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Thirty-six methylcarbazoles were prepared, and their synthetic methods were critically described.

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Methylcarbazoles are often found in coal tar (1), petroleum (2) and plant degradation products (3). It may be worthwhile to present chemical and physical properties of methylcarbazoles, since many investigators have been forced to make laborious efforts to determine these naturally occurring carbazoles. In addition, it is relevant to survey the advantages and disadvantages among several synthetic methods for the carbazoles bearing a definite kind of substituent.

This paper deals with preparation of a complete series of monomethyl- and dimethylcarbazoles, as well as a number of trimethyl- and tetramethylcarbazoles.

Reductive cyclization of 2-nitromethylbiphenyls with triethyl phosphite to methylcarbazoles, which is referred to as the Cadogan synthesis (abbreviated to method C), is most facile and it provides good results. An increasing number of methyl groups tends to decrease yields of carbazoles. In fact, Puskas, *et al.* (4), reported that cyclization

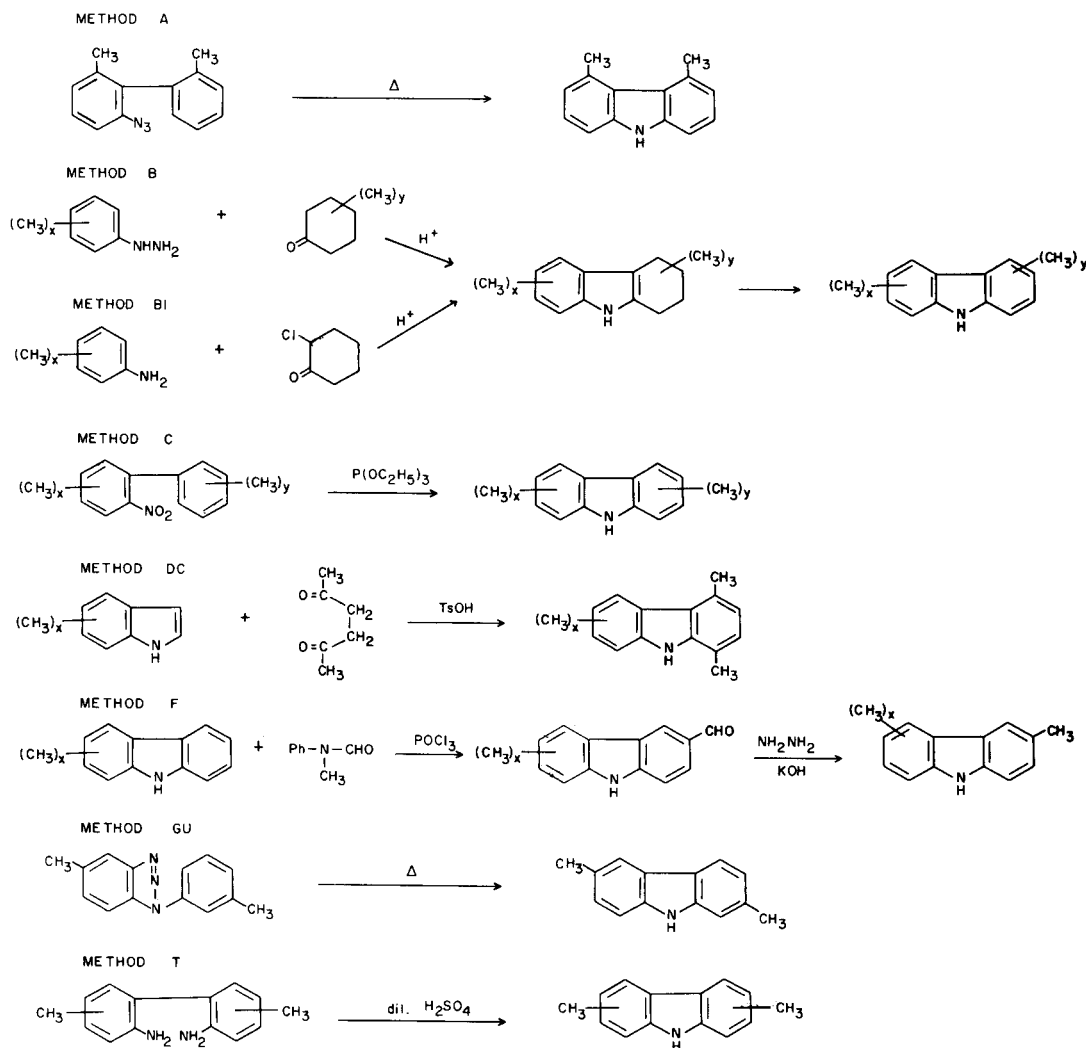


Table I
Methylcarbazoles

Carbazole	Synthetic Method (a)	Yield % (b)	Melting Point, °C [lit.] (c)	¹ H-Nmr (d) δ-CH ₃ , ppm	Anal. Found (e)		
					C%	H%	N%
1-CH ₃	BI	76	121.3-121.7 [121 (12), 122 (13), 120.5 (14), 118-119 (15), 120.5-121 (16), 120-122 (39)]	2.53 (3H) (deuterioacetone)	86.21	6.14	7.67
2-	B	97	264-266 [258-260 (7), 259 (8) (17) (18), 259-260 (39), 260 (20), 261.5-262.5 (19), 260-262 (15), 261-262 (16)]	2.45 (3H) (deuterioacetone)	86.13	6.22	7.70
3-	B	95	207-208 [199-202 (20), 202 (25), 203 (14) (17), 204 (40), 205-207 (7), 205.5-207 (39), 206 (23), 206-207 (15), 207 (21), 206.5-207.5 (16)]	2.47 (3H) (deuterioacetone)	86.18	6.38	7.80
