[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Cyclic Aminoacyloins and Aminoketones. VII. N-Aryl Substitution and Transannular Interaction Between N and C_{CO}[1]

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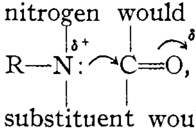
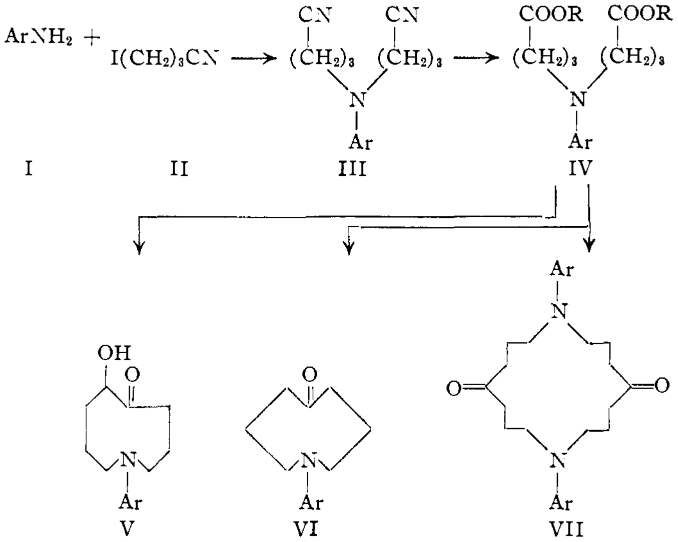
A number of 1-aryl-1-azacyclononan-5-ol-6-ones (V) and 1-aryl-1-azacycloöctan-5-ones (VI) (aryl = phenyl and substituted phenyl) have been synthesized from the corresponding γ,γ′-arylimino-bis-butyric esters. On the basis of infrared determinations and pK'_a comparisons, it is evident that transannular interaction between N and C_{CO} occurs to a lesser extent in these compounds than in their N-alkyl analogs. This may be accounted for by a combination of steric hindrance and the electron-withdrawing power of the phenyl group. From the Dieckmann cyclization of the γ,γ′-arylimino-bis-butyric esters with sodium hydride, several unusual sixteen-membered ring diaminodiketones (VII) have been isolated.

The ring-size,[2,3] steric strain[4–6] and environmental[4,6] limitations of transannular interaction between N and C_{CO} in cyclic aminoacyloins and aminoketones have been described previously. Since one prerequisite for interaction to occur is the availability of the electron pair on nitrogen,[7] it was to be expected that an electron-donating substituent on nitrogen would enhance the N–C_{CO} interaction,  $\overset{|\delta^+}{\underset{|}{\mathrm{R{-}N}}}\!:\curvearrowright\overset{|}{\underset{|}{\mathrm{C}}}{=}\overset{\curvearrowright\delta^-}{\mathrm{O}}$, while an electron-withdrawing substituent would diminish the interaction. For the purpose of studying an electronic effect of the type anticipated, N-aryl substitution appeared to offer convenience and flexibility, since, by varying the *p*-substituent, it should be possible to change the electron-pair availability on the nitrogen without altering the steric hindrance at the nitrogen.



a, Ar = C_6H_5; b, *p*-$CH_3C_6H_4$; c, 2′,4′-$(CH_3)_2C_6H_3$; d, 2′,6′-$(CH_3)_2$-C_6H_3; e, 2′,4′,6′-$(CH_3)_3C_6H_2$; f, *p*-$CH_3OC_6H_4$; g, *p*-$(C_2H_5)_2NC_6H_4$; h, *p*-$(CH_2)_4NC_6H_4$.

Accordingly, we sought to prepare a number of 1-aryl-1-azacylononan-5-ol-6-ones (V) and 1-aryl-1-azacycloöctan-5-ones (VI), basing our selection on the occurrence of transannular nitrogen–carbonyl interaction in the corresponding N-alkyl, nine-membered ring aminoacyloins[3] and eight-membered ring aminoketones.[5] When we found that the infrared carbonyl frequencies for the compounds 1-phenyl-1-azacyclononan-5-ol-6-one (Va) and 1-*p*-tolyl-1-azacycloöctan-5-one (VIb) were near the normal to be expected of non-interacted C=O, we abandoned plans to incorporate electron withdrawing groups in the phenyl ring and concentrated on the synthesis of N-phenyl compounds bearing electron-donating groups. γ-Iodobutyronitrile (II) was employed for the dialkylation of the aromatic amines (I) when it was found that γ-iodobutyric ester did not give the desired diester intermediate IV. The arylamines which were not sterically hindered (Ia, b, f, g, h) were converted to the corresponding dinitriles III by means of potassium carbonate and γ-iodobutyronitrile in aqueous suspension, the hindered amines (Ic, d, e), in amyl alcohol. Alcoholysis of the dinitriles III gave the diesters IV, but two of these intermediates (IVd, g) could not be obtained in the pure state because of their persistent tendency to decompose.

