with water, dried, and evaporated. The resulting solid was recrystallized from ether–hexane to give 183 mg (66%) of white needles, mp 118–121°. A sample for analysis was sublimed at 105° and 0.05 mm to give crystals: mp 118–121°; λ_{max} 225, 304 (ϵ 28,000, 10,000); 2.92 6.15, 6.30, 6.70, 6.96, 7.40 μ.

Anal. Calcd for $C_{11}H_{10}F_3NO$: C, 57.63; H, 4.40; F, 24.87; N, 6.11. Found: C, 57.54; H, 4.48; F, 25.13; N, 6.05.

The nmr spectrum of a sample from a similar experiment showed resonances at 2.42 (singlet, 2-CH_3), 3.88 (singlet, OCH_3), 6.31 (broad, 3-H), 6.83, 7.42 (doublets, 6 and 7 H, J = 9.5 cps), 10.3 ppm (broad, NH).[22]

2,4-Dimethyl-5-methoxyindole (20).—A mixture of 3.5 g of 5-methoxy-2-methyl-4-trifluoromethylindole (**19b**) and 3.5 g of lithium aluminum hydride in 500 ml of tetrahydrofuran was heated at reflux temperature in an inert atmosphere for 3 days. Water was cautiously added, and the reaction mixture was filtered. The filtrate was evaporated and the residue was dissolved in ether, washed with water, dried, and evaporated. The resulting pasty solid was dissolved in dichloromethane and passed through a short column of silica gel. Evaporation gave 2.2 g (82%) of yellow crystals, mp 50–52°. The analytical specimen was prepared by sublimation at 50° and 0.05 mm to give pale yellow crystals: mp 54–55°; λ_{max} 274 (ϵ 8500); 3.00, 3.42, 6.28, 6.66 μ; nmr, 2.26 (singlet, 4-CH_3), 2.35 (singlet, 2-CH_3), 3.73 (singlet, OCH_3), 6.05 (broad, 3-H), 6.68, 7.06 (doublets, 6- and 7-H, J = 8.0 cps), 10.55 ppm (broad, NH).[21]

Anal. Calcd for $C_{11}H_{13}NO$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.78; H, 7.67; N, 8.01.

Registry No.—2-Chloro-5-trifluoromethylhydroquinone, 16052-86-1; 2-chloro-3-trifluoromethylhydroquinone, 16052-87-2; **2b**, 16052-66-7; **3a**, 16052-67-8; **3b**, 16052-68-9; **3c**, 16052-44-1; **3d**, 16052-45-2; **4a**, 16052-46-3; **4b**, 16052-47-4; **4d**, 16052-48-5; **6a**, 16052-49-6; **6b**, 16052-50-9; **6c**, 16052-51-0; **7**, 16052-52-1; **9**, 16052-53-2; **10**, 16052-54-3; **11**, 16052-55-4; **12**, 16052-56-5; **13**, 16109-67-4; **14**, 16052-57-6; **15**, 16052-58-7; **16**, 16052-59-8; **17**, 16052-60-1; **18**, 16052-61-2; **19a**, 16052-62-3; **19b**, 16052-63-4; **20**, 16052-64-5.

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Ring Expansions. I. Ring Expansion of the Epimeric *trans*-2-Aminomethyl-2-decalols and *trans*-2-Decalone

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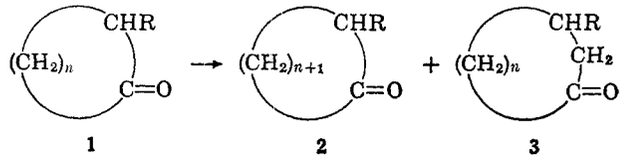
In order to assess the importance of the stereochemistry of the amino alcohols utilized in the Tiffeneau–Demjanov ring expansions of unsymmetrical ketones, the ring expansions of *trans*-2α-aminomethyl-2β-decalol (**10**) and *trans*-2β-aminomethyl-2α-decalol (**11**) have been examined. Ring expansion of amino alcohol **11** gave approximately equal amounts of the two possible ring expanded ketones, *trans*-bicyclo[5.4.0]undecan-3-one (**13**) and *trans*-bicyclo[5.4.0]undecan-4-one (**14**), whereas ring expansion of **10** gave **13** and **14** in the ratio 1:1.6. Ring expansion of *trans*-2-decalone with diazomethane gave a product distribution similar to that obtained from the ring expansion of amino alcohol **10** indicating predominant equatorial attack by diazomethane.

