Wolf–Kishner Reduction of Triketone 6.—Triketone **6** (2.0 g) was reduced by a modification of the procedure of Durham[16] using diethylene glycol as solvent. Distillation of the reaction mixture at 0.1 mm gave 14 g of a mixture of liquids more volatile than diethylene glycol; glpc indicated that a trace of spiro[4.4]-nonane was present. The time-of-flight mass spectrum of the peak was substantially identical with that of spiro[4.4]nonane.

(16) L. J. Durham, D. J. McLeod, and J. Cason, "Organic Syntheses," Coll. Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1963, p 510.

Registry No.—**4**, 4614-01-1; **5**, 17396-77-9; **6**, 17396-18-8; triphenylhydrazone of **6**, 17414-33-4; **7**, 175-93-9.

Nonplanar Cyclobutane. Evidence for a Conformationally Controlled, Classic Mechanism in the Deamination of *cis*- and *trans*-3-Isopropylcyclobutylamine[1]

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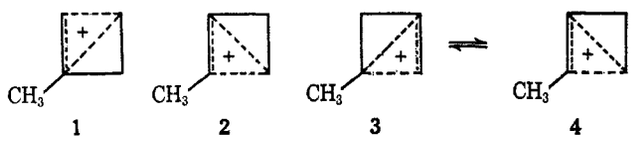
The synthesis and configurational assignments of *cis*- and *trans*-3-isopropylcyclobutylamine are described. Deamination yields the same five products for either isomer, but a major distinction in the ratios of two of these, cyclopropylisopropylcarbinol (68% from *cis* amine, 29% from *trans* amine) and *trans*-(2-isopropylcyclopropyl)-carbinol (0–2% from *cis* amine, 55% from *trans* amine) is observed; no *cis*-(2-isopropylcyclopropyl)carbinol is obtained from either reactant. These data are considered to be most compatible with concerted processes dependent on stereochemical differences; the cyclobutyldiazonium ion is implicated as the branching point in the formation of products, which arise through competing pathways. A mechanism is proposed in which the formation of major product *trans*-(2-isopropylcyclopropyl)carbinol is contingent on conformationally facilitated orbital overlap in the *trans* intermediate, whereas a similar process for the *cis* intermediate is opposed by unfavorable repulsive interactions. It is suggested that cyclobutylamine deaminations may follow a more classic course than has been hitherto generally accepted.

The facile interconversions which often occur among related cyclobutyl, cyclopropylcarbinyl, and homoallyl derivatives in carbonium ion reactions have long been intriguing mechanistically. The bicyclobutonium ion rationale attempts to explain these transformations in terms of a common system of nonclassical carbonium ion intermediates.[3] This concept, while effective in reconciling reactivity for the parent cyclobutyl and cyclopropylcarbinyl derivatives, is less persuasive in application to substituted systems. It was observed that deamination of 1-, 2-, and 3-methylcyclobutylamine[3b] gave no ring rearrangement in the first case, exclusive production of one cyclopropylcarbinol in the second, and a mixture of cyclopropylcarbinols in the third. Preferred stabilization of different bicyclobutonium ions (**1** and **2**) for, respectively,



1 **2** **3** **4**

the 1- and 2-methylamines was invoked to explain the disparity, with a pair of interconverting bicyclobutonium ions (**3** and **4**) accounting for the 3-methyl case. However, it is difficult to understand why such interconversion would occur solely in the latter instance and not the former two. Entry into the same system of rapidly equilibrating intermediates is anticipated in theory, and were electrical stabilization a predominant factor, the same major product(s) might be reasonably expected. Further, although not reflecting a mandatory requirement, absence of homoallylic product implicit in the formulation of the several bicyclobutonium ions was encountered.

Recently, convincing evidence[4-8] has accumulated that the ion derived from the cyclopropylcarbinyl system possesses an unrearranged structure rather than the bicyclobutonium ion structure previously proposed.[3] More recently, extended Hückel theory quantum mechanical calculations have supported a completely classical cyclobutyl cation derived from cyclobutane, with nonclassical structures involving 1,3 bridging in rings with varying dihedral angle all being of higher energy.[9] Further, calculations on the tricyclobutonium ion proposed as a possible initial or intermediary pathway in these reactions[3g] showed that it is of such high energy as to eliminate it clearly from consideration. The suggestion has been previously made that the cyclopropyl cation is in equilibrium with the classical cyclobutyl cation.[10]

It would thus appear that while factors of electrical stability are undoubtedly important in explaining deamination of cyclobutylamines, the specific concept of a system of common, interconverting bicyclobutonium ions must bear renewed examination, particularly

(1) Preliminary reports of this work have been presented: 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, Abstracts, p 167s; I. Lillien and R. A. Doughty, *Tetrahedron Lett.*, 3953 (1967).

(2) Taken in part from the thesis submitted by R. A. D. to the Graduate School of the University of Miami in partial fulfillment of the requirements for the Ph.D. degree in chemistry. Work done primarily at the University of Miami, Coral Gables, Fla.

(3) (a) K. L. Servis and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 1331 (1965); (b) M. S. Silver, M. C. Caserio, H. E. Rice, and J. D. Roberts, *ibid.*, **83**, 3671 (1961); (c) E. F. Cox, M. C. Caserio, M. S. Silver, and J. D. Roberts, *ibid.*, **83**, 2719 (1961); (d) E. Renk and J. D. Roberts, *ibid.*, **83**, 878 (1961); (e) M. S. Silver, P. R. Schaeffer, J. E. Nordlander, C. Rüchardt, and J. D. Roberts, *ibid.*, **82**, 2646 (1960); (f) R. H. Mazur, W. N. White, D. A. Semenov, C. C. Lee, M. S. Silver, and J. D. Roberts, *ibid.*, **81**, 4390 (1959); (g) J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 2509, 3542 (1951).

(4) M. Vogel and J. D. Roberts, *ibid.*, **88**, 2262 (1966).

(5) H. L. Goering and K. E. Rubinstein, Abstracts, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, p 11K.

(6) H. G. Richey, Jr., and J. M. Richey, *J. Amer. Chem. Soc.*, **88**, 4971 (1966).

(7) C. U. Pittman, Jr., and G. A. Olah, *ibid.*, **87**, 2998 (1965); N. C. Deno, J. S. Liu, J. O. Turner, D. N. Lincoln, and R. E. Fruit, Jr., *ibid.*, **87**, 3000 (1965).

(8) P. von R. Schleyer and G. W. Van Dine, *ibid.*, **88**, 2321 (1966).

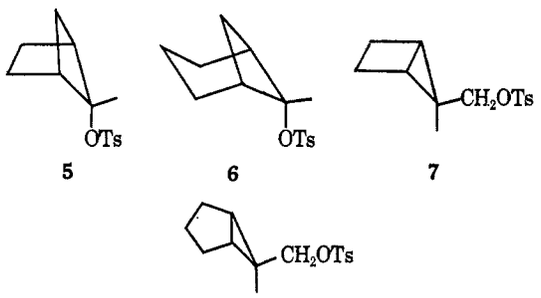
(9) R. E. Davis and A. Ohno, *Tetrahedron*, **24**, 2063 (1968).

