357. *Cyclic Polymerisation of Acetylene. Examination of the $C_{10}H_{10}$ Fraction.*

By D. S. WITHEY.

The presence of 1-phenylbuta-1 : 3-diene and vinyl*cyclo*octatetraene in the $C_{10}H_{10}$ fraction formed during the preparation of *cyclo*octatetraene from acetylene (Craig and Larrabee, *J. Amer. Chem. Soc.*, 1951, **73**, 1191; Cope and Fenton, *ibid.*, p. 1195) has been confirmed. Reactions of vinyl*cyclo*octatetraene with bromine, with hydrogen, and with maleic anhydride are described and discussed. Some halogen derivatives of 1-phenylbuta-1 : 3-diene are described.

REPPE, SCHLICHTING, and MEISTER (*Annalen*, 1948, **560**, 93) isolated two hydrocarbons $C_{10}H_{10}$ from by-products obtained during the polymerisation of acetylene to *cyclo*octatetraene, and considered these to be isomeric *cyclo*decapentaenes. Craig and Larrabee (*J. Amer. Chem. Soc.*, 1951, **73**, 1191) and Cope and Fenton (*ibid.*, p. 1195) have shown that the $C_{10}H_{10}$ fraction is a mixture of *cis*-1-phenylbuta-1 : 3-diene and vinyl*cyclo*octatetraene. Our work concerned with the preparation and identification of the $C_{10}H_{10}$ fraction was almost complete when the above results became available. Some new results are now reported.

Treatment of the fraction with two mols. of bromine gave the two known stereoisomers of 1 : 2 : 3 : 4-tetrabromo-1-phenylbutane and a third unidentified bromide $C_{10}H_{10}Br_4$. As widely differing melting points are quoted for the tetrabromides of phenylbutadiene, these were prepared from *trans*-1-phenylbuta-1 : 3-diene and purified by fractional crystallisation.

trans-1-Phenylbuta-1 : 3-diene was also treated in turn with hydrogen chloride and bromine, to form what is thought to be 1 : 2-dibromo-3-chloro-1-phenylbutane.

In the presence of four mols. of bromine, vinyl*cyclo*octatetraene rapidly formed a tetrabromide which then added one further mol. of bromine at a slower rate. At this stage, reaction had apparently ceased and the product was shown to be a hexabromide. When 12 mols. of bromine were used, a break in the rate of addition was still evident at the tetrabromide stage but in this case a total of four mols. of bromine was added. The product was an octabromide, which resisted further addition. The bromides of *cyclo*octatetraene are derivatives of *bicyclo*[4 : 2 : 0]octane, and by analogy the new bromides may be derivatives of an ethyl*bicyclo*[4 : 2 : 0]octane; the resistance of the octabromide supports this theory.

Reppe, Schlichting, and Meister (*loc. cit.*) treated their $C_{10}H_{10}$ hydrocarbons with maleic anhydride and in both cases obtained the adduct $C_{10}H_{10},3C_4H_2O_3$ as the main crystalline product whilst the adduct $C_{10}H_{10},2C_4H_2O_3$ crystallised from the mother-liquors (in the case of the orange-yellow isomer) in smaller amounts. We find that under similar conditions vinyl*cyclo*octatetraene gives the adduct $C_{10}H_{10},2C_4H_2O_3$. None of the other adduct has yet been isolated from the reaction product although its formation seems reasonable.

Hydrogenation of vinyl*cyclo*octatetraene in methanol or acetic acid over a palladium catalyst indicated the presence of five double bonds. In both solvents the rate of hydrogenation decreased considerably after saturation of the fourth double bond, at which stage the product was presumably 1-ethyl*cyclo*octene which has been identified in the products of incomplete hydrogenation of the $C_{10}H_{10}$ fraction by Craig and Larrabee (*loc. cit.*).

EXPERIMENTAL

M. p.s are uncorrected.

The $C_{10}H_{10}$ fraction was isolated by fractionation of the products obtained by polymerisation of acetylene in the presence of tetrahydrofuran, nickel cyanide, and calcium carbide. It formed an orange-yellow, mobile liquid with a wide boiling range (47·5°/3·8 mm. to 48·5°/2 mm.) and n_D^{20} 1·5780.

Bromination of the $C_{10}H_{10}$ *Fraction.*—Bromine (32 g.) in chloroform (35 c.c.) was added during 1¼ hours to a stirred solution of the $C_{10}H_{10}$ fraction (13 g.) in chloroform (35 c.c.)

at $-50°$ to $-55°$. After the mixture had been kept at room temperature overnight, no free bromine remained, and by washing with water and removal of the solvent under reduced pressure the product was obtained as a dark green syrup (45·8 g.). Treatment of this with cold ether gave two crops of colourless crystals.

