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ARYL SUBSTITUTED DIASTEREOMERIC ALKENES: GAS CHROMATOGRAPHIC BEHAVIOR ON A NON-POLAR *VERSUS* A LIQUID CRYSTAL PHASE

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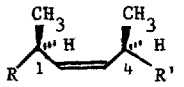
SUMMARY

The preparations and resolutions of a series of aryl substituted diastereomeric alkenes is described using bonded non-polar and cholesteric liquid crystal columns, the latter operated in its mesophase. Separations of diastereomers were notably greater using the more more aligned cholesteric phase. Elution orders of the diastereomers are determined by asymmetric synthesis, and is discussed in terms of molecular size and shape. The greatest diastereomer resolutions are achieved in this study when one of the asymmetric centers bears a 1- or 2-naphthyl group. Hence, it is suggested that a resolved 2-(1′- or 2′-naphthyl)propyl phosphonium salt could be useful as a derivatizing agent via Wittig condensations with chiral aldehydes. That is to say, the resulting diastereomeric alkenes would likely be separable allowing both the assignment of aldehyde absolute configuration by means of elution order and configurational purity by means of diastereomer ratio.

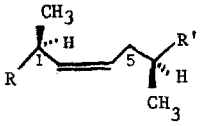
INTRODUCTION

In an earlier report we described the separation by gas–liquid chromatography (GLC) of diastereomeric alkenes (Fig. 1)[1]. The alkenes bore a hydrocarbon asymmetric center on either side of the double bond. The study determined that the separation factor for a (*Z*)-alkene was greater than that for the corresponding (*E*)-alkene. In addition, separations of diastereomeric (*Z*)-pairs were greatest when the asymmetric centers were in a 1,4-relationship (Fig. 1, 1). The *R*S**-diastereomer[2] of 1 eluted first on nonpolar columns, and the diastereomer elution order alternated as the asymmetric centers were methodically shifted apart.

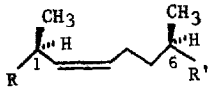
The motivation for such studies is to develop methods for determining configurational purity of such natural products as insect sex pheromones by relatively simple chemical transformations that would generate the alkene double bond. It is intended that one asymmetric carbon be the one for which absolute configuration and configurational purity must be determined; the other must be made available in high, or at least known, configurational purity embodied in a structure suitable for



1. (1*R*,4*S*)-diastereomer



2. (1*R*,5*R*)-diastereomer

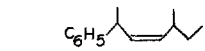
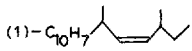
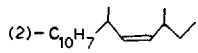
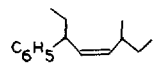
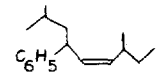
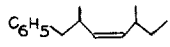
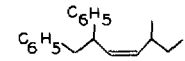
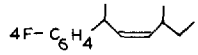
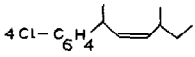


3. (1*R*,6*S*)-diastereomer

Fig. 1. Diastereomeric *Z*-alkenes indicating the relative configuration of the diastereomer that has the lower GLC retention volume.

TABLE I

DATA FOR DIASTEREOMERIC ALKENES OBTAINED FROM 2-METHYLBUTYRALDEHYDE

	Alkene structure	*Column A**			*Column B****		
		T (°C)	*k'***	α_Z**	*T* (°C)	*k'***	α_Z**
1		110	4.24, 4.44	1.048	140	1.44, 1.60	1.111
2		140	9.26, 9.82	1.060	175	8.80, 9.44	1.073
3		140	15.15, 1622	1.071	175	10.16, 11.68	1.150
4		110	18.45§, 18.79§ 7.09. 7.34	1.018§ 1.035	140	13.91§, 14.15§ 2.32, 2.40	1.017§ 1.034
5		110	12.12, 12.52	1.033	140	3.88, 4.08	1.052
6		140	6.40	1.0	140	2.32	1.0
7		150	11.75, 1187	1.011			
8		110	4.44, 4.64	1.045	140	1.76, 1.88	1.068
9		110	12.06, 12.73	1.056	140 160	5.96, 6.44 2.92, 3.12	1.081 1.068

* Column A is a DB-1 fused silica column (0.25 μm film) 15 m × 0.25 mm I.D.; $N_{eff.}$ = 1500 (J&W Scientific, Orangevale, CA, U.S.A.).

