Nonplanar Cyclobutane. Steric Product Control in the Deamination of *cis*- and *trans*-3-Methylcyclobutylamine

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Deamination of the title compounds reveals a significant difference in ratios for the four major products: methylallylcarbinol (*cis*, 18%; *trans*, 59%); cyclopropylmethylcarbinol (*cis*, 60%; *trans*, 20%); *cis*-(2-methylcyclopropyl)carbinol (*cis*, 18%; *trans*, 0%); and *trans*-(2-methylcyclopropyl)carbinol (*cis*, 2%; *trans*, 21%). As in the case of the 3-isopropylcyclobutylamines, stereospecificity in formation of the latter two products is explained in terms of concertion which is conformationally more facile for the *trans*-cyclobutyldiazonium intermediate. The comparatively smaller preponderance of *trans*-(2-methylcyclopropyl)carbinol in the *trans* case, the occurrence of an almost equivalent amount of *cis*-carbinol for the *cis*-amine, and the larger fractions of homoallylic alcohol stand in contrast to the behavior of the isopropyl amines, however. Both the present product ratios and their divergence from those observed in the isopropyl case may be consistently explained in terms of substituent steric effect on orbital opening modes in the parent cyclobutyldiazonium ions and the key 2-alkylcyclopropylcarbinyl cation intermediates.

Within recent years, it has become increasingly apparent that carbonium ion reactivities of substituted cyclobutanes, which have been rationalized by a schema of common bicyclobutonium ion intermediates,[1,2] may require for their more adequate comprehension consideration of competing processes dependent on stereochemical orientation in predominantly puckered[3-10] rings. The solvolysis data of Wiberg and coworkers[8] on fused small ring compounds, and of Dolby[9] and Wilcox[10] and coworkers on polymethylcyclobutyl derivatives, have clearly demonstrated discrete steric requirements for participation in compounds containing the cyclobutane ring. However, such participation appears to show little, if any, relation to the electrical stability factors previously suggested for preferential bicyclobutonium ion stabilization.[11] Moreover, serious doubt has been cast on the viability of the bicyclobutonium ion intermediate as a result of study of cyclopropylcarbinyl reactivity,[12-15] which has implied an essentially unrearranged intermediate. Brown has previously argued in favor of the classical cyclobutane carbonium ion.[16] While recent arguments in support of a symmetrical bicyclobutonium ion have been advanced[17] in consequence of isotope scrambling experiments,[18] the cyclobutyl–cyclopropylcarbinyl cationic rearrangement has been shown to proceed with no positional scrambing in the absence of equilibration in at least one case.[19] Thus, the major support for the bicyclobutonium ion as the intermediate link in the cyclobutyl–cyclopropylcarbinyl rearrangements remains conjectural.

We have recently reported the results of deamination of the isomeric 3-isopropylcyclobutylamines.[20,21] The differences in *cis* and *trans* product ratios are compatible with steric control of an initial orbital overlap process which is concerted with loss of nitrogen in the respective cyclobutyldiazonium intermediates. Pivotal product 2-isopropylcyclopropylcarbinyl cation is formed stereospecifically by suprafacial overlap of C-3 and C-1 orbitals; this is sterically facile in the *trans*-cyclobutyl intermediate. An analogous process is opposed by developing repulsions in the transition state for the *cis*-cyclobutyl intermediate. This factor also appears responsible for *trans* rate preference in solvolysis of the corresponding alcohol brosylates.[22] Wiberg and coworkers have profferred a similar rationale for solvolytic behavior of fused-ring cyclobutanes.[23]

In our work, neither the product distribution nor the rate data were found to be readily reconcilable with bicyclobutonium ion intermediates. As a logical extension of these findings, it appeared of interest to investigate the deamination of the isomeric 3-methylcyclobutylamines to ascertain what effect, if any, the change in substituent would have on relative product distribution. This amine is conveniently available *via* well-known synthetic routes.[11a]

