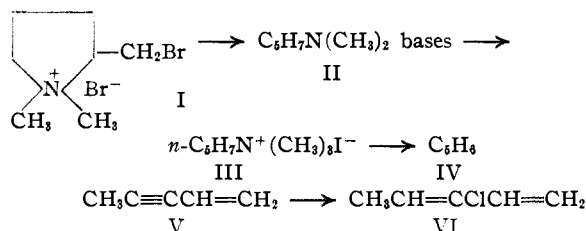


[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 903]

The Constitution of Pirylyene: Chemical Evidence

BY HERBERT SARGENT, EDWIN R. BUCHMAN AND JOHN P. FARQUHAR

The C_6H_6 hydrocarbon pirylyene (IV) was first prepared by Ladenburg¹ starting from piperidine and following essentially the path here indicated over the intermediates (I) to (III). The structure of these intermediates was but imperfectly known in Ladenburg's time,² so that a correct formulation of the pirylyene molecule was out of the question. In 1928, von Braun and Teuffert³ reinvesti-



gated the subject, and concluded that pirylyene must possess a doubly unsaturated ring structure. A number of possibilities were cited; that of methylenecyclobutene⁴ seemed most in accord with their observations. Because of our interest in cyclobutane derivatives the present study was undertaken.

It was found that degradation of (I) led to a mixture of bases (II), a fact which had been overlooked by previous investigators,^{1,2,5} who had assumed the homogeneity of their $C_5H_7N(CH_3)_2$ base. From (II), a methiodide (III) was obtained which is without doubt the parent substance from which pirylyene was formed. The straight-chain nature of the C_5H_7 radical in this quaternary salt was demonstrated by catalytic reduction of the corresponding chloride to *n*-amyltrimethylammonium chloride. From (III) pirylyene (IV) was made in the usual way^{1,3}; its properties, which agreed with the previous descriptions, were those of a pure substance.

A sample of this hydrocarbon has been submitted to Dr. V. Schomaker and Dr. R. Spurr of these Laboratories who have been able to work

(1) Ladenburg, (a) *Ber.*, **15**, 1024 (1882); (b) *Ann.*, **247**, 56 (1888).

(2) It was not until 1900 that Willstätter, *Ber.*, **33**, 365 (1900), elucidated the structure of the *N,N*-dimethyl- α -(bromomethyl)-pyrrolidiniumbromide (I).

(3) von Braun and Teuffert, *ibid.*, **61**, 1092 (1928).

(4) Stevens and Richmond, *THIS JOURNAL*, **63**, 3133, Footnote 14 (1941), have pointed out that it is difficult to explain the formation of this hydrocarbon.

(5) See also (a) Ladenburg, *Ber.*, **14**, 1347 (1881); (b) Merling, *ibid.*, **17**, 2139 (1884); (c) Willstätter, *ref. 2*.

out its structure from the electron diffraction pattern.⁶ Their investigation indicates that (IV) is not a ring compound, but possesses the structure (V) of 1-methyl-2-vinylacetylene, a known substance,⁷ the physical properties of which agree well with those of pirylyene.

The results of our chemical investigation are in full conformity with this conclusion. On catalytic reduction pirylyene readily took up three moles of hydrogen; the reduced product was shown to be *n*-pentane. It also added one mole of hydrogen chloride, as has been demonstrated⁸ for (V), giving 3-chloro-1,3-pentadiene (methylchloroprene) (VI).

Experimental

$C_5H_7N(CH_3)_2$ Bases (II).—The pyrrolidinium bromide (I)⁶ was degraded according to directions in the literature.^{1b,3} From 136.5 g. (0.5 mole) of (I), 39 g. (70%) of mixed bases (II) was obtained, b. p. ca. 56–70° at 50 mm.; the exact composition of this mixture⁹ was not determined due to its unstable nature. Fractionation through a precision column at 50 mm. gave 7.5 g. (13%) of material boiling constantly at 66.5°; examination of this fraction disclosed that it represented a substantially pure substance. It was used directly for conversion to the quaternary salt (III).

A portion of this base was further purified over the diluturate¹⁰ which crystallized from alcohol in well-formed narrow rectangular crystals; m. p. 161–162°. The regenerated base, b. p. 65° at 49 mm., d^{25}_4 0.800, n^{25}_D 1.4430, entirely stable for months in an atmosphere free from carbon dioxide, was obtained by distilling the diluturate with excess aqueous alkali.

Anal. Calcd. for $C_7H_{13}N$: C, 75.60; H, 11.79. Found: C, 75.89; H, 12.10.

The picrate was prepared from the components in ether, cube-like crystals from ethanol-isopropyl ether, m. p. 100.5–101.0°.

Anal. Calcd. for $C_{13}H_{16}N_4O_7$: N, 16.47. Found: N, 16.25.

With methyl iodide the methiodide (III) described below was obtained.

$n\text{-C}_5\text{H}_7\text{N}(\text{CH}_3)_3\text{I}$ (III).—To 54.3 g. of base (from fractionation of (II), b. p. ca. 66.5° at 50 mm.), in 250 cc. of ethanol, 76.4 g. of methyl iodide (10% excess) was added slowly, keeping the temperature at below 35° by cooling in an ice-bath. The crystalline product started to separate

(6) Spurr and Schomaker, *THIS JOURNAL*, **64**, 2693 (1942).

(7) Jacobson and Carothers, *ibid.*, **55**, 1622 (1933).

(8) Jacobson and Carothers, *ibid.*, **55**, 1624 (1933).

(9) A fuller account of the constituents will be published in another connection.

