Stereochemical Study of Sodium–Ammonia Reduction of Acyclic Allenes

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The sodium–ammonia reduction of alkyl-substituted allenes (1,2-octadiene, 1,2-nonadiene, 2,3-nonadiene, 4,5-nonadiene, 3-ethyl-1,2-pentadiene, and 2,4-dimethyl-2,3-pentadiene) and aryl-substituted allenes (phenylpropadiene and 3-phenyl-1,2-butadiene) has been described. Alkyl-substituted allenes were reduced smoothly to give good yields of olefins, while aryl-substituted allenes provided principally alkylbenzenes. Potential routes for the formation of these products have been investigated. Evidence has been obtained for the isomerization of allenes to internal alkynes, wherever possible, before reduction. The allenes, which are not capable of isomerization to internal alkynes, seem to undergo reduction directly.

It has been shown earlier that the blue solution formed by dissolving sodium in liquid ammonia is an excellent reagent for reducing allenes to olefins.[1] This particular method of reduction, in combination with an elegant two-step synthesis of allenes,[2,3] has proved to be advantageous for synthesizing a higher homolog of an olefin in good yield.

Medium-sized cyclic allenes are found to yield *cis* olefins[1,4] on reduction with sodium–ammonia. This reaction has been used recently in the synthesis of *cis,cis*-1,5-cyclononadiene[1,5] and *cis,cis*-1,6-cyclodecadiene[6] because of the advantage offered in selectivity of reduction. Allenes have been proposed as intermediates in the metal–ammonia reduction of certain medium-sized cyclic acetylenes which also form *cis* olefins.[7–9] Since some confusion exists as to the nature of the products in the reduction of acyclic allenes,[1,10] we undertook a study of the reduction of representative acyclic allenes with sodium–liquid ammonia, with the intention of examining the stereospecificity of the reduction and of establishing, if possible, the potential path through which the olefins arise.

Results and Discussion

For the present investigation, we have made use of the following acyclic allenes—mono-, di-, and tetraalkyl allenes (1,2-octadiene, 1,2-nonadiene, 2,3-nonadiene, 4,5-nonadiene, 3-ethyl-1,2-pentadiene, and 2,4-dimethyl-2,3-pentadiene), and aryl allenes (phenylpropadiene and 3-phenyl-1,2-butadiene). All of the allenes except 2,4-dimethyl-2,3-pentadiene were prepared according to the general two-step method for synthesizing allenes.[2,3] They showed properties which were identical with the reported values.[10–13]

The reductions were conducted using commercial ammonia and pieces of freshly cut sodium. The required amount of allene in dry ether was added and worked up after the requisite time.

All the allenes underwent reduction smoothly giving good yields of the products. Yields and product composition are reported in Table I. The products were separated, wherever necessary, by preparative gas chromatography, and subjected to infrared and nuclear magnetic resonance spectral analysis.

TABLE I
REDUCTION OF ACYCLIC ALLENES BY SODIUM IN LIQUID AMMONIA

Allene	Total yield, %	Product (composition, %)
1,2-Octadiene[a]	77	*trans*-2-Octene (96.8) *cis*-2-Octene (2.5) 1-Octene (0.7)
1,2-Nonadiene[a]	80	*trans*-2-Nonene (92.8) *cis*-2-Nonene (7.2)
2,3-Nonadiene[a]	85	*trans*-2-Nonene (49.2) *cis*-2-Nonene (1.5) *trans*-3-Nonene (47.9) *cis*-3-Nonene (1.4)
4,5-Nonadiene[a]	82	*trans*-4-Nonene (96.6) *cis*-4-Nonene (3.4)
3-Ethyl-1,2-pentadiene[a]	81	3-Ethyl-2-pentene (100)
2,4-Dimethyl-2,3-pentadiene[a]	76	2,4-Dimethyl-2-pentene (100)
Phenylpropadiene[b]	72	*n*-Propylbenzene (82.0) Allylbenzene (18.0)
3-Phenyl-1,2-butadiene[b]	42[c]	*sec*-Butylbenzene (100)

[a] Products were analyzed on a 15-ft propylene glycol–$AgNO_3$ column. [b] Products were analyzed on a 10-ft 20% Carbowax column. [c] A large portion of allene was found to undergo polymerization, hence the low yield.