Deamination of 3-methylcyclobutylamine was carried out by Roberts and coworkers several years ago, but on an isomeric mixture.[11a] Major products, methylallylcarbinol, cyclopropylmethylcarbinol, and 2-methylcyclopropylcarbinol, were explained in terms of interconverting bicyclobutonium ions **1** and **2**, with the driving force for formation of **2** being ascribed to greater localization of charge on the carbon bearing the methyl

(1) *Cf.* K. L. Servis and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 1331 (1965), for preceding references; in particular, R. H. Mazur, W. N. White, D. A. Semenov, C. C. Lee, M. S. Silver, and J. D. Roberts, *ibid.*, **81**, 4390 (1959); and J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 2509, 3542 (1951).

(2) S. Winstein and E. Kosower, *ibid.*, **81**, 4399 (1959).

(3) J. B. Lambert and J. D. Roberts, *ibid.*, **87**, 3884, 3891 (1965).

(4) K. B. Wiberg and G. M. Lampman, *ibid.*, **88**, 4429 (1966).

(5) N. L. Allinger and L. A. Tushaus, *J. Org. Chem.*, **30**, 1945 (1965).

(6) I. Lillien and R. A. Doughty, *Tetrahedron*, **23**, 3321 (1967).

(7) G. M. Lampman, K. E. Apt, E. J. Martin, and L. E. Wangen, *J. Org. Chem.*, **32**, 3950 (1967).

(8) *Cf.* K. B. Wiberg and A. J. Ashe, III, *J. Amer. Chem. Soc.*, **90**, 63 (1968), and preceding papers in this series; *cf.* also K. B. Wiberg and J. E. Hiatt, *Tetrahedron Lett.*, 3009 (1968).

(9) L. J. Dolby and C. Wilkins, *ibid.*, 2379 (1964).

(10) C. F. Wilcox, Jr., and D. L. Nealy, *J. Org. Chem.*, **28**, 3450 (1963); C. F. Wilcox, Jr., and R. J. Engen, *Tetrahedron Lett.*, 2759 (1966).

(11) (a) M. S. Silver, M. C. Caserio, H. E. Rice, and J. D. Roberts, *J. Amer. Chem. Soc.*, **83**, 3671 (1961); (b) E. F. Cox, M. C. Caserio, M. S. Silver, and J. D. Roberts, *ibid.*, **83**, 2719 (1961).

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

(13) H. G. Richey, Jr., and J. M. Richey, *ibid.*, **88**, 4971 (1966).

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

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

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

(17) J. E. Baldwin and W. D. Foglesong, *J. Amer. Chem. Soc.*, **90**, 4311 (1968).

(18) J. E. Baldwin and W. D. Foglesong, *ibid.*, **90**, 4303 (1968).

(19) Deamination of 3-isopropylcyclobutylamine-1-*d* leads to specifically deuterated cyclopropylcarbinols: I. Lillien and L. Handloser, *Tetrahedron Lett.*, 1035 (1969).

(20) I. Lillien and R. A. Doughty, *ibid.*, 3953 (1967).

(21) I. Lillien and R. A. Doughty, *J. Org. Chem.*, **33**, 3841 (1968).

(22) I. Lillien, G. F. Reynolds, and L. Handloser, *Tetrahedron Lett.*, 3475 (1968).

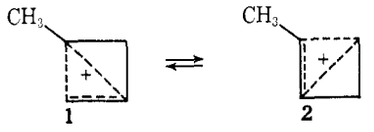
(23) K. B. Wiberg and J. G. Pfeiffer, *J. Amer. Chem. Soc.*, **90**, 5324 (1968).

TABLE I

PER CENT PRODUCT DISTRIBUTION IN THE AQUEOUS DEAMINATION OF ISOMERIC 3-METHYLCYCLOBUTYLAMINES (AVERAGE OF TWO RUNS)[a,b]

Amine	3	4	5[c]	6[c]	7[c]	8[c]
cis[c]	18.3	59.4	17.7	1.8[d]	2.0	0.8
trans[c]	58.8	19.2	0	21.1	0.7	0.2

[a] Percentages are corrected for isomeric amine contamination, which was minor. [b] Small amounts of unidentified material totaling 2–3% for each isomer were observed, with retention time similar to that of known products. [c] Assignment from nmr data. [d] Probably results from thermal inversion of *cis*-cyclopropylcarbonium intermediate: K. B. Wiberg, and G. Szeimies, *J. Amer. Chem. Soc.*, **90**, 4195 (1968).



