The Chemistry of Carbazoles. X (1). Structure of a Pentamethylcarbazole Isolated from a Kuwait Mineral Oil. An Application of the UV Spectral Additivity

Yutaka Tsunashima, Tokunori Sugimoto and Masatane Kuroki*

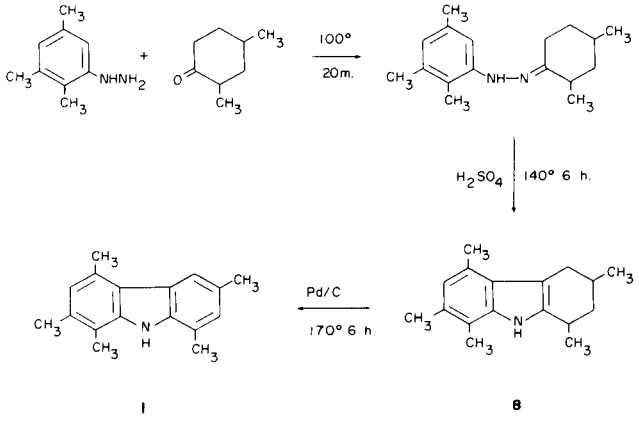
Department of Chemistry,
Shibaura Institute of Technology, Fukasaku,
Ohmiya-shi, Saitama 330, Japan

Received February 18, 1982

The structure of Carruthers' pentamethylcarbazole isolated from Kuwait mineral oil was determined. From the reported spectral data, we deduced methyl-substitutions at the 1-, 2-, 4-, 6- and 8-positions and this was confirmed by synthesis. This is a good example demonstrating the usefulness of uv spectral additivity.

J. Heterocyclic Chem., **19**, 933 (1982).

In 1968, Carruthers (2) isolated a pentamethylcarbazole from a Kuwait mineral oil. Although he presumed it to be 1,2,3,5,7-pentamethylcarbazole on the basis of spectral data, it was not identical with a synthetic specimen. In a previous paper (3) dealing with ultraviolet absorption spectra of 42 methylcarbazoles, we reported that the spectral shifts were additive according to number and positions of the methyl groups, and that this relation could be applied to determination of unknown methylcarbazoles. In this connection, structural determination of Carruthers' pentamethylcarbazole would provide a good example demonstrating the usefulness of the spectral additivity.



I

II

Two singlets at τ 7.21 (3H) and 2.22 (1H) in the nmr spectrum reported by Carruthers can be assigned to methyl protons and a ring proton located in the 4- or 5-positions on the basis of their charateristic low-field shifts. There exist 28 isomeric pentamethylcarbazoles and 14 isomers meet these structural requirements. Moreover, three singlets at τ 2.22, 2.97 and 3.19 and ir absorptions at 840 and 845 cm^{-1} indicate that all the hydrogen atoms on the rings are isolated each other. Consequently, this carbazole should be one of the 7 isomers; 1,2,4,6,8- (**1**), 1,2,3,5,7- (**2**), 1,2,4,6,7- (**3**), 1,3,4,6,7- (**4**), 1,3,4,6,8- (**5**), 1,3,5,6,7- (**6**), and 2,3,4,6,7-pentamethylcarbazole (**7**).

On the other hand, the uv spectral band (340 nm) revealed a bathochromic shift to the extent of 3.0 nm from that of carbazole (337.0 nm in ethanol). As reported previously,

Table I

Expected λ max (a) of Selected Pentamethylcarbazole by Calculation With the Additive Values (nm)

	Pentamethylcarbazole	Calcd. shift	Expected λ max	Difference from Carruthers' data
(**1**)	1,2,4,6,8-(CH_3)$_5$	3.0	340.0	0.0
(**2**)	1,2,3,5,7-	1.2	338.2	-1.8
(**3**)	1,2,4,6,7-	1.2	338.2	-1.8
(**4**)	1,3,4,6,7-	9.5	346.5	6.5
(**5**)	1,3,4,6,8-	11.3	348.3	8.3
(**6**)	1,3,5,6,7-	9.5	346.5	6.5
(**7**)	2,3,4,6,7-	7.7	344.7	4.7

(a) The λ max based on 337.0 nm band of carbazole in ethanol.

Table II

Properties of Pentamethylcarbazoles

	Pentamethylcarbazole in a Kuwait Oil		1,2,4,6,8-Pentamethylcarbazole (**1**)	
Mp (°C)	183-186 (needles)		185-187 (needles)	
Picrate mp (°C)	200 (deep brown needles)		202-203 (deep brown needles)	
UV (Ethanol) λ max (log ε)	245	(4.70)	245.5	(4.70)
	253 infl.	(4.51)	254	(4.56)
	263	(4.20)	263.5	(4.24)
	293	(4.15)	294 (4.21)	
	314 infl.	(3.42)	314 infl.	(3.45)
	326	(3.59)	326	(3.59)
	340	(3.60)	340	(3.59)
NMR (Deuteriochloroform) τ	2.22 (1H, s)		2.26 (1H, s, 5-H)	
	2.97 (1H, s)		2.99 (1H, s)	
	3.19 (1H, s)		3.19 (1H, s)	
	7.21 (3H, s)		7.22 (3H, s, 4-CH_3)	
	7.50 (6H)		7.50 (6H, s)	
	7.60 (6H)		7.58 (6H, s)	
IR (potassium bromide) cm^{-1}	845		847	
	840		842	

additive values of the spectral shift are -0.3, -2.1, 6.2 and -0.5 nm for 1- or 8-, 2- or 7-, 3- or 6- and 4- or 5-methyl substitutions, respectively. The expected absorption maxima were calculated for the probable 7 isomers by using these additive values (Table I).