The use of ring expansion reactions for the homologation of cyclic compounds has been an important method for the synthesis of a variety of compounds which could be obtained only with difficulty by other methods. Among the most widely used methods of ring expansion are the reaction of cyclic ketones with diazo compounds[1] and the Tiffeneau–Demjanov[2] rearrangement of amino alcohols derived from the cyclic ketones. For symmetrical ketones both methods are often satisfactory, although in the reaction of cyclic ketones with a diazo compound the initial ring expanded ketones may undergo further reaction to produce undesired higher homologs. The chief disadvantage of the Tiffeneau–Demjanov sequence is the inconvenience of the several additional steps necessary for conversion of the ketone into the required amino alcohol.



1 2 3

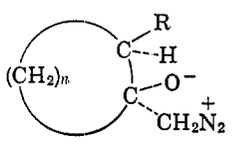
When an unsymmetrical ketone (*e.g.*, **1**) is subjected to ring expansion by one of these methods, two possible ring expanded ketones (**2** and **3**) may be formed and it is difficult to predict in advance which will be the major product of the reaction. An examination of the results available in the literature suggests that several factors may be involved in determining the course of the ring expansion of unsymmetrical ketones. Among these factors are (a) the migratory aptitudes of the competing carbon centers, (b) the method of ring expansion, (c) the experimental conditions, (d) conformational and steric effects in the transition state, and (e) the effect of remote substituents.

On the basis of factor a, it might be anticipated on electronic grounds that the more substituted carbon should migrate preferentially by analogy with other reactions involving migrations to electron-deficient centers[3–6] and this type of behavior has been observed in some cases. For example, the diazomethane ring expansion of 2,2-dimethylcyclohexanone is reported to give only 3,3-dimethylcycloheptanone.[7] In contrast,

(1) C. D. Gutsche, *Org. Reactions*, **8**, 364 (1954).
(2) P. A. S. Smith and D. R. Baer, *ibid.*, **11**, 157 (1960).
(3) M. Stiles and R. P. Mayer, *J. Amer. Chem. Soc.*, **81**, 1497 (1959).
(4) Rearrangements in the semipinacolic deamination reaction are much less sensitive to substituent effects than other rearrangements such as the pinacol rearrangement. For example, in the pinacol rearrangement, the migration ratio *p*-anisyl/phenyl is 500[5] whereas in the semipinacolic deamination of 2-amino-1,1-diarylethanols the ratio is only 1.56.[6]
(5) W. E. Bachman and J. W. Ferguson, *J. Amer. Chem. Soc.*, **56**, 2081 (1934).
(6) D. Y. Curtin and M. C. Crew, *ibid.*, **76**, 3719 (1954).
(7) R. A. Barnes and W. J. Houlihan, *J. Org. Chem.*, **26**, 1609 (1961).

2-methylcyclohexanone gives almost equal amounts of 2- and 3-methylcycloheptanones[8] and 2-phenylcyclohexanone gives predominately 2-phenylcycloheptanone.[9] In a study of the reaction of acyclic ketones with diazomethane, the following order of migratory aptitudes was observed—$C_6H_5 \sim (CH_3)_2C{=}CH > CH_3 \sim CH_3CH_2CH_2 > (CH_3)_2CH \sim (CH_3)_3C$—indicating that the establishment of a unique set of migratory aptitudes applicable to all reactions involving migrations to electron-deficient centers cannot be established.[10] Relatively few examples are available which allow a comparison of the product distributions when a ketone is subjected to ring expansion by both the diazomethane and Tiffeneau–Demjanov methods (factor b). For the ring expansion of carvomenthone, Dev reports that both methods gave the same ratio of the two possible ring expanded ketones.[11] In contrast to the results cited above for the ring expansion of 2-methylcyclohexanone with diazomethane, ring expansion by the Tiffeneau–Demjanov method gave 2- and 3-methylcycloheptanone in the ratio 1:8.7.[12] A comparison of the two methods is further complicated by the possibility that in the diazomethane ring expansion one of the initial products may undergo selective reaction with diazomethane to give higher homologs and thus give misleading results.[10]

Factor c seems to be particularly important in determining the product distribution. Gutsche has shown that changes in temperature, concentration, and method of introducing the diazomethane (*"in situ" vs. "ex situ"*) affected the ratio of the ring expanded ketones in the reactions of diazomethane with *cis*- and *trans*-1-decalone.[13] In the Lewis acid catalyzed ring expansion of menthone and carvomenthone, exclusive migration of $-CH_2-$ relative to $-CHR-$ occurs in contrast to the uncatalyzed ring expansion.[14]



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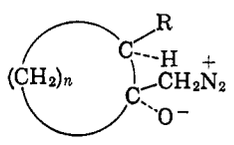