(10) H. C. Brown, "The Transition State," Spec. Publ. No. 16, The Chemical Society, London, 1962, p 140.

in the course of consideration of other factors. A major such factor devolves on the question of conformation. Current awareness of nonplanarity prevalent in many cyclobutanes[3b,11] has heightened interest in what relationship conformation and mechanism may display in these compounds.

This problem becomes more significant in view of substituent effects such as those mentioned above and observed in other cases, when it is recalled that there is very likely an intimate substituent–conformation interdependence in the flexible cyclobutanes[11c,f,g] and that conformational variances can profoundly affect the course of a reaction such as deamination. Because the quite low $\Delta F^{\ddagger}$ for deamination is in the range of conformational energy barriers, it has been eloquently argued that sterically concerted processes critically dependent on conformation may be important pathways for deamination.[12] Since deamination and solvolysis do not necessarily proceed *via* identical mechanisms,[13] it is well to bear in mind that the often cited evidence of rate acceleration in solvolysis used to support the nonclassical hypothesis may have only limited bearing on the mechanism of deamination, specifically, in the case of the cyclobutylamines and cyclopropylcarbinylamines.[3,4,14]

Conformational effects on the solvolysis of bicyclic cyclopropanes and cyclobutanes have been reported in the investigations of Wiberg and coworkers.[14c,15] It was found that *endo*-5-bicyclo[2.1.1]hexyl tosylate[14c,15] (**5**) and *endo*-6-bicyclo[3.1.1]heptyl tosylate[15a] (**6**) solvolyze much faster than their *exo* epimers with almost identical rate ratios, leading to the suggestion that pseudoequatorial leaving group rates may be preferentially accelerated by bicyclobutonium ion participation. The *exo* epimer of **6**, which solvolyzes 10^6 times slower, was considered to react *via* a norbornyl type nonclassical scheme. It is not clear why norbornyl-type participation should be 10^6 times less effective in rate acceleration than bicyclobutonium-type participation, since the ratio of rates of solvolysis of parent norbornyl and cyclobutyl arenesulfonates, upon which these concepts are based, is about 50:1 in favor of the former.[16] Further, the major product of acetolysis of **6** (*endo*-2-norcaranyl acetate, 75%) has a stereochemistry incompatible with *intermediacy* of the bicyclobutonium ion (Figure XIV in ref 15a). It is possible that rate differences in the above cases need not necessarily reflect delocalization, but a combination of factors such as conformational effects causing different ground-state energies,[17] steric hindrance to ionization or solvation,[10,18] and, especially, cyclopropylmethyl carbonium ion stabilization.[14] A plausible alternative explanation which can reconcile the accelerated rates of **5** and **6** relative to their *exo* epimers



5 **6** **7** **8**

is a combination of relative retardation of departure of the *exo* tosyloxy group by the very proximal 6 or 7 hydrogens, similar hindrance to solvated ion-pair formation, and the "push" of concertion by the migrating group backside to the leaving group in the *endo* isomers (which migration is greatly facilitated, in contrast to the *exo* epimers, by generation of cyclopropylmethyl carbonium ions). The generation of such ions may likewise account for the high rates of solvolysis of analogous compounds **7** (which does not undergo rearrangement)[14c] and **8**,[15c] irrespective of rearrangement routes, which can well be regulated by other considerations. Indeed, the formation of cyclopropylmethyl carbonium ion may account in part for the high rates of solvolysis of cyclobutyl and cyclopropylmethyl arenesulfonates themselves.[19]

A further note of caution must precede generalization of rationales derived from results in fused cyclobutane systems to unfused systems, as this will be limited by variances in conformational factors with alterations in cyclobutane dihedral angles prevailing in both ground and transition states. Mechanistic pathways may not be parallel.

With regard to the parent cyclobutane system, Roberts and coworkers have suggested that the formation of 3-methylcyclobutanol in the deamination of 3-methylcyclobutylamine may be due to solvolytic displacement of the equatorial diazonium group.[3b] However, with this exception, the possibility of other mechanistic differences arising from conformationally different *cis* and *trans* isomers has not as yet been much considered or experimentally explored. To gain further insight into such relationships, we have prepared de-

(11) *Cf.*, for example, (a) W. G. Rothschild, *J. Chem. Phys.*, **45**, 1214 (1966); (b) J. B. Lambert and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 3884, 3891 (1965); (c) N. L. Allinger and L. A. Tushaus, *J. Org. Chem.*, **30**, 1945 (1965); (d) K. B. Wiberg and G. M. Lampman, *J. Amer. Chem. Soc.*, **88**, 4429 (1966); (e) I. Lillien and R. A. Doughty, *ibid.*, **89**, 155 (1967); (f) I. Lillien and R. A. Doughty, *Tetrahedron*, **23**, 3321 (1967); (g) G. M. Lampman, K. E. Apt, E. J. Martin, and L. E. Wangen, *J. Org. Chem.*, **32**, 3950 (1967).

(12) A. Streitwieser, Jr., *J. Org. Chem.*, **22**, 861 (1957); A. Streitwieser, Jr., and W. D. Schaeffer, *J. Amer. Chem. Soc.*, **79**, 2888 (1957).

(13) *Cf.*, for example, (a) R. R. Sauers and J. A. Beisler, *Tetrahedron Lett.*, 2181 (1964); (b) S. Winstein and J. Sonnenberg, *J. Amer. Chem. Soc.*, **83**, 3244, 3235 (1961); (c) E. J. Corey, J. Casanova, P. A. Vatakencherry, and R. Winter, *ibid.*, **85**, 169 (1963); (d) J. A. Berson and A. Remanick, *ibid.*, **86**, 1749 (1964).

(14) Of particular relevancy to the present discussion is the viewpoint which has been advanced that the rapid solvolysis of cyclopropylmethyl derivatives is attributable to carbonium ion stabilization by interaction of its p orbital with the "bent" ring orbitals, rather than by formation of a bicyclobutonium ion, *vide supra; cf.* (a) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, p 588; (b) B. Capon, *Quart. Rev.* (London), **18**, 100 (1964); (c) K. B. Wiberg and A. J. Ashe, III, *Tetrahedron Lett.*, 4425 (1965); (d) H. Hart and P. A. Law, *J. Amer. Chem. Soc.*, **84**, 2462 (1962); (e) H. Hart and J. M. Sandri, *ibid.*, **81**, 320 (1959).

(15) (a) K. B. Wiberg and B. A. Hess, Jr., *ibid.*, **89**, 3015 (1967); (b) K. B. Wiberg and B. A. Hess, Jr., *ibid.*, **88**, 4433 (1966); (c) K. B. Wiberg and A. J. Ashe, III, *Tetrahedron Lett.*, 1553, 4265 (1965); (d) K. B. Wiberg and R. Fenoglio, *ibid.*, 1273 (1963); (e) K. B. Wiberg, B. R. Lowry, and T. H. Colby, *J. Amer. Chem. Soc.*, **83**, 3998 (1961); (f) K. B. Wiberg and B. R. Lowry, *ibid.*, **85**, 3188 (1963).

