

From the rate data for *p*-toluenesulfinyl *p*-tolyl sulfone in dioxane and acetonitrile^{3b} one estimates that k_1 at 70° should be about 6×10^{-3} sec.⁻¹. At this temperature in acetic acid–0.56 *M* water–0.6 *M* sulfuric acid, k_2 for *p*-toluenesulfinic acid is 1.5×10^{-3} *M*⁻¹ sec.⁻¹ (Table I). When inserted into eq. 4 these data lead to the conclusion that under these conditions the equilibrium concentration of sulfinyl sulfone in a solution 0.10 *M* in sulfinic acid will be about 8×10^{-4} *M*, or 8/1000ths the concentration of the sulfinic acid. This indication that the sulfinyl sulfone is not too thermodynamically disfavored in solvent systems such as the present one would seem to have significant implications for the chemistry of sulfinic acids.

Experimental

Preparation of Materials.—*p*-Toluenesulfinic,² *p*-chlorobenzenesulfinic,⁵ *p*-bromobenzenesulfinic,⁶ and *p*-methoxybenzenesulfinic⁷ acids were all prepared by published procedures. β -Naphthalenesulfinic acid⁸ and *p*-nitrobenzenesulfinic acid⁹ were prepared from the corresponding sulfonyl chlorides by the same procedure⁶ used for the *p*-bromo acid. Benzenesulfinic acid was liberated by acidification of sodium benzenesulfinate (Aldrich Chemical).

Once prepared, *p*-toluenesulfinic and *p*-methoxybenzenesulfinic acids were further purified by published procedures.^{2,7} Benzenesulfinic acid was recrystallized from water, m.p. 85°. *p*-Chlorobenzenesulfinic acid was recrystallized from 1:1 ether–hexane, m.p. 94–96°. The *p*-bromo acid was purified in the same way, m.p. 112–114°. To purify β -naphthalenesulfinic acid, the crude acid obtained by acidification of an aqueous solution of the sodium salt was filtered off and dissolved in as little ether as possible. The ether solution was dried over anhydrous calcium sulfate and filtered. The acid was precipitated by addition of five times its volume of hexane to the filtrate. Another recrystallization from

ether–hexane gave pure β -naphthalenesulfinic acid, m.p. 103–104.5°. A similar purification procedure, except that only three volumes of hexane were used per volume of ether, was employed for *p*-nitrobenzenesulfinic acid, m.p. 157–158°.

The purification of acetic acid and the preparation of the various stock solutions of sulfuric acid in acetic acid–water were carried out as previously described.^{2,10}

Kinetic Studies.—The general procedure used for the kinetic runs was the one already described by Kice and Bowers.² In all cases except the *p*-nitro acid the progress of the reaction was followed by titrating the residual sulfinic acid with standard sodium nitrite solution in the manner previously described.²

For the *p*-nitro acid an alternate procedure involving the titration of the aliquot from the reaction with standard ceric sulfate, using a potentiometric end point,¹¹ was employed. The rate of oxidation of the sulfinic acid by ceric ion is enough faster than the oxidation by the same reagent of the thiolsulfonate from the disproportionation that a sufficiently sharp end point can be obtained.

Product Studies.—The stoichiometry of the disproportionation reaction was checked with both *p*-chlorobenzenesulfinic and benzenesulfinic acids. A solution of the sulfinic acid in acetic acid–water–sulfuric acid was made up and deaerated using the same procedure as in the kinetic runs. After being heated at 80° for a period of time sufficient to disproportionate most of the sulfinic acid, the solution was cooled, and an aliquot was removed and titrated for residual sulfinic acid. The remainder of the solution was then poured into ten times its volume of water, and the resulting mixture was extracted with ether. The ether extracts were washed first with aqueous sodium bicarbonate, then with water, and finally were dried over anhydrous sodium sulfate. The ether was removed and the infrared spectrum of the residue was determined. The infrared spectrum of the residue in each case was identical with the spectrum of the appropriate thiolsulfonate. In the case of the *p*-chloro compound the residue was also recrystallized from 95% ethanol to give a pure sample of *p*-chlorophenyl *p*-chlorobenzenethiolsulfonate, m.p. 137–139°, lit.¹² m.p. 136–138°. Disproportionation of 3.57 mmoles of *p*-chlorobenzenesulfinic acid gave 1.07 mmoles (90%) of crude *p*-chlorophenyl *p*-chlorobenzenethiolsulfonate, while disproportionation of 4.04 mmoles of benzenesulfinic acid gave 1.24 mmoles (92%) of crude phenyl benzenethiolsulfonate.

