solid (2.8 g.) was extracted with 100 ml. of ethanol to which 0.4 g. of calcium carbonate was added. The filtrate was concentrated *in vacuo* to about 20 ml. On cooling, 1.2 g. of colorless prisms, m.p. 305–310° dec., was obtained. From the filtrate, an additional 1.0 g. of colorless crystals, m.p. 306–308°, was recovered. The m.p. rose to 322–324° dec. after three recrystallizations from water; total yield 2.2 g. (78%).

Anal. Calcd. for $C_6H_3N_4OF_3$: C, 35.30; H, 1.48; N, 27.45; F, 27.93. Found: C, 35.11; H, 1.47; N, 28.20; F, 27.57.

6-Amino-8-trifluoromethylpurine (XXXIII).—4,5,6-Triaminopyrimidine (XXXII)[29,62] (1.5 g., 0.012 mole) was dissolved in melted trifluoroacetamide (8.1 g., 0.072 mole) and refluxed. After a few minutes, a copious white precipitate formed and ammonia was evolved. The refluxing (oil-bath temp. 175–180°) was continued for 2 hr. and the white product washed thoroughly with ether and water to yield 1.95 g. (80%) of colorless crystals which charred at 330–335°. Recrystallization from 50% aqueous ethanol gave prisms with the same m.p.

Anal. Calcd. for $C_6H_4N_5F_3$: C, 35.47; H, 1.98; F, 28.06. Found: C, 35.57; H, 1.98; F, 27.94.

2-Trifluoromethyl-6-hydroxypurine (XXXV).—4-Amino-5-imidazolecarboxamide hydrochloride (XXXIV) (1 g., 0.006 mole) prepared by the method of Shaw,[55] was refluxed with trifluoroacetamide (6.8 g., 0.06 mole) for 4 hr. The solid product was washed thoroughly with ether and water. The yield of crude material was 1 g., m.p. 313–315°. Recrystallization from methanol gave 0.8 g. (78%) of colorless needles, m.p. 324–326° dec.

Anal. Calcd. for $C_6H_3N_4OF_3$: C, 35.30; H, 1.48; N, 27.45. Found: C, 35.73; H, 1.69; N, 27.44.

2-Trifluoromethyl-6-aminopurine (XXXVII).—A mixture of 4-amino-5-imidazolecarboxamidine dihydrochloride (XXXVI) (2.4 g., 0.012 mole), prepared by the method of Shaw,[55] and trifluoroacetamide (13.5 g., 0.12 mole), was refluxed (oil-bath temp. 175–180°) for 2 hr. The reaction mixture was cooled, washed thoroughly with ether and recrystallized from 50% aqueous ethanol; yield 1.4 g. (56%), m.p. 360–362° dec. After three recrystallizations from 50% aqueous ethanol, colorless needles were obtained with the same m.p.

Anal. Calcd. for $C_6H_4N_5F_3$: C, 35.47; H, 1.98; N, 34.48. Found: C, 35.28; H, 1.84; N, 34.59.

Spectrophotometric and Dissociation Studies.—Spectrophotometric measurements were made with a Cary model 11 ultraviolet recording spectrophotometer (Applied Physics Corp., Pasadena, Calif.) using matched 1-cm. silica cells and techniques and buffers previously described.[56] The apparent pK_a values were determined using the methods described by Fox and Shugar[57,23] and Parke and Davis.[58]

Acknowledgments.—The authors wish to thank Dr. George B. Brown, Dr. J. J. Fox, Dr. C. Chester Stock and Dr. D. A. Clarke for valuable advice and discussion. They wish to express their gratitude to Mr. Janis Vitols for assistance.

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(56) J. J. Fox, L. F. Cavalieri and N. Chang, THIS JOURNAL, **75**, 4315 (1953).

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(58) T. V. Parke and W. W. Davis, *Anal. Chem.*, **26**, 642 (1954).

NEW YORK 21, N. Y.

