tallized from 95% ethanol; orange prisms, m.p. 111–112° after sintering at 110°.

Anal. Calcd. for $C_{18}H_{21}N_5O_7$: C, 51.55; H, 5.05; N, 16.70. Found: C, 51.73; H, 5.20; N, 16.58.

1-Methyl-2-methylaminomethyltetrahydroquinoline (XVI).—The general procedure for the N-alkylation of the amide of a primary amine was employed.[19] A mixture of 10.23 g. (0.04 mole) of 1-methyl-2-benzoylaminomethyltetrahydroquinoline (XX) and 150 ml. of xylene was distilled until the distillate was no longer cloudy. To the cooled mixture was added 1.15 g. (0.05 atom) of sodium, and the resulting mixture was heated at about 140° for three hours. Following cooling, 7.10 g. (0.05 mole) of methyl iodide was added, and the mixture was heated at 80° for 12 hours. Excess methyl iodide and xylene were removed by distillation at reduced pressure, and 10 ml. of 95% ethanol was added to remove any unreacted sodium. After the addition of 30 ml. of concentrated hydrochloric acid, the aqueous mixture was refluxed for 48 hours. The benzoic acid which separated upon cooling was removed by filtration, and the filtrate was made strongly alkaline with concentrated sodium hydroxide. Ether extraction followed by drying and removal of the ether gave a liquid which was fractionally distilled *in vacuo;* yield 3.88 g. (51% over-all) of 1-methyl-2-methylaminomethyltetrahydroquinoline, b.p. 134° (8 mm.), $n^{20}D$ 1.5680, and 1.55 g. of 1-methyl-2-aminomethyltetrahydroquinoline (X), b.p. 148° (8 mm.), $n^{20}D$ 1.5943 (by hydrolysis of unreacted amide).

Anal. Calcd. for $C_{12}H_{18}N_2$: C, 75.74; H, 9.53; N, 14.73. Found: C, 75.87; H, 9.55; N, 14.52.

The monohydrobromide of XVI crystallized as prisms from 95% ethanol, m.p. 232–233°.

Anal. Calcd. for $C_{12}H_{19}BrN_2$: C, 53.14; H, 7.06; N, 10.33. Found: C, 52.89; H, 7.24; N, 10.60.

The monopicrate of XVI was formed in and recrystallized from ethanol; red elongated prisms, m.p. 153–154°.

Anal. Calcd. for $C_{18}H_{21}N_5O_7$: C, 51.55; H, 5.05; N, 16.70. Found: C, 51.78; H, 5.19; N, 16.61.

1-Methyl-2-dimethylaminomethyltetrahydroquinoline (XVIII).—To a cooled solution of 9.74 g. (0.055 mole) of 1-methyl-2-aminomethyltetrahydroquinoline (X)[10,18] (b.p. 137° (2 mm.), $n^{20}D$ 1.5945) in 50 ml. of absolute methanol

(19) W. J. Hickinbottom, "Reactions of Organic Compounds," Longmans, Green and Company, London, England, 1948, second edition, p. 300.

were added 9.30 g. (0.111 mole) of sodium bicarbonate and 15.70 g. (0.111 mole) of methyl iodide in 50 ml. of methanol. The reaction mixture was refluxed for twelve hours, cooled, and the insoluble crystalline material was removed by filtration. The filtrate was further concentrated *in vacuo,* and the resulting oil and crystal mixture was treated with three 50-ml. portions of ether. The ether extracts were combined and dried, and the ether was removed. Distillation of the residue through an eight-inch helices-packed column gave two fractions: 4.65 g. (65% yield based on unrecovered starting material) of 1-methyl-2-dimethylaminomethyltetrahydroquinoline, b.p. 109–110° (0.5 mm.), $n^{20}D$ 1.5775, and 3.50 g. of starting material (X), b.p. 119–120° (0.5 mm.), $n^{20}D$ 1.5945.

Anal. Calcd. for $C_{13}H_{20}N_2$: C, 76.42; H, 9.87; N, 13.71. Found: C, 76.45; H, 9.83; N, 13.92.

The crystalline materials isolated in the procedure described above were combined and treated with 50 ml. of cold water to remove the sodium iodide. The water-insoluble residue was recrystallized from 95% ethanol to give 3.50 g. of the methiodide of 1-methyl-2-dimethylaminomethyltetrahydroquinoline (XVIII) as colorless plates, m.p. 191–192°. The melting point reported by Rupe, Paltzer and Engel[10] was 204°.

Anal. Calcd. for $C_{14}H_{23}IN_2$: C, 48.56; H, 6.69; N, 8.09. Found: C, 49.02; H, 6.91; N, 7.98.

The monopicrate of XVIII was made from equimolar quantities of the amine (XVIII) and picric acid. Three recrystallizations from ethanol gave orange-red prisms, m.p. 164–165°. By contrast, Rupe, Paltzer and Engel[10] reported a melting point of 122° for 1-methyl-2-dimethylaminomethyltetrahydroquinoline picrate.

Anal. Calcd. for $C_{19}H_{23}N_5O_7$: C, 52.53; H, 5.57; N, 16.12. Found: C, 52.44; H, 5.37; N, 16.17.

When the hydriodide, m.p. 198.5–200°, obtained from the treatment of XV with methyl iodide in the presence of potassium hydroxide (see above) was treated with an excess of picric acid in ethanol, orange-red prisms, m.p. 164–165°, of monopicrate were isolated.

Anal. Calcd. for $C_{19}H_{23}N_5O_7$: C, 52.53; H, 5.57; N, 16.12. Found: C, 52.57; H, 5.42; N, 16.06.

This picrate sample, when mixed with the picrate made directly from the amine XVIII, gave no depression in melting point.

Urbana, Ill.

[Contribution from the Department of Chemistry of the Ohio State University and the American Petroleum Institute Research Project 45]

The Quantitative Inversion of cis- and trans-Alkene Isomers: A New Synthesis of Normal cis-Alkenes[1]

By Melvern C. Hoff,[2] Kenneth W. Greenlee and Cecil E. Boord

A new method is described for quantitatively inverting the configuration about the carbon to carbon double bond in n-alkenes, involving molecular chlorination (*trans*), alkaline dehydrochlorination (*trans*), and dechlorination (without change in configuration) by sodium in ammonia. The method was applied to the *trans*-isomers of 2-pentene, 2-hexene, 3-hexene, 2-octene and 4-octene and the *cis*-isomer of 3-hexene. Quantitative data are given for the stereospecificity of the reactions, and the corresponding reaction mechanisms are discussed. Physical properties are given for five *cis*-alkenes which were prepared in higher purity than previously reported.

