Synthesis of 1,2-Diaryl-2-imidazolines

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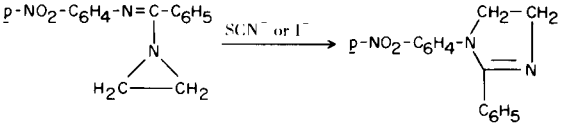
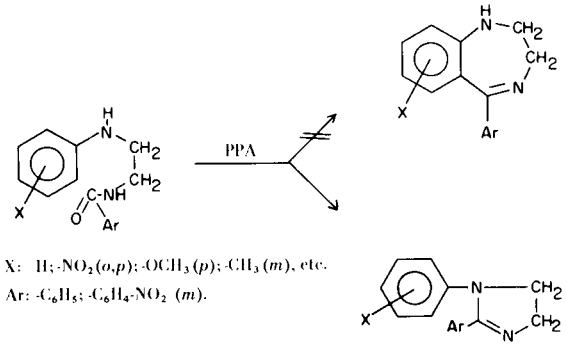
Polyphosphoric acid and *N*-aryl-*N'*-benzoylethylenediamines in a type of Bischler-Napieralski reaction afforded 1,2-diaryl-2-imidazolines in good yields, rather than the 2,3-dihydro-1*H*-[1,4]-benzodiazepines. Blocking of the amino nitrogen by a methyl or ethyl group, to avoid imidazoline formation, gave starting material rather than the expected dihydrobenzodiazepine. When *p*-tosyl was the blocking group, imidazoline was again the only product isolated. Analytical and spectroscopic data of several unreported 1,2-diaryl-2-imidazolines are presented.

The methods most frequently used (1,2,3) in the preparation of 2-substituted-2-imidazolines are not satisfactory for the preparation of 1-aryl derivatives because the necessary arylethylenediamines (except in the case of *ortho* and *para*-nitrophenylethylenediamines) are idfficult to synthesize. Clayton (4) reports the preparation of some 2,5-disubstituted-1-aryl-2-imidazolines using *N*-allylcarboxamides and amine hydrochloride. The best known method to synthesize this type of imidazoline is that of Partridge and Turner (5), based on the conversion of *N*-(2-chloroethyl)carboxamides with phosphorus pentachloride into the corresponding imidochloride. The latter in presence of an arylamine affords a 1,2-disubstituted imidazoline on treatment with alkali. The nine 1,2-diaryl-2-imidazolines reported in the literature were synthesized using this technique.

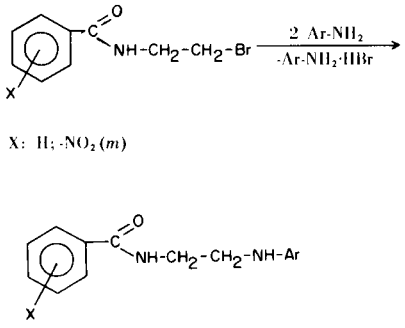
More recently Heine and Bender (6), obtained 1,2-diaryl-2-imidazolines by isomerization of aziridines; 1-(*N*-arylbenzimidoyl)aziridine in acetone, treated with iodide or thiocyanate ions isomerizates into 1-aryl-2-substituted imidazoline (1-*p*-nitrophenyl-2-phenyl-2-imidazoline).



We have shown that the easily prepared *N*-aryl-*N'*-benzoylethylenediamines when heated with PPA lead without any difficulty to the formation of 1-aryl-2-substituted imidazolines in yields of 85-95 percent. Under the selected conditions there was no formation of dihydrobenzodiazepines.



The *N*-aryl-*N'*-benzoylethylenediamines (Table I) were produced from *N*-(2-bromoethyl)benzamide by means of the corresponding arylamine which also functions as a dehydrohalogenating agent (Method A).



