quired by the "C" structure is favored by the trivalent ions of smaller radius. The continuous transition from the fluorite structure to the "C" type M_2O_3 structure is possible because of the close similarities of the two structures.[14]

Although the previous studies indicated rather definite upper solubility limits of around 60–70 atomic per cent. of the trivalent oxides in the tetravalent oxides, only the $Ce^{IV}-Gd^{III}$ system shows an indication of a limit in the present work. Due to tendencies toward supersaturation in this case, however, it is possible to explore the entire range of solid solutions and it is difficult to determine just where the solubility limit is.

Another point of interest is the inability of praseodymium to be oxidized beyond the tetravalent state in the Pr–Y system. This is worth noting because it was their work on this system which Prandtl and Rieder[11] offered as proof of the ability of praseodymium to be oxidized to Pr^V. This claim was later refuted by Marsh[12] and by one of the present authors.[9] The rigorous oxidizing conditions used in the present work leave little doubt about the extreme reluctance of praseodymium to be oxidized beyond the tetravalent state. It was Prandtl and Rieder's belief that the presence of Y_2O_3 should promote the oxidation of praseodymium to the pentavalent state by forming the compound $YPrO_4$. However, the present study indicated a definite increase in the difficulty of oxidizing praseodymium with increasing yttrium content.

(14) L. Pauling and M. D. Shappell, Z. Krist., 75, 138 (1930).

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1,3,5,7,9-Decapentaene and 1,3,5,7,9,11,13-tetradecaheptaene

BY ALEXANDER D. MEBANE

In the series of unsubstituted linear polyenes, $H(CH=CH)_nH$, the first four members are known. By application of the sodamide–liquid ammonia coupling of allylic halides[1] to pentadienyl and heptatrienyl halides, what are undoubtedly the $n = 5$ and $n = 7$ members of the series have now been prepared. Decapentaene was obtained in 5% yield as cream-colored crystals melting at ca. 145°; tetradecaheptaene, in minute yield, only as an impure concentrate.

The ultraviolet absorption spectra (Fig. 1) continue the series defined by those of butadiene, hexatriene[2] and octatetraene.[3] The absorption maxima of the five compounds fall on a smooth curve.[4] The "fine structure" shows a consistent increase as the series is ascended, until in decapentaene and tetradecaheptaene the longest wave length absorp-

(1) M. S. Kharasch and E. Sternfeld, THIS JOURNAL, 61, 2318 (1939); M. S. Kharasch, W. Nudenberg and E. K. Fields, ibid., 66, 1276 (1944); D. R. Howton, J. Org. Chem., 14, 1 (1949).

(2) G. F. Woods and L. H. Schwartzman. THIS JOURNAL, 70, 3394 (1948); D. R. Howton, ref. 1.

(3) G. F. Woods and L. H. Schwartzman, ibid., 71, 1396 (1949).

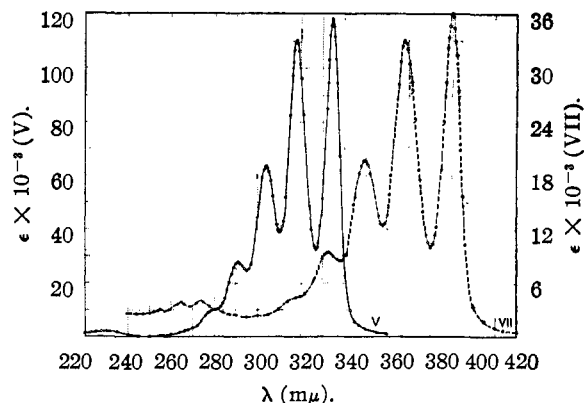(4) Empirical equations for this curve will be discussed in a subsequent communication.

Fig. 1.—Ultraviolet absorption spectra, in "isoöctane," of: V, crystalline all-trans-decapentaene; VII, tetradecaheptaene concentrate.

tion peak has become the most intense one, and the spectrum is clearly approaching, as a limit, a series of equally-spaced discrete absorption "lines" of diminishing intensity. It may be recalled that the absorption spectra of the α,ω-diphenylpolyenes undergo a similar evolution as the series is ascended.[5] The separation between the individual absorption peaks, which in both series ranges from about 1350 to 1550 cm.$^{-1}$, is customarily identified with the stretching frequency of the double bond.

