial cyclohexylamine derivatives

Amine	Solvent	Olefin(s) (%)	Acetate % (Ret : Inv)	Alcohol % (Ret : Inv)	Ref.
(1)	B	77	Saponified	23 (10 : 13)	13
(1)	C	63		37 (52 : 48)	14
(1)	A	50	31 (44 : 56)	19 (78 : 22)	15
3α-NH_2-5α-Cholestane	A	81	19 (45 : 55)		36
3α-NH_2-5α-Cholestane	A	38	15 (40 : 60)	9 (89 : 11)	35
2β-NH_2-5α-Cholestane	A	71	15 (25 : 75)	14 (77 : 23)	36 *a*
4β-NH_2-5α-Cholestane	A	97	2	1	36 *a*
7α-NH_2-5α-Cholestane	A	95	4 (10 : 90)	1	36 *a*
1-*cis*-NH_2-*trans*-Decalin	B	70	Saponified	30 (3 : 27)	33
2-*trans*-NH_2-*trans*-Decalin	B	70	Saponified	30 (3 : 27)	33
2-*trans*-NH_2-*trans*-Decalin	A		71 (46 : 54)	29 (95 : 5)	†

A = CH_3CO_2H; B = 10% CH_3CO_2H–H_2O; C = H_2O–$HClO_4$.

† Acetate + alcohol = 100, calculated from results of ref. 3.

[29] C. N. Berry and B. C. Challis, *Chem. Comm.*, 1972, 627.

[30] J. Mathieu, *Bull. Soc. chim. France*, 1973, 807; M. Cherest, H. Felkin, J. Sicher, F. Sipos, and M. Tichy, *J. Chem. Soc.*, 1965, 2513; R. D. Guthrie, *J. Amer. Chem. Soc.*, 1967, **89**, 6718.

[31] D. Farcasiu, C. Kascheres, and L. H. Schwarz, *J. Amer. Chem. Soc.*, 1972, **94**, 180.

[32] M. Saunders and J. J. Stofko, *J. Amer. Chem. Soc.*, 1973, **95**, 252; W. Kirmse and H. Arold, *Chem. Ber.*, 1970, **103**, 23; Yu. G. Blundel, V. A. Savin, M. A. Ryabtsev, and O. A. Reutov, *Doklady Akad. Nauk S.S.S.R.*, 1965, **165**, 1303 (*Chem. Abs.*, 1966, **64**, 9527d); E. Boelema, J. H. Wieringa, H. Wynberg, and J. Strating, *Tetrahedron Letters*, 1973, 2377.

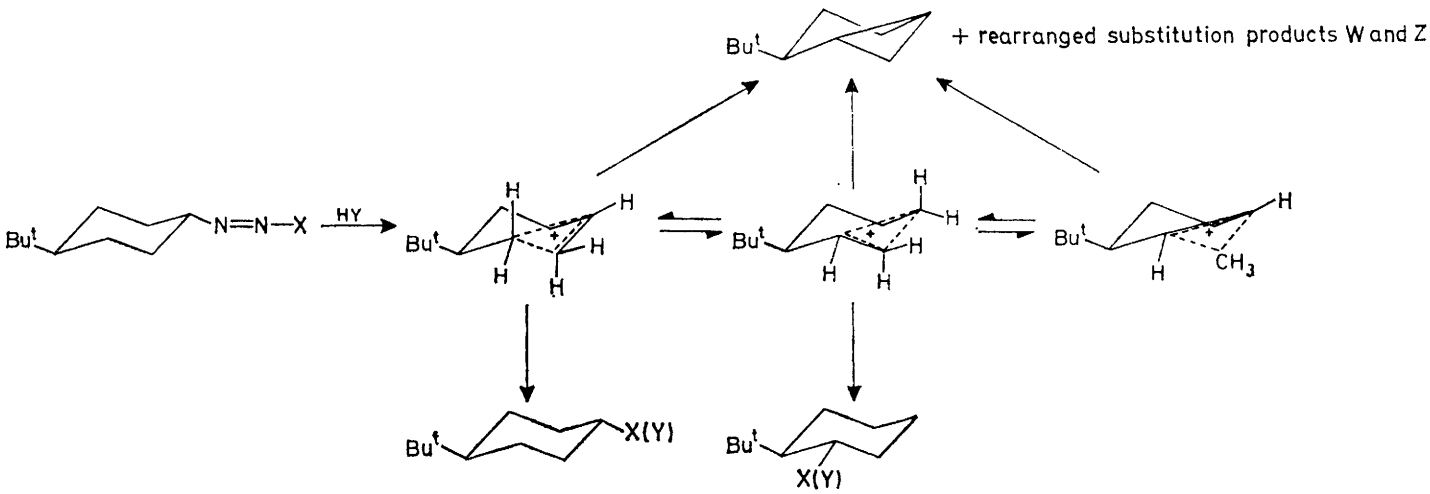
[33] W. G. Dauben, R. C. Tweit, and C. Mannerskantz, *J. Amer. Chem. Soc.*, 1954, **76**, 4420; W. Hückel, *Annalen*, 1938, **533**, 1.

