Some Derivatives of *p*-Aminoarylarylacetonitriles

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The acetyl, acid succinyl, succinyl, carbethoxy, phenylcarbamyl, and some Schiff base derivatives of six *p*-aminoarylarylacetonitriles are described.

THE COMPOUNDS reported here were prepared as part of an investigation of the chemical properties of some *p*-aminoarylarylacetonitriles previously described (*2*), and as intermediates for the syntheses of new aralkylamines.

The acetyl derivatives were prepared by the reaction of acetic anhydride with the *p*-aminoarylarylacetonitriles following a procedure similar to that of Vogel (*5*). The acid succinyl compounds were synthesized using succinic anhydride with the *p*-aminoarylarylacetonitriles, and they were in turn converted to the succinyl derivatives using acetyl chloride according to methods outlined by Fieser (*3*). A procedure similar to that of Damschroeder and Shriner (*1*), employing sodium carbonate and ethyl chlorocarbonate, was used to obtain the carbethoxy substituted *p*-aminoarylarylacetonitriles. The phenylcarbamyl derivatives were prepared using equivalent amounts of phenylisocyanate with the *p*-aminoarylarylacetonitriles in dry benzene. After refluxing for one-half hour, the reaction mixtures were allowed to cool, and the products were precipitated by the addition of petroleum ether (b. p. 60° to 71° C.). The Schiff base compounds were synthesized using aromatic aldehydes and the *p*-aminoarylarylacetonitriles according to the method of Ritchie (*4*).

The following reaction scheme outlines the transformations involved in this investigation, and Table I lists the compounds prepared along with pertinent information. The structures of the products were assigned on the basis of elemental analyses, similarity to known reactions, and infrared spectral data.

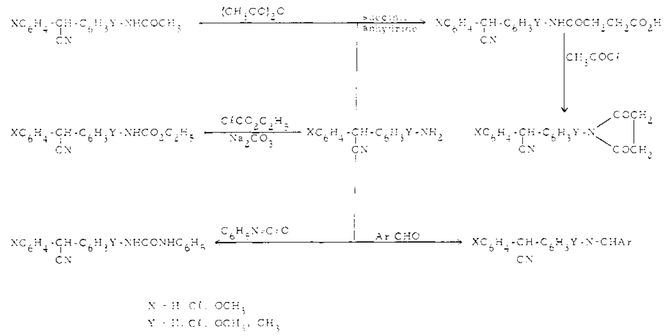

Table I. Derivatives of *p*-Aminoarylarylacetonitriles

Compound	M. P., ° C[a]	Yield, %	Solvent[b]	Analysis, %[c] C	H	N
4-Acetamidophenylphenylacetonitrile	88–9[d]	84	1			
4-Acetamido-3-methylphenylphenylacetonitrile	129–31	90	1	77.25	6.10	
				77.26	6.14	
4-Acetamido-3-chlorophenylphenylacetonitrile	95–7	85	1-2	67.49	4.60	
				67.64	4.80	
4-Acetamido-3-methoxyphenylacetonitrile	89–91	89	1-2	72.83	5.75	
				72.61	5.70	
4-Acetamidophenyl-4-chlorophenylacetonitrile	129–31	88	1	67.49	4.60	
				67.66	4.69	
4-Acetamidophenyl-4-methoxyphenylacetonitrile	127–9	93	1	72.83	5.75	
				73.08	5.77	
4-(Acid succinamido)phenylphenylacetonitrile	151–2	75	3	70.11	5.23	
				70.08	5.30	
4-(Acid succinamido)-3-methylphenylphenylacetonitrile	126–8	94	3-4	70.79	5.63	
				70.61	5.63	
4-(Acid succinamido)-3-chlorophenylphenylacetonitrile	94–6	74	1-3	63.07	4.41	
				63.23	4.67	
4-(Acid succinamido)-3-methoxyphenylphenylacetonitrile	130–1	87	3	67.44	5.36	
				67.31	5.41	
4-(Acid succinamido)phenyl-4-chlorophenylacetonitrile	138–9	82	3	63.07	4.41	
				63.10	4.51	
4-(Acid succamido)phenyl-4-methoxyphenylacetonitrile	146–8	74	3-4	67.44	5.36	
				67.28	5.54	
4-Succinimidophenylphenylacetonitrile	217–18	92	4	74.47	4.86	
				74.72	5.13	
3-Methyl-4-succinimidophenylphenylacetonitrile	130–2	94	4	74.98	5.30	
				75.05	5.36	
3-Chloro-4-succinimidophenylphenylacetonitrile	60–2	80	4-5	66.57	4.03	
				66.53	4.16	
3-Methoxy-4-succinimidophenylphenylacetonitrile	176–8	89	4	71.23	5.04	
				70.99	5.15	
4-Chlorophenyl-4-succinimidophenylacetonitrile	154–5	86	4	66.57	4.03	
				66.65	4.18	
4-Methoxyphenyl-4-succinimidophenylacetonitrile	187–9	96	6	71.23	5.04	
				70.97	5.20	