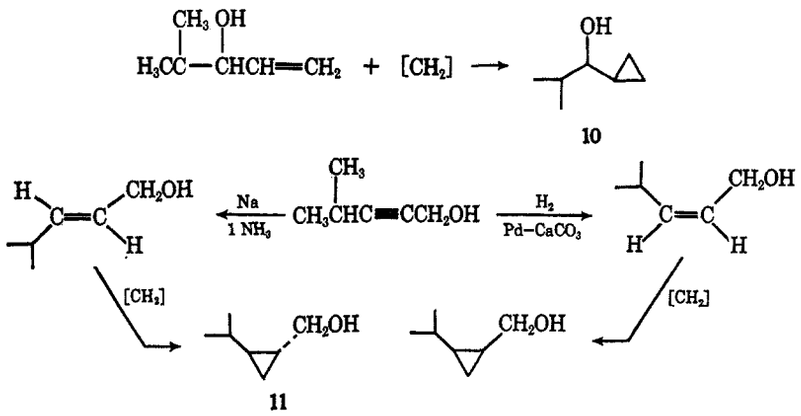
(16) G. D. Sargent, *Quart. Rev.* (London), **20**, 301 (1966).

(17) Note the recent important work emphasizing the significant role that *differences in ground-state energies* may play in creating large rate differences in solvolysis of similar reactants; *cf.* R. S. Bly, R. K. Bly, A. O. Bedenbaugh, and O. R. Vail, *J. Amer. Chem. Soc.*, **89**, 880 (1967).

(18) (a) H. C. Brown, *Chem. Brit.*, 199 (1966); (b) H. C. Brown, *Chem. Eng. News*, **45**, 67 (1967).

(19) Wiberg and Ashe[14c] have favored such an explanation for the high rate of solvolysis of **7**.

SCHEME I



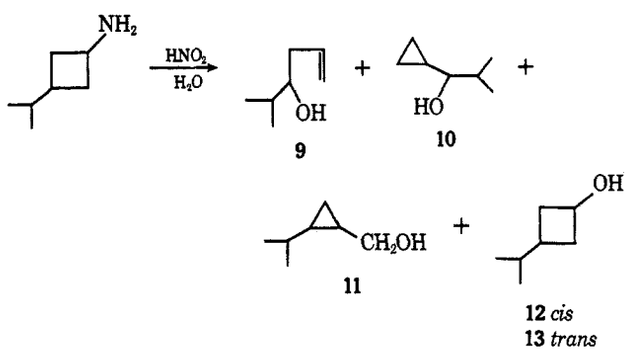
rivatives of the 3-isopropylcyclobutyl system, in which the isopropyl group was intended to serve as a "holding group" to accentuate isomeric differences. We wish herein to report the synthesis, configurational assignments, and results of deamination of the isomeric 3-isopropylcyclobutylamines and consider the possible bearing of these results on the problem of mechanistic pathway for cyclobutane carbonium ion reactions.

Results

3-Isopropylcyclobutanecarboxylic acid was prepared *via* a conventional synthesis from condensation of 2-isopropyl-1,3-dibromopropane with diethyl malonate, followed by hydrolysis, and decarboxylation; this has been described.[11f] Basic equilibration of the monoester[11f] enabled assignment of the isomers as *cis* (the diequatorial conformer is the most thermodynamically stable and therefore predominates at equilibrium) and *trans*. The ester could be hydrolyzed back to acid of the same composition; this in turn could be converted to amine *via* the Schmidt reaction. Since this reaction is known to proceed with retention of configuration, identity of the amine isomers, which formed in identical relative proportions, was established. The amines could be readily separated on a preparative vpc column, and the nmr analysis of each confirmed the assignment.[20] We have interpreted the nmr spectra in terms of puckered rings bearing equatorial isopropyl and equatorial and axial amino groups in the *cis* and *trans* isomers, respectively.[11e]

Deamination of a mixture of unseparated amines (52% *cis*) with aqueous perchloric acid gave, on initial vpc analysis, a 75–80% yield of four products (**9**–**13**) in relative proportions of 8, 47, 28, and 17%. Further analysis of the last product resolved it into two components. The products were separated by preparative vpc. Product **9** was readily identified as an unsaturated alcohol from its ir spectrum, nmr spectrum, and chemical behavior, and its identification as 2-methyl-5-hexen-3-ol was confirmed by comparison with the authentic material.

Products **10** and **11** were identified from their nmr spectra as, respectively, cyclopropylisopropylcarbinol and (2-isopropylcyclopropyl)carbinol. In the latter spectrum, the methinyl and methyl protons have almost identical chemical shifts, resulting in almost no methyl splitting. The spectrum is identical with that of cyclopropylcarbinol[21] with the addition of the isopropyl group. Compound **10** was synthesized in low yield by the reaction of diidomethane with 4-methyl-1-penten-3-ol in the presence of a copper–zinc couple (Scheme I). The stereochemistry of **11** could not be deduced from the nmr spectrum. Further vpc analysis confirmed the homogeneity and purity of the sample. It was therefore necessary to prepare both *cis*- and *trans*-alkenes (Scheme I), which were then treated with diiodomethane in the presence of the copper–zinc couple to give the respective cyclopropanes. Analytical parameters for the *trans*, but not the *cis*, isomer were congruent with those of **11**. Both isomers demonstrated different vpc retention times under the conditions employed and different nmr spectra.



Products **12** and **13** were identified from their nmr spectra[11e] as, respectively, *cis*- and *trans*-3-isopropylcyclobutanol. Synthesis was achieved by converting 3-isopropylcyclobutanecarboxamide into 3-isopropyl-1-acetylcyclobutane *via* the Grignard reaction and the Baeyer–Villiger conversion of the latter into 3-isopropyl-1-acetoxycyclobutane. Since this reaction, like the Schmidt, proceeds with retention of configuration, the *cis*–*trans* mixture of 3-isopropylcyclobutanol obtained from the latter by hydrolysis could be related to equilibrated methyl 3-isopropylcyclobutanecarboxylate in the same fashion as the amines. This experiment confirmed the assignment of configuration from nmr data.

Deamination of the individual amines in the same manner as the mixture produced product compositions listed in Table I.

(20) The *cis* amine was approximately 96–97% isomerically pure, while the *trans* was not less than 98% pure. However, since the *cis* isomer contained 3–4% of the *trans* amine, this may have been responsible for the *ca.* 2% of **11** found in the *cis* deamination (Table I).

(21) K. L. Servis and J. D. Roberts, *J. Amer. Chem. Soc.*, **86**, 3773 (1964).

TABLE I

PER CENT PRODUCTS IN THE AQUEOUS DEAMINATION OF ISOMERIC 3-ISOPROPYLCYCLOBUTYLAMINES (AVERAGES OF SEVERAL RUNS)

Amine	9	10	11[a]	12	13
b *cis*	9.8	68.1	2.2	11.1	8.8
c *trans*	6.0	28.6	55.0	7.3	3.1

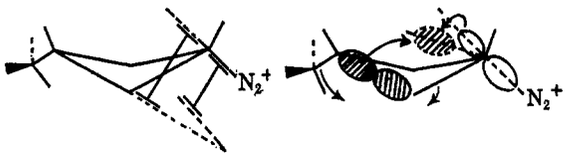
[a] See ref 20. [b] Registry no.: 17393-32-7. [c] Registry no.: 17393-31-6.

