ACETYLENIC ALCOHOLS AND AMINES OF THE DIPHENYL OXIDE SERIES

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It is known that relatively small changes in the structure of acetylenic compounds exert an important effect on their chemical properties. Thus, 4,4'-diethynyldiphenylalkanes unexpectedly react with ketones by the Favorskii reaction many times faster than do the corresponding monoacetylenes [1].

In the present paper we studied the behavior of the previously synthesized acetylenic derivatives of diphenyl oxide [2] in reactions involving the acetylenic hydrogen, and specifically the Favorskii, Iotsich and Mannich reactions. The reaction of 4-ethynyldiphenyl oxide (I) and 4,4'-diethynyldiphenyl oxide (II) with carbonyl compounds by the Favorskii reaction required several times less time than by the Iotsich reaction. Along with this, the yields of secondary alcohols in the latter case were higher (Tables 1 and 3). Acetophenone did not react with acetylene (I) under the selected conditions of the Favorskii reaction. (I) was easily and completely regenerated when tertiary acetylenic alcohols were vacuum-distilled with traces of KOH. In making an approximate estimate of the reactivity of acetylenes (I) and (II) in the Favorskii reaction we were unable to detect an important difference in their behavior, in contrast to the above mentioned case [1]. It was probably for this reason that we were unable to use this method to synthesize monohydric alcohol (III) from diacetylene (II), taken in large excess. Nevertheless, it can be obtained from benzophenone and the monosodium derivative of diacetylene (II) in liquid ammonia. Acetylenes (I) and (II) were also condensed with formaldehyde and various secondary amines by the Mannich reaction (Tables 2 and 4). A noticeable difference in their reactivity was not observed here. Diamines (XXXII)-(XXXVI) represent viscous noncrystallizing liquids that readily form crystalline dipicrates and dihydrochlorides, which can serve for their purification. Acetylenic alcohols (IV)-(X) and monoamines (XXII)-(XXVII) were hydrogenated on skeletal nickel at room temperature and atmospheric pressure to the corresponding saturated compounds (XI)-(XVII) and (XXVIII)-(XXXI).