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Isomeric Arylstearyl Acids

F. D. SMITH, H. E. KENNEY, AND A. J. STIRTON

Eastern Regional Research Laboratory,¹ Philadelphia, Pennsylvania 19118

Received July 27, 1964

The viscous oily arylstearyl acid from oleic acid and an aromatic compound, with aluminum chloride as the condensing agent, was found by gas–liquid chromatography of alkyl aryl ketone oxidation products to be a mixture of 12 position isomers with substitution at C-6–17 in the fatty acid chain. Distribution of isomers depends in part on the relative reactivity of the particular aromatic compound. Substitution predominates at the C-17 atom and at positions near the middle of the chain. Crystalline arylstearyl acids isolated in low yield from the viscous oil are the 17-aryl isomers. Phenylstearyl and ethoxyphenylstearyl acids formed with methanesulfonic acid as the condensing agent are also mixtures of 12 position isomers.

The Friedel–Crafts reaction of oleic acid with excess of aromatic hydrocarbon, with aluminum chloride as the condensing agent, gives an oily arylstearyl acid as the main product. In the case of benzene, *o*- and *p*-xylene, and *o*- and *p*-chlorotoluene it had been possible to isolate a crystalline arylstearyl acid from the main product by repeated crystallization from acetone at –20°, in yields of 1–7% for the crystals compared to 37–75% for the oil.² The oily arylstearyl acid, in the

case of benzene, has been variously considered as primarily a mixture of the 9- and 10-phenyl isomers,³ of, if double-bond migration (hydride ion transfer) is extensive, as a mixture of several isomers² or a mixture in which the 17-phenyl isomer predominates.⁴

By gas–liquid chromatographic separation of alkyl aryl ketone oxidation products we have found that the oily arylstearyl acid is a complex mixture of 12 position isomers, with the aromatic group attached at positions 6–17 on the C₁₈ fatty acid chain. The crystalline



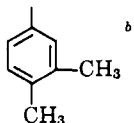
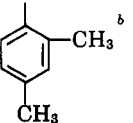
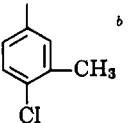
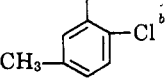
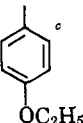
(1) Eastern Regional Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

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TABLE I
 ISOMERIC ARYLSTEARIC ACIDS^a

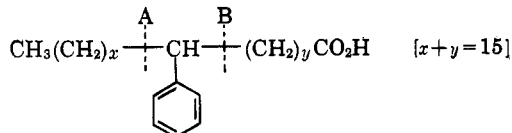
Carbon no. on fatty acid chain	Isomer						
							
17	14.9	28.6	32.5	21.4	20.5	34.3	2.2
16	2.6	5.7	3.5	1.2	4.2	3.6	1.9
15	4.3	7.2	5.8	1.9	6.3	5.5	2.9
14	6.8	8.6	7.0	3.6	9.3	8.0	4.9
13	8.1	8.5	7.6	4.9	10.0	8.7	6.2
12	9.8	8.3	7.7	6.9	10.7	9.2	9.4
11	11.7	8.1	7.6	9.5	10.5	9.1	13.2
10	15.1	7.8	8.6	17.8	10.8	8.8	17.9
9	13.4	7.7	5.3	18.1	9.6	6.8	18.6
8	7.8	5.5	5.3	6.9	5.1	3.9	13.3
7	3.6	3.0	5.0	5.8	1.8	1.3	7.2
6	1.8	1.0	4.2	2.1	1.1	0.5	2.4

^a Values are given as mole %. ^b AlCl₃ condensing agent. ^c CH₃SO₃H condensing agent.

arylsteoric acid, oxidizable to acetophenone or to a ring-substituted acetophenone, is the 17-aryl isomer.


