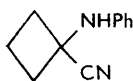


277. Studies in Pyrolysis. Part XXII.¹ 1-Anilino-1-cyano-cycloalkanes.

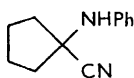
By W. C. BAIN, P. D. RITCHIE, and A. E. WRIGHT.

Liquid-phase pyrolysis (*ca.* 150—300°) of 1-anilino-1-cyanocyclo-pentane, -hexane, and -heptane leads to primary equilibrium dissociation into hydrogen cyanide and the corresponding anil, with no competing primary scission to aniline and olefinic nitrile. For all three anils the reverse reaction at room temperature is rapid and nearly quantitative. At high temperatures the forward reaction is nearly quantitative for the C₇-anilino-nitrile, but for the C₆- and, more particularly, the C₅-homologue the yield of anil is reduced by complex secondary self-condensation of the latter, with elimination of aniline. The C₄-homologue, 1-anilino-1-cyanocyclobutane, gives a complex pyrolysate containing hydrogen cyanide, aniline, and tars. Secondary products are described, and reaction mechanisms suggested.

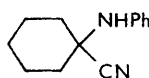
THIS Paper describes the pyrolysis of the homologous 1-anilino-1-cyanocycloalkanes (I)—(IV).



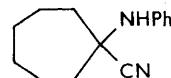
(I)



(II)



(III)



(IV)

In a previous search for new routes to olefinic nitriles, the known thermal breakdown² of the α -anilino-acid (V; R = CO₂H) to aniline and olefinic acid (a breakdown later found³ to compete with other thermal reactions) prompted an attempt⁴ to realise the corresponding pyrolysis of (V; R = CN), *i.e.*, of the anilino-nitrile (III). This seemed a probable reaction in view of an observation⁵ that the lower homologue (II) “decomposes on distillation with formation of some aniline.” The formal possibility was an attractive one, since many α -anilino-nitriles (α -anilino- α -cyanoalkanes) are readily accessible for pyrolysis. However, preliminary work⁴ showed that the total condensate from a flow-reactor (vapour-phase; temperature range *ca.* 450—600°) was substantially unchanged compound (III), with traces of hydrogen cyanide but no detectable olefinic nitrile; and an open-chain analogue (NHPh·CMe₂·CN) gave a similar negative result. The reason

¹ Part XXI, Bengough, Ritchie, and Steedman, *J.*, 1963, 2697.

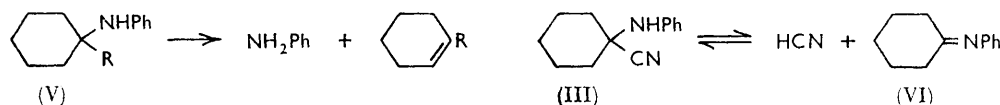
² Betts, Muspratt, and Plant, *J.*, 1927, 1310.

³ Bain and Ritchie, *J.*, 1955, 4407; compare McGee and Ritchie, *J.*, 1961, 1782.

⁴ Ritchie, unpublished observations, 1934.

⁵ Plant and Facer, *J.*, 1925, 127, 2037.

emerged when it was later shown⁶ that in the liquid phase (*ca.* 245°) substance (III) is reversibly dissociated to hydrogen cyanide and the corresponding anil (VI), and that an open-chain analogue (NHPh·CMePh·CN) behaves similarly, the NPh group playing the same role in these equilibria as the oxygen atom in a cyanohydrin. With total condensation of the pyrolysate, the forward reaction in the hot zone is masked by recombination



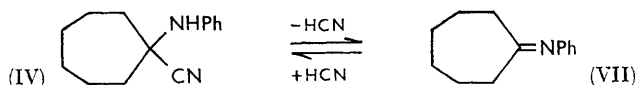
in the cold receiver; however, if hydrogen cyanide is continuously swept from the system, as formed, the anil may be obtained⁶ in high yield. For some open-chain α -anilino-nitriles, however, particularly with a high effective residence-time in the reactor, the yield of anil is much reduced by unexplained secondary reactions.⁷

The present work was designed to elucidate such secondary reactions, and to find whether ring-size (which markedly affects the ratio of reactions competing in the pyrolysis of the corresponding anilino-acids³) might at some point in the series (I)—(IV) introduce a competing scission to aniline and olefinic nitrile.