This method is useful for unsubstituted arylamines (aniline, naphthylamines) as well as those containing electron donating substituents. In these cases this is the preferred method because synthesis of arylethylenediamines is avoided as well as dibenzoylations which generally occur

TABLE I

N-Aryl-*N*′-benzoylethylenediamines

$$Ar-NH-CH_2-CH_2NH-CO-Ar'$$

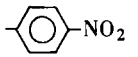
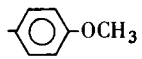
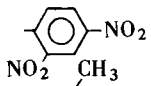
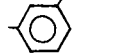
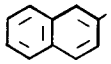
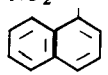
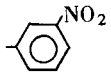
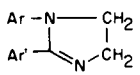
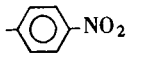
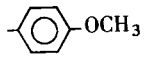
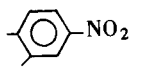
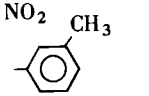
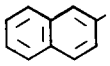
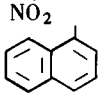
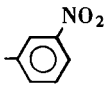
Compound	Ar	Ar′	Method	M.p. °C	Recryst. Solvent	Formula	Anal.	C%	H%	N%
I	$-C_6H_5$	$-C_6H_5$	A	127	Ethanol	$C_{15}H_{16}N_2O$	Calcd.:	75.0	6.66	11.66
							Found:	74.9	6.86	11.54
II		$-C_6H_5$	B	162	Methanol	$C_{15}H_{15}N_3O_3$	Calcd.:	63.1	5.26	14.74
							Found:	62.8	5.30	14.83
III		$-C_6H_5$	A	136.5	Ethanol	$C_{16}H_{18}N_2O_2$	Calcd.:	71.1	6.66	10.37
							Found:	71.0	6.65	10.25
IV		$-C_6H_5$	B	189	Dioxane	$C_{15}H_{14}N_4O_5$	Calcd.:	54.5	4.24	16.97
							Found:	54.7	4.22	16.78
V		$-C_6H_5$	A	104	Ethanol	$C_{16}H_{18}N_2O$	Calcd.:	75.6	7.08	11.02
							Found:	75.4	7.31	11.15
VI		$-C_6H_5$	A	184	Dioxane	$C_{19}H_{18}N_2O$	Calcd.:	78.6	6.21	9.65
							Found:	78.8	6.49	9.64
VII		$-C_6H_5$	B	123.5	Dioxane	$C_{15}H_{15}N_3O_3$	Calcd.:	63.2	5.26	14.74
							Found:	63.1	5.42	14.85
VIII		$-C_6H_5$	A	140	Ethanol	$C_{19}H_{18}N_2O$	Calcd.:	78.6	6.21	9.65
							Found:	78.7	6.44	9.60
IX	$-C_6H_5$		A	132.5	Ethanol	$C_{15}H_{15}N_3O_3$	Calcd.:	63.2	5.26	14.73
							Found:	63.2	5.26	14.90

TABLE II

1,2-Diaryl-2-imidazolines

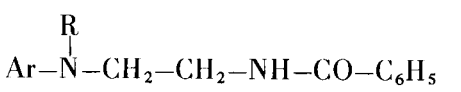


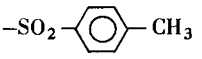
Compound	Ar	Ar′	M.p. °C Bases	Recryst. Solvent	M.p. °C Picrates	Formula Bases	Anal. Bases	C%	H%	N%
X	$-C_6H_5$	$-C_6H_5$	74	Benzene	177.5	$C_{15}H_{14}N_2$	Calcd.:	81.1	6.31	12.61
							Found:	81.0	6.64	12.34
XI		$-C_6H_5$	177	Methanol	174.5	$C_{15}H_{13}N_3O_2$	Calcd.:	67.4	4.87	15.73
							Found:	67.4	5.00	15.52
XII		$-C_6H_5$	77	a	163.5	$C_{16}H_{16}N_2O$	Calcd.:	76.2	6.35	11.11
							Found:	76.1	6.57	11.15
XIII		$-C_6H_5$	144	Ethanol	206	$C_{15}H_{12}N_4O_4$	Calcd.:	57.7	3.85	17.95
							Found:	57.6	3.94	17.50
XIV (b)		$-C_6H_5$	oil	b	152.5	$C_{22}H_{19}N_5O_7$	Calcd.:	56.8	4.09	15.05
							Found:	56.9	4.39	15.45
XV		$-C_6H_5$	129	Benzene	228	$C_{19}H_{16}N_2$	Calcd.:	83.8	5.88	10.29
							Found:	83.5	6.02	10.36
XVI		$-C_6H_5$	79.5	Cyclohexane	164	$C_{15}H_{13}N_3O_2$	Calcd.:	67.4	4.87	15.73
							Found:	67.4	5.13	15.74
XVII		$-C_6H_5$	136	Cyclohexane	240	$C_{19}H_{16}N_2$	Calcd.:	83.8	5.88	10.29
							Found:	83.8	5.86	10.23
XVIII	$-C_6H_5$		50	a	178	$C_{15}H_{13}N_3O_2$	Calcd.:	67.4	4.87	15.73
							Found:	66.9	4.97	15.40

(a) Was obtained by successive dissolution in 10% hydrochloric acid and precipitated with alkali. (b) The remainder base was an oil; analyzed as picrate.