4-	C	70	132-133 [115-116 (25), 115-118 (39), 128 (24), 128-129 (20), 128-130 (15), 129.5-130 (16)]	2.84 (3H) (deuterioacetone)	86.15	6.21	7.69
1,2-(CH ₃) ₂	BI	72	151.3-151.8 [112-114 (27), 147-148 (26)]	2.45 (6H)	86.13	6.78	7.20
1,3-	BI	63	91-93 [94 (26), 95 (14)]	2.50 (6H)	86.01	6.82	7.09
1,4-	DC	58	98.2-98.3 [79-82 (26), 96 (10), 97-98 (9)]	2.48 (3H) 2.82 (3H)	86.21	6.75	7.12
1,5-	C	53*	137-138	2.51 (3H) 2.83 (3H)	86.33	6.89	7.16
1,6-	B	83	174.5-175.5	2.52 (6H)	86.19	6.81	7.12
1,7-	B	79	166-168	2.50 (6H)	85.92	6.71	6.99
1,8-	B	41	178-180 [175-176] (40)]	2.59 (6H)	86.32	6.83	7.01
2,3-	BI	53	254-255 [250-252 (26), 251-253 (28)]	2.41 (6H)	85.98	6.68	7.17
2,4-	B	62	137-138.5 [124-126 (38), 134-136 (7)]	2.48 (3H) 2.82 (3H)	86.23	6.82	7.15
2,5-	C	56	140.5-142	2.50 (3H) 2.84 (3H)	86.35	6.81	7.04
2,6-	GU	30	224-225.5 [208-209 (17), 224 (29)]	2.51 (6H)	86.04	6.68	7.27
2,7-	T	43	288-289 [283 (41)]	2.50 (6H)	86.36	6.74	7.29
3,4-	C	58	168.5-169 [159-160 (26)]	2.46 (3H) 2.81 (3H)	86.22	6.78	7.15
3,5-	C	47*	154-156	2.54 (3H) 2.87 (3H)	85.87	6.81	6.95
3,6-	T	44	213-215 [217-218 (31) (40), 218 (23), 219 (21) (29) (30)]	2.51 (6H)	86.31	6.83	7.23
4,5-	A C	14 trace	177-177.5	3.00 (6H)	86.22	6.86	7.05
1,3,4-(CH ₃) ₃	F	83	148 [143-143.5 (32), 143-145.5 (9), 143-152 (39)]	2.44 (3H), 2.49 (3H), (3H), 2.77 (3H)	86.21	7.22	6.65
1,4,8-	DC	56	154-156 [153-154 (42)]	2.57 (3H), 2.60 (3H), 2.84 (3H)	86.10	7.27	6.61
1,5,7-	B	63	149	2.44 (3H), 2.49 (3H), 2.84 (3H)	86.15	7.48	6.70
2,3,5-	C	30	189-190	2.39 (3H), 2.43 (3H), 2.84 (3H)	86.13	7.23	6.61
2,3,6-	B F	68# 0	211-211.5	2.38 (6H), 2.46 (3H) (deuterioacetone)	86.12	7.24	6.57
2,4,5-	B	32*	139-142.5	2.49 (3H), 2.95 (6H)	86.02	7.07	6.69
2,4,6-	B	83	176 [198 (34)]	2.46 (3H), 2.52 (3H), 2.81 (3H)	86.11	7.25	6.59
2,4,7-	B	65*	145.5-147	2.44 (3H), 2.48 (3H), 2.77 (3H)	86.08	7.28	6.55
3,4,6-	B	30#	205-207.5	2.40 (3H), 2.48 (3H), 2.74 (3H) (deuterioacetone)	85.88	7.25	6.65

