(-$COOCH_3$), which was dissolved in 50 ml of 1:1 ether–methanol and refluxed for 4 hr. The solvent was distilled off and the residue was recrystallized from methanol to give 1.5 g (80%) of **7**: mp 96–97°; ν_{max} 3430, 1740, 1725, 1520, 1225, 775, 648 cm^{-1}; λ_{max} 265 mμ (ϵ 480); nmr δ 4.8–5.2, 3.6 (-OCH_3).

A solution of 1.5 g of the carbamate **7** and 5 g of potassium hydroxide in 50 ml of ethanol and 5 ml of water was refluxed for 30 min.[10] The solution was cooled to room temperature and poured into water. The turbid solution was extracted with benzene, washed thoroughly with water, dried over magnesium sulfate, and filtered and the solvent was evaporated. The residue crystallized upon standing: mp 88–89°; yield 0.8 g (70%); $[\alpha]^{25}D$ +21°; ν_{max} 1730 cm^{-1}; molecular ion *m/e* 383 (calcd, 383).

Anal. Calcd for $C_{29}H_{49}NO_2$: N, 3.1. Found: N, 2.9.

22,23-Iminostigmasteryl Acetate (9).—The reactions were carried out analogously to the preparation of **8**. Thus addition of INCO to stigmasteryl acetate in dry THF gave a 79% yield of an adduct (ν_{max} 2260 and 1725 cm^{-1}). Treatment of the adduct with methanol gave a 90% yield of the iodo carbamate: mp 128°; ν_{max} 3430, 1740, 1725, 1520, 1227, 775, 648 cm^{-1}; λ_{max} 265 mμ (ϵ 450); nmr δ 5.6 (H , broad doublet), 5.0 (NH), 4.8 (CHI), multiplet), 4.2 (CHNHCOOCH$_3$, multiplet). The aziridine **9** was obtained in 90% yield: mp 88–89°; $[\alpha]^{25}D$ −24.5°; ν_{max} 3270 cm^{-1} (-NH); molecular ion *m/e* 409 (calcd, 409).

Anal. Calcd for $C_{31}H_{51}NO_2$: N, 3.2. Found: N, 3.1.

(10) A. Hassner and C. Heathcock, *Tetrahedron*, **20**, 1037 (1964).

Registry No.—**3**, 34389-06-5; **4**, 34389-07-6; **5**, 34389-08-7; **6**, 34389-09-8; **7**, 34389-10-1; **8**, 34388-68-6; **9**, 34388-69-7.

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The Stereochemistry of Azetidine Deaminations. On the Nature of the Trimethylene Intermediate

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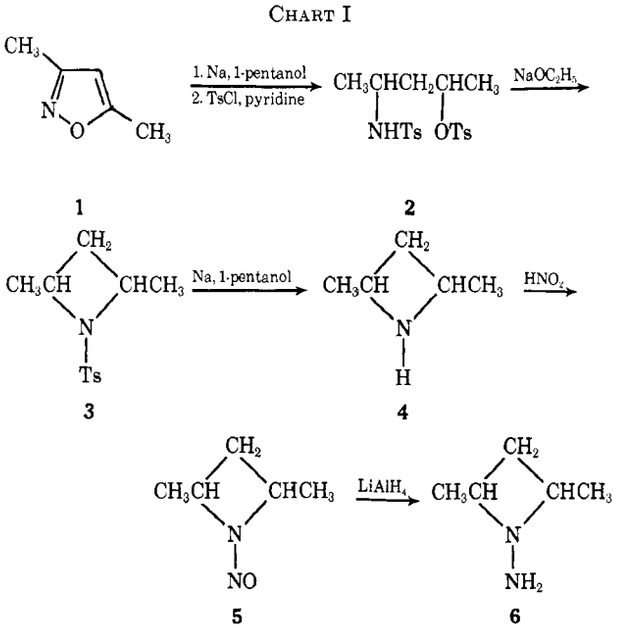
Pure stereoisomers of 2,4-dimethylazetidine (**4**), *N*-nitroso-2,4-dimethylazetidine (**5**), and *N*-amino-2,4-dimethylazetidine (**6**) were prepared. Reaction of *cis*-**4** with difluoramine, of *cis*-**5** with sodium dithionite, and of *cis*-**6** with mercuric oxide produced virtually identical mixtures of *cis*- and *trans*-1,2-dimethylcyclopropanes (**7**), in which *trans*-**7** predominated, thus indicating that these deaminations proceed through a common diazene intermediate. Analogous reactions of *trans*-**5** and *trans*-**6** yielded *cis*-**7** and *trans*-**7** in the ratio of 68:32. It is proposed that a mechanism involving a planar trimethylene intermediate could account for the stereochemical crossover and for the differences in the product distribution between azetidine deaminations and 1-pyrazoline pyrolyses, but that a superposition of "quasi-concerted" processes may offer a more attractive rationalization.

