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ACETYLENIC DERIVATIVES OF ANTHRAQUINONE

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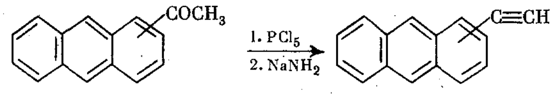
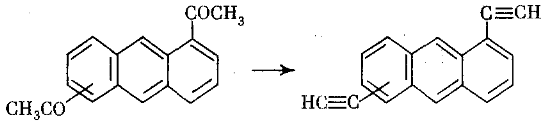
Acetylenic derivatives of condensed aromatic hydrocarbons can be oxidized to the corresponding quinones with a retention of the C≡C bond [1]. In the present paper this path was used to synthesize a number of acetylenylanthraquinones, including ethynylanthraquinones.

Ethynyl compounds (I)-(IV) were synthesized in 46-56% yields by reacting methyl ketones (V)-(VIII) with PCl_5 in benzene at 60°C, or in $POCl_3$ at 110°, and subsequent dehydrochlorination of the formed chlorides with $NaNH_2$ in liquid NH_3. The time of the first of these reactions in benzene is 10-20 times greater than in $POCl_3$; α-anthryl ketones (VI)-(VIII) are much more active than ketone (V).

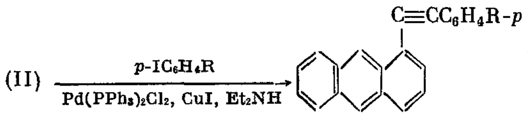


2-(V), 1-(VI) 2-(I), 1-(II)



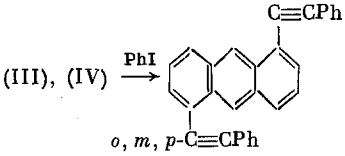
5-(VII), 8-(VIII) 5-(III), 8-(IV)

Compounds (II)-(IV) were used to obtain the disubstituted acetylenes (IX)-(XV). They proved to be active acetylenic components in the condensation with aryl iodides and carboxylic acid chlorides. Their reaction time with PhI in the presence of a complex Pd catalyst and Cu(I) salts in Et_2NH [2] was 0.5-1 h at 45°, and 4-5 h at 20°. The time was quite dependent on the structure of the aryl halide: The time of condensing (II) with p-iodoanisole at 45° reached 4 h, but with p-iodonitrobenzene it decreased to 1.5 h at 15°. The yields of the arylethynylanthracenes (IX)-(XIII) were 70-80% (Table 1).



(IX) — (XI)

R = H (IX), OCH_3 (X), NO_2 (XI)



5-(XII), 8-(XIII)

The benzoylation of (II) under the conditions given in [5] led to 1-(benzoylethynyl)-anthracene (XIV) in 94.5% yield.

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0568-5230/81/3002-0304$07.50

TABLE 1. Ethynylanthracenes and Their Derivatives

Compound	Condensation conditions		Yield, %	mp, °C	Empirical formula	Found/Calculated, %		ν, cm⁻¹ (CHCl₃)	
	time, h	T., °C				C	H	C≡C	C≡CH
(I)	–	–	46	181–182 (decompn., from benzene)	$C_{16}H_{10}$	94,97 95,02	4,98 4,98	2110	3320
(II)	–	–	76	90–91 (from ethanol) [3]	$C_{16}H_{10}$	–	–	2103	3318
(III)	–	–	47–50	>165 (decompn., from benzene)	$C_{18}H_{10}$	95,64 95,55	4,37 4,45	2112	3320
(IV)	–	–	50	141–142 (decompn.) [4]	$C_{18}H_{10}$	–	–	2110	3320
(IX)	0,5	45	77,2	88,5–89,5 (from hexane)	$C_{22}H_{14}$	95,03 94,93	5,09 5,07	2230 (CCl_4)	
(X)	4	45	77,7	123–124 (from ethanol)	$C_{23}H_{16}O$	89,63 89,58	5,20 5,23	2212	
(XI)	1,5	15	70,5	195–196 (from benzene)	$C_{22}H_{13}NO_2$	81,98 81,72	4,00* 4,05	2210	
(XII)	1	45	81,5	205,5–206,5 (from CCl_4)	$C_{30}H_{18}$	95,17 95,21	5,04 4,79	2217	
(XIII)	5	20	78,3	152,5–153,5 (from ethyl acetate)	$C_{30}H_{18}$	95,25 95,21	4,94 4,79	2212	
(XIV)	–	–	94,5	116–117 (from ethanol)	$C_{23}H_{14}O$	90,37 90,17	4,62 4,61	2192†	
(XV)	–	–	80,5	82–83 (from hexane)	$C_{21}H_{19}NO$	83,77 83,69	6,57‡ 6,35	2235 (CCl_4)	