Discussion

The difference in the relative proportions of **10** and **11** is striking. These ratios reflect kinetic control in this nonequilibrium reaction and are significant in enabling speculation directly regarding their preceding transition states. The yield of not only **10**, but all other products, is increased at the expense of **11** for the *cis* isomer,[20] the route to which may be assumed to be unfavorable in that case, but the favored one for the *trans* isomer. A second striking result is the stereoselective formation of exclusively *trans* **11**. It therefore is apparent that, since the major distinction between the isomers is a stereochemical one, the differential behavior of these two compounds must be explained by this determinative factor. Products **12** and **13** may arise readily through solvolytic displacement (*vide infra*) not involving cyclobutane carbonium ions. Attention may therefore be focused on the first three products, of which the relative amounts of **9** are not significantly different. An adequate rationale must thus at least account for (a) the disparity in formation of **11** as a function of stereochemical difference and (b) stereoselectivity in formation of **11**.

We have suggested[1] that the present differences in isomeric behavior may be satisfactorily explained in terms of conformationally controlled concertion which provides a favored route to **11** for the *trans*, but not the *cis* isomer. For deamination in cyclohexane, and indeed in all cyclohexane reactions, rearranging bonds must be in an *anti* configuration;[22] a recent example of such conformational control is in the deamination of the four epimeric 2-amino-4-butylcyclohexanols.[23] Ring contraction occurs with equatorial leaving groups, while *trans* diaxial rearrangement occurs with axial leaving groups. This severe steric limitation evidently involves a critical requirement for overlap of the rear lobe of the developing vacant 2p orbital at C_1 with the approaching orbital of the migrating group in a manner analogous to SN2 substitution. In deamination, the proposal of Streitwieser,[12] that the alkyldiazonium ion was the branching point for pathways leading to other products, including sterically controlled processes, has found important support in recent work which points to the product-determining character of solvated diazonium ion-pairs in this reaction.[13c,d,24] Thus concerted displacement of the diazonium group by migrating bonds in cyclohexane is undoubtedly the significant process leading to deaminative rearrangement in this system.

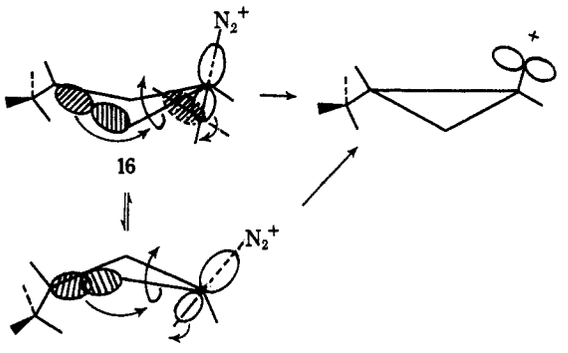
The major distinction between cyclohexane and cyclobutane conformations lies in the degree of ring pucker. Whereas in cyclohexane ring contractions the migrating bond can be exactly parallel to the axis of the leaving group (*i.e.*, N_2 in deamination), in cyclobutane the smaller ring dihedral angle (about 30° as compared to about 54 for cyclohexane) causes a deviation from parallel alignment of bond axes C_2–C_3 and C_1–N_2^+ in the pivotal diazonium ion (**14**) from the *cis* isomer. This should result in minimal overlap as the migrating orbital approaches the vacating orbital at C_1 (**15**).



14 **15**

cis

For favorable overlap, a *conrotatory* orbital movement, as shown by arrows, is required; this leads to a sterically unfavorable *cisoid* transition state with an increase in nonbonded interactions. In contrast, in the *trans* diazonium cation the good degree of angular overlap of the migrating orbital with the C_1 orbital which is already possible (and which is optimized by ring flexion toward planarity)[25] may be enhanced by a *disrotatory* orbital movement (**16**) leading to a sterically favorable *transoid* transition state with net reduction in nonbonded interactions. Alternatively, possible *trans* conformer (**17**) can also proceed through a similarly favorable pathway *via* orbital movement as shown.



16

17

trans

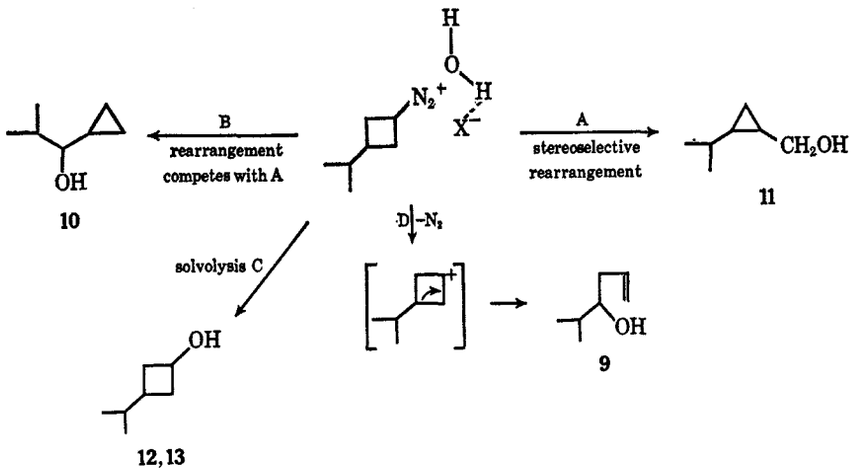
(22) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, New York, N. Y., 1965, Chapter 2.

(23) M. Chérest, H. Felkin, J. Sicher, F. Šipoš, and M. Tichý, *J. Chem. Soc.*, 2513 (1965).

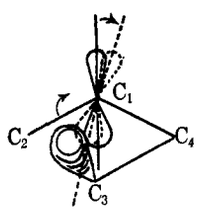
(24) (a) E. H. White and C. A. Aufdermarch, *J. Amer. Chem. Soc.*, **83**, 1174, 1179 (1961). It was proposed that such ion pairs could collapse by nonselective frontal attack. *Cf.* (b) T. Cohen and E. Jankowski, *ibid.*, **86**, 4217 (1964). A similar view has been advocated previously; (c) J. A. Mills, *J. Chem. Soc.*, 260 (1953). NOTE ADDED IN PROOF.—For recent conclusion that carbonium ions are formed as intermediates in deamination of some aliphatic amines *only by concerted rearrangement*, *cf.* J. H. Bayless, A. T. Jurewicz, and L. Friedman, *J. Amer. Chem. Soc.*, **90**, 4466 (1968).

(25) (a) A somewhat more planar *trans* cyclobutyldiazonium cation than depicted in **16** would be even more sterically disposed toward this angular overlap, as the C_1 orbital and C_2–C_3 bond would be more linearly oriented. However, an inspection of models will show that with complete planarity this process should not be favored, since densest portions of the lobes are no longer so oriented; further, steric preference would disappear. (b) I. Lillien, *J. Org. Chem.*, **32**, 4152 (1967).

SCHEME II



The stereoselectivity inherent in the foregoing process may be better apprehended by inspection of **18**,



18

which represents a front view of C_1 looking toward C_3 in the *trans* intermediate (**16**). As the C_2–C_3 orbital becomes relocalized, C_1 undergoes a clockwise torsional rotation in order to maximize orbital overlap. As this occurs, the C_2–C_3 orbital can be seen to be making an inverting displacement on C_1 with respect to mobile substituents CH_2 and H, forcing CH_2 to the same side of the ring as the leaving N_2 group, *i.e.*, *trans* to the isopropyl group. A similar (counterclockwise) process for the *cis* isomer would engender serious repulsive consequences.

