paraform was filtered and the SOCl₂ was evaporated in vacuo. The oily residue was distilled to give 7.5 g (82%) of (II), bp 96-97° (1 mm). PMR spectrum (CDCl₃, δ , ppm): 1.35 s (2 MeCH), 3.05 s (MeSO₂), 4.16 m (CHN), 5.45 s (CH₂). Infrared spectrum (ν , cm⁻¹): 1350, 1165 (S = O), 847 (CCl).

N-Methyl-N-acetamidomethylurethane (X) was isolated from the reaction mixture, bp 90° (1 mm). PMR spectrum (CDCl₃, δ , ppm): 1.97 s (MeCO), 2.82 s (MeN), 3.53 s (MeO), 4.61 d (CH₂). Infrared spectrum (ν , cm⁻¹): 3330 (NH), 1724 (CO₂), 1680 (C = O), 1550, 1280 (NH), 1215 (COC).

CONCLUSIONS

When treated with nitronium tetrafluoborate the N-chloromethyl derivatives of the secondary amides of the carbonic, sulfonic, and nitric acids form either the corresponding N-alkyl-N-nitramides, methylenebis-N-alkylamides, or their mixture.

LITERATURE CITED

- 1. O. A. Luk'yanov, T. G. Mel'nikova, and V. A. Tartakovskii, Izv. Akad. Nauk SSSR, Ser. Khim., 1981, 2335.
- 2. O. A. Luk'yanov, T. G. Mel'nikova, E. G. Kashirskaya, and V. A. Tartakovskii, Izv. Akad. Nauk SSSF, Ser. Khim., <u>1981</u>, 2610.
- 3. V. A. Pal'm, Principles of Quantitive Theory of Organic Reactions [in Russian], Khimiya, Moscow (1977), p. 204.
- 4. E. H. White, M. C. Chen, and L. A. Dolak, J. Org. Chem., <u>31</u>, 3038 (1966).
- 5. O. A. Luk'yanov, V. P. Gorelik, V. A. Tartakovskii, and S. S. Novikov, Izv. Akad. Nauk SSSR, Ser. Khim., 1971, 1804.
- 6. R. C. Brain and A. H. Lamberton, J. Chem. Soc., 1949, 1633.
- 7. L. Goodman, J. Am. Chem. Soc., <u>75</u>, 319 (1953).
- 8. C. Beerman and H. Ramloch, German Patent 1915898 (1970); C. A., 74, 13741v (1971).

ACETYLENIC DERIVATIVES OF ANILINE

 M. I. Bardamova, Z. P. Trotsenko,
 UDC 542.91: 547.551: 547.362

 and I. L. Kotlyarevskii
 UDC 542.91: 547.551: 547.362

In planning a search for new light-sensitive systems it was proposed to develop a scheme for the synthesis of acetylenic aniline derivatives, general methods for whose preparation remain practically undeveloped. The syntheses of the individual acetyleneanilines are characterized by being either multistep, as in the case of obtaining p-ethynyl-N,N-dimethylaniline from p-bromo-N,N-dimethylaniline [1], or restricted, as in the synthesis of ethynyl-N,N-dialkylanilines from phenylacetylene and dialkylamines, or by the inavailability of the starting aminoacetophenones, as in the case of going from the acetyl group to the ethynyl group [2].

We used the method of direct condensation of terminal acetylenes with iodoaryls (I) in the presence of $Pd(PPh_3)_2Cl_2-CuI$ in amines as the medium [3], which leads to the acetylenic carbinols (III) in 70-85% yield, which are cleaved by the reverse Favorskii reaction to give the ethynylanilines (IV) in 70-85% yield.



Institute of Chemical Kinetics and Combustion, Siberian Branch of the Academy of Sciences of the USSR, Novosibirsk. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1184-1186, May, 1982. Original article submitted September 29, 1981. The proposed scheme was successfully used to synthesize p,p'-diethynyldiphenylamine (VII).



The starting iodide (V) was obtained by the iodination of diphenylamine, and its PMR spectrum has the signals characteristic for p-substitution in the phenyl ring as two doublets at 7.03 and 7.6 ppm, and a signal of the NH group at 3.05 ppm. When N,N-dibenzylaniline is iodinated the iodine enters only into the p-position of the phenyl ring attached to the nitrogen, which is confirmed by elemental analysis and the PMR spectrum, in which the signal of the CH₂ group at 4.68 ppm appears as a singlet.

