

629. *Synthesis of cis- and trans-Octadecenes. Selective Catalytic Hydrogenation of Acetylenes.*

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The eight *cis-n*-octadecenes have been prepared by selective catalytic hydrogenation and six of the eight possible *trans-n*-octadecenes by partial reduction of the corresponding octadecynes with sodium and liquid ammonia. The suitability of various catalysts for the selective hydrogenation has been studied. Starch-supported colloidal palladium, poisoned palladium, Raney iron, and pyrophoric Raney nickel were unsuitable: non-pyrophoric Raney nickel and, particularly, a nickel-copper catalyst were, however, sufficiently selective.

OLEFINS of high molecular weight produced by cracking of high-boiling fractions of petroleum constitute new sources of long-chain acids and alcohols. A series of the isomeric *n*-octadecenes, therefore, has been synthesised in a high degree of purity and free from isomers for determination of their physical constants. The usual methods such as dehydration of alcohols, dehalogenation of dihalides, removal of the elements of hydrogen halide from monohalides, thermal cleavage of esters, etc., could not be employed since they cannot be considered unambiguous. For example, Asinger (*Ber.*, 1942, **75**, 1260) has shown that freshly prepared magnesium bromide can cause considerable isomerisation of alk-1-enes; preparation of the latter, therefore, by the Grignard reaction between allyl bromide and alkylmagnesium bromides can no longer be considered unambiguous. In any case such methods are excluded when the synthesis of pure *cis*- and *trans*-olefins is contemplated. In the present work the *cis-n*-octadecenes have been prepared by selective catalytic hydrogenation, and the *trans*-octadecenes by partial reduction of the corresponding octadecynes with sodium and liquid ammonia.

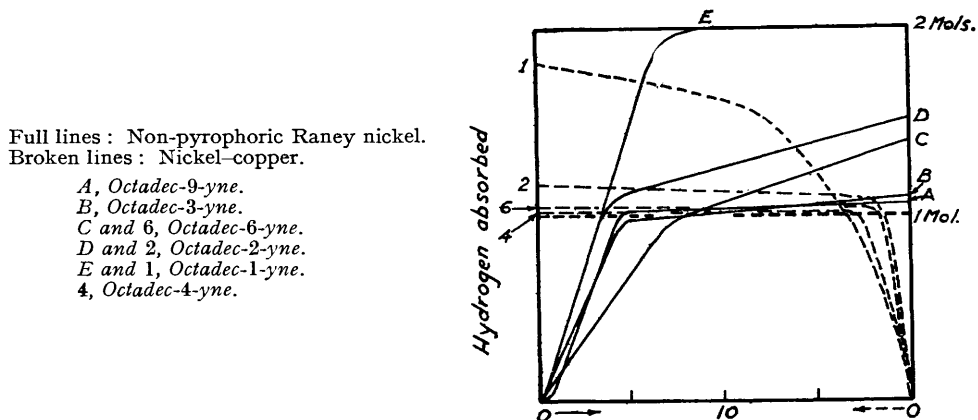
Early workers in this field claimed that the catalytic hydrogenation of acetylenes could be directed to give either the *cis*- or the *trans*-olefins by varying the rate of hydrogenation, the catalyst, or the temperature. Despite contradictory claims it finally became established that catalytic hydrogenation of disubstituted acetylenic hydrocarbons led exclusively to *cis*-olefins; and, further, that addition of the second molecule of hydrogen to an olefin derived from a disubstituted acetylene was much slower, whereas with monosubstituted acetylenes the rates for the first and the second molecule were little different.

In the present work, no evidence of contamination of *cis*- with *trans*-isomers has been found.

Selective Catalytic Hydrogenation of Acetylenes.—The selectivity of the following catalysts was studied. Starch-supported colloidal palladium, prepared according to Bourguel [*Bull. Soc. chim.*, 1927, (4E), **41**, 1444], exhibited only slight specificity with oct-1-yne and octadec-9-yne. In addition, the rate of hydrogenation was very slow. Raney iron, prepared by Paul and Hilly's method [*ibid.*, 1939, (5E), **6**, 218], did not promote hydrogenation of octadec-9-yne at room temperature. This catalyst, although generally considered incapable of promoting the hydrogenation of olefins, caused formation of the alkane when used with *n*-octadec-9-yne at 110°/50 atm. Freshly prepared Raney nickel (cf. Mazingo, *Org. Synth.*, 1941, **21**, 15) gave much higher rates of hydrogenation at atmospheric pressure

