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SYNTHESIS OF NEW DIACETYLENIC MONOMERS

CONTAINING NITROXYL RADICALS

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A series of new symmetrical and asymmetrical disubstituted diacetylenic monomers containing piperidine and carboline nitroxyl radicals were synthesized. These compounds are starting reagents for the synthesis of polyconjugated high-spin species.

The problem of synthesizing disubstituted diacetylenes containing stable free radicals in the side chain arose in the search for organic molecular ferromagnets. This problem has been examined theoretically by a number of workers [1-3]. A polyradical with a conjugated bond system has been proposed as a model for a high-spin "ferromagnetic" molecule, whose total spin is proportional to the number of units in the chain. Mono- and diacetylenic compounds containing nitroxyl radicals are promising starting reagents for the synthesis of such species. For example, the solid-phase polymerization of the diacetylenic diradical BIPO (1,4-bis-(2,2,6,6-tetramethyl-1-oxyl-4-hydroxy-4-piperidyl)butadiyne) gave the first high-temperature organic ferromagnet [4]. However, its polymerization was accompanied by a number of side reactions, including radical annihilation, which was apparently one of the reasons for the extremely low yield of the ferromagnetic fraction.

These difficulties might be overcome by carrying out the reaction through truly topochemical polymerization, which is extremely characteristic for disubstituted diacetylenes [5]. In the case of BIPO, this possibility is excluded since the molecular packing in the crystal lattice of the monomer [6], which specifically determines the feasibility of a truly topochemical reaction, does not satisfy the Baughman criteria [7].

In the present article, we attempted to synthesize new nitroxyl-substituted diacetylenic monomers in order to study their capacity to undergo solid-phase topochemical polymerization. In accord with the scheme given below, we synthesized monomers (III), (IV), (VI), (IX), (X), and (XI).

Asymmetrically substituted diacetylenes were obtained by cross-coupling reactions [8], while symmetrical diradical (XI) was obtained by oxidative dimerization of (VIII) [9]. Furthermore, this diradical was obtained in the syntheses of (IX) and (X) as a side product.



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Radicals (I) and (VII) were obtained by our previous procedures [10,11]. Iodoacetylenes (II) and (V) were synthesized by treating propargyl alcohol and N-propargylcarbazole, respectively, with sodium hypoiodite. The alkylation of carboline (VII) and of the carbazole was carried out under phase transfer catalysis conditions in the presence of triethylbenzylammonium chloride [12] (Table 1).

The EPR spectra of nitroxyls (III), (IV), (VI), (IX), and (X) are triplets (Fig. 1), while the spectrum of diradical (XI) is a quintuplet with  $J \gg a$  (Fig. 1). The ratio of the line intensities is independent of temperature and solvent polarity, which indicates spin-spin exchange through the hexadiyne bridge. The distance between the N-O<sup>-</sup> fragments of the diradical was estimated using the EPR spectrum of a toluene solution of (XI) in the glassy state at 77 K and an empirical parameter for the spectral shape  $d_1/d$  (Fig. 1); r = 15.7 Å [13].

## EXPERIMENTAL

 $\frac{1-(2;2,6,6-\text{Tetramethyl-1-oxyl-1},2,5,6-\text{tetrahydropyridinyl-4})-\text{penta-1},3-\text{diyn-5-ol} (III)}{\text{A solution of 5.45 g (0.03 mole) (II) in 3 ml THF was added dropwise with stirring in an argon stream over 20 min to a mixture of 7 ml THF, 6 ml 70% aqueous ethylamine, 0.3 g CuCl, 0.15 g NH<sub>2</sub>OH·HCl, and 5.35 g (0.03 mole) (I). The reaction mixture was stirred for an$ 

DA monomers	Color, crys- tal shape (solvent)	Mp, °C	Found/Calculated, %				-bec-	IR spectrum
			С	н	N	S	UV sl trum	cm <sup>-1</sup>
C14H18NO2 (III)	Yellow, needles (ethyl acetate- hexane)	128	72,59	7,81 7,76	6,09 6,03	_	218 254 267 283	3350 (−OH) 2230, 2043 (−C≡C−)
C21H2,NO,S (IV)	Pink, needles (hexane)	56	65,33 65,28	<u>6,29</u> 6,22	<u>3,61</u> 3,63	8,03 8,29	219 258 270 284	1178 (-SO <sub>2</sub> -) 2230, 2143 (-C=C-)
C <sub>26</sub> H <sub>25</sub> N <sub>2</sub> O (VI)	Yellow, plate- lets (acetone- hexane)	121	81,98 81,89	6,78 6,57	7,41 7,35	-	214 234 284 289	1460 (carbazole ring) 2230,2144 (-C=C-)
C <sub>21</sub> H <sub>23</sub> N <sub>2</sub> O <sub>2</sub> (IX)	Orange, prisms (acetone-hex- ane)	160	75,34 75,22	7,01 6,87	<u>8,40</u> 8,36	-	224 283	3350 (-OH) 1452 (carboline ring) 2256, 2130, 2042 (-C=C-)
C33H30N3O (X)	Orange, plate- lets (acetone- hexane)	179	81,93 81,81	<u>6,38</u> 6,20	8,59 8,68	_	229 290	1452 (carboline ring) 1460 (carbazole ring) 2260,2187,2143 (-C≡C-)
C36H40N4O2 (XI)	Red orange, prisms (ether)	210	77,18 77,14	7,23 7,14	9,87 10,00	-	224 282	1452 (carboline ring)

