The Synthesis of 1,4-Diphenyl-1,4-di-*p*-tolylbutatriene and 1,4-Diphenyl-1,4-di-*p*-chlorophenylbutatriene.(1)

By Osamu SIMAMURA.

(Received May 27, 1941.)

Kuhn and Wallenfels(2) synthesized tetraphenylbutatriene, which had been obtained by Brand(3) and by Salkind and Kruglow,(4) by treating tetraphenylbutynediol with phosphorus diiodide and accomplished the preparation of tetraarylhexapentaenes from hexaarylhexadiyne-(2, 4)-diols by the same procedure and later by an improved method of reducing with chromous chloride in the presence of hydrogen chloride.(5) The chemistry of these compounds, cumulenes, as Kuhn and Wallenfels call them, is of interest not only because of chemical behaviours which a system of cumulated double bonds diplays. Extending van't Hoff's model which pictures double-bonded carbon atoms by two tetrahedra sharing one edge in common, Kuhn and Wallenfels suggested that asymmetrically substituted cumulenes with an odd number of double bonds such as $R_1R_2C=C=C=CR_1R_2$ should exist in cis and trans isomerides and those with an even number of double bonds should be resolved into optical antipodes. Although the syntheses of allene derivatives in enantiomorphic isomerides(6) were verifications of van't Hoff's prediction, it may be questioned whether the model would be applicable as well to a system of many cumulated double bonds, in view of the electronic concept of valency and the mesomerism in a system of conjugated multiple bonds. A carbon atom which is bound to two neighbouring atoms by two double bonds is of the acetylene type in that it has as atomic orbitals involved in bond formation two derived from *sp*-hybridization(7) lying in a straight line extending in the opposite directions and two $p\pi$ orbitals perpendicular to the former two, the former entering into σ bonds with σ orbitals and the latter into π bonds with $p\pi$ orbitals of the two adjacent atoms. Thus the molecular structure of cumulenes may be assumed to be such that the double-bonded carbon atoms lie in a single straight line just as is the case with carbon suboxide.(8) Then, the question is to what extent the energy of the molecule depends upon the relative orientation of the substituents at one end with respect to those at the other end of the carbon atom chain. In the ethylenic linkage the single π bond makes the energy susceptible to the perturbation by the substituent groups yielding cis and trans positions of the substituents

---

(1) Presented on April 4, 1941, at the 63rd Annual Meeting of the Chemical Society of Japan in Tokyo.

(2) R. Kuhn and K. Wallenfels, *Ber.*, **71** (1938), 783.

(3) K. Brand, *ibid.*, **54** (1921), 1987.

(4) J. Salkind and K. Kruglow, *ibid.*, **61** (1928), 2306.

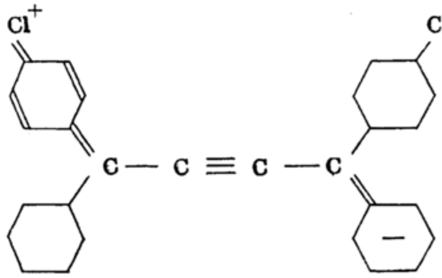
(5) R. Kuhn and K. Wallenfels, *ibid.*, **71** (1938), 1510.

(6) P. Maitland and W. H. Mills, *Nature*, **135**, (1935) 994; *J. Chem. Soc.*, **1936**, 987; E. P. Kohler, J. T. Walker, and M. Tischler, *J. Am. Chem. Soc.*, **57** (1935), 1743.

(7) Cf. J. H. Van Vleck and A. Sherman, *Rev. Modern Phys.*, **7** (1935), 205.

(8) L. O. Brockway and L. Pauling, *Proc. Natl. Acad. Sci.*, **19** (1933), 860. H. Boersch, *Monatsh.*, **65** (1935), 314.

as stable minima;⁽⁹⁾ but in cumulenes, two *p* orbitals of each carbon atom being involved in bond formation, the electronic density of the bonds in the middle part of the chain may presumably be more or less symmetric with respect to the rotation around the axis of the chain and the energy less dependent on the relative orientation of the terminal groups. Further, the intense colour of cumulenes suggests⁽¹⁰⁾ a large contribution of dipolar mesomeric structures such as for example shown by the accompanying formula, and thus the double bonds acquire a single or a triple bond character considerably. It will be inferred from these considerations that the two pairs of terminal groups may rotate around the axis of the carbon atom chain with some freedom and may not be fixed in one plane contrary to the expectation from the van't Hoff model. With a view to settling this point experimentally a synthesis of cumulenes having a set of substituents which, according to the van't Hoff model, makes possible the existence of geometrical isomerides was undertaken.



The meso and racemic forms of 1,4-diphenyl-1,4-di-*p*-tolylbutynediol and 1,4-diphenyl-1,4-di-*p*-chlorophenylbutynediol were synthesized from acetylene dimagnesium bromide and *p*-methylbenzophenone and *p*-chlorobenzophenone respectively. Treatment with phosphorus diiodide converted these butynediols into desired 1,4-diphenyl-1,4-di-*p*-tolylbutatriene and 1,4-diphenyl-1,4-di-*p*-chlorophenylbutatriene. From both meso and racemic forms of each butynediol only one butatriene was obtained. If cis and trans isomerides were formed the synthetic procedure, which involved the use of phosphorus diiodide and hence the liberation of iodine in its course, may have caused the isomerization into the stabler form. By chromatographic analysis with activated alumina no identifiable compounds other than those described above were obtained. As it is a well established fact that the trans isomeride of ethylenic compounds is usually converted into the cis isomeride by irradiation with ultraviolet light, a benzene or petroleum ether solution of 1,4-diphenyl-1,4-di-*p*-tolylbutatriene was exposed to ultraviolet or sun light. It was found that decomposition of the compound took place and that when the decomposition was slight only the starting material was recovered by chromatographic separation.

