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Polymeric Schiff Bases. II. The Synthesis of Azomethines by a Continuous Azeotropic Method

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Polymeric Schiff Bases. II. The Synthesis of Azomethines by a Continuous Azeotropic Method

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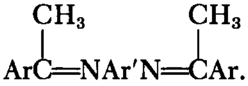
Summary

Various azomethine monomers, including some new Schiff bases, azines, and ketanils have been prepared in high yields by a simple, continuous azeotropic method.

The need for a number of Schiff bases as intermediates and as monomers for use in the synthesis of Schiff base polymers led us to investigate methods of synthesis which would produce high yields of high-purity products. Monomeric Schiff bases are usually prepared (*1,2*) by reacting an aromatic amine, $ArNH_2$, with an aromatic aldehyde, ArCHO, directly or in a solvent or suitable medium, such as ethanol or water, in the presence of a Lewis acid to give an equilibrium yield of the product; thus

$$ArNH_2 + ArCHO \rightleftharpoons ArN{=}HCAr + H_2O$$

In general, this method is satisfactory and the product yield depends on the nature of the reactants, as well as on the solvent. For the particular Schiff bases reported in this study, the yields by this method were found to be in the range of 58–93% of the theoretical amount. Usually, such mono-Schiff bases are purified easily from suitable solvents. However, when the dialdehydes, $Ar'(CHO)_2$, or the diamines, $Ar'(NH_2)_2$, are converted to the corresponding Schiff bases, $Ar'(CH{=}NAr)_2$ and $Ar'(N{=}HCAr)_2$, by this equilibrium method, the crude products are usually contaminated by the mono-Schiff bases, $OHCAr'CH{=}NAr$ and $H_2NArN{=}HCAr$, respectively, and require therefore extensive purification before use in the syntheses of polymers. A complete conversion to the bis-Schiff base would eliminate this complication. This was accomplished using an appropriate azeotroping agent, such as benzene or toluene, as the medium for the reaction, and refluxing the mixture of amine, aldehyde, and azeotroping agent in a Dean-Stark apparatus until the calculated amount of water of reaction is collected in the side-arm trap. This method was extended also to the syntheses of a number of related azines, $ArCH{=}N{-}N{=}HCAr$ and ketanils,  $Ar\overset{CH_3}{\overset{|}{C}}{=}NAr'N{=}\overset{CH_3}{\overset{|}{C}}Ar$. The yield of crude product in all cases was quantitative. Catalysis was not required in the preparation of the Schiff bases or the azines, although their syntheses are accelerated by the addition of catalytic quantities of Lewis acids. The uncatalyzed syntheses of the ketanils were found to proceed very slowly; however, they were accelerated greatly by the addition of 0.10 wt. %, based on the weight of reactants, of either zinc chloride or *p*-toluenesulfonic acid, but not by acetic acid. The isolated crude products were recrystallized easily from benzene or ethanol or a mixture of both, and the yield of purified products in all cases exceeded 92%. Some of the products synthesized by this azeotropic method are given in Table 1.

EXPERIMENTAL

General Procedure

All the reagents used were available from commercial sources and were repurified by distillation or recrystallization before use. Into a 500-ml round-bottom single-neck ground-glass-joint flask was placed 150 ml of dry toluene, 0.1 mole of amine, the stoichiometric quantity of the carbonyl compound, and the catalyst, if used, and the flask was attached to a Dean-Stark apparatus equipped with a reflux condenser. The trap was filled with dry toluene and the mixture refluxed until the theoretical amount of water was collected in the trap. Then the reaction solution was filtered while hot and the filtrate cooled to 0–5°C and allowed to crystallize. The product was recovered by filtration and dried in a vacuum oven at 25°C to