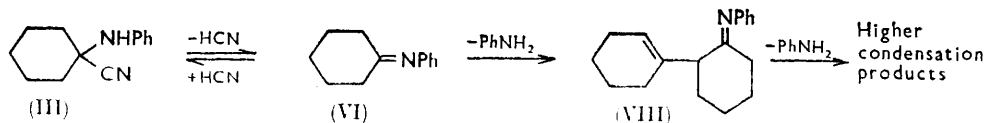
RESULTS

Effect of Ring-size on Rate of Primary Breakdown.—The anilino-nitriles (I)—(IV) all yield hydrogen cyanide on pyrolysis; the rate of elimination does not vary smoothly with ring-size (n), but shows minima where $n = 4$ and 6 (Table 3). It is instructive to compare this with cognate results discussed by Prelog,⁸ who showed that when either pK or free energy of reaction is plotted against n for a series of cycloalkanone cyanohydrins there is again a minimum where $n = 6$. Unfortunately his results do not go further down the series than $n = 5$, so that direct comparison with the pyrolysis of compound (I) ($n = 4$) is precluded.

Effect of Ring-size on Secondary Reactions of the Anilino-nitriles (I)—(IV).—As ring-size decreases, complexity of pyrolysis increases owing to the appearance of secondary reactions. The highest homologue (IV) breaks down very simply; in the liquid phase (*ca.* 250°), with a current of nitrogen to sweep away hydrogen cyanide as formed, elimination of the latter is almost quantitative (*ca.* 99%), giving the C_7 -anil (VII) (85%) as the only other product characterised, though there is also a very little high-boiling tar.



The lower C_6 -homologue (III), under similar conditions, gives less hydrogen cyanide (*ca.* 88%), some aniline, the simple C_6 -anil (VI) (87%), and high-boiling tars which increase in relative amount with the reaction time. In a gas-phase pyrolysis (*ca.* 500°), which gave similar results, the complex anil 2-cyclohex-1-enylcyclohexylideneaniline (VIII) was detected as a minor component of the high-boiling fraction. (The non-conjugated structure ascribed to this complex is discussed later, along with the general constitution of the tars.) The overall breakdown of compound (III) is best represented thus:

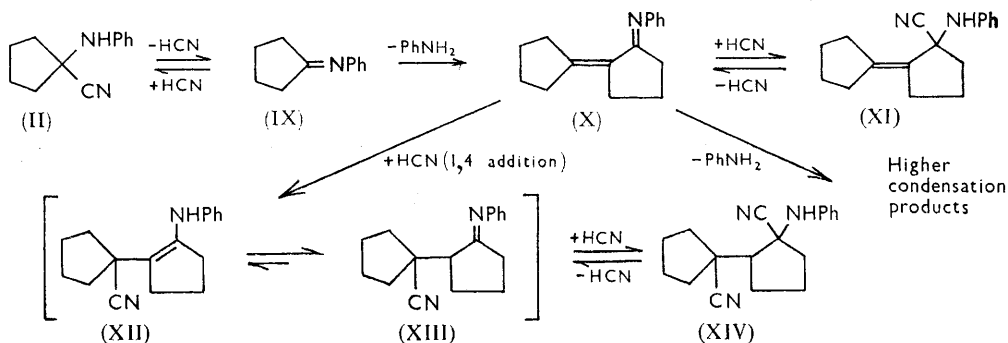


⁶ Drew and Ritchie, *Chem. and Ind.*, 1952, 1104.

⁷ Drew, M.Sc. Thesis, London, 1953.

⁸ Prelog, *J.*, 1950, 420, Fig. 5.

The pyrolysate from the C_5 -homologue (II) contains still less hydrogen cyanide (*ca.* 80%), together with aniline, the simple C_5 -anil (IX), the complex conjugated anil (X), uncharacterised tars, and a crystalline product provisionally identified as 1-anilino-1-cyano-2-(1-cyanocyclopentyl)cyclopentane (XIV). The following scheme is proposed as the best interpretation of these results; the evidence supporting structures (XI)—(XIV) is discussed later, together with the conjugated structure of the complex anil (X).



The aniline formed on pyrolysis of compounds (II) and (III) arises entirely by the various secondary reactions; in neither pyrolysate is there any trace of olefinic nitrile attributable to primary elimination of aniline.

Because of the more difficult accessibility of the C_4 -homologue (I), its breakdown was not examined intensively, but small scale liquid-phase pyrolysis (*ca.* 250°) gives hydrogen cyanide (*ca.* 59%), a little aniline, and much tar. Probably the overall breakdown resembles that undergone by compound (II).