The acyloin condensation of the diesters IV was carried out with the usual precautions,[3] but decomposition usually attended and the only 1-azacyclononan-5-ol-6-ones obtained in comparatively good yield were the 1-*p*-tolyl (Vb) and 1-*p*-N-pyrrolidylphenyl (Vh) compounds. The 1-phenyl compound Va was also obtained. Sodium hydride[5,8] was used to effect Dieckmann ring closure of the diesters IV, leading to 1-*p*-tolyl-, 1-(2′,4′-xylyl)- and 1-*p*-N-pyrrolidylphenyl-1-azacycloöctan-5-one (VIb, c, h), but only the first of these was obtained in good yield. Along with the eight-membered aminoketone bearing N-(2′,4′-xylyl)-substitution, a solid compound with the same empirical formula but double the molecular weight was isolated in a very small amount. The structure assigned was that of the sixteen-membered ring diaminodiketone, 1,9-di-(2′,4′-xylyl)-1,9-diazacyclohexadecane-5,13-dione (VIIc), on the basis of the precursor diester, the aminoketone co-product, molecular weight determination, physical properties and analysis of the

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[1] Presented at the 14th National Organic Chemistry Symposium of the American Chemical Society, Lafayette, Ind., on June 14, 1955.

[2] N. J. Leonard, R. C. Fox, M. Ōki and S. Chiavarelli, THIS JOURNAL, **76**, 630 (1954).

[3] N. J. Leonard, R. C. Fox and M. Ōki, *ibid.*, **76**, 5708 (1954).

[4] N. J. Leonard and M. Ōki, *ibid.*, **76**, 3463 (1954).

[5] N. J. Leonard, M. Ōki and S. Chiavarelli, *ibid.*, **77**, 6234 (1955).

[6] N. J. Leonard, M. Ōki, J. Brader and H. Boaz, *ibid.*, **77**, 6237 (1955).

[7] N. J. Leonard and M. Ōki, *ibid.*, **77**, 6239 (1955).

[8] F. F. Blicke, J. Azuara, N. J. Doorenbos and E. B. Hotelling, *ibid.*, **75**, 5418 (1953).

compound and its diperchlorate salt. Other sixteen-membered ring diaminodiketones (VIIa, e, f) were found where the corresponding eight-membered ring aminoketones could not be isolated following the Dieckmann ring closure. The yields (0.1–0.6%) of these unique large ring compounds were inferior to that reported from this Laboratory (29%) in the analogous synthesis of 1,9-dimethyl-1,9-diazacyclohexadecane-5,13-dione.[5]

For our infrared determinations and pK_a' comparisons, we had to be content with the arylaminoacyloins and arylaminoketones which we had made and which were stable enough for examination. The position of the carbonyl stretching band in the infrared for 1-phenyl-1-azacyclononan-5-ol-6-one (Va) (Table I) bears comment. Its center lies at higher wave number (also a possible inflection point at *ca.* 1692 cm.$^{-1}$) than that observed for solutions of similar concentration in carbon tetrachloride of either the 1-methyl- or the 1-ethyl-1-azacyclononan-5-ol-6-one (1666, 1671 cm.$^{-1}$, respectively).[3] The extent of transannular interaction between N and C_{CO} for the phenyl compound thus appears to be much less than that for the simple alkyl compounds. This may be accounted for by steric interference of the phenyl group or by the electron-withdrawing ability of the phenyl group, or both influences. Our assumption that the limitation of transannular interaction is not due alone to steric strain is based upon the observation that 1-isopropyl- and 1-cyclohexyl-1-azacyclononan-5-ol-6-one, bearing N-groups of bulk at least equivalent to phenyl, have infrared maxima at 1691 cm.$^{-1}$, which is still below that (1704 cm.$^{-1}$) for Va.[9] Substitution of a *p*-methyl on the phenyl group does not alter the frequency of the infrared maximum appreciably (Vb in Table I), despite the contribution to the electron availability on the nitrogen.[10] Moreover, the *p*-N-pyrrolidyl grouping does not have an effect on the carbonyl infrared frequency (comparing dilute solutions of Vb and h in carbon tetrachloride) commensurate with its strong electron-donating power.[11] The increase in pK_a' observed for Vb in shifting solvent from 50% dimethylformamide to water is consistent with attachment of the proton to the nitrogen of the conjugate acid in these solvents.[3]