The trimethylene diradical has frequently been invoked[3] as an intermediate in the isomerization of cyclopropanes[3–6] and in the decomposition of 1-pyrazolines.[3,7,8] Since trimethylenediazene is known[12] to afford cyclopropane and nitrogen under very mild conditions and since the electronic structure of trimethylene is thought[10] to depend critically on the CCC angle, we considered it worthwhile to investigate the stereochemistry of azetidine deaminations.

The synthesis of the starting materials **4**, **5**, and **6** is outlined in Chart I. A crystalline diastereomer of mp 120–120.5° could be obtained from the oily mixture of ditosylates **2** by fractional recrystallizations from methanol. By implication, this must be *threo*-**2**, since it yields pure *cis*-**3** on treatment with sodium ethoxide in ethanol. The stereochemistry of *cis*-**3** is rigorously

CHART I



established by its nmr spectrum, which exhibits three complex groups of signals for the ring protons, centered at about δ 1.3 (1 H), 2.1 (1 H), and 3.65 (2 H). The stereochemical purity of *cis*-**3** follows from its conversion to *cis*-**4** and *cis*-**5**, the latter containing less than 0.3% *trans*-**5** as shown by vpc analysis.

The mother liquors of **2**, enriched in the erythro diastereomer, were subjected to an analogous reaction sequence and afforded a mixture consisting approxi-

(1) This work is based on a dissertation submitted by D. G. P. in partial fulfillment of the requirements for the Ph.D. degree at the University of Notre Dame.

(2) Alfred P. Sloan Research Fellow.

(3) For the extensive earlier literature on this problem and for the intriguing history of the ideas consult the bibliography in ref 4–11.

(4) J. A. Berson and J. M. Balquist, *J. Amer. Chem. Soc.*, **90**, 7343 (1968).

(5) W. L. Carter and R. G. Bergman, *ibid.*, **90**, 7344 (1968); R. G. Bergman and W. L. Carter, *ibid.*, **91**, 7411 (1969).

(6) M. R. Willcott, III, and V. H. Cargle, *ibid.*, **91**, 4310 (1969).

(7) M. P. Schneider and R. J. Crawford, *Can. J. Chem.*, **48**, 628 (1970), and earlier papers in this series.

(8) D. E. McGreer and J. W. McKinley, *ibid.*, **49**, 105 (1971), and earlier papers in this series.

(9) D. M. Lemal in "Nitrenes," W. Lwowski, Ed., Interscience, New York, N. Y., 1970, p 345.

(10) R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968).

(11) L. M. Stephenson and J. I. Brauman, *ibid.*, **93**, 1988 (1971).

(12) C. L. Bumgardner, K. J. Martin, and J. P. Freeman, *ibid.*, **85**, 97 (1963).

TABLE I

PRODUCTS OF AZETIDINE DEAMINATIONS AND 1-PYRAZOLINE PYROLYSES[a]

Reaction	Number of runs	Solvent	Temp, °C	Total yields of hydrocarbons, %	Relative yields, %[b] cis-7	trans-7	Olefins
cis-4 + HNF_2	1	Neat	0	65	16.8	83.2	<0.3
cis-5 + $Na_2S_2O_4$	2	25% Aqueous ethanol	40	67[c]	15.6	84.4	<0.3
trans-5 + $Na_2S_2O_4$	3	25% Aqueous ethanol	40	67[c]	68.5	31.5	<0.3
cis-6 + HgO	2	Ethanol	40	71[c]	15.5	84.5	<0.3
cis-6 + HgO	1	1-Pentanol	140	*d*	18.7	81.3	<0.3
trans-6 + HgO	2	Ethanol	40	71[c]	67.7	32.3	<0.3
cis-9[e] pyrolysis	6	Gas phase	200	98	33.2	66.1	0.7
trans-9[e] pyrolysis	6	Gas phase	200	98	72.6	25.4	2.0

[a] R. J. Crawford and A. Mishra, *J. Amer. Chem. Soc.*, **87**, 3768 (1965); **88**, 3963 (1966). [b] In those cases where more than one run was made, the numbers were reproducible within about ±0.5%, except for the reaction of *trans*-5 + $Na_2S_2O_4$, for which the experimental scatter amounted to ±1.5%. [c] Determined using a mixture of stereoisomeric starting materials. [d] Not determined. [e] 3,5-Dimethyl-1-pyrazoline = 9.