Table I continued

Carbazole	Synthetic Method (a)	Yield % (b)	Melting Point, °C [lit.] (c)	¹ H-Nmr (d) δ-CH ₃ , ppm	Anal. Found (e)		
					C%	H%	N%
1,2,5,7(CH ₃) ₄	C	50	157.5-159	2.39 (3H), 2.46 (6H), 2.80 (3H)	85.78	7.74	6.04
1,2,6,7-	C	64°	210-212.5 [202-205 (4)]	2.36 (6H), 2.40 (3H), 2.42 (3H) (deuterioacetone)	85.82	7.69	6.27
1,3,4,6-	F	63	186-190.5 [190-191.5 (9)]	2.43 (3H), 2.48 (3H), 2.53 (3H), 2.77 (3H)	86.03	7.69	6.18
1,4,5,8-	DC	68	174-175.5 [170-171 (11)]	2.55 (6H), 2.98 (6H)	86.10	7.70	6.21
2,3,5,7-	C	59	187.5-188.5 [185-186 (4)]	2.42 (6H), 2.46 (3H), 2.81 (3H)	86.08	7.68	6.28
	B	66‡					
2,3,6,7-	C	23°	245.5-247.5 [244-246 (4)]	2.40 (12H)	86.23	7.72	6.01
2,4,5,6-	B	21‡	189-192	2.44 (6H), 2.82 (3H), 2.92 (3H)	86.01	7.77	6.25

(a) A: Azidobiphenyl decomposition; BI: Bischler synthesis; B: Borsche synthesis; C: Cadogan synthesis; DC: Dalton and Cranwell synthesis; F: Formylation followed by reduction; GU: Graebe-Ullmann synthesis; T: Täuber synthesis. (b) Based on precursors; couples of symbols (*, #, °, + and ‡) indicate glc yields for isomeric mixtures. (c) Measured on a hot stage melting point apparatus. (d) In deuteriochloroform, unless otherwise stated. (e) Calcd. for monomethylcarbazoles, C₁₃H₁₁N: C, 86.12; H, 6.12; N, 7.73; dimethylcarbazoles, C₁₄H₁₃N: C, 86.11; H, 6.71; N, 7.17; trimethylcarbazoles, C₁₅H₁₅N: C, 86.08; H, 7.22; N, 6.69; and tetramethylcarbazoles, C₁₆H₁₇N: C, 86.05; H, 7.67; N, 6.27.

of pentamethyl- or hexamethyl-2-nitrobiphenyls needed higher temperature under pressure. In spite of this tendency, 2-nitrotetramethylbiphenyls gave corresponding carbazoles in moderate yields under normal conditions.

The method C is inadequate to prepare 4,5-dimethylcarbazole. As was reported in a previous paper (5), formation of 4,5-dimethyl-9-ethylcarbazole was predominant. Hence, thermolysis of 2-azido-2',6-dimethylbiphenyl is recommended for obtaining 4,5-dimethylcarbazole (method A), although the yield was still low (14%).

In comparing the method C with the Borsche synthesis (method B) for the synthesis of 2,3,5,7-tetramethylcarbazole, the former may be preferable. The latter method surpasses the former with regard to yields in the last step, however, the yields of two isomeric tetrahydrocarbazoles were rather low, and separation of two tetramethylcarbazoles was tedious work.

1,5- and 3,5-Dimethylcarbazoles were obtained from 3',6-dimethyl-2-nitrobiphenyl in a 53:47 ratio. This result corresponds to 52-56:44-48 ratios of 1-methyl- and 3-methylcarbazoles from 2-azido- or 2-nitro-3'-methylbiphenyl by the methods A and C, reported by Sauer, *et al.* (6). The similarity of the ratios indicates that a methyl group at the 6-position of biphenyl does not affect isomer distribution on ring closure, and that the intermediacy of nitrene in the Cadogan reaction is strongly supported (Table III).

