SYNTHESIS OF ACETYLENIC DERIVATIVES OF DIPHENYL OXIDE AND m-BITOLYL

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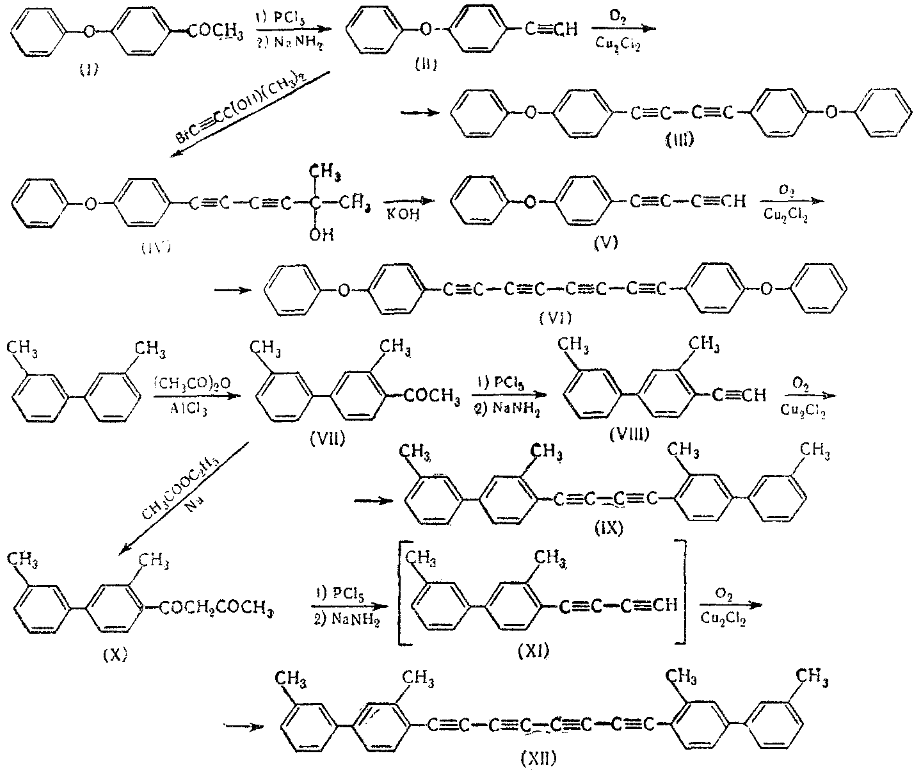
The arylacetylenes may be used to obtain polymeric compounds with conjugated multiple bonds by two schemes; polycondensation [1] and polymerization [2]. Previously we had described the synthesis and polycondensation of the diethynyl and dibutadynyl derivatives of diphenyl oxide and m-bitolyl [3, 4]. In this paper we accomplished the synthesis of some of the simpler acetylenes of the same series, which have importance as monomers. These compounds were obtained in the following manner.



Monoacetylenes (II) and (VIII) were obtained by replacing the oxygen by chlorine in the substituted acetophenones (I) and (VII) by treatment with phosphorus pentachloride and subsequent dehydrochlorination with sodium amide in liquid ammonia. Lengthening of the acetylenic chain of 4-ethynyldiphenyl oxide (II) was effected by condensing the latter with dimethylbromoethynylcarbinol employing the Chodkiewicz reaction [5] and subsequent cleavage of alcohol (IV) in the presence of KOH. An attempt to use an analogous method to lengthen the chain of acetylene (VIII) proved unsuccessful. Butadiyne (XI) was synthesized from β-diketone (X) by the Claisen condensation of (VII) with ethyl acetate. Compounds (II), (V), (VIII) and (XI), having a terminal acetylenic hydrogen,