than did palladium on starch. It was not selective with monoalkylacetylenes. In the case of the dialkylacetylenes, however, the rate of absorption decreased progressively. Campbell and O'Connor (*J. Amer. Chem. Soc.*, 1941, **63**, 216) prepared several *cis*-olefins by partial hydrogenation at 5 atm. in presence of this catalyst. Recent work has shown that a reactive catalyst can be made more selective by poisoning. A quinoline-poisoned palladium-charcoal catalyst has been successfully used by Isler *et al.* (*Helv. Chim. Acta*, 1947, **30**, 1911) and Heilbron, Jones, Toogood, and Weedon (*J.*, 1949, 2028); Ruzicka and Miller (*Helv. Chim. Acta*, 1939, **22**, 755) favoured the use of palladium-calcium carbonate in pyridine suspension; but both of these are insufficiently active for hydrogenation of octadecynes. When, however, palladium-calcium carbonate was used in suspension in ethyl acetate-methanol (2 : 1), containing 0.25% of pyridine, selective hydrogenation did take place although the absorption rate was slow (K. J. Parker, personal communication). The selective palladium catalyst described by Lindlar (*Helv. Chim. Acta*, 1952, **35**, 446) and the piperidine-zinc acetate-poisoned nickel catalyst employed by Oroshnik, Karmas, and Mebane (*J. Amer. Chem. Soc.*, 1952, **74**, 295) were not known to us at the time of the investigation.

Aged Raney nickel was much more selective than freshly prepared Raney nickel. The



marked selectivity of Raney nickel which had been stored under ethanol for six months is demonstrated by the two mean rates of hydrogenation for each of the octadecynes which are listed in Table 1 (p. 3159).

Nickel-Copper Catalyst.—Aged Raney nickel has an obvious disadvantage. A readily available and very selective catalyst was produced by treatment of pyrophoric Raney nickel with ethanolic copper acetate, so that up to 10% of copper was deposited on the nickel. Two factors influence the specificity of this catalyst; first, the activity of Raney nickel which itself depends on the method of preparation and the time of storage; and, secondly, the copper-nickel ratio: the less active the Raney nickel, the less copper is needed and *vice versa*. The selectivity can be varied on this basis to suit the particular acetylenic compound. Hydrogenation of small amounts (0.2—0.5 g.) of the octadecynes to olefins by use of this catalyst at atmospheric pressure and room temperature can be effected in a few minutes, though, of course, it depends also on the amount of catalyst, the effectiveness of stirring, and the age of the catalyst. The selectivities of this catalyst and aged Raney nickel are compared in the Figure.

Non-pyrophoric Raney nickel and the nickel-copper catalyst were used for preparation of the *cis*-octadecenes.

trans-Octadecenes.—No satisfactory method for the partial reduction of acetylenes to *trans*-olefins was available until Campbell and Eby (*ibid.*, 1941, **63**, 216) showed that acetylenes were reduced exclusively to, and only so far as, *trans*-olefins by sodium in liquid ammonia. However, our acetylenes resisted such reduction at -35° ; use of ether as a solvent (cf. Henne and Greenlee, *ibid.*, 1943, **65**, 216, 2683) also proved ineffective. A

modification of Henne and Greenlee's method whereby the reaction was carried out under pressure at room temperature in a tilting autoclave was successful, reaction being complete in 10—12 hours and yields almost quantitative.

Both *cis*- and *trans*-olefin were purified by low-temperature crystallisation from acetone (for method and apparatus see Smith, J., 1939, 944, and Elsner and Paul, J., 1951, 893), in which they were markedly less soluble than the parent acetylenes. This purification, followed by fractional distillation, was repeated until the freezing points were constant; the final physical properties are recorded in Table 2 (p. 3160).

Of the octadecene series, only the *cis*- and the *trans*-9-isomer have been prepared previously, namely, by Boeseken and Belinfante (*Rec. Trav. chim.*, 1926, 45, 914) from oleic and elaidic acid. Their values for the physical constants are not in agreement with ours.

Physical Constants.—*trans*-Octadecenes have higher freezing points than the *cis*-isomers, in agreement with the data for homologues (Campbell and Eby, *loc. cit.*). Further, the difference in freezing point between the corresponding *cis*- and *trans*-isomers increases as the double bond is moved towards the centre of the chain.

Except in the case of the octadec-2-enes, the *trans*-forms have the lower densities, also in agreement with recorded data for the lower homologues.

The refractive indices of *cis*- and *trans*-octadec-2- and -3-ene are the same, whereas in all other cases the *cis*-form has the higher value.

