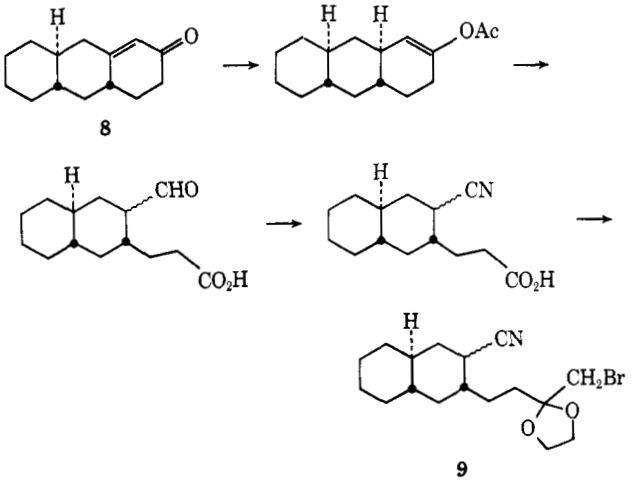
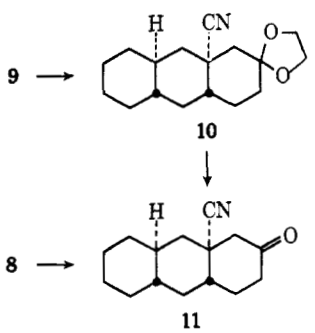
Scheme II



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

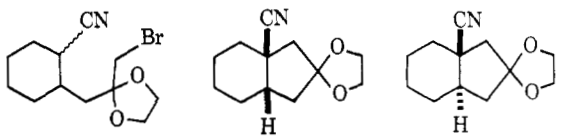


established to lead to *trans*-decalin systems.[5]

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, re-



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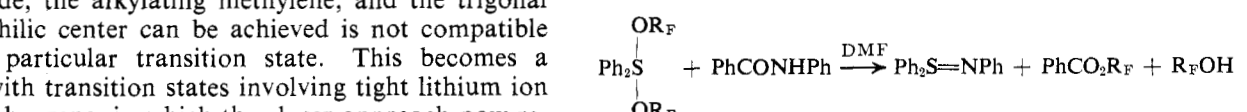
Sulfuranes. X. A Reagent for the Facile Cleavage of Secondary Amides[1]

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).

Table I. Reactions of Amides[a] with **1**

Amide	Solvent	Products[b]	Yield,[c] %	Reaction time[d]
$PhCONHCH_3$	$CDCl_3$	$PhCO_2R_F$	97	Fast[e]
		$Ph_2SNCH_3 \cdot HOR_F$	97, 61[f]	
PhCONHPh	$CDCl_3$, DMF, Et_2O, pyridine-d_5	$PhCO_2R_F$	99	<3 min
		Ph_2SNPh	99, 72[f]	
$CH_3CONHPh$	$CDCl_3$, DMF	$CH_3CO_2R_F$	62	<3 min
		Ph_2SNPh[g]	<35	
		$Ph_2SCHCO_2R_F$[g]	24	
CH_3CONH-*n*-C_4H_9	$CDCl_3$	$CH_3CO_2R_F$	47	10 min
		Ph_2SN-*n*-C_4H_9	47	
		n-$C_4H_9N{=}C(OR_F)CH_3$[h]	49	
$CH_3CONHCH(CH_3)_2$	$CDCl_3$	$(CH_3)_2CHN{=}C(OR_F)CH_3$[h]	94	20 min
$PhCONH$-*n*-C_4H_9	$CDCl_3$	$PhCO_2R_F$	61	2 hr
		Ph_2SN-*n*-C_4H_9	61	
		n-$C_4H_9N{=}C(OR_F)Ph$	36	
$(CH_3)_3CCONHPh$	$CDCl_3$	$PhN{=}C(OR_F)C(CH_3)_3$[h]	96	2.5 hr
		$(CH_3)_3CCO_2R_F$	Trace	
		Ph_2SNPh	Trace	
$PhCONHCH_2Ph$	$CDCl_3$	$PhCO_2R_F$	>50, 42[f]	3 hr
		Ph_2S	71[f]	
		$PhCONH_2$	28[f]	
		PhCN	>20[i]	
		PhCHO	23[i]	
$PhCONHCH_2Ph$	$CDCl_3$	$PhCO_2R_F$	94	3 hr
		$Ph_2SNCH_2Ph \cdot HOR_F$	94[f]	
$PhCONHCH(CH_3)_2$	$CDCl_3$	$(CH_3)_2CHN{=}C(OR_F)Ph$	96	6 hr
$(CH_3)_3CCONH$-*n*-C_4H_9	$CDCl_3$	*n*-$C_4H_9N{=}C(OR_F)C(CH_3)_3$	99	49 hr
$(CH_3)_3CCONHC(CH_3)_3$	$CDCl_3$			No reaction

