SYNTHESIS OF 9,10-DIACETYLENYLANTHRACENES

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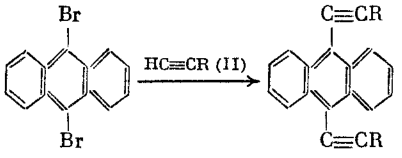
Syntheses are reported for 9,10-bis(phenylethynyl)anthracene and its derivatives containing identical and different substituents in the phenyl groups by the acetylenic condensation of 9,10-dibromoanthracene. The introduction of a donor substituent into one phenyl group and a withdrawing substituent into the other leads to a significant shift of the fluorescence maximum toward longer wavelengths.

9,10-Bis(phenylethynyl)anthracene and its 1-chloro, 2-chloro, and 1,8-dichloro derivatives are components of chemiluminescent compositions [1]. These and related compounds, containing other substituents in the anthracene ring and/or substituents in the phenyl rings, as a rule, are synthesized by the ethynylation of the corresponding anthraquinones by lithium arylacetylenides with subsequent reductive aromatization of the glycols formed using $SnCl_2$ in acetic acid [2-6]. Such anthracenes with two identical acetylene groups at C^9 and C^{10} have attracted the bulk of the attention. Most of these compounds have a fluorescence maximum at 510-550 nm and this maximum is shifted toward longer wavelengths by 10-30 nm only in a few cases [5-9].

We have found that an alternative general method for the synthesis of 9,10-bisacetylenylanthracenes lies in the condensation of dibromoanthracene (I) with terminal acetylenes. This method is applicable for the introduction of both the same and different acetylenic substituents into the anthracene system.



(I) (III)

R = Ph (a), p-C_6H_4OMe (b)

The reaction of (I) with arylacetylenes (IIa) and (IIb) in the presence of $Pd(PPh_3)_2Cl_2$ and CuI in Et_3N [10] at reflux is complete after 1 h. The yields of (IIIa) and (IIIb) were up to 89%. Large amounts of the amine are required due to the poor solubility of (I) in Et_3N. This inconvenience may be eliminated and the bulk of the solvent may be considerably reduced if most of the Et_3N is replaced by pyridine. The yields of (III) in this case are hardly changed.

Bisacetylenes containing a "push-pull" conjugation system, i.e., having an electron-donor substituent at the para position of one phenyl ring and electron-withdrawing substituent at the para position of the other, hold the greatest interest among asymmetric 9,10-disubstituted anthracenes. For these compounds, we should expect significant shifts of the fluorescence maximum toward longer wavelengths. The scope of the proposed method in this regard was demonstrated in the synthesis of 9-*p*-methoxyphenylethynyl-10-*p*-nitrophenylethynylanthracene.

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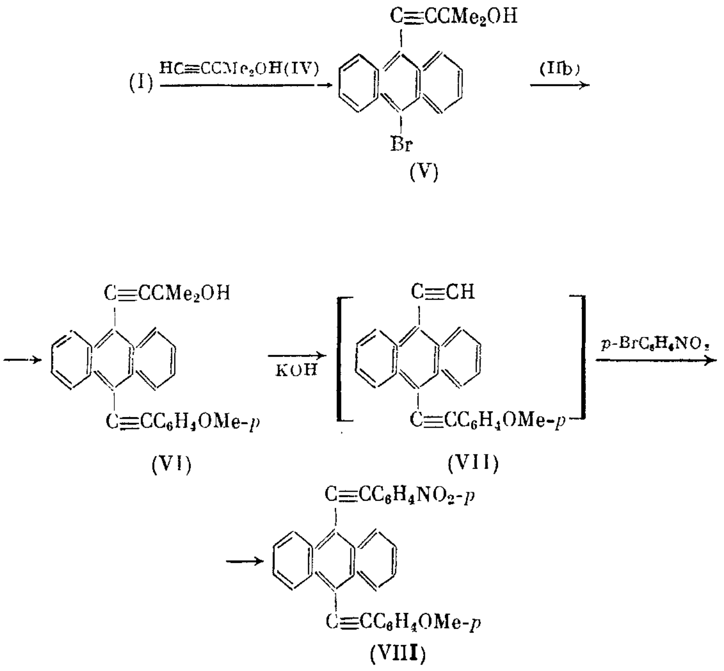

Dibromide (I) was condensed with HC≡CCMe$_2$OH (IV) taken in 25% excess in Et$_3$N-pyridine in the presence of a Pd-Cu catalyst at 100°C over 1.5-2 h. Unreacted (I) was precipitated by the addition of water. Acetylene (V) was separated from the water-pyridine solution by chloroform extraction and chromatography. The yield of (V) was 49% relative to (I). The condensation of (V) with (IIb) was carried out analogously but in Et$_3$N at reflux for 3 h. The yield of (VI) was 72%. The enhanced reactivity of bromides (I) and (V) in the acetylene concentration in comparison with unactivated bromoarenes [11] is probably a consequence of the high nucleofugic lability of the halogen atom in the anthracene meso position, which is further enhanced by the effect of the electron-withdrawing substituents in the ring, namely, a bromine atom or acetylene group.

Tertiary acetylenic alcohol (VI) was cleaved by KOH in toluene in the presence of a crown ether [12]. Labile ethynylanthracene (VII) was purified by chromatography and used without further isolation. The condensation of (VII) with *p*-bromonitrobenzene led to asymmetrically substituted diacetylene (VIII) in 79% yield.

Anthracene (VIII), in contrast to (III), which are orange compounds, is cherry-red with a fluorescence maximum at 590 nm; this maximum for (IIIa) is found at 510 nm.

EXPERIMENTAL

The PMR spectra were taken on a Jeol FX 90Q spectrometer in CDCl$_3$.