Of the physical constants the freezing points show the greatest differences, in agreement with the general rule for such cases (Brooks, "Chemistry of the Non-Benzenoid Hydrocarbons," Reinhold Publ. Corp., New York, 2nd Edn., 1950, p. 240).

Infra-red Spectra.—We are indebted to Dr. E. C. Leisegang (at that time of the Department of Physical Chemistry, University of Oxford) for determination of the infra-red absorption spectra. Marked differences appear between the spectra of the *cis*- and the *trans*-forms in all the cases studied. *trans*-Forms are readily recognised by the very intense absorption band at 970 cm.^{-1} , where the *cis*-isomers have only weak bands. All the compounds have intense bands at 720 cm.^{-1} ; the contours of the bands of the *cis*-forms are, however, broad and rounded, whereas the bands of the *trans*-forms occur as sharp peaks.

The appearance of the spectra support Sheppard and Simpson's interpretation (*Quart. Reviews*, 1952, 6, 1). The intense band at 970 cm.^{-1} in this series of *trans*-disubstituted ethylenes may be due to the out-of-plane-bending vibration of the ethylene grouping, while the broadening of the bands in the *cis*-compounds at 720 cm.^{-1} may be due to the overlap of the out-of-plane-bending mode of the *cis*-form with the rocking-frequency usually found at about this frequency.

EXPERIMENTAL

F. p. and m. p. measurements were made with Anschütz-type thermometers. Analyses were by Mr. F. C. Hall, Dyson Perrins Laboratory.

Hydrogenation Apparatus.—Hydrogenations were carried out under 20 mm. excess pressure. Standard ground-glass joints were used where possible, and glass-to-glass connections were made with "Polythene" tubing. Steady agitation was achieved by means of a magnetic stirrer and was controlled so that the vortex in the liquid just reached the bottom of the flask and no splashing occurred. The reservoir was calibrated by hydrogenation of cinnamic acid.

Selectivity of Catalysts.—(a) *Starch-supported colloidal palladium.* Hydrogenation in ethyl acetate (25 c.c.) solution of oct-1-yne (0.696 g.) and octadec-9-yne (1.685 g.), each in the presence of 25 c.c. of catalyst solution (Bourguel, *loc. cit.*), was complete in 140 min.; 302 and 320 c.c. respectively at $23^{\circ}/763\text{ mm.}$ were absorbed.

A gradual decrease in the rate of hydrogenation after the absorption of the first mol. occurred only in the case of octadec-9-yne.

(b) *Raney nickel.* The catalyst was transferred, when required, to a burette fitted with a 4-mm. cone tap and after settlement, a measured volume was discharged into the hydrogenation flask. Pure oct-1-yne (0.661 g.), octadec-3-yne (0.496 g.), and octadec-9-yne (1.246 g.), in ethyl acetate (25 c.c.), were hydrogenated in the presence of Raney nickel (0.5 c.c.). With oct-1-yne no break occurred in the rate of hydrogenation; with the two octadecynes marked changes in the rate occurred but only after approx. 1.5 mols. had been absorbed.

(c) *Raney iron*. This catalyst did not promote hydrogenation of octadec-9-yne at atmospheric pressure. Hydrogenation in an autoclave (at 110°/50 atm.) for 6 hr. gave octadecane, m. p. 27.5—28° (Found : C, 85.2; H, 14.76. Calc. for C₁₈H₃₈ : C, 85.0; H, 15.0%).

Quinoline-poisoned Palladium-Charcoal.—Octadec-2-yne (0.301 g.) was hydrogenated in ethyl acetate (10 c.c.) in the presence of 8% palladium-charcoal (0.02 g.) and quinoline (0.02 g.). No hydrogen was absorbed in 20 min. When more palladium-charcoal (0.03 g.) was added reduction started after 15 min.; after 2 hours one mol. had been absorbed.

Pyridine-poisoned Palladium-Calcium Carbonate.—Octadec-6-yne (0.395 g.), in ethyl acetate (15 c.c.), methanol (8 c.c.), and pyridine (0.05 g.), was hydrogenated with 5% palladium-calcium carbonate (0.1 g.). One mol. of hydrogen (38 c.c.) was absorbed in 18 min. A further 4 c.c. of hydrogen were absorbed during the next 30 min.

Non-pyrophoric Raney Nickel.—Aged Raney nickel which was no longer pyrophoric when exposed to air was sufficiently active to promote hydrogenation of alkylacetylenes. The rate of addition of the first mol. was still very rapid but with the dialkylacetylenes the second mol. was added at a much reduced rate (cf. Figure and Table 1). With octadec-1-yne there was little difference in the rates of addition of both the first and the second mol. of hydrogen. Hydrogenation curves for octadec-4-, -6-, -7-, and -8-yne have been excluded from the Figure for clarity.