Alkyl-Substituted Allenes.—1,2-Octadiene and 1,2-nonadiene, on reduction, gave good yields of *trans*-2 olefin as the major product instead of *cis*-2 olefin as reported earlier.[1] 4,5-Nonadiene provided *trans*-4-nonene as the major product. The reduction of 2,3-nonadiene gave mainly *trans*-2- and *trans*-3-nonene in almost equal amounts. 3-Ethyl-1,2-pentadiene gave only 3-ethyl-2-pentene. 2,4-Dimethyl-2,3-pentadiene underwent reduction smoothly to yield 2,4-dimethyl-2-pentene.

Scheme I shows the possible routes (A and B) for the reduction of allenes to *trans* olefins. According to route A the *trans* olefin arises by isomerization of allene to acetylene followed by *trans* addition of electrons to form the dianion (I) which then undergoes protonation to give the *trans* olefin. This route is similar to the one

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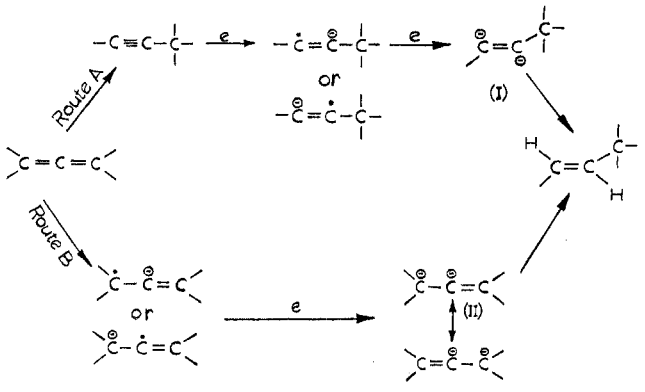
SCHEME I



proposed by earlier workers[14] for the reduction of acetylenes in the absence of an external proton donor. Alternatively, the allene can undergo direct reduction through route B. The reaction presumably proceeds by addition of one electron to give radical anions. Subsequent addition of one more electron followed by rotation of charged carbon atoms gives an allylic dianion (II) which can exist in resonance forms. The intermediate allylic anions can have both *cis* and *trans* configurations. Further, the least substituted end of the molecule probably carries the greater amount of charge, since the electron pair could occupy an orbital containing more s character when concentrated there. If this is so, one expects preferential protonation at the least substituted carbon to yield the thermodynamically more stable olefin (or higher degree of substitution).[15]

The predominance of the *trans*-2 olefin as reduction product made us to suspect that it might be arising from the reduction of a possible 2-alkyne intermediate, in view of the fact that terminal allenes are known to undergo isomerization to 2-alkynes by bases.[16] Also, Moore and Ward[17] have shown by calculations based on heats of formation and hydrogenation that 2-alkynes are thermodynamically more stable than terminal allenes. The most likely reagent in our experiments causing the isomerization seems to be sodium amide, whose concentration increases as reduction proceeds. In support of our proposal, we have observed 36% 2-nonyne along with 18% *trans*-2-nonene and 46% unreacted allene, when 1,2-nonadiene was subjected to partial reduction (using about half the theoretical amount of sodium required to reduce only one double bond). This confirms that some or all of the *trans*-2-nonene is arising *via* a 2-nonyne intermediate. However, the result does not exclude the possibility of the direct reduction of the allene to olefin, since it can be argued that the formation of 2-nonyne could be independent of the reduction of the allene, but the high concentration of 2-nonyne in comparison with that of *trans*-2-nonene could be best explained by 1,2-nonadiene undergoing isomerization faster than the direct reduction. Similar extremely fast isomerization of 1,2-hexadiene to 2-hexyne has been noted by Wotiz and coworkers.[18] The same argument holds for 2,3-nonadiene and 4,5-nonadiene. In the case of the former both 2- and 3-nonyne can be intermediates and the latter can undergo reduction through 4-nonyne. Our results with 1,2-nonadiene and 2,3-nonadiene are completely consistent with the observation of Benkeser and Tincher,[19] who have obtained principally *trans*-2-octene from 1,2-octadiene, and *trans*-2- and *trans*-3-octene in almost equal amounts from 2,3-octadiene, in electrolytic reduction. Similar overall results have been obtained by Brown[10] and also Gardner and de Montellano[20] in the reduction of 2,3-nonadiene by alkali metal in ammonia.