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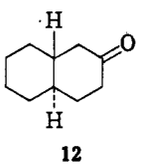
The effect of stereochemistry (factor d) is difficult to assess in the diazoalkane ring expansion because of a lack of information concerning the direction of attack of the diazoalkane. Ring expansion of the unsymmetrical ketone **1** with diazomethane can lead to two isomeric betaine intermediates (**4** and **5**) and it is possible that decomposition of each of these might lead to different ratios of the ring expanded ketones **2** and **3**. Similarly, in the Tiffeneau–Demjanov sequence two isomeric amino alcohols (corresponding to **4** and **5**) can result from **1** and in only a few cases has the stereochemistry of the amino alcohols been rigorously established. Ramirez and Stafiej[15] showed that rearrangement of 3β,17α-dihydroxy-20α-aminoallopregnane afforded 3β-hydroxy-17aα-methyl-D-homoandrostan-17-one while the isomeric 3β,17β-dihydroxy-20β-amino-17-isoallopregnane afforded the 17aβ-methyl-D-homo compound. In both cases, however, it was the more substituted carbon which migrated and molecular models indicate that these results can be interpreted in terms of transition states which involve the least amount of steric interactions. In contrast to these results, in the 3α-acetoxy-11-ketopregnane system both the 17α-hydroxy-17β-aminomethyl and 17β-hydroxy-17α-aminomethyl compounds gave the same 6:1 ratio of 17a-keto- and 17-keto-D-homosteroids.[16] Favre examined the ring expansion of both *cis*- and *trans*-4-*t*-butyl-1-aminomethylcyclohexanol, a case in which only one ring-expanded ketone is possible, and showed that the two isomers gave a different ratio of ring-expanded ketone to epoxide by-product.[17]

Jones and Price have reported a remarkable long-range effect in which the 17β-hydroxyl group of 17β-hydroxy-5α-androstan-3-one appears to control the direction of the ring expansion with diazomethane to give the corresponding A-homo-3-one.[18] This result is in direct contrast with the direction of ring expansion of 5α-cholestan-3-one with diazomethane.[18,19]

As the first part of a general study of the steric factors involved in determining the course of diazomethane and Tiffeneau–Demjanov ring expansions of unsymmetrical ketones we have examined the ring expansion of the epimeric amino alcohols, *trans*-2α-aminomethyl-2β-decalol (**10**) and *trans*-2β-aminomethyl-2α-decalol (**11**)[20] with nitrous acid and the ring expansion of *trans*-2-decalone (**12**) with diazomethane.[21] Ring expansion in these systems can lead to either of the two ring-expanded ketones **13** and **14** and provide an interesting case for the examination of steric and conformational effects since both **13** and **14** arise from migration of electronically similar carbon centers.



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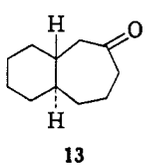

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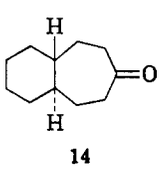

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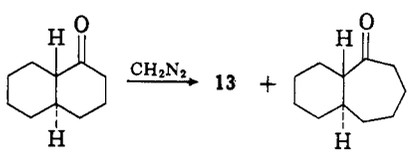


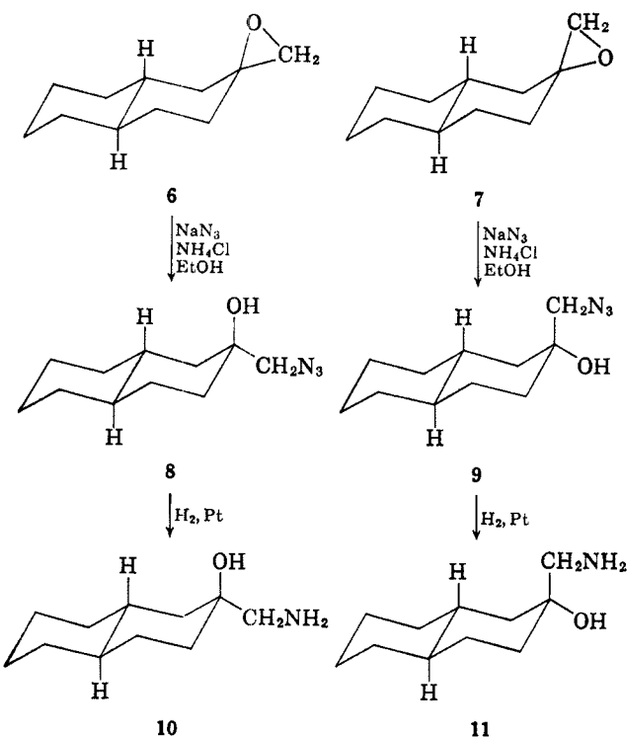
15 16

The required amino alcohols **10** and **11** were prepared from the previously described[22] epoxides **6** and **7** as outlined in Scheme I. The ketones **13** and **14** obtained in the ring expansions of amino alcohols **10** and **11** were

