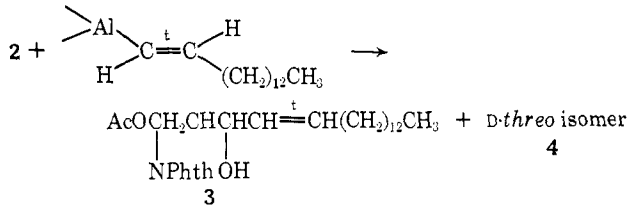
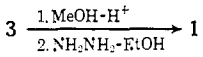


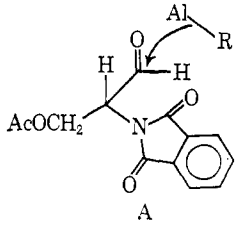
isomers were readily separated by partition chromatography.[12]

This reaction is a further example of our recently reported method[8] for the preparation of trans allylic alcohols stereospecifically from the reaction of aldehydes and ketones and vinylalanes.

Removal of the blocking groups from **3** was accomplished (96% yield) preferentially int wo stages,[13] *viz.* methanolysis in the presence of a trace of acid to remove the acetoxy substituent followed by hydrazinolysis to remove the phthaloyl group to give D-*erythro*-sphingosine (**1**).[6,14]



The aldehyde **2** showed a sharp singlet in its nmr spectrum at δ 9.68 due to the aldehyde proton, suggesting conformation A for this aldehyde, in which the



A

dihedral angle between the aldehydic proton and the one on the α carbon would be *ca.* 90° and as a result show a minimum spin–spin coupling.[16] Preferential attack of this conformation by the organometallic from the least-hindered topside as indicated by the arrow would give predominantly the erythro isomer **3**.[17]

Acknowledgments. The author thanks Mr. J. Baker for the partition chromatography, Mr. L. Brancone and staff for the microanalyses, and Mr. L. Fulmor and staff for the nmr spectra and optical rotation measurements.

(12) Celite 545 and heptane–methyl Cellosolve were the support and developing solvent system used, respectively. A third product, D-*erythro*-1-acetoxy-2-phthalimido-3-hydroxyoctadec-4-yne (i) (0.4 g), was also isolated. The order of elution from the column was first **4**, and then **3**, and finally i. All came off between 7 and 11 holdback volumes. The R_f values of these compounds were *ca.* 0.4 on tlc (silica gel; C_6H_5H–EtOAc, 9:1). (No *threo*-i was present. This compound was obtained in connection with another synthetic approach to sphingosine which we investigated (unpublished results) and would have been detected.) The formation of i is presumably the result of the reaction of some $CH_3(CH_2)_2C{\equiv}C{-}Al<$ (ii) present (formed from pentadecyne and diisobutylaluminum hydride in an acid–base reaction) and **2**. The fact that only *erythro*-i formed suggests that the reaction between ii and **2** proceeds stereospecifically. This could, not unreasonably, be attributed to the decreased reactivity of ii compared to its vinylalane analog which results in a still greater selectivity in its reaction with **2** *via* conformation A (see further on in the discussion above).

(13) Direct hydrazinolysis gave a less pure product. We speculate on the basis of its infrared spectrum which showed absorption in the carbonyl region consistent with the presence of N–Ac that direct hydrazinolysis is complicated by O → N acyl transfer which follows the preferential hydrazinolysis of the phthaloyl moiety.

(14) Obtained as a yellow waxy solid; R_f on tlc (silica gel, $CHCl_3$–MeOH–2 *N* NH_4OH, 40:10:1[15]) −0.57. Unequivocal characterization was effected by conversion to the known *O,O,N*-triacetyl-D-*erythro*-sphingosine (*Beilstein III*, 4, 855) in 92% yield.

(15) P. B. Mendershausen and C. C. Sweeley, *Biochemistry*, **8**, 2633 (1969).

(16) N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, San Francisco, Calif., 1964, p 49.

(17) The recent studies of Hooz[18] and our own unpublished observations indicate organoaluminum additions to carbonyl functions to involve initial coordination of the Al moiety with the carbonyl oxygen followed by attack of the organic moiety at the electron-deficient carbon of the carbonyl component.

(18) J. Hooz and R. B. Layton, *J. Amer. Chem. Soc.*, **93**, 7321 (1971).

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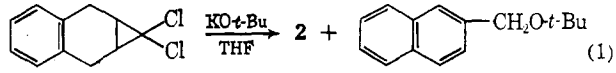
Naphtho[*b*]cyclopropene

Sir:

Although the highly strained but isolable benzocyclopropene (**1**) has been synthesized by two routes,[1] parent members of other aromatic systems incorporating linearly fused cyclopropenes are unknown.[2] We now report the synthesis of naphtho[*b*]cyclopropene (**2**), a compound expected to show a high degree of bond fixation.