[34] C. W. Shoppee, D. E. Evans, and G. H. R. Summers, *J. Chem. Soc.*, 1957, 97; C. W. Shoppee, P. J. W. Cemlyn, D. E. Evans, and G. H. R. Summers, *ibid.*, 4364.

[35] E. H. White and F. W. Bachelor, *Tetrahedron Letters*, 1965, 77; *Canad. J. Chem.*, 1972, **50**, 364.

[36] (*a*) C. W. Shoppee, J. G. Feher, R. M. Hall, R. E. Lack, and L. Tarasoff, *J. Chem. Soc.* (*C*), 1968, 221; (*b*) C. W. Shoppee, R. E. Lack, and P. Ram, *ibid.*, 1966, 1018.

compounds give a much lower yield of olefin (7—18%), very little 1,2-hydride shift (total *ca.* 2%) but a substantial amount of unrearranged substitution product (71—87%), and unidentified substitution products Z (an acetate) and, from the nitrosoamide solvolyses, W (a butyrate). The recoveries are less than complete, 75—85% for the triazenes and nitrosoamides. The nitrosoamides certainly underwent denitrosation [29] besides solvolysis, but the recoveries of the amides were not measured. In triazene solvolyses, it is known [37] that electrophilic nuclear substitution of the aromatic amine by the cationic intermediate of the deamination process occurs, but the extent of this process, also, was not estimated.



SCHEME 1

Samples of the unrearranged olefin, retained acetate, and retained butyrate from the solvolysis of (6a) in buffered butyric [^{2}H]acid were isolated by preparative g.l.c. The integrated 100 MHz n.m.r. spectrum of the compounds showed no loss of protium. Therefore even in butyric acid, very little reaction (if any) occurs *via* the diazoalkane, a route favoured in aprotic media of low dielectric constant.[38]

The elimination process is clearly less dependent upon a particular single stereochemical arrangement than the 1,2-hydride shift. This is in agreement with reports of other cyclohexyl [39] and cyclopentyl [40] derivatives in *E*1 processes. Interestingly, although the total amounts of 1,2-hydride shift from these *trans*-precursors are very low, all the reactions yield 2-t-butylcyclohexyl substitution products whereas the *cis*-precursors, which give substantial total rearrangement, give almost no 2-t-butylcyclohexyl substitution. The low, but fairly constant, yield of 2-t-butylbicyclo[3.1.0]hexane, apparently comparable with the formation of dehydroadamantane from acetolysis of 1-(2-adamantyl)-3-phenyltriazene,[41] could have arisen by 1,3-elimination; the W stereochemistry is particularly favourable for such a process.[42] Alternatively the cyclopropane, the 2-substituted derivatives, and W and Z could arise *via* protonated cyclopropane intermediates [43] as illustrated in Scheme 1. The structures of W and Z are clearly of considerable importance in the description of the cationic intermediate, and are under investigation.

In contrast to the results from the *cis*-derivatives, the decomposition of the nitrosoamides (6) shows that the extents of the preference for retention in the unrearranged internal and external substitution products are similar when internal and external nucleophiles are comparable. (The yields of rearranged substitution products are too small to be stereochemically significant.) Because there is very little rearrangement in the acetolysis of the *trans*-compounds (4) and (6), the two alcoholic compounds from direct deamination of (2) may be taken to be *cis*- and *trans*-4-t-butylcyclohexanols without the introduction of any serious error. It then seems that there is a larger difference in stereoselectivity between the internal and the external nucleophiles, compared

[37] E. H. White, H. Maskill, D. J. Woodcock, and M. A. Shroeder, *Tetrahedron Letters*, 1969, 1713; R. A. Moss and G. H. Temme, *ibid.*, 1968, 3219.

[38] R. A. Moss, D. W. Reger, and E. M. Emery, *J. Amer. Chem. Soc.*, 1970, **92**, 1366.