(8) C. D. Gutsche and C. T. Chang, *J. Amer. Chem. Soc.*, **84**, 2263 (1962).
(9) C. D. Gutsche, *ibid.*, **71**, 3513 (1949); C. D. Gutsche, H. F. Strohmayer, and J. M. Chang, *J. Org. Chem.*, **23**, 1 (1958).
(10) H. O. House, E. J. Grubbs, and W. F. Gannon, *J. Amer. Chem. Soc.*, **82**, 4099 (1960).
(11) T. M. Jacob and S. Dev, *J. Indian Chem. Soc.*, **38**, 674 (1961).
(12) M. B. Tchoubar, *Bull. Soc. Chim. Fr.*, 629 (1946).
(13) C. D. Gutsche and H. H. Peter, *J. Amer. Chem. Soc.*, **77**, 5971 (1955).
(14) E. Müller, W. Lurken, and M. Bauer, *Tetrahedron Lett.*, 775 (1962).
(15) F. Ramirez and S. Stafiej, *J. Amer. Chem. Soc.*, **78**, 644 (1956).
(16) N. L. Wendler, D. Taub, and H. L. Slates, *ibid.*, **77**, 3559 (1955).
(17) H. Favre and D. Gravel, *Can. J. Chem.*, **41**, 1452 (1963).
(18) J. B. Jones and P. Price, *ibid.*, **44**, 999 (1966).
(19) M. W. Goldberg and H. Kirchensteiner, *Helv. Chim. Acta*, **26**, 288 (1943); N. A. Nelson and R. N. Schut, *J. Amer. Chem. Soc.*, **81**, 6486 (1959).
(20) The nomenclature used here is that suggested in E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformation Analysis," John Wiley and Sons, Inc., New York, N. Y., 1965, p 89.
(21) The boron trifluoride catalyzed ring expansion of **12** with diazomethane has been reported to produce 49% of a mixture of ketones **13** and **14** along with 12% of a mixture of higher homologs: E. Muller and M. Bauer, *Ann.*, **654**, 92 (1962).
(22) R. G. Carlson and N. S. Behn, *J. Org. Chem.*, **32**, 1363 (1967).

isolated by preparative vapor phase chromatography (vpc) and one of the ketones was identical (vpc retention time and infrared spectrum) with one of the ketones obtained in the diazomethane ring expansion of *trans*-1-decalone (**15**)[13] and therefore must have structure **13**. The remaining ketone obtained from the ring expansion of amino alcohols **10** and **11** must then have structure **14**. The nmr spectra of **13** and **14** at 100 Mc are also in agreement with these assignments as **14** shows a better resolved and more symmetrical pattern for the methylene protons adjacent to the carbonyl group.

SCHEME I



The distribution of products from the various ring expansion reactions is summarized in Table I. The diazomethane ring expansions were carried out with only 0.05–0.1 equiv of diazomethane to minimize the possibility of one of the products undergoing selective reaction with diazomethane. It is apparent from an examination of the data in Table I that the stereochemistry of the starting amino alcohol is important in determining both the relative amount of each of the ring expanded ketones and the ratio of ring-expanded ketones to epoxide by-product. A comparison of the product distribution from the reaction of **12** with diazomethane with the product distributions obtained in the deamination of **10** and **11** indicates that **12** undergoes predominate, but not exclusive, equatorial attack by diazomethane. To our knowledge this represents the first evidence for the stereochemistry of attack by diazomethane on a rigid cyclohexanone and it has been suggested previously that axial attack would be expected.[18,23]

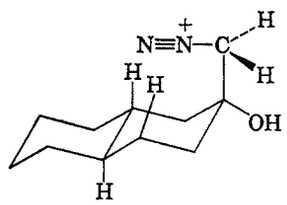
TABLE I

DISTRIBUTION OF PRODUCTS FROM RING-EXPANSION REACTIONS

Reaction	Products, vpc volatile material,[a] % 6	7	13	14	16	Ratio of ketone/oxide[a]
12 + 0.1 equiv of CH_2N_2	4	1	40	50	..	18
10 + HONO	7	..	34	54	..	8
11 + HONO	..	3	47	48	..	30
15 + 0.05 equiv of CH_2N_2[b]	..	..	55	..	11	2

[a] All values are the averages of two or more runs. [b] A mixture (33% of product) of the corresponding epoxides was also obtained.