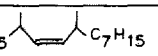
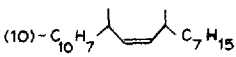
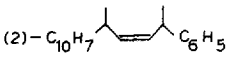
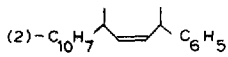
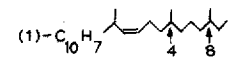
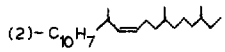
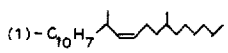
** Partition coefficients, *k'*, and separation factors for *cis*-alkenes, α_Z, are defined in ref. 20. Diastereomer elution orders are discussed in the text.

*** Column B is a CpCC (see text) glass column (static coating of 0.25% solution in dichloromethane) 26 m × 0.20 mm I.D.; $N_{eff.}$ = 1500.

§ *E*-isomers.

TABLE II

DATA FOR DIASTEREOMERIC ALKENES OBTAINED FROM VARIOUS ALDEHYDES

Alkene structure	*Column A*			*Column C***		
	*T k'** (°C)		α_z**	*T k'** (°C)		α_z*
10*** 	160	4.77, 5.33	1.157	140	4.50, 5.40	1.200
11 	180	9.35,12,12	1.296	180	14.80, 23.47	1.586
12 	190	8.77, 10.69	1.219	180	9.00, 1707 20.79§, 30.10§	1.897 1.448§
13 				180	9.77, 23.38	2.393
14 	200	15.15, 15.31	1.011	180	29.8 , 30.4	1.027
15 	200	17.38, 1769	1.018	190	33.2 , 34.2	1.030
16 	200	13.93, 14.29	1.026	180	14.21, 15.00	1.056

* See Table I.

** Column C is a CpCC (see text) glass column (static coating of 0.10% in dichloromethane) 13.6 m × 0.20 mm I.D.; $N_{eff.}$ = 1300.

*** This material on Column B of Table I at 175°C gave k' values of 3.36 and 3.96; α_z = 1.179.

§ *E*-isomers.

the derivatization, or diastereomer-forming, reaction. This report describes an investigation for such a chiral derivatizing agent, and a comparison of the separation factors for the subject diastereomeric alkenes on the bonded nonpolar phase DB-1 and a cholesteric liquid crystal phase cholesterol-*p*-chlorocinnamate (CpCC)[3].

EXPERIMENTAL*

GLC was performed on user-modified Varian-1400 instruments employing the columns described in Tables I and II. The inlet split ratio was 40–50:1, linear flow velocities of helium were set to 18 cm/sec, and detector make-up (nitrogen) was 30 ml/min. All synthetic intermediates and alkene products were routinely characterized [infrared (IR), ^{1}H NMR, and chemical ionization mass spectrometry (CI-MS)].

General procedures for preparing the alkenes (Fig. 2A)

The alkene-forming step is the well known Wittig condensation[4] and it was conducted in the usual manner so as to maximize the amount of *cis*-alkene formed. An example is given in our initial report[1]. The 2-methyl butyraldehyde was purchased

* Mention of a commercial or proprietary product does not constitute an endorsement by the USDA.