(*Continued*)

Table I. Derivatives of *p*-Aminoarylarylacetonitriles (*Continued*)

Compound	M.P., ° C.[a]	Yield, %	Solvent[b]	Analysis, %[c]		
				C	H	N
4-*N*-Carbethoxyaminophenylphenylacetonitrile	69	83	6-5	72.83 72.87	5.75 5.93	10.00 10.26
4-*N*-Carbethoxyamino-3-methylphenylphenylacetonitrile	74–5	88	1-2	73.45 73.19	6.16 6.36	9.52 9.60
4-*N*-Carbethoxyamino-3-chlorophenylphenylacetonitrile	70	93	6-5	64.86 64.76	4.80 4.82	8.90 8.81
4-*N*-Carbethoxyamino-3-methoxyphenylphenylacetonitrile	[e]	97				
4-*N*-Carbethoxyaminophenyl-4-chlorophenylacetonitrile	95–6	92	2	64.86 65.09	4.80 4.92	8.90 8.77
4-*N*-Carbethoxyaminophenyl-4-methoxyphenylacetonitrile	114–15	91	6-5	69.66 70.14	5.84 5.91	9.03 9.45
4-(Phenylureido)phenylphenylacetonitrile	164–6	72	4	77.04 77.34	5.25 5.48	
3-Methyl-4-(phenylureido)phenylphenylacetonitrile	201–03	94	3-4	77.39 77.15	5.61 5.57	
3-Chloro-4-(phenylureido)phenylphenylacetonitrile	177–9	73	4	69.71 69.64	4.46 4.68	
3-Methoxy-4-(phenylureido)phenylphenylacetonitrile	178–80	81	4	73.93 74.06	5.36 5.47	
4-Chlorophenyl-4-(phenylureido)phenylacetonitrile	166–7	77	4	69.71 69.61	4.46 4.47	
4-Methoxyphenyl-4-(phenylureido)phenylacetonitrile	160–2	80	4	73.93 74.17	5.36 5.62	
4-*N*-Benzylideneaminophenylphenylacetonitrile	120–2	95	1-2	85.10 84.98	5.44 5.55	9.64 9.70
4-*N*-(*p*-Dimethylaminobenzylidene)aminophenylphenylacetonitrile	157–8	80	1	81.38 81.17	6.23 6.35	12.38 12.18
4-*N*-(*p*-Hydroxybenzylidene)aminophenylphenylacetonitrile	174–6	98	4	80.74 81.06	5.17 5.12	
4-*N*-(*p*-Acetamidobenzylidene)aminophenylphenylacetonitrile	134–135	92	4	78.16 78.08	5.42 5.49	11.89 12.06
4-*N*-(*p*-Methoxybenzylidene)aminophenylphenylacetonitrile	156	91	1	80.96 81.25	5.56 5.72	8.58 8.73
4-*N*-(*p*-Chlorobenzylidene)aminophenylphenylacetonitrile	143–145	92	1	76.24 75.97	4.57 4.72	8.67 8.66
4-*N*-(4′-Pyridylmethylene)aminophenylphenylacetonitrile	130–131	97	1	80.78 80.69	5.08 5.16	14.13 13.72
4-*N*-Benzylideneaminophenyl-4-chlorophenylacetonitrile	88	80	1-2	76.47 76.63	4.27 4.56	8.50 8.51