[a] Using 0.54 *M* **1** and 0.27 *M* amide in $CDCl_3$ for each reaction. [b] In addition to R_FOH and unreacted **1** or, in the reactions leading to imidates, Ph_2SO. [c] Determined by nmr analysis of ^{19}F and ^1H spectra. All peaks were assigned and integrated. [d] Time for 50% reaction at room temperature, *ca.* 25°. [e] Reacts rapidly at 0°. [f] Yield by isolation based on amide in a preparative scale reaction. [g] Isolated and characterized from a preparative scale reaction in ether. [h] Identified by ir and ^{19}F and ^1H nmr but not independently prepared. [i] Yield determined by glpc.

dependently prepared and isolated (as the R_FOH complexes) by the reaction of **1** with the appropriate amine. The sulfilimines are freed from their complexes by dissolving them in chloroform and extracting R_FOH into 20% aqueous NaOH. Recrystallization yields pure sulfilimine. All esters were identified by comparison with authentic samples prepared by the reaction of R_FOK with the appropriate acid chlorides. Primary amides and sulfonamides do not undergo the cleavage reaction but give *N*-acyl and *N*-sulfonyl sulfilimines. Thus the preparative scale reactions of benzamide and *p*-toluenesulfonamide with sulfurane **1** give *N*-benzoyl- or *N*-*p*-toluenesulfonylsulfilimine[3] in excellent yields.

The amides in Table I are arranged in order of decreasing rates of reaction with **1**. This order corresponds roughly to the order of increasing steric hindrance about the amide function, with the rate of reaction being sensitive to steric bulk of either the N-alkyl group or the acyl group.

A less regular dependence on steric bulk is seen for the degree of intrusion of a competing second reaction leading to imidate products. Authentic imidates were prepared for comparison by the reaction of KOR_F with the imidoyl chloride from the reaction of a secondary amide with $SOCl_2$.[4] The imidates of Table I are directly hydrolyzed in aqueous DMF primarily to regenerate the amide. Treatment of one of these imidates with methanol–H_2SO_4 rapidly provides the methyl imidate which is hydrolyzed in aqueous methanol during *ca.* 2 hr of standing at room temperature to give the methyl ester and the free amine.

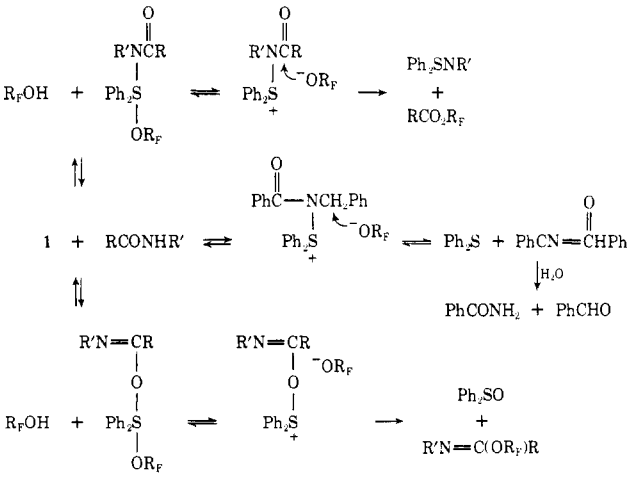
(3) A. Kucsman, I. Kapovits, and M. Balla, *Tetrahedron*, **18**, 75 (1962).

(4) I. Ugi, F. Beck, and U. Fetzer, *Chem. Ber.*, **95**, 126 (1962).