1 **2**

Treatment of **3**[3] with an eightfold excess of KO-*t*-Bu in dry THF for 18 hr gives **2** (38% yield) and its solvolysis product **4**, eq 1. Purification of **2**, mp 86–87°,



3 **4** (1)

was accomplished by adsorption chromatography using Florisil (100–200 mesh) and pentane eluent followed by sublimation.

The structural assignment of **2** was based on its spectral and chemical properties: $uv_{max}^{C_6H_{12}}$ 221 nm (ϵ 58,000); ir_{max}^{KBr} 1673 (aromatic double bond) and 843, 745 cm^{-1} (aromatic); mol wt (mass spectrum) 140 (base peak). The nmr spectrum is displayed in Figure 1. The significant feature of this spectrum is the singlet at δ 7.40 assigned to the two central ring protons. Since these protons reside among the remaining four

(1) E. Vogel, W. Grimime, and S. Korte, *Tetrahedron Lett.*, 3625 (1965); W. E. Billups, A. J. Blakeney, and W. Y. Chow, *Chem. Commun.*, 1461 (1971).

(2) The synthesis of 1,1-dichloro-2,7-diphenylnaphtho[*b*]cyclopropene in low yield has just been reported; see A. R. Browne and B. Halton, *J. Chem. Soc., Chem. Commun.*, 1341 (1972). A compound originally believed to be a keto tautomer of naphtho[*b*]cyclopropenediol was later shown not to contain a three-membered ring: L. F. Fieser and M. A. Peters, *J. Amer. Chem. Soc.*, **53**, 4080 (1931); A. R. Bader and M. G. Ettlinger, *ibid.*, **75**, 730 (1953). For interesting synthetic approaches to the naphtho[*b*]cyclopropene system, see M. P. Cava and K. Narasimhan, *J. Org. Chem.*, **36**, 1419 (1971); K. Geibel and J. Heindl, *Tetrahedron Lett.*, 2133 (1970).

(3) Addition of dichlorocarbene (KO-*t*-Bu, $CHCl_3$, 5°) to 1,4-dihydronaphthalene[4] gives **3**, mp 49–51°, in 27% yield: nmr δ 1.97 (m, 2 H), 2.49–3.45 (m, 4 H), and 7.02 (s, 4 H).

(4) E. S. Cook and A. J. Hill, *J. Amer. Chem. Soc.*, **62**, 1995 (1940),

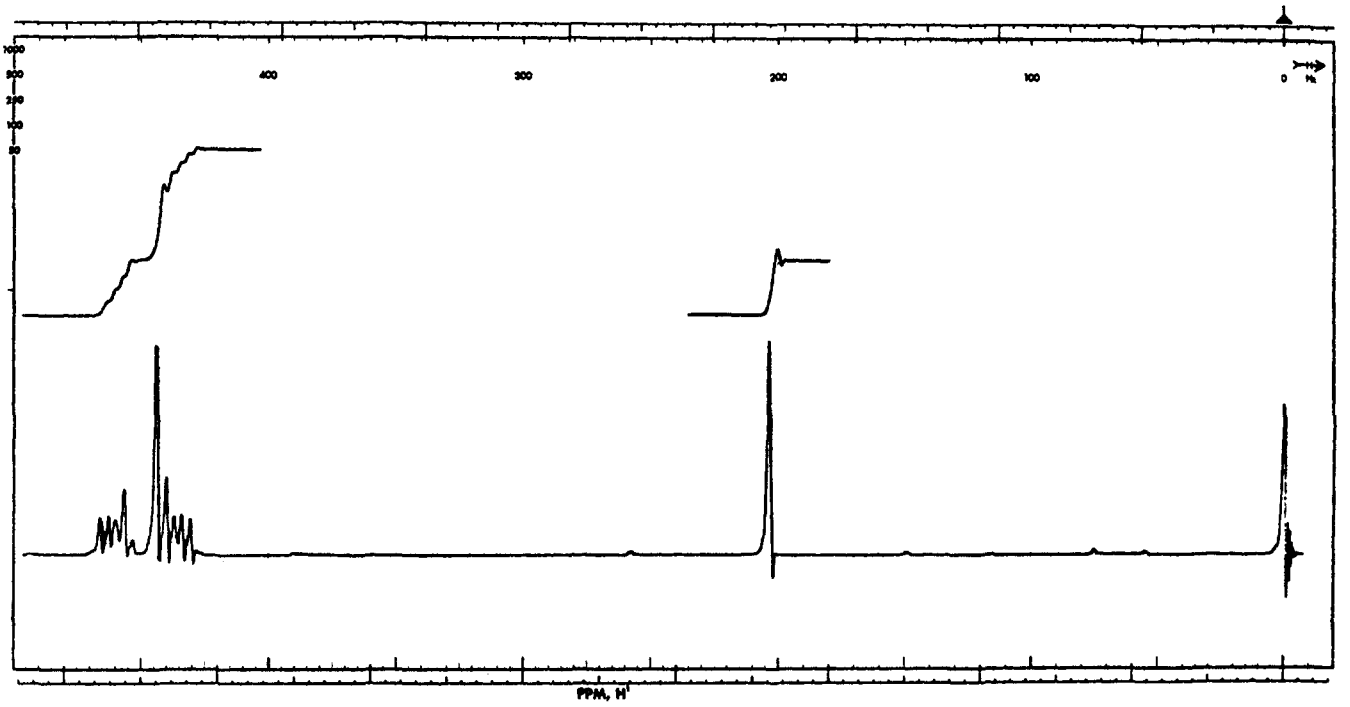
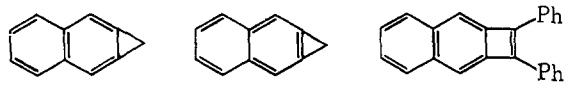


