UDC 542.91 + 547.362

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In the synthesis of aryldiacetylenes, aryl-substituted butynediols, butadienes, and acetylenes are usually used as starting compounds. For the preparation of a diacetylene from a diol the hydroxy groups are replaced by halogen and then two molecules of hydrogen halide are eliminated from the dihalide [1]. When an arylbutadiene is used, two molecules of bromine are added, and the resulting tetrabromide is dehydrobrominated [2]. An arylacetylene is condensed with a tertiary acetylenic alcohol, and the product is split by the reverse Favorskii reaction [3].

$$\label{eq:archieve} \begin{split} &\operatorname{ArCHOHC} \equiv \operatorname{CCH}_2\operatorname{OH} \to \operatorname{ArCHClC} \equiv \operatorname{CCH}_2\operatorname{CI} & & & \\ & & \\ & \operatorname{ArCH} = \operatorname{CH} = \operatorname{CH}_2 \to \operatorname{ArCHBrCHBrCHBrCH}_2\operatorname{Br} \to & \operatorname{ArC} \equiv \operatorname{C-C} \equiv \operatorname{CH} \\ & & \\ & & \\ & \operatorname{ArC} \equiv \operatorname{CH} \to \operatorname{ArC} \equiv \operatorname{C-C} \equiv \operatorname{CC} (\operatorname{OH}) \operatorname{RR'} & & & \\ & &$$

The application of these methods sometimes meets considerable difficulty associated with the poor accessibility of the starting substances, the instability of the intermediate products, etc. One of the most convenient methods for the synthesis of aromatic monoacetylenes consists of the replacement of the carbonyl oxygen of acetophenones by chlorine and subsequent dehydrochlorination [4]. This method has also been applied successfully for the preparation of a considerable number of mono- and poly-nuclear di- and triethynylarenes [5-11]. In the present work we have shown that β -diketones of general formula ArCOCH₂. COCH₃ may be used for the preparation of aryldiacetylenes by an analogous scheme. We synthesized the 1-aryl-1.3-butanediones (Ia)-(Ie) by the reaction of the corresponding aromatic hydrocarbon or acetophenone with acetic anhydride in presence of boron trifluoride. The need to use the monoketone arose only in the synthesis of (Ib) and (Ie), for under acetoacetylation conditions nitrobenzene does not react with acetic anhydride and can be used as a solvent [12], and benzene forms the diketone in very low yield [13]. The reaction temperature has a substantial effect on the yields of the β -diketones (I). Thus, at 50° 4'-nitroacetophenone is converted into the diketone (Ie) in 70% yield, but at $0-5^{\circ}$ the yield falls to 12%, and at from -10 to -15° (Ie) is practically absent in the reaction products. On the other hand, by lengthening of the side chain of acetophenone at 55° we obtained about 23% of (Ib), whereas at 0° the yield of the diketone attained 83.3% [14]. The replacement of the oxygen of the carbonyl groups in (I) by chlorine was effected by means of phosphorus pentachloride in benzene. To avoid violent reaction and the resinification of unsaturated chlorides. (I) was added gradually with vigorous stirring to a cooled (0°) suspension of phosphorus pentachloride in solvent. To complete the reaction the temperature was slowly raised to 50-60°. The mixture of chlorides obtained at this stage was dehydrochlorinated into (II) by means of sodamide in liquid ammonia. At the end of this reaction excess of sodamide was decomposed with dry ammonium chloride, and after the removal of ammonia and separation of the precipitate the product was chromatographed on alumina. The "dry method" shortened the time required for the isolation of the diacetylenes (II) considerably and made it possible to avoid their further resinification, which occurred when the treatment of the reaction mixture was prolonged. The aryldiacetylenes (IIa)-(IIe) are unstable substances, which can be preserved only in solution in the cold and in the dark. By oxidative dimerization they were converted into the relatively stable 1,8-diaryloctatetraynes (III), and by Favorskii reaction with cyclohexanone — into the diacetylenic alcohols (IV). From the latter the aryldiacetylenes (II) can readily be regenerated by cleavage in presence of potassium hydroxide [3] (see scheme on following page).

This method of converting an acetoacetyl group into a butadiynyl group has been extended by us to polynuclear diacetoacetyl derivatives and has formed the basis for the development of a method for the synthesis of dibutadiynylarenes [12, 15].

*This article is published in accordance with a Resolution of the Conference of Editors of Journals of the Academy of Sciences of the USSR of July 12, 1962, as a dissertation paper by V. N. Andrievskii.

Institute of Chemical Kinetics and Combustion, Siberian Division, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 882-886, May, 1966. Original article submitted July 25, 1964.