Although the evidence obtained so far is not conclusive to decide between the two possibilities discussed above—which will be possible by dipole moment measurement—the synthesis may be worth reporting in

---

(9) E. Hückel, *Z. Physik*, **60** (1930), 423.

(10) L. Pauling, Gilman's "Organic Chemistry", 1888, New York (1938).

view of the attempted synthesis by Kuhn and Platzer,(11) who could obtain no asymmetrically substituted cumulenes in crystalline state by means of exactly the same procedue that proved successful in the case of symmetrically substituted ones.

Experimental.

1,4-Diphenyl-1,4-di-*p*-tolylbutynediols. To an ethyl magnesium bromide solution prepared from 2.4 g. of magnesium and 11 g. of ethyl bromide in 100 c.c. of ether dry acetylene was passed until no further increase of the viscous oily precipitate was observed. A solution of 15 g. of *p*-methylbenzophenone in 50 c.c. of ether was added to the acetylene dimagnesium bromide so prepared and the mixture was heated on a water bath with stirring for six hours. The reaction mixture was decomposed with dilute sulphuric acid and ice water. The ether layer was washed with aqueous sodium bicarbonate and after drying with anhydrous sodium sulphate the ether was evaporated. The remaining brown oil was brought to crystallization by rubbing with a small quantity of petroleum ether. Repeated crystallization from methanol effected the separation into two apparently pure crystalline products, one melting at 154–155.5° and the other at 145.5–151.5°, in the yields of 2.3 g. and 1.4 g. respectively. A mixture melted at 134–140°. They correspond to the theoretically expected meso and racemic forms of 1,4-diphenyl-1,4-di-*p*-tolylbutynediol. They effloresced on keeping and, as the presence of methanol of crystallization was suspected, they were recrystallized from benzene—petroleum ether mixture up to the melting points of 156–157° and 151.5° respectively. The di-*p*-chlorophenyl derivative described below was demonstrated to crystallize with one molecule of ethanol. Found for the higher melting butynediol: C, 85.9; H, 6.5; for the lower melting one: C, 86.3; H, 6.6. Calculated for $C_{30}H_{26}O_2$: C, 86.09; H, 6.20%.

Salkind and Martinsson(12) reported the synthesis of 1,4-diphenyl-1,4-di-*p*-tolylbutynediol melting at 146.° It appears to have been a mixture of the two isomerides or, if it was crystallized from alcohol, the lower melting point may be attributed to alcohol of crystallization.

1,4-Diphenyl-1,4-di-*p*-tolylbutatriene. To a solution of 1 g. of the higher melting 1,4-diphenyl-1,4-di-*p*-tolylbutynediol in 15 c.c. of dry ether was added about 1 g. of phosphorus diiodide dissolved in carbon bisulphide. The colour of the solution grew darker and suddenly yellow needles precipitated. The mixture was shaken with an aqueous solution of sodium thiosulphate and sodium hydroxide, and the crystals were collected on a filter, washed with water, and dried in a vacuum desiccator. Repeated precipitation from a hot chloroform solution by adding methanol gave lemon yellow needles melting at 236° with decomposition, yield 23% of the theory. The lower melting butynediol yielded the identical product, the mixed melting point having not been depressed. The products were combined, recrystallized from chloroform—methanol and analyzed. Found: C, 94.1; H, 6.4. Calculated for $C_{30}H_{24}$: C, 93.71; H, 6.29%.

---

(11) R. Kuhn and G. Platzer, *Ber.*, **73** (1940), 1410.

(12) J. Salkind and E. E. Martinsson, *Chem. Zentr.*, **1938**, II, 3678.

1,4-Diphenyl-1,4,-di-*p*-chlorophenylbutynediols. The synthetic procedure was the same as described above for the di-*p*-tolyl derivatives. Two isomerides corresponding to the meso and racemic forms were obtained, m.p. 133–134° and 148–148.5°. Found for the higher melting butynediol: C, 73.5; H, 4.5; Cl, 15.5; for the lower melting one: C, 73.0; H, 4.4; Cl, 15.4. Calculated for $C_{28}H_{20}O_2Cl_2$: C, 73.21; H, 4.39; Cl, 15.44%.

1,4-Diphenyl-1,4-di-*p*-chlorophenylbutatriene. On treatment with phosphorus diiodide in the same manner as described for the di-*p*-tolyl derivative the above butynediols gave in the yield of 13% of the theory the corresponding butatriene melting at 246–247° with decomposition, orange yellow needles. Found: C, 79.0; H, 4.5; Cl, 16.7. Calculated for $C_{28}H_{18}Cl_2$: C ,79.06; H, 4.27; Cl, 16.67%.

The author wishes to express sincere thanks to Prof. Y. Urushibara for his kind guidance and encouragement throughout this work.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.