

CONFIGURATIONAL RETENTION IN THE SILVER ION CATALYZED

SOLVOLYSIS OF AN ALKYL BROMIDE IN ACETONITRILE

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Rather extensive mechanistic studies of the reactions of secondary alkyl halides in acetonitrile with silver salts, such as the nitrate, nitrite, perchlorate and tetrafluoroborate, have led to the conclusions that the silver ion removes the halide ion and that the counteranion is involved in the rate determining step<sup>2-5</sup>. The nitrate<sup>3,4</sup> and nitrite<sup>4</sup> yield some alkene but mainly substitution products (nitrates, nitrites and nitro compounds) of largely inverted configuration. When the counterion is perchlorate<sup>3</sup> or tetrafluoroborate,<sup>4</sup> the major products, obtained after aqueous work-up, are N-alkylacetamides, undoubtedly formed by aqueous quenching of the solvolysis products which are N-alkylacetonitrilium ions,<sup>6</sup> the stereochemistry of this solvolysis reaction has apparently not been studied, although it holds promise of providing interesting mechanistic information.

In connection with studies<sup>7</sup> of the trapping by acetonitrile of the intermediates in the decomposition of N-nitroso-N-decalylamides,<sup>8</sup> we have had occasion to determine the stereochemistry of the silver assisted solvolysis of trans-trans-2-bromodecalin (1, X=Br) in acetonitrile. Treatment of trans-cis-2-decalol (2, X=OH) with phosphorus pentabromide in methylene chloride provided a decalyl bromide fraction containing 90% of the axial trans-trans-2-bromodecalin (1; X=Br) and 10% of another, presumably rearranged, isomer,<sup>9</sup> the mass spectra of the two isomers were essentially identical and the nmr spectrum of the major component exhibited a peak typical of an equatorial carbinyl hydrogen of a cyclohexyl bromide (neat liquid,  $\tau$  5.40, width at half height 7 Hz, for cis-4-t-butylcyclohexyl bromide the corresponding nmr absorption occurs at  $\tau$  5.42<sup>10</sup>). A bromide mixture consisting of 95% 1(X=Br) and 5% of an unidentified component was prepared by reaction of the equatorial mesylate (2, X=CH<sub>3</sub>SO<sub>3</sub>) with lithium bromide in acetone.<sup>10</sup> When either bromide mixture (0.029 M) was

treated with silver perchlorate (0.029 M) in a refluxing homogeneous acetonitrile solution and the product mixture was quenched with water, there was obtained a mixture of *N*-decalyl-acetamides which, within experimental error, contained the same proportion of the axial *N*-(*trans-trans*-2-decalyl)acetamide (1, X=CH<sub>3</sub>CONH)<sup>11</sup> as the proportion of *trans-trans*-bromide (1, X=Br) in the bromide mixture (Table I). The major product was found by coinjection to have identical retention times with those of an authentic sample<sup>11b</sup> on three glpc columns.



In order to examine the possibility<sup>3</sup> that perchlorate ion may have executed a backside displacement of the bromide ion (coordinated to silver ion) and that the resulting alkyl perchlorate had been solvolyzed with inversion of configuration, the bromide mixture containing 95% of the axial bromide (1, X=Br) was subjected to the action of silver tetrafluoroborate in refluxing acetonitrile, once again, the *N*-decalylacetamide product contained about the same proportion of the 2-axial isomer as did the starting material (Table I).

Table I

Steric Results of Silver Ion Assisted Solvolysis of *trans,trans*-2-DecalylBromide (1; X=Br) in Acetonitrile

Run	Silver counterion	Percent <u>1</u> (X=Br) in alkyl bromide	Percent <u>1</u> (X=CH <sub>3</sub> CONH) in <i>N</i> -decalylacetamide <sup>d</sup> product
1. <sup>a</sup>	ClO <sub>4</sub> <sup>-</sup>	90	89
2. <sup>b</sup>	ClO <sub>4</sub> <sup>-</sup>	95	93
3. <sup>c</sup>	BF <sub>4</sub> <sup>-</sup>	95	93
4. <sup>c</sup>	BF <sub>4</sub> <sup>-</sup>	95	94

<sup>a</sup>192 hrs., total yield of amides, 54%. <sup>b</sup>120 hrs., total yield of amides, 63% <sup>c</sup>120 hrs.