A	Yield,		- 1	Found %		Calculated %		IR spectrum, cm ⁻¹	
Ar	%	м.р., °С	Formula	C	Н	C	Η	C = C	$C \equiv CH$
C ₆ H ₅ -	42.2	B.p. 34-40° (0.04 mm) [18]	$C_{10}H_6$	-	_	-		—	
$p-CH_3OC_6H_4-$	24.4	61-62 (decomp.)	C ₁₁ H ₈ O	84.42	5.23	84.59	5,16	2207 s, 2060 w	3311 s
2,4,6-(CH ₃) ₃ . C ₆ H ₂ -	41.2	42-44 (decomp.)	$C_{13}H_{12}$	93.03	7,33	92.81	7.19	2215 s, 2188 m 2070 w	33 17 s
$p-C_6H_5C_6H_4-$	40.6	104-106 (de- comp.)	$C_{16}H_{10}$	95.02	4,98	95.24	5.11	2210 s	3313 s
$p-NO_2C_6H_4-$	41.8*	Decomp. > 100°, explodes at ~ 185°	$\mathrm{C_{10}H_5O_2N}^{\dagger}$		_			2225 w, 2076 w	3311 s

TABLE 1. Synthesis of Arylbutadiynes (II)

*In chromatography it was eluted with a 1:1 mixture of ether and CHCl₃.

† Found %: N 8.15. Calculated %: N 8.18. We could not carry out analysis for C and H because of high explosiveness.

TABLE 2. Freparation of the Diaryloctatetraynes (in	TABLE 2	2.	Preparation	of	the	Diaryloctatetraynes	(Π)	í)
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Ar		Mn °C	Formula	Found %		Calculated%		IR spectrum, cm ⁻¹	
	% Hip., C Formu		Tormula	С	Н	С	н	C = C	
C ₆ H ₅	90	114-115 (decomp., from pet. ether) [18]	$C_{20}H_{10}$		_		-	name.	
$p-CH_3OC_6H_4-$	80.5	190-192 (decomp., from CCl_4)	$\mathrm{C}_{22}\mathrm{H}_{14}\mathrm{O}_{2}$	85.20	4.50	85.14	4,55	2205s,2090w	
$2,4,6-(CH_3)_3C_6H_2-$	81	227-228 (decomp., from ethyl acetate)	$C_{26}H_{22}$	93.37	6.81	93.37	6.63	2200 s ,2090w	
$\mathrm{p}\text{-}\mathrm{C}_{6}\mathrm{H}_{5}\mathrm{C}_{6}\mathrm{H}_{4}-$	88,5	253-254 (decomp., from C_6H_6)	$\mathrm{C}_{32}\mathrm{H}_{18}$	95.68	4.56	95.49	4.51	2210 s, 2095 w	
$p-NO_2C_6H_4-$	80.7	Decomp. > 200° , explodes at ~ 260°	$C_{20}H_8O_4N_2*$	-	-	-	—	2210 s, 2135 m	

* Found %: N 8.44. Calculated %: N 8.23.



EXPERIMENTAL

Preparation of 1-Aryl-1,3-butanediones (I)

1-(4-Biphenyly1)-1,3-butanedione (Ia). Boron trifluoride, prepared from 150 g of boron oxide, 300 g of calcium fluoride, and 1500 ml of 5% oleum, was passed for 5.5 h into a solution of 80 g of biphenyl in 270 g of freshly distilled acetic anhydride at 55°, and the reaction mixture was stirred further

_	Yield, %	M.p., °C	Formula	Found %		Calculated %		IR spectrum, cm ⁻¹		
Ar				C	Η	C	Η	$C \equiv C$	ОН	
С ₆ Н ₅ —	68,5	102-103 (from pet. ether)	С ₁₆ Н ₁₆ О	86.07	7.25	85.68	7.19	2245 m, 2155 w	3605 s	
р-СH ₃ OC ₆ H ₄ —	46.8	88–90 (from pet. ether)	$\mathrm{C_{17}H_{18}O_2}$	80,63	7.26	80.28	7.13		-	
2,4,6−(CH ₃) ₃ · C ₆ H ₂ −	71.4	131-132 (from pet. ether)	$C_{19}H_{22}O$	85.54	8.40	85.67	8.33	2236 s, 2147 w	3605 s	
$p-C_6H_5C_6H_4$	72.4	118-119 (from C_6H_6 - pet. ether)	$\mathrm{C_{22}H_{20}O}$	88,13	6.78	87.96	6.71	2242 m, 2155 w	3605 s	

TABLE 3. Favorskii Reaction of Arylbutadiynes with Cyclohexanone

for 2 h at the same temperature and then decomposed by boiling it for 2 h with a solution of 400 g of $CH_3COONa \cdot 3H_2O$ in 1 liter of water. The mixture was cooled, and the precipitate was separated, washed with water and then a little alcohol, and dried. We obtained 121 g of product, m.p. 140-148°. Two crys-tallizations from propyl alcohol gave 100.5 g (81.4%) of (Ia), m.p. 158.5-159° [16].

<u>1-Phenyl-1,3-butanedione (Ib)</u>. This was prepared in a similar way to (Ia) from 120 g of acetophenone and 204 g of acetic anhydride at 55°. After the decomposition of the reaction mixture the product was dissolved in 500 ml of ether, and (Ib) was extracted with 2% NaOH solution. The cooled solution of the enolate was acidified with 1:3 hydrochloric acid, (Ib) was extracted with ether, and the extract was dried over $CaCl_2$ and distilled. Yield 37.2 g (22.9%); b.p. 137-141° (18 mm) [14].