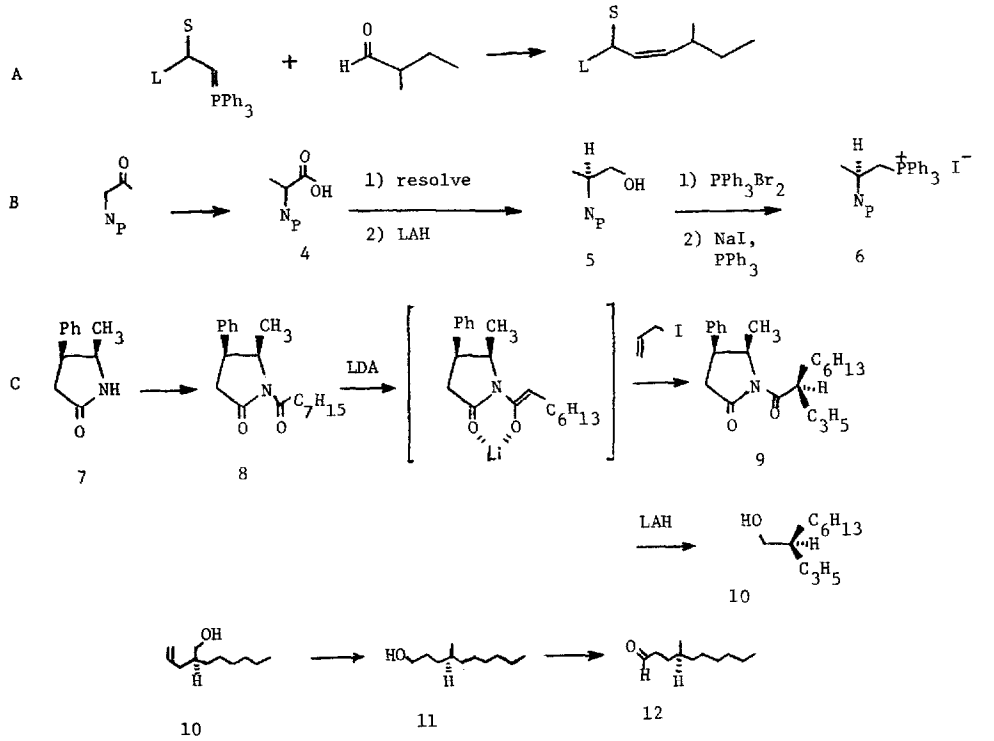


Fig. 2. Synthetic schemes. Ph = Phenyl; Np = (1)-naphthyl; LAH = lithium aluminum hydride; LDA = lithium diisopropylamide; S = small, *e.g.*, alkyl group; L = large, *e.g.* aryl group.

from Aldrich and used directly with phosphonium ylids that had been synthesized starting with arylacetic acids (Aldrich). An example is given below in the description of the synthesis of configurationally biased compounds. The 4,8-dimethyldecanol was obtained from Zoecon, 2-methylnonanal was previously described[1], and 4-methyldecanal will be described below.

(R)-2-(1'-naphthyl)propyl triphenyl phosphonium iodide, 6 (Fig. 2B)

1-Naphthylacetic acid was converted to its dianion[5] and treated with methyl iodide to provide the racemic C-methylated acid, 2-(1'-naphthyl)propionic acid in 70% yield after recrystallization from ethylene dichloride-hexane: ^{1}H NMR (C^2HCl_3) δ 1.65 (3H, J = 7.2 Hz, CH_3CH), 4.51 (1H, q, J = 7.0 Hz, $CHCH_3$), 7.4–8.2 (aryl H) ppm; methyl ester CI-MS, m/e 215 (M+1), 155 (M+1−60). The acid was converted via its acid chloride to an amide of (*S*)-α-methylbenzylamine (Hexcel) and recrystallized 4 times from ethanol whereupon GLC analysis indicated ⩾99.8% diastereomeric amide purity (column A, 220°C, k' values: $S_{Acid}S_{Amine}$ 7.00, $R_{Acid}S_{Amine}$ 7.36, α = 1.051). The relative retention volumes of these amides were used to assign the purified (later) isomer as *RS*: yield 45.6% of theory; m.p. 143°C; IR (CCl_4) 3460 and 1680 cm^{-1}; ^{1}H NMR (C^2HCl_3) δ 1.25 (3H, d, J = 6.9 Hz, CH_3CHN), 1.71 (3H, d, J = 7.1, $CH_3CHC{=}O$), 4.30 (1H, q, J = 7.1, $CH_3CHC{=}O$), 5.09 (1H, m, CH_3CHN), 5.39 (1H, s, NH), 7–8 (aryl H) ppm; CI-MS m/e 304 (M+1).

The purified amide was cleaved by carbomethoxylation of the amide nitrogen and treatment of the resulting acyl urethan with lithium aluminum hydride[5] to give the corresponding (*R*)-alcohol (5) in 68.3% yield: b.p. 110–118°C/0.01 mmHg; $[\alpha]_D^{23}$ − 21.2° (*c*, 5, $CHCl_3$); ^1H NMR (C^2HCl_3) δ 1.43 (3H, d, J = 6.4 Hz, CH_3CH), 3.85 (2H, m, CH_2OH), 7.4–8.2 (aryl H) ppm; CI-MS *m/e* 187 (M+1), 169 (M+1−18). The alcohol 5 was reoxidized to the 4 so that it could be analyzed for configurational purity. This was done by reconverting the acid to its amide with (*S*)-α-methylbenzylamine and examining diastereomer content by GLC (*vide supra*). The alcohol 5 was determined to be 94% (*R*) — evidently some racemization occurred during the process of recovering the acid residue by cleaving the purified amide.