TABLE III

N,N-Disubstituted Benzoylethylenediamines



Compound	Ar	R	M.p. °C	Recryst. Solvent	Formula	Anal.	C%	H%	N%
XIx	C_6H_5	CH_3	90	Ethanol	$C_{16}H_{18}N_2O$	Calcd.:	75.6	7.08	11.02
						Found:	75.4	7.26	10.90
XX	C_6H_5	C_2H_5	97	Methanol	$C_{17}H_{20}N_2O$	Calcd.:	76.1	7.46	10.45
						Found:	76.3	7.39	10.35
XXI		C_2H_5	80	Ethanol	$C_{18}H_{22}N_2O$	Calcd.:	76.6	7.80	9.93
						Found:	76.5	8.05	9.68
XXII	C_6H_5		151	Ethanol	$C_{22}H_{22}N_2O_3S$	Calcd.:	67.0	5.58	7.10
						Found:	67.2	5.72	7.30

on treatment of arylethylenediamines with benzoyl chloride. However, with amines containing electron attracting substituents such as *ortho* and *para*-nitrophenylethylenediamines, direct benzoylation gives a good yield of the *N*-monobenzoylated derivative without difficulties (Method B).

These *N*-aryl-*N'*-benzoylethylenediamines, I-IX (listed in Table I) were identified by elementary analysis, hydrolysis under acidic conditions and infrared spectra (see Table VI).

The *N*-aryl-*N'*-benzoylethylenediamines were dehydrated with polyphosphoric acid (PPA) in a 1 to 15 ratio by weight by heating at 150° for one hour. Several probe runs were performed to fix the reaction conditions: between 100 and 120° there was practically no transformation of the *N*-aryl-*N'*-benzoylethylenediamines, while between 160-200° resins were formed; a temperature of 150° gave the best results. Imidazolines were isolated on dilution and neutralization of the reaction mixtures, performing solvent extractions when necessary. They were crystallized as the free bases, except in only one case (Compound XIV in Table II) that was an oil. The respective picrates of all the bases were also prepared.

The structure of the imidazolines was confirmed by elementary analysis, IR and NMR spectra, and by comparison with the products provided by Partridge's technique.

After acid, neutral and basic extractions, traces of benzoic acid, arylethylenediamine and starting material were identified by TLC. No traces of dihydrobenzodiazepines were found. Apparently a side reaction of little importance, hydrolysis of the amide, takes place and the presence of traces of the starting material could be a consequence of the hydrolysis of the imidazoline during the neutralization process.

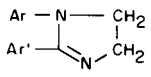
In attempts to alter the course of reaction so that dihydrodiazepine rather than imidazoline ring formation was favored, the amino hydrogen was replaced by an alkyl or tosyl group. Compounds shown in Table III were prepared. Compounds XIX and XX were synthesized by Method A, XXI by benzoylation of the *N*-(*m*-tolyl)-*N*-ethylethylenediamine and XXII from *N*-phenyl-*N'*-benzoylethylenediamine in acetone solution of *p*-tosyl chloride in the presence of potassium carbonate.

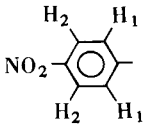
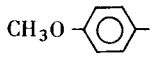
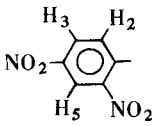
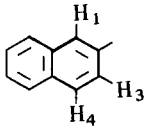
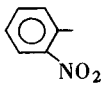
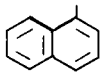
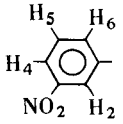
These *N,N*-disubstituted-*N'*-benzoylethylenediamines, XIX-XXII (listed in Table III) were identified by elementary analysis, hydrolysis in 30% hydrochloric acid and IR spectra (see Table VI). Heating of XIX, XX and XXI with PPA at 150° for four hours gave unreacted starting material almost quantitatively. When the reaction was forced by heating at 180°, hydrolysis of the amides was observed. Heating of XXII at 150° for one hour caused the *p*-tosyl group to split off and X was quantitatively formed.