[39] T. Cohen and A. R. Daniewski, *J. Amer. Chem. Soc.*, 1969, **91**, 533; see also T. Cohen, A. R. Daniewski, G. M. Deeb, and C. K. Shaw, *ibid.*, 1972, **94**, 1786.

[40] K. Humski, V. Sendijarevic, and V. J. Shiner, *J. Amer. Chem. Soc.*, 1974, **96**, 6187.

[41] M. L. Sinnott, H. J. Storesund, and M. C. Whiting, *Chem. Comm.*, 1969, 1000.

[42] A. Nickon and N. H. Werstiuck, *J. Amer. Chem. Soc.*, 1967, **89**, 3914.

[43] H. Maskill, 'Specialist Periodical Reports (Chem. Soc.), Aliphatic, Alicyclic, and Saturated Heterocyclic Chemistry', vol. 1 part 2, 1970–1971; *ibid.*, vol. II, 1972; C. J. Collins, *Chem. Rev.*, 1969, **69**, 543; M. Saunders, P. Vogel, E. L. Hagen, and J. Rosenfeld, *Accounts Chem. Res.*, 1973, **6**, 53; C. H. Depuy, A. H. Andrist, and P. C. Funfschilling, *J. Amer. Chem. Soc.*, 1974, **96**, 948; G. J. Karabatsos, C. E. Orzech, and S. Meyerson, *ibid.*, 1965, **87**, 4394; R. L. Baird and A. A. Aboderin, *Tetrahedron Letters*, 1963, 235; *J. Amer. Chem. Soc.*, 1964, **86**, 252, 2300; W. E. Depuy, H. R. Hudson, and P. A. Karam, *Tetrahedron Letters*, 1971, 3193; W. Kirmse, W. Gruber, and J. Knist, *Chem. Ber.*, 1973, **106**, 1376.

with the nitrosoamide decomposition. This is in agreement with the literature as seen from Table 4 and may be because the monodentate nature of water is less conducive to an intramolecular inversion process.[4b,23,25]

Conclusions.—The high measure of stereospecificity of these deaminations rules out significant reaction through free or symmetrically solvated carbonium ions.[7,13,45] The results can be accommodated by a mechanism