Gas-liquid chromatography applied to oily phenylsteoric acid and to the crystalline phenylsteoric acid, in the form of the methyl esters, gave the same picture in each case indicating lack of resolution of the isomeric esters because of low vapor pressure and great similarity in adsorption characteristics.


The products from the chromic acid oxidation of an oily arylsteoric acid are represented in the case of phenylsteoric acid.⁵



A-I, CH₃(CH₂)_{x-1}CO₂H

B-I, HO₂C(CH₂)_{y-1}CO₂H

A-II,  CO(CH₂)_yCO₂H

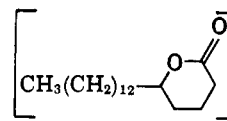
B-II,  CO(CH₂)_xCH₃

After neutralization and removal of the acid fractions A-I, A-II, and B-I, the B-II fraction was obtained as a neutral oil. The alkyl aryl ketones of B-II were recognized by gas-liquid chromatography using acetophenone, propiophenone, valerophenone, hexanophenone, and laurophenone as reference ketones.

By the use of acetophenone, 2,4-dimethyl-, 2,5-dimethyl-, 3,4-dimethyl-, 4-chloro-3-methyl-, and 2-chloro-5-methylacetophenones, the crystalline acids from benzene, *o*- and *p*-xylene, and *o*- and *p*-chlorotoluene were found to be the respective 17-aryloctadecanoic acids with the orientation shown in Table I. The chlorine atom of *o*- and *p*-chlorotoluene directs substitution on the benzene ring *para* and *ortho*, respectively.

The condensation of benzene with oleic acid in the Friedel-Crafts reaction apparently proceeds through proton addition (from H⁺[AlCl₄]⁻) carbonium ion formation and hydride ion transfer to create a series of 12 position isomers with the phenyl group at positions 6-17 on the fatty acid chain. No alkyl aryl ketones with an alkyl group of 13 carbon atoms or

more were found and therefore no substitution occurs at carbon-5, -4, -3, or -2. In the mechanism of proton addition, carbonium ion formation, and hydride ion transfer, lactone formation may become possible as shown and if this happens the carbonium ion no longer exists and attachment of an aryl group is no longer possible.^{5,6}



Experiments in which no crystalline arylsteoric acids had been isolated were also included. These were the condensation of oleic acid with *m*-xylene, catalyzed by AlCl₃, and the condensation of oleic acid with benzene and with phenetole, catalyzed by methanesulfonic acid.⁷

The reaction conditions had been chosen for the greatest yield of the mixture of isomeric arylsteoric acids and are not particularly appropriate for a comparison of the relative rates of the double-bond migration and the condensation reaction. Differences in reactivity of the aromatic compound and in the efficiency of the two condensing agents result in a different distribution of isomers. In both the aluminum chloride and the methanesulfonic acid catalyzed reaction the highest ratio of penultimate to midpoint substitution is found with the less reactive aromatic compounds. This is true from the figures of Table I in the comparison of *o*- with *m*-xylene, *p*- with *o*-chlorotoluene (aluminum chloride catalyst), and benzene with phenetole (methanesulfonic acid catalyst). The use of methanesulfonic acid, a less vigorous catalyst, results in a higher ratio of the 17-phenyl isomer as can be seen from the two benzene experiments.

Experimental

Arylsteoric Acids.—The oily arylsteoric acids, with aluminum chloride as the condensing agent, were prepared from purified oleic acid as described in an earlier publication.² The crystalline

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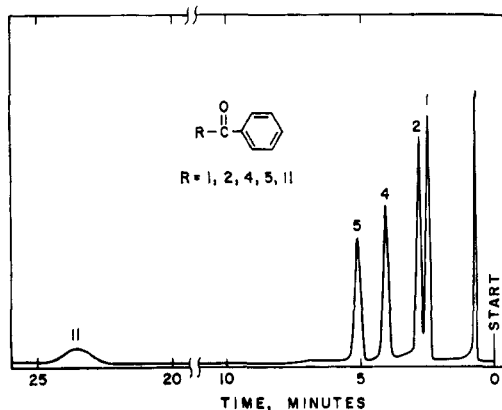


Figure 1.—Separation of reference compounds.

