working up in a customary manner there were obtained 0.66 g. of triphenylbismuth, and 0.15 g. of a product which melted at 179–180° (with prior shrinking) after crystallization from chloroform–methanol.

Anal. Calcd. for $C_{18}H_{15}OBi$: Bi, 45.83. Found: Bi, 40.98.

The chloroform–methanol filtrate (from which was obtained the product melting at 179–180°) deposited, on standing, triphenylbismuth. Apparently, the expected diphenyl-*p*-hydroxyphenylbismuth is very unstable.

Diphenylbismuth Sodium and Halogenated Benzoic Acids.—Addition of 1.24 g. (0.005 mole) of *o*-iodobenzoic acid in ether to 0.005 mole of diphenylbismuth sodium discharged the red color. In addition to 0.95 g. (65%) of triphenylbismuth, there was obtained an alkali soluble compound which contained bismuth. This as yet unidentified product melted at 152° with shrinking at 145°.

From a corresponding reaction with *m*-bromobenzoic acid there was obtained a 75.3% yield of triphenylbismuth and a quantitative recovery of *m*-bromobenzoic acid.

From a reaction with methyl *p*-bromobenzoate, the only product identified was *p*-bromobenzoic acid. A mixture, soluble in alkali and containing bismuth, has not been resolved.

From a reaction with sodium *o*-iodobenzoate there was obtained a 42.5% yield of triphenylbismuth, and 0.65 g. of a mixture which was soluble in water and contained bismuth. Some orienting attempts at purification resulted in general decomposition.

A reaction between diphenylbismuth sodium and one-half the required amount of *p*-iodobenzoic acid (previously dissolved in a little liquid ammonia) yielded 24.5% of triphenylbismuth, together with an alkali-soluble, bismuth-containing product.

Diphenylbismuth Iodide and Triphenylmethylsodium.—To a solution of triphenylmethylsodium (prepared from 0.01 mole of triphenylmethane) in 150 cc. of liquid ammonia was added 0.01 mole of diphenylbismuth iodide. The chief product, melting between 57–60° after crystallization from chloroform–methanol, was probably a mixture. (See preceding paper.)

Anal. Calcd. for $(C_6H_5)_2BiC(C_6H_5)_3$: Bi, 34.48. Found: Bi, 24.99 and 24.05.

From a reaction between diphenylbismuth sodium and triphenylchloromethane, triphenylbismuth and triphenylmethane were obtained.

Ammonolysis of Diphenylbismuth Iodide and Bromide.—A solution of 2 g. of freshly prepared diphenylbismuth iodide in 150 cc. of liquid ammonia was stirred as the ammonia evaporated (three hours). From the residue there was obtained 0.27 g. (21%) of triphenylbismuth and 1.3 g. (65%) of unreacted diphenylbismuth iodide.

A corresponding experiment with diphenylbismuth bromide yielded 38.2% of unreacted diphenylbismuth bromide. No triphenylbismuth was isolated subsequent to ammonolysis, and the ether insoluble material appeared to consist mostly of inorganic bismuth.

Summary

Diarylbismuth halides react in liquid ammonia with equivalent quantities of lithium, sodium, potassium, calcium or barium to give highly reactive, deep red colored R_2BiM compounds. These diarylbismuth metallic compounds react with $R'X$ compounds to give unsymmetrical organobismuth compounds ($R_2R'Bi$), and a water-soluble type ($R_2BiC_6H_4CO_2H$).

The radical diphenylbismuth is formed transitorily in the reaction between diphenylbismuth halides and alkali or alkaline earth metals.

A new type of halogen–metal interconversion appears to be involved in the reaction between diphenylbismuth sodium and α-iodonaphthalene.

