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Continuing the search for light-sensitive compounds among aryl acetylenes [1] we synthesized a series of diacetylene alcohol derivatives of simple aromatic amines. As the amine components we used residues of aniline, N,N-dimethylaniline, N,N-diethylaniline, N,N-dibenzylaniline, diphenylamine and also triphenylamine. The synthesis was carried out by the method of direct condensation of the appropriate p-iodo derivatives of the aromatic amines with diacetylene alcohols in the presence of palladium-copper catalysts [2] according to the scheme



The iodides prepared (Ia-d) and (IV) were described by us in [1] and (VI) was synthesized according to [3]. For the purpose of comparing its properties with those of (IX), having a diacetylene substituent on each benzene ring, we synthesized (VIII) with monoacetylene substituents.

In connection with the presence of a strong electron donor amino group in each of the aromatic iodides which we used nucleophilic replacement of iodine by an acetylene group was difficult. We noted that the reaction proceeds much more rapidly and with much higher yields if the mixture of iodide, catalysts, and solvent is stirred 30-60 min at 20-60°C previous to the addition of the acetylene component. This may be the result of the formation at this point of an activated complex of the iodide with the catalysts. Substantially lower yields were obtained when all components were stirred simultaneously with the catalyst, i.e., under the standard conditions described by the Japanese authors [2], in which it is usually noted that the diacetylene component is polymerized somewhat in this particular application. Observing the progress of the reaction with the aid of TLC, we did not detect any dehydro-dimers of either mono- of diacetylene alcohols in the normal course of the reaction. These should be formed according to the mechanism proposed in [4].

We also noted that the interactions of (IV) and (VI) with alcohols (VII) and (II) proceed stepwise as verified from the TLC data. At the beginning of the reaction in addition to triethylamine and the acetylene alcohol appearing close to the start, and iodide with a high R_f value, a product appears corresponding to replacement of one atom of iodine by an

Institute of Chemical Kinetics and Combustion, Siberian Branch, Academy of Sciences of the USSR, Novosibirsk. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 821-823, April, 1984. Original article submitted January 25, 1983. acetylene group. As the reaction proceeds a compound appears with a lower R_f corresponding to the product with two (and in the case of (VI), three) iodines replaced by acetylenic al-cohol residues. Later the starting iodides and products with high R_f values disappear and only the completely substituted product remains. This definitely points to the feasibility of obtaining all the intermediate products in case of necessity.

It is known that in nucleophilic reactions (for example, the Favorskii reaction) the diacetylene compounds are more active than the monoacetylene. Also in the examples studied the diacetylene alcohol reacts twice as fast as the monoacetylene, and the reaction of (II) with tris(p-iodophenyl)amine (VI) is accompanied by significant evolution of heat and the reaction mixture requires cooling to prevent tar formation and drastic lowering of the yield of (IX). The structures of the synthetic compounds were established spectrally and by analytical methods.

EXPERIMENTAL

The PMR spectra were taken on a Varian XL-200 spectrometer in CD₃COCD₃.

<u>p-(5-Methyl-5-hydroxy-1,3-hexadiynyl)aniline (IIIa)</u>. A solution of 5.5 g (Ia), 290 mg Pd(PPh₃)₂Cl₂, and 150 mg CuI in 120 ml Et₃N was stirred for 1 h in a stream of inert gas, 5 g of (II) in 50 ml Et₃N was added dropwise at 19°C over a period of 15 min, the mixture stirred 3 h at 50°C, diluted with 300 ml ether, the precipitate filtered off, the solvent removed by distillation and the crystalline residue chromatographed on Al₂O₃ (activity II), eluting initially with hexane, then with benzene. There was isolated 3.2 g of (IIIa), yield 60%, mp 102-103.5°C (from benzene). Found: C 78.15; H 6.40; N 7.01%. C₁₃H₁₃NO. Calculated: C 78.36; H 6.58; N 7.03%. IR spectrum (CHCl₃, \lor , cm⁻¹): 2150 and 2230 (C=C-C=C), 3410 and 3500 (NH₂), 3600 (OH). PMR spectrum (δ , ppm): 1.47 s (2CH₃ next to COH), 4.60 (OH), 5.17 broad (NH₂), 6.64 d and 7.18 d (C₆H₄).

p-(5-Methyl-3-hydroxy-1,3-hexadiynyl)-N,N-dimethylaniline (IIIb). To a solution of 15.4 g of (Ib), 730 mg Pd(PPh₃)₂Cl₂, and 360 mg CuI in 160 ml Et₃N heated to 50°C in an inert atmosphere was added 10 g of (II) in 50 ml Et₃N during 30 min. The mixture was stirred 4 h at 50°C, and after working up as with (IIIa), 12.24 g of (IIIb) (86%) was isolated, mp 103-104°C (from ether). Found: C 79.21; H 7.47; N 6.27%. C₁₅H₁₇NO. Calculated: C 79.26; H 7.54; N 6.16%. IR spectrum (CCl₄, ν , cm⁻¹): 2150 and 2240 (C≡C-C≡C), 3610 (OH)). PMR spectrum (δ , ppm): 1.47 s (2CH₃ next to COH), 2.97 s (2CH₃ next to N), 4.58 s (OH), 6.69 d and 7.29 d (C₆H₄).

p-(5-Methyl-5-hydroxy-1,3-hexadiynyl)-N,N-diethylaniline (IIIc). The analog of (IIIb) was obtained, yield 85%, mp 99.5-100.5°C (from ether). Found: C 79.81; H 8.05; N 5.32%. C₁₇H₂₁NO. Calculated: C 79.96; H 8.29; N 5.49%. IR spectrum (CCl₄, \vee , cm⁻¹): 2150 and 2230 (CΞC-CΞC), 3620 (OH). PMR spectrum (δ , ppm): 1.13 m (CH₃ next to CH₂), 1.47 s (2CH₃ next to COH), 3.38 m (CH₂), 4.56 (OH), 6.66 d and 7.26 d (C₆H₄).