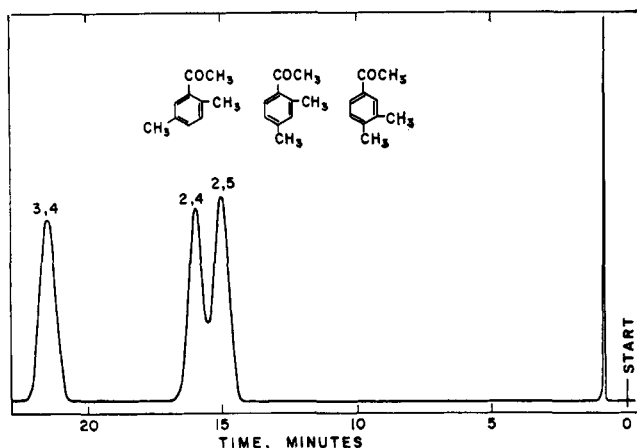


Figure 2.—Separation of reference compounds.

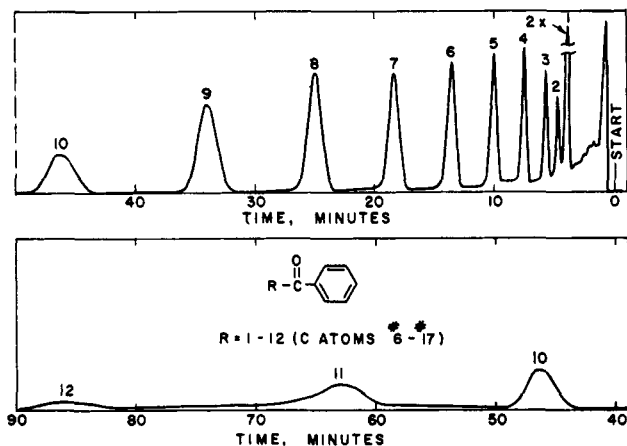


Figure 3.—Ketones from oily phenylstearic acid.

arylstearic acids from benzene, *o*- and *p*-xylene, and *o*- and *p*-chlorotoluene, m.p. 64.8–65.4°, 59.8–61.2°, 76.4–77.6°, 53.1–54.1°, 69.4–70.2°, respectively, were obtained from the oil by repeated crystallization from acetone at –20°. Oily phenylstearic and ethoxyphenylstearic acids were also prepared from oleic acid in a homogeneous reaction system with methanesulfonic acid as the condensing agent.⁷

Alkyl Aryl Ketones.—Acetophenone, propiophenone, valerophenone, hexanophenone, laurophenone, 2,4-dimethylacetophenone, 2,5-dimethylacetophenone, and 3,4-dimethylacetophenone were commercial reagent chemicals. The 4-chloro-3-methylacetophenone and 2-chloro-5-methylacetophenone were prepared from acetic anhydride and *o*- and *p*-chlorotoluene, respectively, by the Friedel-Crafts reaction.⁸

Chromic Acid Oxidation.—Chromic acid, 15.3 g., was added in the course of 2 min. to a stirred solution of 10 g. of phenyl-

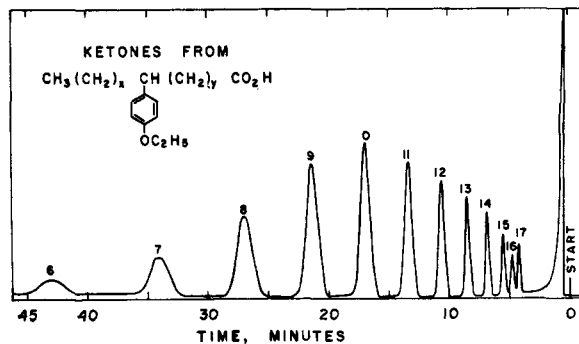


Figure 4.