The alcohol was converted to a bromide with triphenylphosphine dibromide in the usual manner[6]: ^1H NMR (C^2HCl_3) δ 1.58 (3H, d, J = 6.9 Hz, CH_3CH), 3.52, 3.77 (2H, m's, H_A and H_B of C^*CH_2Br), 4.02 (1H, m, CH_3CHCH_2), 7.4–8.2 (aryl H) ppm; CI-MS *m/e* 169 (M+1−HBr). The crude bromide was allowed to react with one equivalent of triphenylphosphine and excess sodium iodide to produce the phosphonium iodide, 6, in 33% yield: m.p. 211–216°C (ethylene dichloride–diethyl ether); $[\alpha]_D^{23}$ − 42.8° (*c*, 5, $CHCl_3$); ^1H NMR (C^2HCl_3) α 1.71 (3H, d, J = 5.0 Hz, CH_3CH).

(S)-4-Methyl-1-decanol, 11 (Fig. 2C)

The route is that developed by Evans *et al.*[8] and involves asymmetric induction via a chiral oxazolidone. The oxazolidone 7 (Fig. 2C) was synthesized by the general method of Pirkle and Simmons[9], using (+)-1*R*,2*S*-norephedrine (Aldrich) as a starting material. The yield was 95.1% by Pirkle's procedure. The oxozalidone was then alkylated with *n*-octanoyl chloride as described by Evans *et al.*[8] to give, after crystallization of some unalkylated material from hexane, an 88% yield of oily 8: IR (CCl_4) absence of NH, OH, 1790, 1735 and 1700 cm^{-1}; ^1H NMR (C^2HCl_3) δ 0.89 (6H, m, CH_3 groups), 1.29 (CH_2 envelope), 1.64 (2H, m, $CH_2C{=}O$), 4.77 (1H, m, $NCHCH_3$), 5.66 (1H, d, J = 7.3 Hz, $CHCHO$), 7.1–7.3 (5H, m, aryl H) ppm.

The *n*-octanoyl derivative 8 was then asymmetrically alkylated with allyl iodide using Evans' general procedure the stereochemical outcome of which is known[8]. The alkylated oxazolidone 9 was purified by gravity column chromatography with silica gel [thin-layer chromatography: R_F 0.70 for 9, 0.62 for 8, 0.10 for 7 with ethyl acetate–hexane (20:80)] eluting with ethyl acetate–hexane (5:95). Reduction of 9 with lithium aluminum hydride (tetrahydrofuran), 2 h, reflux) and distillation gave impure alcohol 10 in low yield: b.p. 57–62°C/0.02 mmHg. The crude alcohol 10 was converted to alcohol 11 by a process we have previously described[10] whereby alcohol 10 is converted to its bromide, the double bond is hydroborated with disecondary isoamylborane, addition of lithium triethylborohydride replaces Br with H, and an oxidative work-up produces the terminal alcohol 11: b.p. 64–66°C/0.1 mmHg; $[\alpha]_D^{23}$ + 2.5 (*c*, 1.4, $CHCl_3$); IR (CCl_4) 3640 cm^{-1}; ^1H NMR (C^2HCl_3) δ 0.87 (6H, m, CH_3 groups), 1.2–1.7 (CH_2 envelope), 3.63 (2H, t, 6.7 Hz, CH_2CH_2OH) ppm.

Configurationally biased alkenes

Condensation of the ylid of 6 with the aldehyde 12 that was obtained by pyridinium chlorochromate oxidation of alcohol 11[11], led to the *Z*-alkene of entry 16 in which the ratio of *cis*-diastereomers was >90:10. The *S,S*-stereoisomer predominated and this accords with an expected high stereoselectivity in oxazolidone alkyl-

ation of about 97:3. The alkene of entry 11 was obtained with a configurational bias by carrying out the alkene preparation with the same ylid and (*R*)-2-methylnonanal[1]. All of the alkenes were characterized by CI-MS. In particular, the *cis*-alkenes of entry 11 were purified by high-performance liquid chromatography (HPLC) ($AgNO_3$–silica gel). The earlier eluting isomer (both LC and GLC): ^1H NMR (C^2HCl_3) δ 0.90 (9H, m, CH_3 groups), 1.25 (CH_2 envelope), 2.6 (1H, m, allylic CH), 4.52 (1H, m, allylic CH), 5.19, 5.61 (2H, t's, J = 10 Hz, vinyl H); CI-MS m/e 309 (M+1), 181 (M+1−$C_{10}H_7$). The later isomer had identical spectral characteristics except that the vinyl H's resonated at 5.15 and 5.57 ppm. The identities of *trans*-isomers were verified by equilibrating the geometrical isomers with nitrous acid[11].

