To the extent that *cis*-decalin systems can be obtained *via* the α-haloketal cyclization, the process is complementary to the Nagata process;[9] *cis*-9-cyano-2-decalones are available by our method and the trans isomers by Nagata's.

We consider in an accompanying communication[13] the factors which lead to *cis*-decalin stereochemistry and the situations in which this result can be altered or reversed.[14]

(13) Gilbert Stork and Robert K. Boeckman, Jr., *J. Amer. Chem. Soc.*, **95**, 2016 (1973).

(14) We thank the National Science Foundation and the National Institutes of Health for their support of this work.

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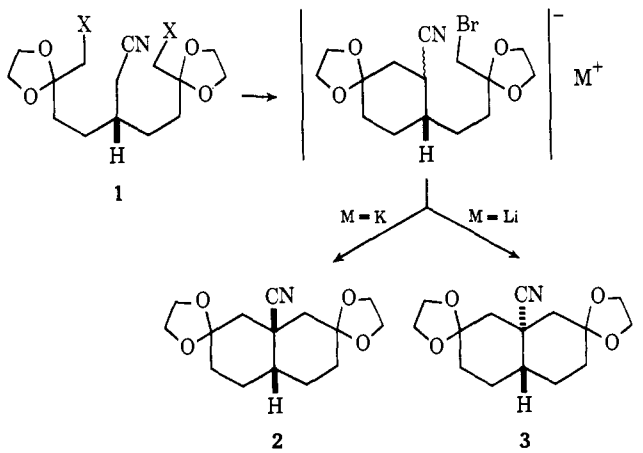
## Mechanism and Stereochemical Control in the α-Haloketal Cyclization. A Remarkable Effect of Metal Cations

*Sir:*

We report in an accompanying communication[1] that *cis*-decalin and hydrindan systems are formed in high yields from suitable α-haloketal nitriles and esters (Scheme I).

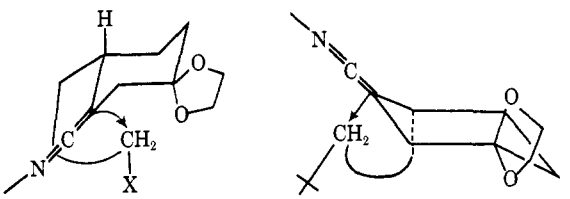
**Scheme I**




We have made the surprising observation that whereas, as previously reported,[1] the cyclization of **1** (X = Br) with *potassium* hexamethyldisilazane in benzene leads, in high yield, to a mixture consisting of 95% of the *cis*-decalin (**2**), mp 108–109°, the use of *lithium* hexamethyldisilazane, also in benzene, leads to a complete reversal of stereochemistry and the formation of a mixture which now consists of 95% of the *trans*-decalin (**3**), mp 163–164°. This is, to our knowledge, the most dramatic effect yet encountered of the metal cation on the stereochemistry of an alkylation.

Before passing to a discussion of the mechanism of the cyclization, we draw attention to further remarkable observations relating to the control of stereochemistry in the formation of **2** and **3**. First, changing the departing group in **1** from chloride to bromide to iodide had very little effect on the stereochemical result, with either the potassium or sodium base. Even with the lithium base, we only observed a change in product composition from 70% trans from **1** (X = Cl) to 90% trans from the corresponding dibromide or diiodide. In striking contrast, cyclization of the ditosylate **1** (X = OTs) with the same lithium base changed the product composition to 90% *cis*-decalin (**2**). Second, cyclization of the bis(chloroketal) with the lithium base in tetrahydrofuran, rather than in benzene, changes the product ratio from 70:30 in favor of the *trans*-decalin (**3**) to 80:20 in favor of the *cis*-decalin (**2**).

In considering the mechanism of these cyclizations, two possibilities come to mind. If the chain is equatorial at the transition state, the formation of a *cis*-decalin requires that it enter from the axial side at the nitrile α carbon (*cf.* **4**). Conversely, if the transition-state




**4** **5**

conformation of the chain is axial (*cf.* **5**), the formation of a *cis*-decalin requires equatorial side connection to that same α carbon.