Pyrolysis of the Simple Anils from Compounds (II)—(IV).—Separate pyrolyses of these simple anils confirm the above reaction schemes, and also provide an interesting parallel with the observation by Wallach⁹ that the readiness of the analogous cyclic ketones to undergo catalysed self-condensation follows the sequence: $C_5 > C_6 > C_7$. In the liquid phase (*ca.* 230°), the C_5 -anil (IX) readily yields aniline, the complex anil (X), and tars, whereas the C_6 -anil (VI) yields less aniline, and only uncharacterised tars. In the gas phase (*ca.* 500°), the C_6 -anil yields aniline, the complex anil (VIII), tars, and unchanged (VI), in roughly the ratio observed on pyrolysis of the anilino-nitrile (III) itself, whereas the C_7 -anil (VII) remains very largely unchanged, yielding only a trace of aniline and no tar.

At room temperature, the C_6 -anil is still fairly reactive, becoming yellow within a few hours, and dark orange within a few weeks, with gradual accompanying formation of aniline. Even the much less reactive C_7 -anil undergoes self-condensation at room temperature, though extremely slowly; a pure sample, kept for five years in a sealed glass ampoule, decomposed almost entirely to aniline and tars.

Small amounts of carbazole are formed as a by-product in the vapour-phase pyrolysis (*ca.* 500°) of the three anils, presumably by the known¹⁰ pyrolytic sequence: aniline → diphenylamine → carbazole. It is also observed in the gas-phase pyrolysate from the anilino-nitrile (III).

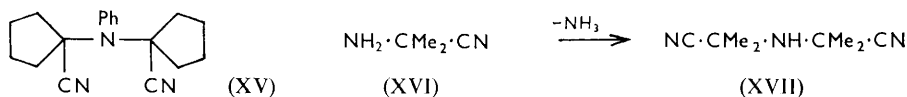
DISCUSSION

Constitution of the Crystalline Product from the Anilino-nitrile (II).—Although this crystalline product ($C_{18}H_{21}N_3$) has not been rigorously identified, much evidence supports the constitution (XIV) proposed above. At first sight, the symmetrical dinitrile structure

⁹ Wallach, *Ber.*, 1896, **29**, 2964; 1897, **30**, 1095.

¹⁰ Graebe, *Annalen*, 1873, **167**, 125; 1874, **174**, 177.

(XV) is suggested by an earlier observation¹¹ that pyrolysis of the α -amino-nitrile (XVI) yields ammonia and the dinitrile (XVII). This, however, is ruled out by detection of the NHPH grouping in the present product and by the fact that there cannot be two cyano-groups with identical environments, because only one is hydrolysed during a Kjeldahl determination, which suggests the unsymmetrical isomeric dinitrile (XIV) as a probable alternative.



An attempt to synthesise compound (XIV) by direct addition of hydrogen cyanide to the conjugated anil (X) at room temperature gave no crystalline material, but only a crude liquid product containing *ca.* 0.8 mole of combined hydrogen cyanide, which was readily and completely eliminated on pyrolysis (*ca.* 250°) in a stream of nitrogen. This liquid is probably mainly the olefinic anilino-nitrile (XI), formed by 1,2-addition to the conjugated system (X); it should dissociate thermally, like other α -anilino-nitriles, and would therefore not persist under pyrolytic conditions. It is suggested that when 1,2-addition is thus reduced or eliminated, 1,4-addition becomes the sole reaction of hydrogen cyanide, although heavily outweighed at lower temperatures in a competition between the 1,2- and 1,4-reactions. The analogous 1,4-addition of hydrogen cyanide to various $\alpha\beta$ -unsaturated ketones is known,¹² and, although this does not appear to have been recorded for 2-cyclopentylidenecyclopentanone itself, it is possible that its anil (X) will behave in this way. The immediate product (XII), a labile substituted vinylamine, would isomerise to the cyano-anil (XIII), and this, in turn, like other anils, should react further with hydrogen cyanide, yielding structure (XIV). 1,4-Addition would not be expected to be so readily reversible by heat as 1,2-addition; and in fact the crystalline product (XIV) is rather stable up to *ca.* 200°, though at *ca.* 300° (1 hr.) it eliminates *ca.* 0.8 mole of hydrogen cyanide, yielding a crude product whose ultraviolet absorption is compatible with an anil structure such as (XIII).