Products **12** and **13** may be ascribed to both the process of direct solvolytic displacement of the diazonium group[3b,24,26] and front-side collapse of the solvated diazonium ion pair in a process reminiscent of the SNi reaction.[24,27] Direct nucleophilic displacement (SN2) is expected to lead to inversion, and it can be tentatively concluded that this process occurs to a comparable extent for both isomers (*i.e.*, *cis* = 8.8% *trans* alcohol, *trans* = 7.3% *cis* alcohol). On the other hand, front-side collapse apparently occurs to a larger extent (11.1%) for the *cis* isomer than for the *trans* (3.1%); this is a significant difference. This fact, taken together with the larger total yield of alcohols for the *cis* (19.1%) than the *trans* (10.4%) amine, implies that the lifetime of the *cis* diazonium intermediate is longer than that of the *trans*. This is perfectly in keeping with the greater conformational stability expected of the *cis* isomer and also the absence for the *cis* isomer of the sterically limited route to **11**, which would consume diazonium ion.

Not only is the total yield of alcohols greater for the *cis* amine, but other products as well, except **11**. Together with the other factors discussed, this argues persuasively for competing pathways diverging at the cyclobutyldiazonium ion (shown as a solvated ion-pair in Scheme II). Where conformational factors do not favor the route to **11**, others become more prominent.

Rearrangement by route B, which competes directly with A, must be a more complex one and require a larger $\Delta E^{\ddagger}$. The path to its formation, in the absence of delocalized ions, must involve either a $C_2 \rightarrow C_1$ hydride migration or rearrangement of an intermediate (2-isopropylcyclopropyl)carbinyl cation. However, the high proportion of **10** found in the *cis* case, in which little or no (2-isopropylcyclopropyl)carbinol results, makes the latter choice less attractive and strengthens speculation regarding a hydride-shift pathway. This is indeed more complex than the simple one-step route to **11**. It may occur in either the cyclobutyldiazonium ion, with concertion providing the anchimeric assistance for loss of nitrogen, or in the cyclobutyl carbonium ion itself. The former is favored for several reasons, including the premise that the concerted path must be considerably less energetic than the generation of a bare carbonium ion.

Hydride shifts concurrent with heterolysis of the leaving group are widely known to occur in cationic reactions.[28] Pertinent to the present discussion is the relative ease of hydride shifts which have been well studied in, for example, cyclodecylamine deamination[28c] and in deamination and solvolysis of norbornyl derivatives.[28d-g] It has been recently observed that "..... there is an increasing recognition of the importance of hydride transfer."[28b] There is nothing in

(26) Berson and coworkers have advanced the argument that direct nucleophilic displacement by solvent competes with simple ionization in the norbornyldiazonium ion; *cf.* ref 13d and J. A. Berson and D. A. Ben-Efraim, *J. Amer. Chem. Soc.*, **81**, 4094 (1959). The present results are in line with this viewpoint as well as prior suggestions (ref 3b,d). The objection of Sargent (ref 16, p 358) to this viewpoint, based on alleged absence of the sovolytic displacement reaction in the closely related decomposition of N-nitrosamides, is frivolous, since it ignores the fact that the latter decomposition has almost always been carried out in aprotic media. Indeed, diazo esters *do* yield solvolysis products in protic media; *cf.* E. H. White, *ibid.*, **77**, 6011 (1955); E. H. White, *ibid.*, **76**, 4497 (1954).

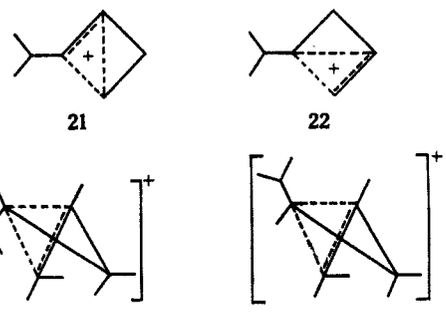
(27) Strong evidence implicating intramolecular (*i.e.*, retentive) diazonium ion-pair collapse is available; *cf.* E. H. White and J. Stuber, *ibid.*, **85**, 2168 (1963); E. H. White and F. W. Bachelor, *Tetrahedron Lett.*, 77, (1965).

(28) (a) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 141 ff; (b) N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, 129 (1963); (c) V. Prelog, H. J. Urech, A. A. Bothner-By, and J. Würsch, *Helv. Chim. Acta*, **38**, 1095 (1955); (d) J. D. Roberts, C. C. Lee, and W. H. Saunders, *J. Amer. Chem. Soc.*, **76**, 4501 (1954); (e) J. A. Berson, *Mol. Rearrangements*, **1**, 163 (1963); (f) B. M. Benjamin and C. J. Collins, *J. Amer. Chem. Soc.*, **88**, 1556 (1966); (g) J. A. Berson, R. G. Bergman, J. H. Hammons, and A. W. McRowe, *ibid.*, **89**, 2581 (1967); J. A. Berson and P. W. Guibb, *ibid.*, **87**, 4016 (1965); (h) L. G. Cannel and R. G. Taft, *ibid.*, **78**, 5812 (1956).

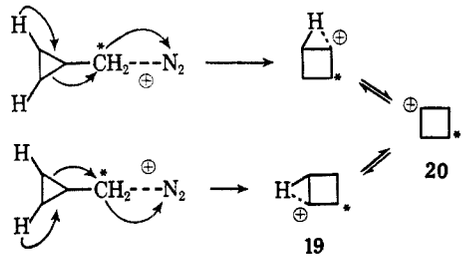
the cyclobutane system which is inherently preclusive of the possibility of hydride shifts, and, although this process has not been specifically shown to be present in cyclobutane reactions, neither has it been uniquely shown to be absent.[29] The seeming ease of formation of **10** from both isomers in the present work, in contrast to **11**, suggests a lesser steric differentiation and possibly a different intermediary genesis. Such a genesis can well be from a more planar cyclobutyldiazonium ion which has "aged" within its lifespan and more closely resembles the cyclobutyl carbonium ion, with rearranging hydride still providing "push" for final heterolysis of N_2^+. The almost equivalent but low yield of **9** for both isomers likewise indicates a sterically poorly defined process. It seems unlikely that **9** results from a pathway concurrent with the formation of **10**, however, since the **9**:**10** ratio is so different for the two isomers. Interestingly, the homoallylic alcohols do not appear significantly in the deamination of 1-methyl- and 2-methylcyclobutylamine.[3a,b,21] Hypothesizing that classical intermediates prevail in these systems, the driving force for their fate can be simply laid to the formation of a tertiary carbonium ion in the first by direct ionization, and a cyclopropyl stabilized secondary carbonium ion in the second by direct concertion assisted ionization.[29] Both are simple processes and are far less complex than route B in Scheme II. Thus thermodynamic factors may be sufficient to preempt complete consumption of diazonium by sufficiently lowering the energy of a single transition state in each instance, precluding other pathways. Where such a situation does not prevail, as in the 3-alkyl cases, other fates may befall the diazonium ion. It may be validly speculated that the homoallylic alcohol is the consequence of simple ionization by the residual, undiverted diazonium ion to the relatively unstable carbonium ion[30] (Scheme II), and that this, as an unfavored route (Roberts and coworkers have previously commented on the high-energy barrier to formation of homoallylic alcohols in these reactions),[3b] represents a "last recourse" for that intermediate. In the *planar carbonium ion*, stereoelectronic factors are not conducive to formation of **10** or **11**.