The infrared spectrum of decapentaene (Fig. 2) closely resembles those of hexatriene[2] and octatetraene,[3] except in the extreme lowness of the $7.1\text{-}\mu$ peak and the differing appearance of the $6.1\text{-}6.6\text{-}\mu$ system.[6] The entire absence of the infrared cis-peak (14.0 ± 0.5 μ) shows that the all-trans stereoisomer was the one isolated in crystalline form. This conclusion was confirmed by the results of catalytic iodine treatment.
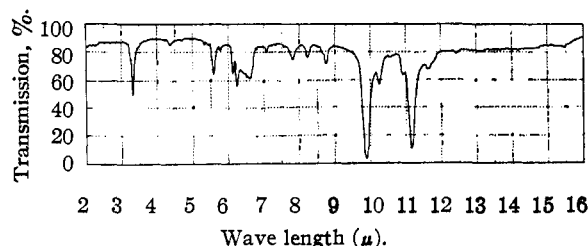

Fig. 2.—Infrared spectrum of all-trans-decapentaene (1.7% solutions, 0.2-mm. cell).

In the chromatographic forerun of decapentaene, a cis-isomer or isomers (not obtained in solid condition) appeared to be present.

The tetradecaheptaene was obviously not sterically homogeneous, since the absorption maxima at the beginning and end of the chromatographic fraction differed by more than 2 mμ. However, the highest λ_{max} obtained probably corresponds

(5) K. W. Hausser, R. Kuhn and A. Smakula, Z. physik. Chem., 29B, 384 (1935). In this series the first peak is just reaching equality with the second by $n = 7$, the highest member studied. (The $n = 8, n = 11$ and $n = 15$ members of the series have been reported by Kuhn and his co-workers, but their absorption curves have apparently not been published.)

(6) Since the solutions measured had been in transit at ordinary temperatures for about 24 hours, it is probable that some polymer was present at the time the spectrum was taken.

to the all-*trans* isomer, since iodine equilibration gave an intermediate spectrum.

Neither compound gives any appreciable color with antimony trichloride in chloroform; it appears therefore that the Carr–Price reaction requires the participation of alkyl substituents.

Experimental

2,4-Pentadien-1-ol.—Vinylacrylic acid[7] (50 g.) was reduced with 18.7 g. of lithium aluminum hydride. The reaction and work-up were carried out as described below for methyl heptatrienoate, except that the temperature of reduction was −25°. The dried ethereal extracts were fractionated through a 20-cm. vacuum-jacketed Vigreux column. The fraction coming over at 70–72.5° (31 mm.) weighed 14.9 g. (35% yield), n^{22}D 1.4808, λ_{max} 223.7 mμ (alc.), ϵ 23,700.[8] This pentadienol was impure, analyzing 1.4% low in carbon; but the impurity (possibly water) was removed in the next step.

5-Chloro-1,3-pentadiene.—Crude pentadienol (12.6 g., 0.15 mole) was shaken for a few minutes with 100 ml. of cold, concentrated hydrochloric acid, and the mixture was extracted with petroleum ether. The extract was washed with hydrochloric acid, dried over anhydrous magnesium sulfate, and fractionated as above, in the presence of a little hydroquinone. The only significant fraction (6.1 g., 40% yield) came over at 65–67° (130 mm.), n^{24}D 1.4923[9]; d^{24} 0.946, λ_{max} 226.5 mμ (isoöctane), ϵ 25,300; sharp odor.

Anal. Calcd. for C$_5$H$_7$Cl: C, 58.54; H, 6.88; Cl, 34.57; MR_D, 27.9. Found: C, 58.74; H, 6.87; Cl, 34.18; MR_D, 31.5.