In its reaction with *N*-benzylbenzamide, **1** also acts as an oxidizing agent, forming benzonitrile and a Schiff's base which is hydrolyzed to benzamide and benzaldehyde.[5]

We favor a mechanistic scheme for these reactions related to that postulated[6] for the reaction of **1** with alcohols (Scheme I). The ligand exchange reaction in-

Scheme I



volving the ambident amides can introduce either an oxygen-centered ligand (leading to imidate) or a nitrogen-centered ligand (leading to amide cleavage or, for species with relatively acidic protons α to nitrogen, to oxidation products).

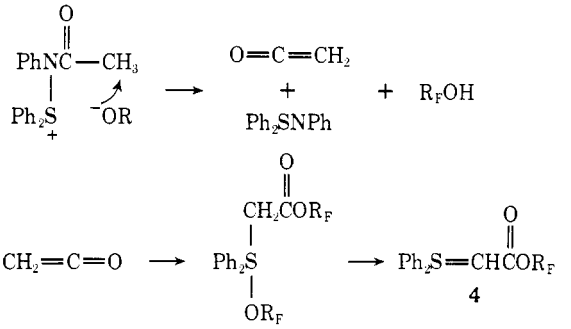
The reaction of **1** with secondary amides to form

(5) This reaction and other reactions of sulfurane-derived sulfilimines are the subject of a separate paper, manuscript in preparation.

(6) J. C. Martin and R. J. Arhart, *J. Amer. Chem. Soc.*, **93**, 2339, 2341 (1971); R. J. Arhart and J. C. Martin, *ibid.*, **94**, 4997, 5003 (1972).

imidates is mechanistically related to the alternative two-step routes which generate from the amide a more readily hydrolyzable species, by treatment with thionyl chloride,[7,8] phosphorus pentachloride,[9] or triethyloxonium fluoroborate,[10] after which the amide is liberated by acidic hydrolysis.

The reaction of **1** with acetanilide gives, in addition



to sulfilimine **2** and the acetate ester analogous to **3**, 24% of ylid **4**, which was isolated and characterized by elemental analysis, mass spectrometry, and ^{1}H and ^{19}F nmr and infrared spectroscopy. Since the acetate ester is stable in the presence of sulfurane **1** and sulfilimine **2**, it cannot serve as a precursor to **4**. We suggest that ketene, formed directly from acetanilide and **1**, reacts with another molecule of sulfurane to give **4**.

The reaction of sulfurane **1** with secondary amides, when combined with the reduction of the sulfilimines (or R_FOH complexes of sulfilimines) to free amines[11] and the acid hydrolysis of imidates, is a cleavage reaction of general applicability. Since the sulfurane reacts rapidly with active hydrogen compounds (*i.e.*, alcohols, amines, and carbon acids such as malonic esters), these functional groups must be protected if the cleavage of a multifunctional amide is attempted. The mild conditions for the cleavage by **1**, the high overall yields observed and the pattern of selectivities which is emerging, make further studies of this reaction very appealing. Applications to peptide links are currently being studied in our laboratory.

Acknowledgment. This work was supported in part by grants from the National Science Foundation (GP 30491X) and a grant used to purchase a 220-MHz nmr spectrometer and in part by a grant from the National Institutes of Health (CA13963).

(7) J. v. Graun and W. Pinkernelle, *Chem. Ber.*, **67**, 1218 (1934).
(8) G. D. Lander, *J. Chem. Soc.*, **81**, 591 (1902).
(9) H. W. O. Weissenberger and M. G. van der Hoeven, *Recl. Trav. Chim. Pays-Bas*, **89**, 1081 (1970).
(10) S. Hanessian, *Tetrahedron Lett.*, 1549 (1967).
(11) For examples of reduction of *N*-*p*-toluenesulfilimines to sulfides and *p*-toluenesulfonamide, see M. A. McCall, D. S. Tarbell, and M. A. Havill, *J. Amer. Chem. Soc.*, **73**, 4476 (1951).

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Ion–Solvent and Ion–Ion Interactions. Solvent Effects on ^{27}Al–^{13}C Spin–Spin Coupling in $NaAlR_4$ Salts

Sir:

There has been considerable research in recent years seeking to understand the nature and properties of species present in solutions of alkali metal salts. A broad variety of solvents has been employed in these studies, with the consequent determination that ion–ion interactions, which are relatively insignificant in solvents of high polarity, exert an increasingly profound effect as the solvating ability and the dielectric constant of the solvent decrease. Direct observation of the extent to which the cation is solvated has been achieved by examining the spectral properties of either the complexing agent[1] or, in favorable cases, the cation[2] itself. Indirect inference of the extent of cation solvation has been accomplished by consideration of the degree to which ion–ion interactions are reflected in the spectral properties of the anion.[3] Since the nature of the ionic species in solution is determined both by ion–solvent and by ion–ion interactions, the ideal experiment would allow one to observe cation solvation and anion involvement in the same system and to employ solvents representing the broadest possible spectrum of dielectric and complexing properties.