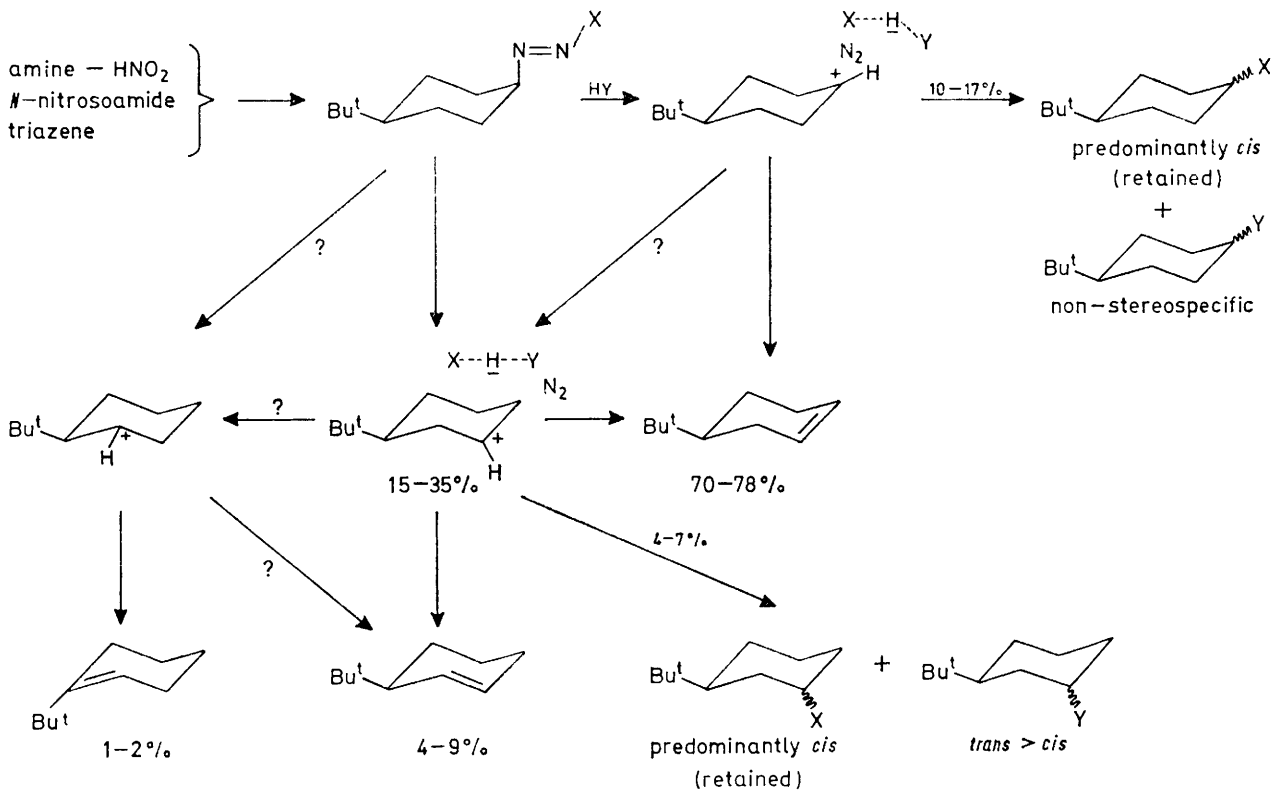
TABLE 4

Nitrous deamination of equatorial cyclohexylamine derivatives

Amine	Solvent	Olefin(s) (%)	Acetate % (Ret : Inv)	Alcohol % (Ret : Inv)	Ref.
(2)	B	10	Saponified	90 (73 : 13)	13
(2)	C	2		98 (100% ret)	14
(2)	A	6	52 (78 : 22)	42 (95 : 5)	15
3β-NH_2-5α-Cholestane	A	5	53 (66 : 34)	41 (90 : 10)	35
3β-NH_2-5α-Cholestane	A	9	59 (61 : 39)	32 (94 : 6)	36
2α-NH_2-5α-Cholestane	A	18	47 (78 : 22)	33 (95 : 5)	36*a*
4α-NH_2-5α-Cholestane	A	22	46 (80 : 20)	32 (100% ret)	36*a*
7β-NH_2-5α-Cholestane	A	10	49 (60 : 40)	41 (98 : 2)	36*a*
cis-[2-^{2}H]Cyclohexylamine	C			(<94% ret)	44
1-*trans*-NH_2-*cis*-Decalin	B		Saponified	(100% ret)	33
1-*trans*-NH_2-*trans*-Decalin	B		Saponified	(100% ret)	33
2-*cis*-NH_2-*cis*-Decalin	B		Saponified	(100% ret)	33
2-*cis*-NH_2-*trans*-Decalin	B		Saponified	(100% ret)	33
2-*cis*-NH_2-*trans*-Decalin	A		73 (75 : 25)	27 (97 : 3)	†

A = CH_3CO_2H; B = 10% CH_3CO_2H–H_2O; C = H_2O—$HClO_4$.

† Acetate + alcohol = 100, calculated from unpublished results kindly supplied by Cohen and Jankowski.



SCHEME 2 Principal reaction pathways for deamination of derivatives of (1)

The combination of very low amounts of rearrangement and the preference for retention of configuration for both internal and external substitution processes accounts for the good agreement in the early literature concerning the stereochemical consequences of deamination of equatorial cyclohexylamines.[11–15,33–36,44]

involving a concerted fragmentation of diazo-intermediates to give unrearranged and rearranged ion-pairs, initially separated by nitrogen[46] (Schemes 2 and 3). The cations are simple secondary carbonium ions, rather than diazonium ions as proposed by Cohen and Jankowski,[3] and are generated *ca.* 60 pm from the anions,