The first crop (3·5 g.; m. p. 122—133°), after five crystallisations from ethanol, yielded 1 : 2 : 3 : 4-tetrabromo-1-phenylbutane as colourless rhombs, m. p. 151—152° (Found : C, 26·7; H, 2·2; Br, 71·2. Calc. for $C_{10}H_{10}Br_4$: C, 26·7; H, 2·2; Br, 71·1%). The mixed m. p. with an authentic sample (see below) was 151—152°.

From the mother-liquors, a small quantity of an unidentified *tetrabromide*, $C_{10}H_{10}Br_4$, m. p. 91° (unchanged by crystallisations from ligroin, ethanol, or acetic acid), was obtained as fine colourless needles (Found : C, 26·6; H, 2·2. $C_{10}H_{10}Br_4$ requires C, 26·7; H, 2·2%).

The second crop (7·8 g.; m. p. 58—63°) was recrystallised from ethanol and then from light petroleum (b. p. 60—80°), to give colourless needles, m. p. 74—75°, which did not depress the m. p. of an authentic sample of the lower-melting stereoisomer of 1 : 2 : 3 : 4-tetrabromo-1-phenylbutane (Found : C, 26·7; H, 2·4; Br, 71·4%).

Preparation of trans-1-*Phenylbuta*-1 : 3-*diene and Some of its Halides.*—The hydrocarbon was prepared in 41% yield by Klages's method (*Ber.*, 1904, **37**, 2309), which gives the *trans*-form (Grummitt and Christoph, *J. Amer. Chem. Soc.*, 1951, **73**, 3479). It formed a colourless liquid, b. p. 41—42°/0·8 mm., n_D^{16} 1·6098.

The tetrabromides were prepared by treating it (4 g.) with bromine (9·9 g.) in carbon tetrachloride at 0—10°. Formation of the dibromide took place rapidly, but absorption of the second molar equivalent of bromine required several hours. After a week, a crop of colourless crystals had separated (*A*; 2·5 g.; m. p. 139—140°). The mother-liquor deposited a further quantity of colourless crystals (*B*; 11·2 g.; m. p. 64—68°). Fractional crystallisation of *A* gave colourless rhombs, m. p. 151·5—152° (from ethanol–benzene), and of *B* gave colourless needles, m. p. 75° (from ligroin). M. p.s recorded for these stereoisomers are : 142° (Liebermann and Riiber, *Ber.*, 1900, **33**, 2400), 146° (Klages, *Ber.*, 1902, **35**, 2651), 76° and 151° (Riiber, *Ber.*, 1903, **36**, 1406), 146° (Heide, *Ber.*, 1904, **37**, 2101), 146—147·5° and 147·2—147·7° (Grummitt and Christoph, *loc. cit.*).

An ethereal solution of *trans*-3-chloro-1-phenylbut-1-ene was prepared from *trans*-1-phenylbuta-1 : 3-diene (10 g.) in ether (30 c.c.) by passing in dry hydrogen chloride at $-10°$ until no more was absorbed (cf. Muskat and Huggins, *J. Amer. Chem. Soc.*, 1934, **56**, 1240). The resulting straw-coloured solution was washed with water, dried (Na_2SO_4), and treated with a solution of bromine (12·3 g.) in carbon tetrachloride. Next day colourless needles (4·7 g.), m. p. 136—140°, were separated. By recrystallisation in turn from ethanol, light petroleum, and benzene–light petroleum, (?) 1 : 2-*dibromo*-3-*chloro*-1-*phenylbutane* was obtained as colourless needles, m. p. 150—151° (Found : C, 36·4; H, 3·3%; 10·655 mg. gave 16·926 mg. of silver halide. $C_{10}H_{11}Br_2Cl$ requires C, 36·8; H, 3·4%; 16·93 mg. of silver halide).

*Vinyl*cyclo*octatetraene.*—The $C_{10}H_{10}$ fraction (79 g.) was dissolved in an equal volume of light petroleum (b. p. 40—60°), and the solution cooled to about $-80°$ for 12 hours. A bright yellow crystalline solid separated and, after separation by decantation, was again crystallised as above. The recrystallised material was distilled under reduced pressure. After a forerun (0·5 g.; n_D^{20} 1·5716) the main fraction, b. p. 31·5°/0·7 mm., m. p. $-20°$ to $-19°$, n_D^{20} 1·5724, was collected. One more low-temperature crystallisation from light petroleum gave vinyl*cyclo*octatetraene (32 g.; 40% of starting material), b. p. 27°/0·5 mm., m. p. $-19°$ to $-18°$, n_D^{20} 1·5723, d_4^{20} 0·9325 (Found : C, 92·2; H, 7·8. Calc. for $C_{10}H_{10}$: C, 92·3; H, 7·7%).