To further a program for the preparation of hydrocarbons[3] it was desired to develop a method for the production of normal *cis*-alkenes suitable

(1) The material in this paper was abstracted from the dissertation submitted by Melvern C. Hoff to the Graduate School of The Ohio State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy in 1948. Part of it was presented before the Organic Division at the 115th Meeting of the American Chemical Society, San Francisco, March, 1949.

(2) Standard Oil Company of Indiana, Whiting, Indiana.

(3) The American Petroleum Institute Research Project 45, for the "Synthesis and Properties of Hydrocarbons of Low Molecular Weight," administered by The Ohio State University Research Foundation.

for use in the preparation of standard samples[4] and for engine testing.[5] Fairly high purity of the product and ease of further purification were therefore of primary importance. Although *cis-n*-alkenes are readily produced by catalytic hydrogenation of the corresponding alkynes,[6,7] cryoscopic examination of the *cis* isomers produced in this manner has shown them not to be of high

(4) Demmerle, *Chem. Eng. News,* **24,** 2020 (1946).

(5) Lovell, *Ind. Eng. Chem.,* **40,** 2388 (1948).

(6) Campbell and O'Connor, This Journal, **61,** 2897 (1939).

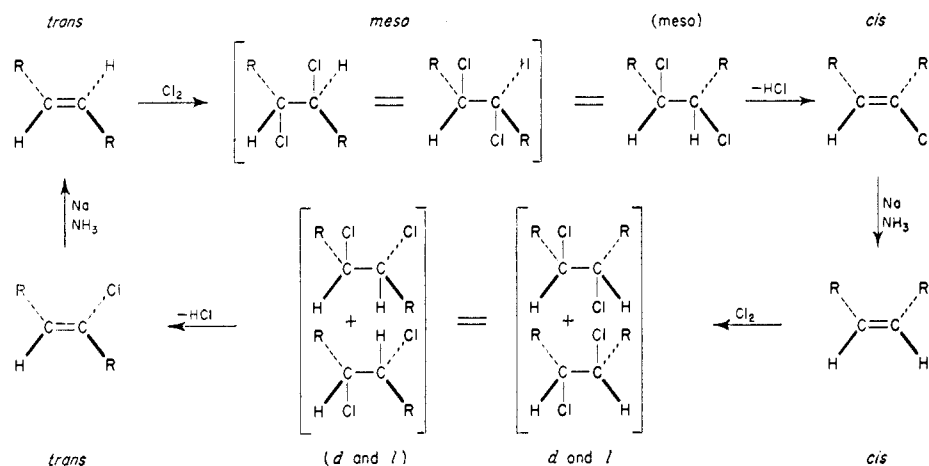(7) Campbell and Eby, *ibid.,* **63,** 216, 2683 (1941).

Fig. 1.—The chemical inversion of double bond configuration. The following method of representing stereochemical courses of reactions has been adopted for use in this paper. Double bonds are in the plane of the printed page, groups behind the plane of the page are indicated by dotted bonds, and groups in front of the plane of the page are indicated by bold-faced bonds. Reactions at the double bond are shown in the plane of the printed page with the position of the original alkene groups unchanged. The intermediate step between the chlorination and dehydrochlorination (above) constitutes a rotation of half of the molecule to place the hydrogen and chlorine atoms in the reacting position.

purity.[8] Pure trans-n-alkenes, however, are readily prepared by reduction of the alkynes with sodium in liquid ammonia.[7,8] The inversion of cis–trans-isomers by physical or chemical methods to yield equilibrium mixtures is well known.[9] The complete inversion of one isomer to its antipode has been accomplished by Wilson and Lucas[10] using six chemical steps. However, this method is long and is dependent upon considerable purification of intermediates to yield high purity products.[11]

In the present work a chemical method was developed, involving a series of three stereospecific chemical reactions, by which a pure trans- or cis-alkene can be converted to its antipode, the purity of which is 94–97%. The physical properties of the cis-alkenes obtained by inversion were compared with those of samples prepared by an improved catalytic hydrogenation procedure. The purities of the starting materials, final products, and intermediates were determined by cryoscopic methods, allowing quantitative estimation of the stereospecificity of the reactions employed.

Discussion

The Inversion Method.—The reversal of configuration about the double bond was effected in three steps: (1) direct catalytic chlorination to yield a dichloride, (2) dehydrochlorination with propanolic potassium hydroxide to form a chloroalkene, and (3) dechlorination with sodium in liquid ammonia to produce the alkene. The nearly quantitative inversion is readily explained on the assumptions that the addition of chlorine is trans to the double bond, that the removal of hydrogen chloride is also trans and that the dechlorination, which results in replacement of the remaining chlorine atom by hydrogen, takes place with retention of configuration. Thus, in the first

(8) Henne and Greenlee, ibid., **65**, 2020 (1943).

(9) Gilman, "Organic Chemistry," 2nd Edition, Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 453.

(10) (a) Wilson and Lucas, THIS JOURNAL, **58**, 2396 (1936); (b) Lucas, Schlatter and Jones, ibid., **63**, 22 (1941).

(11) Van Risseghem, Bull. soc. chim. Belg., **47**, 194 (1936).

step, symmetrical trans- and cis-alkenes yield meso- and dl-dichlorides, respectively; in the second step, the dehydrohalogenation of the meso- and d- or l-dichlorides yields cis- and trans-chloroalkenes, respectively; and in the third step, the replacement of the halogen on the cis or trans chloro-alkene yields an alkene of the same respective geometric structure (see Fig. 1). With a dichloride derived from an unsymmetrical alkene, dehydrochlorination produces a pair of chloroalkenes differing only in the position of the chlorine, each yielding the same alkene upon dechlorination.