The larger amount of epoxide obtained from amino alcohol **10** as compared with the amount of epoxide from **11** is readily explained if it is assumed that the oxygen of the hydroxyl group attacks the methylene carbon from the side opposite the departing nitrogen. In the case of **11** this would require the unfavorable conformation shown in **17**. Gutsche has suggested[23] that the



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epoxide product obtained in the reaction of diazomethane with cyclic ketones arises from electrophilic attack of diazomethane at the carbonyl oxygen and has cited considerable evidence to support this hypothesis. It is apparent, however, that some epoxide product can also form from the betaine intermediate arising from nucleophilic attack of diazomethane at the carbonyl carbon since epoxides are formed (although usually in lesser amount) in the deamination of the corresponding amino alcohols. The smaller amounts of epoxides formed in the deamination of the amino alcohols may simply reflect the decreased nucleophilicity of the oxygen in the intermediate hydroxy diazonium ion as opposed to what is formally an alkoxide ion in the betaine intermediate from the diazomethane reaction.[10] Although we agree with Gutsche's analysis of the effect of substituents in determining the stereochemistry of attack by the diazomethane on various substituted cyclohexanone derivatives,[23,24] we suggest that the high ketone/oxide ratios observed when axial attack is relatively favorable reflect the necessity for unfavorable conformations similar to **17** for epoxide formation.

The decreased amount of ketone **13** obtained in the deamination of **10** is of particular interest and indicates the importance of steric control in determining the course of the ring expansion reaction. Unfortunately the details of the rearrangements accompanying the deamination of aliphatic amines are not clear, although there is general agreement that migration is not very far advanced in the transition state and little assistance is required by the migrating groups for the expulsion of nitrogen.[6,25–27] If it is assumed that migration occurs with inversion of configuration at the migration terminus,[28] it is apparent from an examination of molecu-

(23) C. D. Gutsche and J. E. Bowers, *J. Org. Chem.*, **32**, 1203 (1967).

(24) Molecular models indicate that introduction of an α-equatorial alkyl group or β-axial alkyl group should make axial attack less favorable.

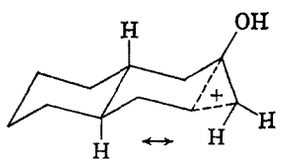
(25) A. Streitweiser, Jr., *J. Org. Chem.*, **22**, 861 (1957).

(26) B. M. Benjamin, P. Wilder, Jr., and C. J. Collins, *J. Amer. Chem. Soc.*, **83**, 3655 (1961).

(27) J. H. Ridd, *Quart. Rev.* (London), **15**, 418 (1961).

(28) For an example of a rearrangement accompanying deamination which occurs with net retention of configuration at the migration terminus, see B. M. Benjamin and C. J. Collins, *J. Amer. Chem. Soc.*, **83**, 3662 (1961).

lar models that the predominant formation of **14** from **10** does not reflect the existence of a preferred ground-state conformation of **10**. Models indicate that in both amino alcohols **10** and **11** the conformers required for a concerted migration of either C_1 or C_3 are equally probable and therefore there must be some type of steric interaction which arises during the migration of C_3 in the electron-deficient species obtained in the deamination of **10** which is less severe or absent in the migration of C_1. A careful examination using Dreiding models of the various conformational and steric interactions which are introduced as C_1 or C_3 migrate by reasonable hypothetical pathways to the electron-deficient methylene group generated in the deamination of amino alcohols **10** and **11** suggests a possible reason for the decreased amount of **13** obtained in the deamination of **10**. Although transannular hydrogen interactions are generated as migration occurs in each of the four possible migration paths, they appear to be far more severe in the case in which C_3 migrates in the deamination of **10**. The nature of this interaction is illustrated in **18**.



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A decision as to whether it is this type of transannular interaction which causes predominant formation of ketone **14** from amino alcohol **10** or other subtle conformational and electronic effects must await further studies in related systems. It is apparent, however, that an understanding of the factors controlling the course of the Tiffeneau–Demjanov ring expansions of unsymmetrical ketones will require an examination of the product distribution obtained from each of the possible isomeric amino alcohols.

Experimental Section[29]

Preparation of *trans*-2α-Azidomethyl-2β-decalol (8).—A solution of 3.17 g (0.019 mol) of epoxide **6**,[22] 6.5 g (0.10 mol) of sodium azide, 5.3 g (0.10 mol) of ammonium chloride, 60 ml of ethanol, and 18 ml of water was heated at reflux for 15 hr. The reaction mixture was diluted with water and extracted with ether. The combined ether extracts were washed with saturated sodium bicarbonate solution, dried, and evaporated under reduced pressure to afford 3.73 g of crude azide which crystallized on standing. Recrystallization from pentane–ether afforded 2.60 g (65%) of the pure[30] azide, mp 37–39°. The product exhibits infrared absorption at[31] 3605 (OH) and 2205 cm^{-1} (N_3) and nmr absorption at δ 3.17 (singlet, 2 H, $-CH_2N_3$) and unresolved absorption in the region 0.7–2.0 (17 H).