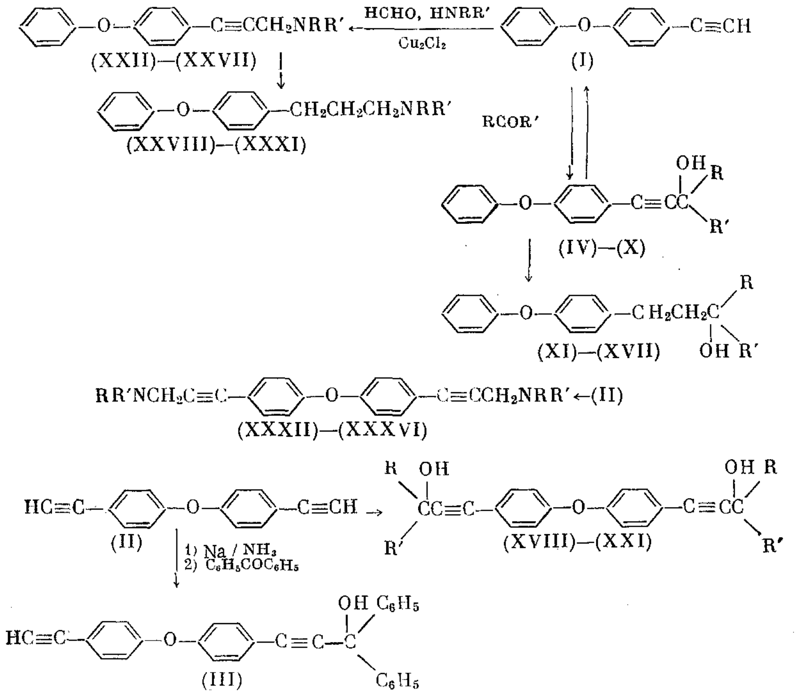

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TABLE 1

R	R′	Acetylenic alcohols									Hydrogenated alcohols							
		No.	yield, % method		b.p., °C (p, mm of Hg)	found, %		empirical formula	calc., %		No.	yield, %	b.p., °C (p, mm of Hg)	found, %		empirical formula	calc., %	
			A	B		C	H		C	H				C	H		C	H
CH_3	CH_3	IV	50	85,5	151—153 (1) M.p. 46,5—47,5	80,85	6,30	$C_{17}H_{16}O_2$	80,92	6,36	XI	79,5	165—166 (1)	79,64	7,80	$C_{17}H_{20}O_2$	79,65	7,86
—$(CH_2)_5$—		V	59	95,2	198—200 (1) M.p. 66—67	82,47	6,95	$C_{20}H_{20}O_2$	82,15	6,89	XII	89,5	187—189 (1)	80,92	8,07	$C_{20}H_{24}O_2$	81,04	8,16
CH_3	C_2H_5	VI	52,4	47,5	169—171(2,5)	81,22	6,78	$C_{18}H_{18}O_2$	81,17	6,81	XIII	83,6	184—185(2,5)	79,74	8,02	$C_{18}H_{22}O_2$	79,96	8,20
CH_3	p-C_4H_9	VII	48,4	80	190—193 (3)	81,92	7,30	$C_{20}H_{22}O_2$	81,60	7,53	XIV	92,1	184—185 (2)	80,82	8,72	$C_{20}H_{26}O_2$	80,49	8,78
CH_3	C_6H_5	VIII	51,2	—	226—229 (1)	84,11	5,94	$C_{22}H_{18}O_2$	84,05	5,77	XV	85	218—220 (2)	83,27	6,97	$C_{22}H_{22}O_2$	82,98	6,96
H	$(CH_3)_2CH$	IX	52,5	39,2	172—175 (3)	81,35	6,85	$C_{18}H_{18}O_2$	81,17	6,81	XVI	86,9	183—185(2,5)	79,64	8,02	$C_{18}H_{22}O_2$	79,96	8,20
H	$(CH_3)_2CHCH_2$	X	69	44,7	184—186 (3)	81,51	7,15	$C_{19}H_{20}O_2$	81,39	7,19	XVII	74,4	193—194(2,5)	80,13	8,58	$C_{19}H_{24}O_2$	80,24	8,51

TABLE 2

R	R′	Acetylenic amines						Hydrogenated amines					
		No.	yield, %	b.p., °C (p, mm of Hg)	found N, %	empirical formula	calc. N, %	No.	yield, %	b.p., °C (p, mm of Hg)	found N, %	empirical formula	calc. N, %
—$(CH_2)_5$—		XXII	79	199—200 (2)	4,91	$C_{20}H_{21}ON$	4,81	XXVIII	74,6	190—192 (2)	5,00	$C_{20}H_{25}ON$	4,74
—$CH_2CH_2OCH_2CH_2$—		XXIII	81,8	197—199 (2)	4,78	$C_{19}H_{19}O_2N$	4,77	XXIX	73,2	199—200 (2,5)	4,69	$C_{19}H_{23}O_2N$	4,71
C_2H_5	C_2H_5	XXIV	79	181—182 (2) *	5,11	$C_{19}H_{21}ON$	5,01	XXX	82,3	168—169 (2)	4,99	$C_{19}H_{25}ON$	4,94
$HOCH_2CH_2$	$HOCH_2CH_2$	XXV	96,7	M.p. 73—73,5 (ether)	4,69	$C_{21}H_{21}O_3N$	4,50	—	—	—	—	—	—
cyclo-C_6H_{11}	cyclo-C_6H_{11}	XXVI	84,8	M.p. 37—39†	—	$C_{27}H_{33}ON$	—	—	—	—	—	—	—
CH_3	CH_3	XXVII	50	166—168 (2)‡	5,50	$C_{17}H_{17}ON$	5,57	XXXI	80	170—172 (4)	5,53	$C_{17}H_{21}ON$	5,49

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*Picrate, m.p. 140-141° (alcohol). Found %: N 10.98. $C_{25}H_{24}O_8N_4$. Calculated %: N 11.02.

†Crude product; picrate, m.p. 172-172.5° (decomp.) (alcohol). Found %: N 8.90. $C_{33}H_{36}O_8N_4$. Calculated %: N 9.09

‡Picrate, m.p. 135.5-136.5° (alcohol). Found %: N 11.85. $C_{23}H_{20}O_8N_4$. Calculated %: N 11.66.

TABLE 3

Compound No.	R	R'	Yield, %	M.p., °C	Found, %		Empirical formula	Calculated, %	
					C	H		C	H
XVIII	CH_3	CH_3	79.4*	141.5-142.5 (benzene)	79.24	6.74	$C_{22}H_{22}O_3$	79.01	6.63
XIX	$-(CH_2)_5-$		94.3	138-138.5 (petroleum ether)	80.86	7.42	$C_{28}H_{30}O_3$	81.12	7.30
XX	CH_3	C_2H_5	> 90 †	119-119.5	79.72	7.12	$C_{24}H_{26}O_3$	79.53	7.23
XXI	CH_3	$(CH_3)_3C$	75	107.5-109	80.56	8.38	$C_{28}H_{34}O_3$	80.34	8.19

*Yield 69.7% by the Iotsich reaction.

†Crude product.