This sequence was applied to trans-2-pentene, trans-2-hexene, trans-3-hexene, trans-2-octene, trans-4-octene and cis-3-hexene, and produced in each case the isomer of opposite configuration. The physical properties of these compounds are shown in Table II. In each reaction carried out, the close proximity of the boiling points of the desired product and its undesired isomer (e.g., dl-3,4-dichlorohexane in meso-3,4-dichlorohexane), precluded the removal of the principal impurity by distillation. Hence, the purities of the intermediate and final products were dependent on the stereospecificity of the reactions employed. The data for the individual inversions are summarized in Table I.

The stereospecificities for the chlorination step vary only slightly from the average and are reasonably constant. Except in the case of meso-3,4-dichlorohexane → 3-chloro-cis-3-hexene → cis-3-hexene, in which the stereospecificities were 99.8% and 95.9%, respectively, quantitative data could not be obtained on the dehydrochlorination and dechlorination reactions, separately; neither 3-chloro-trans-3-hexene nor 4-chloro-cis-4-octene could be induced to crystallize and yield freezing curves, and all the other chloro-cis-alkenes were mixtures of positional isomers with respect to chlorine. However, since the dehydrohalogenation reaction appears to be highly stereospecific in the one case noted, it may be inferred that the over-all stereospecificities for dehydrochlorination and de-

chlorination shown in Table I represent essentially the latter reaction. The variation in stereo-specificity for this reaction may be explained by the presence of sodium amide which is formed during the course of the reaction and which can cause undesirable side reactions in an extent dependent upon such mechanical variables as temperature and rate of stirring.

TABLE I

CHEMICAL INVERSION OF DOUBLE BOND CONFIGURATION

|	Original alkene Purity, %	S.S.,[a] %	Dichloride Purity, %	S.S.,[b] %	Inverted alkene Purity, %
trans-2-pentene to cis-2-pentene	100.0	98.3	98.3	95.4	93.6
trans-2-hexene to cis-2-hexene	100.0	99.0	99.0	98.0	97.0
trans-3-hexene to cis-3-hexene	98.7	100.0	98.9	95.7	94.5
cis-3-hexene to trans-3-hexene	96.3	98.0	94.4	99.0	93.5
trans-2-octene to cis-2-octene	99.4	98.4	97.7	97.9	95.7
trans-4-octene to cis-4-octene	100.0	98.7	98.7	96.8-97.8	95.5-96.5

[a] Stereospecificity (purity of product)/(purity of reactant). [b] Over-all stereospecificity for dehydrochlorination plus dechlorination.

Determination of Configuration.—Alkenes produced from alkynes by reduction with sodium in liquid ammonia have a *trans* configuration and olefins produced by catalytic hydrogenation of alkynes have a *cis* configuration.[7,12,13,14] In the present work, the identities of the inversion products from *trans*- and *cis*-3-hexene were established as their antipodes, *cis*- and *trans*-3-hexene, respectively, by mixed melting points with authentic samples. The configurations of 3-chloro-*cis*- and 3-chloro-*trans*-3-hexene were determined by relative dehydrohalogenation rates, the faster reacting compound being assigned the *trans* configuration.[15,16,17] No determination of configuration was made on the dichlorides, but in view of the known *trans* addition of halogens[18,19] it appears certain that the chlorination of *trans*-3-hexene, for example, yields *meso*-3,4-dichlorohexane. Alkaline dehydrochlorination of this dichloride to 3-chloro-*cis*-3-hexene confirms this since alkaline dehydrochlorination preferentially proceeds by a *trans* mechanism[20] and 3-chloro-*cis*-3-hexene can therefore arise only from *meso*-3,4-dichlorohexane. The actual determination of structure and identity was carried out only for the compounds involved in the inversion of *cis*- and *trans*-3-hexene. Since the reactions used on the other

(12) Kistiakowsky, et al., THIS JOURNAL, **58**, 144 (1936).
(13) Brockway and Cross, ibid., **58**, 2407 (1936).
(14) Carr and Stucklen, ibid., **59**, 2138 (1937).
(15) Wislicenus and Schmidt, Ann., **313**, 216 (1900).
(16) Michael, THIS JOURNAL, **40**, 704, 1674 (1918).
(17) Chavanne, Compt. rend., **154**, 776 (1912).
(18) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 148.
(19) Lucas and Gould, THIS JOURNAL, **63**, 2541 (1941).
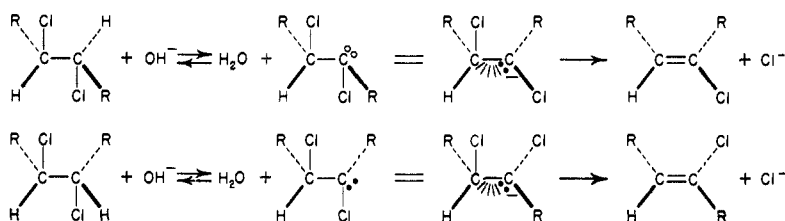(20) Cristol, ibid., **69**, 339 (1947).

olefins were carried out in a completely analogous manner, the same assignment of configuration was applied to their derivatives.

Reaction Mechanisms.—It is of particular importance to note that both the inversion of a *trans*-alkene to a *cis*-alkene and the inversion of a *cis*-alkene to a *trans*-alkene can be carried out with the same degree of stereospecificity. This fact shows that the configurational changes occurring are fixed by the mechanism of the reaction causing the change, and that no intermediate such as a planar carbonium ion exists which can react from more than one direction in space. Any mechanisms proposed must be in agreement with the known stereochemical results of the reactions and must account for the high degree of stereospecificity observed.

Chlorination.—The chlorinations were carried out under conditions chosen to preclude all but ionic mechanisms. The catalyst, antimony pentachloride, functions in a manner similar to aluminum chloride to enhance the polarity of the chlorine, the driving force being the completion of octahedral symmetry

$$SbCl_5 + Cl_2 \rightleftharpoons (SbCl_6)^- Cl^+$$
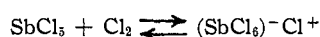
Both the specificity and the stereochemistry of the chlorination are well accounted for by the mechanism presented by Hammett[18] in which the chlorine reacts stepwise; first by addition of the positive ion to produce a cyclic chloronium ion,[19] and then by nucleophilic attack of the negative ion to yield the final product.
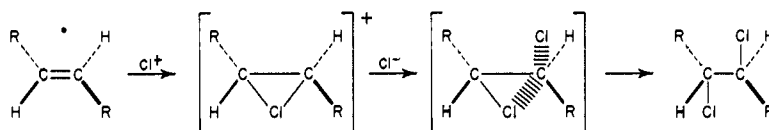
A rigid structure, such as the cyclic chloronium ion, for the intermediate, and a straightforward displacement reaction in the second step are required to account for the high specificity of the over-all reaction.