[CONTRIBUTION FROM THE INSTITUT FÜR KRISTALLOGRAPHIE UND PETROGRAPHIE OF THE EIDG. TECHN. HOCHSCHULE]

The Determination of *cis–trans* Isomerism by Length Measurements of Molecules in Urea or Thiourea Adducts

BY N. NICOLAIDES[1] AND FRITZ LAVES

RECEIVED MARCH 22, 1958

In X-ray photographs of single crystals of urea or thiourea adducts taken by the Laue technique continuous layer lines appear. The distance between these lines enables one to compute the length of the adducted molecule. This length measurement has been used to differentiate between *cis* and *trans* isomers. A *cis* double bond shortens a molecule 0.9 ± 0.1 Å. while a *trans* double bond shortens it 0.15 ± 0.1 Å. compared to the length of the saturated molecule. The method can be applied to mono- and to some polyunsaturated substances, to some trisubstituted double-bonded systems, and, to some extent, to mixtures.

When a *cis* double bond is present in a hydrocarbon chain, the length of the most extended structural conformation is somewhat less than is that of the corresponding *trans* isomer. This fact has been used to elucidate the structures of rubber and guttapercha, two isomeric, acyclic, polyisoprenoid hydrocarbons. Thus, on the basis of the X-ray work of Bunn[2] and earlier investigators,[3,4] the double bonds in rubber were assigned the *cis* configuration while those of guttapercha were given the *trans* configuration, since the periodicity in stretched rubber was found to be shorter than it was in guttapercha.

Recently it was shown[5-8] that the over-all molecular length of certain compounds can be measured if they can be made to form an inclusion type of complex with urea or thiourea known as urea or thiourea adducts. These adducts yield continuous layer lines when Laue photographs of single crystals are taken, and the distance between these lines can be used to compute the molecular length of the included compound. In the present work this length measurement has served as a basis for differentiating between *cis* and *trans* isomers.[9]

Materials.—To ensure length measurements as exact as the method permits, every attempt was made to employ only substances of the highest purity. Samples of stearic, oleic and elaidic acids of very high purity were kindly provided by R. R. Allen[10] of the Research Division of Armour and Co., Chicago, Ill.

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(1) Western Fish Nutrition Laboratory, Fish and Wildlife Service, Cook, Wash. Guggenheim Fellow for 1955–1956 during which time most of this work was performed.

(2) C. W. Bunn, *Proc. Roy. Soc. (London)*, **180A**, 40 (1942).

(3) K. H. Meyer and H. Mark, "Der Aufbau der hochpolymeren organischen Naturstoffe," Akad. Verlag, Leipzig, 1930, p. 189 ff.

(4) C. S. Fuller, *Eng. Chem.*, **28**, 907 (1936).

(5) A. E. Smith, *Acta Crystallogr.*, **5**, 224 (1952).

(6) W. Borchert, *Heidelberger Beitrage z. Min. u. Petr.*, **3**, 124 (1952).

(7) F. Laves and N. Nicolaides, Abstr. of the Am. Cryst. Assoc. Mtg. Proc., pp. 16–17 (1952).

(8) C. Hermann and H. U. Lenné, *Naturwiss.*, **39**, 234 (1952).

(9) A preliminary statement of this method and its application to the stereochemistry of squalene has appeared already: THIS JOURNAL, **76**, 2596 (1954).

(10) R. R. Allen and A. A. Kiess, *J. Am. Oil Chemists' Soc.*, **32**, 400 (1955); **33**, 301 (1956).

A second sample of elaidic acid, and samples of linoleic and linolelaidic acids as well as samples of methyl *trans*-10,-*trans*-12-linoleate and the methyl ester of a conjugated *cis*-*trans*-linoleic acid were kindly provided by the Research Department of General Mills, Inc., Minneapolis 13, Minn. Dr. Raymond F. Paschke of that group has provided[11] the following information about these compounds: The elaidic acid was prepared by selenium elaidinization of very pure oleic acid followed by further extensive purification. Its melting range was 44.4 to 44.6° and its purity was estimated to be above 99%. The linoleic acid was obtained by solvent crystallization of the fatty acids from safflower oil. Its purity was estimated to be 97% from its iodine value of 178.6 and from its spectral absorption at 233 mμ after isomerization with alkali, the most probable impurities being oleic and palmitic acids. The linolelaidic acid was prepared by isomerizing linoleic acid.[12] It contained about 5% conjugated double bonds and perhaps a small amount of *cis* isomers. The methyl *trans*-10,*trans*-12-linoleate was prepared by isomerizing the non-conjugated esters of dehydrated castor oil with alkali.[12] It was estimated to be 96% pure, the impurities probably being saturates. The conjugated *cis-trans*-methyl linoleate was prepared from a "debromination" linoleic acid after isomerizing with alkali[12]; 90% of it consisted of approximately equal parts of the *trans*-10,*cis*-12 and the *cis*-9,*trans*-11 isomers, the remaining 10% being a mixture of the unconjugated *trans*-9,*cis*-12 isomer, the *cis*-9,*trans*-12 isomer and the original *cis*-9,*cis*-12 isomer.

