values of $\tau_a$ and $\tau_e$ (5.57 and 5.77),[4] together with the reported value of $\tau$ (5.72 for nitrocyclohexane),[2] an equilibrium constant of 3 was calculated. This latter method is likely to be less accurate in this case, compared to the band-width method, due to the small difference in chemical shift between the equatorial and axial X protons in conformers I and II. However, both methods indicate that approximately 13–25% of conformer II is present in nitrocyclohexane at room temperature.

It now remains to explain why a septet was observed for the X proton in nitrocyclohexane. Recent work[3,7] has shown that interchanging conformations do not show a quintet with coupling constant $J_{av} \approx 7$ c.p.s. (i.e., $J_{av} \neq (J_{aa} + J_{ea})/2$), and in order to calculate the time-averaged coupling constants the method as applied by Booth[7] to mobile cyclohexane systems must be used. Thus the averaged coupling constants are $J_{AX} = mJ_{aa} + (1 - m)J_{ee}$, and $J_{BX} = mJ_{ea} + (1 - m)J_{ae}$.

It has recently been shown that in a *fixed* cyclohexyl system containing a nitro group the coupling constants are $J_{aa} = 11.0–11.5$ and $J_{ea} = 4.0–4.2$[8] c.p.s. Unfortunately, as yet no value of $J_{ee}$ for nitro systems has been measured; however, it was reasonable to assume that $J_{ee} = 2.7$ c.p.s.[9] as used in calculating $w_a$. It was also assumed for the present that $J_{ea} = J_{ae}$, although it has been pointed out that this need not necessarily be so.[10] With these assumptions it was calculated that $J_{AX} = 9.95 \pm 0.45$ c.p.s. while $J_{BX} = 4.1 \pm 0.1$ c.p.s. It was then observed that these *average* coupling constants were very close to the coupling constants used by Urbanski[2] to calculate the theoretical spectrum. For this reason, among others, a very good agreement was found between the experimental and theoretical spectra. However, if the theoretical spectrum for a fixed system was recalculated using the *fixed* coupling constants (and correcting the mathematical mistakes in Table 1 of Urbanski's paper[2]), it was seen that there was very poor agreement with the experimental curve (spectrum 1 of Figure 2). However, using the average coupling constants[11,12] it was observed from spectrum 2 (Figure 2) that these fit the experimental curve more accurately.[13]

It is of interest at this point to comment on the results of Neikam and Dailey[14] for nitrocyclohexane. On cooling, no separation of the methine (X) proton into its axial and equatorial components was observed. This is most likely due to the very small chemical shift ($\tau$ 0.2) between the two components; however, it is possible, if extremely low temperatures are used, that such a splitting may be observed. Against this though is the fact that assuming the $\Delta G$ value of the

(7) H. Booth, *Tetrahedron*, 20, 2211 (1964).

(8) A. C. Huitric, J. B. Carr, W. F. Trager, and B. J. Nist, *ibid.*, 19, 2145 (1963).

(9) F. A. L. Anet, *J. Am. Chem. Soc.*, 84, 1053 (1962).

(10) D. H. Williams and N. S. Bhacca, *ibid.*, 86, 2742 (1964).

(11) The second-order perturbation method[12] was used with the constants $\gamma_A = \tau\ 5.72$, $\gamma_B = \tau\ 8.00$, $\gamma_C = \tau\ 8.20$,[13] $J_{AC} = 9.7$ c.p.s., $J_{AB} = 4.2$ c.p.s.

(12) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 151–156.

(13) Values of $\gamma_B$ and $\gamma_C$ were taken from 3-nitropentane, as it was believed that a straight chain nitroalkane does not provide the best model for nitrocyclohexane. The differences, however, lie within the limits of experimental accuracy.