Dehydrohalogenation.—Cristol,[20] working with benzene hexachlorides, has established conclusively the *trans* steric requirement for the hydrogen and chlorine atoms in the second order, E_2-type, dehydrochlorination, and has pictured the mechanism as a simultaneous removal of a proton to form a carbanion and expulsion of a chloride ion by a typical Walden inversion displacement. Considering this reaction as occurring in two steps and satisfying the steric requirements by rotation about the central carbon to carbon bond, it can be predicted that a *meso* dichloride must yield a chloro-*cis*-alkene and that a *d*- or *l*-dichloride must yield a chloro-*trans*-alkene (below).

These predictions are in complete agreement with the experimental results. In view of the high stereospecificity of the reaction, it must be concluded that, if carbanions exist as such during the course of the reaction, they maintain their configuration. In no case was there any evidence for the formation of allylic halides, and, only in the case of *dl*-3,4-dichlorohexane, which yields a chloro-

alkene with hydrogen and chlorine atoms in a *trans* relationship across the double bond, was there any evidence of further dehydrochlorination.

Dechlorination.—The dehalogenation of organic compounds with sodium in liquid ammonia has been used extensively for analytical and purification procedures and to a lesser extent as a preparative method. The work of many investigators is complicated by the fact that solutions of sodium in liquid ammonia were added to halides, whereby the sodium amide formed can also react with the halide, to yield various products. Generally, however, the reaction of saturated monohalides produces the corresponding paraffins.[21] The stereochemical aspects of this reaction have not been previously investigated.

In the present investigation, the over-all steric effect of the dechlorination with sodium in liquid ammonia was the replacement of chlorine atoms by hydrogen atoms without change of configuration. Thus, 3-chloro-*cis*-3-hexene yields *cis*-3-hexene and 3-chloro-*trans*-3-hexene yields *trans*-3-hexene. Fernelius and Watt[21] class these dehalogenation reactions as bond ruptures proceeding either in one or two steps depending on the stability of R
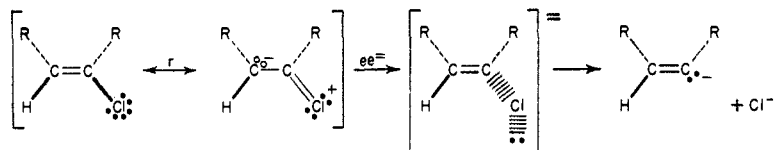
$$\text{RX} \xrightarrow{\text{e}^-} \text{R}\cdot + \text{Cl}^- \xrightarrow{\text{c}^-}$$

$$\bar{\text{R}} + \text{Cl}^- \text{ or } \text{RX} \xrightarrow{2\text{e}^-} \text{R}^- + \text{Cl}^-$$
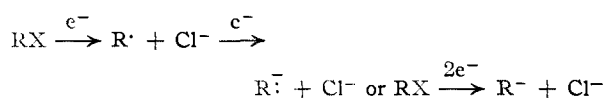
as a free radical. The reaction is completed by ammonolysis to yield a paraffin and an amide ion. Application of this mechanism to the de-

$$\bar{\text{R}} + \text{NH}_3 \longrightarrow \text{RH} + \text{NH}_2^-$$
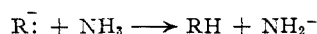
chlorination of chloro-alkenes to alkenes, which is found to proceed with a high degree of specificity, implies that the vinylic carbanion formed
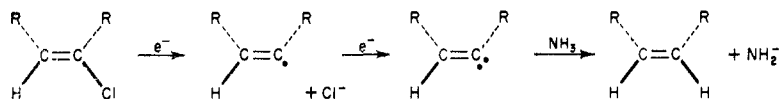
does not isomerize and that the formation of the carbanion from the chloride is essentially a single step reaction, since free radicals are not optically stable.[22] Possibly a more satisfactory interpretation of the mechanism is that the chlorine atom, which is normally electron attracting and which in

the vinylic chlorides is even more so due to resonance, is the point of attack by an electron pair[23] which, in effect, displaces the carbanion from the chlorine.

The dechlorination is the least stereospecific of the three reactions employed in the inversion process. This may be inherent in the mechanism of the reaction, or may be due to impurities caused by reaction of the chloro-alkene with the by-product sodium amide despite the threefold excess of sodium employed.

Preparation of Normal *cis* Alkenes by Partial Hydrogenation of Alkynes.—The catalytic hydrogenation of alkynes to produce the same *cis*-alkenes prepared by inversion was carried out using only 20% (50% in the case of 3-hexyne) of the theoretical amount of hydrogen in order to minimize conversion of alkenes to alkanes. For the alkenes produced in this manner, the refractive indices were considerably higher (av. 0.0012 unit), and the densities were the same as or higher than those of the same alkenes prepared by Campbell and Eby (see Table II) who also used Raney nickel, but employed higher temperatures and 85–100% of the theoretical hydrogen.[7] This average difference in refractive index corresponds to about 5–6% more paraffin in their products.

Campbell and O'Connor[6] noted that symmetrical alkynes exhibited much sharper changes in rates of hydrogenation near the midpoint than did 1-alkynes. As a parallel to this, it was found in the present work that the symmetrical alkynes, 3-hexyne and 4-octyne, yielded relatively high purity *cis*-alkenes, distilling within a narrow refractive index range, whereas the unsymmetrical alkynes, 2-hexyne and 2-octyne, yielded *cis*-alkenes of only moderate purity, distilling over fairly wide refractive index ranges; 2-pentyne, being nearly symmetrical, yielded *cis*-2-pentene which was of intermediate purity (Table II).