A second sample of stearic and oleic acids as well as samples of linoleic and linolenic acids and the methyl esters of the latter two acids were purchased from the Hormel Foundation, Austin, Minn. The linoleic and linolenic acids and their methyl esters had been prepared by the bromination–debromination technique of Rollett.[13] They were not stereoisomerically pure as is indicated below.

A sample of methyl eicos-*cis*-11-enoate was kindly provided by C. Y. Hopkins.[14] This substance was assumed to be the *cis* isomer (from its melting point), and the measurements herein reported support this assumption.

Methyl docos-*cis*-13-enoate was prepared from erucic acid by esterifying with methyl alcohol and sulfuric acid, chromatographing on alumina and then carefully fractionating on a 25-cm. spinning band column similar to the one described by Nerheim and Dinerstein.[15] A fraction distilling from 185 to 186° at 0.50 mm. was employed.

Samples of 2,2,4-trimethylpentane and 2,4,4-trimethylpentene-2 were purchased from the American Petroleum Institute, Carnegie Institute of Technology, Pittsburgh 13, Penna. A second sample of 2,2,4-trimethylpentane was purchased from the Matheson Co., Inc., Joliet, Ill.

Methods.—Crystals of urea or thiourea adducts suitable for X-ray studies were prepared by heating to boiling in a small vial 50 to 100 mg. of substance to be adducted with 4 to 6 ml. of a methanol solution saturated with either urea or thiourea (Merck analytical reagents). Up to 1 ml. of benzene was added to dissolve difficultly soluble substances. The vial was then stoppered, wrapped in cotton and allowed to cool slowly to 4° in a Dewar flask. The supernatant liquid was poured off and the crystals blotted on filter paper. A crystal about 0.2 mm. in diameter was selected with the aid of a 14-power binocular microscope.

Differentiation between adduct crystals and crystals of either pure urea or thiourea was made on the basis of crystal form and index of refraction. Urea adducts are transparent or translucent hexagonal needles (sometimes hollow), while pure urea crystallizes in very clear, transparent tetragonal needles usually with a wedge-shaped end. To determine whether a given crystal was adduct or urea it usually was sufficient to get an end view of the crystal and to observe the hexagonal form. Thiourea adducts, on the other hand, frequently cannot be differentiated from pure thiourea visually by means of the hexagonal shape since thiourea itself occasionally crystallizes in pseudohexagonal needles. But by measuring the interfacial angles of the crystal on an optical goniometer, it is possible to make such a differentiation quickly. For adducts, the interfacial angles of the hexagonal needles are exactly 60°, while those of pure thiourea are either 54°15′ or 71°30′.

As an additional quick test to determine whether adduct formed or not, a comparison can be made easily of the index of refraction of the two different axes of the crystal with that of a reference liquid (in which the crystal is placed) by observing the Becke line effect through the polarizing microscope. To distinguish between urea adducts and urea, a suitable reference liquid is xylene (any isomer). For urea adducts the indices of refraction along both axes are greater than that of xylene while pure urea shows an index along only one axis greater than that of xylene. For thiourea adducts a reference liquid consisting of a mixture of iodobenzene and bromobenzene adjusted to give an index of refraction of 1.60 is suitable. Here in contrast, the indices of refraction along both axes of pure thiourea are greater than that of the reference liquid, while thiourea adducts show only one axis greater than that of the reference liquid.