1,3,5,7,9-Decapentaene.—Sodamide (2.0 g., 0.05 mole) was added portionwise, over a 10-minute period, to 5.1 g. (0.05 mole) of chloropentadiene dissolved in 10 ml. of ether and 50 ml. of liquid ammonia. After a further 10 minutes, 20 ml. of hexane was added, and the ammonia was evaporated by gentle warming. The reaction mixture was drowned in ice-water, and the ether-hexane extract (50 ml.) dried over anhydrous potassium carbonate and poured onto an adsorption column (4 × 30 cm.) of Alcoa F-20 activated alumina. Development with 10% ether-hexane gave a single zone, white-fluorescent under a G.E. Purple-X bulb, which was eluted with increasing proportions (finally 40%) of ether in hexane. The eluate containing the first eighth of the zone was rejected; the remainder (400 ml.) was concentrated from lukewarm water under partial vacuum in the presence of a trace of hydroquinone, finally admitting nitrogen. The concentrate (oil and pale-yellowish plates) was washed by decantation with a few ml. of cold petroleum ether, again evacuated, and then taken up in 80 ml. of lukewarm 95% ethanol containing a little hydroquinone, and filtered. After 18 hours at −5° under nitrogen, the precipitated crystals (minute flat needles, of irregular form, cream-colored in mass) were filtered off with cold-alcohol rinses and vacuum-dried, finally admitting nitrogen; yield 160 mg. (4.8%). The rather spicy-sweet, allylic odor was strong and persistent.

(7) E. P. Kohler and F. R. Butler, THIS JOURNAL, **48**, 1041 (1926); H. Burton and C. K. Ingold, *J. Chem. Soc.*, 2028 (1929). In this preparation, it proved to be best to isolate the crude product by a very rapid vacuum distillation (b.p. 82° at 4 mm.); a single crystallization from 1.7 parts of hexane then furnished large, transparent prisms of m.p. 71–73°, in 25% yield.

(8) L. Crombie, S. H. Harper and D. Thompson, *ibid.*, 2906 (1951), obtained by this reaction an 18% yield of pentadienol of n^{20}D 1.4838. By substituting pentadienal for pentadienoic acid as starting material, they obtained a 77% yield of pure *trans*-pentadienol, n^{20}D 1.4890, in good agreement with n^{25}D 1.4857 by Meerwein-Ponndorf reduction of pentadienal (G. F. Woods and H. F. Lederle. THIS JOURNAL, **73**, 2245 (1951)) and n^{18}D 1.4902 by rearrangement of divinylcarbinol (E. R. H. Jones, J. T. McCombie and B. C. L. Weedon, *J. Chem. Soc.*, **84** (1945)). The latter authors found λ_{max} 223 mμ (alc.), ϵ 25,000; Crombie *et al.* report λ_{max} 226 mμ, ϵ 25,200.

(9) G. F. Woods and H. F. Lederle (ref. 8) found n^{25}D ranging from 1.4696 to 1.4919 for material of correct boiling point and analysis prepared by means of thionyl chloride. Although this was obtained from *trans*-pentadienol, it appears to have been a *cis-trans* mixture. For material obtained, in 92% yield, by means of phosphorus trichloride, Crombie *et al.* (ref. 8) found "n^{20}D 1.492–1.493," only slightly lower than the n^{20}D 1.494 of the present product, which should be the nearly-pure *trans*-isomer.

Anal. Calcd. for C$_{10}$H$_{12}$: C, 90.85; H, 9.15. Found: C, 90.69; H, 9.19.

The m.p. could not be determined in the usual way, because of rapid polymerization when warmed. When a crystal was slipped under the cover-glass of a preheated Fisher–Johns block, the lowest temperature at which fusion was observed before polymerization supervened was 145 ± 2°.

Antimony trichloride in chloroform gave no color. (In contrast, decatetraene gives a raspberry-red.[10])

The absorption spectrum in 2,2,4-trimethylpentane ("isoöctane") exhibited maxima at 230, 280 (infl.), 290.8, 303.9, 318.0 and 334.3 mμ; $\epsilon_{max}^{334.3}$ 118,000 (Fig. 1). In 95% ethanol, the spectrum was identical in shape, with λ_{max} 335.3 mμ.