Judging from the agreement between the calculated and the found values, we conclude that the pentamethylcarbazole in the Kuwait oil is 1,2,4,6,8-pentamethyl isomer.

This structure was subsequently confirmed by synthesis. Fischer indole cyclization of 2,3,5-trimethylphenylhydrazone of 2,4-dimethylcyclohexanone was carried out by boiling in dilute sulfuric acid to give 1,3,5,7,8-pentamethyl-1,2,3,4,-tetrahydrocarbazole (**8**). On account of its instability toward air and light, the tetrahydrocarbazole was dehydrogenated *in situ* by refluxing with Pd/C in pseudocumene to give 1,2,4,6,8-pentamethylcarbazole (**1**).

Its melting point and spectral data are listed in Table II and compared with Carruthers' data. All the data are in good agreement with those reported.

EXPERIMENTAL

Melting point were taken on a hot-stage apparatus and uncorrected. The uv spectrum was determined in 95% ethanol solution with a Hitachi EPS-3T spectrophotometer. The nmr spectra were recorded on a JEOL PS-100 (100MHz) with TMS as an internal standard and ir spectrum was obtained with a JASCO IRA-1 spectrophotometer for potassium bromide pellet.

2,3,5-Trimethylphenylhydrazine Hydrochloride.

2,3,5-Trimethylaniline (4) (18.9 g, 0.14 mole) was diazotized with 13.1 g of sodium nitrite in 250 ml of 20% hydrochloric acid. The diazotized solution was treated with a solution of stannous chloride (90 g, 0.14 mole in 120 ml of 20% hydrochloric acid) and stirred overnight at room temperature. The collected complex was digested with aqueous sodium hydroxide (40%, 100 ml) and the mixture was extracted with ether repeatedly (total 200 ml). 2,3,5-Trimethylphenylhydrazine hydrochloride (4.1 g, 16%) was obtained from the dried ethereal solution by introduction of dry hydrogen chloride, mp 200° dec; ir: 3145, 2920, 2680, 850 cm^{-1}.

Anal. Calcd. for $C_9H_{15}ClN_2$: C, 57.91; H, 8.10; N, 15.00. Found: C, 57.65; H, 7.91; N, 14.78.

1,3,5,7,8-Pentamethyl-1,2,3,4-tetrahydrocarbazole (**8**).

All the operations were carried out in an atmosphere of nitrogen.

2,3,5-Trimethylphenlhydrazine hydrochloride (3.2 g, 0.017 mole) was shaken with 5% aqueous sodium hydroxide (20 ml) and extracted with ether, washed with water and dried. After removal of the ether, 2,4-dimethylcyclohexanone (2.2 g, 0.018 mole) was added and heated at 100° for 20 minutes. The 15% sulfuric acid (50 ml) was added and heated at 140° for 6 hours. The reaction mixture was extracted with hot benzene (200 ml). The benzene solution was divided into two parts. From a fraction of the solution (one-third volume), a picrate of 1,3,5,7,8-pentamethyl-1,2,3,4-tetrahydrocarbazole was obtained as dark red needles of mp 207-208°.

Anal. Calcd. for $C_{23}H_{26}N_4O_7$: C, 58.72; H, 5.57; N, 11.91. Found: C, 58.49; H, 5.59; N, 11.70.

Although the tetrahydrocarbazole **8** regenerated as a brown gum by treating a benzene solution of the picrate with aqueous sodium hydroxide solution, the mp and analysis could not be determined on account of its instability; nmr (carbon tetrachloride): τ 2.80 (1H, s, 6-H), 7.33 (3H, s, 5-CH_3), 7.50-7.95 with dominant peaks at 7.58, 7.69, and 7.80 (12H, m, 1,3,7,8-CH_3), 8.78-8.92 (6H, m, -CH_2-CH).

1,2,4,6,8-Pentamethylcarbazole (**1**).

The Residual benzene solution of the tetrahydrocarbazole mentioned above was evaporated to dryness under reduced pressure. Pseudocumene (30 ml) and 5% palladium charcoal (2.0 g) was added and refluxed at 170° for 6 hours. After removal of the catalyst, pure 1,2,4,6,8-pentamethylcarbazole crystallized from the concentrated solution, 0.2 g (5% yield based on the trimethylphenylhydrazine hydrochloride). Its properties are shown in Table II.

Anal. Calcd. for $C_{17}H_{19}N$: C, 86.03; H, 8.07; N, 5.90. Found: C, 86.15; H, 7.91; N, 5.72.

REFERENCES AND NOTES

(1) Part IX. T. Nakazawa, M. Kuroki and Y. Tsunashima, *J. Chromatogr.*, **211**, 388 (1981).

(2) W. Carruthers, *J. Chem. Soc. (C)*, 2244 (1968).

(3) Y. Tsunashima and M. Kuroki, *J. Heterocyclic Chem.*, **18**, 715 (1981).

(4) F. M. Beringer and I. Ugelow, *J. Am. Chem. Soc.*, **75**, 2635 (1953).