The decreasing order of relative reactivities of diarylbismuth halides is: R_2BiCl, R_2BiBr, R_2BiI. This is a reversal of the stabilities of R_3BiX_2 types.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Preparation of Higher *cis* and *trans* Olefins[1]

BY KENNETH N. CAMPBELL AND LAWRENCE T. EBY

In recent years there has been considerable interest in the preparation of the pure geometrical isomers of olefins. Most methods of preparing olefins yield a mixture of the two geometrical isomers, but in the case of 2-butene these can be separated by fractional distillation.[2] As the length of the carbon chain increases, however, the boiling points of the two forms approach each other, and separation by distillation fails. For this reason attention has been turned to methods of preparation which will yield one form and not the other. Several such methods have been proposed, but they are of limited applicability and do not always give the pure isomers. The *cis* and *trans* forms of 2-butene[3] and 2-pentene[4] have been made from the corresponding *cis* and *trans* α-β un-

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[1] Paper XLI on the chemistry of substituted acetylenes and their derivatives; previous paper, THIS JOURNAL, **62**, 1798 (1940). Part of the material in this paper was presented before the Organic Division at the Detroit meeting, September, 1940.

[2] Kistiakowsky, *et al.*, *ibid.*, **57**, 876 (1935).

[3] Lucas and Prater, *ibid.*, **59**, 1682 (1937).

[4] Sherrill and Matlack, *ibid.*, **59**, 2134 (1937).

saturated acids, through the hydrogen iodide addition products, but as Young and his co-workers[5] have pointed out, this is not a promising method for making the pure geometrical isomers of higher olefins, since it is difficult to obtain and keep the pure geometrically isomeric acids.

Young, Jasaitis and Levanas[5] have reported the preparation of the pure *cis* and *trans* forms of 4-octene from the *meso* and *dl* forms of 4,5-octanediol through the intermediate dibromides. Van Risseghem[6] has used a similar method to prepare the *cis* and *trans* forms of 3-hexene. She determined the purity and structure of her products by means of Raman spectra, and thereby found the *cis* form obtained from the *meso* glycol contained 15–20% of the *trans* isomer, and the *trans* form obtained from the *dl* glycol was contaminated with 5–10% of the *cis* compound. This method of preparing olefins from glycols through the dibromides suffers also from the disadvantage that it is tedious, expensive and in many cases the over-all yield of olefin is poor.

In earlier work we have shown that the easily obtained dialkyl acetylenes form a logical starting material for the preparation of pure olefins of known position of the double bond, for the reduction can be stopped at the olefin stage.[7] If the reduction could be controlled from a stereochemical standpoint, it would seem possible to use them also for the preparation of the individual geometrical isomers of a given olefin. A study of the stereochemical reduction of dialkylacetylenes was undertaken, and in this paper are described the preparation and proof of configuration of four pairs of geometrical isomers, namely, those of 4-octene, 3-octene, 3-hexene and 5-decene.

Other workers have shown that dialkylacetylenes when reduced catalytically in the presence of colloidal palladium[6,8] or Raney nickel[9] yield the corresponding *cis* olefins. Some of these workers[8a,b,9] have shown by means of Raman spectra that the *cis* olefins so obtained have a high degree of purity. More vigorous catalysts such as platinum black do not always permit selective reduction to the olefin, and may lead to the formation of both the *cis* and *trans* isomers, as well as of the saturated product.[10] There thus appears to be no way of hydrogenating a dialkylacetylene catalytically so as to obtain the *trans* olefin, free from the *cis* isomer and the saturated hydrocarbon.

Attention was therefore turned to chemical reducing agents. The literature contains but few references to the chemical reduction of substituted acetylenic hydrocarbons, and still less to the stereochemical course of such reduction. Straus[11] and Aronstein and Holleman[12] found that certain reducing agents, such as sodium in methyl alcohol, zinc dust and acetic acid, red phosphorus and iodine, caused the reduction of tolane to stilbene (*trans*), while other reducing agents yielded isostilbene (*cis*) as did catalytic hydrogenation with colloidal palladium.[13]

In the present study, it was found that dibutylacetylene was not reduced by granulated zinc in either acetic acid or hydrochloric acid solution, or by zinc amalgam in hydrochloric acid. When zinc amalgam and hydrochloric acid were used together in acetic acid solution, a complex mixture was obtained from which were isolated chlorinated products and an ester, doubtless formed by addition of the solvents to the triple bond. Sodium in boiling amyl alcohol caused no reduction of diamylacetylene. It was found, however, that the dialkylacetylenes could be reduced smoothly and easily by sodium in liquid ammonia solution to olefins to which were assigned the *trans* structures, for reasons discussed below. These olefins were obtained in good yields and a remarkable state of purity.