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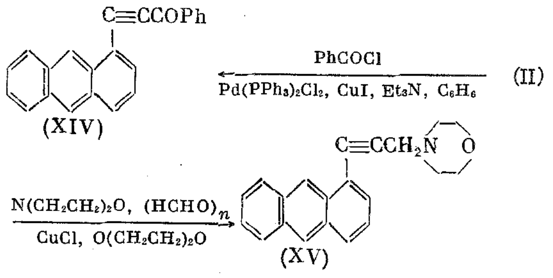
*Found: N 4.17%. Calculated: N 4.33%.

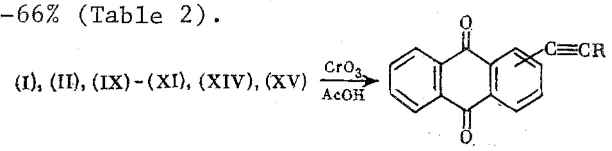
†νC=O 1640 cm⁻¹.

‡Found: N 4.82%. Calculated: N 4.65%. PMR spectrum (in CCl_4, δ, ppm): 2.58 t (4H, CH_2NCH_2), 3.63 t (4H, CH_2OCH_2), 3.54 s (2H, $NCH_2C≡$), 8.71 s and 8.13 s (2H, H^9 and H^{10}), 7.0-8.0 m (7H, H^2-H^8).



Aminopropynylanthracene (XV) was obtained in 80% yield by the aminomethylation of (II) with paraform and morpholine in dioxane at 80° in the presence of CuCl.

The synthesized acetylenylanthracenes (I)-(III) and (IX)-(XV) were oxidized to the quinones with CrO_3 in AcOH at 20-90°. The need to raise the temperature simultaneously with a decrease in the reaction time and (or) the use of dilute solutions of the reactants is due to the low solubility of some of the diacetylenes [(XI)-(XIV)] in AcOH. The yields of quinones (XVI)-(XXV) were 18-66% (Table 2).



β-, R=H (XVI); α-, R=H (XVII), Ph (XVIII), p-$CH_3OC_6H_4$ (XIX), p-$O_2NC_6H_4$ (XX), PhCO (XXI), $O(CH_2CH_2)_2NCH_2$ (XXII).

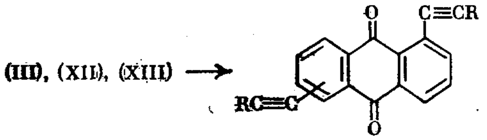
TABLE 2. Actylenylanthraquinones

Compound	Yield, %	Oxidation time, min	mp, °C	Empirical formula	Found/Calculated, %		Infrared spectrum (CHCl$_3$), ν, cm^{-1}		
					C	H	C≡C	HC≡C	C=O
(XVI)	62,5	250	~232–234 (from benzene)	$C_{16}H_8O_2$	82,92/82,75	3,65/3,47	2120	3310	1680
(XVII)	66	130	~222–225 (decompn.)	$C_{16}H_8O_2$	82,77/82,75	3,51/3,47	2115	3315	1680
(XVIII)	57	25	159–160 (from benzene) [6]	$C_{22}H_{12}O_2$	–	–	–	–	–
(XIX)	18	20	193–194 (from benzene–ethanol)	$C_{23}H_{14}O_3$	81,61/81,64	4,29/4,17	2210	–	1678
(XX)	43	10 *	214–215,5 (decompn., from ethyl acetate)	$C_{22}H_{11}NO_4$	74,83/74,78	3,07†/3,14	2212	–	1680
(XXI)	45	15	~223–224 (from dichloroethane)	$C_{23}H_{12}O_3$	81,46/82,13	3,64/3,60	2202	–	1680, 1643
(XXII)	34	25	154–155 (decompn., from MeCOEt)	$C_{21}H_{17}NO_3$	76,28/76,12	4,92†/5,17	2232	–	1680 ‡
(XXIII)	62	40	>220 (explosive decompn.)	$C_{18}H_8O_2$	84,24/84,36	3,17/3,15	2103 (KBr)	3270	1678
(XXIV)	49	6 *	~235–237 (decompn., from benzene–ethyl acetate)	$C_{30}H_{16}O_2$	88,15/88,22	4,04/3,95	2228	–	1690
(XXV)	31,5	6 *	166–167 (decompn. from ethyl acetate)	$C_{30}H_{16}O_2$	87,87/88,22	4,11/3,95	2215	–	1680

Reaction temperature for (XX) = 40°, (XXIV) = 90°, and (XXV) = 60°.