Compound No.	Yield, %	m.p. °C	Empirical formula	Found, %		Calc., %		Infrared spectrum
				C	H	C	H	C≡C, cm^{-1}
IX	68,8	175,5—176,2 from (n-C_3H_7OH)	$C_{32}H_{26}$	93,57	6,52	93,62	6,38	2148, 2222
VI	ca. 90	120 from alcohol	$C_{32}H_{18}O_2$	88,42	4,34	88,46	4,18	2139, 2205
XII	15*	172—172,5 from n-C_3H_7OH	$C_{36}H_{26}$	94,06	5,98	94,29	5,71	2137, 2200

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*Based on diketone (X).

were dimerized by oxidation in the presence of cuprous chloride to polyynes (III), (VI), (IX) and (XII). It is interesting to mention that when going from diacetylenes (III) and (VI) to tetraacetylenes (IX) and (XII) the intensity of the absorption at 2200-2235 cm^{-1}, corresponding to the stretching vibrations of the C ≡C bond, increases sharply in the infrared spectrum.

EXPERIMENTAL

Acetylation of m-bitolyl. To a solution of 43.7 g of m-bitolyl in 250 ml of carbon disulfide was added 89 g of aluminum chloride, and then in 40 min, with cooling in ice water, was added 28.3 g of acetic anhydride. The temperature was gradually raised to 50° in 4 h and the stirring was continued for another 3.5 h. The formed complex was decomposed with a mixture of dilute HCl and ice. The ketone (VII) was isolated by distillation (b.p. 136-143° (2 mm)), filtered in ether solution through a bed of aluminum oxide, and recrystallized from petroleum ether (b.p. 48-60°). The yield of (VII) was 20.7 g (38.5%), m.p. 52-53°. Found: C 85.75; H 7.22%. $C_{16}H_{16}O$. Calculated: C 85.68; H 7.19%.

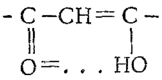
Synthesis of 3,3'-dimethyl-4-ethynylbiphenyl (VIII). To a solution of 18 g of ketone (VII) in 50 ml of dry benzene at 0° was added 20.2 g of phosphorus pentachloride and the mixture was stirred for 4.5 h, gradually raising the temperature up to 65°. After cooling, the reaction mass was poured into a mixture of ether and ice, and the ether-benzene layer was washed with Na_2CO_3 solution and then with water. After drying over calcium chloride, the solution of mixed chlorides was added to the sodium amide prepared from 10 g of sodium in 0.8 liter of liquid ammonia. After stirring for 5 h, the ammonia was removed and the solution of the product was washed with water, dried, vacuum-distilled, and chromatographed in petroleum ether solution on aluminum oxide. We obtained 11.2 (69.5%) of ethynylbiphenyl (VIII), b.p. 117-120° (2 mm); n_D^{20} 1.6285. Found: C 93.05; H 6.96%. $C_{16}H_{14}$. Calculated: C 93.16; H 6.84%. Infrared spectrum: C ≡CH 3320 cm^{-1}, C≡C 2108 cm^{-1}.

Synthesis of 4-ethynyldiphenyl oxide (II). (II) was obtained in the same manner as acetylene (VIII) from 4-acetyldiphenyl oxide (I), yield 75.4%, b.p. 92-94° (1 mm); n_D^{19} 1.6072. Found: C 86.26, H 5.33%. $C_{14}H_{10}O$. Calculated: C 86.57; H 5.19%. Infrared spectrum: C ≡ CH 3355 cm^{-1}, C ≡C 2128 cm^{-1}, ether bridge 1247 cm^{-1}.