It may now be instructive to compare present product ratios with those obtained for 3-methylcyclobutylamine.[3b] Making the reasonable assumption that the *cis* and *trans* isomers of the latter were present in about equivalent amounts (on the basis that amine preparations in the present work contained approximately equal amounts of isomers), the product percentages of 39, 47, 9, and 5 in that deamination are directly comparable with those of 8, 47, and 28, and 17 for analogous products **9**, **10**, **11**, and **12** + **13**, respectively, obtained for the present mixed isomers (52% *cis*). The major difference is in the homoallylic alcohol and the products corresponding to **11**. The homoallylic alcohol forms at the expense of this product in the 3-methyl case (the product corresponding to **10** being equal in yield to **10**) and the cyclobutanol. The lesser priority for a sterically favored, concerted route to 2-methylcyclopropylcarbinol, as opposed to the present results, *substantiates the significance of conformation in product determination.* The methyl group is expected to be less effective in holding the puckered conformation of the ring. Consequently, the *trans*-3-methylcyclobutyldiazonium ion may be more planar than its isopropyl homolog[25] and therefore less stable. Indeed, both isomers may be less puckered and less stable. In line with the views presented above, the result would be a greater rate of collapse to cyclobutyl carbonium ion, which yields homoallylic alcohol, as is borne out in the fraction of that product obtained. This factor is also reflected in the lower yield of 3-methylcyclobutanol, which, as a product of diazonium solvolysis, may be due primarily to *cis* isomer present.

As an alternative to mechanistic insight into the present results, we find the bicyclobutonium ion rationale relatively unattractive. In terms of explicit bicyclobutonium ions, **21** would be the precursor of **10** and thus implicated as the major species involved in the *cis* transformations; and **22**, which would be the



precursor of **11**, the major species formed from the *trans* isomer. However, **21** cannot arise directly from the *cis* but would have to ensue from **22**; **22** would also have to "leak" to **21** in the *trans* case to account for the substantial amount of **10** formed. This proposal becomes tenable only if, considering the differences in behavior, ion **22** can differ in important structural aspects for the two isomers. Configurationally different



(29) The isotope-label studies of J. D. Roberts and coworkers (*cf.* ref 3, 4, 21, and references cited therein), while considered by these authors as presumptive evidence for delocalized intermediates, can be equally well interpreted in terms of equilibration of, or limited hydride shifts in charge-localized ions; *cf.*, *e.g.*, footnote 13 in ref 3c, and ref 3f. A mechanism which can plausibly account for the seeming conflict raised by the rearrangement of (1-methylcyclopropyl)carbinylamine-α-^{14}C to 1-methylcyclobutanol containing 3% ^{14}C at C_3, as opposed to rearrangement of cyclopropylcarbinylamine-α-^{14}C to cyclobutanol containing 28% ^{14}C at C_3 is the strong driving force toward formation of the tertiary carbonium ion which is predominant in the first case, which does not require hydride "push" for N_2^+ ionization; while in the second case anchimeric assistance from migrating hydride is concerted with loss of nitrogen accounting for the approximately equivalent distribution of ^{14}C with $C_2 = C_4 = 36\%$ label larger in accord with the likelihood of nucleophilic capture of species **19** before complete conversion into **20**. Note that complete equilibration is neither necessary nor demanded, in accord with the data. For a recent related opinion, *cf.* K. B. Wiberg and A. J. Ashe, III, *J. Amer. Chem. Soc.*, **90**, 63 (1968). It is quite essential to bear in mind the recent conclusions that scrambling of carbons and hydrogens prior to the carbonium ion reaction with solvent can no longer be accepted as evidence for equivalence of carbons in carbonium structures or as evidence of hybrid structures; *cf.* ref 28b and P. S. Skell and R. J. Maxwell, *ibid.*, **84**, 3963 (1962).

(30) The introduction of an sp^2-hybridized carbonium ion in cyclobutane must cause an increase in strain; *cf.* P. von R. Schleyer and R. D. Nicholas, *ibid.*, **83**, 182 (1961).

bicyclobutonium ions **23** and **24**, which are variants of **22**, may be postulated to arise from *cis* and *trans* reactants having equatorial amino and, respectively, equatorial and axial isopropyl groups; these may possibly interconvert through the cyclobutyl carbonium ion. It is difficult, however, to relate these ions to the product distribution observed or offer a sound rationale for their divergent behavior (*i.e.*, differential tendency to form **21**) in terms of explicit processes. Other specific objections tend to vitiate the likelihood of their intervention: ion **23** might be expected to lead to *cis*-(2-isopropylcyclopropyl)carbinol, which is not presently observed; the homoallylic alcohol corresponding to **21** is not observed;[31] ion **24**, with an axial isopropyl group which is quite crowded transannularly, must be less stable than ion **23**, with an equatorial isopropyl group; however, data for solvolysis of the analogous brosylates indicates a rate factor of 6.4 (aqueous acetone) favoring the *trans* isomer;[32] 1,3 bridging of this type has been shown to be energetically unfavorable even in a puckered ring.[9] Further, viewing the intervention of bicyclobutonium ion intermediates (*i.e.*, **23** and **24**) as an energy-lowering process ensuing from favorably arranged bonds in the immediate precursors and assisting in loss of the leaving group, it is evident that ion **24** can only result *directly* from conformation **17**, having an axial isopropyl group, whereas it cannot result from **16** prior to inversion at C_1, which must be completed *after* loss of nitrogen. However, the most reasonable conformations for the two isomeric diazonium intermediates, like their amine precursors,[11e] maintain relatively equatorial isopropyl groups.[33] In **16**, thus considered to be the more likely conformation for the *trans* isomer, transformation to the *trans*-(2-isopropylcyclopropyl)carbinyl cation may simply occur by inversion at C_1 *during* the bond-making process in a transition state resembling this product, rather than ion **24**.

It is evident from the present work that conformational control can be a vital factor in cyclobutylamine deamination. We have offered the premise that, together with well-established thermodynamic principles, classical routes prominently involving sterically limited concertive processes can explain the present results simply and directly. We suggest that extrapolation of these results to other cyclobutylamine deaminations can perhaps serve better to reconcile the data uniformly in terms of classical processes developing from the cyclobutyldiazonium ion. It appears that further scrutiny may be profitably applied to the general viability of delocalized ion concepts in cyclobutane reactions.

Experimental Section

Boiling and melting points are uncorrected. Melting points were taken with a Thomas–Hoover capillary apparatus. Microanalyses were carried out by Dr. Weiler and Dr. Strauss, Oxford, England. Infrared spectra were routinely recorded on the Baird-Atomic Model KM-1 and Beckman IR-10 spectrophotometers. Nmr spectra were run in CCl_4 solution with reference TMS on a Varian A-60 spectrometer. Vpc analyses and preparations were carried out on Aerograph A-90-P and A-700 instruments, using the following columns: $^1/_2$ in. × 30 ft stainless steel, 20% KOH, 2% Carbowax 20M on Chromosorb W (column A); $^3/_8$ in. × 7 ft stainless steel, 20% Carbowax 20M on Chromosorb P (column B); $^3/_8$ in. × 20 ft stainless steel, 5% Carbowax 20M on Chromosorb P (column C).