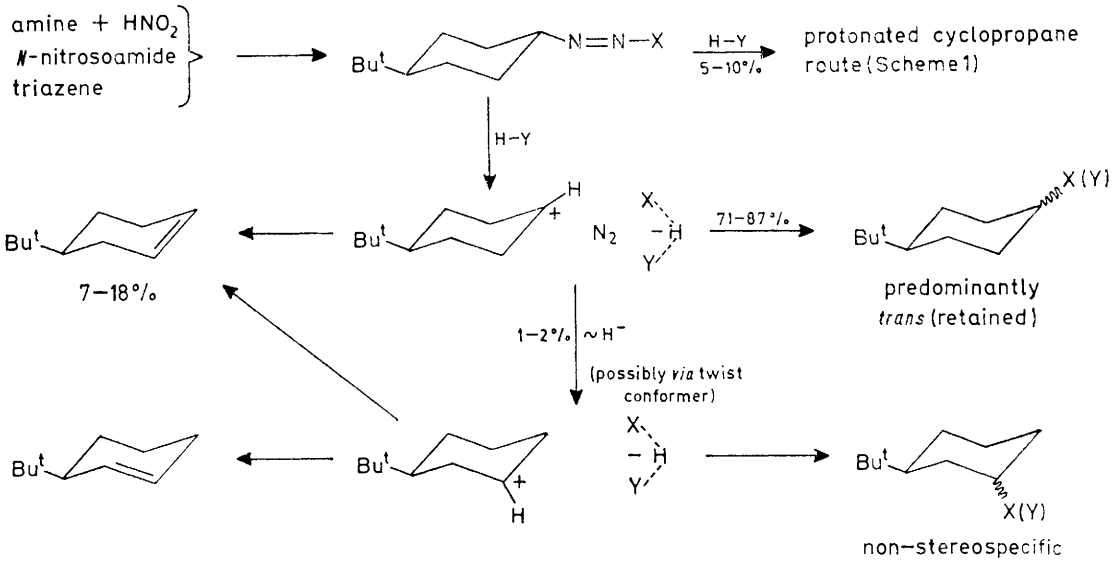
[44] A. Streitwieser and C. E. Coverdale, *J. Amer. Chem. Soc.*, 1959, **81**, 4275.

[45] D. G. Cooper and R. A. Jones, *J. Chem. Soc.* (*C*), 1971, 3920.

[46] R. A. Moss, *Accounts Chem. Res.* 1974, **7**, 421.

probably hydrogen-bonded species $[X \cdots H \cdots Y]^-$ (or higher oligomers). Twinned, hydrogen-bonded anions are well known in the solid state.[47] This mechanism involving ion-pairs having hydrogen-bonded anions, *e.g.* $[CH_3CO_2 \cdots H \cdots O_2CC_3H_7]^-$, accounts for the approximately equal yields of products from internal and external nucleophiles, and supersedes the explanation formerly advanced by one of us,[5] which is incompatible with the stereochemical results now reported. It explains the strong preference for retention of configuration in the internal substitution product and, if we assume that some substitution also occurs from the solvation shell around the cation, the smaller preference for retention in the external substitution product. These generalisations apply to the unrearranged products from both stereoisomeric series, and also to the rearranged products in the *cis*-series. The solvent isotope effect upon the product ratios for the butyrolysis of (6a) (Table 5) is interesting in these respects. There is no effect upon the stereospecificity of the unrearranged internal substitution. There is, however, a modest reduction (9%) in the stereospecificity of the unrearranged external substitution and a substantial increase (17%) in the proportion of unrearranged internal substitution product. These effects are compatible with the above mechanisms, as the deuteriated solvent has the stronger hydrogen bonds.[48]

The results of the acetolysis of 1-diazo-4-t-butylcyclohexane are shown in Table 6. The low recovery is probably due to a low overall yield in the diazoalkane preparation, and an unknown proportion of the olefinic products and of the cyclopropane might conceivably be due to decomposition *via* a carbene before the mixture reached the acetic acid. The very low proportion of



SCHEME 3 Principal reaction pathways for deamination of derivatives of (2)

TABLE 5

Solvent isotope effect upon unrearranged products of butyrolysis of (6a)

	Butyric acid	Butyric [²H]acid	Change (%)
4-Ene	17.3	18.3	+1
Ret : Inv(4-OAc)	6.92	7.00	+1
Ret : Inv(4-OBt)	4.03	3.72	−9
4-OAc/4-OBt	1.15	1.35	+17

rearranged acetate would fit initial formation of the same cations as were formed in the acetolysis of the *N*-nitrosoamides only if the protonation were almost entirely (>95%) axial. In that case, however, the unidentified acetate Z would also have been formed in detectable yield. Accordingly, we presume that protonation of the diazoalkane gives an incipient carbonium ion very close to the conjugate base of the proton donor, acetate (presumably hydrogen-bonded to acetic acid); there is no internal nucleophile in this reaction. Nucleophilic capture or proton abstraction will follow more rapidly

TABLE 6

Products of acetolysis of 1-diazo-4-t-butylcyclohexane[a] at 25° in acetic acid–0.15M-potassium acetate

4-Ene	61.4
3-Ene	0.4
Cyclop.	3.1 [b]
c-4-OAc	21.7
t-4-OAc	14.2
c-3-OAc	0.1
t-3-OAc	0.1
Total hydride shift	<1%
Recovery	9%

[a] Calculated on the basis of acetates + hydrocarbons = 100 (see text). [b] May contain up to 0.1% 1-ene.

See Table 1 for abbreviations.