†Found/Calculated N, %: 3.90/3.96 (XX); 4.38/4.23 (XXII).

‡PMR spectrum (CDCl$_3$, δ, ppm): 2.69 t (4H, CH_2NCH_2), 3.74 t (4H, CH_2OCH_2), 3.60 s (2H, $NCH_2C\equiv$), 7.4-8.4 m (7H, ring H).



5-, R=H (XXIII), Ph (XXIV); 8-, R=Ph (XXV).

Ethynylquinones (XVI), (XVII), and (XXIII) are yellowish powders that change color when exposed to sunlight and gradually decompose when heated. Their melting points can be recorded with low accuracy only if the sample is heated rapidly (~3°/sec). Quinones (XVIII)-(XXII), (XXIV), and (XXV) range in color from yellow to orange, and they are more light stable. The structure of (XVI)-(XXV) was confirmed by the analytical and spectral data, while (XVIII) is identical with the sample synthesized by the condensation of 1-iodoanthraquinone with PhC≡CCu [6].

EXPERIMENTAL

The PMR spectra were taken on a Tesla BS 487-C spectrometer at a frequency of 80 MHz and a temperature of 25° (internal standard - MHDS), while the IR spectra were taken on a UR-20 instrument.

2-Acetylanthracene (V). To 16 g of anthracene in 10 ml of PhNO$_2$ at 15° were added 9.4 g of AcCl and 15 g of AlCl$_3$ in 50 ml of PhNO$_2$, and the mixture was stirred for 2 h and let stand for 2 days. The precipitate of the complex was filtered, washed twice with a little PhNO$_2$, and decomposed with dilute HCl solution. The product was extracted with CHCl$_3$, the extract was filtered through Al$_2$O$_3$ (II activity), the CHCl$_3$ was distilled off, and the residue was dissolved in methyl ethyl ketone and refluxed with active carbon. After filtration, concentration, and recrystallization, we obtained 4 g (20.2%) of (V), mp 188-189° [7].

1-Acetylanthracene (VI). The compound was obtained by acetylating anthracene as described in [8], but using the reverse order of mixing the reactants; yield 49%, mp 108-108.5° (from ethanol).

1,5-(VII) and 1,8-Diacetylanthracene (VIII). Anthracene was acetylated as described in [8]. Compounds (VII) and (VIII) were isolated by chromatography on Al_2O_3 (II activity) (eluants = CH_2Cl_2 and $CHCl_3$) and recrystallization from $CHCl_3$. Yield of (VII) = 38%, and mp 210-211°; yield of (VIII) - 15.1%, and mp 179.5-180°.

1,5-Diethynylanthracene (III). a) A mixture of 10.5 g of (VII) and 20 g of PCl_5 in 100 ml of abs. benzene was stirred for 22 h at 60°, cooled, poured into 300 ml of an ether—ice mixture, and the organic layer was separated, washed with water until neutral, and dried over $MgSO_4$.

b) A mixture of 10.5 g of (VII) and 25 g of PCl_5 in 100 ml of $POCl_3$ was refluxed for 2 h, the $POCl_3$ was vacuum-distilled, and the residue was dissolved in benzene and worked up as described above.

Dehydrochlorination. The benzene—ether solution of the obtained chlorides was added in 50 min to a suspension of $NaNH_2$ (from 21 g of Na in 800 ml of NH_3), stirred for 3 h, diluted with 300 ml of ether, and let stand to evaporate the NH_3. After removal of the NH_3, 200 ml of water were added cautiously with stirring, and the organic layer was separated, washed with water, and dried over $CaCl_2$. The obtained (III) in benzene was filtered through Al_2O_3 (II activity) and recrystallized from benzene.

In a similar manner were obtained: (I) (reaction time of (V) with PCl_5 in benzene = 140 h, and 12 h in $POCl_3$, but here the yield of (I) drops to 25.7%); (II) (reaction time of (VI) with PCl_5 in benzene = 16 h), and (IV) (reaction time of (VIII) with PCl_5 in $POCl_3$ = 6 h). The yields and constants of (I)-(IV) are given in Table 1.

1-(Phenylethnyyl)anthracene (IX). A mixture of 3 g of (II), 3.4 g of PhI, 90 mg of $(PPh_3)_2PdCl_2$, and 45 mg of CuI in 180 ml of Et_2NH was heated at 45° under N_2 for 30 min, diluted with 500 ml of benzene, washed with water, filtered through Al_2O_3 (II activity), and the solvent was removed. The residue was extracted with boiling petroleum ether (bp 70-100°), and (IX) was isolated by chromatography on Al_2O_3 (II activity, 50 × 150 mm) (eluant = 2:1 light petroleum ether—benzene mixture); the yields and constants are given in Table 1.