Anal. Calcd for $C_{11}H_{19}N_3O$: C, 63.13; H, 9.15; N, 20.08. Found: C, 63.17; H, 9.17; N, 19.94.

Preparation of *trans*-2β-Azidomethyl-2α-decalol (9).—A solution of 2.0 g (0.012 mol) of epoxide **7**,[22] 6.5 g (0.10 mol) of sodium azide, and 5.3 g (0.10 mol) of ammonium chloride in 65 ml of ethanol and 20 ml of water was heated at reflux for 30 hr and worked up as above to give 2.58 g of crude azide. Distillation afforded 1.88 g (75%) of pure[30] azide, bp 93–94° (0.07 mm), which crystallized on standing, mp 25–27°. The product exhibits infrared absorption[31] at 3605 (OH) and 2210 cm^{-1} (N_3) and nmr absorption at δ 3.35 (singlet, 2 H, $-CH_2N_3$) and unresolved absorption in the region 0.8–2.1 (17 H).

Anal. Calcd for $C_{11}H_{19}N_3O$: C, 63.13; H, 9.15; N, 20.08. Found: C, 63.36; H, 9.26; N, 20.31.

Preparation of *trans*-2α-Aminomethyl-2β-decalol (10).—A solution of 2.60 g (0.013 mol) of azide **8** in 50 ml of ethanol and 0.18 g of platinum oxide were shaken in a hydrogen atmosphere (50 psi) at room temperature for 3 days. The catalyst was removed by filtration and the solvent removed under reduced pressure leaving 2.15 g of crude solid which was recrystallized from hexane to afford 1.61 g (71%) of the amino alcohol as white needles, mp 88–89°. Sublimation at 60° and 0.01 mm afforded the analytical sample, mp 89–89.5°. The product exhibits infrared absorption[32] at 3200, 3600, 3400, and 1600 cm^{-1} and nmr absorption[33] at δ 7.0 (3 H, broad, NH_3^+), 3.41 (1 H, doublet, J = 5.7 cps), and 3.19 (1 H, doublet, J = 5.7 cps) for the nonequivalent protons ($-CH_2N^+<$) and unresolved absorption in the range 0.9–2.1 (17 H).

Anal. Calcd for $C_{11}H_{21}NO$: C, 72.08; H, 11.55; N, 7.64. Found: C, 71.91; H, 11.61; N, 7.53.

Preparation of *trans*-2β-Aminoethyl-2α-decalol (11).—Reduction of 1.80 g (0.0086 mol) of azide **9** by the method used in the preparation of **10** afforded 1.80 g of crude liquid which crystallized on standing. Recrystallization from hexane gave 1.00 g (64%) of amino alcohol **11** as white needles, mp 84–88°. Sublimation at 55° and 0.1 mm afforded pure **11**, mp 93–94.5° (mmp 58–60° with **10**). The product exhibits infrared absorption at 3690, 3600, 3400, and 1600 cm^{-1} and nmr absorption[33] at δ 7.1 (3 H, broad, NH_3^+), 3.62 (1 H, doublet, J = 6.0 cps), and 3.40 (1 H, doublet, J = 6.0 cps) for the nonequivalent protons ($-CH_2N^+<$) and unresolved absorption in the region 0.8–2.1 (17 H).

Anal. Calcd for $C_{11}H_{21}NO$: C, 72.08; H, 11.55; N, 7.64. Found: C, 71.87; H, 11.52; N, 7.64.

Preparation of an Authentic Sample of Ketone (13). Ring Expansion of *trans*-1-Decalone (15) with Diazomethane.[13]—A solution of 1.00 g (6.5 mmol) of *trans*-1-decalone in 30 ml of 3% methanolic potassium carbonate was cooled in an ice bath and a solution of 0.68 g (6.5 mmol) of N-nitroso-N-methylurea in 10 ml of methanol was added over a 10-min period. The resulting mixture was stirred for 5 hr and the methanol removed under reduced pressure. The residue was taken up in water and extracted with ether. The combined ether layers were washed with brine, dried, and evaporated to leave 0.85 g of crude product. Vpc analysis[34] showed the presence of 78% unreacted **15**, 11% a mixture of epoxides, 10% a ketone subsequently shown to be **13**, and 1% a ketone shown to be **16**.

