

active. However, they did not measure the parent compound itself. Our results for mandelic acid in dioxane solution are shown in Figure 3. A negative Cotton effect is observed which crosses the zero axis at 224 m μ . No anomalous dispersion is found in the benzene absorption region.^{8a} The optically active absorption band controlling the dispersion may be the first absorption band of the carboxyl group or the second absorption region of the phenyl group.

Because of the contributions of other chromophoric groups in the molecule, the effective rotatory dispersion of the benzene chromophore may be very small (methylphenylcarbinol) or unobservable (mandelic acid). Accordingly, we examined the o.r.d. of 2-phenylbutane (IV)⁹ as an example of a molecule with a benzene ring at the asymmetric center but containing no other chromophore which could contribute appreciably to the rotatory dispersion. The results are shown in Figure 4. A very small but real Cotton effect is observed at 263 m μ . From the data of Benson, Kenyon, and Shepherd¹⁰ on the rotation of 2-phenylbutane in the visible region, a λ_0 of 233 m μ is calculated. We have measured the rotation directly to 230 m μ . The o.r.d. curve rises very steeply in this region and it is possible that a Cotton effect lies at somewhat shorter wave length.

The results obtained with 2-phenylbutane indicate that the o.r.d. curves of open chain compounds may be due to the superposition of the spectra of several rotational isomers.¹¹ Further, the rotatory contributions of various conformations may be markedly different.^{11,12}

Acknowledgment. The encouragement and advice of Professor Andrew Streitwieser, Jr., are very gratefully acknowledged.

(8a) NOTE ADDED IN PROOF. Dirkx and Sixma recently measured the o.r.d. of II in 0.1 N HCl. Their results are in agreement with ours: I. P. Dirkx and F. L. J. Sixma, *Rec. trav. chim.*, **83**, 522 (1964).

(9) Kindly donated by Professor H. S. Mosher. The 2-phenylbutane was purified by g.l.p.c. (polybutylene glycol column) and had $[\alpha]_D +23.70^\circ$.

(10) P. W. Benson, J. Kenyon, and J. R. Shepherd, *J. Chem. Soc.*, 658 (1926).

(11) K. M. Wellman and C. Djerassi, *J. Am. Chem. Soc.*, **87**, 60 (1965).

(12) A variable-temperature c.d. study is in progress with Professor C. Djerassi and Dr. E. Bunnenberg.

(13) (a) U. S. Public Health Service Postdoctoral Fellow, 1963-1964; (b) address correspondence to Department of Chemistry, State University of New York at Binghamton, Binghamton, N. Y.

Lawrence Verbit¹³

Department of Chemistry, University of California
Berkeley, California

Received February 2, 1965

Optically Active R₃Si*Li from Lithium Metal Cleavage of an Optically Active Disilane

Sir:

The synthesis of optically active neo-C₅H₁₁Ph-MeSi*Li, neopentylphenylmethylsilyllithium, involved the preparation of optically active neo-C₅H₁₁PhMeSi*-SiMePh₂ according to eq. 1.

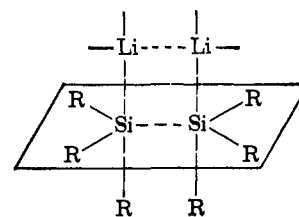
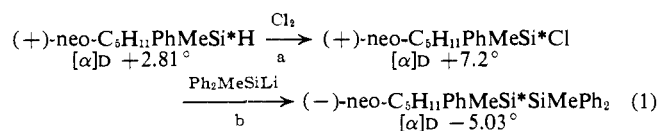
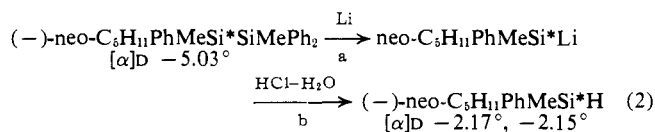


Figure 1. Representation of a proposed model for the lithium metal cleavage of a hexaorganodisilane, having over-all trigonal bipyramidal geometry at each silicon atom and concerted breaking of Si-Si and formation of two Si-Li bonds.