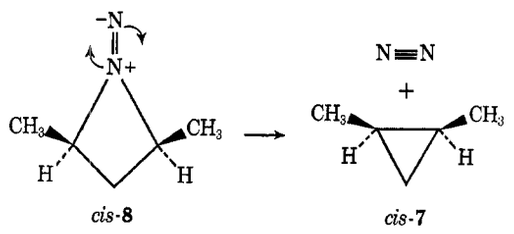
mately of 30% *cis*-**5** and 70% *trans*-**5**. Separation on a preparative vpc column yielded *trans*-**5** in greater than 99.7% purity. Its stereochemistry is proved by the isochronism of the ring methylene protons, which give rise to a triplet at δ 2.14 (2 H).

The reagents used for the deaminations of **4**, **5**, and **6** and the reaction conditions are summarized in Table I. The low-boiling products were collected in traps and analyzed by vpc and nmr. The *cis*- and *trans*-1,2-dimethylcyclopropanes (**7**) needed for comparison were prepared from the authentic 1,1-dibromo-2,3-dimethylcyclopropanes[13] by reduction with sodium in 1-pentanol.

Discussion

On the basis of the results in Table I we draw the following conclusions. (1) The three different deamination reactions proceed through a common intermediate, the diazene **8**. (2) In analogy to the stereospecific deaminations of *cis*- and *trans*-2,3-butenimines[14] one might have expected that the diazenes **8** could produce the dimethylcyclopropanes **7** stereospecifically under retention of configuration (*cis*-**8** → *cis*-**7**; *trans*-**8** → *trans*-**7**) in a concerted cheletropic reaction characterized by a nonlinear departure of the nitrogen molecule (Chart II). This possibility, tentatively

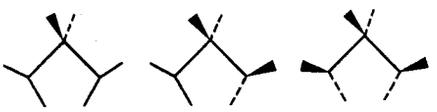
CHART II



cis-**8** *cis*-**7**

favored by Lemal[9] on general grounds, can at best only partially account for the results. Since the formation of a cyclopropane bond under inversion of configuration at one of the α carbons concerted with a linear nitrogen extrusion does not seem possible sterically, we conclude that at least a major fraction of the deaminations involve additional intermediates. (3) The observed partial crossover in stereochemistry is reminiscent of the analogous phenomenon detected in the pyrolyses of 3,5-dimethyl-1-pyrazolines[15] (**9**), the results of which are included in Table I. The most economical explanation of the observations therefore appears to consist in the hypothesis of a concerted linear expulsion of nitrogen from **8** concomitant with disrotation to a planar trimethylene diradical of the type **10a** (Chart III) (the 0,0 species in Hoffmann's[10] terminology), which subsequently undergoes preferential controtatory ring closure.[10,15]

CHART III



0,0 0,90 90,90

10a **10b** **10c**

The obvious difficulty with this explanation stems from the quantitative differences in the isomer distribution observed for the azetidine deaminations and pyrazoline pyrolyses and from the fact that no olefins could be detected in the former reactions. As the data in Table I show, this discrepancy is not easily disposed of by blaming it on spurious effects such as temperature and reaction conditions. A similar insensitivity of the product composition in the pyrazoline thermolyses to changes in temperature has also been noticed by Crawford.[15] McGreer's[16] data suggest a general decrease in the degree of stereochemical crossover in going from the gas phase to the solution phase, whereas the deamination of *cis*-2,4-dimethylazetidine yields more *trans*-**7** than the pyrolysis of *cis*-**9**. Nitrogen-containing intermediates do not seem to provide an escape hatch either. Crawford[7,15] has presented experimental evidence supporting[17] a concerted fission of both carbon–nitrogen bonds in 1-pyrazolines. If a nitrogen-containing intermediate with a lifetime sufficient for rotation and back-side displacement[17] were

(13) P. S. Skell and A. Y. Gardner, *J. Amer. Chem. Soc.*, **78**, 3409 (1956).
(14) J. P. Freeman and W. H. Graham, *ibid.*, **89**, 1761 (1967).
(15) R. J. Crawford and A. Mishra, *ibid.*, **87**, 3768 (1965); **88**, 3963 (1966).
(16) D. E. McGreer, N. W. F. Chiu, M. G. Vinje, and K. C. K. Wong, *Can. J. Chem.*, **43**, 1407 (1965).
(17) For a dissenting view, see P. B. Condit and R. G. Bergman, *Chem. Commun.*, 4 (1971).