1-p-Methoxyphenyl-1, 3-butanedione (Ic). Boron trifluoride was passed for 4 h into a solution of 90 g of 4'-methoxyacetophenone in 122 g of acetic anhydride at 0°. The reaction mixture was stirred for 2 h at 0°, and the reaction mixture was decomposed. (Ic) was isolated in the same way as (Ib). We obtained 34.5 g (30%) of (Ic) after two distillations; b.p. 143-146° (1 mm) [13].

<u>1-Mesityl-1,3-butanedione (Id)</u>. This was prepared by passing boron trifluoride into a solution of 60 g of mesitylene in 204 g of acetic anhydride for 4.5 h at 0° and then stirring for 3 h. The mixture was decomposed by boiling it with a solution of 400 g of $CH_3COONa \cdot 3H_2O$ in 1 liter of water for 20 min. An ether extract of the product was washed with saturated $NaHCO_3$ solution and water, dried over $CaCl_2$, and distilled twice. The yield of (Id) was 93.4 g (91.5%); b.p. 93-95° (1 mm) [13].

<u>1-p-Nitrophenyl-1,3-butanedione (Ie)</u>. Boron trifluoride was passed to saturation into a stirred mixture of 60 g of 4'-nitroacetophenone, 74 g of acetic anhydride, and 70 ml of nitrobenzene at 50°, after which the mixture was stirred for 2 h, a solution of 184 g of $CH_3COONa \cdot 3H_2O$ in 730 ml of water was added, and nitrobenzene was steam-distilled off. The mixture was cooled, and the precipitate was separated, washed with water, dried, and crystallized twice from 350 ml of alcohol. We obtained 52.5 g (70%) of (Ie), m.p. 109.5-110.5° [17]. Found %: C 58.04; H 4.21; N 6.86. $C_{10}H_9O_4N$. Calculated %: C 57.97; H 4.38; N 6.76.

Synthesis of Arylbutadiynes (II)

<u>(4-Biphenylyl) butadiyne (IIa)</u>. 4.6 g of the dione (Ia) was added with stirring and cooling with ice to a suspension of 9.5 g of PCl_5 in 50 ml of dry benzene. The reaction mixture was stirred for 30 min at 0° and for 30 min at 20°, and then the temperature was raised to 50° in the course of 1 h and kept at this temperature for 5 h. The cooled mixture was poured into 150 ml of ether containing ice, and the ether—benzene solution was washed with saturated NaHCO₃ solution and water and was dried over CaCl₂. The solution of chloro compounds was added in the course of 20 min to sodamide prepared from 7 g of sodium in 500 ml of liquid ammonia. After 90 min 17.5 g of NH₄Cl and 200 ml of ether were added, and ammonia was evaporated. The filtered solution of (IIa) with ether. The main fraction (120 ml) was diluted with an equal volume of light gasoline (b.p. 80-100°), and ether was removed in a vacuum. We obtained 1.6 g (40.6%) of (IIa). When heated rapidly on a block, (IIa) melted at about 104-106° (decomp.); when heated in a capillary it polymerized and darkened at 90-100°.

The arylbutadiynes (IIb)-(IIe) were synthesized similarly. The yields, constants, elemental analyses, and IR spectrum data of (II) are given in Table 1.

<u>Oxidative Dimerization of (II)</u>. A solution of 10 g of (IIa) and 0.5 g of Cu_2Cl_2 in 60 ml of pyridine was shaken in an atmosphere of oxygen for 90 min. The calculated amount of oxygen was absorbed. The reaction mixture was poured into 400 ml of acidified water, and the precipitate was filtered off, carefully washed with water, and dried. After two crystallizations from 1200-ml portions of benzene we obtained 8.8 g (88.5%) of the tetrayne (IIIa) in the form of yellow crystals, m.p. 243-245° (decomp.).

By the same method we dimerized the diacetylenes (IIb)-(IIe). The results are presented in Table 2.

<u>Reactions of the Aryldiacetylenes (II) with Cyclohexanone.</u> A solution of 4.5 g of (IIa) in 25 ml of ether was added gradually to a suspension of 3.8 g of KOH powder in 10 ml of dry ether at 0-5°. The reaction mixture was stirred for 2 h at this temperature, and then 3.2 g of cyclohexanone was added in the course of 10 min. The mixture was stirred for a few hours and then left overnight. The mass, which had become thick, was decomposed with water with cooling, and (IVa) was extracted with ether. The ethereal solution was neutralized with 3-5% sulfuric acid and dried over potassium carbonate. Solvent was driven off, and the residue was crystallized from a 1:5 mixture of benzene and petroleum ether. After two crystallizations the yield of (IVa) was 4.9 g (72.4%); m.p. 118-119°.

The diacetylenic alcohols (IVb)-(IVd) were synthesized in a similar way (Table 3).

CONCLUSIONS

1. A method is proposed for the synthesis of aryldiacetylenes from 1-aryl-1,3-butanediones.

2. By this method the synthesis was carried out of some previously undescribed aryldiacetylenes and also some of their derivatives — diacetylenic alcohols and diaryloctatetraynes.

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