Compounds (X)-(XIII) were synthesized in a similar manner (see Table 1).

1-(Benzoylethynyl)anthracene (XIV). A mixture of 3 g of (II), 2.7 g of PhCOCl, 30 mg of $(PPH_3)_2PdCl_2$, and 30 mg CuI in a mixture of 30 ml of Et_3N and 30 ml of benzene was stirred under argon for 4 h (checked by TLC; Silufol, hexane), poured into 200 ml of dichloroethane, washed with ∿200 ml of 1:6 HCl solution, then with water, and filtered through Al_2O_3 (II activity, 30 × 100 mm). See Table 1 for yield and constants.

1-(3'-N-Morpholino-1'-propynyl)anthracene (XV). A mixture of 3 g of (II), 1.8 g of morpholine, 0.6 g of paraform, and 30 mg of CuCl in 150 ml of dioxane was heated at 80° under argon for 2 h, cooled, poured into an ether—water mixture, and the ether layer was separated, washed in succession with water, aqueous NH_3 solution, and water, dried over $MgSO_4$, and purified by chromatography on anhydrous Al_2O_3 (eluants = benzene and ether) (see Table 1).

1,5-Diethynylanthraquinone (XXIII). A solution of 0.8 g of CrO_3 in 25 ml of 80% AcOH was added in 10 min to a suspension of 0.6 g of (III), which was prepared by dissolving (III) in 50 ml of hot AcOH and then cooling to 20°. The reaction mixture was stirred for 30 min, poured into 300 ml of water, and the precipitate was filtered and washed in succession with water and chilled ethanol. We obtained 0.4 g (62%) of practically pure (XXIII). The analytical sample of (XXIII) was prepared by dissolving it in a large volume of benzene, filtration through a silica gel bed, concentration in the cold in vacuo, and filtration of the (XXIII) precipitate.

Acetylenylanthracenes (I), (II), and (IX)-(XV) were oxidized in a similar manner. The yields and constants of the obtained anthraquinones are given in Table 2.

CONCLUSIONS

1. A method was developed for the synthesis of the acetylenic, including the ethynyl, derivatives of anthraquinones by oxidizing acetylenylanthracenes with CrO_3 in AcOH.

2. The ethynylanthracenes are reactive acetylenic components in the condensation with aryl halides and carboxylic acid chlorides in the presence of Pd and Cu catalysts.

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VALENCE PHOTOISOMERIZATION OF 2H-PYRANS

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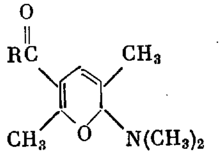
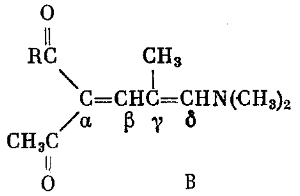
A study of the photoisomerization of 2H-pyrans is of interest from the standpoint of a detailed study of the mechanism of the reversible cleavage of the C-O bond. The reaction for the reversible cleavage of the C-O bond lies at the base of the photochromism of spiropyrans, which is one of the very important classes of photochromic compounds that find broad practical use, while the 2H-pyrans make it possible to directly study the cleavage of the C-O bond, not complicated by interaction with the heterocycle. In addition, it could be expected that the 2-amino-2H-pyrans themselves will exhibit photochromism, since the absorption spectrum of the dienic form B of the studied compounds is found at longer wavelengths than the spectrum of the 2H-pyran form A, in which the amino group is drawn out of the conjugation chain [1].



A



B

$R=CH_3$ (I), OCH_3 (II).

The purpose of the present paper is to study the mechanism of the photochemical opening of the ring and cyclization on the example of the 2-amino-2H-pyrans (IA) and (IIA), and also to ascertain the role of various isomers in the process of photo and dark isomerization.

Previously it was shown that, depending on the solvent and aggregate state, (I) and (II) can be found either as the cyclic pyran form A or as the acyclic dienone B, and also as an equilibrium mixture (EM) of these two forms [1, 2]. When the PMR method was used to study the stereochemistry of dienic δ-aminocarbonyl compounds of type $RCOCH_3COC{=}CH{-}CH{=}CHN(CH_3)_2$ it was shown that they represent an equilibrium mixture of geometric isomers relative to the $C_\alpha{=}C_\beta$ bond, with a trans configuration of the protons at the $C_\gamma{=}C_\delta$ bond, and exist predominantly as the s-trans conformers relative to the $C_\beta{-}C_\gamma$ bond [3].

Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow. N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 390-394, February, 1981. Original article submitted March 12, 1980.