TABLE I

ARYLAMINOACYLOINS

Compound	Infrared C=O max, cm.$^{-1}$ (CCl$_4$) 3%	0.01 *M*	$pK_a'^{a}$ DMF 66%	50%	33%	H$_2$O
Va	1704					
Vb	1705	1702		2.5	2.7	3.2
Vh	1698	1700	4.8	5.5	5.8	6.2

[a] We are indebted to Mrs. Helen Arndt for the electrometric titrations and to Dr. Harold E. Boaz, both of Eli Lilly and Company, Indianapolis, Ind., for aid in their interpretation.

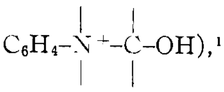
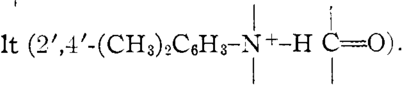
The frequencies of the infrared carbonyl maxima (mid-point of each band) for the arylaminoketones (Table II) suggest less transannular nitrogen–carbonyl interaction in these examples than in their 1-methyl (1683 cm.$^{-1}$) and 1-cyclohexyl (1687 cm.$^{-1}$) analogs.[5] Here again, the electron-withdrawing power of the phenyl group submerges the electron-donating power of the substituents on phenyl. Nevertheless, an interesting example of the importance of the steric limitation of transannular N–C_{CO} bonding is provided in a comparison of the solid perchlorates of 1-*p*-tolyl- and 1-(2′,4′-xylyl)-1-azacyclooöctan-5-one (VIb, c). The former exists in the transannular quaternary form (*p*-CH$_3$-$C_6H_4\text{–}\overset{|}{\underset{|}{N}}{}^{+}\text{–}\overset{|}{\underset{|}{C}}\text{–}OH$),[12] while the latter exists as the normal salt ($2',4'\text{-}(CH_3)_2C_6H_3\text{–}\overset{|}{\underset{|}{N}}{}^{+}\text{–}H\ \overset{|}{\underset{|}{C}}=O$). The steric strain (F-strain)[13] provided by the additional *o*-methyl in the xylyl grouping prevents bonding between N and C_{CO} and favors bonding between nitrogen and the proton.[14] To conclude, the aryl compounds studied have thus provided additional information on the steric limitation of transannular nitrogen–carbonyl interaction and have indicated the possibility of an electronic limitation of this type of interaction.

TABLE II

ARYLAMINOKETONES

Compound	Infrared C=O max, cm.$^{-1}$ (CCl$_4$) 5%	Perchlorate max. (mull) C=O	O-H/N-H
VIb	1698^{a}	None	3310
VIc	1697	1713	3460,3090
VIh	1694		

[a] 1701 cm.$^{-1}$ for 0.01 *M* solution.

Experimental[15,16]

γ,γ'-Arylimino-bis-butyronitriles (III).—A mixture of 0.5 mole of the arylamine I,[17] 1.0 mole of γ-iodobutyronitrile (II), 0.5 mole of potassium carbonate and 700 ml. of water was heated under reflux with efficient stirring for 15–20 hours. After cooling the mixture, 10 g. of potassium carbonate was added and the whole was extracted with chloroform. The

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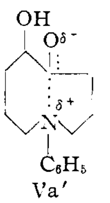
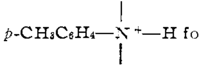
[9] An alternative explanation, which cannot be discarded completely, lies in the assumption that transannular nitrogen–carbonyl interaction does occur in Va, but that the frequency of carbonyl stretching in the interacted form[6] Va′, will be higher than that for the corresponding methyl compound and hence close to that of a normal carbonyl, as in the non-interacted form. The closest analogy available is in the finding of R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, 1248 (1947), that the C=O maximum for $CH_3CON(CH_3)C_6H_5$ is 15–20 cm.$^{-1}$ higher than that for $CH_3CON(C_2H_5)_2$.



Va′

[10] *Cf.* pK_a in 50% ethanol at 20° for dimethylaniline = 4.35, for N,N-dimethyl-*p*-toluidine = 4.94 (R. A. Benkeser and H. R. Krysiak, THIS JOURNAL, **75**, 2421 (1953)).