 $\frac{p-(5-Methyl-5-hydroxy-1,3-hexadiynyl)-N,N-dibenzylaniline (IIId). The analog of (IIIb) was obtained, yield 70%, mp 107-108°C (from ether). Found: C 85.26; H 6.63; N 3.51%. C₁₇H₂₅NO. Calculated: C 85.45; H 6.64; N 3.69%. IR spectrum (CHCl₃, <math>\nu$, cm⁻¹): 2150 and 2250 (C=C-C=C), 3620 (OH). PMR spectrum (δ , ppm): 1.46 s (CH₃ next to COH), 4.58 s (OH), 4.76 s (2CH₂), 6.72 d (C₆H₄), 7.2-7.3, m (C₆H₄ and 2C₆H₅).

Bis-[p-(5-methy1-5-hydroxy-1,3-hexadiyny1)pheny1]amine (V). To a solution of 5.17 g (IV), 240 mg Pd(PPh₃)₂Cl₂, 120 mg CuI in 60 ml Et₃N heated to 60°C in a stream of argon was added 4 g of (II) in 15 m1 Et₃N during 30 min. At the end of the addition of (II) A spot for the monosubstitution product appeared on a TLC chromatogram. Within 5 min after finishing the addition of (II) the spot due to the (IV) present at the beginning became very weak, and the spot due to the monosubstituted product was notably diminished and the spot due to (V) became the most intense one. The mixture was stirred 2 h at 60°C, diluted with 500 ml ether, filtered, the solvents distilled off, chromatographed an Al203 (activity II), sequentially eluted with pentane, benzene, and ether. Isolated was 2.55 g of (V), yield 54.6%, mp 161-162°C (from benzene). Found: C 81.48; H 6.04; N 3.75%. C26H23NO2. Calculated: C 81.86; H 6.08; N 3.67%. IR spectrum (CHCl3, v, cm⁻¹): 2160 and 2240 (CEC-CEC), 3440 (H), 3615 (OH). PMR spectrum (ô, ppm): 1.5 s (2CH3 next to COH), 4.6 (OH), 7.18 d and 7.44 d (CoH4), 8.14 (NH) (see [1]). In diphenylamines signals of H in NH are found at 7.3 ppm, in p,p'-diododiphenylamine at 7.6 ppm, in p,p'-diethyldiphenylamine at 7.9 ppm, and in bis[p-(3-methyl-3-hydroxy-1-butynyl)phenyl]amine at 7.8 ppm. Referencing signals for H in NH at 3 ppm is incorrect.

 $\frac{\text{Tris}[p-(3-\text{methyl}-3-\text{hydroxy}-1-\text{butynyl})\text{phenyl}]amine (VIII).}{240 \text{ mg Pd}(PPh_3)_2Cl_2, and 120 \text{ mg of CuI in 100 ml diethylamine in an argon atmosphere was added 6.7 g of (VII) in 20 ml diethylamine during 30 min, whereupon the temperature rose to 50°C. On the chromatogram besides the (VI) present initially three spots were evident for the products from replacement of one, two, and three iodine atoms. After stirring the mixture at 50°C for 3 h the spots due to the (VI) initially present and to the monosubstitution product disappeared from the chromatogram. The spot evidently associated with the disubstituted product became the most intense, but after 3 h it disappeared and an intensive spot for the trisubstituted product (VIII) remained. After standard processing of the reaction mixture and chromatography (Al_2O_3, activity II, eluant benzene—ether) 8.77 g of (VIII) was isolated, yield 89%, mp 205-206°C. Found: C 80.66; H 6.64; N 2.87%. Cl_3 H_3NO_3. Calculated: C 80.62; H 6.77; N 2.85%. IR spectrum (CHCl_3, v, cm⁻¹): 2240 (CEC), 3620 (OH). PMR spectrum (<math>\delta$, ppm): 1.5 s (CH₃ next to COH), 4.45 (OH), 7.00 d and 7.3 d (C_6H_4).

Tris-p-(5-methyl-5-hydroxy-1,3-hexadiynyl)phenylamine (IX). A mixture of 12.4 g (VI), 240 mg Pd(PPh₃)₂Cl₂, and 120 mg CuI was dissolved in 100 ml Et₃N and 15 ml dimethylformamide at 50°C in an argon atmosphere. Cooling to 20°C 10 g of (II) in 20 ml Et₃N was added during 15 min, not allowing the temperature to rise above 40°C. After 1 h of stirring at 40°C the (VI) initially present disappeared and the product from replacement of one iodine atom (from the TLC data on Silufol with ether eluant). After 2 h the product from replacement of two iodine atoms disappeared and only (IX), the product from replacement of three iodine atoms, remained. After working up as usual and chromatographing (Al₂O₃, activity (II) with benzene and ether) 7.1 g of (IX) was isolated, yield 63%, mp 134-135°C. Found: C 83.27; H 5.92; N 2.22%. C₃₉H₃₉O₃N. Calculated: C 83.10; H 5.90; N 2.48%. IR spectrum (CHCl₃, ν , cm⁻¹): 2160 and 2240 (C=C-C=C), 3600 (OH). PMR spectrum (δ , ppm): 1.48 (CH₃ next to COH), 4.64 s (OH), 7.06 d and 7.46 d (C₆H₄).

CONCLUSIONS

We have developed methods of synthesis of acetylenic and diacetylenic alcohol derivatives of simple aromatic amines.

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