4-*N*-(*p*-Dimethylaminobenzylidene)aminophenyl-4-chlorophenylacetonitrile	139	69	1-2	74.26 74.13	5.43 5.43	10.76 10.91
4-*N*-(*p*-Hydroxybenzylidene)aminophenyl-4-chlorophenylacetonitrile	217–218	80	7	72.71 72.81	4.36 4.36	8.08 8.19
4-*N*-(*p*-Acetamidobenzylidene)aminophenyl-4-chlorophenylacetonitrile	197	96	7	71.22 71.31	4.68 4.86	10.81 10.92
4-*N*-(*p*-Methoxybenzylidene)aminophenyl-4-chlorophenylacetonitrile	165	98	1-2	73.22 72.97	4.75 4.87	7.76 7.69
4-*N*-(*p*-Chlorobenzylidene)aminophenyl-4-chlorophenylacetonitrile	149	80	4	69.07 69.06	3.86 3.84	7.67 7.57
4-*N*-(4′-Pyridylmethylene)aminophenyl-4-chlorophenylacetonitrile	130	97	1-2	72.40 72.29	4.25 4.52	12.66 12.50
4-*N*-Benzylideneaminophenyl-4-methoxyphenylacetonitrile	119–120	94	6	80.96 80.92	5.56 5.53	8.59 8.58
4-*N*-(*p*-Dimethylaminobenzylidene)aminophenyl-4-methoxyphenylacetonitrile	137–138	97	6	78.02 78.19	6.27 6.39	11.38 11.58
4-*N*-(*p*-Hydroxybenzylidene)aminophenyl-4-methoxyphenylacetonitrile	184–186	77	1	77.17 77.58	5.30 5.57	8.18 7.98
4-*N*-(*p*-Acetamidobenzylidene)aminophenyl-4-methoxphenylacetonitrile	189–190	72	7	75.18 75.61	5.53 5.71	10.93 10.61
4-*N*-(*p*-Methoxybenzylidene)aminophenyl-4-methoxyphenylacetonitrile	195	70	1	77.50 77.63	5.66 5.80	7.86 7.62
4-*N*-(*p*-Chlorobenzylidene)aminophenyl-4-methoxphenylacetonitrile	165	67	1	73.22 72.97	4.75 4.93	7.77 7.76
4-*N*-(4′-Pyridylmethylene)aminophenyl-4-methoxyphenylacetonitrileacetonitrile	146	51	1-2	77.04 77.25	5.33 5.33	12.83 12.57

[a] Melting points were determined using a copper block and are uncorrected. [b] Solvents used for recrystallization: 1. benzene, 2. petroleum ether (b.p. 60° to 71° C.), 3. chloroform, 4. methanol, 5. water, 6. ethanol, 7. toluene. Two numbers indicate co-solvents were used. [c] Analyses by Midwest Microlab, Inc., Indianapolis, Ind. First series calculated, second found. [d] Lit. 90° C. (*6*). [e] Isolated as an oil and used as such in subsequent reactions which demonstrated its authenticity.