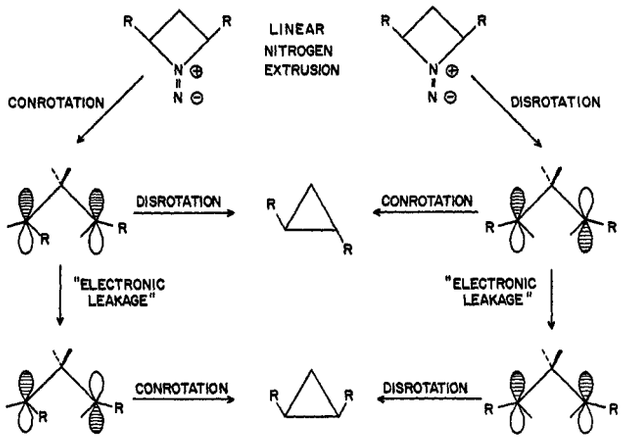


Figure 1.—Possible azetidine deamination pathways.

involved in the decomposition of **8**, it would be surprising if it could not also close the ring to form the 1-pyrazoline, which is thermally stable at that temperature, in analogy to the diradical rearrangement mechanism frequently observed for open-chain ylides.[18] No such reaction was observed for the deaminations of Table I; control experiments established that 0.2% of pyrazolines could easily have been detected.

Beyond this point we can only speculate. If one postulates a competing conrotatory pathway from **8** to **10a** one arrives at the scheme shown in Figure 1. It should be noted that such a competing conrotatory pathway does *not* require a nonlinear cheletropic extrusion of nitrogen. Hoffmann[10] predicted a crossover of π levels in **10a** at a CCC angle of about 100°. A 0,0 species with a CCC angle smaller than 100° could thus be produced initially by conrotation and linear departure of nitrogen from **8** in a concerted fashion, and this species could become a doubly excited electronic configuration of **10a** within one period of a CCC bending vibration. "Electronic leakage" (see Figure 1) could then produce an electronic configuration in which two electrons occupy the MO of opposite symmetry. In this scheme the observed stereochemical crossover emerges as a consequence of faster ring closure as compared to the rate of electronic leakage along *both* pathways, and the differences in the product distributions between the azetidine deaminations and 1-pyrazoline pyrolyses can be accounted for by suitable choices of the various rate constant ratios.[19]

In the light of recent theoretical work[20,21] there can be no question that the scheme of Figure 1 is grossly oversimplified. A single-configuration description of the diradical singlet state of **10a** is clearly inadequate; according to Salem's calculations[20] the two single-determinant singlet wave functions obtained by placing two electrons into the MO's of either symmetry mix almost equally at the equilibrium geometry of **10a**. The process termed "electronic leakage" in Figure 1 therefore only amounts to a small change in the mixing

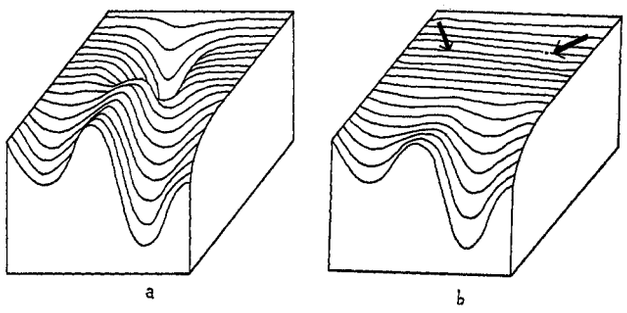


Figure 2.—Schematic potential hypersurfaces: (a) for a reaction proceeding through a genuine intermediate; (b) for a reaction proceeding through a twixtyl.

coefficients as a function of the CCC angle. Of perhaps even more serious consequence is the assumption, implicit in the scheme of Figure 1, that **10a** represents a genuine intermediate residing in a subsidiary energy minimum and capable of discriminating between two or more competing rate processes. Salem's work[20] casts serious doubt on the validity of such an assumption and suggests that this "species" rather represents a more or less flat plateau (with respect to certain internal coordinates) in the potential hypersurface, a situation for which Hoffmann, *et al.*,[22] have recently introduced the term "twixtyl." Finally, the scheme of Figure 1 does not readily explain the relative rates of diastereomerizations and enantiomerizations in the pyrolysis of cyclopropanes,[4,5] for which intermediates of a different structure have been invoked.[4,5] It seems desirable, therefore, to seek a modification of the scheme in Figure 1 that can simultaneously accommodate the results of the nitrogen elimination reactions[23] and the cyclopropane isomerizations. We should like to suggest that such a modification might be found along the following lines.[25]

It has traditionally been supposed[26] that a reliable criterion for the intervention of a high-energy intermediate in a chemical reaction is the possibility of "branching" after the rate-determining step and that the product ratios are controlled by the relative heights of the potential troughs leading out of a subsidiary energy minimum (Figure 2a), independent of how the intermediate itself had been generated. In a genuinely concerted reaction, on the other hand, the structural characteristics of the rate-determining transition state are thought to be sufficient to seal the further fate of the reaction. If Salem's[20] *ab initio* calculations, which yielded species closely resembling **10b** and **10c** with energies virtually equal to that of **10a**, should prove to be sufficiently reliable, we may be dealing with an intermediate situation of a "quasi-concerted" reaction, indicated schematically in Figure 2b. In such a quasi-concerted reaction there is no "resting point" along the reaction coordinate, but the structural characteristics of the "transition state" do *not* completely deter-

(18) J. E. Baldwin, J. E. Brown, and G. Höfle, *J. Amer. Chem. Soc.*, **93**, 788 (1971), and earlier papers in this series.