3-Isopropylcyclobutylamine.—In a 500-ml three-necked flask equipped with a mechanical stirrer and reflux condenser were placed 28.4 g (0.02 mol) of 3-isopropylcyclobutanecarboxylic acid,[11f] 165 ml of chloroform, and 38 ml of concentrated sulfuric acid. With stirring, 15.5 g (0.024 mol) of sodium azide was added in small portions. After addition was complete, the solution was stirred for 3 hr, then diluted with ice and made alkaline with sodium hydroxide. The reaction mixture was distilled, and the fraction which came over at 50–100° was collected. It was dried over anhydrous magnesium sulfate and poured into an ethereal solution of 25.2 g (0.20 mol) of oxalic acid. Filtration yielded 33.8 g (0.107 mol, 53%) of di(3-isopropylcyclobutylammonium) monooxalate, mp 242–243°, after crystallization from ethanol. *Anal.* Calcd for $C_{16}H_{32}N_2O_4$: C, 60.76; H, 10.11. Found: C, 60.70; H, 10.19.

The amine was regenerated by adding 22.5 g (0.07 mol) of monooxalate to a concentrated solution of sodium hydroxide followed by stirring for 2 hr. The solution was extracted with ether, and the ether solution dried over barium oxide. Distillation of the residue after removal of ether yielded 9.5 g (0.084 mol, 60%) of 3-isopropylcyclobutylamine, bp 140–142°, $n^{20}D$ 1.4365. Vpc analysis on column A gave two peaks with retention times of 24 and 26 min at 40° with a helium flow rate of 60 cc/min. Proportions varied slightly with the preparation; the above contained 52% of peak 1 (*cis*). Preparation of an amine sample from carboxylic acid in turn prepared from equilibrated methyl 3-isopropylcyclobutanecarboxylate[11f] gave 68.7% peak 1. Pure isomers were prepared by condensing the effluent vpc vapors, using column A, in a Dry Ice–acetone bath; peaks 1 and 2 had 97 and 98% isomeric purity, respectively. *Anal.* Calcd for $C_7H_{15}N$: C, 74.26; H, 13.36. Found: C, 74.25; H, 13.42.

Deamination of 3-Isopropylcyclobutylamine.—The procedure used was similar to that of Roberts and Mazur.[3g] In a 100-ml flask equipped with a stirrer and condenser set for downward distillation were placed ice cold solutions of 1.0 g (0.009 mol) of isopropylcyclobutylamine (mixed isomers) in 10 ml of water, 30 ml of 1 *N* perchloric acid, and 5.5 g (0.08 mol) of sodium nitrite in 20 ml of water. The stirrer was started, and the solution allowed to warm to room temperature over a period of 1 hr. The solution was then slowly heated to boiling over a period of 1 hr, and the mixture distilled until about 30 ml of distillate was collected. The distillate was saturated with sodium carbonate and extracted with two 15-ml portions of ether. The extracts were dried over anhydrous sodium sulfate, and the ether was removed by distillation to give ~0.7–0.8 g of alcohols (70–80% yield). Vpc of the mixture on column B showed four peaks with peak 4 evidently a fusion of two peaks, having retention times of 4.2, 6.2, 8.1, 10.3, and 10.8 min at 125° and a helium flow rate of 60 cc/min. Four runs were carried out, giving the percentages mentioned in the text as an average, with no more than 1.5% deviation from reproducibility. Peaks 4 and 5 were adequately resolved by use of column C at the same temperature and flow rate, and this column was used for isolation of the five products by condensation of effluent vapors in a Dry Ice–acetone bath.

Deamination of the individual isomers was carried out on a smaller scale and in the same fashion as above, and the products were analyzed on columns B and C to give the percentages mentioned in the text, as an average of four runs for each isomer with no more than 1% deviation from reproducibility.

Peak 1 from the deaminations was identified as 2-methyl-5-hexen-3-ol (**9**) by virtue of complete congruence with synthetic material prepared from allylmagnesium bromide and isobutyraldehyde.[34,35] A mixture of *cis* and *trans* isomers of synthetic 5-methyl-3-hexen-1-ol[36] displayed different retention times than **9** under the same vpc conditions, with good resolution of the two

(31) The vpc method employed was accurate to a fraction of a per cent and could cleanly separate the isomeric homoallylic alcohols.

(32) I. Lillien, G. F. Reynolds, and L. Handloser, *Tetrahedron Lett.*, 3475 (1968); indeed the rate acceleration for either isomer *vs.* cyclohexyl tosylate does not support nonclassical ion intervention. Note that the present rationale predicts greater *trans* reactivity, while the bicyclobutonium ion scheme does not.

(33) Evidence from the study of the temperature-dependent infrared spectra of the isomeric methyl 3-isopropylcyclobutanecarboxylates indicates that axial isopropyl is not observed in the *trans* isomer; *cf.* ref 25b.

(34) K. I. Karasev and A. V. Khabarova, *J. Gen. Chem. USSR*, **10**, 1641 (1940).

(35) H. R. Henze, B. B. Allen, and W. B. Leslie, *J. Org. Chem.*, **7**, 326 (1942).

(36) L. Crombie, J. Gold, and B. J. Stokes, *J. Chem. Soc.*, 136 (1956).

geometric isomers. Compounds responsible for the remaining peaks were identified through nmr analysis and synthesis as described below.

Cyclopropylisoproylcarbinol.—A solution of 27 g (0.1 mol) of diiodomethane, 0.1 g (0.0004 mol) of iodine, and 8.2 g (0.125 g-atom) of copper–zinc couple in 100 ml of anhydrous ether was refluxed for 30 min.[37] External heating was discontinued and 10 g (0.1 mol) of 4-methyl-1-penten-3-ol in 50 ml of anhydrous ether was added over 30 min, and the solution was refluxed for 20 hr. The solution was cooled and filtered through a Büchner funnel; the residue was washed with ether, and the washings were combined with the main solution. The ether solution was washed with 3% hydrochloric acid (three 50-ml portions) and water (two 50-ml portions) and dried over anhydrous magnesium sulfate. The ether was removed by distillation, and residue was distilled to yield 1.2 g (0.01 mol, 10%) of cyclopropylisopropylcarbinol, bp 144°, $n^{20}D$ 1.4400. This alcohol had vpc and spectral characteristics completely congruent with those of peak 2 of the deamination. Nmr (CCl_4) peaks appeared at 0.10–0.55 ppm (multiplet, 4 H), 0.58–0.90 (multiplet, 1 H), 0.91 (center of CH_3 doublet, 6 H), 1.63 (center of symmetrical quintet), 2.0 (OH), 2.48 (center of X quartet, J = 7 cps, 1 H). *Anal.* Calcd for $C_7H_{14}O$: C, 73.63; H, 12.36. Found: C, 73.42; H, 12.38. The α-naphthylurethan was prepared, and had a mp of 113–113.5°. *Anal.* Calcd for $C_{18}H_{21}NO_2$: C, 76.29; H, 7.47. Found C, 76.41; H, 7.58.