The infrared spectra were obtained using solutions of the derivatives in chloroform for those compounds which were reasonably soluble in chloroform. For the other derivatives, the spectra were obtained using mulls in Nujol. All derivatives showed retention of the cyano group as demonstrated by characteristic absorption peaks in the 4.47-micron region. All derivatives showed at least some modification of the amino absorption bands in the 2.8 to 3.0-micron region in comparison with the spectra of the corresponding underivatized compounds. The acetyl, acid succinyl, succinyl, carbethoxy, and phenylcarbamyl derivatives showed characteristic carbonyl absorption bands in the 5.85 to 5.96-micron region. The Shiff base compounds showed no nitrogen to hydrogen absorption in the 2.8 to 3.0-micron region, but did show imino stretching absorption in the 6.1-micron region.

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Reaction of Hydrazine and Iodomethane

Removal of Iodomethane from a Gas Phase in Contact with Alkaline Hydrazine Solution

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The removal of iodomethane from the gas phase over alkaline solutions of hydrazine is a bimolecular interfacial reaction unretarded by the reaction products. The reaction was studied from 21° to 50.1° C. by a gas chromatographic technique from 0 to 0.77 mole fraction of hydrazine hydrate in the solution. The rate of disappearance of iodomethane from the gas phase is directly proportional to the concentration of iodomethane in the gas phase, the mole fraction of hydrazine hydrate in the solution, the interfacial area of the solution, and the reciprocal of the volume of the gas phase.

THE DIRECT reaction of macro amounts of alkyl iodides with hydrazine has been known for some time (*4*). Kinetic studies of the reaction of hydrazine and iodine have been reported (*8*) but not an investigation of the kinetics and mechanism of the iodomethane-hydrazine reaction.

This investigation is part of an effort (*6, 10*) now in progress to determine the mechanism and kinetics of the reaction between iodomethane and hydrazine. The application and verification of reaction models in predicting the behavior of iodomethane in the presence of reactive sprays in large columns and in defining reaction parameters is the primary goal of this project. These results cover the case where a gas phase, which contains a very low concentration of iodomethane, is in contact with an alkaline hydrazine solution.

EXPERIMENTAL

Iodomethane, iodoethane, and 95% hydrazine (Eastman Organic Chemicals) were used without further purification. The iodomethane and iodoethane were stored at 4° C. until needed. To obtain the desired initial concentration of iodomethane (ca. 20 mg. per cu. meter or ca. 4×10^{-3} torr) in the experiments, appropriate dilutions were made of the vapors saturated with iodomethane. The hydrazine stock solution was 93.4 ± 0.5 wt. % hydrazine. The direct iodate method (using solvent) described by Audrieth and Ogg (*1*) was used.

Alkaline hydrazine solutions were prepared by dilution of the hydrazine stock solution and standardized sodium hydroxide solution. There was no indication of deterioration of the alkaline hydrazine solution stored at ambient conditions during the course of the experiments.

A Research Specialties gas chromatograph equipped with a Warner Chilcot electron-capture detector was used. The column was either a 6- or 12-foot length of 0.25-inch I.D. column packed with 20% SE 30 on Chromosorb-P (60- to 80-mesh) and was operated under isothermal conditions (ca. 60° C.). Nitrogen was the carrier gas at flow rates of ca. 100 ml. per minute.

The electron-capture detector used a Sr^{90} source and was compatible with water vapor, which was present in the aliquots of the gaseous reaction mixtures.

The reaction cells consisted of two types. Both types of cells were jacketed borosilicate glass vessels. The first type of vessel was cylindrical with an I.D. of 2.7 cm. and a volume of 55.3 ± 0.1 ml. Access to the interior of the reaction vessel was through a 6-mm. I.D. tube located at the top of the vessel. The system was sealed with a rubber serum bottle stopper. Iodomethane was absorbed by the rubber stopper, but both the rate and extent of absorption were negligible during the time of observation of a reaction. In smaller reaction vessels where the ratio of surface area of rubber to glass is larger by a factor of 10 than in the vessel used in these studies, the extent of iodomethane absorption was appreciable.