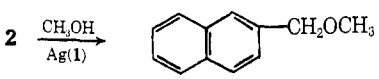
Figure 1. ^1H nmr spectrum (60 MHz) of naphtho[*b*]cyclopropene in CCl_4.

low-field aromatic protons, double bond fixation (**2a** *vs.* **2b**) may not be as extreme for this system as expected. In contrast, 1,2-diphenylnaphthocyclobutadiene (**5**) shows a high degree of double bond fixation and the central ring protons appear at δ 6.50, very close to the olefinic protons of *cis*-stilbene.[5] An X-ray structure determination of **2** is under way.



2a 2b 5

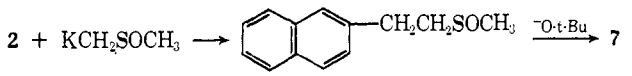
Hydrogenation of **2** over PtO_2 in ether at 25° gives benzocycloheptene (86%) and β-methylnaphthalene (14%). Naphtho[*b*]cyclopropene, like benzocyclopropene,[6] is sensitive to acid reagents. Thus, both **1** and **2** react slowly with acetic acid to give the corresponding benzylic acetates. The methanolysis of **2** is not detectable (nmr) after 4 hr at 25°; however, addition of 1 mol % Ag(I) to a 10% solution of **2** in methanol gives a quantitative yield of the ether **6** in <1 min at 25°, eq 2.



(2)

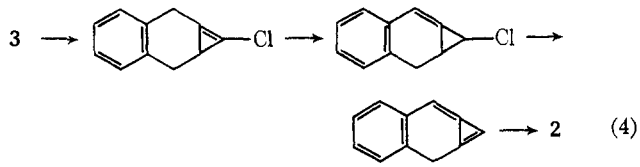
6

Attempts to find a base–solvent combination that gives a more rapid conversion of **3** → **2** than the KO-*t*-Bu–THF system have been largely unsuccessful. When KO-*t*-Bu in Me_2SO was used a low yield (<10%) of **2** was produced. The major products were **4** and β-vinylnaphthalene (**7**). The formation of **7** probably arises by reaction of **2** with potassium dimsyl to give **8**. This compound would be expected to undergo elimination under the reaction conditions, eq 3.[7]



8 (3)

Finally, we can only speculate on the structure of the intermediates produced in the conversion **3** → **2**. The sequence shown in eq 4 seems reasonable.



(4)

Acknowledgment. We gratefully acknowledge the Robert A. Welch Foundation for support of this work.

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Received February 21, 1973

(5) M. P. Cava, B. Hwang, and J. P. van Meter, *J. Amer. Chem. Soc.*, **85**, 4032 (1963).
(6) Unpublished observations; see also S. Korte, Ph.D. Thesis, University of Köln, 1968.
(7) J. E. Hofmann, T. J. Wallace, P. A. Argabright, and A. Schriesheim, *Chem. Ind. (London)*, 1243 (1963).

The Rapid Quantitative Reaction of Potassium Hydride with Weak Lewis Acids. A Highly Convenient New Route to Hindered Complex Borohydrides[1,2]

Sir:

Potassium hydride reacts rapidly and quantitatively with weak Lewis acids such as hindered trialkylboranes, borate esters, and tetraalkyldiboranes. The reaction provides with unprecedented ease complex potassium borohydrides, certain of which have been demonstrated to be highly stereospecific reducing agents.

Potassium hydride (KH) is highly reactive toward metalation of weak organic acids such as dimethyl sulfoxide, amines, and hindered alcohols;[2] reactivity

(1) Kaliation. II.
(2) Part I: C. A. Brown, *J. Amer. Chem. Soc.*, **95**, 982 (1973).