[11] H. C. Brown, J. H. Brewster and H. Shechter, *ibid.*, **76**, 467 (1954).

[12] In solution, the pK_a' data tend to suggest existence in the $p\text{-}CH_3C_6H_4\text{—}\overset{|}{\underset{|}{N}}{}^{+}\text{—}H$ form (2.1 ± 0.3 for 66% DMF, ≃2.6 for water).

[13] H. C. Brown, H. Bartholomay, Jr., and M. D. Taylor, THIS JOURNAL, **66**, 435 (1944).

[14] The pK_a for N,N-dimethyl-2,4-xylidine is 5.28 in 50% ethanol at 25° (G. Thompson, *J. Chem. Soc.*, 1113 (1946)); compare ref. 10.

[15] All melting points are corrected; boiling points are uncorrected.

[16] We wish to thank Mr. James Brader for determination of the infrared absorption spectra and Mrs. Lucy Chang, Mrs. Esther Fett and Mr. Joseph Nemeth for the microanalyses.

[17] 1-(*p*-Aminophenyl)-pyrrolidine (Ih) was prepared according to the method of J. E. LoValle, D. B. Glass and A. Weissberger, THIS JOURNAL, **70**, 2223 (1948).

TABLE III

γ,γ'-ARYLIMINO-BIS-BUTYRONITRILES

Compound, -bis-butyronitrile (III)	Yield, %	B.p., °C.	B.p., Mm.	n^tD	t, °C.	Infrared C≡N max, cm.$^{-1a}$	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
γ,γ-Phenylimino (a)	67	177	0.1	1.5560	18.5	2250	$C_{14}H_{17}N_3$	73.97	74.23	7.54	7.51	18.49	18.24
γ,γ'-(p-Tolylimino) (b)	79	188	.3	1.5497	19	2250	$C_{15}H_{19}N_3$	74.65	74.46	7.94	7.98	17.41	17.15
γ,γ'-(2,4-Xylylimino) (c)	60^b	170–171	.1	1.5259	20	2255	$C_{16}H_{21}N_3$	75.25	75.01	8.29	8.27	16.46	16.59
γ,γ'-(2,6-Xylylimino) (d)	63^b	177–179	.1	1.5269	21	2255	$C_{16}H_{21}N_3$	75.25	74.94	8.29	8.13	16.46	16.74
γ,γ'-(Mesitylimino) (e)	48^b	176–177	.1	1.5278	22.5	2250	$C_{17}H_{23}N_3$	75.79	75.94	8.61	8.57	15.60	15.62
γ,γ'-(p-Methoxyphenylimino) (f)	79	204	.3	1.5493	17.5	2250	$C_{15}H_{19}N_3O$	70.01	69.92	7.44	7.33	16.33	16.05
γ,γ'-(p-Diethylaminophenylimino) (g)	63	205–207	.3	1.5432	30	2260	$C_{18}H_{26}N_4$	72.44	72.49	8.78	8.74	18.78	18.93
γ,γ'-(p-N-Pyrrolidylphenylimino) (h)	54	227–228	.2	1.5632	28	2250	$C_{18}H_{24}N_4$	72.94	71.95	8.16	7.72		

[a] 10% solution in carbon tetrachloride. [b] Prepared using amyl alcohol as the reaction medium. See Experimental section.

TABLE IV

DIALKYL γ,γ'-ARYLIMINO-BIS-BUTYRATES

Compound -bis-butyrate (IV)	Yield, %	B.p., °C.	B.p., Mm.	n^tD	t, °C.	Infrared C=O max, cm.$^{-1a}$	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
Diethyl γ,γ'-phenylimino (a)	72	166	0.3	1.5140	23	1735	$C_{18}H_{27}NO_4$	67.26	67.72	8.47	8.17	4.36	4.72
Diethyl γ,γ'-(p-tolylimino) (b)	73	164–166	.2	1.5152	25	1735	$C_{19}H_{29}NO_4$	68.03	68.19	8.71	8.79	4.18	4.91
Dimethyl γ,γ'-(p-tolylimino)	80	157	.1	1.5187	23		$C_{17}H_{25}NO_4$	66.42	66.55	8.20	8.05	4.56	4.89
Diethyl γ,γ'-(2,4-xylylimino)(c)	68	157–158	.1	1.4975	21	1735	$C_{20}H_{31}NO_4$	68.74	68.95	8.94	8.78	4.01	4.31
Diethyl γ,γ'-(mesitylimino) (e)	72	165	.1	1.5006	21	1737	$C_{21}H_{33}NO_4$	69.39	69.74	9.15	9.19	3.85	4.31
Diethyl γ,γ'-(p-methoxyphenylimino) (f)	70	185	.3	1.5152	22	1737	$C_{19}H_{29}NO_5$	64.93	65.24	8.32	8.13	3.99	4.13
Dimethyl γ,γ'-(p-N-pyrrolidylphenylimino) (h)	78	235–237	.7^b			1732^c	$C_{20}H_{30}N_2O_4$	66.27	66.30	8.34	8.63		