Three other observations support the foregoing ideas: (i) the enhanced yield of crystalline solid (*ca.* 16% as against *ca.* 5%) when (II) is simply refluxed, instead of being heated in a stream of nitrogen to sweep away hydrogen cyanide as formed; (ii) the two-stage elimination of hydrogen cyanide from (II) when the temperature is raised from *ca.* 150° to *ca.* 300° (Table 2); and (iii) the absence of any corresponding crystalline product in the pyrolysates from the higher anilino-nitriles (III) and (IV), neither of which yields a complex conjugated anil and which hence cannot undergo 1,4-addition.

Constitution of Higher Self-condensation Products of the Anils.—Recent work¹³⁻¹⁷ on the self-condensation of cyclopentanone and cyclohexanone (which markedly modifies the earlier views of Wallach⁹) suggests the probable nature of the complex glassy or tarry residues from the present pyrolysates. The annexed scheme (R = oxygen) summarises these recent results. The three-ring condensates from both ketones are mixtures of isomers; furthermore, although all the products from cyclopentanone have a fully conjugated structure, all but one of those from cyclohexanone are either partly or fully non-conjugated. The importance of this latter difference between the pair of two-ring condensed ketones has been stressed in the previous section.

¹¹ Snessarev, *J. prakt. Chem.*, 1914, **89**, 361; Dubsky and Wensink, *Ber.*, 1916, **49**, 1134.

¹² Michael and Weiner, *J. Amer. Chem. Soc.*, 1937, **59**, 744.

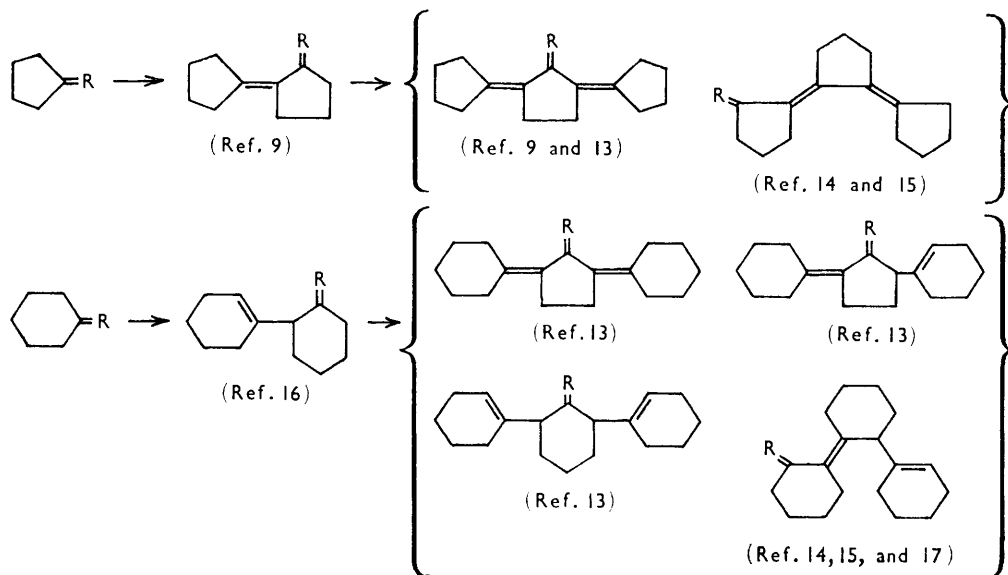
¹³ Plesek, *Chem. listy*, 1956, **50**, 252.

¹⁴ Mleziwa, *Coll. Czech. Chem. Comm.*, 1954, **19**, 505, 517.

¹⁵ Edgar and Johnson, *J.*, 1958, 3925.

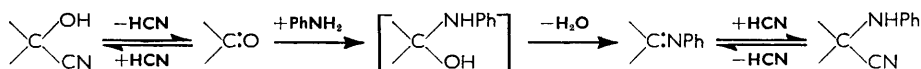
¹⁶ Brown and Ritter, *Ber.*, 1922, **55B**, 3792; Kon and Nutland, *J.*, 1926, 3106.

¹⁷ Svetozarskii, Zilbermann, and Rayuvaev, *J. Gen. Chem. (U.S.S.R.)*, 1959, **4**, 1454.