The first possibility is, *a priori*, unlikely because closure of the chain would produce strong 1,3-diaxial interaction with one of the ring ketal oxygens as shown in **4**. In spite of this, cyclization of the bromoketal **6**, in


**6** **7**

which axial entry would not be subject to such an interaction, actually gives *less* cis cyclization (to **7**) than is obtained from **1** (X = Br) under the same conditions (cis:trans ratio = 83:17 and 95:5, respectively).

The second possibility was demonstrated to be the correct one by showing that no *cis*-decalin results when the cyclizing chain is constrained to an equatorial position. This is achieved in the bicyclic bromoketal **9**, synthesized as shown in Scheme II,[2] in which there is a considerable barrier to axial orientation of the chain since such an orientation would require a boat (or twist) conformation of the ring to which it is attached.[3,4]

Cyclization of **9** with potassium hexamethyldisilizane in benzene, conditions which give very largely *cis*-deca-

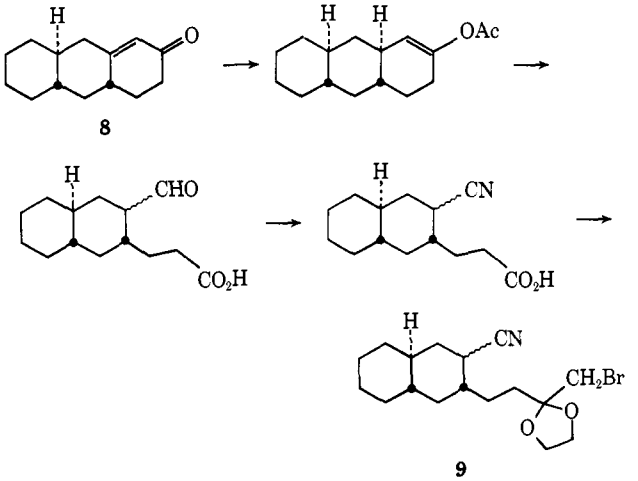
(1) G. Stork, J. O. Gardner, R. K. Boeckman, Jr., and K. A. Parker, *J. Amer. Chem. Soc.*, **95**, 2014 (1973).

(2) The starting enone **8** was made by pyrrolidine enamine annelation of *trans*-2-decalone (G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Amer. Chem. Soc.*, **85**, 207 (1963)), followed by enolate trapping (G. Stork, P. Rosen, N. Goldman, R. V. Coombs, and J. Tsuji, *ibid.*, **87**, 275 (1965)) with acetic anhydride (*cf.* G. Stork, M. Nussim, and B. August, *Tetrahedron Suppl.*, **8**, 105 (1966)), ozonolysis to the aldehyde acid, and transformation of the related nitrile acid to **13** *via* the diazoketone route. This sequence was selected to establish rigorously the stereochemistry of the chain in **9**.

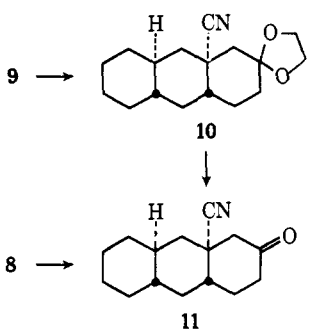
(3) This barrier might be of the order of 5–6 kcal/mol; *cf.* E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, p 206.

(4) For the use of this approach, albeit in a mechanistically unrelated case, *cf.* P. T. Lansbury, P. C. Briggs, T. R. Demmin, and G. E. DuBois, *J. Amer. Chem. Soc.*, **93**, 1311 (1971).

**Scheme II**



lin from **6**, now gives a single product **10**, mp 105–106°. This anthracene derivative was shown to be trans by the identity of the corresponding ketone **11**, mp 93–94°, with the sole product of diethylaluminum cyanide addition to the enone **8**, mp 70–72°, a process which is well

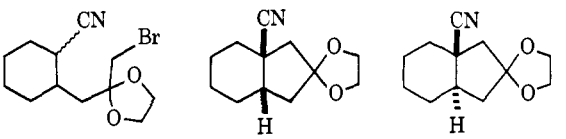


established to lead to *trans*-decalin systems.[5]

It is thus clear that, when no special constraints prevent it, cyclization to a six-membered ring is more rapid from an axially held haloketal chain, and a *cis*-decalin results, *e.g.*, **1** → **2**.