The infrared spectrum was determined by Samuel P. Sadtler & Son, Inc., of Philadelphia. A 1.7% solution in carbon tetrachloride was used from 2 to 7.5 μ, a 1.7% solution in carbon disulfide from 7.5 to 16 μ. Since these solutions spent about 24 hours in transit before examination, the curves obtained are probably not entirely representative of the freshly-made solutions.

The isoöctane spectroscopic solution, after five days at room temperature under nitrogen, showed practically no alteration in the ultraviolet absorption curve. Iodine, 15% by weight of the decapentaene, was then added. Eighty minutes later, all of the four main $\lambda\lambda_{max}$ had decreased by 0.3–0.4 mμ, $\epsilon_{max}^{334.0}$ had dropped to 106,000 (although $\epsilon^{290.4}$ remained unchanged), and the *cis*-peak, now at 235 mμ, had nearly tripled in height. These changes are similar to those observed when all-*trans*-phytofluene (a substituted pentaene) is stereo-equilibrated with iodine.[11]

The first eluates from the chromatogram showed (in addition to a major proportion of diene, λ_{max} 226) a three-peaked absorption curve of much less conspicuous fine structure, $\lambda\lambda_{max}$ 303.3–*316.8*–332.6 mμ (isoöctane), the long wave length peak being the lowest of the triplet. An excess of iodine (barely-visible pink tint) was added to this solution. Twenty minutes later, all of the $\lambda\lambda_{max}$ had increased by 0.6–1.0 mμ, and the shape of the spectrum much more nearly resembled that of all-*trans*-decapentaene, the longest wave length peak (now at 333.6 mμ) having risen strikingly while the third peak dropped. Evidently a *cis* form of decapentaene had been present initially.

Decapentaene was also obtainable by sodamide coupling of *bromo*pentadiene.[12] The spectrum of the product was the same as that obtained from the chloride, and the yield was of the same order.

As would be expected, decapentaene is a delicate substance, very prone to polymerize during handling, although it can be kept for long periods at −40° under nitrogen. On prolonged exposure to air, it forms peroxides that puff vigorously on the hot block.

2,4,6-Heptatrien-1-ol.—Methyl 2,4,6-heptatrienoate[13] (50.9 g., 0.365 mole) in 150 ml. of dry ether was added dropwise during one-half hour to a stirred suspension of 10.3 g. (0.27 mole, 50% excess) of commercial lithium aluminum hydride in 200 ml. of dry ether, maintaining the temperature at −45° with a Dry Ice-bath. After a further half-hour stirring, during which the temperature was permitted to reach 10°, the mixture was treated at 0–10° with 20 ml. of ethyl acetate followed by 150 ml. of 20% sulfuric acid. The aqueous phase was separated, diluted with water, and twice ether-extracted; the combined ethereal extracts were bicarbonate-washed, dried over magnesium sulfate, and rapidly distilled at 0.005 mm. through a 30-cm. Vigreux column. Two arbitrary fractions were collected: bulk, 43–"58°" (superheated), n^{23}D 1.5540, m.p. 11–14°, 33.1 g.; tails: "50"–43°, n^{23}D 1.5576, m.p. 14–16°, 1.4 g. Both

(10) R. Kuhn, *Angew. Chem.*, **50**, 705 (1937).

(11) F. J. Petracek and L. Zechmeister, THIS JOURNAL, **74**, 184 (1952).

(12) This was obtained (in only 3% yield) by Ziegler bromination of piperylene: b.p. 65–68° (58 mm.), n^{24}D 1.5308, lachrymatory. *Anal.* Calcd. for C$_5$H$_7$Br: Br, 54.36. Found: Br, 52.7.

(13) G. H. Kalb and J. C. Sauer, U. S. Patent 2,540,736 (to E. I. du Pont de Nemours & Co.), 1951. Dr. Kalb very kindly furnished us with a generous sample of this compound, which has λ_{max} 285.5 mμ in *n*-heptane, ϵ 28,400. Its lithium aluminum hydride reduction had previously been carried out in the du Pont laboratories (personal communication from Dr. Kalb; T. L. Cairns, *et al.*, Abstracts of Papers, 120th Meeting of the A.C.S., 1951, p. 14-M).

fractions were pale greenish-yellow and had a sweet, oily, alcoholic odor; total yield 85.5%.