The reaction time favoring maximum imidazoline formation was determined. After 30-40 minutes the concentration of imidazoline and starting material remained constant but traces of the arylethylenediamines appeared. Reaction times required for the nitrated derivatives were slightly less which agrees with the greater acidity for the hydrogen of the secondary amine. Summarily, when the reaction time was increased, neither the imidazoline yields nor the decomposition increased. Therefore conditions of 150° for one hour were chosen in all cases.

TABLE IV

Nuclear Magnetic Resonance



Compound	Ar	Ar′	δ ppm	Multiplicity	Assignment
X	$-C_6H_5$	$-C_6H_5$	4	(Q)	$-CH_2-CH_2-$
			6.6-7.65	(M)	aromatic
XI		$-C_6H_5$	4.13	(S)	$-CH_2-CH_2-$
			6.75	(D)	2 x H_1
			7.12-7.84	(M)	$-C_6H_5$
			8.03	(D)	2 x H_2
XII		$-C_6H_5$	3.75	(S)	CH_3-
			4.01	(S)	$-CH_2-CH_2-$
			6.81	(S)	$-O-C_6H_4-$
			7.15-7.70	(M)	$-C_6H_5$
XIII		$-C_6H_5$	4.03-4.30	(M)	$-CH_2-CH_2-$
			7.15	(D)	H_2
			7.32-7.66	(M)	$-C_6H_5$
			8.25	(D) two	H_3
			8.70	(D)	H_5
XV		$-C_6H_5$	4.12	(S)	$-CH_2-CH_2-$
			6.95	(D) two	H_3
			7.72-7.8	(M)	the remaining H
XVI		$-C_6H_5$	3.72-4.46	(M)	$-CH_2-CH_2-$
			7.02-7.96	(M)	aromatic
XVII		$-C_6H_5$	4.27	(S) broad	$-CH_2-CH_2-$
			6.86-9	(M)	aromatic
XVIII	$-C_6H_5$		4.10	(S)	$-CH_2CH_2-$
			6.76-7.98	(M)	$-C_6H_5$, H_5, H_6
			8.26	(Q) two	H_4
			8.47	(T)	H_2

Since no spectroscopic data for 1,2-diaryl-2-imidazolines is presented in the literature, we present NMR and IR spectral data for eight imidazolines of this type, which we obtained in the course of our investigations (see Tables IV and V).

EXPERIMENTAL

All melting points are uncorrected and were taken on a Buchi Capillary melting point apparatus. Infrared spectra were determined with a Perkin-Elmer Model 21 spectrometer using potassium bromide pellets of the compounds. NMR spectra were measured

TABLE V

Infrared Spectral Data of 1,2-Diaryl-2-imidazolines

Compound	X	3.35-3.42	6.16	6.22	6.32	6.65	6.73	6.88	7.26	7.82	8.87	12.88	14.31
		(w-m)	(m)	(s)	(m)	(s)	(m)	(m)	(s)	(s)	(m)	(m)	(s)
"	XI	3.35-3.42	6.17	6.28	6.30	6.64	6.75	6.68	7.24	7.84	8.78	12.98	14.35
		(w-b)	(m)	(s)	(m)	(s)	(m)	(w-m)	(m)	(s)	(w-m)	(m)	(s)
"	XII	3.38-3.50	6.20	6.25	6.35	6.61	6.70	6.90	7.24	7.82	8.83	12.85	14.25
		(w-b)	(m)	(m)	(m)	(s)	(m)	(w-m)	(m)	(m)	(m)	(s)	(s)
"	XIII	3.40-3.50	6.16	6.25	6.33	6.62	6.73	6.90	7.28	7.87	8.80	12.94	14.32
		(w-b)	(m)	(s-b)	(m)	(m)	(m)	(w)	(m)	(s)	(m)	(m)	(s)
"	XV	3.40-3.53	6.22	6.29	6.30	6.70	6.78	6.82	7.20	7.87	8.83	12.90	14.35
		(w-b)	(m)	(s)	(m)	(m)	(w)	(m)	(s)	(s)	(m)	(s)	(s)
"	XVI	3.38-3.45	6.18	6.24	6.34	6.60	6.78	6.88	7.21	7.83	8.90	12.90	14.30
		(w-m)	(m)	(s)	(m)	(s)	(m)	(m)	(s)	(s)	(m)	(m)	(s)
"	XVII	3.40-3.47	6.19	6.25	6.35	6.70	6.78	6.85	7.27	7.85	8.86	12.85	14.32
		(w)	(s)	(m)	(s)	(s)	(w-m)	(m)	(s)	(s)	(m-s)	(s)	(s)
"	XVIII	3.36-3.45	6.16	6.25	6.32	6.65	6.75	6.90	7.19	7.85	8.85	12.95	14.40
		(m)	(m)	(m-s)	(m)	(w-m)	(m)	(m)	(m)	(s)	(m)	(s)	(s)