The X-ray photographs of single crystals of adducts were taken on a calibrated Buerger precession camera (60 mm. crystal to film distance) using copper radiation at 40 kv. and 15 ma. To observe the continuous layer lines the Laue technique was used (X-ray beam perpendicular to the *c*-axis which is the channel axis). The exposure time usually varied from 12 to 48 hours depending on such factors as the quality and size of the crystal, the diameter of the collimator used, etc. From the distances between these layer lines the periodicities of the adducted molecules within the channels can be calculated.[16] These periodicities are related to the average length of channel occupied by single molecules in the adduct and will be designated here as the channel length of the molecule.[17] To determine the lattice constants of the urea or thiourea framework, zero level precession pictures were taken with the *a*-axis as precession axis and a precession angle of 30°. A complete description and discussion of all the X-ray techniques and procedures will be given in a forthcoming paper.[18]

Results and Discussion

Table I lists the channel lengths of a number of unsaturated molecules along with the corresponding lengths of the saturated analogs when these are adducted with either urea or thiourea. The first thing to note is that all the C_{18}-unsaturated acids, *i. e.*, oleic, linoleic, elaidic and linolelaidic acids are shorter than stearic acid. (All the fatty acids adducted as dimers.) Furthermore oleic acid which has a *cis* double bond in the hydrocarbon chain is appreciably shorter than the *trans* isomer, elaidic acid. The shortening due to a *cis* double bond is approximately the same whether it occurs in an acid such as oleic acid or an ester such as methyl oleate, methyl eicosenoate or methyl docosenoate.

Thus it may be concluded that in urea adducts, a single *cis* double bond shortens a molecule an average of 0.9 Å. whereas a single *trans* double bond shortens it only approximately 0.15 Å. when the channel lengths of the molecules are compared with those of the corresponding saturated analogs. These values are probably accurate within a range of ±0.1 Å. The magnitude of the error is affected

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(11) Private communication.

(12) J. E. Jackson, R. F. Paschke, W. Tolberg, N. M. Boyd and D. H. Wheeler, *J. Am. Oil Chemists' Soc.*, **29**, 229 (1952).

(13) A. Rollett, *Z. Physiol. Chem.*, **62**, 410 (1909).

(14) C. Y. Hopkins and H. J. Chisholm, *Can. J. Chem.*, **32**, 37 (1954).

(15) A. G. Nerheim and R. A. Dinerstein, *Anal. Chem.*, **28**, 1029 (1956).

(16) Let R be the crystal to film distance, D_n the distance between the continuous layer line of the nth order and the equator, and λ the wave length of the characteristic radiation used; then $D_n/R = \tan \sigma_n$ from which the periodicity, l, can be computed: $l = (n\lambda/\sin \sigma_n)$. See for example, J. M. Bijvoet, N. H. Kolkmeyer and C. H. MacGillavry, "X-ray Analysis of Crystals," Butterworths Scientific Publications, London, 1951, Fig. 27 and pp. 30–32.

(17) The channel length of the molecule depends on several factors, such as the degree of coiling and the extent to which the ends of the molecules overlap when they are projected on the channel axis. A fuller discussion of these factors is presented in a forthcoming paper.