Comparison of *cis*-Alkenes Prepared by Catalytic Hydrogenation and by Inversion.—The curves of refractive index *versus* volume % distilled (Figs. 2 and 3) for *cis*-2-hexene and *cis*-2-octene prepared by hydrogenation are lower at all points than the corresponding curves for the purer products prepared by the inversion method. This is easily accounted for by the fact that alkanes are the most probable low-index impurities in alkenes made by hydrogenation of alkynes, and these impurities are so close-boiling that no significant separation can be expected with the distillation efficiency employed. However, the gradual rise in refractive index and the more gradual approach to constant boiling point are probably due to the presence of the corresponding *trans*-isomers and/or lesser amounts of the 1-alkenes. These compounds both have lower refractive indices than the corresponding *cis*-alkenes

(21) Fernelius and Watt, *Chem. Revs.*, **20**, 226 (1937).
(22) Gilman, ref. 9, p. 383.

(23) Yost and Russel, "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1944, p. 142.

TABLE II

COMPARISON OF THE PHYSICAL PROPERTIES OF NORMAL cis ALKENES

cis-Alkene	Preparation	n^{20}D	B.p., °C. (760)	d^{20}_4	M.p., °C.	$t_{t_0},^a$ °C.	$K_p,^b$ °C.	Mole % purity
2-Pentene	Inversion (this work)	1.3821–1.3830 (1.3826)	36.88	0.6556	−152.48	−151.38	0.17	93.6
	Cat. H_2 (this work)	1.3803–1.3830 (1.3822)	....	.6551	−152.56	......	..	93.2
	Inversion (Lucas, et al.[10b])	1.3828	36.69c	.6554	......	......	..	..
2-Hexene	Inversion[d] (this work)	1.3976	68.86	.6869	−141.80	−141.38	.14	97.0
	Cat. H_2 (this work)	1.3948–1.3970 (1.3965)	....	.6845	−143.16	......	..	88
	Cat. H_2 (Campbell and Eby[7])	1.3954	68.6c	.6845	−146	......	..	..
3-Hexene	Inversion (this work)	1.3951	66.52	.6794	−138.93	......	..	94.5
	Cat. H_2[d] (this work)	1.3950	66.51	.6795	−138.45	−137.88	.19	97.0
	Cat. H_2 (Campbell and Eby[7])	1.3934	67.6c	.6796	−135	......	..	..
2-Octene	Inversion (this work)	1.4158	125.64	.7245	−100.96	−100.27	.16	95.7
	Cat. H_2 (this work)	1.4138–1.4151 (1.4146)	....	.7231	−101.70	......	..	91.2
	Cat. H_2 (Campbell and Eby[7])	1.4139	125.1c	.7229	−104	......	..	..
4-Octene	Inversion (this work)	1.4150	122.52	.7212	−119.32	......	..	95.5–96.5
	Cat. H_2 (this work)	1.4151	122.54	.7212	−119.02	−118.7	.21	97–98
	Cat. H_2 (Campbell and Eby[7])	1.4136	122.6c	.7205	−118	......	..	..

^{a} t_{t_0} = ultimate freezing (melting) point, i.e., calculated f.p. of 100% pure material. ^{b} K_p = degrees lowering per mole % impurity. ^{c} This boiling point datum corrected to 760 mm. from the reported incidental pressure. ^{d} The following data were received after this paper was written: cis-2-hexene: t_{t_0} −141.135°, K_p 0.171, n^{25}D 1.3947; cis-3-hexene; t_{t_0} −137.820°, K_p 0.192, n^{25}D 1.3920. These data were obtained from samples prepared by the American Petroleum Institute Research Project 45 by inversion and catalytic hydrogenation, respectively, and submitted to the American Petroleum Institute Research Project 6 at the National Bureau of Standards for final purification.

and the boiling point differentials are large enough for partial separation to be expected during the distillation (Table III).

TABLE III

PHYSICAL PROPERTIES OF RELATED HYDROCARBONS

Compound	B.p., °C. (760 mm.)	n^{20}D
n-Hexane[24]	68.74	1.3794
1-Hexene[24]	63.55	1.3876
trans-2-Hexene[25]	67.87	1.3940
cis-2-Hexene	68.86	1.3976
n-Octane[24]	125.67	1.3974
1-Octene[24]	121.27	1.4088
trans-2-Octene[8]	124.94	1.4132
cis-2-Octene	125.64	1.4158

From the best available values for refractive index and density of pure cis-2-pentene, cis-2-hexene, cis-2-octene and the corresponding alkanes, these properties were calculated for mixtures of the same purity as those obtained by catalytic hydrogenation, but containing only the corre-

(24) Rossini, et al., "Selected Values of Properties of Hydrocarbons," N. B. S. Circular C461, U. S. Govt. Printing Office, Washington, D. C. (1947).

(25) Unpublished data, American Petroleum Institute Research Project 45.

sponding alkanes as impurity (see Table IV). In all cases, the calculated values are lower than the cryoscopically measured values, indicating that all the impurity cannot be paraffin but must consist partly of isomerization products.

TABLE IV

ACTUAL AND CALCULATED PROPERTIES OF cis-2-ALKENES

Compound	Mole % purity	d^{20}_4 Actual	d^{20}_4 Calcd.[a]	n^{20}D Actual	n^{20}D Calcd.[a]
cis-2-Pentene	93.2	0.6551	0.654	1.3822	1.3813
cis-2-Hexene	87–88	.6845	.6835	1.3695	1.3943
cis-2-Octene	91.2	.7231	.7226	1.4146	1.4142

^{a} Assuming all the impurity to be the corresponding paraffin.

The refractive indices and densities of the symmetrical cis-3-hexene and cis-4-octene prepared by catalytic hydrogenation and by inversion are nearly identical. The rectification curves of these products are characterized by rapid rise of refractive index and boiling point to values which remain nearly constant throughout the entire alkene fraction. The most probable impurities in the cis-3-hexene and cis-4-octene prepared by hydrogenation are the corresponding trans-isomers and alkanes, and the trans-isomers boil so close to the
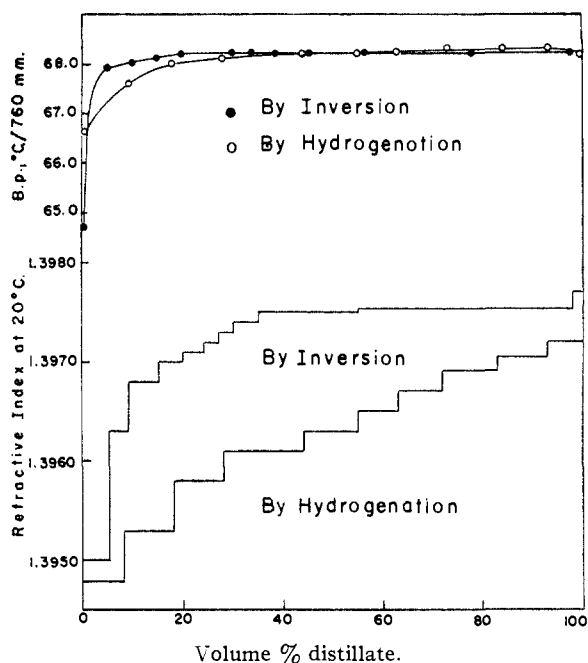
Fig. 2.—Comparative distillations of cis-2-hexene.