Data in microns; w:weak; m:medium; s:strong; b:broad.

in deuteriochloroform on a Varian A-60 instrument and chemical shifts are reported in parts per million (δ) downfield from an internal TMS reference. The abreviations: S for singlet; D for doublet; T for triplet; Q for quartet and M for multiplet are used. Thin layer chromatography (TLC) was run on Merck Silica Gel G and G.F.254.

N-(2,4-Dinitrophenyl)ethylenediamine (7).

To a solution of 10.25 g. (0.17 mole) of ethylenediamine in 30 ml. of acetone was added dropwise with stirring and cooling, 5 g. (0.025 mole) of 1-chloro-2,4-dinitrobenzene in 30 ml. of acetone. The mixture was left in the ice bath for 30 minutes and then at room temperature another 30 minutes. The solvent was removed *in vacuo* and the residue was dissolved in 20 ml. of ethanol and adjusted to *p*H 2 with hydrochloric acid. After cooling, the precipitate was collected by filtration, washed with alcohol and dried. The dried residue was dissolved in 80 ml. of boiling water, the solution was filtered to remove any insoluble material (bis derivative) and made alkaline with 5% sodium hydroxide. After standing at 5° overnight, 4.7 g. of product was obtained, m.p. 84-85°, yield 85%.

N-(2,4-Dinitrophenyl)-*N'*-benzoylethylenediamine (IV) (Method B).

A mixture of 2.6 g. (0.01 mole) of 2,4-dinitrophenylethylenediamine and 2.1 g. (0.015 mole) of benzoyl chloride was heated for 30 minutes in a water bath at 100° and protected from moisture. The reaction mixture was treated with cooled 5% sodium hydroxide and the product was collected and washed successively with cold water, 10% hydrochloric acid and water. Crystallization from dioxane afforded orange needles of IV, m.p. 188-189°, yield 95% (see Table I).

N-(*p*-Nitrophenyl)-*N'*-benzoylethylenediamine (II). (Method B).

To a stirred cooled suspension of 0.99 g. (0.005 mole) of *p*-nitrophenylethylenediamine (prepared according to Fourneau and Lestrange (8)) in 15 ml. of 5% sodium hydroxide and 10 ml. of acetone, was added dropwise 0.98 g. (0.007 mole) of benzoyl chloride in 10 ml. of acetone. Stirring was continued for two hours and the mixture was treated with water and filtered. The resulting solid was washed and crystallized from methanol affording yellow needles of II, m.p. 162°.

N-(*o*-Nitrophenyl)-*N'*-benzoylethylenediamine (VII). (Method B).

This compound was prepared in an identical manner but starting from *o*-nitrophenylethylenediamine hydrochloride (8). The yellow solid obtained was crystallized from dioxane to give VII, m.p. 123°.

N-Aryl-*N'*-benzoylethylenediamines (I, III, V, VI, VIII and IX). (Method A).

A mixture of 0.02 mole of *N*-(2-bromoethyl)benzamide or *m*-nitrobenzamide (9) and 0.04 mole of the amine, was heated in an oil bath at 100-130° (according to the amine employed) for one hour. The crude product was washed twice with boiling water, dried and crystallized from a suitable solvent (see Table I).

1-Aryl-2-aryl'-2-imidazolines (X-XVIII).