The haloketal chain may, however, be forced to assume an equatorial conformation either, as in **9**, because of conformational restrictions, or because the rather large distance at which proper alignment of the departing halide, the alkylating methylene, and the trigonal nucleophilic center can be achieved is not compatible with a particular transition state. This becomes a factor with transition states involving tight lithium ion pairs in benzene, in which the closer approach now required of the relevant centers can be reached only with the chain equatorial. Completion of the ring by approach from either the equatorial or axial side is geometrically feasible and therefore leads to equatorial side closure and a *trans*-decalin (**1** → **3**). It should conversely follow that, with this same lithium salt, loosening the ion pair by solvating the cation (*e.g.*, with tetrahydrofuran or with a dipolar departing group like tosylate) again allows transition states in which the chain can cyclize from an axial position, with the formation of a *cis*-decalin.

On the other hand, the closure of a five-membered ring to form a hydrindan should lead to cis stereochemistry, regardless of the equatorial/axial attachment of the chain. Models show that the deformation required in either case for the proper orientation of the entering methylene can be achieved readily only in transition states leading to the cis product. It is thus found that the haloketal nitrile **12** which gives (94% yield) the cis and trans products **13** and **14** in a ratio of 89 to 11, respectively, with potassium hexamethyldisilazane in benzene (8 hr at room temperature) gives almost the same stereochemical result (**13**:**14** = 80:20) with the lithium base (benzene, 17 hr, room temperature).[6]



Although the mechanistic considerations given here can only be considered tentative, it is clear that the nature of the cation must be added to the several other factors which can have a profound effect on the stereochemistry of alkylation reactions.[7]

(5) W. Nagata, M. Yoshioka, and T. Terasawa, *J. Amer. Chem. Soc.*, 94, 4672 (1972).

(6) These experiments were performed by Mr. Rick Danheiser.

(7) We thank the National Science Foundation and the National Institutes of Health for their support of this work.

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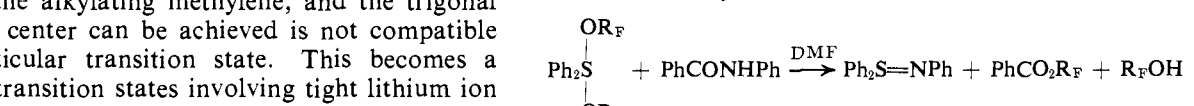
## Sulfuranes. X. A Reagent for the Facile Cleavage of Secondary Amides[1]

*Sir:*

The reaction of diphenyldialkoxysulfurane (**1**) (where $OR_F$ is $OC(CF_3)_2Ph$) with a suitable substituted secondary amide results in a uniquely facile single-step cleavage of the amide at room temperature or below. For example, the very clean cleavage of benzanilide with 0.5 *M* **1** in dimethylformamide (DMF) solvent to give sulfilimine **2** and benzoate ester **3** is observed to be essentially complete in 3 min in an nmr tube at probe temperature, 41°. No evidence is seen for reaction of **1** with the tertiary amide solvent.



Sulfilimine **2** (mp 109.5–110.5°), which was isolated in 72% yield from this reaction in ether,[2] was independently synthesized by the direct reaction of **1** with aniline in ether at room temperature. It was characterized by elemental analysis and ir, nmr, and mass spectrometry. It is rapidly hydrogenolyzed over 5% Pd–C in ethanol to give diphenyl sulfide and aniline. The ester is easily saponified in ethanolic KOH.

The other sulfilimines listed in Table I were also in-

(1) For paper IX in this series, see L. J. Kaplan and J. C. Martin, *J. Amer. Chem. Soc.*, **95**, 793 (1973).

(2) This compound was reported by W. C. Smith, C. W. Tullock, R. D. Smith, and V. A. Engelhardt, *ibid.*, **82**, 551 (1960), to be formed in the reaction of phenyllithium and phenyliminosulfur difluoride, but the compound was not isolated and was characterized only by the mixture infrared spectrum (details not reported).