Several laboratories[3b,c,e] have studied the ^{27}Al–^{1}H spin–spin coupling interaction in solutions of tetraalkylaluminate salts. The dependence of this interaction on the degree of electrical dissymmetry about the quadrupolar aluminum nucleus can be used to evaluate, by pmr spectroscopy, the solvation of these salts. Extension of these studies is limited, however, by the fact that the tetraalkylaluminate salts exhibiting interpretable pmr spectra show only very limited solubility in noncoordinating solvents, whereas the corresponding information in the pmr spectrum of sodium tetra-*n*-butylaluminate ($NaAlBu_4$), which exhibits satisfactory solubility characteristics[1a,4] in an extremely broad range of solvents, is inaccessible because of inadequate proton resonance separation.

In an effort to determine the feasibility of extending the nmr technique to $NaAlBu_4$, we measured the heteronuclear proton noise decoupled ^{13}C nmr (cmr) spectra (Figure 1) of $NaAlBu_4$, together with those of the well-characterized analog $NaAlEt_4$, in the strongly coordinating solvent DMSO and in the effectively noncoordinating solvent benzene. Several important features are evident in these spectra.

Firstly, the methylene α-carbon resonances of both $NaAlBu_4$ and $NaAlEt_4$ in DMSO are observed as evenly spaced, six-line multiplets from which the values of $^{1}J_{^{27}Al,^{13}C}$ (=71.6 Hz) recorded on traces 1 and 2 in Figure 1 may be measured. Although heteronuclear couplings to carbon-13 nuclei are a relatively common[5]

(1) (a) E. Schaschel and M. C. Day, *J. Amer. Chem. Soc.*, **90**, 503 (1968); (b) R. H. Ehrlich and A. I. Popov, *ibid.*, **93**, 5620 (1971); (c) E. G. Höhn, J. A. Olander, and M. C. Day, *J. Phys. Chem.*, **73**, 3880 (1969).
(2) (a) E. G. Bloor and R. G. Kidd, *Can. J. Chem.*, **46**, 3425 (1968); (b) R. H. Ehrlich, E. Roach, and A. I. Popov, *J. Amer. Chem. Soc.*, **92**, 4989 (1970); (c) A. M. Grotens, J. Smid, and E. DeBoer, *Chem. Commun.*, 759 (1971).
(3) (a) T. E. Hogen Esch and J. Smid, *J. Amer. Chem. Soc.*, **88**, 307 (1966); (b) E. S. Gore and H. S. Gutowsky, *J. Phys. Chem.*, **73**, 2515 (1969); (c) J. F. Ross and J. P. Oliver, *J. Organometal. Chem.*, **22**, 503 (1970); (d) W. F. Edgell, J. Lyford, A. Barbetta, and C. I. Tose, *J. Amer. Chem. Soc.*, **93**, 6403 (1971); (e) T. D. Westmoreland, Jr., N. S. Bhacca, J. D. Wander, and M. C. Day, *J. Organometal. Chem.*, **38**, 1 (1972).
(4) J. A. Olander and M. C. Day, *J. Amer. Chem. Soc.*, **93**, 3584 (1971), and references therein.
(5) (a) E. F. Mooney and P. H. Winson, *Annu. Rev. NMR (Nucl. Magn. Resonance) Spectrosc.*, **2**, 153 (1969); (b) A. Allerhand and E. A. Trull, *Annu. Rev. Phys. Chem.*, **21**, 317 (1970); (c) P. S. Pregosin and E. W. Randall in "Determination of Organic Structures by Physical Methods," Vol. 3, F. C. Nachod and J. J. Zuckerman, Ed., Academic Press, New York, N. Y., 1971; (d) G. C. Levy and G. L. Nelson, "Carbon-13 NMR for Organic Chemists," Interscience, New York, N. Y., 1972.