1 2

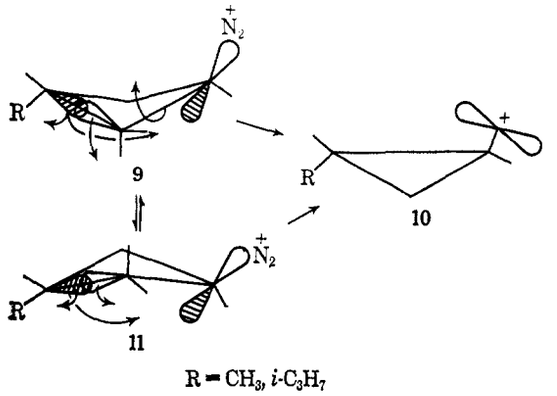
group. An important problem in this rationale lies in the fact that, while **2** may explain the large fraction (47%) of cyclopropylmethylcarbinol obtained, **1** must simultaneously acount for the small proportion (9%) of 2-methylcyclopropylcarbinol and the large proportion (39%) of allylmethylcarbinol. However, the former carbonium ion is more stable thermodynamically,[24] and the reverse was observed for the isopropyl case.[21] These facts argue against such a common progenitor for both of these products. Other objections to this general scheme have been cited,[21] and recent results militate against the likelihood of a **1**–**2** interconversion in this system.[19] In consequence of the foregoing considerations, we consider it of interest to report our observations in the deamination of the individual isomers.

Results and Discussion

Separation of the individual amine isomers was readily achieved by preparative vpc, employing a 30-ft Carbowax–KOH column. Isomeric assignment was made on the basis of nmr; the proton geminal to the NH_2 is further downfield (3.52 ppm) in the *trans* than in the *cis* isomer (3.15 ppm).[25] Results of two runs agreed closely, and are shown in Table I.

Stereospecificity in formation of 2-methylcyclopropylcarbinol is evidenced as in the isopropyl case, and as is demanded by orbital symmetry considerations.[26] However, in contrast to the isopropyl case, the present yields of **5** and **6** are almost equivalent.[27] Conversely, the proportion of **6** produced for *trans*-amine is substantially less than in the isopropyl case (where it is 55%). This difference corresponds to only a small change in the free energy of activation (*i.e.*, *ca.* 0.6 kcal/mol), which falls in the same range as the small magnitudes of conformational free-energy differences which prevail in this system.[5–7] Perhaps the most singular datum in the present results is the quite high proportion of **3** observed for the *trans*-amine, in contrast to the corresponding 3-isopropylamine, in which the homoallylic alcohol was a minor product.

The suggestion was previously made that products may arise directly from the cyclobutyldiazonium ion.[21] However, it now appears more likely that the common precursor is the 2-alkylcyclopropylcarbinyl cation or ion pair formed by initial rate-determining rearrangement of the cyclobutyldiazonium ion. A concerted, suprafacial overlap pathway from *trans*-diazonium intermediate **9** or **11** to *trans*-cyclopropylcarbinyl cation **10** (large arrows) subsequent to disrotatory C-2–C-3 bond opening[23] (small arrows) appears facile for both R = CH_3 and R = *i*-C_3H_7, since the transition state involves a net reduction in nonbonded interactions. It is difficult to make an *a priori* decision as to whether **9** or **11** more correctly represents the actual intermediate. Both can undergo the disrotatory orbital process preceding formation of **10** with comparative ease, although ensuing overlap is more direct for **11**. A simple conformational first approximation would tend to favor **9** on the basis that axial diazonium is more readily accommodated than axial alkyl. However, this may be a naive assumption, since it neglects the small differences which separate the conformational free energies of pseudoaxial and pseudoequatorial substituents in flexible cyclobutanes,[5–7] as well as the possibility that bulky solvation of the charged group may tip the delicate conformational balance. Wiberg and coworkers have argued, on the basis of calculations,[28] that cross-ring σ-bond stabilization is more effective for an equatorial leaving group. When this conclusion is accepted, it