(19) Alternatively, the partial randomization of stereochemistry may be attributed to competitive bond rotation in the intermediate **10a** instead of electronic leakage, an interpretation corresponding more closely to that preferred by previous workers.[3]

(20) L. Salem, *Bull. Soc. Chim. Fr.*, 3161 (1970); Y. Jean and L. Salem, *Chem. Commun.*, 382 (1971).

(21) L. Salem and C. Rowland, *Angew. Chem.*, **84**, 86 (1972); *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972).

(22) R. Hoffmann, S. Swaminathan, B. G. Odell, and R. Gleiter, *J. Amer. Chem. Soc.*, **92**, 7091 (1970).

(23) There exists the possibility that some related elimination reactions[24] leading to cyclopropanes also fall into this category.

(24) B. M. Trost, W. L. Schinski, and I. B. Mantz, *J. Amer. Chem. Soc.*, **91**, 4320 (1969); P. S. Skell, K. J. Klabunde, and J. H. Plonka, *Chem. Commun.*, 1109 (1970); H. A. J. Carless and E. K. C. Lee, *J. Amer. Chem. Soc.*, **92**, 6683 (1970).

(25) This suggestion is closely akin to the conclusions reached by Salem.[20,21]

(26) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **9**, 751 (1970).

mine the final outcome of the reaction. Conventional activated-complex theory is ill suited for describing such a situation and one should therefore explicitly consider individual trajectories.[27] The product distribution then emerges as the result of a superposition of individual quasi-concerted trajectories, ensemble averaged over the "momentum" distribution at the point of entry into the plateau (indicated schematically by arrows in Figure 2b), and would be expected to depend on subtle details of that "momentum" distribution, in contrast to genuinely concerted reactions.[28,30]

The preceding analysis should not be construed to mean that there are no energetic preferences on the potential hypersurface, but only that they may not be exclusively controlling the course of a quasi-concerted reaction. If this proposal should turn out not to be totally unreasonable, there would no longer be any need for invoking a different type of intermediate in the cyclopropane isomerizations.[4,5] By the same token, the difficulty of having to require[4] that the cyclopropane ring opening could not be the microscopically reverse process of the ring closure from Crawford's[15] intermediate would be eliminated, provided only that the principle of microscopic reversibility is applied correctly, as recently shown by Kinsey.[32]

The experimental evidence now available, including that presented in this paper, can at best only furnish a hint that a description in terms of an ensemble average of quasi-concerted trajectories may sometimes provide an attractive alternative to the usual picture of a diradical intermediate whose fate is determined by a competition between ring closure, bond rotation, hydrogen migration, etc. It would be a pointless alternative, however, if a twixtyl really were operationally indistinguishable from a true intermediate.[22] It seems to us that this can only be part of the whole story. In particular we wish to point out that the analysis presented here leads to two novel conclusions, each of which is, in principle, amenable to experimental test. (1) The fate of a twixtyl, as reflected in its product distribution, should depend on the nature of its chemical precursor. (2) A twixtyl emanating from one and the same chemical precursor should still show different chemistry if one succeeds in controlling its mode of generation selectively by external means.

(27) This has already been pointed out by Hoffmann, *et al.*,[22] for the closely related case of the tetramethylene diradical twixtyl.

(28) It is important to realize that there is an essential difference between this hypothetical situation and that of "hot-molecule" reactions[29] of the conventional type. The possibility that activated species are involved in certain photochemical reactions purportedly proceeding through diradical intermediates has recently been discussed by Stephenson and Brauman.[11] In the thermal reactions considered here the initial distribution of the energy over translational, rotational, and vibrational states need not deviate from a normal Boltzmann distribution. Rather, the difference between genuinely concerted and quasi-concerted reactions has to be attributed to the following two features. (i) Every individual transition state (there may of course be more than one) leads to just one single product (or its enantiomer) in a concerted reaction, but to more than one product in a quasi-concerted reaction. (ii) Since there is, by hypothesis, no resting point along the reaction coordinate in a quasi-concerted reaction, differences in the "momentum" distribution at the point of entry into the plateau, which are to be expected if the "same" twixtyl is generated from different precursors, should stand a much higher chance not to become completely equilibrated before the system reaches one of the exit valleys leading to product than in the case of ordinary "hot" molecules. In other words, "reactive relaxation" may effectively compete with nonreactive relaxation, even in solution and for large molecules. The product ratios are expected to be a sensitive function of this distribution, whereas in a concerted reaction such differences, if not too drastic, would only change the macroscopic rate of the reaction but not the product.