[a] 10% solution in carbon tetrachloride. [b] Sublimed, needles, m.p. 61–62.5°. [c] Crystal melt.

TABLE VI

1,9-DIARYL-1,9-DIAZACYCLOHEXADECANE-5,13-DIONES

Compound	Yield, %	M.p., °C.	Crystal form	Infrared C=O max, cm.$^{-1}$	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Mol. wt. Calcd.	Mol. wt. Found^a
-1,9-Diazacyclohexadecane-5,13-dione													
1,9-Diphenyl (VIIa)	0.4	168–169	Ndls.^{b}	1715^c	$C_{26}H_{34}N_2O_2$	76.81	76.97	8.43	8.33	6.89	6.87	407	425
1,9-Di-(2′,4′-xylyl) (VIIc)	.1	138–139	Plates^b	1717^c	$C_{30}H_{42}N_2O_2$	77.88	78.04	9.15	9.35	6.06	6.05	463	483
1,9-Dimesityl (VIIe)	.6	171–172	Plates^b	1712^c	$C_{32}H_{46}N_2O_2$	78.32	78.12	9.45	9.32	5.71	5.73	491	468
1,9-Di-(p-methoxyphenyl) (VIIf)	.3	132–133	Ndls.^{b}	1715^c	$C_{28}H_{38}N_2O_4$	72.07	72.04	8.21	8.03	6.00	6.26	467	492
-1,9-Diazacyclohexadecane-5,13-dione diperchlorate													
1,9-Diphenyl	..	>335	Prisms^d	1704^e	$C_{26}H_{36}Cl_2N_2O_{10}$	51.40	51.31	5.97	5.70	4.61	4.49		
1,9-Di-(2′,4′-xylyl)	..	259^f	Ndls.^{d}	1693^e	$C_{30}H_{44}Cl_2N_2O_{10}$	54.30	54.20	6.68	6.52	4.22	4.12		
1,9-Dimesityl	..	258^f	Prisms^d	1695^e	$C_{32}H_{48}Cl_2N_2O_{10}$	55.57	55.32	7.00	7.05	4.05	4.06		
1,9-Di-(p-methoxyphenyl)	..	284^f	Ndls.^{d}	1693^e	$C_{28}H_{40}Cl_2N_2O_{12}$	50.38	50.19	6.04	5.93	4.20	4.02		

[a] Rast, camphor. [b] From petroleum ether (b.p. 90–110°) or ethanol–petroleum ether. [c] Carbon tetrachloride solution. [d] Diperchlorate was made in ethanol and recrystallized from ethanol containing a small quantity of perchloric acid. [e] Nujol mull. [f] With decomposition.

TABLE V

CYCLIC AMINOACYLOINS AND AMINOKETONES

Compound	Yield, %	M.p., °C.	Crystal form[a]	Formula	Carbon, %		Hydrogen, %		Nitrogen, %	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
-1-Azacyclononan-5-ol-6-one										
1-Phenyl (Va)	3	98–99	Ndls.	$C_{14}H_{19}NO_2$	72.07	72.00	8.21	7.96	6.00	6.05
1-*p*-Tolyl (Vb)	38	103–104	Ndls.	$C_{15}H_{21}NO_2$	72.84	73.10	8.56	8.33	5.66	5.68
1-*p*-N-Pyrrolidylphenyl (Vh)	37	134–136[b]	Prisms	$C_{18}H_{26}N_2O_2$	71.49	70.95	8.67	8.40		
-1-Azacycloöctan-5-one										
1-*p*-Tolyl (VIb)	64	108–109	Ndls.	$C_{14}H_{19}NO$	77.38	77.22	8.81	8.75	6.45	6.34
1-(2′,4′-Xylyl) (VIc)	3	[c]	.....	$C_{15}H_{21}NO$	77.88	78.22	9.15	9.19	6.05	5.90
1-*p*-N-Pyrrolidylphenyl (VIh)	0.7	126–127[b]	Ndls.	$C_{17}H_{24}N_2O$	74.96	74.81	8.88	8.79		
-1-Azacycloöctan-5-one perchlorate										
1-*p*-Tolyl	..	178[d]	Prisms[e]	$C_{14}H_{20}ClNO_5$	52.91	52.78	6.34	6.15	4.41	4.39
1-(2′,4′-Xylyl)	..	90–92	Prisms[e]	$C_{15}H_{22}ClNO_5$	54.30	54.35	6.68	6.83		