Anal. Calcd. for $C_7H_{10}O$: C, 76.30; H, 9.15. Found (main fraction): C, 76.40; H, 9.27.

The absorption spectrum of the purer "tail" fraction consisted of a sharp triplet system: $\lambda\lambda_{max}$ 252, 261.2, 271.7 mμ in 95% ethanol, ϵ_{max} 26,500, 34,300, 25,800. No diene was present. The bulk fraction gave a curve of identical shape, but lower ϵ_{max} (30,600).

This preparation was probably sterically heterogeneous (variation in ϵ) and in any case was not the pure *trans–trans* isomer, for which a melting point of 79–80° has been reported.[14]

1-Bromo-2,4,6-heptatriene.—With stirring and cooling, 3.9 ml. (0.041 mole) of phosphorus tribromide was dropped into a mixture of 11 g. (0.1 mole) of heptatrienol with 2.7 ml. (0.035 mole) of dry pyridine. The viscous mixture, intermittently stirred, was kept in a −10° bath for 30 min., at room temperature for 30 min., and in a 45° bath for 15 min.; then poured into 30 ml. of ice and water and thrice extracted with ether–petroleum ether. (Considerable tar remained undissolved.) The water-washed extract, dried over magnesium sulfate, was distilled through a 15-cm. center-rod column, giving a single fraction, b.p. 48–49° (0.8 mm.), n^{25}D 1.5983, d^{25} 1.295, m.p. 2–6.2°. The light-yellow, fragrant, rather lachrymatory liquid weighed 8.2 g. (51% yield). Stored at −70° under nitrogen, it remained unchanged for nearly a year.

Anal. Calcd. for C_7H_9Br: C, 48.58; H, 5.24; Br, 46.18; MRD, 39.0. Found: C, 49.04; H, 5.19; Br, 46.15, 45.75; MRD, 45.7.

The absorption spectrum consisted of a smooth peak entirely devoid of fine structure; λ_{max} 272 mμ (isoöctane), ϵ 31,200.

The steric configuration of this bromide would be expected to be the same as that of the starting material, or approximately so.

1,3,5,7,9,11,13-Tetradecaheptaene.—When bromoheptatriene was coupled with sodamide as previously described, the expected heptaene peaks appeared, but only a minute trace of the compound was formed. A better yield (though still well below 1%) was obtained by quickly adding the bromide (2.2 g., in 10 ml. of ether) to a liquid ammonia solution of slightly less than one equivalent of potassamide, prepared *in situ* from potassium. A transient dark-violet color was observed. The final orange extract, in 50% methylene dichloride–hexane, was dried, filtered, and immediately chromatographed on a 3 × 25-cm. alumina column, precooled to 5°, developing with the same solvent. The main, red-fluorescent zone required 750 ml. of solvent for substantially complete elution. It was sterically inhomogeneous, the first λ_{max} (isoöctane) ranging from 388.1 mμ early in the fraction to 390.4 mμ at its end. This eluate was considerably richer in a triene, λ_{max} 264 mμ, than in the desired heptaene. The first two-thirds (A) and the final third (B) were separately vacuum-concentrated to dryness with a trace of hydroquinone; nitrogen was admitted, and 10 ml. of 10% ether–alcohol was added to dissolve the non-heptaene constituents. After 12 hours at −40°, filtration with cold alcohol rinses gave 7.5 mg. (vacuum-dry weight) of minute golden-yellow flakes from (A) and 2 mg. from (B). The material from (B) was dissolved in a little ether (not all was soluble) and diluted with isoöctane. The resulting absorption spectrum (Fig. 1) showed an ϵ_{max} of only 36,000; the compound was therefore still very impure. The 255-265-275 triplet system in this spectrum is no doubt attributable in large measure to persisting triene contamination rather than to the true *cis*-peak.