(29) For a review see B. S. Rabinovitch and M. C. Flowers, *Quart. Rev., Chem. Soc.*, **18**, 122 (1964).

(30) There is a close relationship to the previously proposed "recoil" effect in the pyrolysis of bicyclic azo compounds.[31]

(31) E. L. Allred and R. L. Smith, *J. Amer. Chem. Soc.*, **89**, 7133 (1967); W. R. Roth and M. Martin, *Justus Liebigs Ann. Chem.*, **702**, 1 (1967).

(32) J. L. Kinsey, *J. Chem. Phys.*, **54**, 1206 (1971).

Experimental Section

4-Aminopentan-2-ol (Threo–Erythro Mixture.)—The following procedure proved to be superior to that described in the literature.[33] To a refluxing solution of 10.0 g (103 mmol) of 3,5-dimethylisoxazole (**1**) in 250 ml of 1-pentanol was added 24 g of sodium in 1-g pieces over a period of 6 hr. Water (150 ml) was added to the cold solution, the layers were separated, and the aqueous phase was extracted with four 15-ml portions of chloroform. The chloroform solution was concentrated and the residue was added to the alcoholic layer. The product was extracted from the alcohol with 75 ml of 6 *N* hydrochloric acid, and the acidic solution was washed twice with 10-ml portions of ether and made strongly alkaline with potassium hydroxide pellets. Extraction with ten 10-ml portions of chloroform and work-up by distillation afforded 4.2 g (41 mmol, 40%) of the amino alcohol mixture, bp 72–75° (20–25 mm) [lit.[33] bp 72–77° (20 mm)]. The *threo-p*-nitrobenzamide derivative melted at 129–130° (lit.[33] mp 131–132°).

4-(*p*-Toluenesulfonamido)-2-pentyl *p*-Toluenesulfonate (2).—*p*-Toluenesulfonyl chloride (18.5 g, 97 mmol) was added to a cold (−3°) solution of 5.0 g (48.5 mmol) of the 4-aminopentan-2-ol diastereomer mixture in 100 ml of dry pyridine and the solution was kept at −15° for 4 days, during which time pyridine hydrochloride precipitated. The mixture was poured onto 400 g of ice, and the red oil was washed with cold, dilute hydrochloric acid, dissolved in chloroform, dried (Na_2SO_4), and treated with Norit. Addition of petroleum ether (bp 35–60°) to the filtrate gave 12.5 g (30.5 mmol, 63%) of the ditosylate mixture **2** as a tan oil which slowly solidified, mp 55–90°.

When a solution of 140 g of the diastereomer mixture **2** in 300 ml of methanol was refrigerated at −20° for 20 hr, 62 g of crude crystalline material was obtained, which yielded 33.5 g of pure *threo*-**2** upon three additional recrystallizations from methanol: mp 120–120.5°; $\delta_{TMS}^{CDCl_3}$ 7.5 (m, 8), 4.8 (m, 2), 3.4 (m, 1), 2.43 (s, 6), 1.72 (t, 2), 1.16 (d, 3), 0.98 (d, 3).

Anal. Calcd for $C_{19}H_{25}NO_5S_2$: C, 55.45; H, 6.12; N, 3.40. Found: C, 55.55; H, 6.15; N, 3.16.

The erythro isomer of **2** was not obtained in pure form, but only as enriched material from the mother liquors.

***cis*-2,4-Dimethyl-*p*-toluenesulfonazetidide (*cis*-3).**—To a refluxing solution of 2.5 g (37 mmol) of sodium ethoxide in 500 ml of absolute ethanol was added a solution of 11.5 g (37 mmol) of *threo*-**2** in 300 ml of absolute ethanol over a period of 40 hr. The solution was heated for an additional 10 hr, concentrated to a volume of 200 ml, and poured onto 600 g of ice to yield 5.0 g (28 mmol, 75%) of *cis*-**3** as a precipitate: mp 141.5–142°; $\delta_{TMS}^{CDCl_3}$ 7.52 (AB pattern, 4), 3.65 (m, 2), 2.42 (s, 3), 2.1 (m, 1), 1.36 (d, 6), 1.3 (m, 1).

Anal. Calcd for $C_{12}H_{17}NO_2S$: C, 60.22; H, 7.16; N, 5.85. Found: C, 60.28; H, 7.06; N, 5.69.