(18) To be published in *Z. Kristallographie.*

TABLE I

CHANNEL LENGTHS OF SOME COMPOUNDS OF KNOWN *cis-trans* CONFIGURATION IN UREA AND THIOUREA ADDUCTS

Substance	Carbon chain length	Double bonds	Type of adduct	Channel length in Å.	Shortening per double bond	Prepn. of adducting cmpds.	Laue films taken	The order of the lines measured	*c*-axis of host in Å.
Stearic acid	C_{18}	None	Urea	50.10[a]	..	2	6	5th	11.03
Oleic acid	C_{18}	*cis*-9	Urea	48.44[a]	0.83	2	3	5th	10.99
Linoleic acid	C_{18}	*cis*-9,*cis*-12	Urea	46.63[a]	0.87	1	2	5th	10.98
Elaidic acid	C_{18}	*trans*-9	Urea	49.82[a]	0.14	2	7	5th	11.00
Linolelaidic acid	C_{18}	*trans*-9,*trans*-12	Urea	49.18[a]	0.23	1	3	5th	11.00
Methyl stearate	C_{18}	None	Urea	27.42	..	1	6	3rd, 4th, 5th	...
Methyl oleate	C_{18}	*cis*-9	Urea	26.39	1.03	1	3	3rd, 4th, 5th	11.01
Methyl eicosanoate	C_{20}	None	Urea	29.92[b]	..	..	..	....	...
Methyl eicosenoate	C_{20}	*cis*-11	Urea	28.95	0.97	1	1	3rd, 4th, 5th	11.00
Methyl docosanoate	C_{22}	None	Urea	32.45[b]	..	..	..	....	...
Methyl docosenoate	C_{22}	*cis*-13	Urea	31.47	0.98	1	1	3rd, 4th, 5th	10.99
Methyl linoleate	C_{18}	*trans*-10,*trans*-12	Urea	26.96	0.23	1	2	2nd, 3rd, 4th, 5th	...
Methyl linoleate[c]	C_{18}	*cis & trans*[d]	Urea	26.14	0.64[e]	1	2	2nd, 3rd, 4th, 5th	...
2,2,4-Trimethylpentane	C_5	None	Thiourea	8.36	..	2	2	1st, 2nd	12.50
2,4,4-Trimethylpentene-2	C_5	*trans*-2	Thiourea	8.31	0.05	1	1	1st, 2nd	...

[a] Dimeric length. [b] Length obtained by extrapolation from data on methyl esters to be published. [c] Obtained by alkali isomerization: a mixture approximately 45% *trans*-10,*cis*-12 and 45% *cis*-9,*trans*-11, plus 10% other isomers, see text. [d] A *cis* and a *trans* double bond conjugated. [e] Average shortening, see text.

by the purity of the sample and the accuracy with which the X-ray data were taken. The latter depends on the number of different cameras used, the number of films taken, the number and fuzziness of the lines read, the magnitude of the line-to-line distance measured and the precision of multiple readings.[19]

In thiourea adducts the same effect seems to hold. Thus 2,4,4-trimethylpentene-2 appears to be somewhat shorter than its saturated analog 2,2,4-trimethyl pentane, and for *trans* molecules at least the shortening effect in the thiourea system is similar to that of the urea system. No example of a known high purity *cis* compound which will adduct with thiourea has been obtained as yet, but the length of a thiourea adduct of a mixture rich in isomers of squalene containing one or more *cis* double bonds[20] was measured. The length as compared to natural squalene was measurably shorter, some 0.3 Å. These measurements will be discussed in greater detail in a forthcoming paper.

Some insight into the nature of this shortening effect can be gained by referring to Fig. 1. Here hydrocarbon chains are shown schematically in their most extended form in which a contains one *trans* double bond, b no double bonds, and c one *cis* double bond. To calculate distances along the chain, bond lengths and bond angles known from other structures (approximate values) were employed[21]: C—C, 1.54 Å.; C=C, 1.33 Å; $\sphericalangle$ C—C—C, 111°; $\sphericalangle$ C—C=C, 123°. Comparison of Fig. 1b with 1c shows that the kink produced in the chain by a *cis* double bond leads to a shape that would not fit into the host channel as a planar molecule without considerable (and improbable) bending. Also, even if such bending were admitted, its effect would not then be large enough to explain the experimentally observed amount of shortening. It is thus concluded that some coiling has to be considered. Coiling need not necessarily be assumed to explain the shortening effect of the *trans* double bond (Fig. 1a) as even in the most extended form of this hydrocarbon chain, the *trans* molecule is slightly shorter than the saturated analog.[22] However, this does not preclude the possibility that superimposed on this shortening effect there is some coiling or a very small amount of bending of C–C–C angles for both the saturated and the unsaturated substances. Indeed, the lengths of a series of normal hydrocarbons in urea were found to be somewhat less than those in the pure hydrocarbon crystals suggesting that this is actually the case.[18] By the term "coiling" it is not here simply meant a uniform coiling in one direction leading to either a "right" or a "left" molecule of an average cylindrical shape. There might well be an alternating (right-left-right-left. . .) coiling or "wiggling" such that a plane of gravity could be defined leading to an average shape comparable to that of a thick lath. Of course, a combination of coiling and "wiggling" also may be possible. Thus, the amount of shortening in a special case can be visualized as a combination of three effects: (1) shortening connected with a variation of bond angles, (2) shortening due to either double or triple bonds and (3) coiling and/or "wiggling" of the molecule.