Fig. 3.—Comparative distillations of cis-2-octene.

cis-isomers (see Table IV) that no significant separation would be expected under the distillation conditions employed. In the case of cis-3-hexene several large runs were made with 50% instead of 20% of the theoretical amount of hydrogen, and the refractive index dropped 0.0004 during distillation of the last 20% of the olefin product, indicating an increase of 2–3% of n-hexane in these fractions. Undoubtedly a small amount of n-hexane is present in the earlier fractions. The boiling point differential between cis-3-hexene and n-hexane is large enough (Table V) that this increase in concentration of n-hexane in the end fractions is to be expected.

TABLE V

PHYSICAL PROPERTIES OF RELATED HYDROCARBONS

Compound	B.p., °C. (760 mm.)	$n^{20}D$
cis-3-Hexene	66.52	1.3950
trans-3-Hexene[25]	67.12	1.3943
n-Hexane[24]	68.74	1.3794
cis-4-Octene	122.54	1.4151
trans-4-Octene[25]	122.10	1.4122
n-Octane[24]	125.67	1.3974

Experimental

Preparation of Alkynes.—The alkynes were prepared by the stepwise alkylation[26,27] of acetylene with sodium amide[28] and the appropriate alkyl halide or sulfate in liquid ammonia.
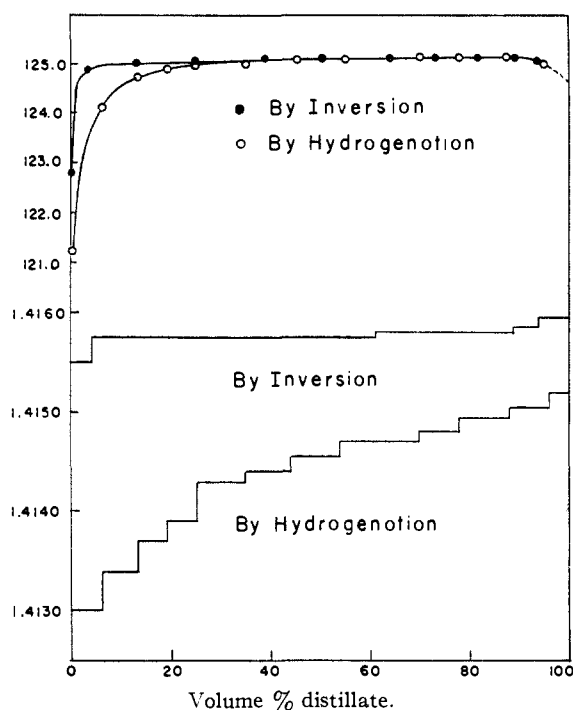
Preparation of trans-Alkenes.—The trans-alkenes were prepared by sodium reduction in liquid ammonia[7] of the corresponding alkynes by the experimental procedures of Henne and Greenlee.[8,28] With the exception of trans-2-pentene, the crude trans-alkenes were fractionated at 25 to 30 plate efficiency prior to chlorination.

Chlorination of Olefins.—The same chlorination procedure was used to prepare all the dichlorides. The reaction

(26) Vaughn, Hennion, Vogt and Nieuwland, J. Org. Chem., **2**, 1 (1937).

(27) Henne and Greenlee, THIS JOURNAL, **67**, 484 (1945).

(28) Greenlee and Henne, "Inorganic Syntheses," McGraw-Hill Book Co., Inc., New York, N. Y., Vol. II, pp. 75 and 128.

was carried out in a three-neck flask shielded from direct light and fitted with a chlorine inlet tube (leading to the bottom of the flask), stirrer, thermometer and gas outlet tube. The chlorination was carried out at Dry Ice temperature using 200 ml. of chloroform and 7.5 ml. of antimony pentachloride per mole of alkene.

In order to prevent tar formation, the solvent and catalyst were added to the reaction flask and cooled to –70° before the alkene was added. Gaseous chlorine was introduced at a rate of about 0.5 mole/hr. in runs of less than 2 moles and at about 0.7–0.8 mole/hr. in larger runs. To prevent the formation of trichlorides, only 95% of the theoretical amount of chlorine was added. The reaction mixture was stirred 15 minutes to complete the reaction, poured into an equal volume of water, and steam distilled to separate the solvent and the dichloride from the precipitated antimony oxides.

The steam distillate was fractionated under reduced pressure through a 2.5 cm. × 95 cm. column packed with $^1/_8$ inch glass helices. The chloroform was removed at 200 mm. pressure up to a kettle temperature of 100° and the dichloride distilled at a pressure at which it would boil at 60° to 80°. Under these conditions there was no evidence of decomposition during distillation. The average yield of constant refractive index product was 81% based on alkene employed.

The physical properties of the dichlorides produced in the above manner are shown in Table VI.

Dehydrochlorination of Dichlorides.—The dehydrochlorination was carried out in a three-neck flask fitted with a dropping funnel, condenser, thermometer and sealed stirrer. With each mole of dichloride, 2 moles of potassium hydroxide and 200 ml. of propanol were used; this solvent was chosen, rather than ethanol, because the higher reaction temperature obtained at reflux increased the speed of the reaction markedly. This amount of solvent allows both easy solution of the potassium hydroxide and smooth stirring of the slurry formed by the potassium chloride which precipitates.

The reaction, which is exothermic, was easily controlled by heating the propanolic potassium hydroxide to 80°, and then adding the dichloride at a rate sufficient to maintain a temperature of 85 to 90° (slow reflux). After the addition of dichloride was complete (1 to 2 hours), heat was applied to maintain this temperature for 15 to 18 hours; titration of unreacted potassium hydroxide indicated 90% dehydrochlorination at 5–6 hours.