9,10-Bis(phenylethynyl)anthracene (IIIa). *a*. A mixture of 0.67 g (I), 0.51 g (IIa), 24 mg Pd(PPh$_3$)$_2$Cl$_2$, and 12 mg CuI in 140 ml Et$_3$N was stirred at 89°C for 1 h and Et$_3$N was distilled off in vacuum. The residue in 100 ml dioxane was heated to reflux. A sample of 100 ml hot water was added. The mixture was cooled. The precipitate was cooled and washed with water, acetone, and ether to give 0.67 g (IIIa) (see Table 1).

b. A mixture of 3.36 g (I) and 2.55 g (IIa) was condensed in the presence of 70 mg Pd(PPh$_3$)$_2$Cl$_2$ and 190 mg CuI in 50 ml pyridine and 30 ml Et$_3$N at reflux (102°C) over 1.5 h. Then, 150 ml hot water was added and the mixture was cooled to give 3.15 g (IIIa).

9,10-Bis(p-methoxyphenylethynyl)anthracene (IIIb) was obtained from 0.67 g (I) and 0.66 g (IIb) by analogy to (IIIa) (procedure *a*). The yield of (IIIb) was 0.78 g (see Table 1).

9-Bromo-10-(3-hydroxy-3-methylbutynyl)anthracene (V). A mixture of 6.72 g (I), 2.10 g (IV), 0.24 g Pd(PPh$_3$)$_2$Cl$_2$, 0.24 g CuI in 90 ml pyridiene and 30 ml Et$_3$N was stirred in an argon atmosphere at reflux for 1.5 h. Then, 600 ml water was added. The precipitate formed was filtered off and washed with water and acetone. A total of 3.62 g (I) was recovered. Then, 200 ml chloroform was added to the filtrate and the organic layer was washed with 500

TABLE 1. Acetylenic Anthracene Derivatives

Compound	Mp, °C (from	Chemical formula	Found/Calculated, %			PMR spectrum (δ, ppm)
			C	H	Br(N)	
(IIIa)	253–4 [6]	$C_{30}H_{18}$	–	–	–	7,41—7.48 m (6H, Ph), 7,58—7,80 m (8H, Ph, $H^{2,3,6,7}$), 8,64—8,75 m ($H^{1,4,5,8}$)
(IIIb)	240–1 [6]	$C_{32}H_{22}O_2$	–	–	–	3,88 (OCH_3), 6,97 d ($H^{3',5'}$), 7,56—7,76 m ($H^{2,2',3,6,6',7}$), 8,62—8,74 m ($H^{1,4,5,8}$)
(V)	123–4 (C_6H_6–hexane)	$C_{19}H_{15}BrO$	67.35 67,27	4.42 4,46	23.59 23,55	1,84 (CH_3), 2,28 (OH), 7,54—7,56 m ($H^{2,3,6,7}$), 8,47—8,58 m ($H^{1,4,5,8}$)
(VI)	155–6 (C_6H_6–hexane)	$C_{28}H_{22}O_2$	86.13 86,12	5.69 5,68	–	1,85 (CH_3), 2,27 (OH), 3,38 (OCH_3), 6,97 d ($H^{3',5'}$), 7,54—7,75 m ($H^{2,2',3,6,6',7}$), 8,46—8,71 m ($H^{1,4,5,8}$)
(VIII)	255.5–6.5	$C_{31}H_{19}NO_3$	82.06 82,10	4.19 4,22	(3.08) (3,09)	3,86 (OCH_3), 7,06 d ($H^{3',5'}$), 7,70—7,79 m ($H^{2,2',3,6,6',7}$), 8,03 d, 8,29 d ($H^{2'',3'',5'',6''}$), 8,56—8,69 m ($H^{1,4,5,8}$)*

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*In DMSO-d_6.

ml water, 1.5 liter 5% hydrochloric acid, and 1.5 liter water. The solvent was distilled off in vacuum. Chromatography on silica gel in benzene with subsequent recrystallization from benzene-hexane gave 1.54 g (V) (Table 1).

9-(3-Hydroxy-3-methylbutynyl)-10-(p-methoxyphenylethynyl)anthracene (VI). A mixture of 1.70 g (V), 0.79 g (IIb), 100 mg $Pd(PPh_3)_2Cl_2$, and 50 mg CuI in 100 ml Et_3N was stirred in an argon atmosphere at 89°C for 3 h. Then, 100 ml ether was added. Triethylamine hydrochloride was filtered off and the solvent was distilled off in vacuum. In order to remove all traces of Et_3N, 100 ml toluene was added to the residue and the solvent was distilled off in vacuum. Chromatography on 200 cm^3 silica gel in benzene and 1:1 benzene-dichloroethane gave 1.41 g (VI) (Table 1).

9-(p-Methoxyphenylethynyl)-10-(p-nitrophenylethynyl)anthracene (VIII). A mixture of 1.17 g (VI), 0.17 roasted KOH powder, and 0.10 g dibenzo-18-crown-6 in 80 ml dry toluene was stirred at 70°C for 15 min. KOH was filtered off. The reaction mixture was placed on a 2.8 × 10-cm silica gel column and (VII) was eluted with benzene. The fractions containing (VII) were reduced to a volume of 150 ml and used in the next step.

Then, 0.70 g p-bromonitrobenzene and 100 ml Et_3N were added to the solution of (VII). A sample of 0.10 g $Pd(PPh_3)_2Cl_2$ was added at reflux. The reaction mixture was stirred for 15 min and the solvent was distilled off in vacuum. The residue was treated as described for (IIIa) (procedure a). The yield of (VIII) was 1.08 g (Table 1).

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