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Abstract

Full Text

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Synthesis of N-Substituted Aromatic Amines

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N-substituted aromatic amines are known as inhibitors of polymer aging; they are widely used for the stabilization of rubbers and rubber products (^1). The inhibiting activity of this class of compounds depends on their chemical structure and on the nature of the substituent. We have proposed, as such inhibitors, the condensation products of *p*-aminodiphenylamine, *p*-anisidine, and *p*-phenylenediamine with acetophenone (^2).

The condensation reaction of aromatic amines with aldehydes and ketones leads to the formation of azomethine bases ([3,4]), which are readily reduced by hydrogen in the presence of catalysts to secondary amines (^4). According to (^3), the condensation of aromatic amines with ketones proceeds only in the presence of the complex salt $ZnCl_2(amine)_2$ as catalyst. Later (^5) it was established that azomethine bases, when heated with water, are readily hydrolyzed.

We investigated the condensation reaction of aromatic amines with acetophenone and found that the condensation of *p*-aminodiphenylamine with acetophenone readily proceeds upon direct interaction of the reagents in toluene medium, but with obligatory removal of the reaction water through a Dean–Stark trap. Introduction into the reaction medium of a small amount of anhydrous zinc chloride (0.1 g per 0.5 g-mol of amine) considerably accelerates the reaction and increases the yield of the azomethine base by 10–15%. The condensation of *p*-anisidine with acetophenone proceeds similarly. *p*-Phenylenediamine reacts very slowly with acetophenone without catalyst ($ZnCl_2$), and the azomethine base is formed in 60–70% yield. The presence of a small amount of zinc chloride considerably accelerates the reaction and increases the yield of the azomethine base to quantitative. Carrying out the condensation reaction in the presence of the complex salt $ZnCl_2(amine)_2$ gives no advantages whatsoever compared with anhydrous zinc chloride (Table 1). The rate of the condensation reaction of aromatic amines with acetophenone and the yield of the azomethine base are practically unchanged by the amount of zinc chloride introduced into the reaction within the range from 0.01 to 1.0 g per 0.5 g-mol of amine.

The hydrogenation of the resulting azomethine bases was carried out with hydrogen in an alcoholic medium in the presence of a copper–chromium oxide catalyst. The hydrogenation reaction proceeds rapidly; the yield of secondary amines is 90%.

Experimental Part

N-(α-Methylbenzylidene)-*p*-aminodiphenylamine. In a round-bottom flask equipped with a stirrer, thermometer, and reflux condenser with a Dean-Stark trap, 150 g (1.25 g-mol) of acetophenone, 95 ml of toluene, and 0.1 g of zinc chloride were added to 92.0 g (0.5 g-mol) of *p*-aminodiphenylamine. The mixture was heated with stirring for 1 h at 144° until the evolution of water had completely ceased. The solvent was then distilled off and

Table 1

Results of experiments on the condensation of amines with acetophenone

Starting amine	Amine, g-mol	Acetophenone, g-mol	Solvent, ml	Catalyst, g	Reaction temperature, °C	Reaction duration, h	Yield, %
p-Aminodiphenylamine	0.5	1.25	95	–	146	3.0	87.3
p-Aminodiphenylamine	0.5	1.25	95	–	145	3.0	87.4
p-Aminodiphenylamine	0.5	1.25	95	–	145	4.0	90.6
p-Aminodiphenylamine	0.5	1.25	95	0.1	144	1.0	99.0
p-Aminodiphenylamine	0.5	1.25	95	0.1	142	1.2	97.5
p-Anisidine	0.4	0.6	45	–	158	5.7	76.0
p-Anisidine	0.4	0.6	45	–	157	5.0	80.0
p-Anisidine	0.4	0.6	45	0.1	152	1.0	88.6
p-Anisidine	0.4	0.6	45	0.1	156	1.2	89.6
p-Anisidine	0.4	0.6	45	0.5*	156	2.0	90.0
p-Phenylenediamine	0.4	1.6	100	–	154	13.5	57.0
p-Phenylenediamine	0.4	1.6	100	–	153	13.0	65.8
p-Phenylenediamine	0.4	1.6	100	0.1	150	4.0	94.0
p-Phenylenediamine	0.4	1.6	100	0.1	152	4.0	96.5

Starting amine	Amine, g-mol	Acetophenone, g-mol	Solvent, ml	Catalyst, g	Reaction temperature, °C	Reaction duration, h	Yield, %
p-Phenylenediamine	0.4	1.6	100	0.5*	150	4.5	92.0
p-Phenylenediamine	0.4	1.6	100	3.0*	152	4.0	92.1

* Complex salt.