By utilizing catalytic hydrogenation with Raney nickel for the preparation of the *cis* olefins, and sodium–liquid ammonia reduction for the *trans* forms, the four pairs of geometrical isomers mentioned above were prepared. The physical constants of these substances, given in Table I, were obtained consistently, on several different runs. There is no apparent relationship between configuration and boiling point, as has already been pointed out by van Risseghem,[6] but in all cases the boiling points of the two forms are very close together. In every case the *trans* form has the lower density, and therefore the higher molecular refraction, but there is not always a difference in index of refraction between the two forms.

(5) Young, Jasaitis and Levanas, THIS JOURNAL, **59**, 403 (1937).

(6) Van Risseghem, *Bull. soc. chim. Belg.*, **47**, 194 (1938).

(7) Campbell and O'Connor, THIS JOURNAL, **61**, 2897 (1939).

(8) (a) Grédy, *Bull. soc. chim.*, [5] **2**, 1029 (1935); (b) Bourguel, *Compt. rend.*, **180**, 1753 (1925); (c) Sherrill and Launspach, THIS JOURNAL, **60**, 2562 (1938).

(9) Du Pont, *Bull. soc. chim.*, [5] **3**, 1030 (1936).

(10) Ott and Schurmann, *Ber.*, **61**, 2119 (1928).

(11) Straus, *Ann.*, **342**, 261 (1905).

(12) Aronstein and Holleman, *Ber.*, **21**, 2833 (1888).

(13) Kelber and Schwartz, *ibid.*, **45**, 1951 (1912).

Table I

Physical Constants of *cis* and *trans* Olefins

Compound	B. p., °C.	Press., mm.	F. p., °C.	n^{20}_D	d^{20}_4	n^{25}_D	d^{25}_4	MR_D[a] obsd.	MR_D calcd.	ϵ^{25}	P_t	P_0
cis-5-Decene	169.5– 9.6	739	−112	1.42521	0.74451	1.42296	0.74063	48.22	47.91	2.071	49.82	1.60
trans-5-Decene	170.2	739	− 73	1.42351	.74012	1.42126	.73626	48.34	47.91	2.030	48.69	0.35
cis-4-Octene[b]	121.7	739	−118	1.41361	.72048	1.41127	.71628	38.92	38.68	2.053	40.70	1.78
trans-4-Octene[b]	121.4	739	− 84	1.41157	.71467	1.40909	.71044	39.05	38.68	2.004	39.60	0.55
cis-3-Octene	122.3	741	−126	1.41246	.71888	1.41008	.71470	38.91	38.68	2.062	41.05	2.14
trans-3-Octene	122.4	741	−107	1.41241	.71630	1.40998	.71210	39.04	38.68	2.002	39.45	0.41
cis-3-Hexene[c]	66.8–66.9	741	−135	1.39338	.67964	1.39076	.67489	29.61	29.44	2.062	32.60	2.99
trans-3-Hexene[c]	67.4–67.6	741	−113	1.39377	.67788	1.39116	.67303	29.72	29.44	2.000	31.26	1.54