For polyunsaturated compounds the shortening

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(19) A more detailed discussion of the errors involved will be given in ref. 18.

(20) This material was kindly provided by D. W. Dicker and M. C. Whiting and was a by-product in their synthesis of squalene [*Chemistry & Industry*, 351 (1956)]. This liquid mixture was stated by them to contain mainly the *cis*-10 and the *cis*-10,*cis*-14 isomers of squalene (all other double bonds being *trans*), to be analytically pure, and to show an infrared spectrum almost identical to that of natural squalene. Although it did not adduct with thiourea in benzene–methanol in their experiments, some adduct crystals suitable for X-ray analysis were obtained by the method for the preparation of adducts here described.

(21) The values used here are based on summaries given by (a) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 163 ff., and Appendix; and (b) L. Crombie, *Quart. Revs.*, **6**, 101 (1952).

(22) In this connection see two papers of Bunn in which evidence is presented for a tendency of chain molecules with double bonds to coil more than molecules without double bonds; C. W. Bunn, *Proc. Roy. Soc.* (*London*), **180A**, 67 (1942); 82 (1942). See also Jeffrey's critic with Bunn's reply, *Trans. Faraday Soc.*, **38**, 382 (1942), and G. A. Jeffrey, *ibid.*, **40**, 517 (1944).

effect appears to be distinctly additive for those cases where double bonds of the same kind (*i. e.*, all *cis* or all *trans*) are separated each by one methylene group in the hydrocarbon chain. Thus, the shortening for the two *cis* double bonds of linoleic acid (Table I) is very close to twice that of oleic acid, and the shortening for the two *trans* double bonds of linolelaidic acid, while somewhat greater than twice that of elaidic acid, is within the experimental error. The discrepancy may be due to a small amount of *cis* double bond present in this difficultly prepared material.

As for conjugated double bonds, a shortening effect also was observed. For methyl *trans*-10, *trans*-12-linoleate in urea we find a shortening of 0.46 Å. for two *trans* double bonds, and for the methyl linoleate containing a conjugated *cis* and *trans* double bond per molecule the shortening is 1.28 Å. Considering the purity of the materials and the experimental error, these values are comparable to those here derived from isolated double bonds.

It remains to be seen how far the method can be extended, *i. e.*, to what combinations of *cis* and *trans* double bonds the method can be applied. It already has been applied to the solution of the problem of the stereochemistry of squalene.[9] Further details on this application will be discussed in another paper.

It should be pointed out that this method can be applied successfully to systems containing trialkylethylenes of the type $RC(CH_3){=}CHR_1$. Infrared spectroscopy which can differentiate between *cis* and *trans* isomers of dialkylethylenes can be applied to trialkylethylenes only with considerable difficulty, it being necessary to have on hand the spectra of both isomers for comparison.[21b] Thus, by means of the method here described, it should be possible to determine the *cis–trans* isomerism of naturally occurring acyclic terpenes.

Since many preparative procedures result in mixtures of *cis* and *trans* isomers, some experiments were made to get an idea of what kind of length measurements one might expect from mixtures. To begin with, a clear-cut case consisting of a 50–50 mixture of palmitic and stearic acid adducted with urea was examined. The length measurements for this mixture as well as those of the individual components are listed in Table II. It is seen that the length given by the mixture is approximately the average length of the components. Similar results were obtained for two mixtures of oleic and elaidic acids. However, care must be exercised in interpreting such values since partial fractionation during urea adduct formation may occur.[23] It is thus possible that crystals formed at the beginning of the crystallization can be different from those at the end.

TABLE II

AVERAGE CHANNEL LENGTH OF MIXTURES OF COMPOUNDS IN UREA ADDUCTS

Composition	Channel length of the components, Å.	Mixture length computed,[a] Å.	Mixture length measured, Å.
50% palmitic acid	45.10	47.60	48.02
50% stearic acid	50.10		
50% oleic acid	48.44	49.13	48.92
50% elaidic acid	49.82		
11.5% oleic acid	48.44	49.66	49.69
88.5% elaidic acid	49.82		

[a] Sum of percentage × length of each component/100.