The result with 3-ethyl-1,2-pentadiene reveals that the least substituted double bond of the allene is reduced specifically to yield the highly substituted olefin. Since this allene cannot isomerize to the corresponding 2-alkyne, and because of the conspicuous absence of conjugated dienes in the partial reduction product of 1,2-nonadiene, we propose, in this case, that the reduction follows only route B of Scheme I to give the resonance stabilized allylic dicarbanion followed by preferential protonation at the least substituted carbon atom, for reasons already discussed. The result with 2,4-dimethyl-2,3-pentadiene demonstrates that a simple tetrasubstituted allene offers no hindrance to sodium–ammonia reduction.

Aryl-Substituted Allenes.—In this series the allenes used for the present investigation were phenylpropadiene and 3-phenyl-1,2-butadiene, both of which have the allenic double bond in conjugation with the phenyl ring. The former gave *n*-propylbenzene with some amount of allylbenzene, and the latter gave only *sec*-butylbenzene. These results, wherein the alkyl benzenes are formed, are very similar to those observed by Wooster and Ryan,[21] who obtained 1,1,3,3-tetraphenylpropane by sodium–ammonia reduction of tetraphenylpropadiene. It can also be pointed out here that the complete reduction of unsaturated bonds in conjugation with phenyl ring can be a general phenomenon, which has been noticed by Benkeser and coworker,[19] who have shown the formation of alkylbenzenes by electrolytic reduction of 1-arylacetylenes.

The observed facts can be rationalized as follows. In the case of phenylpropadiene it can be presumed that both allene and its isomerized product, 1-phenylpropyne, are undergoing reduction. The former gives rise to the intermediates allylbenzene and propenylbenzene, and the latter gives rise to propenylbenzene which, we think, undergoes further reduction to *n*-propylbenzene, while allylbenzene undergoes isomerization to propenylbenzene before reduction. This assumption of isomerization of allylbenzene to propenylbenzene is not unreasonable since such isomerization under the influence of various bases has been well established by many workers.[22] It is interesting to note at this point that we have found in a separate experiment that even allylbenzene, on reduction with excess sodium under similar conditions, gives rise to *n*-propylbenzene.

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To check the possibility of the aforesaid intermediates, partial reduction (with about half the amount of sodium required to reduce only one double bond) of phenylpropadiene was carried out. When the reaction was arrested after about 15 min, the gas chromatographic analysis of the product after usual work-up showed the presence of *n*-propylbenzene, allylbenzene, and 1-phenylpropyne. No other product including the starting allene itself was observed. In another experiment, when the partial reduction was allowed to proceed for about 3 hr, the product analysis showed *n*-propylbenzene, propenylbenzene, and 1-phenylpropyne only. This clearly indicates that the reduction proceeds, at least partly, through a 1-phenylpropyne intermediate, and that allylbenzene, which is observed in the short-period experiment, isomerizes to the propenylbenzene observed in the long-period experiment. Formation of allylbenzene in the absence of formation of 3-phenylpropyne in the partial reduction of phenylpropadiene, indicates that the former arises out of direct reduction of the allene.

The reduction of 3-phenyl-1,2-butadiene to *sec*-butylbenzene can be explained as arising from direct reduction of allene through the possible 2-phenyl-2-butene and 3-phenyl-1-butene intermediates. Among these two intermediates one cannot be favored over the other, but it can be recalled, however, that 3-ethyl-1,2-pentadiene gives exclusively 3-ethyl-2-pentene, which suggests the likelihood of formation of 2-phenyl-2-butene in preference to the other isomer which, of course, can go over to the former reasonably fast.