Dehydrogenation of 1,2,3,4-tetrahydrocarbazoles on palladium charcoal catalyst in trimethylbenzene (7) is also an excellent method. Accordingly, the success depends

upon outcome of Borsche synthesis or Bischler synthesis (method BI). Difficulties in these methods reside in the instability of polymethylphenylhydrazines and hydrazones to air or light, as well as polymethyl-1,2,3,4-tetrahydrocarbazoles. Therefore, these reactions sometimes require to operate without isolation of individual intermediates.

As given in Table II, the yields of tetrahydrocarbazoles are generally satisfactory. However, *o*-methylphenylhydrazones gave 8-methyl substituted tetrahydrocarbazoles in somewhat low yields. Thus, the yield of 1,8-dimethyl-1,2,3,4-tetrahydrocarbazole was only 18%. One reason for the low yields is realized in the sterically hindered cyclization by the methyl group at the *o*-position of benzene ring.

In the reactions giving two isomeric tetrahydrocarbazoles, isomer ratios could not be determined on account of their instabilities, therefore, the ratios were determined for methylcarbazoles as dehydrogenated products (Table III). Yields of tetrahydrocarbazoles bearing a methyl group at the 5-position were inferior in comparison with those of the corresponding isomers. The most typical case is the cyclization of the *m*-tolylhydrazone of cyclohexanone, where 5-methyl-1,2,3,4-tetrahydrocarbazole could not be obtained. Ring closure of the phenylhydrazone of 3-methylcyclohexanone, reported by Campbell, *et al.* (8), gives solely 2-methyl-1,2,3,4-tetrahydrocarbazole. Both results indicate that the methods B and BI are inadequate for preparing 4-methylcarbazole.

The Täuber synthesis (method T), which is ring closure of 2,2'-diaminobiphenyls in mineral acid, gave 2,7- and

Table II
Tetrahydrocarbazoles

1,2,3,4-Tetrahydrocarbazole	Method (a)	Starting materials	Yield %	m.p./b.p. [lit.]
8-methyl-	I	2-chlorocyclohexanone <i>o</i> -toluidine	54	91-92 [95-96 (35) 96-97 (15), 97-98 (8) (13) (16), 98 (36), 97-99 (26)]
7-methyl-	II	cyclohexanone <i>m</i> -tolylhydrazine	70	134-137 [125-138 (13), 126-138 (16)]
6-methyl-	II	cyclohexanone <i>p</i> -tolylhydrazine	82	145-147 [141-142 (8) (17), 143 (22), 145-146 (16), 148-150 (15)]
7,8-dimethyl-	I	2-chlorocyclohexanone 2,3-dimethylaniline	72	84-86[84-86 (26)]
6,8-dimethyl-	I	2-chlorocyclohexanone 2,4-dimethylaniline	61	b.p. (6 torr) 195 [b.p. (25 torr) 235- 242 (28), m.p. 92-94 (26), 101-105 (28)]
3,8-dimethyl	III	4-methylcyclohexanone <i>o</i> -tolylhydrazine	51	108-109.6
2,8-dimethyl-	II	3-methylcyclohexanone <i>o</i> -tolylhydrazine	85(b)	
1,8-dimethyl-	III	2-methylcyclohexanone <i>o</i> -tolylhydrazine	18	75-78
6,7-dimethyl-	I	2-chlorocyclohexanone 3,4-dimethylaniline	79	120-127 [109 (28), 119-130 (26)]
2,4-dimethyl-	II	3,5-dimethylcyclohexanone phenylhydrazine	58	99-100 [96-99 (38), 103-106 (37)]
2,4,8-trimethyl-	II	3,5-dimethylcyclohexanone <i>o</i> -tolylhydrazine	51	b.p. (2 torr) 120-140
2,6,7-trimethyl-	II	4-methylcyclohexanone	86 (c)	97-115
2,5,6-trimethyl-		3,4-dimethylphenyl- hydrazine		
2,4,7-trimethyl	II	3,5-dimethylcyclohexanone	65 (c)	b.p. (6 torr) 192
2,4,5-trimethyl-		<i>m</i> -tolylhydrazine		
2,4,6-trimethyl-	II	3,5-dimethylcyclohexanone <i>p</i> -tolylhydrazine	64	109-113.5
2,4,5,6-tetramethyl-	II	3,5-dimethylcyclohexanone	51 (c)	b.p. (2 torr) 152-180
2,4,6,7-tetramethyl-		3,4-dimethylphenylhydrazine		

(a) Method I: refluxed for 10 hours in ethanol; method II: refluxed for 2-2.5 hours in acetic acid; method III: heated for 10 hours in boiling dilute sulfuric acid. (b) Yield of crude product. (c) Yield of two isomers mixture.