(14) W. C. Neikam and B. P. Dailey, *J. Chem. Phys.*, 38, 445 (1963).

nitro group as approximately 1 kcal./mole, then at −75° only 8.5% of nitrocyclohexane would exist with the nitro group axial, and thus the equatorial hydrogen signal is liable to be very small and perhaps not observed. As proof of this suggestion it may be mentioned that no splitting was observed on cooling cyclohexylamine,[14] although it is known that the $\Delta G$ value of the amino group is 1.2 kcal./mole.[15] This would, however, give only 7% of axial amine at −75°.

Further studies are in progress on the synthesis of a number of nitro compounds with a view to determining more accurately the conformational free energy of this group, and the results will be published in due course.

(15) H. Feltkamp, N. C. Franklin, and K. D. Thomas, *Ann. Chem.*, 683, 64 (1965).

(16) NATO Postdoctoral Research Fellow, 1963–1965.

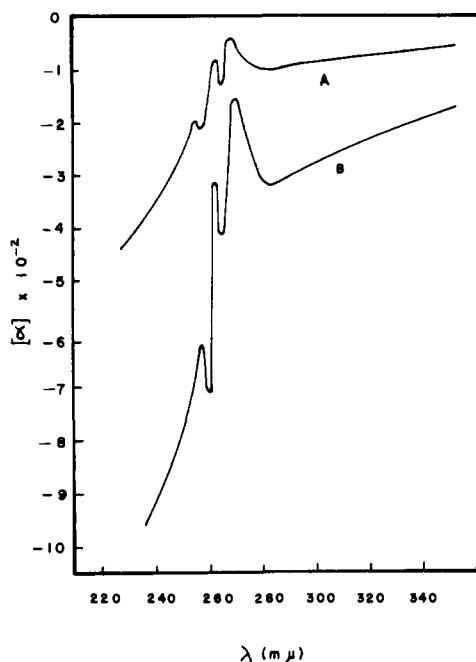Herbert Feltkamp, Norman C. Franklin[16]
Pharmazeutisch-Chemisches Institut
University of Tübingen, Tübingen, Germany

## The Benzene Ring as an Optically Active Chromophore

Sir:

Although the carbonyl group has proved to be extremely useful as an optically active chromophore in optical rotatory dispersion (o.r.d.) studies,[1] increasing attention is being given to compounds possessing other chromophoric groups. Because of conflicting reports in the literature concerning the behavior of a benzene ring attached to an asymmetric carbon center we have undertaken a study of this chromophore.

An o.r.d. investigation of methylphenylcarbinol (I) and its derivatives led Kuhn and Biller[2] to the conclu-



I, R = OH, R' = CH₃
II, R = OH, R' = CO₂H
III, R = CH₃, R' = CO₂H
IV, R = C₂H₅, R' = CH₃
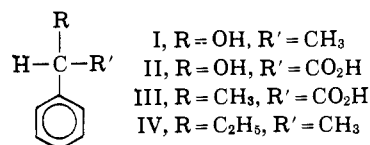
sion that the benzene absorption band in the 260 m$\mu$ region of this compound is not optically active. On the other hand, several derivatives of mandelic acid (II) showed anomalous rotatory dispersion in the benzene absorption region.[2] Sjöberg[3] was able to observe the peak of a Cotton effect at 270 m$\mu$ for atrolactic acid (III) although this wave length was close to the limit of his instrument. Lyle[4] has shown that in certain amines and alcohols having a benzene ring attached to the asymmetric center, the aromatic group exhibits a Cotton effect. The results of calculations utilizing the Drude equation led to the conclusion that the aromatic ring of steroids such as estradiol is optically active.[5] L-Tyrosine, in which the phenolic ring is one carbon removed from the asymmetric center, displays a Cotton effect associated with the aromatic absorption band near 280 m$\mu$.[6] In contrast, the aromatic absorp-

(1) C. Djerassi, *Proc. Chem. Soc.*, 314 (1964).

(2) W. Kuhn and H. Biller, *Z. physik. Chem.*, B29, 1 (1935).

(3) B. Sjöberg, *Acta Chem. Scand.*, 14, 273 (1960).

(4) G. G. Lyle, *J. Org. Chem.*, 25, 1779 (1960).