EXPERIMENTAL

The PMR spectra were taken in deuteroacetone relative to TMS, and the IR spectra were taken in CCl_4 solution.

<u>N,N-Dibenzyl-4-iodoaniline (Id)</u>. The compound was obtained as described in [4] from 13 g of N,N-dibenzylaniline, 10 g of iodine, 6 g of NaHCO₃, 20 ml of MeOH, and 60 ml of water in 3 h at 8-20°C in 79% yield, mp 121-122° (from acetone). Found: C 60.31; H 4.62; I 31.74%. $C_{20}H_{18}NI$. Calculated: C 60.16; H 4.54; I 31.78%. PMR spectrum (δ , ppm): 4.68 s (2CH₂); 6.53 d and 7.28 d ($C_{6}H_{4}$); 7.25 s (2 $C_{6}H_{5}$).

p,p'-Diiododiphenylamine (V). A mixture of 25 g of Ph₂NH, 125 g of I₂, 100 g of HgO, and 1 liter of EtOH was refluxed for 2 h and then worked up as described in [5]. For additional purification the benzene solution was filtered through silica gel. We isolated 56 g (62%) of (V), mp 125-126°. Found: C 34.3; H 2.11; I 59.95%. $C_{12}H_9NI_2$. Calculated: C 34.23; H 2.15; I 60.28%.

<u>p-(3-Methyl-1-butyn-3-ol)-N,N-dibenzylaniline (IIId)</u>. To a mixture of 12 g of (Id), 210 mg of Pd(PPh₃)₂Cl₂, and 105 mg of Cul in 100 ml of Et₂NH was added in 15 min 4 g of (II) in 20 ml of Et₂NH in a helium stream, after which the mixture was stirred for 3 h at 50°, diluted with 200 ml of ether, filtered from the obtained precipitate, and the solvent was removed and chromatographed on Al₂O₃ (II activity), eluting first with hexane and then with ether. We isolated 7.7 g (72%) of (IIId), mp 93.8° (from ether). Found: C 84.46; H 6.89; N 4.20%. C₂₅H₂₅NO. Calculated: C 84.47; H 7.09; N 3.94%.

Infrared spectrum (CHCl₃, ν , cm⁻¹): 2220 (-C \equiv C-), 3610 (OH); PMR spectrum (δ , ppm): 1.28 s (2CH₃); 4.03 s (OH), 4.56 s (2CH₂); 6.54d and 7.00 d (C₆H₄); 7.13 s (2C₆H₅).

In a similar manner we obtained: p-(3-methyl-1-butyn-3-ol)aniline (IIIa). 70% yield, mp 85-86° (from benzene). Found: C 75.56; H 7.30; N 7.82%. C₁₁H₁₃NO. Calculated: C 75.40; H 7.48; N 7.99%. Infrared spectrum (ν , cm⁻¹): 2220 ($-C \equiv C-$); 3400 and 3500 (NH₂), 3600 (OH). Infrared spectrum (δ , ppm): 1.46 s (CH₃), 4.16 (NH₂), 4.76 br. (OH), 6.48 d and 7.02 d (C₆H₄).

p-(3-Methyl-1-butyn-3-ol)-N,N-dimethylaniline (IIIb), 87% yield, mp 89°. Found: C 76.78; H 8.48; N 6.83%. C₁₃H₁₇NO. Calculated: C 76.81; H 8.43; N 6.89%. Infrared (ν, cm⁻¹): 2210 (C \equiv C); 3610 (-OH); PMR spectrum (δ, ppm): 1.5 s (2CH₃ at COH), 2.23 s (2CH₃ at -N <); 4.47 s (OH); 6.6 d and 7.13 d (C₆H₄).

<u>p-(3-Methyl-1-butyn-3-ol)-N,N-diethylaniline (IIIc)</u>, 87% yield, mp 81-82°. Found: C 77.77; H 9.04; N 6.24%. C₁₅H₂₁NO. Calculated: C 77.88; H 9.15; N 6.05%. Infrared spectrum (ν , cm⁻¹): 2210 (C≡C); 3600 (O-H). Infrared spectrum (δ , ppm): 1.11 m (2CH₃); 2.85 s (OH); 3.35 m (CH₂CH₃); 6.6 d and 7.3 d (C₆H₄).