Ketone **13** was collected by preparative vpc[34] and exhibited spectral properties similar to those reported by Gutsche.[13] The semicarbazone was obtained as colorless crystals, mp 206–208° (lit.[13] mp 210.5–211.5°). Ketone **16** was also collected by preparative vpc and exhibited infrared absorption similar to that reported.[13]

When the reaction was carried out using only 0.10 equiv of N-nitroso-N-methylurea the crude product contained 91% **15**, 3% of the epoxide mixture, 5% ketone **13**, and 1% ketone **16**.

Ring Expansion of Amino Alcohol 10.—To a solution of 0.100 g (0.54 mmol) of amino alcohol **10** in 4.5 ml of 5% acetic acid at 0° was added a solution of 0.172 g (2.5 mmol) of sodium nitrite in 2 ml of water. The resulting solution was stirred at 0° for 30 min, room temperature for 30 min, and finally heated on the steam bath for 15 min. After extraction with ether, the combined organic layers were washed with saturated sodium bicarbonate solution and brine and dried. Removal of the solvent gave 0.051 g of crude product. Vpc analysis[34] indicated the presence of 11% epoxide **6**, 31% ketone **13**, 51% ketone **14**, and 8% of unidentified products. In another experiment using the same amounts of materials, 0.087 g of crude product was obtained which was composed of 4% epoxide **6**, 36% ketone **13**, 57% ketone **14**, and 3% of unidentified products.

(29) All boiling points are uncorrected and all melting points are corrected. The infrared spectra were recorded on a Beckman IR-8 spectrophotometer and the nuclear magnetic resonance spectra were recorded on a Varian A-60, A-60-A, or HA-100 instrument using tetramethylsilane as an internal standard. Gas chromatography studies utilized an Aerograph A-90-P or F & M Model 700 gas chromatograph and a Beckman 10-in. recorder equipped with a Disc integrator. Unless otherwise stated, magnesium sulfate was employed as the drying agent. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn., and Weiller and Straus Microanalytical Laboratory, Oxford, England.

(30) A thin layer chromatographic plate coated with silica gel was employed for this analysis.

(31) Determined as a solution in carbon tetrachloride.

(32) Determined as a solution in chloroform.

(33) Determined in trifluoroacetic acid solution. The amino alcohols could be recovered unchanged from this solvent.

(34) A 6 ft × 0.25 in. column packed with 10% PDEAS on 60–80 mesh Chromosorb W was employed.

Preparative vpc[34] provided a sample of pure **13** which had spectral properties identical with the sample obtained from *trans*-1-decalone. The semicarbazone, mp 207–208°, showed no depression on mixture melting point determination with the semicarbazone prepared above.

Ketone **14** was collected by preparative vpc and exhibited infrared absorption[35] at 1702 cm^{-1} (C=O) and nmr absorption at δ 2.31–2.48 (4 H, multiplet, $-CH_2C(=O)CH_2-$) with unresolved absorption in region 0.90–1.90 (14 H).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.39; H, 11.01.

The semicarbazone was prepared and after recrystallization from aqueous alcohol had mp 212–213.5°.

Ring Expansion of Amino Alcohol 11.—Using the same procedure as for the ring expansion of amino alcohol **10**, 0.100 g of **11** afforded 0.060 g of crude product which was composed of 5% epoxide **7**, 45% ketone **13**, 48% ketone **14**, and 2% unidentified products. In another run 0.064 of crude product was obtained which consisted of 0.5% **7**, 48% **13**, 48% **14**, and 4% unidentified products.

Ring Expansion of *trans*-2-Decalone (12) with Diazomethane.—To a solution of 1.00 g (6.5 mmol) of **12** in 20 ml of 3% methanolic potassium carbonate solution at 0° was added a solution of 0.068 g (0.65 mmol) of N-nitroso-N-methylurea in 5 ml of methanol over a 10-min period. The reaction mixture was stirred at room temperature for 12 hr and the methanol removed under reduced pressure. Work-up in the usual manner afforded 1.00 g of crude product. Analysis by vpc[34] indicated the presence of 91% unreacted **12**, 0.4% epoxide **6**, 0.1% epoxide **7**, 3.8% ketone **13**, and 4.8% ketone **14**. Ketones **13** and **14** were collected and had spectral properties identical with those of previously obtained samples.

(35) Determined as a solution in carbon disulfide.

Registry No.—**8**, 16021-09-3; **9**, 16033-87-7; **10**, 16021-04-8; **11**, 16021-05-9; **12**, 16021-08-2; **14**, 16021-06-0; **14**, semicarbazone, 16021-07-1.