9 10 11

R = CH_3, *i*-C_3H_7

(24) M. Hanack and H.-J. Schneider, *Angew. Chem. Intern. Ed. Engl.*, **6**, 666 (1967).

(25) *Cf.* for analogy I. Lillien and R. A. Doughty, *J. Amer. Chem. Soc.*, **89**, 155 (1967).

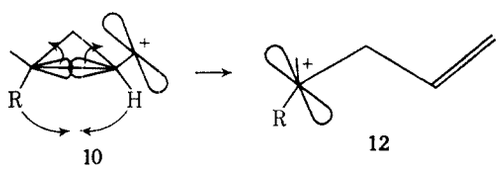
(26) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

(27) Repetition of the deamination reported in ref 20 and 21 has revealed that *cis*-3-isopropylcyclobutylamine does yield some *cis*-(2-isopropylcyclopropyl)carbinol. This product escaped prior detection, as under the vpc conditions then employed, it was not separated from *cis*-3-isopropylcyclobutanol. The adjusted product percentages for the *cis*-amine follow: *cis*-(2-isopropylcyclopropyl)carbinol, 11.1%; *cis*-3-isopropylcyclobutanol, 7.6%; *trans*-3-isopropylcyclobutanol, 1.2%. No *cis*-(2-isopropylcyclopropyl)carbinol was found for the *trans*-amine. The presence of this product for the *cis*-amine, however, does not vitiate the accompanying rationale, which is based in large part on the greater preponderance of the *trans*-cyclopropylcarbinol for the *trans*-3-isopropylcyclobutylamine.

(28) K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968).

becomes evident that the differing yields of the carbinols corresponding to **10** cannot be attributed to a difference in the conformational effects of isopropyl and methyl on the stability of **11**. Axial methyl should favor this route as opposed to axial isopropyl, but the converse appears to be reflected in the respective yields of these carbinols. Thus it seems most likely that an explanation of *trans*-product variation when the substituents isopropyl and methyl are compared must be sought in the differing effects of these groups on the collapse of the 2-alkylcyclopropylcarbinyl cation intermediate **10**.

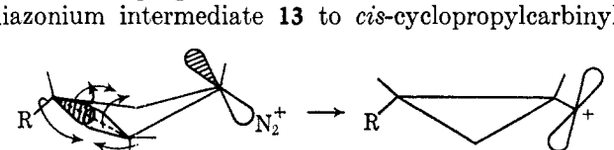
Consideration of the path from **10** to **3** carbonium ion reveals that disrotatory orbital opening of the C-1–C-2 bond is required for conservation of maximum bonding during rearrangement.[26] It is seen that this process will engender R–H repulsive interactions. One may therefore anticipate that in the close proximity of the ensuing transition state, such motion will be energetically less restricted when $R_4^{\bullet} = CH_3$ than when $R = i\text{-}C_3H_7$.[29] Thus, the much larger proportion of homoallylic alcohol obtained for the *trans*-3-methyl deamination (as opposed to the *trans*-3-isopropyl case) becomes readily intelligible in terms of the same kind of steric factors as govern the initial cyclobutyl rearrangement (*i.e.*, **11** → **10** *vs.* **13** → **14**). One might be tempted to cite the differing electrical capabilities of methyl and isopropyl to stabilize the homoallylic carbonium ion as a significant factor in this context. This might in part account for the greater yield of homoallyl alcohol for the *cis*-3-methylcyclobutyl as opposed to the *cis*-3-isopropylcyclobutyl case. However, the large *trans*/*cis* homoallylic yield ratio for the methylcyclobutyl isomers (*ca.* 3) clearly implicates a steric factor.