The reaction mixture was cooled, poured into twice its volume of water, and the upper phase was separated and

TABLE VI
PHYSICAL PROPERTIES OF DICHLORIDES

Compound	B.p., °C. (760 mm.)	B.p., °C.	Mm.	n^{20}D	d^{20}_4	M.p., °C.	t_{f_0}, °C.	K_p, °C.	Mole % purity
erythro-2,3-Dichloropentane	138.9–139.0	58	50	1.4464	1.0789	−77.82	−77.35	0.28	98.3
meso-3,4-Dichlorohexane	161.4–161.5	55	15	1.4508	1.0589	−44.84	−44.48	.30	98.9
		59.5	20						
		68	30						
dl-3,4-Dichlorohexane	167.7	62	20	1.4514	1.0617	−34.57	−33.00	.51	97.0
erythro-2,3-Dichlorohexane	162.2	70.5	30	1.4487	1.0522	−64.50	−64.35	.27	99.0
meso-4,5-Dichloroöctane	202.5	..	..	1.4538	1.0175	−35.06	−34.36	.55	98.7
erythro-2,3-Dichloroöctane	206.1–206.2	78	10	1.4523	0.9712	−55.11	−54.53	.28	97.7

TABLE VII
PHYSICAL PROPERTIES OF CHLOROALKENES AND AZEOTROPES

Compound	B.p., °C. (760 mm.)	n^{20}D	d^{20}_4	Azeotroping agent	n^{20}D (azeo.)	%^{a}	B.p., (azeo.) °C.	Mm.
Mixed 2- and 3-chloro-cis-2-pentene	....	1.4312	....	n-Propanol	1.4163	67	85.2	751
3-Chloro-cis-3-hexene^b	119.6–119.7	1.4360	0.9009	Methyl Cellosolve	1.4240	65	109.0	736
				n-Propanol	1.4050	39	93.4	743
3-Chloro-trans-3-hexene	114.8–114.9	1.4340	0.8982	Methyl Cellosolve	1.4242	69	106.0	750
Mixed 2- and 3-chloro-cis-2-hexene	....	1.4370	....	Methyl Cellosolve	1.4237	62	110.8	748
4-Chloro-cis-4-octene	165.33	1.4447	0.8912	Ethyl Cellosolve	1.4146	17	133.6	755
Mixed 2- and 3-chloro-cis-2-octene	....	1.444	....	^{c}	....	..	...	...

^{a} Per cent. of chloride in the azeotrope, by volume. ^{b} Cryoscopic data for 3-chloro-cis-3-hexene: mole % purity 98.6, m.p. −110.93°; t_{f_0} −110.69°; K_p 0.19°. ^{c} Not azeotropically distilled.

steam distilled in the presence of sodium bicarbonate. The organic distillate was freed of propanol, by washing with equal volumes of ice-water, clarified by shaking with a 50% aqueous solution of glycerol and dried by percolation through a column of granular anhydrous sodium sulfate. The average yield of this crude product was 90%.[29]

Final purification from possible impurities such as alkynes, traces of propanol, and unreacted dichlorides was effected by azeotropic distillation with a suitable Cellosolve[30] in a 1.2 cm. × 100 cm. column packed ·with $^3/_{32}$ inch glass helices and operating at about 25-plate efficiency. The chloride and somewhat less than the amount of azeotroping agent thought to be required were charged to the still and fractionation started. The approximate composition of the azeotrope was estimated from the refractive index of early fractions of distillate, the correct amount of agent added to produce this composition in the kettle, and the distillation continued. Several grams of sodium bicarbonate, to act as scavenger for hydrogen chloride and to prevent isomerization, were included in each charge for azeotropic distillation. The purified chloroalkene was isolated from the constant refractive index portion of the azeotrope by five washings with equal volumes of ice-water, was clarified by shaking with a 50% aqueous solution of glycerol and was dried by percolation through silica gel at Dry Ice temperature. The recovery of purified chloroalkene from the distillation was 85–90%. The physical properties of chloroalkenes and their azeotropes are shown in Table VII.

Dechlorination of Monohalides.—The dechlorinations were carried out with 3 M solutions of sodium in liquid ammonia using a three-neck flask immersed in a Dry Ice–acetone mixture and fitted with a mercury-sealed Hershberg stirrer and a Dry Ice-cooled reflux condenser.[28] The flask used was chosen so that the solvent and reactants would occupy somewhat less than one-half the total volume in order to leave ample room for subsequent hydrolysis and to minimize the spattering of sodium onto the upper walls of the flask during the reaction.

The required amount of liquid ammonia was charged to the reaction flask, and sodium (6 g.-atoms per mole of chloride to be dehalogenated) was added in 3–7 g. pieces. When

(29) In the case of 3-chloro-cis-3-hexene, this crude product was 1% lower in purity and produced an olefin 0.5% lower in purity than part of the same material purified further by azeotropic distillation.

(30) Vinylic halides are not thermally stable and may isomerize to cis-trans equilibrium mixtures. Lepingle, Bull. soc. chim., [4] **39**, 741 (1926), showed that alcohols stabilize these compounds. Cellosolves were used because of their satisfactory boiling points and complete water solubility.

the sodium had dissolved, the chloride, diluted with one to two volumes of suitable solvent (methylcyclohexane for the C_6 compounds and butylcyclohexane for the C_8 compounds), was added dropwise to the stirred sodium solution. After the addition was complete, the mixture was stirred an additional 30 to 60 minutes to ensure complete reaction.

The excess sodium and the sodium amide formed during the reaction were neutralized with solid ammonium chloride added gradually from a flask attached to a side-neck of the reactor by a section of Gooch tubing. The cooling bath was removed and water was added slowly until the reaction vessel was nearly full. The lower layer (concd. solution of ammonia and sodium chloride) was siphoned off, and the remaining organic layer was washed in the reactor (three times with water, once with dilute acid, and finally with dilute bicarbonate), then was dried. The crude product was topped from the solvent and fractionated at 25 to 40 plate efficiency. Yields of crude products, prior to final distillation, were about 90%. Physical properties of the alkenes prepared in this manner are shown in Table II.