It was unchanged on storage in nitrogen in the dark for several months, but in light and air rapidly afforded a pale yellow solid.

*Bromination of Vinyl*cyclo*octatetraene.*—(*a*) A solution of vinyl*cyclo*octatetraene (1·622 g.) in carbon tetrachloride (total volume 25 c.c.) was added rapidly with agitation to a solution of bromine in carbon tetrachloride (175 c.c.) which contained sufficient bromine to saturate four double bonds of the sample. The mixture was kept agitated at room temperature in artificial light and 5-c.c. aliquots were periodically treated with excess of potassium iodide solution, and the liberated iodine was determined by titration against 0·1N-sodium thiosulphate. It was thus found that, under the conditions employed, two double bonds were saturated almost instantly, whereas the third required 25 minutes. Very little further bromination was detected after 12 hours. After removal of excess of bromine and evaporation of the solvent, the *hexabromide* was obtained as a colourless gum which crystallised when treated with methanol. Recrystallisation from ethanol gave laths, m .p. 122—123° (Found : C, 19·9; H, 1·7; Br, 78·7. $C_{10}H_{10}Br_6$ requires C, 19·7; H, 1·6; Br, 78·7%.)

(*b*) Bromine (96 g.) in carbon tetrachloride (90 c.c. of solution) was delivered into a solution of vinyl*cyclo*octatetraene (6·5 g.) in carbon tetrachloride (50 c.c.) at −10° to 0°. Two molar equivalents of bromine were decolorised rapidly, after which the reaction slowed down and the remaining bromine was added all at once. The reaction mixture was diluted to 250 c.c. and kept at room temperature in the dark. After 20 and 40 hours, the unused bromine was determined by treatment of 2-c.c. aliquots with potassium iodide and titration against standard sodium thiosulphate. Utilization of bromine was found to be 31·5 and 30·8 g. respectively (Calc. for $C_{10}H_{10}Br_8$: 32 g.). After removal of excess of bromine by sodium hydroxide solution and water, the solution was dried and evaporated in a vacuum, leaving a colourless gum (34·9 g., 90·7%) which crystallised when treated with ether. Successive crystallisations of this from benzene and finally from acetic acid gave an *octabromide* as colourless rhombs, m. p. 176—177° (decomp.) (Found : C, 15·8; H, 1·4; Br, 83·6. $C_{10}H_{10}Br_8$ requires C, 15·6; H, 1·3; Br, 83·1%).

*Maleic Anhydride Adduct of Vinyl*cyclo*octatetraene*.—Maleic anhydride (6 g.) and vinyl*cyclo*octatetraene (2·6 g.) were heated together in an oil-bath at 140°; a vigorous reaction set in which caused the mixture to boil for some 30 seconds. Heating was then continued for an hour, the bath-temperature being slowly raised to 160°. After cooling, the colourless crystals which had first formed after 50 minutes' heating, were collected and washed with dry acetone [yield 1·5 g.; m. p. 281—288° (decomp.)]. After several recrystallisations from acetic acid, the pure adduct was obtained as small colourless parallelograms, m. p. 303—305° (decomp.) (after rapid heating to 260°) (Found : C, 66·4; H, 4·4%; equiv., 81·4. Calc. for $C_{10}H_{10},2C_4H_2O_3$: C, 66·3; H, 4·3%; equiv., 81·5).

*Hydrogenation of Vinyl*cyclo*octatetraene*.—When vinyl*cyclo*octatetraene (2·00 g.), 5% palladium–barium sulphate (0·7 g.), and methanol or acetic acid (20 c.c.) were shaken in an atmosphere of hydrogen, absorption of hydrogen corresponding to four double bonds occurred during 2 hours and a slower absorption corresponding to the fifth double bond during the following 4 hours, after which reaction ceased.

I am indebted to Mr. H. Wright-Hodgson for the microanalyses, Dr. W. O. Jones for helpful advice, and the Directors of the British Oxygen Company Ltd. for the supply of raw material and laboratory facilities.

British Oxygen Company, Ltd.,
Lombard Road, London, S.W.19.

[*Received, October 29th,* 1951.]