***cis*-2,4-Dimethylazetidine (*cis*-4).**—To a refluxing solution of 10.4 g (43 mmol) of *cis*-**3** in 300 ml of 1-pentanol was added 23 g of sodium in 1-g pieces over a period of 6 hr. Water (150 ml) was added to the cold solution, the layers were separated, and the aqueous phase was subjected to distillation, which was discontinued when the temperature of the vapors reached 100°. The distillate was combined with the alcoholic phase and the amine was extracted with dilute hydrochloric acid. The acidic solution was washed with ether, made strongly basic, and partially distilled. Upon addition of potassium hydroxide pellets to the first 20 ml of distillate, 3.6 g of an oil separated, which on distillation afforded 3.2 g (38 mmol, 89%) of *cis*-**4** as a hygroscopic oil: bp 84–86° (750 mm); δ_{TMS}^{neat} 3.7 (multiplet overlapping a broad singlet, total intensity approximately 4.5), 2.3 (m, 1), 1.4 (m, 1), 1.13 (d, 6). The *p*-bromobenzenesulfonyl derivative melted at 131°.

Anal. Calcd for $C_{11}H_{14}NO_2SBr$: C, 43.42; H, 4.64; N, 4.60. Found: C, 43.15; H, 4.75; N, 4.54.

***N*-Nitroso-*cis*-2,4-dimethylazetidine (*cis*-5).**—A solution of 1.0

(33) J. Sicher, M. Pankova, J. Jonas, and M. Svoboda, *Collect. Czech. Chem. Commun.*, **24**, 2727 (1959).

g (12 mmol) of *cis*-4 in 30 ml of 50% aqueous acetic acid was heated with 2.0 g of sodium nitrite to 80° for 3 hr. The oil precipitated with potassium hydroxide was chromatographed on a neutral silica gel column. Elution with chloroform afforded 1.1 g (10 mmol, 85%) of *cis*-5: bp 55° (2.5 mm); δ_{TMS}^{neat} 5.0 (m, 1), 4.2 (m, 1), 2.7 (m, 1), 1.63 (d, 3), 1.38 (d, 3), 1.5 (m, 1). Its mass spectrum (70 eV) showed prominent peaks at *m/e* 114, 84, 70, 42, 41, and 30. Its stereochemical purity was checked on two vpc columns[34,35] and found to be greater than 99.7%.

N-**Nitroso-*trans*-2,4-dimethylazetidine** (*trans*-5).—The solid material isolated from the mother liquors remaining after crystallization of pure *threo*-2 was subjected to procedures identical with those described above. The product thus obtained was shown by vpc[35] to consist of 30% *cis*-5 and 70% *trans*-5. Preparative separation on a 15 ft × 0.5 in. 20% Carbowax 20M on Chromosorb G column, using an Aerograph Autoprep Model A-700 gas chromatograph, yielded pure (>99.7%[34,35]) *trans*-5: bp 40° (0.9 mm); $\delta_{TMS}^{CDCl_3}$ 5.2 (m, 1), 4.7 (m, 1), 2.14 (t, 2), 1.67 (d, 3), 1.40 (d, 3). Its mass spectrum was identical with that of *cis*-5.

N-**Amino-*cis*-2,4-dimethylazetidine** (*cis*-6).—A solution of 1.5 g (13 mmol) of *cis*-5 in 10 ml of dry ether was added dropwise to a slurry of 2.0 g of lithium aluminum hydride in 20 ml of dry ether under stirring and the mixture was heated under reflux for an additional 12 hr. Water (2.0 ml) was then added dropwise under cooling, followed by gradual addition of 2.0 ml of 10% sodium hydroxide and an additional 4.0 ml of water. The mixture was filtered and the ether solution was extracted with dilute hydrochloric acid. The residual ether was removed from the aqueous solution by an air stream, and the solution was made strongly alkaline and partially distilled. Addition of potassium hydroxide pellets to the first 15 ml of the distillate precipitated 1.2 g (12 mmol, 92%) of *cis*-6 as a yellow oil: δ_{TMS}^{neat} 4.4 (broad singlet), 2.9 (m, 2), 2.1 (m, 1), 1.16 (d, 6), 1.1 (m, 1). Its mass spectrum (70 eV) showed a parent peak at *m/e* 100. Vpc analysis[34] demonstrated a stereochemical purity of >99.7%.

In a preliminary experiment a *p*-nitrobenzaldehyde derivative of mp 74–76° was prepared from a 2:3 mixture of *cis*-6 and *trans*-6.

Anal. Calcd for $C_{12}H_{15}N_3O_2$: C, 61.79; H, 6.48; N, 18.01. Found: C, 61.52; H, 6.32; N, 17.94.

N-**Amino-*trans*-2,4-dimethylazetidine** (*trans*-6).—When a procedure identical with that used for the preparation of *cis*-6 was applied to *trans*-5, *trans*-6 was obtained in greater than 99.7% stereochemical purity: δ_{TMS}^{neat} 4.4 (broad singlet), 3.52 (sextet, 2), 1.62 (t, 2), 1.19 (d, 6).

