BRIEF COMMUNICATIONS

SYNTHESIS OF ACETYLENE DERIVATIVES OF 9-METHYLCARBAZOLE

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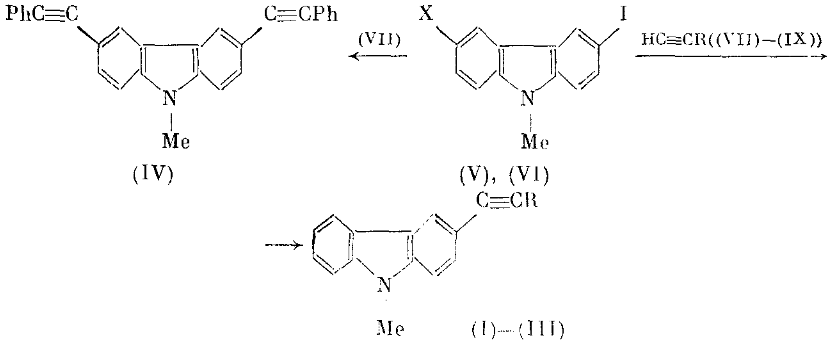
A number of mono- and diacetylene derivatives of 9-methylcarbazole were synthesized.

Acetylene derivatives of aromatic nitrogen heterocycles are monomers or polymers with semiconductor properties and intermediates in the production of components of photoconducting films [1, 2].

We have synthesized a series of new acetylenylcarbazoles. Compounds (I)-(IV) are obtained as condensed iodocarbazoles (V) and (VI) with terminal acetylenes (VII)-(IX) in the presence of $Pd(PPh_3)_2Cl_2$–CuI in Et_2NH at 50°C [3].

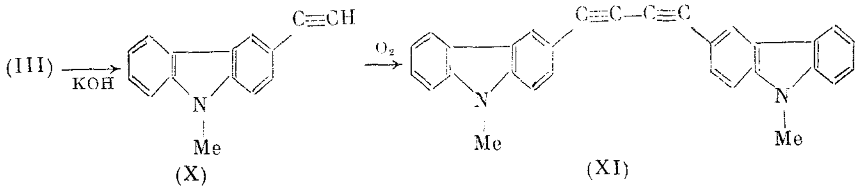


X = H (V), I (VI).

R = Ph (I), (VII); C_6H_{13} (II), (VIII); C(OH)Me_2 (III), (IX).

The yields of (I)-(IV) were 70-93% (Table 1).

Carbazolylacetylenic alcohol (III) was cleaved by the action of KOH in toluene upon heating at reflux [4, 5]. The yield of ethynylcarbazole (X) was 75%. Oxidation of (X) by O_2 in the presence of CuCl in pyridine at 20-30°C gave the dehydrodimer (XI) in 74% yield.



EXPERIMENTAL

The PMR spectra were taken on a Varian XL-200 spectrometer. The IR spectra were taken on a UR-20 spectrometer.

9-Methyl-3-phenylethynylcarbazole (I). A mixture of 10.8 g (V) [6], 8 g (VII), 80 mg $Pd(PPh_3)_2Cl_2$, and 40 mg CuI in 80 ml Et_2NH was heated in an argon atmosphere for 8 h at 50°C

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TABLE 1. Acetylenic Derivatives of 9-Methylcarbazoles