10 12

Where the route to homoallyl alcohol, *via* its precursor carbonium ion, is more favorable, it may successfully compete with unrearranged solvolysis. Thus, the smaller proportion of **6** observed, as opposed to its isopropyl counterpart, probably reflects better competitive diversion of **10** to **3** for the reasons given above, rather than abrupt change in mechanism.

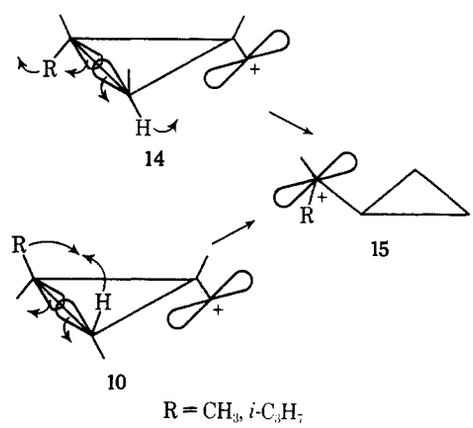
A similar course of reasoning can account for the *cis*-amine product distribution. The CH_3–H interactions in the developing transition state for conversion of *cis*-diazonium intermediate **13** to *cis*-cyclopropylcarbinyl cation **14** (large arrows), subsequent to disrotatory orbital opening (small arrows), are less than those for the analogous isopropyl-H interactions. This is therefore an energetically more favorable process. Indeed, the relative proportions of the *cis* and *trans* isomers of this carbinol are almost equivalent. The small amount of *trans*-carbinol obtained from *cis*-amine may simply reflect an energetically advantageous consumption of some **14** by thermal inversion[30] to **10** prior to conversion to carbinol.[31]



13 14

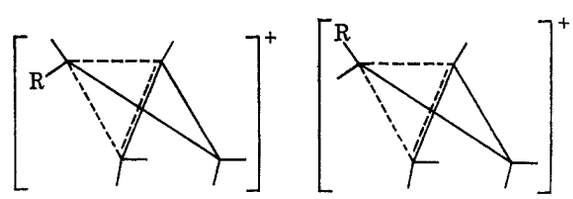
R = CH_3, i-C_3H_7

Major *cis*-amine product **4**, as well as its isopropyl homolog, is formed[19] *via* the process indicated below from **14**, again assuming disrotatory orbital opening of the C-2–C-3 bond. For the *cis* precursor **14**, no steric difficulties are expected. However, for the *trans* process from **10**, R–H oppositions arise, resulting in a smaller yield of **4**, even though **15** may be expected to be more stable than either **14** or **10**.[24]



R = CH_3, i-C_3H_7

Any attempt to rationalize these results through a scheme of bicyclobutonium ion *intermediates* meets with several serious objections. The difficulty of trying to relate the two ions **16** and **17**, derivable from *cis*- and *trans*-amines, respectively, to differential product distribution has been pointed out for the isopropyl case,[21] and is equally evident in the present instance. Moreover, there is an immediate dilemma inherent in attempting to account for the quite different homoallyl alcohol/*trans*-(2-alkylcyclopropyl)carbinol ratios, 0.1 for the *trans*-isopropylamine, but 2.8 for the *trans*-methylamine. This reflects a change in relative rates by a factor of about thirty; yet, in both cases, both products would ostensibly ensue from the same ion **17**.



16 17

Finally, the interconversion of ions **1** and **2** previously called on[11a] to rationalize product formation in the deamination of 3-methylcyclobutylamine may be *specifically excluded* by the results of deamination of the analogous 3-isopropylcyclobutylamine-1-*d*.[19]

(29) It has been shown [N. L. Allinger and L. A. Freiberg, *J. Org. Chem.*, **31**, 894 (1966)] that the conformational free energies of methyl and isopropyl in cyclohexanes (ΔG_{CH_3} = 1.8, $\Delta G_{i\text{-}C_3H_7}$ = 2.1) are similar because isopropyl can adopt a conformation in which its methyl groups are rotated away from a hydrogen atom in axial opposition ("*meso*"). However, in the closer proximity of the smaller ring systems under present consideration, increased restriction of rotational degrees of freedom may be expected to result in a greater loss of entropy, and thus in increased energy of activation, for transition states involving such isopropyl interactions.