RESULTS AND DISCUSSION

The limiting factors to separations of hydrocarbon diastereomeric alkenes appear to be (1) the degree to which the substituents on the asymmetric centers influence the solute's presumed solution conformation preferences, and (2) the sensitivity of the solvent to those conformations. At the present time studies designed specifically to learn of the solution conformations of this type of substrate have not been conducted. However, an evaluation of molecular models of these alkenes was coupled with strong analogy to the (HPLC) studies of diastereomeric amides and carbamates[13,14] (Fig. 2A). Conceptual models were envisioned by those authors in which the central amide and carbamate units including the attached asymmetric carbons and carbinyl hydrogens were coplanar. Any structural alteration that increased the acidity of a carbinyl hydrogen that could hydrogen-bond to the carbonyl oxygen served to legitimize the model further. We found that for alkyl substituents R^1 and R^2 that had no polar functional groups, GLC separation could be predicted in terms of the relative lengths of the two alkyl groups (the amine residue carried a methyl and a phenyl substituent as R^3 and R^5)[15]. The structures of Fig. 3 may be rotated 90° to permit a view from the top. If $R^1 > R^2$ and $R^4 > R^3$, and in the cases reported[15] phenyl > methyl for the amine portion of these structures, then the structure is *trans*-like. The other diastereomer in each case is *cis*-like and less extended, *i.e.*, its length-to-breadth ratio is less. Accordingly, we rationalized the greater retention time for the *trans*-like diastereomers as an enhanced ability to align with the

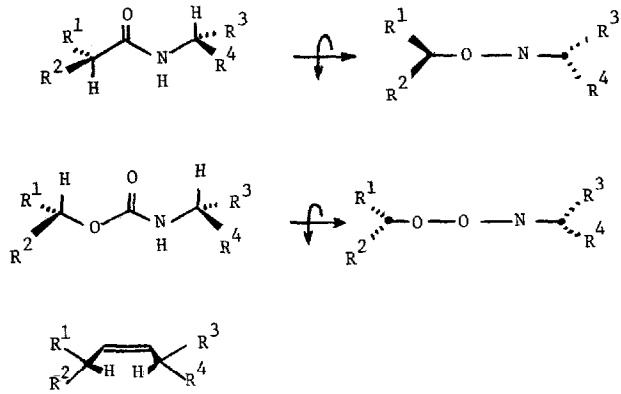


Fig.3. Solution conformation preferences of amides, carbamates, and possibly the diastereomeric alkenes.

solvent molecules of the GLC stationary phase. The degree of separation of diastereomeric amides and carbamates was greatest in columns coated with the cholesteric liquid crystal, CpCC[3]. As one might expect, such a liquid phase is very highly ordered in its mesophase, and separations based primarily on solute shape are likely to be exalted[16–18].

The separations of diastereomeric alkenes reported[1] dealt only with structures that have alkyl groups on the asymmetric centers. In order to develop a useful chiral derivatizing agent we wished to optimize diastereomer separations. Although the natural products obtained from insects that are our laboratory's prime concern are usually aliphatic, the attachment of an aryl ring to the asymmetric center of the projected derivatizing agent was expected to lead to greater differentiation of diastereomers by GLC solvents, especially by the liquid crystal CpCC. Since the most difficult separations are realized when the aliphatic asymmetric center is substituted by methyl and ethyl groups[1,15], 2-methylbutyraldehyde was chosen as the aldehyde component for a series of alkene-forming condensations (Fig. 2A, Table I). The components bearing an aryl ring were each synthesized from commercially available chemicals by known methods (see Experimental) to provide the derivatizing agent as a phosphonium salt. Condensations of 2-methylbutyraldehyde with ylids of the phosphonium salts were conducted to maximize *cis*-content in the alkene product.

A comparison of the first three entries of Table I shows that aryl substitution indeed aids diastereomer separations in comparison with alkyl substitution as previously described. Alkenes in which the aryl substituents of entries 1–3 are replaced with a normal alkyl group gave a separation factor no greater than 1.033 on the same DB-1 column. Moreover, CpCC afforded equivalent separation to that obtained on DB-1 for a strictly aliphatic diastereomer pair, whereas separations are greater on CpCC than on DB-1 for diastereomers with aryl substituents. The 2-methyl group provides the greatest separation of diastereomers, though both naphthyl substituted alkenes (entries 2 and 3) reduce volatility greatly, and may therefore have a more limited range of usefulness. The chromatographic separations of the diastereomers implicit in entries 2 and 3 of Table I are shown in Fig. 4.