[47] J. C. Speakman and H. H. Mills, *J. Chem. Soc.*, 1961, 1164; J. C. Speakman, *Chem. Comm.*, 1967, 32.

[48] S. N. Vinogradov and R. H. Linnell, 'Hydrogen Bonding', Van Nostrand Reinhold, New York, 1970, p. 160,

than in the reactions through separated ion-pairs and consequently rearrangement is less able to compete.

EXPERIMENTAL

4-t-Butylcyclohexanone.—4-t-Butylcyclohexanol was oxidised by the two-phase method of Brown and Garg [49] [91%; m.p. 46—48° (lit.,[13] 47.8—48.7°)]. The oxime was made by the base catalysed reaction of the ketone and hydroxylamine hydrochloride at room temperature [84%; m.p. 139—140° (lit.,[13] 133—134.6°)].

cis- *and* trans-*4-t-Butylcyclohexylamines* (1) *and* (2).—These were made by the method of Hückel and Heyder [13] with only minor modifications and were isolated and recrystallised as the hydrochlorides [59%; m.p. 264—266° (lit.,[50] 281—282°) for the *cis* isomer; 64%; m.p. 316—318° (lit.,[51] 330°) for the *trans*]. The *N*-(4-t-butylcyclohexyl)-amides were prepared from the amines by standard methods. After the usual work-up procedures they were recrystallised from light petroleum (b.p. 80—100°): *N*-(*trans*-4-t-butylcyclohexyl)acetamide, 80% [m.p. 118—120° (lit.,[13] 117.2—118.1°)]; *N*-(*cis*-4-t-butylcyclohexyl)acetamide, 74% [m.p. 171—173° (lit.,[13] 170.3—171.2°)]; *N*-(*cis*-4-t-butylcyclohexyl)butyramide, 71% [m.p. 105—106 and 110—111° after a phase change (Found: C, 74.6; H, 11.9; N, 6.15. $C_{14}H_{27}NO$ requires C, 74.6; H, 12.1; N, 6.2%)]; and *N*-(*trans*-4-t-butylcyclohexyl)butyramide, 58% [m.p. 121—122° (Found: C, 74.85; H, 12.05; N, 6.4%)].

The two *N*-(*trans*-4-t-butylcyclohexyl)amides were *N*-nitrosated by a solution of redistilled dinitrogen tetroxide (15 g) in dry dichloromethane (100 cm³) which was stored in a dark bottle at 0°.

N-*Nitroso*-N-(trans-*4-t-butylcyclohexyl*)*butyramide* (6b).—To the stirred CH_2Cl_2–N_2O_4 reagent (10 cm³; 11 mmol N_2O_4) at −70° was added powdered, freshly fused sodium acetate (1.7 g; 21 mmol) followed by a solution of the amide (0.34 g; 1.5 mmol) in dichloromethane. The stirred mixture was protected from atmospheric moisture and gradually allowed to warm to 0° over *ca.* 1.5 h. The solution was extracted with ice-cold, aqueous sodium carbonate, then with ice-cold water, and the separated organic phase was dried (Na_2SO_4) and filtered. The solvent was evaporated under a stream of nitrogen and the residual golden yellow oil (0.38 g, 99%), $\bar{\nu}_{max.}$ (CCl_4) 1 728 and 1 509 cm^{-1}, $\lambda_{max.}$ (C_2H_5OH) 429 and 410 nm, was solvolysed directly. By the same procedure N-*nitroso*-N-(trans-*4-t-butylcyclohexyl*)*acetamide* (6a) was prepared, m.p. 63—64° (from light petroleum, b.p. 30—40°) (Found: C, 63.4; H, 9.7. $C_{12}H_{22}N_2O_2$ requires C, 63.7; H, 9.8%), $\bar{\nu}_{max.}$(CCl_4) 1 728 and 1 509 cm^{-1}, $\lambda_{max.}$(EtOH) 410 (ε 83.8) and 429 nm (86.7).

N-*Nitroso*-N-(cis-*4-t-butylcyclohexyl*)*acetamide* (5).—A standardised solution of n-butyl-lithium in hexane (containing 1.1 mmol C_4H_9Li) was added by hypodermic syringe through a septum fitted to one of two necks of a flask containing a degassed, magnetically stirred solution of *N*-(*cis*-4-t-butylcyclohexyl)acetamide (0.21 g, 1.1 mmol) in dry tetrahydrofuran. After being stirred for 5 min at room temperature, the flask was fitted to a vacuum line, and cooled to −196°, and non-condensed gases were evacuated. Dinitrogen tetroxide (*ca.* 0.1 g, 1.1 mmol) was distilled into the flask and the mixture was then stirred for 30 min at −70°. The volatile components were distilled out of the flask at −15° under reduced nitrogen pressure to leave a waxy yellow oil which was solvolysed immediately.