Treatment of the levorotatory disilane with shiny lithium foil in tetrahydrofuran solvent at 0° for 6 hr. gave the optically active silyllithium as a green-brown solution. Addition of the latter to a mixture of dilute hydrochloric acid and ether yielded optically active (-)-silane according to eq. 2. Duplicate runs on



portions of the same optically active disilane gave product R₃Si*H having $[\alpha]_D -2.17$ and -2.15° .

Present assignment of *retention* of configuration for reaction 2a is based on: previous¹ assignment of *retention* to reaction 1a; *inversion* for 1b based on general inversion for R₃Si*Cl with strong nucleophiles² including R'Li³; *retention* for (2b) which is an electrophilic displacement on silicon free from any special features which might lead to inversion.

To our knowledge stereospecific reaction of an active metal with a metaloid-metaloid bond to give an optically active compound, as in (2a), is unique, and our rationale of retention of configuration for this reaction involves operation of a quasi-cyclic four-center mechanism⁴ whose geometry approximates that shown in Figure 1.

Gilman and his students have contributed many excellent studies of the preparation of R₃SiLi from lithium metal cleavage of R₃SiSiR₃, and the present work should aid in the interpretation of their results.⁵

The present results show that neopentylphenylmethylsilyllithium, like the recently reported α -naphthylphenylmethylgermyllithium,⁶ has considerably enhanced optical stability relative to simple acyclic alkylsilyllithium compounds, such as *sec*-butyllithium, in solvents such as tetrahydrofuran.⁷

(1) L. H. Sommer, K. W. Michael, and W. D. Korte, *J. Am. Chem. Soc.*, **85**, 3712 (1963).

(2) L. H. Sommer, C. L. Frye, G. A. Parker, and K. W. Michael, *ibid.*, **86**, 3271 (1964).

(3) A. G. Brook and C. M. Warner, *Tetrahedron Letters*, 815 (1962); L. H. Sommer, P. G. Rodewald, and G. A. Parker, *ibid.*, 821 (1962).

(4) Quasi-cyclic mechanisms for nucleophilic displacements on asymmetric silicon have been proposed for retention reactions: cf. L. H. Sommer, C. L. Frye, and G. A. Parker, *J. Am. Chem. Soc.*, **86**, 3271 (1964). In the present work nucleophilic displacement at both silicon atoms in the disilane is impossible, and the cleavage of Si-Si may be either heterolytic or homolytic, but bond-breaking of Si-Si and bond-making of two R₃SiLi species is postulated to be concerted.

(5) For a review see: H. Gilman and H. J. S. Winkler in H. Zeiss, "Organometallic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1960, Chapter 6.

(6) A. G. Brook and G. J. D. Peddle, *J. Am. Chem. Soc.*, **85**, 2338 (1963). Synthesis of the germyllithium used a procedure not applicable to preparation of R₃Si*Li, e.g., *n*-BuLi and R₃Ge*H.

(7) D. Y. Curtin and W. J. Koehl, *ibid.*, **84**, 1967 (1962).

Reaction Ia has been reported,¹ and methylphenylsilyllithium, prepared from the disilane,⁸ was added to an ether solution of the (+)-chlorosilane and gave the (-)-disilane (*Anal. Calcd.*: C, 77.25; H, 8.30; Si, 14.45. *Found*: C, 77.40; H, 8.21; Si, 14.45) as a clear colorless liquid having $[\alpha]_D -5.03^\circ$ (*c* 6.3, benzene), in 82% yield after purification by chromatography over silica gel. In reaction sequence 2, a solution of (-)-disilane in tetrahydrofuran was added all at once to shiny lithium foil at 0° in an atmosphere of dry oxygen-free nitrogen. After 6 hr. of stirring the reactants, the solution of R_3Si^*Li in THF was syringed out of the flask and into a mixture of ether and dilute hydrochloric acid. Fractional distillation gave 50–60% yields of optically active neopentylphenylmethylsilane, R_3Si^*H .

Acknowledgment. We thank Dow Corning Corporation for continued generous support.

(8) H. Gilman and G. D. Lichtenwalter, *J. Am. Chem. Soc.*, **80**, 608 (1958).

Leo H. Sommer, Richard Mason

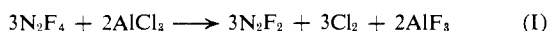
Whitmore Laboratory, The Pennsylvania State University
University Park, Pennsylvania

Received February 1, 1965

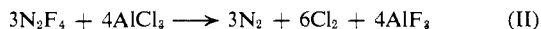
Preparation of *trans*-Difluorodiazine

Sir:

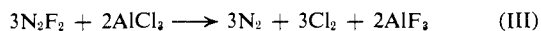
Pure *trans*-difluorodiazine can readily be prepared in about 45% yield from commercially available tetrafluorohydrazine and aluminum chloride.