(5) E. W. Foltz, A. E. Lippmann, and C. Djerassi, *J. Am. Chem. Soc.*, 77, 4359 (1955).

(6) T. M. Hooker and C. Tanford, *ibid.*, 86, 4989 (1964).

Figure 1. Optical rotatory dispersion of methylphenylcarbinol in (A) methanol, (B) isooctane.



Figure 3. Optical rotatory dispersion of mandelic acid in dioxane.



Figure 2. Circular dichroism curve of methylphenylcarbinol in heptane.
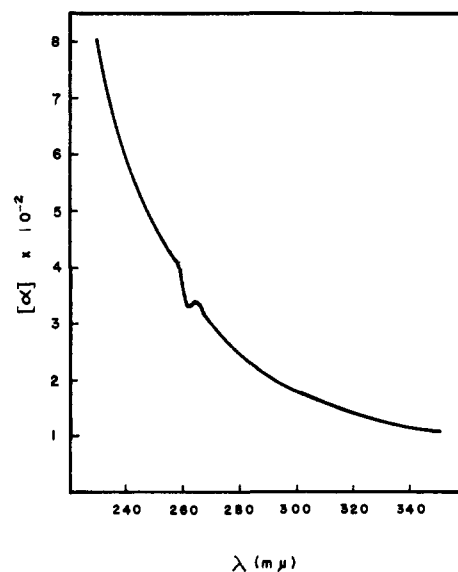


Figure 4. Optical rotatory dispersion of 2-phenylbutane in iso-octane.

tion bands of L-phenylalanine in the 260 m$\mu$ region are not optically active.[6]

Using a Cary 60 recording spectropolarimeter we have measured the o.r.d. spectra of methylphenyl-carbinol (I), mandelic acid (II), and 2-phenylbutane (IV) from 350 m$\mu$ to below 230 m$\mu$. Rotations were measured through the aromatic absorption region and great care was taken to make certain of the validity of our results.

Figure 1 shows the results for methylphenylcarbinol (I)[7] in methanol (curve A) and isooctane (curve B). The o.r.d. spectra show a positive multiple Cotton effect of relatively small magnitude. Independent evidence is obtained from measurement of the circular dichroism (c.d.,[8] Figure 2), which clearly shows the

electronic transitions in the aromatic region to be optically active. The c.d. curve also shows strong optically active transitions at 205 and 212 m$\mu$ which have the opposite sign from those in the 260 m$\mu$ region. It is evident that these short wave length Cotton effects contribute importantly to the observed rotation in the 260 m$\mu$ region.

From their o.r.d. results on derivatives of mandelic acid (II), Kuhn and Biller[2] demonstrated that the benzene chromophore in these molecules was optically

(7) Two different samples of methylphenylcarbinol were used. Both were purified by g.l.p.c. (Carbowax 20M column). The sample whose o.r.d. is shown in curve A had [$\alpha$]D $-15.44°$ while the sample shown in curve B had [$\alpha$]D $-38.45°$.
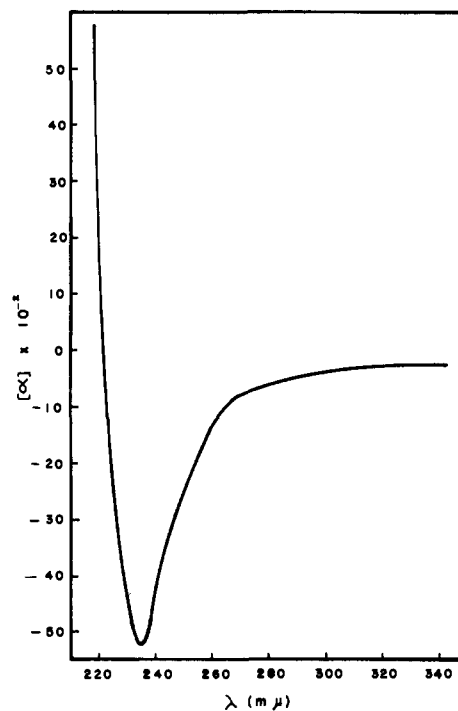
(8) We are indebted to Dr. M. Legrand, Roussel-UCLAF, Romainville, France, for this measurement.