TABLE 4

Compound No.	R	R'	Yield, %	Characterized as	M.p., °C	Found, %		Empirical formula	Calculated, %	
						N	Cl		N	Cl
XXXII	$-(CH_2)_5-$	-	87.6	Dihydrochloride	265.5-266 (decomp.) (alcohol)	-	14.56	$C_{28}H_{34}ON_2Cl_2$	-	14.61
				Dipicrate	145-146 (C_3H_7OH)	12.85	-	$C_{40}H_{38}O_{15}N_8$	12.87	-
XXXIII	$-CH_2CH_2OCH_2CH_2-$	-	86.3	Dihydrochloride	245.5-247.5 (decomp.) (alcohol)	-	14.42	$C_{26}H_{30}O_3N_2Cl_2$	-	14.49
				Dipicrate	193.5-194 (decomp.) (alcohol)	12.66	-	$C_{38}H_{34}O_{17}N_8$	12.81	-
XXXIV	C_2H_5	C_2H_5	93.5	Base	-	7.41	-	$C_{26}H_{32}ON_2$	7.21	-
				Dipicrate	170.5-171 (decomp.) (C_3H_7OH)	13.38	-	$C_{38}H_{38}O_{15}N_8$	13.23	-
XXXV	$HOCH_2CH_2$	$HOCH_2CH_2$	80.2-86.5	Base	-	6.24	-	$C_{26}H_{32}O_5N_2$	6.19	-
XXXVI	CH_3	CH_3	35	Dihydrochloride	239-240 (decomp.)*	-	17.26	$C_{22}H_{26}ON_2Cl_2$	-	17.49

*In a sealed capillary.

EXPERIMENTAL

Preparation of 1-p-Phenoxyphenyl-2-(1'-hydroxycyclohexyl)acetylene (V). By the Iotsich Reaction (Method A). To the C_2H_5MgBr, obtained from 1.3 g of Mg and 6 g of C_2H_5Br in 45 ml of absolute ether, was added 10 g of acetylene (I) in 30 ml of ether. After stirring for 12-15 h, the heavy layer of the Iotsich complex was separated. Then, at 0°, was gradually added 4 g of cyclohexanone in 5-10 ml of ether and the reaction mass was stirred at 20° for another 1 to 2 days. The mixture was decomposed in conventional manner. Distillation gave 2-3 g of starting acetylene (I) and 7 g (59%) of acetylenic alcohol (V).

By the Favorskii Reaction (Method B). To a suspension of 8.6 g of powdered KOH in 50 ml of absolute ether, with vigorous stirring and ice cooling (0-5°), was added 10 g of acetylene (I) in 30 ml of ether in 15 min, and 6.9 g of cyclohexanone in 5-30 min. After stirring for 2 h the solid reaction mass was treated with water, the ether layer was separated, and the aqueous alkaline layer was extracted with ether. Vacuum-distillation gave 14.3 g (95.2%) of alcohol (V). In a similar manner were synthesized acetylenic alcohols (IV)-(X) using methods A and B (see Table 1), and glycols (XVIII)-(XXI) using method B (see Table 3).

Preparation of p-Ethynyl-p'-(3-hydroxy-3,3-diphenyl-1-propynyl)diphenyl Oxide (III). To a solution of 6.5 g of diacetylene (II) in a mixture of ml of absolute ether and 500 ml of liquid NH_3 was added in 30 min 0.7 g of Na in 300 ml of liquid NH_3. Then an ether solution of 5 g of benzophenone was added to the reaction mixture, after which the mixture was stirred for 3 h, followed by the addition of 300 ml of ether and 30 ml of water. After removal of the NH_3 the ether solution was washed with water, dried over potassium carbonate, and the solvent was distilled off. The residue (11 g) was chromatographed on an Al_2O_3 column, and the products were eluted in sequence with a mixture of benzene and petroleum ether (1:1 and 2:1), ether, and CH_3OH. We isolated 4.1 g of crude alcohol (III) with m.p. 100-117°, which was recrystallized from CH_3OH; yield 3 g (27.3%), m.p. 117-117.5°. Found %: C 86.99; H 4.92. $C_{29}H_{20}O_2$. Calculated %: C 86.99; H 5.03.

Preparation of 1-N-Piperidyl-3-p-phenoxyphenyl-2-propyne (XXII). A mixture of 1.9 g of acetylene (I), 0.94 g of piperidine, 0.4 g of paraform and 0.01 g of Cu_2Cl_2 in 10 ml of dioxane was refluxed for 2 h, after which it was diluted with 10 ml of ether and the amine (XXII) was extracted with dilute HCl solution. The HCl solution was washed with ether and then made alkaline with a mixture of concentrated NaOH solution and ice. The obtained oil was extracted with ether and then distilled. The yield of amine (XXII) was 2.3 g (79%). Acetylenic amines (XXIII)-(XXVII) and (XXXII)-(XXXVI) were synthesized in a similar manner (see Tables 2 and 4).

CONCLUSIONS

A number of alcohols and amines – derivatives of 4-ethynyldiphenyl oxide and 4,4'-diethynyldiphenyl oxide – were synthesized. Important differences in the reactivity of the starting mono- and diacetylenes in the Favorskii and Mannich reactions were not detected.

LITERATURE CITED

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