3,6-dimethylcarbazoles in moderate yields.

The Graebe-Ullmann synthesis (method GU) was adopted for the preparation of 2,6-dimethylcarbazole. This method has no merit as compared with other methods.

One or more methyl groups are added to methylcarbazoles by formylation with *N*-methylformanilide and phosphoryl chloride, followed by Wolff-Kischner-Huang-Minlon reduction (method F) (9). Although 1,3,4-trimethylcarbazole was successfully obtained by this method, syntheses of 2,3,6-trimethyl-, 1,3,4,6- and 2,3,4,6-tetramethylcarbazoles failed. In these cases, reductions of 2,3-dimethyl-6-formyl-, 3,6-diformyl-1,4-dimethyl- and 3-formyl- 2,4,6-trimethylcarbazoles led curiously to decarbonylation to give 3,4-dimethyl-, 1,4-dimethyl- and 2,4,6-trimethylcarbazoles, respectively.

The reaction of indoles with hexan-2,5-dione (method

DC) is the most useful method for preparing 1,4-dimethylcarbazoles (9-11).

1,4,8-Trimethylcarbazole was obtained by this method in a good yield.

EXPERIMENTAL

All melting points were uncorrected. Nmr spectra were recorded on Jeol JNM-PS-100 (100 MHz) and Hitachi R-600 (FT, 60 MHz) spectrometers using tetramethylsilane as an internal standard. Isomer ratios were determined by gas liquid chromatography using an Hitachi 106 instrument at 210° on an SE-30 column.

General Procedure of the Method B (Borsche Synthesis) 2,4,5- and 2,4,7-Trimethylcarbazoles.

m-Tolylhydrazine (5.1 g.) was added to solution of 3,5-dimethylcyclohexanone (5.0 g.) in acetic acid (16 g.) under nitrogen over a period of an hour. The mixture was then refluxed for an hour. The reaction mixture was taken up in 50 ml. of benzene and washed with a sodium bicarbonate solution and water. The benzene solution was dried with sodium sulfate

and distilled. After 3,5-dimethylcyclohexanone and *m*-tolylhydrazine were distilled at 50-60° (5-6 mm), the mixture of 2,4,5- and 2,4,7-trimethyl-1,2,3,4-tetrahydrocarbazoles was distilled at 192° (6 mm) as a viscous pale yellow oil, 5.78 g. (65%). The tetrahydrocarbazoles were dehydrogenated by boiling with 1.5 g. of 10% palladium charcoal in 15 ml. of 1,2,4-trimethylbenzene for 5.5 hours. After removal of the catalyst by filtering while hot, the trimethylbenzene was distilled off *in vacuo*, and 5.45 g. of white crystals was obtained. Fractional recrystallization in a cyclohexane-benzene mixture (10:1) gave 0.10 g. of 2,4,5-trimethylcarbazole and 0.45 g. of 2,4,7-trimethylcarbazole.

The Method BI (Bischler Synthesis).

Methyl-substituted tetrahydrocarbazoles were obtained from 2-chlorocyclohexanone and methylanilines by following Campbell's procedure (28). Dehydrogenation of 8-methyl-1,2,3,4-tetrahydrocarbazole over Raney nickel (13) required a long reaction time (27 hours). The dehydrogenations of 1,2-, 1,3- and 2,3-dimethyl-1,2,3,4-tetrahydrocarbazoles with palladium on charcoal were better than the chloranil dehydrogenations reported by Barclay and Campbell (8).

General Procedure of the Method C (Cadogen Synthesis) 1,5- and 3,5-Dimethylcarbazoles.

A mixture of 3',6-dimethyl-2-nitrobiphenyl (4.5 g.) and triethyl phosphite (9.3 g.) was refluxed for 5.5 hours under nitrogen. Triethyl phosphate and excess triethyl phosphite were distilled, and the residue was chromatographed on alumina with benzene-petroleum ether (2:1) to give 3.9 g. of white crystals. This isomeric mixture was recrystallized from a cyclohexane-benzene mixture (10:1) repeatedly, and 0.23 g. of 3,5-dimethylcarbazole and 0.03 g. of 1,5-dimethylcarbazole were isolated.

General Procedure of the Method DC (Darton and Cranwell Synthesis) 1,4,8-Trimethylcarbazole.