1,2-Dimethylcyclopropanes (*cis*-7 **and** *trans*-7).—To a solution of 8.3 g (36 mmol) of *cis*- or *trans*-1,1-dibromo-2,3-dimethylcyclopropane, prepared according to the procedure of Skell and Gardner,[18] in 300 ml of 1-pentanol was added with stirring 3.3 g of sodium in small pieces over a period of 3 hr. After the reaction had subsided, the mixture was warmed to 45° and the cyclopropane was distilled into a Dry Ice trap under a slow stream of nitrogen. The nmr spectra of the products are very complex, but sufficiently different to permit approximate analysis of mixtures.[36] Injection of the pure isomers and of mixtures into two different vpc columns[34,37] showed that *trans*-7 was the faster eluting isomer in both cases.

Reaction of 5 with Sodium Dithionite.—To a slurry of 6.0 g (33 mmol) of sodium dithionite in 25 ml of 20% sodium hydroxide was added a solution of 1.0 g (8.8 mmol) of a mixture consisting of 30% *cis*-5 and 70% *trans*-5 in 9 ml of ethanol. The mixture was stirred at 40° and the low-boiling products were swept out by a slow stream of nitrogen. After 4 hr 0.28 g of a colorless liquid had been collected in a Dry Ice trap, shown by nmr (CCl_4) to be a mixture of *cis*-7 and *trans*-7. The liquid was further analyzed by vpc[34,37] and found to consist of 39% *cis*-7 and 61% *trans*-7 as the only detectable products. Addition of *cis*- and *trans*-2-pentene to the product mixture gave two additional peaks in the gas chromatogram;[38] a control experiment established that 0.3% of 2-pentenes could be detected. The dithionite reaction mixture was extracted with ether to give 0.3 g of starting material, for an overall yield of isolated cyclopropanes of 67%.

The stereochemically pure isomers of 5 were subjected to identical reaction conditions and the product compositions were determined by vpc analysis.[34,37] Reisolated unreacted starting materials were in both cases shown by vpc[35] to be identical with the original, uncontaminated by the other isomer or by detectable side products.

In a further control experiment a trace of *trans*-3,5-dimethyl-1-pyrazoline[39] was added to the 30:70 mixture of *cis*- and *trans*-5, which was then subjected to the above reaction conditions. Vpc analysis[35] of the recovered starting material showed three additional unidentified components.

Reaction of 6 with Mercuric Oxide.—A solution of 0.85 g (8.5 mmol) of a 29:71 mixture of *cis*- and *trans*-6 in 4 ml of absolute ethanol was added to 6.3 g (30 mmol) of yellow mercuric oxide in 20 ml of absolute ethanol and the mixture was stirred for 3 hr at 40° under a slow stream of nitrogen. The material (0.42 g, 71%) collected in a Dry Ice trap was found by vpc[34,37] to consist exclusively of dimethylcyclopropanes. The individual isomers were subjected to an identical procedure; *cis*-6 was also deaminated at 140° using refluxing 1-pentanol as a solvent.

Reaction of *cis*-4 with Difluoramine.—The procedure previously described[12] was followed using 20 mmol of *cis*-2,4-dimethylazetidine and 5 mmol of difluoramine (generated by the hydrolysis of triphenylmethyldifluoramine[40]). A total of 3.3 mmol (65%) of a mixture of 1,3-dimethylcyclopropanes (Table I) was collected in a methylcyclohexane slush bath and analyzed by gas chromatography. The other gaseous product, nitrogen (67%), was identified by its mass spectrum.

Registry No.—*threo*-2, 34414-32-9; *erythro*-2, 34414-33-0; *cis*-3, 34414-34-1; *cis*-4, 34414-35-2; *cis*-4 *p*-bromobenzenesulfonyl derivative, 34414-36-3; *cis*-5, 34414-37-4; *trans*-5, 34414-38-5; *cis*-6, 34414-39-6; *trans*-6, 34414-40-9; 6 *p*-nitrobenzaldehyde derivative, 34414-41-0.

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(34) 6 ft × 0.12 in. 10% UCW 98 Chromosorb W.

(35) 10 ft × 0.25 in. 20% Carbowax 20M on Chromosorb G.

(36) The cis isomer displays an isolated group of signals around 458 Hz upfield from internal $CHCl_3$ at 60 MHz, which is absent in the trans isomer.

(37) 20 ft × 0.25 in. 20% SE-30 on Chromosorb W.

(38) The order of elution was *trans*-7, *trans*-2-pentene, *cis*-2-pentene, *cis*-7.

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