Experimental Section

All boiling points are uncorrected. The infrared spectra were recorded on a Perkin-Elmer Model 521 spectrophotometer using cesium bromide plates for liquid film spectra and sodium chloride cells for solution spectra. The nmr spectra were recorded on a Varian Associates A-60 spectrometer, in carbon tetrachloride with tetramethylsilane as the internal standard. The peaks are reported in δ (ppm). Gas chromatographic analysis of the reduction products of the alkyl-substituted allenes was carried out on a 0.25 in × 15 ft column packed with 20% propylene glycol–silver nitrate (F & M Scientific Corp., Avondale, Pa.) on 60–80 mesh Chromosorb P. The efficiency of the column was checked with authentic samples of *cis*- and *trans*-nonenes and was found to be quite satisfactory for our present investigation. The glpc analysis of the reduction products of phenyl substituted allenes was carried out using a 1/4 in. × 10 ft 20% Carbowax column. 2,4-Dimethyl-2,3-pentadiene was obtained from Aldrich Chemical Co. and showed no detectable impurities by glpc and nmr. All of the other allenes were prepared by known procedures reported in the literature,[2,3] and their properties corresponded well with those reported.[10–13] The elemental analyses were carried out by A. H. Siddiqui, microanalyst of this department.

General Procedure for Sodium–Ammonia Reduction.—Commercial ammonia was directly condensed without purification into the reaction flask fitted with a dropping funnel, a stirrer, and a Dry Ice condenser. A calculated quantity of dried sodium (freshly cut with a clean stainless steel knife) was dissolved in liquid ammonia. To the blue solution, the allene in dry ether was added dropwise. After complete addition of the allene, the stirring was continued for *ca.* 1 hr to ensure completion of the reaction, even though the reaction was found to be instantaneous. The excess sodium was then destroyed by adding ammonium chloride in small amounts. The excess ammonia was allowed to evaporate. The product was isolated by adding water to the residue and extraction of the product with ether. The combined extracts were washed twice with water and dried over anhydrous magnesium sulfate. The product was distilled after removal of the solvent through an efficient column.

Reduction of 1,2-Octadiene.—1,2-Octadiene (3.30 g, 0.03 mol) was reduced with 2.76 g (0.12 g-atom) of sodium in *ca.* 100 ml of liquid ammonia to give 2.57 g (77%) of octene mixture, bp 121–122° (754 mm). Analysis by glpc showed that the product consisted of 1-octene (0.7%), *cis*-2-octene (2.5%), and *trans*-2-octene (96.8%). The infrared spectrum (liquid film) showed a strong band at 963 cm^{-1} (*trans* out-of-plane hydrogen bending). All three components were identified by comparing the glpc retention times with those of authentic samples. Only *trans*-2-octene was separated by glpc, and it was identified by comparison of the infrared and nmr spectra with those of an authentic sample.

Reduction of 1,2-Nonadiene.—1,2-Nonadiene (2.48 g, 0.02 mol) was reduced with 2.06 g (0.09 g-atom) of sodium in *ca.* 80 ml of liquid ammonia. The usual work-up gave 2.0 g (80%) of nonenes, bp 69–70° (45 mm). The glpc analysis showed that the product consisted of *cis*-2-nonene (7.2%) and *trans*-2-nonene (92.8%). The identity of each of these isomers was established by comparison of glpc retention times with those of authentic samples. The major component was isolated by glpc, and its identity was established by comparison of the infrared and nmr spectra with those of an authentic sample.

Reduction of 2,3-Nonadiene.—A 2.48-g (0.02 mol) sample of 2,3-nonadiene was reduced by 2.08 g (0.09 g-atom) of sodium in *ca.* 80 ml of liquid ammonia. The usual work-up and distillation yielded 2.16 g (85%) of product, bp 68–69° (49 mm). Careful analysis by glpc indicated that the product consisted of *cis*-2-nonene (1.5%), *trans*-2-nonene (49.2%), *cis*-3-nonene (1.4%), and *trans*-3-nonene (47.9%). The minor components were identified by glpc analysis, while the major components were separated by glpc and identified by comparison of the infrared and nmr spectra with those of authentic samples.

Reduction of 4,5-Nonadiene.—4,5-Nonadiene (2.48 g, 0.02 mol) was reduced with 2.06 g (0.09 g-atom) of sodium in *ca.* 80 ml of liquid ammonia to obtain 1.98 g (79%) of 4-nonene isomers, bp 58–59° (49 mm). Analysis by glpc indicated 3.4% *cis*-4-nonene and 96.6% *trans*-4-nonene. *trans*-4-Nonene was separated and identified by infrared and nmr. The infrared spectrum had a strong band at 966 cm^{-1} (lit.[23] 969 cm^{-1}). The nmr spectrum showed a triplet at δ 0.9 (6 H), multiplets at 1.22 (6 H) and 1.95 (4 H), and a septet at 5.38 (2 H).