Bis[p-(3-methyl-1-butyn-3-ol)-phenyl]amine (VI). To a suspension of 8.4 g of (V) in 50 ml of Et₂NH, in the presence of 240 mg of Pd(PPh₃)₂Cl₂ and 120 mg of CuI, in a helium stream, was added 5.1 g of (II) in 20 ml of Et₂NH in 1 h at 45-50°, and the mixture was stirred for 8 h. We isolated 4.5 g (87%) of (VI), mp 122-123°. Found: C 79.41; H 6.86; N 4.27%. C₂₂H₂₃NO₂. Calculated: C 79.25; H 6.95; N 4.20%. Infrared spectrum (CHCl₃, ν , cm⁻¹); 2220 (C = C), 3440 (NH), 3610 (OH). PMR (δ , ppm): 1.5 s (4CH₃): 3.15 s (NH); 4.5 s (2OH); 7.02 d and 7.22 d (C₆H₄).

<u>N,N,-Dibenzyl-4-ethynylaniline (IVd)</u>. A mixture of 1 g of (IIId), 50 mg of well ground KOH, and 10 mg of hydroquinone was heated in vacuo (0.5 mm). Brisk foaming occurred at 120°, while 0.6 g (70%) of (IVd) sublimed at 170°, mp 111-112°. The yield is retained if the reaction is run in a high-vacuum inert oil [7] with bp > 170° (0.1 mm). Found: C 88.63; H 6.55; N 4.47%. C₂₂H₁₉N. Calculated: C 88.85; H 6.44; N 4.71%. Infrared spectrum (ν , cm⁻¹): 2100 (C \equiv CH), 3320 (\equiv CH). PMR spectrum (δ , ppm): 3.24 s (\equiv CH); 4.64 s (2CH₂); 6.6 d and 7.16 d (C₆H₄); 7.22 s (2C₆H₅).

Using a high-vacuum oil and a vacuum of 0.5 mm, compounds (IIIa-c) were decomposed under analogous conditions. From (IIIa) at 120° we isolated 75% of (IVa), mp 101-102° [6]. Infrared spectrum (ν , cm⁻¹): 2110 (C = CH), 3310 (= CH), 3420 and 3500 (NH₂); PMR spectrum (δ , ppm): 3.28 s (= CH); 4.9 br, s (NH₂); 6.57 d and 7.15 d (C₆H₄). From (IIIb) at 110° we obtained 90% of (IVb), mp 52-52.5° [1]. From (IIIc) at 115° we obtained 85% of (IVc), bp 62° (0.1 mm) [2], mp 23-24°

p,p'-Diethynyldiphenylamine (VII). A mixture of 1 g of (VI), 100 mg of KOH, 20 mg of hydroquinone, and 3-4 drops of high-vacuum oil was heated up to 110° (0.5 mm), and 0.45 g (69%) of (VII) sublimed at 120°, mp 92-93°. Found: C 88.34; H 5.30; N 6.49%. C₁₆H₁₁N. Calculated: C 88.45; H 5.10; N 6.46%. Infrared spectrum (ν , cm⁻¹): 2110 (C = CH), 3320 (= CH), 3440 (NH); PMR spectrum (δ , ppm): 3.23 s (NH); 3.47 s (= CH); 7.12 d and 7.38 d (C₆H₄).

CONCLUSIONS

The direct condensation of iodoanilines with 2-methyl-3-butyn-2-ol gave acetylenic carbinols, whose cleavage by the reverse Favorskii reaction leads to ethynylanilines.

LITERATURE CITED

- 1. A. Janousova, M. J. Benes, M. Janic, and J. Peska, Preprints of Papers presented at the International Symposium on Macromolecules, Helsinki, Finland (1972), Vol. 2, Sect. 1, pp. 699-702.
- 2. M. P. Terpugova, I. L. Kotlyarevskii, Yu. I. Amosov, and R. N. Myasnikova, Izv. Akad. Nauk SSSR, Ser. Khim., <u>1975</u>, 2808.
- 3. H. Jamanaka, Shiraiwa, Edo Kiyoto, and Sakamoto Makuo, Chem. Pharm. Bull. (Tokyo), 27, 270 (1979).
- 4. R. Q. Brewster, Org. Syntheses, Coll. Vol. 2 (1943), p. 347.
- 5. A. Classen, German Patent 81928 (G. 5107); Friedländer, Vol. 4 (1896), p. 1096.
- 6. A. Burawoy and J. P. Critchley, Tetrahedron, 5, 340 (1959).
- 7. S. F. Vasilevskii, M. S. Shvartsberg, I. L. Kotlyarevskii, and A. N. Sinyakov, Inventor's Certificate 596567 (1977); Byull. Izobr., No. 9 (1978).