## TABLE 1. Physical Indices and Elemental Analysis Data for Diacetylenic Monomers



Fig. 1. EPR spectra of diacetylenic monomers (IX) (a) and (XI) (b,c) in toluene at 293 (a,b) and 77 K (c).

additional 1 h. The reaction was exothermal. The temperature was maintained at 27-30°C. The reaction mixture was poured into 60 ml 1% aqueous NaCN and then extracted with ether. The extract was washed with water and dried over MgSO<sub>4</sub>. Chromatography on a column packed with silica gel L100/160 with 3:7 ethyl acetate-hexane as the eluent gave 1.6 g (23%) (III). 1-(2.2.6.6-Tetramethyl-1-oxyl-1.2.5.6-tetrahydropyridinyl-4)-5-(1-sulfonyloxy-4-

<u>methylphenyl)penta-1,3-diyne (IV)</u>. A sample of 0.55 ml pyridine was added to a solution of 0.76 g (0.003 mole) (III) in 3.5 ml chloroform and then 0.78 g finely ground p-toluene-

sulfonyl chloride was added in small portions over 25 min with stirring to the solution at  $-5^{\circ}$ C. The reaction mixture was stirred for an additional 2 h and, then, 4 ml water and 10 ml ether were added. The ethereal layer was separated and repeatedly washed with hydrochloric acid (pH = 4) and then water. The solution was dried over MgSO<sub>4</sub>. Chromatography as described above and recrystallization from hexane gave 0.67 g (58%) (IV).

<u>1-(2.2.6.6-Tetramethyl-1-oxyl-1.2.5.6-tetrahydropyridinyl-4)-5-(N-carbazolyl)- penta-1.</u> <u>3-diyne (VI)</u>. A solution of 1.49 g (V) in 3 ml DMF was added dropwise over 20 min with stirring in an argon stream to a mixture of 7 ml DMF, 2.2 ml 70% aqueous ethylamine, 0.025 g CuCl, 0.05 g NH<sub>2</sub>OH·HCl, and 1.15 g (0.0065 mole) (I). The reaction mixture was stirred for an additional 1.5 h. The product was isolated by analogy to (III) by chromatography with chloroform as the eluent to give 0.79 g (32%) (VI).

2.2.4.4.-Tetramethyl-1.2.3.4-tetrahydro-3-oxyl-9-(2-propynyl)- $\gamma$ -carboline (VIII). A solution of 2 ml propargyl bromide in 3 ml DMSO was added dropwise with stirring to a mixture of 3.4 g (0.014 mole) (VII), 100 ml CH<sub>2</sub>Cl<sub>2</sub>, 3 ml DMSO, 5.5 ml 50% aq. NaOH, and 0.02 g C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>N(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>Cl (TEBA). The reaction mixture was stirred for 10-12 h at 20°C and then diluted with an equal volume of water. The colored layer was separated, washed with water, and dried over MgSO<sub>4</sub>. Column chromatography as described above and recrystallization from ether gave 1.79 g (46%) (VIII) as red orange crystals with mp 146°C. Found: C, 76.78; H, 7.40; N, 10.15%. Calculated for C<sub>18</sub>H<sub>21</sub>N<sub>2</sub>O: C, 76.85; H, 7.52; N, 9.96%. M = 281.38.

<u>1-[9-(2,2,4,4-Tetramethyl-1,2,3,4-tetrahydro-3-oxyl- $\gamma$ -carbolinyl)]hexa-2,4-diyn-6-ol</u> (<u>IX</u>). A solution of 1.45 g (II) in 1 ml THF was added dropwise with stirring over 20 min in an argon stream to a mixture of 2.8 g (0.01 mole) (VIII), 0.025 g CuCl, 2 ml 70% ag. ethylamine, 0.05 g NH<sub>2</sub>OH·HCl, and 8 ml THF and then stirred for an additional 1.5 h. The product was separated by analogy to (III). Column chromatography as described above and recrystallization from acetone-hexane gave 0.81 g (24%) (IX).

<u>1-[9-(2,2,4,4-Teramethyl-1,2,3,4-tetrahydro-3-oxyl- $\gamma$ -carbolinyl)]-6-(N-carbazolyl)-hexa-2,4-diyne(X)</u>. A solution of 2.2 g(V) in 3 ml DMF was added dropwise over 20 min in an argon stream to a mixture of 1.8 g (0.0064 mole) (VIII), 0.013 g CuCl, 1.2 ml 70% aq. ethylamine, 0.03 g NH<sub>2</sub>OH·HCl and 7 ml DMF. After stirring for 2 h the product was separated by analogy to (III). Column chromatography as described above and recrystallization from acetone-hexane gave 0.88 g (28.3%) (X).

<u>1.6-Bis-[9-(2.2.4,4-tetramethyl-1,2.3,4-tetrahydro-3-oxyl- $\gamma$ -carbolinyl)]hexa-2,4-diyne</u> (XI). A sample of 0.1 g CuCl and 7 ml acetone were added to a flask equipped with a stirrer, reflux condenser, and oxygen bubbler, and dropping funnel and then 0.12 g N,N,N',N'-tetramethylethylenediamine (TMEDA) was added with stirring. Oxygen was introduced for 10-15 min with stirring. A solution of 2.8 g (0.01 mole) (VIII) in 3 ml acetone was then added dropwise over 15 min with cooling of the flask when necessary in a water bath so that the temperature did not exceed 35-40°C. The mixture was stirred for an additional 2 h and poured into water. The product was obtained as a yellow precipitate, which was separated by filtration, dried, subjected to column chromatography as described above to give 1.06 g (38%) (XI).

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