A mixture of 1 g. of *N*-aryl-*N'*-benzoylethylenediamine and 15 g. of polyphosphoric acid was placed in a closed tube and heated in an oil bath at 150° for one hour. The mixture was cooled and after addition of 150 ml. of ice water, was neutralized with solid sodium carbonate. If the imidazoline precipitated, it was collected; if not, the solution was extracted four times with 30 ml. of methylene chloride. The organic solution, after washing with water, was dried and evaporated *in vacuo*. The imidazolines were crystallized from the solvents indicated in Table II and also transformed into picrates. The latter were obtained after dissolving the bases in dilute hydrochloric acid and precipitating with aqueous solution of picric acid. The resulting picrates were crystallized from ethanol (see Table II).

TABLE VI

Infrared Spectral Data of *N*-Aryl-*N'*-benzoylethylenediamines Listed in Tables I and III

Compound	NH	Amide I	C=C	Amide II	C–N
I	2.98 (s)	6.12 (s)	6.25, 6.33 (w) (m)	6.56 (s)	7.74, 8.12 (m) (s)
II	2.94, 3.08 (s) (s)	6.04 (s)	6.25, 6.33 (s) (m)	6.49 (m)	7.75, 8.13 (s) (m)
III	2.97 (s)	6.12 (s)	6.25, 6.33 (w) (m)	6.58 (s)	7.72, 8.11 (m) (s)
IV	2.99, 3.02 (s) (s)	6.12 (s)	6.25, 6.31 (m) (s)	6.58 (s)	7.74, 8.16 (s) (s)
V	3.01, 3.04 (s) (s)	6.14 (s)	6.23, 6.33 (m) (m)	6.54 (m)	7.75, 8.20 (m) (w)
VI	2.94, 3.00 (m) (s)	6.14 (s)	6.25, 6.35 (m) (m)	6.58 (s)	7.73, 8.17 (w) (m)
VII	2.96, 2.99 (s) (s)	6.11 (s)	6.27, 6.33 (m) (s)	6.54 (s)	7.70, 8.13 (m) (s)
VIII	2.98, 3.07 (s) (s)	6.14 (s)	6.24, 6.31 (m) (s)	6.56 (m)	7.75, 8.13 (m) (m)
IX	2.93, 2.98 (s) (s)	6.13 (s)	6.25, 6.37 (m) (m)	6.60 (s)	7.70, 8.13 (m) (m)
XIX	2.99 (s)	6.12 (s)	6.25, 6.33 (m) (m)	6.62 (s)	7.72, 8.10 (s) (m)
XX	3.03 (s)	6.10 (s)	6.24, 6.33 (m) (m)	6.62 (s)	7.75, 8.10 (w) (s)
XXI	3.03 (s)	6.12 (s)	6.24, 6.33 (s) (s)	6.54 (s)	7.70, 8.09 (s) (s)
XXII	3.07 (s)	6.11 (s)	6.24, 6.33 (w) (m)	6.49 (m)	7.71, 8.21 (w) (m)

Data in microns; w:weak; m:medium; s:strong.

N-(*m*-Tolyl)-*N*-ethyl-*N'*-benzoylethylenediamine (XXI). (Method B).

To a stirred and cooled suspension of 0.01 mole of *N*-(*m*-tolyl)-*N*-ethylethylenediamine in 25 ml. of 5% sodium hydroxide and 20 ml. of acetone, was added dropwise, a solution of 0.013 mole of benzoyl chloride in 20 ml. of acetone during 45 minutes. Stirring was continued for 2 hours and the mixture was treated with water. Upon cooling in ice, the oil solidified. Crystallization from ethanol afforded a solid XXI, m.p. 80°. (see Table III).

N-(Phenyl)-*N*-tosyl-*N'*-benzoylethylenediamine (XXII).

A solution of 0.015 mole of *p*-toluenesulfonyl chloride in 60 ml. of acetone was added during 30 minutes to a boiling mixture of 0.01 mole of *N*-phenyl-*N'*-benzoylethylenediamine (I), in 25 ml. of acetone and 0.015 mole of anhydrous potassium carbonate. The mixture was refluxed for 5 hours and filtered; the potassium chloride was washed with 10 ml. of acetone. The acetonic solution was concentrated *in vacuo* and the resulting solid was washed with dilute hydrochloric acid and then with water, yield of XXII was 95%, m.p. 151° (ethanol).

N-Phenyl-*N*-methyl-*N'*-benzoylethylenediamine (XIX) and *N*-Phenyl-*N*-ethyl-*N'*-benzoylethylenediamine (XX).