***trans*-(2-Isopropylcyclopropyl)carbinol.**—The same method was used in the reaction of 2.7 g (0.01 mol) of diiodomethane, 0.1 g of iodine, and 0.82 g (0.0125 g-atom) of copper–zinc couple with 1.0 g (0.01 mol) of *trans*-4-methyl-2-penten-1-ol[38] in 30 ml of anhydrous ether. Work-up gave 0.2 g (0.0017 mol, 17%) of *trans*-(2-isopropylcyclopropyl)carbinol, bp 76° (20 mm), $n^{20}D$ 1.4320. Vpc and spectral characteristics were completely identical with those of peak 3 from the deamination. Nmr (CCl_4) peaks appeared at 0.15–0.45 ppm (multiplet, 3 H), 0.50–1.05 (multiplet merging with sharp singlet at 0.95, 8 H), 2.90 (OH), 3.25 (center of symmetrical doublet, J = 6.5 cps, 2 H). *Anal.* Calcd for $C_7H_{14}O$: C, 73.63; H, 12.36. Found: C, 73.43; H, 12.28.

***cis*-(2-Isopropylcyclopropyl)carbinol.**—Using the same method, 2.7 g (0.01 mol) of diiodomethane, 0.1 g of iodine, and 0.82 g (0.0125 g-atom) of copper–zinc couple were reacted together in 30 ml of anhydrous ether, followed by reaction with 0.7 g (0.007 mol) of *cis*-4-methyl-2-penten-1-ol,[39] to yield 0.05 g (0.425 mmol, 4%) of product, bp 67–70° (18 mm). This alcohol and peak 3 of the deamination were demonstrably different in vpc retention time both singly and in mixtures (column C). Nmr ($CDCl_3$) peaks appeared at 0.45–0.85 ppm (multiplet, 2 H), 0.91–1.15 (two fused singlets, 9 H), 2.30 (OH), 3.60 (center of quartet, 2 H). *Anal.* Calcd for $C_7H_{14}O$: C, 73.63; H, 12.36. Found: C, 73.37; H, 12.45.

3-Isopropylcyclobutanecarboxamide.—A solution of 96 g (0.676 mol) of 3-isopropylcyclobutanecarboxylic acid and 90 g (0.891 mol) of triethylamine in 3 l. of chloroform was cooled in an ice–salt bath, and 100 g (0.92 mol) of ethyl chlorocarbonate was added rapidly with continuous agitation.[40] After the solution was stirred for 15 min, anhydrous ammonia gas was passed through it for 15 min. The mixture was removed from the cooling bath, stirred at room temperature for 1 hr, and allowed to stand overnight. The suspension was filtered, and the chloroform removed by distillation. The residual material was boiled with 350 ml of benzene, and the resultant solution was filtered hot. Dilution with 1 l. of *n*-hexane and cooling produced a precipitate of 59 g (0.42 mol, 62%) of 3-isopropylcyclobutanecarboxamide, mp 117–127°. The melting point was not improved on further crystallization, and undoubtedly exhibits a wide range owing to isomeric composition. An analytical sample was obtained by sublimation and had the same melting point. *Anal.* Calcd for $C_8H_{15}NO$: C, 68.04; H, 10.71. Found: C, 67.94; H, 10.67.

3-Isopropyl-1-acetylcyclobutane.[41]—A Grignard reagent was prepared from 107 g (0.76 mol) of methyl iodide and 17.1 g (0.71 g-atom) of clean magnesium turnings in 350 ml of anhydrous ether. To the solution of the Grignard reagent was added slowly over a 30-min period 35 g (0.25 mol) of 3-isopropylcyclobutanecarboxamide. The fluffy amide adhered to the walls of the flask and was washed down with fresh anhydrous ether. The solution was refluxed gently for 20 hr. The mixture was decomposed with ice and saturated ammonium chloride solution, followed by dilute hydrochloric acid. The ether layer was separated, the aqueous solution was extracted with several fresh portions of ether, and the ether extracts were combined. These were washed with sodium bicarbonate and dried over anhydrous sodium sulfate. The ether was distilled through a 20 in. Vigreux column; as the residual solution became concentrated, unreacted amide precipitated and was removed by filtration to yield 7 g. The remainder of the ether was removed, and the residue was distilled to give 17.0 g (0.12 mol, 60% based on reacted amide) of 3-isopropyl-1-acetylcyclobutane, bp 92–93° (18 mm), $n^{20}D$ 1.4330 (52% *cis*). Distillation was rendered difficult by active foaming of the ketone. *Anal.* Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.98; H, 11.47.

3-Isopropyl-1-acetoxycyclobutane.[42]—A solution of peroxytrifluoroacetic acid was prepared by the dropwise addition of 15.2 g (0.072 mol) of trifluoroacetic anhydride to 3 ml of 90% hydrogen peroxide in 50 ml of cold methylene chloride. This solution was added slowly to a suspension of disodium hydrogen phosphate in a mixture of 50 ml of cold methylene chloride and 8 g (0.057 mol) of 3-isopropyl-1-acetylcyclobutane. After addition was complete, the solution was refluxed for 30 min. It was filtered, and the filtrate was washed with 10% sodium bicarbonate solution and dried over anhydrous sodium sulfate. Distillation of the residue remaining after removal of methylene chloride through a 20 in. Vigreux column gave badly foaming 3-isopropyl-1-acetoxycyclobutane: bp 94–96° (18 mm); 7.7 g (0.049 mol, 86%); $n^{20}D$ 1.4210 (52% *cis*). *Anal.* Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.33. Found: C, 69.11; H, 10.24.

3-Isopropylcyclobutanol.—A solution of 40 ml of 25% sodium hydroxide solution and 4.0 g (0.026 mol) of 3-isopropyl-1-acetoxycyclobutane was stirred at room temperature for 30 min and then refluxed for 1 hr. The solution was distilled, and the two-phase distillate was collected. The distillate was saturated with sodium carbonate, and the organic layer was separated. The aqueous layer was extracted with ether, and the combined organic layers were dried over anhydrous sodium sulfate. The ether was removed through a Vigreux column, and distillation of the residue (which foamed badly) gave 2.45 g (0.021 mol, 81%) of 3-isopropylcyclobutanol, bp 165–168°. Vpc analysis demonstrated identical retention times for the two peaks of this compound as peaks 4 and 5 of the amine deamination (column C). Spectral properties of these isomers and the corresponding peaks were completely congruent.

An experiment in which equilibrated methyl 3-isopropylcyclobutanecarboxylate was used to prepare 3-isopropylcyclobutanol gave a ratio of peak 1/peak 2 of 2.20:1.00, identifying them as, respectively, *cis* and *trans* and confirming the assignment from the nmr spectra.[11e] *Anal.* Calcd for $C_7H_{14}O$: C, 73.63; H, 12.36. Found: C, 73.56; H, 12.27.

Registry No.—**10**, 17393-35-0; **10** α-naphthylurethan, 17393-36-1; **11** (*trans*), 17393-31-6; **11** (*cis*), 17393-32-7; 3-isopropylcyclobutylamine, 17398-33-8; di(3-isopropylcyclobutylammonium) monooxalate, 17393-34-9; 3-isopropylcyclobutanecarboxamide, 13363-92-3; 3-isopropyl-1-acetylcyclobutane, 17393-38-3; 3-isopropyl-1-acetoxycyclobutane, 17414-49-2; 3-isopropylcyclobutanol, 17448-26-9.

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