TABLE 1

Some Azomethines Synthesized by an Azeotropic Method

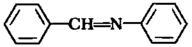
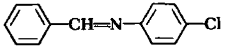
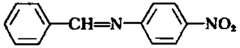
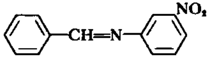
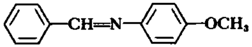
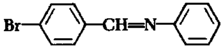
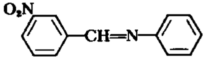
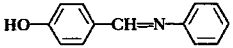
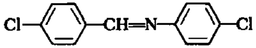
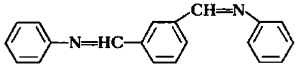
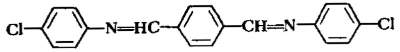
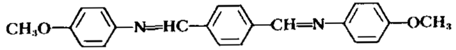
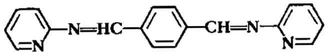
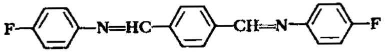
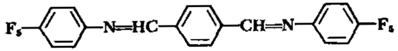
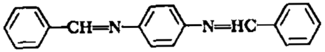
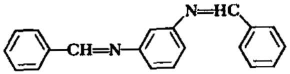
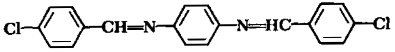
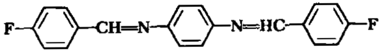
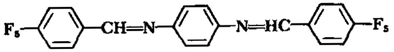
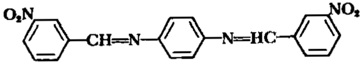
Product	Melting point, °C[a]		Analyses[b]									
			Found					Calcd.				
	Found	Lit.	C	H	N	X[c]	S	C	H	N	X	S
	49	49(2)	—	—	7.73	—	—	86.18	6.07	7.73	—	—
	62	—	72.52	4.60	6.50	16.48	—	72.46	4.64	6.49	16.45	—
	93	93 (3)	69.10	4.40	12.41	—	—	69.03	4.42	12.39	—	—
	73	—	69.08	4.41	12.37	—	—	69.03	4.42	12.39	—	—
	72	72 (4)	79.66	6.19	6.66	—	—	79.62	6.16	6.64	—	—
	65	—	60.10	3.90	5.36	30.81	—	60.02	3.86	5.38	30.74	—
	66	66 (5)	69.00	4.44	12.41	—	—	69.03	4.42	12.39	—	—
	200	200 (6)	79.28	5.55	7.14	—	—	79.19	5.58	7.11	—	—
	112	—	62.36	3.58	5.57	28.42	—	62.42	3.60	5.60	28.37	—
	166	164 (7)	84.47	5.59	9.86	—	—	84.51	5.63	9.86	—	—
	53	—	84.52	5.61	9.84	—	—	84.51	5.63	9.86	—	—

TABLE 1 (*Continued*)

Product	Melting point, °C[a]		Analyses[b]									
			Found					Calcd.				
	Found	Lit.	C	H	N	X[c]	S	C	H	N	X	S
	180	180 (*8*)	67.96	4.01	7.91	20.11	—	68.00	3.99	7.93	20.07	—
	221	—	76.63	5.68	8.17	—	—	76.70	5.82	8.14	—	—
	204	—	75.90	5.23	19.82	—	—	75.52	4.89	19.58	—	—
	154	—	74.55	4.27	8.82	12.52	—	75.01	4.42	8.75	11.87	—
	208	—	51.71	1.27	6.28	40.84	—	51.74	1.30	6.04	40.92	—
	140	140 (*9*)	84.49	5.60	9.89	—	—	84.51	5.63	9.86	—	—
	106	105 (*10*)	84.50	5.62	9.85	—	—	84.51	5.63	9.86	—	—
	199	—	67.98	4.20	7.91	20.11	—	68.00	3.99	7.93	20.07	—
	175	—	74.81	4.67	8.81	11.92	—	75.01	4.42	8.75	11.87	—
	140	—	51.70	1.26	6.16	41.02	—	51.74	1.30	6.04	40.92	—
	251	249 (*8*)	64.36	3.77	15.01	—	—	64.17	3.74	14.97	—	—
	234	234 (*11*)	86.43	5.59	7.79	—	—	86.67	5.55	7.78	—	—