<sup>d</sup>by glpc

In the first run described in the table the amide product mixture was monitored throughout the reaction and its composition was found to be invariant with time indicating that the reactants do not isomerize during the course of the reaction, that the products are

stable to the reaction conditions, and that the precipitated silver bromide does not influence the steric course of the solvolysis. The latter conclusion is consistent with the report that the silver bromide product does not alter the rate of reaction of 2-octyl bromide with silver nitrate.<sup>3</sup>

It appears that the displacement of the axial bromide by acetonitrile occurs with overwhelming retention of configuration.<sup>12</sup> It is clear that this is an extremely unusual solvolysis in view of the high degree of inversion of configuration that has consistently been observed in the solvolysis of both axial and equatorial cyclohexyl sulfonates.<sup>14,15</sup> The high ratio of substitution to elimination is also noteworthy (Table I) since solvolysis of axial compounds nearly always give very predominant elimination.<sup>14</sup>

At least three factors may be involved in the stereochemical result, the weak nucleophilicity of acetonitrile,<sup>4,16,17</sup> the presence of perchlorate or tetrafluoroborate ions on the backside of the carbon atom from which the halogen is being removed<sup>2,18</sup> (providing steric hindrance to solvent attack) and the ability of acetonitrile to complex the silver ion<sup>19</sup> which removes the halogen. With regard to this last effect, it may be that the binding of the bromide to the silver ion weakens the bond between the latter and the acetonitrile ligands, thus allowing one of these ligands to attack the developing carbonium ion from the front side. This concept would place this displacement in the category of an S<sub>N</sub>1 reaction and, as will be reported later, the solvolysis of decalyl N-nitrosocarbamates in acetonitrile, a process believed to proceed by an S<sub>N</sub>1 mechanism,<sup>8</sup> also furnishes a large proportion of retained solvent-derived product.<sup>7</sup> The low degree of elimination may also be due to the weak basicity of the solvent.

#### Footnotes and References.

1. Andrew Mellon Predoctoral Fellow.
2. G. S. Hammond, M. F. Hawthorne, J. H. Waters, and B. M. Graybill, J. Amer. Chem. Soc. 82, 704 (1960).
3. Y. Pocker and D. N. Kevill, ibid. 87, 4760, 4771, 4778 (1965).
4. N. Kornblum and D. E. Hardies, ibid. 88, 1707 (1966).
5. R. A. Bartsch and G. M. Pruss, J. Org. Chem. 37, 458 (1972).
6. L. I. Krimen and D. J. Cota, Org. Reactions 17, 213 (1969).
7. J. Solash, Ph.D. Thesis, University of Pittsburgh, 1972

8. T. Cohen, A. R. Daniewski, G. M. Deeb, and C. K. Shaw, J. Amer. Chem. Soc. 94, 1786 (1972); T. Cohen and A. R. Daniewski, ibid. 91, 533 (1969).
9. This method was reported to yield inverted bromide in addition to a small quantity of rearranged bromide from trans-4-t-butylcyclohexanol. E.L. Eliel and R. G. Haber, J. Org. Chem. 24, 143 (1959).
10. E. L. Eliel and J. L. Martin, J. Amer. Chem. Soc. 90, 689 (1968).
11. a) W. G. Dauben, R. C. Tweit, and C. Mannerskantz, ibid. 76, 4220 (1954), b) J. L. Pinkus, G. Pinkus, and T. Cohen, J. Org. Chem. 27, 4356 (1962).
12. It should be noted that the major product could also result from an axial C3 to C2 hydride migration with configurational retention at the migration origin, although nearly complete rearrangement in this type of system would be extremely surprising.<sup>13,14</sup> However, this must not be a major source of the 2-axial acetamide since such a migration would almost certainly result in the production of 1-axial acetamide, as well, formed by an analogous hydride shift from the 1-position,<sup>13</sup> extensive experience with decalin derivatives suggests that the latter amide would elute before the 2-axial isomer and would thus be easily detectable.
13. A. D. Botelho, Ph.D. Thesis, University of Pittsburgh, 1970.
14. S. Winstein and N. J. Holness, J. Amer. Chem. Soc. 77, 5562 (1955).
15. Unpublished work of M. Malaiyandi cited in footnote 31b of ref. 11b.
16. C. E. Boozer and E. S. Lewis, J. Amer. Chem. Soc. 75, 3182 (1953).
17. A. F. Diaz and S. Winstein, ibid. 86, 5010 (1964).
18. Pocker and Kevill<sup>3</sup> found that at the concentration of silver salt used here (0.029 M) the solvolysis of 2-octyl bromide in acetonitrile was of order 1.2 in silver perchlorate.
19. I. M. Kolthoff and J. F. Coetsee, ibid. 79, 1852 (1957).