Reaction of 4-ethynyldiphenyl oxide (II) with 1-bromo-3-methyl-1-butyn-3-ol. To a solution of 9.8 g of acetylene (II), 5.3 g of ethylamine, 0.2 g of cuprous chloride and 0.5 g of hydroxylamine hydrochloride in a mixture of 40 ml of methanol and 15 ml of tetrahydrofuran, with vigorous stirring and cooling in ice water, was slowly added 8.2 g of 1-bromo-3-methyl-1-butyn-3-ol, in which connection the temperature of the reaction mass was 30-35°. At the end of addition the temperature was maintained in the same range for another 1-1.5 h. The periodic addition of small amounts of hydroxylamine hydrochloride keeps the monovalent copper from oxidizing to the divalent stage. After distilling off the solvent in vacuo the residue was dissolved in benzene and chromatographed on an aluminum oxide column (27 x 450). The yield of 2-methyl-6-p-phenoxyphenyl-3,5-hexadiyn-2-ol (IV) was 10.9 (79%), m.p. 79.5-80° (from petroleum ether). Found: C 82.85; H 5.89%. $C_{19}H_{16}O_2$. Calculated: C 82.58; H 5.84%. Infrared spectrum: C ≡C 2240 cm^{-1}, OH 3615 cm^{-1}, ether bridge 1247 cm^{-1}.

Preparation of p-phenoxyphenylbutadiyne (V). A mixture of 4 g of carbinol (IV) and 12 g of powdered KOH in 65 ml of dry ether was shaken in an acetylene atmosphere for 7-8 h, after which, with cooling, a small amount of water was added until all of the precipitate had dissolved, and then the ether solution was neutralized with carbon dioxide and dried over potassium carbonate. The product was chromatographed in benzene solution on aluminum oxide and then kept in solution. To obtain a sample for analysis a portion of the solution was vacuum-distilled in the cold and in the dark to give the diacetylene (V) as an extremely unstable liquid. The yield of (V) was 2-2.2 g (63.3-69.7%). Found: C 88.05; H 4.81%. $C_{16}H_{16}O$. Calculated: C 88.05; H 4.62%.

Synthesis of 3,3'-dimethyl-4-acetoacetylbiphenyl (X). A mixture of 8.1 g of ketone (VII), 8.1 g of ethyl acetate and 1.1 g of finely cut sodium in 70 ml of ether was stirred at 38-40° for 5 h, after which the reaction mass was filtered, the ether distilled off, and the residue dissolved in water. Acidification of the solution with acetic acid gave crystals of the diketone (X), which were washed with water, dried, and recrystallized from alcohol. The yield of (X) was 5.8 g (60%), m.p. 83.5-84.5°. Found: C 81.46; H 7.05%. $C_{18}H_{18}O_2$. Calculated: C 81.17; H 6.81%. Infrared spectrum: C=O group, contained in the ring



$$-\underset{\underset{\displaystyle O=\ldots}{\|}}{C}-CH=\underset{\underset{\displaystyle \ldots HO}{|}}{C}-$$

1615 cm^{-1}.

Preparation of 3,3'-dimethyl-4-butadiynylbiphenyl (XI). The reaction of 4.6 g of diketone (X) with 11.1 g of phosphorus pentachloride was run at 0-40°, in the same manner as in the case of ketone (VII). The obtained mixture of products was dehydrochlorinated with sodium amide (from 5.8 g of sodium) in liquid ammonia at -50° for 3 h. The excess sodium amide was decomposed with 17 g of ammonium chloride, the ammonia was removed, and the dilute solution of diacetylene (XI) was filtered and passed through a short bed of aluminum oxide, and without further purification was used in the next step.

Oxidative dimerization of acetylenes (II), (V), (VIII) and (XI). A mixture of 11.8 g of 4-ethynyldiphenyl oxide (II) and 0.5 g of cuprous chloride in 40 ml of pyridine was shaken in an oxygen atmosphere until the absorption of the latter ceased. After decomposition with water we isolated 10.5 g (89.5%) of 1,4-bis(p-phenoxyphenyl) butadiyne (III), m.p. 130-130.2° (from alcohol). Found: C 87.27; H 4.72%. $C_{28}H_{18}O_2$. Calculated: C 87.02; H 4.69%. Infrared spectrum: C=C 2164 and 2235 cm^{-1}, ether bridge 1247 cm^{-1}.

The other disubstituted polyynes (Table) were obtained in a similar manner.

SUMMARY

A number of acetylenic derivatives of diphenyl oxide and m-bitolyl were synthesized.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.