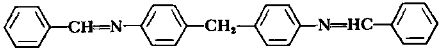
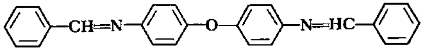
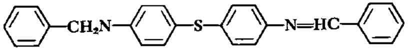
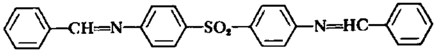
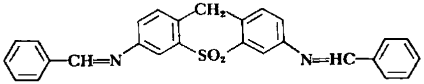
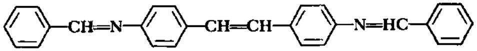
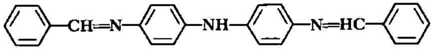
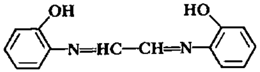
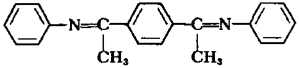
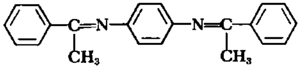
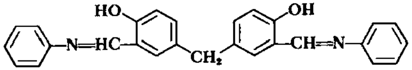
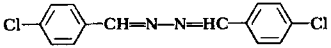
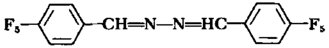
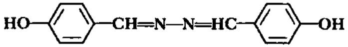
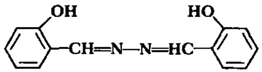
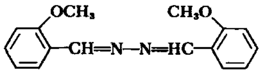
	130	126 (*12*)	86.68	5.90	7.44	—	—	86.63	5.88	7.48	—	—
	183	181 (*13*)	83.01	5.36	7.49	—	—	82.98	5.32	7.46	—	—
	180	178 (*14*)	79.88	5.14	7.18	—	8.21	79.59	5.10	7.14	—	8.16
	236	232 (*15*)	73.68	4.74	6.62	—	7.59	73.59	4.72	6.60	—	7.55
	208	—	74.47	4.65	6.48	—	7.44	74.50	4.58	6.44	—	7.35
	270	—	87.08	5.77	7.38	—	—	87.05	5.70	7.25	—	—
	186	182 (*13*)	83.28	5.60	11.27	—	—	83.20	5.60	11.20	—	—
	204	—	70.31	5.12	11.67	—	—	70.00	5.00	11.67	—	—
	214	—	85.19	5.79	9.08	—	—	85.16	5.81	9.03	—	—
	216	—	85.22	5.77	9.07	—	—	85.16	5.81	9.03	—	—
	146	—	79.89	5.46	6.94	—	—	79.80	5.42	6.90	—	—
	213	211 (*16*)	60.70	3.59	10.15	25.66	—	60.67	3.61	10.11	25.61	—
	137	—	43.09	0.79	7.42	48.95	—	43.31	0.52	7.22	48.95	—

TABLE 1 (*Continued*)

Product	Melting point, °C[a]		Analyses[b]									
			Found					Calcd.				
	Found	Lit.	C	H	N	X[c]	S	C	H	N	X	S
	287	270 (*17*)	69.98	5.04	11.65	—	—	70.00	5.00	11.67	—	—
	219	216 (*17*)	70.08	5.02	11.96	—	—	70.00	5.00	11.67	—	—
	144	144 (*17*)	71.60	6.01	10.46	—	—	71.64	5.97	10.45	—	—

[a] All melting points were taken on a calibrated Fisher-Johns melting point apparatus.

[b] Microanalyses were performed by Midwest Microlab, Inc., Indianapolis, Ind., and by the Schwartzkopf Microanalytical Laboratories, Woodside, N.Y.

[c] X, halogen.

constant weight. The yields varied from 94–96% of the theoretical amount. Evaporation of the filtrate at 15 mm Hg pressure yielded an additional 4–6% of product, usually of slightly lower melting point than the first crystalline crop. Recrystallization of the products to constant melting points were performed from 95% ethanol, or benzene, or a mixture of both.

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Zusammenfassung

Eine Reihe von Azomethinmonomerer, einschliesslich, einiger neuer Schiff'schen Basen, Azine, und Ketanile wurden in hoher Ausbeute nach einer einfachen, kontinuierlich-azeotropen Methode dargestellt.

Résumé

On a preparé avec un rendement elevé, par une simple méthode continue azéotrope, des différents monomères azomethine, y compris quelques bases de Schiff nouvelles, des azines et des cétanils.

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