(30) *Cf.* Wiberg and Szeimies, footnote *d*, Table I.

(31) A similar result was noted in the solvolysis of *cis*-3-isopropylcyclobutyl brosylate; *cf.* ref 22. Indeed, solvolysis of *trans*-(2-isopropylcyclopropyl)carbinyl 3,5-dinitrobenzoate yields no *cis*-carbinol, whereas the *cis* ester gives a substantial yield of *trans*-carbinol (I. Lillien, unpublished work).

The present results provide further support for a picture of conformationally dependent, classical processes functioning in carbonium ion reactivity of substituted cyclobutanes, and contribute to an increasing mass of evidence which impugns the concept of nonclassical bicyclobutonium ion intermediates.

Experimental Section

3-Methylenecyclobutanecarbonitrile was prepared from a bomb reaction of allene and acrylonitrile as described.[32] However, a run of 2 mol (80 g) of allene, 8 mol (424 g) of acrylonitrile, and 4 g of hydroquinone in the presence of 100 ml of dry benzene diluent, in a 2-l. bomb under autogenous pressure at 196° for 14 hr, produced a yield of 155 g (1.62 mol, 81%) of material with n^{28}D 1.4596 (lit. n^{25}D 1.4590). This represents a considerable improvement over the *ca.* 60% reported in the absence of diluent, and in a smaller vessel for a shorter time.[32] Conversion to 3-methylcyclobutylamine was carried out as reported.[11a] Isomers were separated by freezing the effluent vapors from a 30 ft × 0.25 in., 5% KOH–20% Carbowax 20M on Chromosorb W column maintained at 70° with a helium flow rate of *ca.* 35 ml/min. Under these conditions, the retention times of the *cis* and *trans* isomers were 13.07 and 14.53 min, respectively.

Deamination was carried out on the individual isomers and the mixture as previously described.[11a] The deamination mixture was analyzed on a 30 ft × 0.25 in., 5% CO-990 on Chromosorb W column. Components were obtained by isolation of effluent vapors from a mixed amine deamination. With the CO-990 column operated at 100° and a helium flow rate of 40 ml/min., retention times were as follows:

Inadequate separation of *trans*-(2-methylcyclopropyl)carbinol and *cis*-3-methylcyclobutanol resulted in isolation of mixtures. However, content could be assayed by nmr integration and comparison with authentic material.

(32) J. D. Roberts and C. M. Sharts, *Org. Reactions*, **12**, 32 (1962).

Table II

Product	Retention time, min
4-Penten-2-ol	7.70
Cyclopropylmethylcarbinol	9.63
trans-(2-Methylcyclopropyl)carbinol	12.61
cis-3-Methylcyclobutanol	12.70
trans-3-Methylcyclobutanol	13.46
cis-(2-Methylcyclopropyl)carbinol	15.00

Authentic 4-penten-2-ol was synthesized from allylmagnesium bromide and acetaldehyde. Its retention time was found to differ widely from its isomers 1-penten-3-ol and 3-penten-2-ol under these conditions. Cyclopropylmethylcarbinol was prepared by lithium aluminum hydride reduction of commercial cyclopropyl methyl ketone. *cis*- and *trans*-(2-methylcyclopropyl)carbinol were prepared by a Simmons–Smith reaction[33] with commercial crotyl alcohol, whose *cis*/*trans* ratio was about 3:1, and were isolated by freezing of effluent vapors from the CO-990 column. Isomeric configuration was assigned on the bssis of retention time (*cis* longer) and nmr, as has been discussed[34] and also observed for the homologous 2-isopropylcyclopropylcarbinols.[21] The methylene protons were at higher field for the *trans* isomer, and were seen as a ABX multiplet for the *cis* carbinol, and an A_2X doublet for the *trans*. 3-Methylcyclobutanol was prepared as described,[11a] and the isomers were separated by preparative vpc on the CO-990 column. Configuration was assigned by analogy with the 3-isopropylcyclobutanols.[25] The proton geminal to hydroxy was centered at 3.9 ppm for the *cis* and 4.4 ppm for the *trans* isomer.