Entries 4 and 5 show that increasing the size of the alkyl substituent on the derivatizing agent from methyl to ethyl or isopropyl tends to reduce the separation of diastereomers. Similarly shifting the aryl ring from the asymmetric center (entry 6) and placing two aryl rings on the center (entry 7) also cause separations to decline. Substitution on the aryl ring was briefly examined (entries 8 and 9) since substitution in the *para* position might aid solute alignment and a selection of substituents is available to enhance detection by electron capture techniques. Both *p*-fluoro and *p*-chloro derivatives were separated to about the degree of the unsubstituted aryl derivative.

Selected condensations involving other aldehydes produced a series of diastereomeric alkenes that are presented in Table II. Entry 10 of Table II, 8,11-dimethyl-*Z*-9-octadecene diastereomers were well separated by both types of GLC column. Replacing one of the normal heptyl chains by an aryl group (1-naphthyl, entry 11) increased the separation factor by 1.1 on the DB-1 phase and by a dramatic 1.3 on the chloresteric phase even though column temperature had to be raised 40°C. When both asymmetric centers bore an aryl group (entries 12 and 13) the separation factors were even greater on the CpCC column.

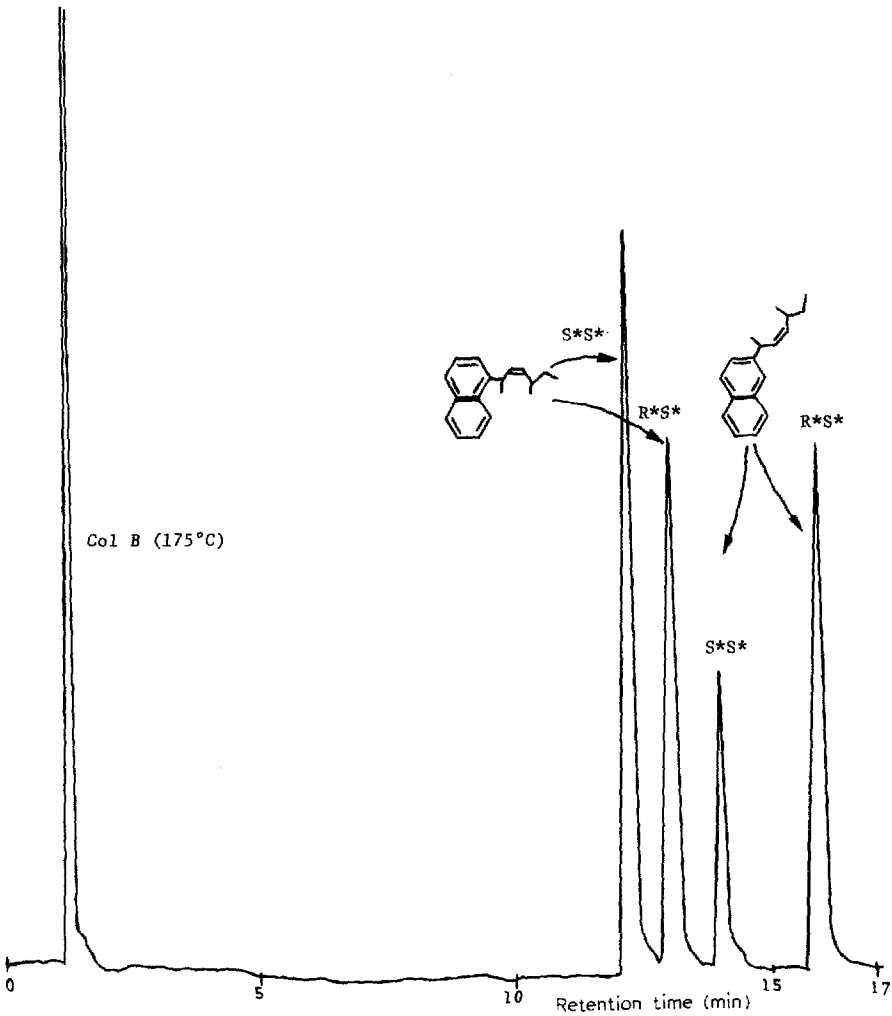


Fig. 4. Separations of diastereomeric alkenes (entries 2 and 3 of Table I) on cholesterol-*p*-chlorocinnamate column B.