7-Methylindole (1.00 g.), hexane-2,5-dione (0.92 g.) and *p*-toluene sulfonic acid monohydrate (0.78 g.) were dissolved in 4.1 ml. of ethanol and refluxed for an hour. The reaction mixture was taken up 50 ml. of ether, and the ethereal solution was washed with water and dried. Removal of the solvent left white-green crystals (1.41 g.), which were recrystallized from cyclohexane to give 0.90 g. (56%) of white flakes.

2,3-Dimethyl-6-formylcarbazole.

2,3-Dimethylcarbazole (2.0 g.) was added to a mixture of *N*-methylformanilide (1.82 g.), phosphoryl chloride (1.86 g.) and chloroform (5.2 ml.) at 0° and refluxed for 5.25 hours. The solution was shaken with sodium acetate solution (3.5 g. in 17.4 ml. of water), and steam distilled. The residue was a colorless oil which solidified by scratching under ice cooling (2.20 g.). Recrystallization from cyclohexane gave 1.98 g. (87%) of 2,3-dimethyl-6-formylcarbazole as flakes, m.p. 85.2°; ν (potassium bromide): 3370, 2915, 2870, 1700 cm^{-1} ; nmr (deuteriochloroform): δ 2.40 (6H, s, -CH₃), 7.25-7.87 (5H, m, ring protons), 9.60 ppm (1H, s, -CHO).

Anal. Calcd. for C₁₅H₁₃NO: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.54; H, 5.80; N, 6.32.

The 2,4-dinitrophenylhydrazine was obtained as pale yellow plates, m.p. 260-262°.

3-Formyl-2,4,6-trimethylcarbazole.

From 3.55 g. of 2,4,6-trimethylcarbazole, 3.20 g. (80%) of formylated product was obtained, m.p. 149-150.5°; ν (potassium bromide): 3340, 2910, 2860, 1682 cm^{-1} ; nmr (deuteriochloroform): δ 2.49 (6H, s, 2- and 6-CH₃), 2.51 (3H, s, 4-CH₃), 6.99 (1H, s, 1-H), 7.15-7.40 (2H, m, 7- and 8-H), 7.79 (1H, s, 5-H), 9.60 (1H, s, -CHO).

Anal. Calcd. for C₁₆H₁₅NO: C, 80.98; H, 6.37; N, 5.90. Found: C, 80.87; H, 6.35; N, 5.92.

Attempted Reduction of Formylcarbazoles.

A solution of 2,3-dimethyl-6-formylcarbazole (1.60 g.), hydrazine hydrate (0.92 ml.) and potassium hydroxide (1.37 g.) in ethylene glycol (13.7 ml.) was heated to 190° gradually, and maintained at the same

Table III
Isomer Ratios

Method	Carbazole	Ratio
C	1,5-dimethyl-	53
	3,5-dimethyl-	47
C	1,2,6,7-tetramethyl-	74
	2,3,6,7-tetramethyl-	26
B	2-methyl-	100
	4-methyl-	0
B	2,3,6-trimethyl-	68
	3,4,6-trimethyl-	32
B	2,4,7-trimethyl-	67
	2,4,5-trimethyl-	33
B	2,3,5,7-tetramethyl-	76
	2,4,5,6-tetramethyl-	24

temperature for 3.5 hours. The reaction mixture was poured into water, and the white precipitate was recrystallized from toluene to give 1.17 g. of flakes, m.p. 257-258.5°. This was identical to 2,3-dimethylcarbazole.

Under similar reaction conditions, 3,6-diformyl-1,4-dimethyl- (9) and 3-formyl-2,4,6-trimethylcarbazoles were decarbonylated to give 1,4-dimethyl- and 2,4,6-trimethylcarbazoles, respectively.

3',6-Dimethyl-2-nitrobiphenyl.

Copper bronze (22.0 g.) was added to the mixture of 2-bromo-3-nitrotoluene (18.0 g.) and *m*-iodotoluene (22.0 g.) at 175° and heated at 230° for half an hour. From a chloroform extract, 3',6-dimethyl-2-nitrobiphenyl was distilled at 145-146° (2.5 mm) as a pale yellow oil, 5.0 g. (27%).

Anal. Calcd. for C₁₄H₁₃NO₂: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.72; H, 5.68; N, 6.12.

4',6-Dimethyl-2-nitrobiphenyl.

This compound was obtained from 2-bromo-3-nitrotoluene and *p*-iodotoluene in 36% yield by the same method described above, b.p. 78-88° (1.5 mm), m.p. 55-56°, pale yellow crystals.

Anal. Calcd. for C₁₄H₁₃NO₂: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.82; H, 5.76; N, 6.10.

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