[a] These molecular refractions are calculated from the data obtained at 25°. [b] Young, Jasaitis and Levanas[5] found the following values for *cis*-4-octene: b. p. 120.0–120.5° (760) n^{24}_D 1.4111, d^{20}_4 0.7186, f. p. −115°; and for *trans* 4-octene: b. p. 120.0–120.5° (760), n^{24}_D 1.4110, d^{20}_4 0.7165, f. p. −105°. They prepared the olefins from the *meso* and *dl*-octanediols through the dibromides. Gibson, Doctorate Thesis, Ohio State University, 1938, prepared *trans* 4-octene from *trans* 1,4-dibromo-2-butene and found: b. p. 120.7° (760), n^{20}_D 1.4131, d^{20}_4 0.7167. [c] Van Risseghem[6] prepared *cis* and *trans* 3-hexene from the diols, and obtained the following constants: *cis*, b. p. 66.9–67.05° (760), n^{20}_D 1.3926, d^{20}_4 0.6784; *trans*, 67.3–67.35° (760), n^{20}_D 1.3946, d^{20}_4 0.6779. Gibson, *loc. cit.*, made *trans* 3-hexene from *trans* 1,4-dibromobutene and reported: b. p. 66.4–66.7° (760), n^{20}_D 1.3943, d^{20}_4 0.6784.

The configurations assigned to the olefins were established in three ways. The first was by means of dielectric constants. It has long been known that the *cis* and *trans* forms of dichloroethylene and similar substances have markedly different orientation polarizations and dipole moments, and that the *trans* form in every case has the lower polarization and moment, since the effects of the two polar groups tend to cancel each other. Although alkyl groups are not strongly polar as are halogen atoms, nevertheless the *cis* and *trans* forms of olefins should also have different orientation polarizations, since in the *cis* form the two alkyl groups work in the same direction, and in the *trans* in opposite directions. The dielectric constants of the olefins prepared in this work were determined by means of the heterodyne beat method of Otto and Wenzke.[14] In every case the olefin obtained by the sodium–liquid ammonia reduction had the lower dielectric constant, and calculations of the orientation polarizations showed that the values for the *trans* forms were significantly lower than those for the *cis*. These data are also summarized in Table I.

The second evidence for the configurations assigned was obtained from Raman spectra. Through the kindness of Dr. Eugene Rosenbaum of the University of Chicago the Raman spectra of three of the four pairs were determined. The details of this work will be published elsewhere, but, in brief, the Raman spectra showed that the olefins prepared by catalytic hydrogenation had the characteristic olefin line at the same position, and the value was in agreement with that found for *cis* olefins by other workers, about 1658 cm.$^{-1}$. The olefins prepared by sodium–liquid ammonia reduction all showed the olefin line at the same displaced position, and this also was in agreement with the value found by other workers for *trans* olefins, namely, 1674 cm.$^{-1}$. Furthermore, the Raman spectra showed that the *trans* olefins were free from unreduced acetylene, *cis* olefin or saturated hydrocarbon. The *cis* olefins were in the same way shown to be free from acetylene or saturated hydrocarbon, but in some cases were contaminated with 2–3% of the *trans* isomer.

The third evidence was obtained from freezing point data. The freezing points of the four pairs of olefins were determined, and in every case the olefin prepared by catalytic hydrogenation had a lower freezing point than that of its isomer prepared by sodium–liquid ammonia reduction. These data are recorded in Table I.

These results appear to establish the fact that individual geometrical isomers of a given olefin can be made by selective reduction of a dialkylacetylene, and we believe that we have proved the configurations of the olefins prepared in this work. In future publications, now in preparation, we expect to describe studies on the addition reactions of geometrically isomeric olefins, and the preparation of aryl-substituted olefins from acetylenes.

Experimental Part

Columns.—All the compounds used or prepared in the course of this work were purified by repeated distillation through Whitmore–Fenske total condensation, partial take-off columns, packed with single-turn glass helices. The physical constants were determined on the middle

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[14] Otto and Wenzke, *Ind. Eng. Chem., Anal. Ed.*, **6**, 187 (1934).

cuts from the fractionation of 50–100 g. quantities. The constants were determined immediately after distillation, and the materials used for the measurements were shown to be free from peroxides.

Dialkylacetylenes.—These were prepared from alkyl bromides and sodium acetylide in liquid ammonia solution.[15] Only materials of constant index of refraction and constant boiling point were used in the reduction studies. The physical constants of the acetylenes used are recorded in Table II.