TABLE I.

Octa- dec- <i>x</i> -yne, <i>x</i>	Wt. (g.)	Theor. H ₂ absorption (c.c./temp./mm.)	Change in rate at (c.c.)	Rates of hydrogenation (c.c./min.)	
				Initial	Secondary
1	0.326	64.1/21°/747	—	9.15	7.1
2	0.378	74.4/21°/746	40	10.0	1.5
3	0.412	81.4/21°/744	39.5	7.9	0.5
4	0.423	83.8/20°/738	39.0	6.5	0.2
5	0.413	80.3/17°/745	40.0	6.0	0.25
6	0.416	80.2/20°/759	40.0	5.0	0.5
7	0.392	75.9/19°/754	38.0	6.5	0.2
8	0.401	76.9/20°/763	39.0	7.0	0.4
9	0.354	68.5/20°/756	35.0	7.0	0.5

Preparation of the Nickel-Copper Catalyst.—Ethanol-moist pyrophoric Raney nickel (18 g.) was stirred in a solution of copper acetate (2 g.) in ethanol (120 c.c.) on the water-bath for 20 min. The catalyst was washed by decantation with ethanol (3 × 60—80 c.c.), then with ethyl acetate (3 × 60—80 c.c.). The catalyst was kept under ethyl acetate.

In the hydrogenation of octadec-4-yne, for example, the catalyst (0.5 c.c.), suspended in ethyl acetate (20 c.c.), was stirred under hydrogen until saturated, before the acetylene (0.286 g.) was added. The theoretical volume of hydrogen (28 c.c.) was absorbed in 3 min. and no further absorption occurred during the next 10 min. The other dialkylacetylenes behaved similarly. In the case of octadec-1-yne (0.323 g.) the first mol. (32 c.c.) was absorbed in 4 min. but the reduction did not then cease: the second mol. was absorbed, however, in 40 min. (cf. Figure).

The same catalyst could be used for the hydrogenation of a fresh specimen of the same acetylene or of another isomer with similar results, thus demonstrating that the activity of the catalyst was not impaired.

Selectivity of Nickel-Copper Catalyst.—The catalyst prepared from Raney nickel W.7 (Billica and Adkins, *Org. Synth.*, 29, 24) made 2 weeks previously was inactive towards octadec-4-yne. This acetylene (0.26 g. each time) was used to test three nickel-copper catalysts prepared from highly pyrophoric Raney nickel (6 g. of ethanol-moist) made 2 days previously (cf. Mazingo, *loc. cit.*) and treated as above, but as follows: (a) Copper acetate (0.7 g.). One mol. of hydrogen was absorbed in 3 min.; reduction went on slowly until the second mol. was absorbed. (b) Copper acetate (1.0 g.). After 1 mol. had been absorbed in 5 min. the reduction stopped for about 3 min., then went on until the second equiv. was absorbed in 25 min. This catalyst was used 4 days later: absorption of the first mol. required 8 min., and reduction stopped for 6 min., then went on until the second equiv. was absorbed in 68 min. (c) Copper acetate (1.4 g.). The first mol. was absorbed in 5 min. and the reaction stopped during the next 6 min. Hydrogenation with this catalyst 7 days later reached the half-way stage in 8 min. and no further absorption of hydrogen occurred in the following 10 min.

cis-Octadecenes.—Non-pyrophoric Raney nickel or nickel-copper catalyst was employed in the preparation of the *cis*-olefins. Hydrogenation was interrupted when 1 mol. of hydrogen was absorbed. The crude olefins were purified immediately and their physical constants determined. Approx. 8 g. of the parent hydrocarbon were hydrogenated in each case. With

octadec-9-yne, for example, the acetylene (7.833 g.), in ethyl acetate (25 c.c.), was stirred under hydrogen in the presence of non-pyrophoric Raney nickel (0.5 c.c.). The rate of hydrogen absorption was constant (7 c.c./min.), and, when the theoretical volume had been absorbed (1 mol., 761 c.c. at 20°/752 mm.), stirring was discontinued and the catalyst removed immediately filtered off. The solvent was removed under reduced pressure and the product distilled immediately (b. p. 164°/9 mm.). A solution of the crude olefin in acetone (180 c.c.) was allowed to crystallise at -50° in the low-temperature filtration apparatus (cf. *J.*, 1951, 893). The f. p. (-30.4°) of the purified olefin was unaltered on further low-temperature recrystallisation. *cis*-Octadec-9-yne (5.5 g., 70%) was obtained as a colourless, odourless oil (b. p. 162°/8.5 mm., n_D^{20} 1.4470, and d_4^{20} 0.7916) (Found: C, 85.8; H, 14.4. Calc. for $C_{18}H_{34}$: C, 85.7; H, 14.3%). Boeseken and Belinfante (*loc. cit.*) record b. p. 190°/15 mm., m. p. < -15°, n_D^{20} 1.4483, d_4^{20} 0.7968.