The Reactions of Carbamoyl Chlorides with Thiocyanate Ion

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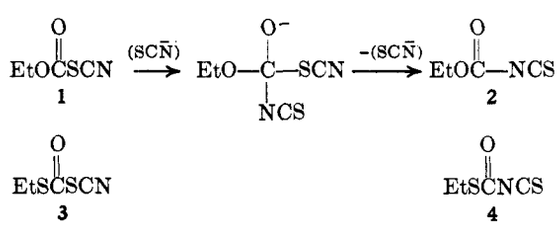
Diphenylcarbamoyl thiocyanate (**6**) and dimethylcarbamoyl isothiocyanate (**9**) were prepared by reaction of the corresponding carbamoyl chlorides with potassium thiocyanate in acetonitrile. Dimethylcarbamoyl thiocyanate (**17**) could only be prepared by an indirect method. Thiocyanates **6** and **17** were found to isomerize to their respective isothiocyanates **7** and **9** at drastically different rates (**17** ≫ **6**). Some mechanistic implications of these results are discussed in relation to other acyl thiocyanate isomerizations.

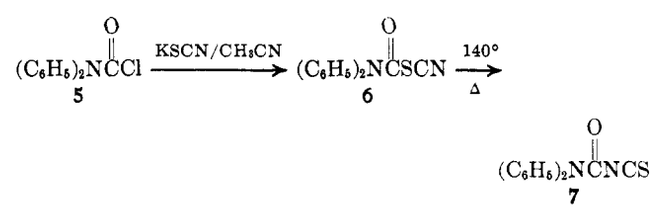
In the course of our investigations of thiocyanate isomerizations, we became interested in the preparation of certain dialkyl- and diarylcarbamoyl thiocyanates.

Previous reports,[1] and our own observations, indicated that the reaction of an acyl chloride with thiocyanate ion produces, with a few exceptions, exclusively the acyl isothiocyanate. These exceptions led us to believe that the stability of acyl thiocyanates may be related to the facility of nucleophilic attack by thiocyanate ion on the acyl carbon. The mode of isomerization is assumed to be a simple addition–elimination sequence (illustrated by the conversion of **1** into **2**). Lending support to this theory is the report that ethoxycarbonyl thiocyanate (**1**) can be isolated [and isomerized to ethoxycarbonyl isothiocyanate (**2**) in the



presence of additional thiocyanate ion] while ethylthiocarbonyl isothiocyanate (**4**) is the only isolable product from its similar preparation.[2] It is probable that the stability of **1** is the result of electronic overlap by the ether oxygen with the adjacent carbonyl π system. This could reduce nucleophilic attack on the acyl carbon, rendering **1** isolable. By contrast, the adjacent sulfur of the thio analog, **3**, cannot provide overlap of a similar magnitude,[3] and so any intermediate thiocyanate would be subject to rapid attack by thiocyanate ion giving the isomerized product, **4**.

Because of the probability that a nitrogen atom, in contrast to sulfur, could provide better electronic overlap than an oxygen atom with the carbonyl π system, it seemed likely that the carbamoyl derivatives would provide an adequate test for this theory. One compound of this type, diphenylcarbamoyl thiocyanate (**6**), had been previously reported[4] when our investigation was initiated. A reinvestigation of its preparation was undertaken.



From the reaction of diphenylcarbamoyl chloride (**5**) with potassium thiocyanate was obtained a crystalline solid, which could be identified as **6** on the basis of elemental analysis and infrared absorption at 2160 (-SCN) and 1725 cm^{-1} (C=O). The employment of acetonitrile as solvent for this reaction resulted in substantially better yields of **6** (35%) than with ethanol

(1) A. E. Dixon and J. Taylor, *J. Chem. Soc.*, **93**, 684 (1908); J. C. Ambeland and T. B. Johnson, *J. Amer. Chem. Soc.*, **61**, 632 (1939); I. B. Douglass and F. B. Dains, *ibid.*, **56**, 719, 1408 (1934); R. H. Patton and J. H. Simens, *ibid.*, **77**, 2017 (1955); D. T. Elmore and J. R. Ogle, *Tetrahedron*, **3**, 310 (1958); W. Ruske and M. Keilert, *Ber.*, **94**, 2695 (1961).

(2) A. Takamizawa, K. Hirai, and K. Matsui, *Bull. Chem. Soc. Jap.*, **36**, 1214 (1963).

(3) The analogous positive mesomeric effect of the CH_3S- group has been shown to be roughly half that of the CH_3O- group. See H. Lumbroso and C. Marschalk, *J. Chim. Phys.*, **49**, 385 (1952); H. Lumbroso, *ibid.*, **49**, 394 (1952).

(4) T. B. Johnson and L. H. Levy, *Amer. Chem. J.*, **38**, 456 (1907).