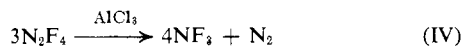
Reaction I is invariably accompanied by the formation of elementary nitrogen which accounts for the bulk of the N_2F_4 used.



The product N_2F_2 is also relatively slowly reduced by $AlCl_3$ to give elementary nitrogen and chlorine.



An additional undesirable reaction which may occur is the disproportionation of N_2F_4 to give nitrogen and NF_3 .



Reaction IV proceeds almost quantitatively at room temperature in the presence of trace quantities of $AlCl_3$.

Fortunately, both reactions III and IV can be inhibited effectively by adjusting conditions of temperature and pressure, respectively. Reaction III is extremely slow at -80° while reactions I, II, and IV are still quite rapid. The rate of disproportionation of N_2F_4 in the presence of $AlCl_3$ (reaction IV) is strongly pressure dependent, becoming almost negligible at pressures below 20 mm.

Consistent yields of 45–48% *trans*- N_2F_2 have been obtained from both batch and flow reactions involving

excess $AlCl_3$ and N_2F_4 at 15–20 mm. and -80° with contact times ranging from 0.5 to 5 min. Because of the necessarily low pressures, flow systems are strongly recommended.

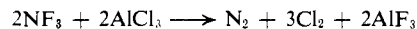
A convenient reactor can be prepared by subliming anhydrous $AlCl_3$ (15–20 g. for 30–50 mmoles of N_2F_4) onto the side-arm walls of a conventional Pyrex U-tube (16 mm. o.d.) by heating the material in the bottom of the vessel with a bunsen burner. It is necessary to activate the $AlCl_3$ before use by keeping it in contact with a small quantity of N_2F_4 at room temperature for 30 min. *Caution.* Do not use glass wool in the reaction tube as it may ignite.

The product is purified by washing with aqueous caustic soda followed by trap-to-trap vacuum distillation. Any unchanged N_2F_4 in the product can be destroyed by shaking it with water in the presence of elementary oxygen and a trace of nitric oxide. Concentrated nitric acid has also been used to remove N_2F_4 but this reagent should be avoided because of the danger of possible detonation. Samples of *trans*- N_2F_2 prepared in 48% yield in this laboratory contained approximately 0.2% NF_3 as the only impurity detectable in the infrared spectrum.

Observations made during the investigation of the above reactions indicate that at least two unstable solid NF-containing compounds are also formed in small amounts. Below -132° the activated $AlCl_3$ described above absorbs some N_2F_4 which cannot be pumped off. On warming, the solid liberates a mixture of N_2F_4 , *trans*- N_2F_2 , N_2 , and Cl_2 . Similarly, the reaction of N_2F_4 with $AlCl_3$ at -80° yields not only gaseous products but also a solid which slowly decomposes to give N_2 and Cl_2 at this temperature. In the presence of traces of moisture, N_2O is also formed in small amounts.

Additional work in this area is now in progress, including the study of reactions involving other metal salts and the nitrogen fluorides. Preliminary results indicate that $FeCl_3$ is similar to $AlCl_3$ in its action on N_2F_4 but the iron compound is considerably less reactive.

Contrary to an early report¹ by Ruff, NF_3 is also readily reduced to nitrogen by $AlCl_3$ at 70° .



Acknowledgment. This research was supported by the Advanced Research Projects Agency through the U. S. Army Research Office (Durham) under Contract No. DA-31-124-ARO(D)-76

(1) O. Ruff, *Z. anorg. allgem. chem.*, **197**, 283 (1931).

Gerald L. Hurst, S. I. Khayat

Research Department, Harshaw Chemical Company
Cleveland, Ohio 44106

Received January 19, 1965

Electronic Spectra and Photochemistry of Adsorbed Organic Molecules. I. Spectra of Ketones on Silica Gel

Sir:

We have observed that silica gel-cyclohexane and silica gel-benzene matrices, if of sufficiently short path length, are highly transparent in the near-ultraviolet