Catalytic Hydrogenation.—The same procedure was employed in all the hydrogenations. A Parr low-pressure apparatus was used in which a metal bomb with a cooling jacket replaced the customary glass bottle. The alkyne (100 ml.), absolute ethanol (100 ml.) and Raney nickel (5 g., as an alcohol slurry) were charged. The bomb was then flushed twice with hydrogen, and shaking was started, usually at 60 to 70 p.s.i.; ice-water cooling was used throughout the reaction period (20 to 30 minutes).

After the desired amount of hydrogen had been consumed, the crude mixture was decanted from the catalyst, filtered, and mixed with water to effect separation of the hydrocarbon which was then freed from traces of nickel by steam distillation. The steam distilled alkyne–alkene mixture was then washed five times with equal volumes of ice-water to remove alcohol, clarified by washing with a 50% aqueous solution of glycerol, and dried by percolation through a column of anhydrous sodium sulfate. The material balance to this point was 90–98%. The alkyne–alkene mixture was then fractionated at about 30-plate efficiency to obtain an alkene fraction and an intermediate fraction which was redistilled separately to give an additional amount of alkene. The combined product fractions were refractionated at 30 to 50 plate efficiency to give purified alkene in yield of 70–80% of the theoretical based on hydrogen consumed; recovered alkyne could be recycled.

Proof of Configuration.—To prove the identity of the cis-3-hexene made by inversion, a sample (m.p. −139.45°, corresponding to 91.7 mole % purity) was mixed with a smaller amount (5% of the mixture) of authentic cis-3-hex-

ene (m.p. −138.45°, purity 97.0%), *i.e.*, a sample made by catalytic hydrogenation of 3-hexyne; the m.p. of the mixture was an intermediate value (m.p. −139.41°, purity 91.9%).

Similarly, the identity of the *trans*-3-hexene made by inversion (b.p. 67.07°, m.p. −114.54°, purity 93.5 mole %) was proved by a mixed melting point. On the authentic sample (98.7% pure), which had been made by reduction of 3-hexyne with sodium in ammonia, the following properties were determined: b.p. 67.12° (760 mm.), $n^{20}D$ 1.3943, d^{20}_4 0.6772, m.p. −113.66°, t_{t0} −113.43°, K_p 0.17°. The mixture containing 5% of the authentic material had an intermediate melting point (m.p. −114.50°, purity 93.7%), indicating that the component samples were identical.

The determination of the relative dehydrochlorination rates of the 3-chloro-3-hexenes was done by heating small samples with alkali in sealed tubes and titrating at intervals. Several tubes were prepared for each chloroalkene, each tube being charged with 4 ml. of standard propanolic potassium hydroxide (0.0088 mole) and 1.00 ml. of one of the 3-chloro-3-hexenes. They were simultaneously immersed in an oil-bath at 120° and pairs were removed at intervals, cooled and opened; the contents were titrated at once with standard acid, and the per cent. of dehydrohalogenation was calculated. The percentages of the supposed 3-chloro-*cis*-3-hexene reacted at 12, 24 and 35 hours were 15, 18 and 21%, respectively; the percentages of the supposed 3-chloro-*trans*-3-hexene reacted were 44, 63 and 69, respectively, at the same intervals. This indicated that the 3-chloro-3-hexene presumed to be *trans* was dehydrohalogenated about 3 times as fast as the other isomer, thus confirming the identification.

Determination of Physical Properties.—The alkenes, alkynes and chloro-alkenes employed in this investigation become peroxidized even on short contact with air. Since traces of peroxides produce marked effects upon the physical properties, only samples freshly prepared or freshly treated with sodium thiosulfate and/or silica gel to eliminate peroxidic material were used for the measurement of physical properties.

The apparatus used in determining freezing points, melting points and mixed melting points was essentially that used at the National Bureau of Standards.[31] Temperatures were measured by a platinum resistance thermometer (calibrated to ±0.01° in the range used) in connection with a Mueller resistance bridge (Leeds and Northrup, Type G-2). The melting points obtained were precise to about ±0.02° and were believed accurate to about ±0.05°.

The purities of the compounds for which no cryoscopic constants are available were determined by essentially the same method as that described by Mair, Glasgow and Ros-

sini.[32] The purities in the range of 99% are believed to be accurate to about 0.2%, those in the range of 95% to ±0.5%, and those in the range of 90% to ±1.0%. The values for *cis*-4-octene are reported as ranges since the crystalline character of compound was anomalous,[33] and freezing and melting points of the usual accuracy could not be obtained.

The standard boiling points of the compounds prepared in the course of this investigation were determined in a modified Cottrell apparatus[34] attached to a barostat which maintained a constant pressure of 760 mm. The actual temperatures were measured with the same platinum resistance thermometer and Mueller bridge used for the cryoscopic determinations, and should be accurate to ±0.02°. Refractive indices were determined with a Valentine Precision Refractometer (Industro–Scientific Co.) with a waterbath controlled to ±0.1°, and are accurate to ±0.0001. Densities were measured to a precision of ±0.00005 with double-arm 15-ml. glass pycnometers and a water-bath controlled to ±0.02°.

Conclusions

The data from the preparation of *cis*-alkenes by catalytic hydrogenation indicate that the impurities present in these alkenes are principally alkanes and the *trans*-isomers. The impurities in the *cis*-alkenes prepared by the inversion method herein described are principally the *trans*-isomers and possibly some positional isomers.

Examination of the data in Table II shows that this inversion method yields purer *cis*-2-hexene and *cis*-2-octene (unsymmetrical alkenes) and that catalytic hydrogenation produces purer *cis*-3-hexene and *cis*-4-octene (symmetrical alkenes).

The inversion method appears to be of general applicability to isolated double bonds.[35] However, the degree of strain associated with the change in configuration can be expected to affect the stereospecificity in the individual case.

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(32) Mair, Glasgow and Rossini, *ibid.*, **26**, 591 (1941).

(33) Hoff and Boord, THIS JOURNAL, **72**, 2770 (1950).

(34) Quiggle, Tongberg and Fenske, *Ind. Eng. Chem., Anal. Ed.*, **6**, 466 (1934).

(35) Preliminary experiments on inverting oleic acid to elaidic acid and *trans*-2-*trans*-7-nonadiene to *cis*-2-*cis*-7-nonadiene indicated satisfactory results.

(31) Glasgow, Streiff and Rossini, *J. Research Natl. Bur. Standards*, **35**, 355 (1945).