3-Aryl-1-(4-t-butylcyclohexyl)triazenes which are unstable crystalline solids were made by the general procedure described for (4a). An ice-cold solution of benzenediazonium tetrafluoroborate [52] (2.59 g, 13.5 mmol) in acetonitrile (20 cm³) was added dropwise to a stirred suspension of anhydrous sodium carbonate (30 g, 0.28 mol), (2) (2.11 g, 13.6 mmol), and acetonitrile (20 cm³) cooled to −10 to −15° over 15 min. After a further 1 h the mixture was warmed to 0°, filtered, and extracted five times with cold light petroleum (b.p. 30—40°). Evaporation of the solvent at 0° followed by recrystallisation of the residue from light petroleum gave very pale pink *needles* (1.19 g, 34%), m.p. 116—118°. Although charcoal removes the colour from the triazene, it also catalyses decomposition (Found: C, 74.1; H, 9.55; N, 16.1. $C_{16}H_{25}N_3$ requires C, 74.1; H, 9.7; N, 16.2%). By the same procedures *triazene* (3a) was obtained in 35% yield, m.p. 55.5—56.5° (Found: C, 73.15; H, 9.55; N, 16.95%) and *triazene* (3b) in 20%, m.p. 84.0—85.5° (Found: C, 62.75; H, 7.95; N, 14.6. $C_{16}H_{24}N_4O_2$ requires C, 63.15; H, 7.95; N, 18.4%). Compound (4b) was obtained in 23% yield, m.p. 92—94°, but was not successfully recrystallised (Found: C, 63.8; H, 8.1; N, 16.95%).

4-t-Butylcyclohexanone Hydrazone.—A solution of 4-t-butylcyclohexanone (1.5 g, 9.7 mmol; shown by g.l.c. to contain <0.02% of the corresponding alcohols) in dry methanol (12 cm³) was added during 10 min to a stirred slurry of hydrazine (95%; [53] 4 g), barium oxide (10 g, 65 mmol), and methanol (17 cm³) at room temperature. After 30 min, dry ether (240 cm³) was added and the mixture was filtered. The solvents and the excess of hydrazine were evaporated at reduced pressure and the residual hydrazone, $\bar{\nu}_{max.}$(CCl_4) 1 615, 1 650, and 3 400 cm^{-1}, was oxidised directly [attempts to purify it resulted in an increased conversion to the corresponding azine, $\bar{\nu}_{max.}$(CCl_4) 1 648 cm^{-1}].

1-*Diazo*-*4-t-butylcyclohexane* (7).—Yellow mercury(II) oxide (10 g, 46 mmol) was added to an ice-cold, stirred slurry of 4-t-butylcyclohexanone hydrazone (as prepared above), calcium oxide (1.1 g, 0.20 mmol), several drops of a methanolic potassium hydroxide solution, and dry ether (20 cm³) over 3 min. After 1 h the mixture was filtered and the solvents were evaporated at 0° under reduced pressure. The pink effervescing residue, $\bar{\nu}_{max.}$(CCl_4) 2 030 cm^{-1}, was solvolysed immediately.

Solvolytic Media.—Acetic acid was fractionally distilled, b.p. 118°, from acetic anhydride, and n-butyric acid was fractionally distilled, b.p. 162—163°, from butyric anhydride. Butyric [^{2}H]acid was made from n-butyryl chloride and deuterium oxide and was fractionally distilled, b.p. 162—163°. The n.m.r. spectrum showed that there was no deuterium on carbon. Each of the three acids was made 0.15M in the corresponding anhydrous potassium salt.

Potassium Butyrate.—Freshly cut potassium (5.2 g, 0.133 mol) was cautiously added to ice-cold methanol under nitrogen and the solution was filtered through glass

[49] H. C. Brown and C. P. Garg, *J. Amer. Chem. Soc.*, 1961, **83**, 2952.
[50] J. L. Pinkus, G. Pinkus, and T. Cohen, *J. Org. Chem.*, 1962, **27**, 4356.
[51] D. Y. Curtin, R. D. Stolow, and W. Maya, *J. Amer. Chem. Soc.*, 1959, **81**, 3330.
[52] A. Roe and G. F. Hawkins, *J. Amer. Chem. Soc.*, 1947, **69**, 2443.
[53] L. I. Smith and K. L. Howard, *Org. Synth.*, 1944, **24**, 53.

wool. To the filtrate was cautiously added redistilled n-butyric acid (11.8 g, 0.134 mol) and the methanol was removed by distillation at reduced pressure. The residue was fused under a low nitrogen pressure then cooled, ground, and stored in a desiccator.