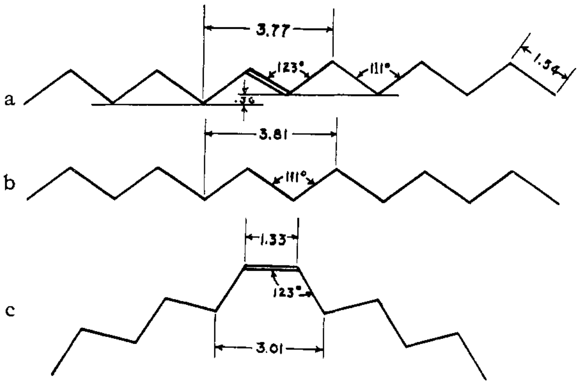

Fig. 1

It was interesting to make the comparison of the channel lengths of linoleic and linolenic acids and their methyl esters, prepared by the bromination–debromination procedure,[18] with values that can be calculated for these substances under the assumption that all double bonds are *cis*. This calculation of the channel length, l, in Ångstrom units can be made for the acids with the use of the formula $l = 50.1 - 2n \times 0.9$ and for the methyl ester $l = 27.4 - n \times 0.9$, where n is the number of double bonds in the molecule. The values 50.1 and 27.4 represent the average channel lengths of stearic acid (dimer) and methyl stearate, respectively (Table I), while 0.9 represents the average value of the shortening effect for one *cis* double bond, as indicated above. Table III lists these calculated values as well as the measured ones. It can be seen that in 3 of the 4 cases, the measured lengths are greater than the calculated ones. This indicates that some transformation of *cis* to *trans* double bonds occurred during the bromination–debromination period. An idea of the approximate magnitude of this transformation may be obtained by using the observed differences for a calculation of percentage of *trans* double bond present, assuming that the above-determined shortening effect of a *trans* double bond (0.15 Å.) can be applied here. These results are in accord with those of Allen and Kiess[24] who find that for linoleic acid and methyl

TABLE III

CHANNEL LENGTHS OF SUBSTANCES PREPARED BY THE BROMINATION–DEBROMINATION PROCEDURES

	Measured channel length, Å.	Expected length,[a] Å.	Approximate % *trans* isomers
Linoleic acid	46.8	46.5	10
Methyl linoleate	25.6	25.6	0
Linolenic acid	46.3	44.7	35
Methyl linolenate	25.3	24.7	27

[a] See text.

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[23] H. Schlenk and R. T. Holman, THIS JOURNAL, **72**, 5001 (1950).

[24] R. R. Allen and A. A. Kiess, *J. Am. Oil Chemists' Soc.*, **33**, 355 (1956).

linoleate "the debrominated material contained large amounts of positional and geometric isomers and less than 75% of the 9,12-di-*cis*-octadecadienoic acid."

In conclusion it should be said that although the method may be used in some cases to determine whether one or more double bonds in a molecule are *cis* or *trans*, it could not, of course, from length measurements alone locate the position of these double bonds. The solution of such a problem would depend on an evaluation of the intensities of the continuous lines in the X-ray photographs. The applicability of line intensities for the problem of locating the position of functional groups has already been demonstrated.[25]

Acknowledgment.—The authors wish to acknowledge gratefully the assistance of Dr. K. C. Peng who took many of the X-ray photographs used in the work.

[25] N. Nicolaides, F. Laves and A. Niggli, THIS JOURNAL, **78**, 6415 (1956).