The final entries of Table II (14, 15 and 16) demonstrate (1) that the use of an aryl substituted asymmetric center as part of the chiral derivatizing agent provides sufficient diastereomer differentiation for the resulting alkene and (2), that the asymmetric center of a natural product under investigation may be relatively distant from the eventual double bond. The aliphatic residue of entries 14 and 15 was derived from 4,8-dimethyldecanal, an aggregating pheromone of beetles of the genus *Tribolium*[19]. Although the 8-methyl group of that residue is also part of an asymmetric construction, its distance from the double bond of the derivative is still too remote to be sensed by this method. Fig. 5 shows the separation of the diastereomers of entry 15 on CpCC. Entry 16 was derived from 4-methyldecanal that was stereochemically biased. Its reaction with a similarly biased phojsphonium salt produced an alkene enriched in the *S,S*-diastereomer. Similarly the derivative of entry 11 was also

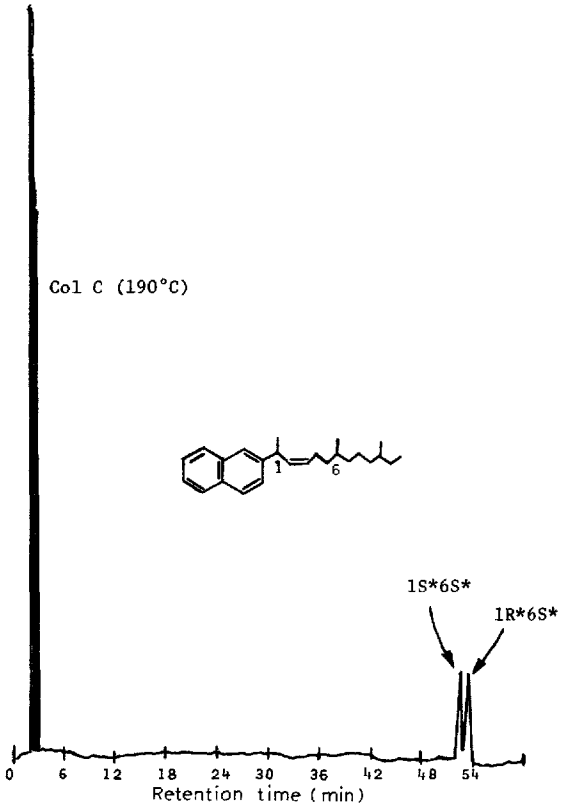


Fig. 5. Separations of diastereomeric alkenes (entry 15 of Table II) on cholesterol-*p*-chlorocinnamate column C.

synthesized to provide unequal amounts of the diastereomers. In this fashion it was possible to assign elution orders of the diastereomers specifically to those entries, and by analogy to the others. The elution orders paralleled those of the strictly aliphatic alkenes previously reported[1], and fitted the conceptual model that had been tentatively advanced to explain elution orders (Fig. 1). Unfortunately, the *R-S* convention leads to alteration of the letter designation of the aryl substituted carbon's configuration. Thus the diastereomer of lower retention volume when the asymmetric carbons are in a 1,4-relationship, *e.g.*, entry 11, or a 1,6-relationship, *e.g.*, entry 16, has the *S*,S** configuration[2]. The elution order is reversed for the intermediate 1,5-relationship. More simply, the relative configurations of these compounds can be ascertained by using Fig. 3 (the *Z* alkene structure) and inverting elution order for each additional chain (carbon) atom inserted between the asymmetric centers. If $R^1 > R^2$ and $R^3 > R^4$ in the general sense of chain length, then this is the *cisoid* diastereomer and is expected to have the lower GLC retention volume.

In summary, improved separations of diastereomeric alkenes can be realized if the projected derivatizing agent has an aryl substituent on its asymmetric center. A 2-naphthyl substituent appears to have the greatest influence on separations though derivative volatilities will be greatly reduced as the cost of an increased sep-

aration factor. Since compounds with variously substituted phenyl rings are commercially available, the individual faced with a configuration assignment can choose to prepare a suitable derivatizing agent, for example in analogy to the Experimental section or by employing other known synthetic methods, in order to optimize volatility and electron capture–UV detection, as well as separation.

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