In isoöctane, the absorption peaks appeared at 332.3, 349.7, 367.9 and 390.0 mμ. In 95% ethanol, the long wave length peak occurred at 391.4 mμ; the shape was identical. The solid from fraction (A) gave a curve of substantially identical shape, though much higher at 265 mμ, with the $\lambda\lambda_{max}$ occurring at 331.1, 348.4, 366.4 and 388.5 mμ (isoöctane). A catalytic amount of iodine was added, and the solution was illuminated with a 100-watt bulb. After 80 minutes, all of the $\lambda\lambda_{max}$ had increased by 1.0 mμ; and al-

though the height of the main absorption peaks had scarcely altered, that of the 265-mμ peak had decreased by 50%. These changes indicate the presence of a *cis* isomer (or isomers) in fraction (A).

Tetradecaheptaene had no detectable odor. The Carr-Price reagent gave a faint greenish-blue, which was stronger in the specimens richer in the triene contaminant. (Tetradecahexaene gives an indigo-blue.[10])

Apparatus.—The spectrophotometer used was a Beckman model DU, whose wave length scale, above 250 mμ, had been calibrated to the nearest 0.05 mμ against a mercury lamp.

Acknowledgment.—For the analyses, I am indebted to Mr. Joseph Grodsky of this Laboratory.

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Diaryloxyalkane Derivatives. Some Miscellaneous Diphenoxypropanes[1]

BY FREEMAN H. McMILLAN[2]

As part of a program leading to the preparation of some moderately high molecular weight compounds several new derivatives of 1,3-diphenoxypropane have been prepared.

It has been found that by substituting ethylene glycol for ethanol as the solvent for the reaction between trimethylene bromide and the potassium salt of a phenol and heating to 130° the time required for the reaction is materially shortened. For example, potassium p-nitrophenoxide was condensed with trimethylene bromide in ethylene glycol at 130° for one hour giving a 61% yield of p,p'-dinitro-1,3-diphenoxypropane[3] whereas the same reaction in refluxing ethanol for three hours gave only a 22% yield. An additional advantage of this procedure is that even the more difficultly soluble potassium salts, *e.g.*, potassium p-nitrophenoxide, are more soluble in this solvent than in ethanol. Either the anhydrous potassium salt of the phenol may be used or the theoretical amount of 85% potassium hydroxide may be dissolved in the ethylene glycol with the phenol and the trimethylene bromide.

p,p'-Dinitro-1,3-diphenoxypropane was reduced with Raney nickel in quantitative yield to the corresponding diamine. This in turn was converted to the N,N'-dibenzyl derivative by reduction with Raney nickel in the presence of benzaldehyde. The intermediate Schiff base was also isolated and characterized. Treatment of p,p'-diamino-1,3-diphenoxypropane with hydrogen chloride and phosgene in refluxing toluene gave 1,3-diphenoxypropane p,p'-diisocyanate.

Two carboxylic acid derivatives of 1,3-diphenoxypropane were prepared. Ethyl p-hydroxybenzoate was condensed with trimethylene bromide in a solution of potassium hydroxide in ethylene glycol. The resulting diester was hydrolyzed to 1,3-diphenoxypropane-p,p'-dicarboxylic acid

(14) I. N. Nazarov and L. B. Fisher, *Zhur. Obshchei Khim.*, **20**, 1107 (1950) [*C. A.*, **44**, 9460 (1950)]. These authors prepared heptatrienol by an allylic rearrangement, which by analogy with pentadienol (I. M. Heilbron, *et al.*, reference 8) would undoubtedly furnish a *trans–trans* product.

(1) For previous papers *cf.* J. A. King, THIS JOURNAL, **66**, 2076 (1944), and J. A. King and F. H. McMillan, *ibid.*, **67**, 336 (1945).

(2) Warner Institute for Therapeutic Research, 113 West 18th Street, New York 11, N. Y.

(3) J. A. Goodson, *et al.*, *Brit. J. Pharmacol.*, **3**, 62 (1948), report m.p. 132°.