TABLE II

PHYSICAL CONSTANTS OF ACETYLENES

Compound	B. p., °C.	Press., mm.	n^{20}D	d^{20}_4	F. p., °C.
Dibutylacetylene	177.1–177.2	751	1.4331	0.7690	− 77
Dipropylacetylene	131.8–132.1	747	1.4245	.7521	−102
Et-Bu-acetylene	132.8–133.0	747	1.4250	.7529	−104
Diethylacetylene	81.2– 81.3	747	1.4111	.7231	−101

Catalytic Hydrogenation.[7]—To a solution of 0.2 mole of dialkylacetylene in 50 ml. of 95% ethyl alcohol was added 1 g. of Raney nickel catalyst[16] (wet weight) and the mixture was shaken with hydrogen at an initial pressure of 60 lb. per sq. in. until 0.2 mole had been absorbed. The reaction mixture was filtered from the catalyst, poured into two volumes of water, the organic layer washed with water, dried over anhydrous potassium carbonate and distilled from fresh carbonate. The material from several such runs was combined and refractionated. The yield of *cis* olefin of constant boiling point, constant index of refraction was about 75–90% of the theoretical amount.

Sodium–Liquid Ammonia Reduction.—To a solution of 1.5 gram atoms of sodium in 1.5 liters of liquid ammonia, 0.5 mole of the dialkylacetylene was added dropwise, with stirring, below the surface of the liquid. The addition usually required about forty minutes. Stirring was continued for one to two hours longer, and the mixture was then hydrolyzed by the addition of ammonium hydroxide and water. The organic layer was separated, washed with water, dilute acid, dilute carbonate solution and finally with water. It was dried over anhydrous potassium carbonate and distilled from fresh carbonate. For the higher olefins the yield of pure compound was 80–90%. In the case of 3-hexene (*trans*) it was necessary to carry the reaction out in a dry-ice-bath, and to do the hydrolysis very slowly. In this case the yield was about 40%.

Physical Constants. (a) **Densities.**—A carefully calibrated 10 ml. Ostwald–Sprengel type pyknometer was used, and the determinations were carried out in triplicate. The weighings were made on a five-place balance, and were corrected to vacuum. The thermostat used was constant to ±0.005° at 25° and to ±0.01° at 20°, as determined by a Bureau of Standards calibrated thermometer and a Beckmann thermometer.

(b) **Indices of Refraction.**—The five-place indices were measured on a Zeiss Pulfrich refractometer, the accuracy of which had been checked by means of conductivity water and by a sample of methylcyclohexane furnished through the courtesy of Dr. Rossini of the Bureau of Standards. The other indices of refraction were measured on an Abbe refractometer which had been checked against the Pulfrich. The thermostat used in these measurements was the one described above.

(c) **Boiling Points.**—These were determined with a semimicro Cottrell apparatus,[17] using calibrated Anschütz thermometers.

(d) **Dielectric Constants.**—These were measured at 25.0° on the pure liquids, using the heterodyne beat method of Otto and Wenzke.[14]

(e) **Freezing Points.**—These were determined in the usual way, using a calibrated pentane thermometer and a liquid air cooling-bath. The freezing points recorded in Table II are values corrected for stem exposure.[18] The freezing points have a probable accuracy of ±1°.

Summary

1. The reduction of dialkylacetylenes can be controlled so as to yield either *cis* or *trans* olefins. *cis* Olefins can be prepared by catalytic hydrogenation in the presence of Raney nickel, and *trans* olefins can be made by reducing dialkylacetylenes with sodium in liquid ammonia.

2. Four pairs of *cis* and *trans* isomers have been described: those of 5-decene, 4-octene, 3-octene and 3-hexene, and their configurations established by means of Raman spectra, freezing points and dielectric constant data.

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[15] Bried and Hennion, THIS JOURNAL, **59**, 1310 (1937).

[16] Covert and Adkins, *ibid.*, **54**, 4116 (1932).

[17] Willard and Crabtree, *Ind. Eng. Chem., Anal. Ed.*, **8**, 79 (1936).

[18] "International Critical Tables," Vol. I, p. 56.