These compounds were synthesized by Method A reported for *N*-aryl-*N'*-benzoylethylenediamines (see Table III).

Attempted Synthesis of 1-Alkyl-5-phenyl-1*H*-2,3-dihydro-[1,4]-benzodiazepines.

An intimate mixture of 0.5 g. of *N*-aryl-*N*-alkyl-*N'*-benzoylethylenediamine and 7.5 g. of polyphosphoric acid was heated in an oil bath at 150° for one hour. After cooling, the mixture was dissolved in 75 ml. of ice water; the solution was neutralized with solid sodium carbonate and extracted with methylene chloride. The organic solution was washed, dried, and after concentration, gave a white solid which upon crystallization from ethanol afforded

0.45 g. of a product, identical with starting material (no m.p. depression with an authentic sample, identical chromatographic results and infrared spectrum). Even after heating the mixture for four hours at 150° the recovery of the starting material was also nearly quantitative. Thin layer chromatography of the organic extracts from the reaction mixture (under acidic, neutral and alkaline conditions) showed the presence of only traces of benzoic acid and the debenzoylated amine as the only contaminants. No traces of the dihydrobenzodiazepine was observed. After heating the mixture for four hours at 180°, however, working under the same conditions as above, abundant debenzoylation was observed.

Attempted Synthesis of 1-*p*-Tosyl-5-phenyl-1*H*-2,3-dihydro-[1,4]-benzodiazepine.

Starting from *N*-phenyl-*N*-tosyl-*N'*-benzoylethylenediamine, the same procedure as for 1-aryl-2-aryl'-2-imidazoline was followed. The neutral extract gave a solid, m.p. 70-72°, which was crystallized from benzene, m.p. 74° and was identical by mixture melting point and infrared spectrum with 1,2-diphenyl-2-imidazoline, yield, 92%.

Optimal Temperature and Time of Reaction.

One g. of *N*-aryl-*N'*-benzoylethylenediamine in 15 g. of polyphosphoric acid was heated in an oil bath at 100° for five minutes and an aliquot of 1 ml. was taken; the temperature was raised to 120° and after five minutes another aliquot was taken. This procedure was repeated at 140°, 160°, 180° and 200°. The 1 ml. samples were dissolved in 10 ml. of ice water, the solutions were made alkaline with solid sodium carbonate and extracted with three portions of 5 ml. of methylene chloride. The organic layer was decanted, washed, dried and then examined by thin layer chromatography.

While maintaining the reaction mixture at 150° under the conditions described above, aliquots were taken every five minutes for 5-60 minutes, and then examined by thin layer chromatography.

Nature of the Reaction Products.

The reaction products were determined in the prescribed conditions and analyzed by chromatography after extraction in acidic, neutral and alkaline mediums: 1). The crude extract was dissolved in ice water and extracted with methylene chloride (acidic extract); the organic layer was treated with 5% sodium hydroxide, the solutions were separated and the alkaline solution was brought to *p*H 2 with concentrated hydrochloric acid and extracted again with methylene chloride and examined for benzoic acid. 2). The remaining acid solution was neutralized to *p*H 7, with solid sodium carbonate, and extracted with several portions of methylene chloride (neutral extract). 3). The neutral solutions of 2) were made strongly alkaline with 20% sodium hydroxide and again extracted with methylene chloride (alkaline extract). Solutions 2) and 3) were examined for imidazolines and other basic products.

All of the organic extracts obtained above were examined by thin layer chromatography. The thin layer plates (10 x 20 cm.) were prepared from Silica Gel G and Silica Gel GF-254. The reference compounds were: a) *N*-aryl-*N'*-benzoylethylenediamines; b) *N*-arylethylenediamines; c) 1,2-diaryl-2-imidazolines; d) 5-phenyl-1*H*-2,3-dihydro-[1,4]benzodiazepines.

The solvents were: benzene-methanol (95:5), methanol-acetone-triethanolamine (10:10:0.3), chloroform-diethylamine (90:10) and methanol. On silica Gel G plates, the visualization was achieved by spraying with Draggendorf reagent and on Silica Gel GF-254 plates by exposition to ultraviolet light. In the analysis of benzoic acid in the acidic extract 1), the reagent was bromocresol green and the solvent, benzene-methanol-acetic acid (90:16:8) using as reference compound pure benzoic acid in methylene chloride.

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