Registry No.—*cis*-3-Methylcyclobutylamine, 20826-76-0; *trans*-3-methylcyclobutylamine, 20826-77-1.

(33) L. Fieser and M. Fieser, "Reagents for Organic Synthesis," John Wiley & Sons, Inc., New York, N. Y., 1967, p 1019.

(34) G. W. Van Dine, Ph.D. Thesis, Princeton University, Princeton, N. J., 1967, p 152.

Ring-Cleavage Reactions of 2-Bicyclo[2.1.1]hexyl Grignard Reagents[1]

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Ring-cleavage reactions of 2-bicyclo[2.1.1]hexyl Grignard reagents have been investigated. Preparation of the chloride or bromide from β-5,5-dimethylbicyclo[2.1.1]hexan-2-ol (1) leads to a mixture of halides including α- and β-2-halo-5,5-dimethylbicyclo[2.1.1]hexanes (**2** and **3**) and 2-halo-3,3-dimethylbicyclo[2.1.1]hexane (**4**) as major products. The Grignard reagents from these halides rearrange on heating to the Grignard reagent derivable from 4-halomethyl-3,3-dimethylcyclopentene (**5**). In the preparation of the halide, **5** is also a minor product, which is postulated to form by nucleophilic attack of halide ion on an intermediate ester or carbonium ion. During formation of the Grignard reagent, an alternative cleavage occurs yielding eventually 4-isopropylcyclopentene and 4-isopropenylcyclopentene. A radical process is believed responsible for these latter products. The Grignard reagent from 2-chlorobicyclo[2.1.1]hexane rearranges cleanly to the reagent derivable from 4-chloromethylcyclopentene. The ring cleavages observed are all slower than the analogous cleavage of the Grignard reagents from α-cyclobutylethyl halides, despite substantially greater relief of ring strain in the bicyclic system. These results are in agreement with predictions from a concerted four-center mechanism for the ring-cleavage reactions. However, hybridization effects, the *gem*-dimethyl effect, and overlap control, the magnitude of which are difficult to assess, may contribute to the slowness of the observed cleavages.

A kinetic and mechanistic study of the ring cleavage of cyclobutylmethyl organomagnesium compounds has been reported previously.[3,4] A concerted four-center process was considered to be more consistent with observed solvent, α-deuterium, and methyl substituent effects than were alternative radical and carbanionic mechanisms. The proposed mechanism, in which transfer of the magnesium is synchronous with bonding

(1) (a) Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research, and to the National Science Foundation and the Shell Oil Co. for summer and academic year fellowships, respectively, for R. J. T. (b) Presented in part at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, Abstracts, p 19-K.

(2) (a) To whom inquiries should be addressed: University of Wisconsin-Milwaukee, Milwaukee, Wis. 53201. (b) Taken in part from the Ph.D. Thesis of R. J. Theissen, University of Minnesota, 1966. (c) National Science Foundation Undergraduate Research Participant, University of Wisconsin-Milwaukee, 1967.

(3) E. A. Hill and J. A. Davidson, *J. Amer. Chem. Soc.*, **86**, 4663 (1964).

(4) Analogous cleavages of other cyclobutylmethyl and cyclopropylmethyl organometallic compounds are known: M. S. Silver, P. R. Shafer, J. E. Nordlander, C. Ruchardt, and J. D. Roberts, *ibid.*, **82**, 2646 (1960); P. T. Lansbury, *ibid.*, **85**, 1886 (1963); H. G. Richey, Jr., and E. A. Hill, *J. Org. Chem.*, **29**, 421 (1964).