trans-Octadecenes.—Prolonged treatment of the octadecynes with sodium and liquid ammonia by the methods of Campbell and Eby and of Henne and Greenlee (*loc. cit.*) failed. When the reductions were carried out in an autoclave at room temperature, however, the reactions proceeded to completion and the olefins were obtained in good yield. *E.g.*, octadec-9-yne (8.0 g.) in anhydrous ether (150 c.c.) was added to a pre-cooled stainless-steel tilting autoclave (1 l.). A solution of sodium (2.0 g.) in liquid ammonia (200 c.c.) was added quickly and the autoclave sealed and was shaken for about 14 hr. The liquid ammonia was then allowed to evaporate through the needle-valve. Ice (100 g.) was added and the product extracted with ether. The olefin (7.6 g.; b. p. 178—180°/18 mm.) was crystallised twice from acetone (175 c.c.) at -35° before being fractionally distilled. *trans*-Octadec-9-ene (6.6 g., 82%) was obtained as a colourless, odourless oil, b. p. 180°/18 mm., n_D^{20} 1.4460, d_4^{20} 0.7852, f. p. 4.8° (Found: C, 85.5; H, 14.3%). Boeseken and Belinfante (*loc. cit.*) report m. p. 2.0°, n_D^{19} 1.4478, d_4^{19} 0.7917.

TABLE 2.

Octadecenes	B. p. (°/mm.)	F. p.	M. p.	n_D^{20}	n_D^{25}	d_4^{20}	d_4^{25}
<i>cis</i> -2-	173.5°/13	7.7°	7.6°	1.4470	1.4451	0.7922	0.7890
<i>trans</i> -2-	174.0/15	13.5	13.2	1.4470	1.4450	0.7938	0.7902
<i>cis</i> -3-	171.5/13	4.2	4.3	1.4447	1.4427	0.7902	0.7870
<i>trans</i> -3-	177.0/16	10.3	10.2	1.4447	1.4427	0.7876	0.7847
<i>cis</i> -4-	171.5/13	-15.8	-16.0	1.4468	1.4449	0.7910	0.7876
<i>trans</i> -4-	183.5/22	-0.6	-0.7	1.4460	1.4441	0.7880	0.7851
<i>cis</i> -5-	177.0/17	-25.2	-25.5	1.4460	1.4439	0.7898	0.7868
<i>cis</i> -6-	181.0/19	-19.2	-19.0	1.4468	1.4450	0.7905	0.7874
<i>trans</i> -6-	178.5/19	0.7	0.6	1.4461	1.4440	0.7894	0.7857
<i>cis</i> -7-	186.0/23	-33.5	-33.2	1.4469	1.4450	0.7911	0.7880
<i>trans</i> -7-	183.0/21	-3.8	-3.6	1.4460	1.4440	0.7877	0.7849
<i>cis</i> -8-	182.5/21	-19.5	-19.5	1.4465	1.4448	0.7924	0.7993
<i>cis</i> -9-	162.0/9	-30.4	-30.5	1.4470	1.4450	0.7916	0.7884
<i>trans</i> -9-	180.0/18	4.8	5.0	1.4461	1.4440	0.7883	0.7852

Infra-red Spectra of the Octadecenes.—The spectra were obtained by means of a single-beam infra-red spectrometer with a rock-salt prism. A 0.2-mm. rock-salt liquid cell was used. The specimen of octadec-1-ene was warmed to 20—25°.

The spectra of the 2-, 4-, and 6-*cis*- and -*trans*-isomers were also measured by Dr. F. B. Strauss (Dyson Perrins Laboratory, Oxford) with a Perkin Elmer double-beam instrument, in cells of 0.01 and 0.1 mm. length.

These measurements show that the bands near 968 cm^{-1} have extinction coefficient Ex/l of 2.5—2.7 in the *cis*- and 39 in the *trans*-series, where $Ex = \log I_0/I$ and l is in mm.

Although no attempt was made to observe the variation of the spectra during purification to constant f. p., we assume that the very small bands of the *cis*-forms are peculiar to these compounds and are not due to the presence of *trans*-isomers.

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