Reduction of 2,4-Dimethyl-2,3-pentadiene.—2,4-Dimethyl-2,3-pentadiene (2.88 g, 0.03 mol) was reduced with 2.76 g (0.12 g-atom) of sodium in 100 ml of liquid ammonia to give 1.23 g (76%) of 2,4-dimethyl-2-pentene, bp 78–79° (754 mm), $n^{28}D$ 1.4005 (lit.[24] bp 83–84°, $n^{20}D$ 1.4016). The product was found to be pure by glpc. The infrared spectrum showed a band at 1670 cm^{-1} (C=C). The nmr spectrum had a doublet at δ 0.87 (6 H), multiplets at 1.56 (6 H), 2.42 (1 H), and 4.88 (1 H).

Reduction of 3-Ethyl-1,2-pentadiene.—3-Ethyl-1,2-pentadiene (1.92 g, 0.02 mol), on reduction with 2.06 g (0.09 g-atom) of sodium in *ca.* 80 ml of liquid ammonia, gave 1.57 g (81%) of 3-ethyl-2-pentene, bp 91–92° (754 mm), $n^{28}D$ 1.4135 (lit.[25] bp 94–95°, $n^{20}D$ 1.4148). The glpc analysis showed the sample to be pure. The infrared spectrum exhibited a band at 1673 cm^{-1} (C=C). The nmr spectrum had a triplet (with further fine splitting) at δ 0.98 (6 H), a doublet at 1.59 (3 H), mainly a quartet with fine structure at 2.05 (4 H), and a quartet at 4.19 (1 H).

Reduction of Phenylpropadiene.—Phenylpropadiene (2.90 g, 0.025 mol) was reduced with 2.30 g (0.10 g-atom) of sodium in *ca.* 100 ml of liquid ammonia to obtain 2.15 g (72%) of the product, bp 52–55° (16 mm). The glpc analysis showed the presence of *n*-propylbenzene (82%) and allylbenzene (18%). They were separated by glpc and identified by comparison of the infrared and nmr spectra with those of authentic samples.

Reduction of 3-Phenyl-1,2-butadiene.—3-Phenyl-1,2-butadiene (2.60 g, 0.02 mol) was reduced with 0.06 g (0.09 g-atom) of sodium in *ca.* 80 ml of liquid ammonia to yield 1.62 g (42%) of product, bp 60–62° (12 mm). The undistilled polymeric residue accounted for *ca.* 40% of the product. The glpc analysis of the product indicated it to be pure. The product was identified as *sec*-butylbenzene by comparison of the infrared and nmr spectra with those of an authentic sample.

Partial Reduction of 1,2-Nonadiene.—Partial reduction of 1,2-nonadiene (1.24 g, 0.01 mol) using 0.23 g (0.01 g-atom) of sodium in 50 ml of liquid ammonia gave a product mixture (1.01 g) which was found to contain *trans*-2-nonene (18%), 1,2-nonadiene

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(46%), and 2-nonyne (36%) by glpc analysis. These were separated by glpc and identified by infrared and nmr.

Partial Reduction of Phenylpropadiene.—Phenylpropadiene (1.16 g, 0.01 mol) was reduced with 0.23 g (0.01 g-atom) of sodium in 50 ml of liquid ammonia. The reaction product was stirred for 3 hr and worked up in the usual manner. The glpc analysis of the product (0.95 g) showed the presence of *n*-propylbenzene (17.2%), propenylbenzene (22.5%), 1-phenylpropyne (56.8%), and an unidentified product (3.5%). The first three components were separated by glpc and identified by nmr.

When the reaction in another lot was arrested and worked up after just 15 min, the product analysis showed 15.7% *n*-propylbenzene, 19.5% allylbenzene, and 64.8% 1-phenylpropyne.