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$\mu$. 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$\mu$. From the data of Benson, Kenyon, and Shepherd[10] on the rotation of 2-phenylbutane in the visible region, a $\lambda_0$ of 233 m$\mu$ is calculated. We have measured the rotation directly to 230 m$\mu$. 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°.

(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.

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## Optically Active R$_3$Si*Li from Lithium Metal Cleavage of an Optically Active Disilane

*Sir:*

The synthesis of optically active neo-C$_5$H$_{11}$PhMeSi*Li, neopentylphenylmethylsilyllithium, involved the preparation of optically active neo-C$_5$H$_{11}$PhMeSi*-SiMePh$_2$ according to eq. 1.

$$(+)\text{-neo-C}_5\text{H}_{11}\text{PhMeSi*H} \xrightarrow[\text{a}]{\text{Cl}_2} (+)\text{-neo-C}_5\text{H}_{11}\text{PhMeSi*Cl}$$
$$[\alpha]\text{D} +2.81° \qquad [\alpha]\text{D} +7.2°$$

$$\xrightarrow[\text{b}]{\text{Ph}_2\text{MeSiLi}} (-)\text{-neo-C}_5\text{H}_{11}\text{PhMeSi*SiMePh}_2 \quad (1)$$
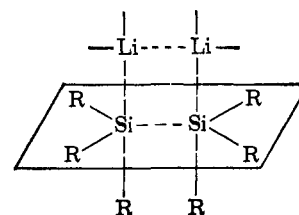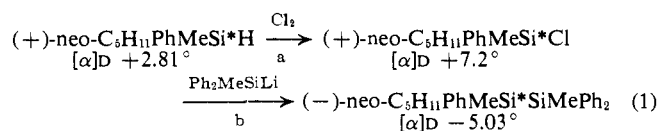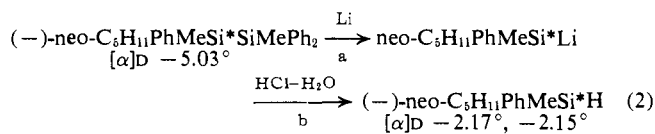$$[\alpha]\text{D} -5.03°$$



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

$$(-)\text{-neo-C}_5\text{H}_{11}\text{PhMeSi*SiMePh}_2 \xrightarrow[\text{a}]{\text{Li}} \text{neo-C}_5\text{H}_{11}\text{PhMeSi*Li}$$
$$[\alpha]\text{D} -5.03°$$

$$\xrightarrow[\text{b}]{\text{HCl-H}_2\text{O}} (-)\text{-neo-C}_5\text{H}_{11}\text{PhMeSi*H} \quad (2)$$
$$[\alpha]\text{D} -2.17°, -2.15°$$

portions of the same optically active disilane gave product R$_3$Si*H having [$\alpha$]D −2.17 and −2.15°.

Present assignment of *retention* of configuration for reaction 2a is based on: previous[1] assignment of *retention* to reaction 1a; *inversion* for 1b based on general inversion for R$_3$Si*Cl with strong nucleophiles[2] including R'Li[3]; *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 mechanism[4] whose geometry approximates that shown in Figure 1.

Gilman and his students have contributed many excellent studies of the preparation of R$_3$SiLi from lithium metal cleavage of R$_3$SiSiR$_3$, and the present work should aid in the interpretation of their results.[5]

The present results show that neopentylphenylmethylsilyllithium, like the recently reported $\alpha$-naphthylphenylmethylgermyllithium,[6] has considerably enhanced optical stability relative to simple acyclic alkyllithium 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* R$_3$SiLi 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 R$_3$Si*Li, *e.g.*, *n*-BuLi and R$_3$Ge*H.

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