Excess acetophenone and the residue were transferred into a beaker. After cooling, the yellow crystals that separated were filtered off and washed on the filter with alcohol. 141.5 g were obtained (99.0% of theory). After recrystallization from alcohol, m.p. 135°. Soluble in benzene, toluene, and acetone; less soluble in alcohol; insoluble in water.

$C_{20}H_{18}N_2$.	Found, %:	C 83.95; H 6.29; N 9.76
	Calculated, %:	C 83.88; H 6.33; N 9.78

N-(α-Methylbenzyl)-*p*-phenylenediamine. Into a rotating autoclave of 0.5 l capacity were placed 57.2 g (0.2 g-mol) of the acetophenone base, 100 ml of alcohol, and 3.5 g of a copper chromite catalyst; hydrogen was introduced into the autoclave under a pressure of 70 atm. The autoclave was heated with constant rotation at 140° for 40 min, until hydrogen absorption ceased. The autoclave was cooled and discharged. The reaction mass was heated to 70° and the catalyst was filtered off. The mother liquor was cooled to room temperature, and the light-gray crystalline product that separated was filtered off, washed on the filter with a small amount of cold alcohol, and dried. 52.7 g were obtained (91.5% of theory). After recrystallization from alcohol, m.p. 85.5°.

$C_{20}H_{20}N_2$.	Found, %:	C 83.10; H 7.05; N 9.58
	Calculated, %:	C 83.29; H 6.99; N 9.71

N-(α-Methylbenzylidene)-*p*-anisidine. Into the apparatus described above were charged 49.2 g (0.4 g-mol) of *p*-anisidine, 72 g (0.6 g-mol) of acetophenone, 45 ml of toluene, and 0.1 g of zinc chloride. The reaction was carried out with constant stirring and heating at 152° for 1 h, until the evolution of water ceased. The solvent and excess acetophenone were then distilled off through a Dean–Stark trap, and the residue was transferred into a beaker. After cooling, the crystalline precipitate of the acetophenone base that separated was filtered off and washed on the filter with alcohol. 79.7 g were obtained (88.6% of theory). M.p. 86°, corresponding to the literature data (2).

N-(α-Methylbenzyl)-*p*-anisidine. Reduction of the acetophenone base obtained above was carried out in an autoclave. Into the autoclave were charged –

90.0 g of the azomethine base (0.4 mole), 75 ml of alcohol, and 7.0 g of copper-chromium oxide catalyst were charged, and hydrogen was introduced under a pressure of 120 atm. The reaction was carried out at 140° for 60 min. The reaction mixture was worked up as described above. 87.1 g (96.0% of theory) of N-(α-methylbenzyl)-*p*-anisidine, m.p. 66°, was obtained.

Found, %: C 79.32; H 7.62; N 6.19
$C_{15}H_{17}ON$. Calculated, %: C 79.26; H 7.53; N 6.16

N,N′-di-(α-methylbenzylidene)-*p*-phenylenediamine. The condensation of *p*-phenylenediamine with acetophenone was carried out analogously. 43.2 g of *p*-phenylenediamine (0.4 g-mole), 192 g of acetophenone (1.6 g-mole), 100 ml of toluene, and 0.1 g of zinc chloride were heated at 150° for 4 hr. 117.3 g (94.0%) of the azomethine base, m.p. 205°, was obtained.

Found, %: C 84.52; H 6.43; N 9.00
$C_{22}H_{20}N$. Calculated, %: C 84.58; H 6.45; N 8.97

N,N′-di-(α-methylbenzyl)-*p*-phenylenediamine. 128.9 g (0.4 g-mole) of the azomethine base, 200 ml of alcohol, and 7.0 g of copper–chromium oxide catalyst were charged into an autoclave; hydrogen was introduced under a pressure of 120 atm. The reaction was carried out at 145° for 60 min. 113.6 g (90.0%), m.p. 174°, was obtained.

Found, %: C 83.31; H 7.86; N 8.82
$C_{22}H_{24}N_2$. Calculated, %: C 83.50; H 7.64; N 8.85

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CITED LITERATURE

[1] B. S. Bigss, *Rubber Chem. Techn.*, **31**, 1015 (1958). [2] A. A. Grinberg, T. F. Bebikh, USSR Author' s Certificate No. 156674, 1963; No. 159858, 1964. [3] G. Reddelien, *Ber.*, **42**, 4759 (1909); *Ber.*, **43**, 2476 (1910); *Ann.*, **388**, 165 (1912). [4] V. Emerson, Organic Reactions, collected volume 5, 345 (1951). [5] B. A. Porai-Koshits et al., ZhOKh, **17**, 1774 (1947); ZhOKh, **24**, 372 (1954).

Note: Figure translations are in progress. See original paper for figures.