Reduction of Phenylpropadiene with Equivalent Quantity of Sodium.—Phenylpropadiene (1.16 g, 0.01 mol) in dry ether was added into a solution of 0.46 g (0.02 g-atom) of sodium in 50 ml of liquid ammonia. The reaction mixture was stirred only for 15 min and worked up in the usual way. The product (0.92 g) analysis by glpc showed the presence of *n*-propylbenzene (21.9%), allylbenzene (15.3%), and 1-phenylpropyne (62.8%). These were separated and identified by nmr.

Registry No.—1,2-Octadiene, 1072-19-1; 1,2-nonadiene, 22433-33-6; 2,3-nonadiene, 22433-34-7; 4,5-nonadiene, 821-74-9; 3-ethyl-1,2-pentadiene, 2384-96-5; 2,4-dimethyl-2,3-pentadiene, 1000-87-9; phenylpropadiene, 2327-99-3; 3-phenyl-1,2-butadiene, 22433-39-2.

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Syntheses of All of the Racemic Diastereoisomers of Phytosphingosine

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Ethyl 2-acetamido-3-octadecynoate (**8**), derived from the 2,4-dinitrophenylhydrazone (**4**) of ethyl 2-oxo-3-octadecynoate (**1**) by reductive acetylation, was converted into *trans*- and *cis*-2-acetamido-1-acetoxy-3-octadecenes (**13** and **16**). Dihydroxylation in *trans* fashion of the *trans* compound **13** with performic acid followed by saponification afforded racemic N-acetyl phytosphingosine, the DL-*ribo* isomer **14**, together with the DL-*arabino* isomer **15**. From the *cis* compound **16** there was obtained in the same way the DL-*lyxo* isomer **17**, but the DL-*xylo* compound **18** was not obtained. *cis* dihydroxylation of **13** by silver iodoacetate furnished the DL-*xylo* isomer **18**.

In the previous paper,[1] a synthesis of racemic phytosphingosine and the *lyxo* isomer was described. The procedure was based on the stereospecific reaction of *trans*-glycidic acid with benzylamine to give 2,3-*erythro*-2-benzylamino-3-hydroxy acid.[2] The present paper deals with syntheses of all of the racemic diastereoisomers of phytosphingosine by stereospecific dihydroxylations[3] of 3-octadecene derivatives.

The stereochemical assignments of the products as compared with the natural and the diastereomeric compounds described in the previous paper[1] confirmed that all of the reactions proceeded with known stereochemistry.

The reaction of *n*-hexadecynylmagnesium bromide with diethyl oxalate[4] gave ethyl 2-oxo-3-octadecynoate (**1**) (identified by the semicarbazone **1'**) accompanied by a small amount of tetrakis(1-hexadecynyl)ethylene glycol (**2**), whose constitution was confirmed by oxidation with lead tetraacetate to afford bis(1-hexadecynyl) ketone (**3**) (identified by the 2,4-dinitrophenylhydrazone **3'**). On heating an alcoholic solution of the 2,4-dinitrophenylhydrazone (**4**) of the acetylenic keto ester **1** cyclization into the pyrazole derivative (**5**)[5] was observed. When **1** was treated with hydroxylamine hydrochloride, similar cyclization reaction occurred and the isoxazole derivative (**6**)[6] was formed. On the other hand, the treatment of **1** with hydroxylamine hydrochloride in the presence of sodium acetate furnished an addition–cyclization product (**7**).[7]

Reductive acetylation of the 2,4-dinitrophenylhydrazone **4** to the acetylenic amido ester **8** was carried out with zinc dust.[8] The ester group of **8** was selectively reduced with lithium aluminum hydride to give acetylenic amido alcohol **9**, which was partially hydrogenated to 2-acetamido-1-hydroxy-*trans*-3-octadecene (**10**) with sodium in liquid ammonia,[9] or to the *cis* isomer **12** with Lindlar's catalyst.[10] Alternatively, the same *cis* compound **12** was obtained from **8** by catalytic hydrogenation followed by reduction with lithium aluminum hydride or lithium borohydride.[11]

The *trans*-amido alcohol **10** was transformed into the O-acetate **13** and dihydroxylated in *trans* fashion with performic acid[12] followed by saponification to furnish racemic N-acetyl phytosphingosine (**14**) and the DL-*arabino* isomer **15**. The separation was carried out by fractional recrystallization. Excellent crystallizability of the DL-*arabino* compound **15** aided the isolation of both isomers. The compound **14** was identical

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