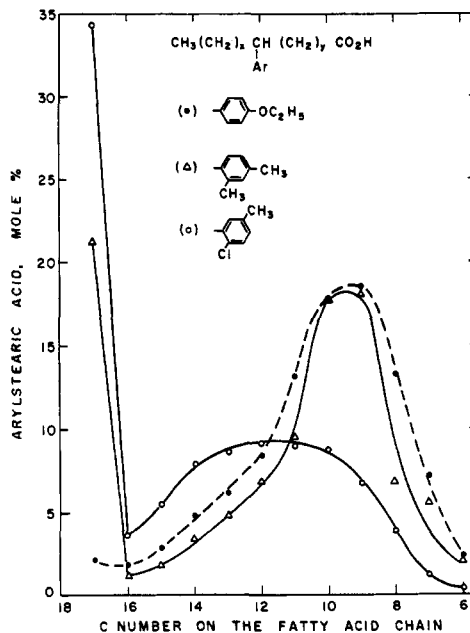


Figure 5.

stearic acid in 170 ml. of glacial acetic acid at 20°. The mixture was stirred for 2 hr., the temperature rising to 28°. Water and ethyl ether, 200 ml. each, were added, and the mixture was transferred to a 4-l. separatory funnel containing 2 l. of water and 200 ml. of ether. The aqueous layer was re-extracted twice with 300 ml. of ether and the combined ether extracts were washed free of water-soluble acids with a saturated sodium sulfate solution. The light green ether layer was neutralized with 6 *N* sodium hydroxide, until the ether layer was colorless and the aqueous layer green. The ether layer was separated, washed, concentrated to about 2 ml., dried with anhydrous sodium sulfate, and analyzed by gas-liquid chromatography.

Chromatography.—The chromatographic separations were carried out on a F and M Model 500 control panel with a F and M Model 720 dual column oven.⁹ Gow-Mac W-2 filaments were used in the thermal conductivity cell and the d.c. power was supplied with a Gow-Mac Model 405-C:1.

A stainless steel coiled column 6 ft. × 0.25 in. o.d. packed with Diatoport W (60–80 mesh) coated with 10% Carbowax 20M gave the best separation with these homologous series of ketones.

The separations were carried out at temperatures ranging from 220° for phenylstearic acid oxidation products to 240° for the ketones from the arylstearic acids from the chlorotoluenes. All of the analyses were run isothermally since this gave the best log retention plots and the most accurate quantitative analysis with known reference mixtures.

Reliability and Validity of Results.—A known mixture of five acetophenone homologs, 20% each by weight, was separated as shown in Figure 1. A plot of log retention times against the

(9) Reference to specific manufactured items does not constitute recommendation by the U. S. Department of Agriculture over similar articles not mentioned.

(8) C. F. H. Allen and M. P. Bridgess, *J. Am. Chem. Soc.*, **49**, 1846 (1927).

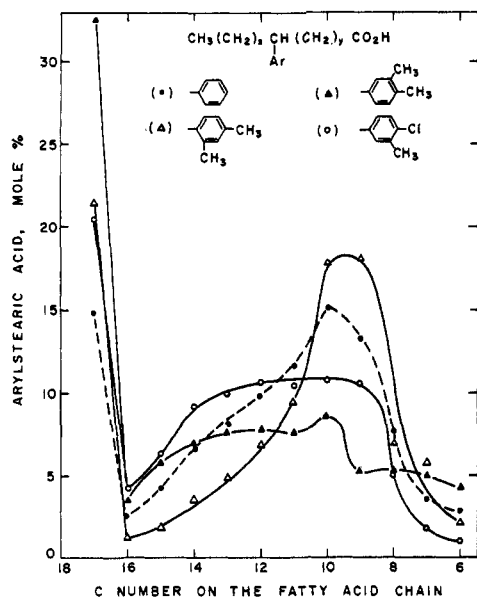


Figure 6.

number of carbon atoms gave a nearly straight line. Quantitative analysis of the mixture by gas-liquid chromatography gave the following results, % by weight: acetophenone, 18.2; propiophenone, 19.3; valerophenone, 21.0; hexanophenone, 22.2; laurophenone, 19.3. The chromatographic separation of a mixture of equal parts of three isomeric dimethylacetophenones is shown in Figure 2.

The separation of the alkyl aryl ketones obtained by chromic acid oxidation of oily arylstearic acids from benzene (aluminum chloride catalyst) and phenetole (methanesulfonic acid catalyst) is shown in Figures 3 and 4.

Distribution of isomeric arylstearic acids from benzene, *o*- and *m*-xylene, *o*- and *p*-chlorotoluene, and phenetole is shown in Table I and Figures 5 and 6. Oxidation and chromatographic separation experiments showed that the values of Table I for phenylstearic acid (aluminum chloride catalyst) could be closely duplicated with an average deviation of 0.24 mole %. As in the case of the reference acetophenone homologs, plots of the log retention time against numbers of carbon atoms gave a nearly straight line for each family of alkyl aryl ketones.