ZÜRICH, SWITZERLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON UNIVERSITY]

Experiments in the Colchicine Field. V. The Thermal and Photochemical Decomposition of Various 2-(β-Phenylethyl)-phenyldiazomethanes and 2-(γ-Phenylpropyl)-phenyldiazomethanes[1]

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For an investigation of reactions leading to tricyclic cycloheptatriene compounds, 2-[β-(4′-methoxyphenyl)-ethyl]-phenyldiazomethane, 2-(γ-phenylpropyl)-phenyldiazomethane, 2-[γ-(4′-methoxyphenyl)-propyl]-3,4,5-trimethoxyphenyldiazomethane and 2-[γ-(3′,4′-dimethoxyphenyl)-propyl]-3,4,5-trimethoxyphenyldiazomethane have been prepared and subjected to thermal and/or photochemical decomposition. From the first two diazo alkanes small amounts of tricyclic cycloheptatriene may be formed, but no evidence for this type of compound is found in the products from the second two diazo alkanes. In all cases, the major cyclic material is the indan and/or tetralin resulting from attack at a point on the polymethylene bridge between the aromatic nuclei. The decomposition of 2-(γ-phenylpropyl)-phenyldiazomethane was studied in detail, and the products have been shown to include 2-phenyltetralin, 2-benzylindan, 2-(γ-phenylpropyl)-benzaldehyde, 2-(γ-phenylpropyl)-benzonitrile and 2-(γ-phenylpropyl)-benzal azine. The indan/tetralin ratio was studied as a function of reaction conditions and was found to be temperature dependent. Independent syntheses for the indans and tetralins are described.

An intramolecular counterpart of the reaction of phenyldiazomethane with benzene to form phenylcycloheptatriene (*cf.* Experimental) involves the decomposition of 2-(β-phenylethyl)-phenyldiazomethane (I) to 6,6a-dihydro-5*H*-cyclohepta[a]naphthalene (VI) and 2-phenylindan (VIII) as reported in the previous paper of this series.[4] In the hope of extending this procedure to the synthesis of compounds related to colchicine a variety of 2-(β-phenylethyl)-phenyldiazomethanes and 2-(γ-phenylpropyl)-phenyldiazomethanes have been prepared and decomposed. Although the results are singularly disappointing from the standpoint of a colchicine synthesis, they have some pertinence to the currently expanding field of carbene chemistry and are, therefore, reported in detail.

Thermal and Photochemical Decomposition of 2-(Arylalkyl)-phenyldiazomethanes.—The formation of the tricyclic cycloheptatriene (VI) from the irradiation of the diazo compound I gave encouragement that a similar reaction with the diazo compounds IV and V might lead to substances closely resembling colchicine. This hope was abetted by a consideration of the probable mechanism for the reaction. Considerable data have accumulated which suggest that the initial action of heat or light on a diazoalkane is to release molecular nitrogen and produce a fragment which has been designated as a "carbene."[5] A carbene might be expected to be electrophilic and as a consequence to react with centers of highest electron density.[6] Thus, a compound of the type IV would be predicted to form a tricyclic cycloheptatriene more readily than an unmethoxylated analog. In actual fact, however, the photochemical decomposition of IV in dilute petroleum ether solution at 65° or the thermal decomposition at 175° yielded a mixture which showed no spectral evidence for this type of substance. Instead, the products included the aldehyde XXXIV, the nitrile XVI, the azine and the tetralin XII. Similarly, the photochemical decomposition of V under comparable conditions yielded no spectrally detectable tricyclic cycloheptatriene derivative but instead produced the aldehyde XXXV, the nitrile XVII, the azine and the tetralin XIII.

Further study of the reaction was carried out with the diazo compounds II and III, the first to test more definitely the effect of a methoxyl group and the second to test the effect of the length of the bridge between the two aryl groups. When II was subjected to photochemical decomposition in dilute petroleum ether solution at 65° an amount of tricyclic cycloheptatriene (VII) was formed which was equal to or smaller than the amount of

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[4] C. D. Gutsche and H. E. Johnson, THIS JOURNAL, **77**, 5933 (1955).

[5] For a definition of "carbene" *cf.* W. von E. Doering and L. H. Knox, *ibid.*, **78**, 4947 (1956), footnote 9.

[6] P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956); W. E. Parham and C. D. Wright, *J. Org. Chem.*, **22**, 147 (1957); and P. S. Skell and R. M. Etter, *Chemistry & Industry*, 624 (1958), have adduced data in support of the electrophilic character of dihalocarbenes and carbethoxycarbene. The degree of similarity between these and alkyl- or arylcarbenes, however, has not been delineated.