Compound	Yield, % (time, h)	Mp, °C (hexane)	Chemical formula	$\frac{\text{Found}}{\text{Calculated}}$, %			PMR spectrum in $CDCl_3$ (δ, ppm)	IR spectrum ($CHCl_3$, $\nu C{\equiv}C$, cm^{-1})
				C	H	N		
(I)	93,4 (8)	125–126	$C_{21}H_{15}N$	$\frac{89{,}62}{89{,}65}$	$\frac{5{,}67}{5{,}37}$	$\frac{5{,}31}{4{,}98}$	3,75 (CH_3), 7,2–7,8 **m** ($H^{1,2,6-8}$ and Ph), 8,10 **d** (H^5), 8,35 (H^4)	2225
(II)	75,0 (10,5)	37–38	$C_{21}H_{23}N$	$\frac{86{,}88}{87{,}15}$	$\frac{7{,}99}{8{,}01}$	$\frac{5{,}24}{4{,}84}$	0,95 **t** ($\underline{CH_3}CH_2$), 1,3–1,7 **m** (CH_3, $\underline{(CH_2)_4}$), 2,48 **t** ($C-CH_2$), 3,77 ($N-CH_3$), 7,2–7,6 **m** ($H^{1,2,6-8}$), 8,10 **d** (H^5), 8,25 (H^4)	2230
(III)	70,4 (24)	89–90	$C_{18}H_{17}NO$	$\frac{82{,}13}{82{,}10}$	$\frac{6{,}56}{6{,}51}$	$\frac{5{,}57}{5{,}32}$	1,60 ($(CH_3)_2$), 2,05 (OH), 3,72 ($N-CH_3$), 7,2–7,4 ($H^{1,2,6-8}$), 8,01 **d** (H^5), 8,10 (H^4)	2235 (3625, OH)
(IV)	70,0 (8,5)	217–218	$C_{29}H_{19}N$	$\frac{91{,}13}{91{,}31}$	$\frac{5{,}33}{5{,}02}$	$\frac{3{,}62}{3{,}67}$	3,89 (CH_3), 7,2–7,7 **m** ($H^{1,2,7,8}$ and Ph), 8,24 ($H^{4,5}$)	2200
(X)	74,9 (2)	76–77	$C_{15}H_{11}N$	$\frac{87{,}73}{87{,}77}$	$\frac{5{,}41}{5{,}40}$	$\frac{6{,}68}{6{,}82}$	3,00 (CH), 3,74 (CH_3), 7,2–7,5 **m** ($H^{1,2,6-8}$), 7,95 **d** (H^5), 8,17 (H^4)	2115 (3300, CH)
(XI)	74,3 (2)	212–213 (dichloroethane)	$C_{30}H_{20}N_2$	$\frac{88{,}23}{88{,}21}$	$\frac{5{,}12}{4{,}94}$	$\frac{6{,}80}{6{,}86}$	3,85 (CH_3), 7,3–7,7 **m** ($H^{1,2,6-8}$), 8,07 **d** (H^5), 8,30 (H^4)	(KBr) 2130, 2205 ($C{\equiv}C-C{\equiv}C$)

until (V) was no longer present as indicated by thin-layer chromatography on Silufol plates with elution by 1:1 hexane—benzene. The mixture was poured into 500 ml ether and filtered through a 50 × 40-mm alumina column. The solvent was distilled off and the residue was recrystallized from CCl_4—hexane. The yield of (I) was 9.2 g (Table 1).

Products (II) and (III) were obtained analogously from (V) and (IV) was obtained analogously from (VI) [7].

9-Methyl-3-ethynylcarbazole (X). A mixture of 6.0 g (III) and 1.2 g powdered KOH in 80 ml abs. toluene was heated for 2 h at 110°C, cooled, and filtered through a 20 × 20-mm alumina column. The solvent was distilled off and the residue was recrystallized from hexane to give 3.5 g (X) (Table 1).

1,4-Di(9-methyl-3-carbazolyl)-1,3-butadiyne (XI). Air was bubbled through a mixture of 3.9 g (X) and 0.5 g CuCl in 35 ml pyridine and 10 ml methanol with vigorous stirring for 2 h. The temperature of the reaction mixture rose to 30°C. The reaction mixture was poured into 300 ml water. The residue was filtered off, washed with dilute ammonium hydroxide and, then, water, dissolved in dichloroethane, and filtered through a 20 × 20-mm alumina column. The solvent was distilled off and recrystallization of the residue from dichloroethane gave 2.9 g (XI) (Table 1).

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