Point of Substitution on the Benzene Ring.—Chromic acid oxidation of a crystalline arylstearic acid isolated from the condensation of *p*-xylene with oleic acid² gave a dimethylacetophenone identical in retention time by gas-liquid chromatography with 2,5-dimethylacetophenone. The crystalline arylstearic acid is therefore 2',5'-dimethyl-17-phenyloctadecanoic acid.

Similarly the first member of the two series of alkyl aryl ketones from oily arylstearic acids from *o*- and *m*-xylene were found to have identical and superimposable retention time with 3,4-dimethylacetophenone and 2,4-dimethylacetophenone, respectively. The point of substitution of aliphatic carbon on the benzene ring is therefore as shown in Table I.

The chlorine atom of *o*- and *p*-chlorotoluene was found to direct the point of substitution of aliphatic carbon *para* and *ortho* to itself, respectively, as shown in Table I. This is true also in the Friedel-Crafts reaction of chlorotoluenes with acetic anhydride.⁸ The first member of the series of alkyl aryl ketones from the oily arylstearic acid from *o*-chlorotoluene was found identical in retention time with 4-chloro-3-methylacetophenone.

Oxidation of a crystalline arylstearic acid from *p*-chlorotoluene gave a ketone identical with 2-chloro-5-methylacetophenone in retention time and in the melting point of the oxime, 114–115°.

Reaction Products of Alloocimene and Maleic Anhydride

J. E. MILKS

Arizona Chemical Company, Stamford, Connecticut

AND J. E. LANCASTER

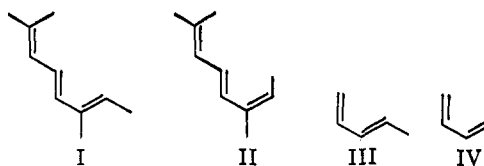
American Cyanamid Company, Research Service Department, Stamford, Connecticut

Received October 8, 1964

Alloocimene, a mixture of two stereoisomers of 2,6-dimethyl-2,4,6-octatriene, when treated with maleic anhydride gives two isomeric adducts, resulting from the addition of maleic anhydride to positions 4 and 7 of the alloocimene isomers. The structure of the adducts was established by n.m.r. analysis. The two acids produced by hydrolysis showed a large difference in the ionization of the second carboxyl group. A third adduct was also formed in significant amounts when traces of maleic acid were present. The latter adduct was suggested by n.m.r. analysis to be formed from a third triene produced by an acid-catalyzed isomerization of the alloocimene.

Alloocimene (2,6-dimethyl-2,4,6-octatriene), a terpene produced from the thermal isomerization of α -pinene exists in two geometric forms,^{1,2} I and II. In two separate studies^{1,3} both isomers were reported to give the same addition product (m.p. 84°) when treated separately with maleic anhydride. Only this adduct was isolated from the reaction of maleic anhydride and a mixture of the isomers.^{4,5} Recently, however, Alder and co-workers² reported that the alloocimene isomers gave different adducts. The adduct which melted at 84° was derived from the 4:5-*trans*-6:7-*cis* isomer⁶ I,

and a different adduct which melted at 38° was produced from the 4:5-*trans*-6:7-*trans* isomer⁶ II.



trans-Piperylene (III) and *cis*-piperylene (IV), which are related to I and II in the steric configuration of the terminal methyl group, differ markedly in their reactivity with maleic anhydride. With a mixture of the two piperylenes only the *trans* isomer gives an isolable

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(5) B. A. Arbuзов and A. R. Vil'chinskaya, *J. Gen. Chem. USSR*, **25**, 168 (1955).

(6) This nomenclature, based on the relationship of like groups, was adopted to permit further characterization of each triene according to ref. 1, 14, and O'Connor and Goldblatt, *Anal. Chem.*, **26**, 1726 (1954). Alder and co-workers employ a different convention and refer to isomer I as 4:5-*trans*-6:7-*trans*, or alloocimene, and to isomer II as 4:5-*trans*-6:7-*cis*, or neoalloocimene.