[a] From petroleum ether (b.p. 90–110°) unless otherwise specified. [b] Sealed tube; compound is unstable. [c] B.p. 137–140° (1 mm.), n^{25}_D 1.5490. [d] With slight decomposition. [e] Perchlorate was prepared in ethanol and recrystallized from ethanol–ether containing excess perchloric acid.

combined chloroform extracts were fractionated. In the case of IIIg and h, sodium bisulfite was added to the original reaction mixture, which was then refluxed under nitrogen. For the hindered amines, the same proportions of reagents were used with 500 ml. of amyl alcohol and the reflux time was 24 hours for IIIc, 48 hours for IIId and e. The solids were filtered after cooling the reaction mixture, the alcohol was removed by distillation and the residue was taken up in chloroform, filtered and treated as described above. The yields, physical properties and analytical data are given in Table III. Compounds IIIg and h are extremely unstable and absorb oxygen from the air. Some of the monoalkylated compounds were isolated in this reaction, but most of them were not obtained pure. The only compound purified was **γ-(*p*-methoxyphenyl)-butyronitrile**, b.p. 156° (0.4 mm.), m.p. 46–47°, colorless plates from petroleum ether (b.p. 40–60°), characteristic infrared absorption maxima at 3370, 2245 cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{14}N_2O$: C, 69.44; H, 7.42; N, 14.73. Found: C, 69.23; H, 7.53; N, 14.76.

Dialkyl γ,γ′-Arylimino-bis-butyrates (IV).—A solution of 0.1 mole of the dinitrile III and 0.25 mole of water in 100 ml. of ethanol or methanol was saturated with hydrogen chloride and was heated at the reflux temperature with stirring for 2 hours. The mixture was cooled, the ammonium chloride was separated by filtration, and the filtrate was evaporated. The residue was made basic with aqueous sodium carbonate at <10°. The product was worked up by ether extraction and fractional distillation. Since the hydrochloride of IIIg was practically insoluble in ethanol, complete alcoholysis could not be effected in this case. The diesters tended to decompose on distillation, with the result that some of them were not obtained as pure as desired (Table IV). Compound IVh was especially unstable.

1-Aryl-1-azacyclononan-5-ol-6-ones (V).—The acyloin condensation was run in the usual manner[3] using 0.1 mole of diester IV, 0.44 gram atom of sodium and 1.5 l. of dry xylene. Addition of the diester required 5–6 hours. Many modifications in procedure were applied in those cases where the standard procedure resulted in failure initially. The final isolation involved a fractional distillation that gave a crude oil which then solidified and was recrystallized from petroleum ether (Table V). Severe decomposition took place during distillation in many cases, but attempts to extract the desired product with petroleum ether and thereby omit distillation offered no advantage.

1-Aryl-1-azacycloöctan-5-ones (VI).—The Dieckmann ring closure was run with sodium hydride as described for 1-cyclohexyl-1-azacycloöctan-5-one.[5] Following hydrolysis and decarboxylation, the product was extracted with chloroform. The combined chloroform extracts were evaporated and the residue was extracted with hot petroleum ether (b.p. 90–110°). If the product did not separate as crystals on cooling the petroleum ether solution, the solvent was evaporated and the residue was either distilled or recrystallized (Table V). Due to the instability of Vh, the addition period for the ring closure was shortened from 24 to 6 hours.

1,9-Diaryl-1,9-diazacyclohexadecane-5,13-diones (VII).—Compounds of this type (Table VI) were obtained from the petroleum ether extract of the Dieckmann condensation product and were easily separated, due to lower solubility in petroleum ether or higher boiling range, from the eight-membered ring aminoketone and petroleum ether-soluble by-products.

Infrared Absorption Spectra.—The spectra were obtained with a Perkin–Elmer recording spectrophotometer, model 21. For high resolution with dilute solutions (1.00 ± 0.05 × 10^{-2} *M*) in carbon tetrachloride, Rascher and Betzold reagent grade, the machine was operated as described previously.[6]

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