(10) Compare Redemann and Niemann, *ibid.*, **62**, 590 (1940).

almost immediately; after recrystallization from aqueous alcohol, the yield of (III) was 104 g. (84%), m. p. 259° d. (lit.⁸ m. p. 257°), entirely stable when heated with water at 100° (compare ref. 3).

Anal. Calcd. for C₈H₁₀N: C, 37.96; H, 6.36; N, 5.53. Found: C, 38.33; H, 6.60; N, 5.57.

The same methiodide (III) was obtained when the mixed bases (II) were methylated according to directions¹ in the literature. As a characteristic derivative, the picrate was prepared from concentrated aqueous solutions of (III) and of sodium picrate, needles from ethanol, m. p. 112.5–113.0°.

(III) was not amenable to catalytic reduction; it was converted to the corresponding chloride³ which was hydrogenated in aqueous solution under two atmospheres pressure using a palladium–charcoal catalyst. Two moles of hydrogen was taken up; the product was characterized by conversion to the picrate, prisms, m. p. 93.2–94.0°, from ethanol–isopropyl ether, and to the bromide, needles, m. p. 181.0–181.5°,¹¹ from ethanol. These derivatives gave no depression when mixed with authentic samples of the corresponding *n*-amyltrimethylammonium salts made from *n*-amyl bromide and trimethylamine.

Pirylene (IV)¹.—Quaternary iodide (III) (57.5 g.) was introduced together with 27 g. of potassium hydroxide and 70 cc. of water into a flask, and the mixture distilled from an oil-bath into a receiver immersed in a bath at –15°. A smooth decomposition took place (bath temperature 120–135°); the distillate was acidified with 6 *N* hydrochloric acid, and the hydrocarbon separated and dried over potassium carbonate, and over sodium. After distillation through a precision column, 8.9 g. (59%) of (IV) was obtained which boiled constantly; in

(11) von Braun and Murjahn, *Ber.*, **59**, 1205 (1926), reported the m. p. 175–176°.

a second similar experiment the yield was 11.0 g. (73%) of material having a 0.3° range. The constants observed were: b. p. 59.4° at 744 mm., d_{20}^{25} 0.7339, n_D^{25} 1.4467 (lit. piryrene³: b. p. 60°, d_{19}^{19} 0.7443, n_D^{19} 1.4505; methylvinylacetylene (V)⁷: b. p. 59.2° at 760 mm., d_{20}^{20} 0.7401, n_D^{20} 1.4496); the material polymerized slowly (much less rapidly than (VI)) on standing (compare refs. 3, 7).

The hydrocarbon (IV) (2.140 g.) was hydrogenated in ethanol solution using a palladium–charcoal catalyst. The hydrogen adsorbed (2.415 l. at 23° and 745 mm.) corresponded to 3 double bonds. The reduced hydrocarbon was distilled from the reduction mixture, treated with concentrated sulfuric acid and redistilled through a precision column; the sole product detected was *n*-pentane, yield 1.0 g., b. p. 36.3–36.5° (lit.¹² 36.1°).

Methylchloroprene (VI) was prepared from 3.7 g. of (IV) according to directions in the literature.⁸ Two and two-tenths grams of (VI) b. p. 98.5–101°, n_D^{25} 1.4745 (lit.⁸ b. p. 99.5–101.5°, n_D^{25} 1.4785) was obtained, and 1.5 g. of hydrocarbon was recovered. (VI) was identified by condensing with α -naphthoquinone; the derivative⁸ melted at 180.7–181.0° cor. (lit.⁸ 181°). When excess of (IV) and α -naphthoquinone were heated for two hours in a sealed tube at 100° no reaction¹³ was observed.

Summary

The conclusion, first arrived at as a result of the electron diffraction investigation,⁶ that piryrene and 1-methyl-2-vinylacetylene are identical, is supported by the chemical evidence.

(12) Egloff, "Physical Constants of Hydrocarbons," Vol. I, Reinhold Publishing Corp., New York, N. Y., 1939, p. 33.

(13) Compare Butz and Joshi, *THIS JOURNAL*, **63**, 3344 (1941). Under the same conditions, piperylene gave an adduct which was oxidized to 1-methylanthraquinone, m. p. 170–171°.

PASADENA, CALIF.

RECEIVED JULY 7, 1942

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 902]

The Constitution of Piryrene: Electron Diffraction Investigation

BY ROBERT SPURR AND VERNER SCHOMAKER

In connection with the studies described in the foregoing article¹ we have carried out an electron diffraction investigation of the C₈H₈ hydrocarbon piryrene with the object of determining its structural formula. Our results show that piryrene does not contain a three or four-membered ring as suggested by von Braun and Teuffert² but that it is methylvinylacetylene, CH₃—C≡C—CH=CH₂. This identification is substantiated by the agreement¹ of the physical properties of piryrene with those reported for methylvinylacetylene and by chemical evidence.¹ We wish to express our thanks

to Dr. E. R. Buchman for suggesting the problem and to him and his collaborators for providing the sample of piryrene used in the investigation.

Experimental

The preparation of the piryrene has been described.¹ The apparatus and technique used have been reviewed by Brockway.³ Twenty photographs were taken of the scattering from the vapor. The camera distance was about eleven or about twenty centimeters, and the wave length of the electrons was about 0.06 Å. (based on $a_0 = 4.070$ Å. for Au). The diffraction pattern showed fine structure indicative of long inter-

(1) Herbert Sargent, Edwin R. Buchman and John P. Farquhar, *THIS JOURNAL*, **64**, 2692 (1942).

(2) von Braun and Teuffert, *Ber.*, **61**, 1092 (1928).

(3) L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).