Isolation of 2-t-Butylbicyclo[3.1.0]*hexane*.—Compound (4a) (13.5 g, 52.1 mmol) was added batchwise to stirred acetic acid (50 cm^3) at 25°. After 30 min, light petroleum (b.p. 30—40°; 50 cm^3) was added and the solution was cooled in ice. An excess of saturated aqueous tripotassium phosphate was added, the petroleum phase was separated, and the aqueous phase was re-extracted with more light petroleum. The combined petroleum solution was washed with cold dilute sulphuric acid and water, then most of the solvent was removed by fractional distillation. The residue was chromatographed on alumina, eluted with light petroleum, and hydrocarbon fractions were combined. Again the bulk of the light petroleum was fractionally distilled. The residue was added to a solution of sodium periodate (12.6 g, 59 mmol), potassium permanganate (0.16 g, 1 mmol), sodium carbonate decahydrate (3.0 g), water (600 cm^3), and pyridine (900 cm^3) and the mixture was maintained at room temperature for 20 h with occasional shaking. It was then extracted twice with light petroleum and the combined petroleum phase was washed with dilute sulphuric acid, dilute potassium hydroxide solution, sodium thiosulphate solution, and water. The bulk of the light petroleum was fractionally distilled and the residue was again chromatographed on alumina, and eluted with light petroleum. Fractions containing unoxidised hydrocarbon were combined and fractionally distilled. Final traces of volatile solvent were removed by reduced pressure at −80° and the residue was dissolved in CCl_4 for n.m.r. analysis.

Solvolysis of Triazenes.—All solvolyses were in anhydrous acetic (or butyric) acid 0.15M in the corresponding potassium salt and containing a known concentration of decalin as internal calibrant. The following procedures are typical.

(a) *Analysis of hydrocarbons and acetates*. The triazene (80.0 mg, *ca.* 0.3 mmol) was carefully added batchwise to the stirred decalin-containing acetolysis medium (5 cm^3) at 25°. After 30 min, light petroleum (3 cm^3) was added and the solution was cooled before an excess of an aqueous ice-cold solution of tripotassium phosphate was added. The organic phase was separated, washed with water and dilute acid and used directly for g.l.c. analysis.

(b) *Estimation of total secondary amine product*. The above procedure was used except that ether rather than light petroleum was used to extract the products, and no acid wash was included. The ether and volatile products were evaporated at 0° and the residue was chromatographed on deactivated alumina using light petroleum as eluant. The fractions containing the secondary amines were combined, evaporated at 0°, and made up to a standard volume in ethanol. From the optical density of this solution and knowledge of the extinction coefficient of the chromophore [19] [ε 1 514 (294 nm) for the *N*-alkylaniline and 19 050 (387 nm) for *N*-alkyl-*p*-nitroaniline], the yield of the secondary amine was calculated.

Solvolysis of N-*Nitrosoamides*.—To the *N*-nitrosoamide (150—250 mg), immediately after preparation for (5), was added decalin-containing solvolysis solution (5 cm^3). The flask was fitted with a septum, through which was inserted a hypodermic needle, and maintained at 25° for a period not less than ten half-lives of the reaction. The work-up procedure was as for the triazene reactions.

Nitrous Deaminations.—The amine hydrochloride (*ca.* 250 mg) was extracted between light petroleum and freshly made sodium hydroxide solution. The petroleum phase was separated and the light petroleum was evaporated at 0°. To the free amine was added the decalin-containing acetolysis medium (5 cm^3) and the solution was stirred at 25° as sodium nitrite (*ca.* 0.2 g, 3 mmol) was added over 40 min. In later experiments this addition was under nitrogen. The reaction was worked-up as for the triazenes.

Analysis of Products.—The analytical procedures for the olefins, alcohols, and acetates have already been described.[6b,10] The butyrates were analysed on the same column as the acetates but at 130 rather than 120°. Samples of all isomers were separately prepared from the corresponding alcohols and shown to be well resolved with the exception of the pair *trans*-2- and *trans*-3-t-butylcyclohexyl butyrates which partially overlapped.

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