It is highly probable that the analogous simple anils produced by pyrolysis in the present work, which also undergo self-condensation, will thereby give the corresponding series of condensates ($R = NPh$), and Sapiro and P'eng¹⁸ have reasonably assumed that the anil derived from condensation of aniline with the two-ring ketone from cyclohexanone does, in fact, have the non-conjugated structure (VIII) mentioned previously. Furthermore, it is likely that self-condensation of some of the anils will in part proceed beyond the three-ring stage, thus developing considerable isomeric complexity, and explaining the non-crystallisable nature of the glassy or tarry residues from the present pyrolysates.

Mechanisms of Formation and Primary Thermal Dissociation of α -Anilino-nitriles.—**Formation.** α -Anilino-nitriles are in general formed rapidly and in high yield when an equimolar mixture of aniline and ketone (or aldehyde) reacts at room temperature with an excess of anhydrous hydrogen cyanide (Mulder¹⁹) or of alkali-metal cyanide acidified with acetic acid. If, however, aniline is mixed with a pre-formed cyanohydrin⁵ the reaction is slow and the yield poor. This marked difference may be interpreted as follows:



The uncatalysed reaction of the three-component system most probably proceeds by way of the transient α -anilino-alcohol, yielding anil to which hydrogen cyanide then rapidly adds. However, in the presence of a basic catalyst such as piperidine the cyanohydrin is first formed rapidly; thereafter, the now essentially two-component system must undergo slow reversal of the cyanohydrin equilibrium before ketone (or aldehyde) can be removed by interaction with aniline, and hydrogen cyanide by interaction with anil. Mulder's method¹⁹ is found to work with aniline but not with *N*-methylaniline (which cannot form an anil); this supports the above concept.

It is of interest that chloroform²⁰ and nitromethane,²¹ which like hydrogen cyanide react with cyclohexanone to give a 1-substituted cyclohexanol, and might be expected to react similarly with the anil (VI), do not do so; also, they do not react with a mixture of cyclohexanone and aniline.

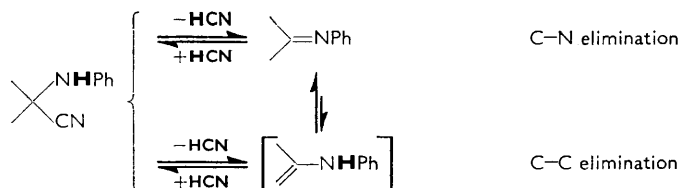
¹⁸ Sapiro and P'eng, *J.*, 1938, 1171.

¹⁹ Mulder, *Rec. Trav. chim.*, 1907, **26**, 180.

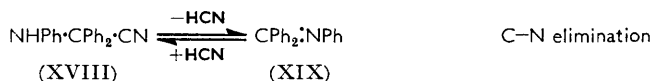
²⁰ Weizmann, Bergman, and Sulzbacher, *J. Amer. Chem. Soc.*, 1948, **70**, 1189.

²¹ Fraser and Kon, *J.*, 1934, 604; Wood and Cadorin, *J. Amer. Chem. Soc.*, 1951, **73**, 5504.

Primary thermal dissociation. Formally, the reversible thermal scission of an α -anilino-nitrile may occur by elimination of the C_α -nitrile group along with either the N -hydrogen atom **H** or the C_β -hydrogen atom, by reactions which may thus be termed C-N and C-C eliminations, respectively:



Since the labile vinylamine resulting from C-C elimination will rearrange to anil, formation of the latter must not, of itself, be taken as evidence for C-N rather than C-C reaction; but other considerations do in fact favour the former mechanism. For example, anilino-cyanodiphenylmethane (XVIII), in which C-C elimination is precluded by the absence of a β -hydrogen atom, still very readily and rapidly yields hydrogen cyanide (*ca.* 100%) and anil (XIX) (*ca.* 98%) at *ca.* 200° by what can only, in this case, be a C-N elimination:.



Here, in fact, the backward reaction from anil (XIX) is the only method available for synthesis²² of compound (XVIII), since with benzophenone as the starting point the conventional methods of preparing α -anilino-nitriles fail. This agrees with the known failure of benzophenone to form a cyanohydrin, the dissociation constant, K , being immeasurably high; similarly, 1-tetralone ($K = 8.06$) forms no α -anilino-nitrile.

Clearly, if an N -methylated anilino-nitrile could be shown to yield hydrogen cyanide on pyrolysis, this could only have occurred by C-C elimination, with formation of a stable NN -disubstituted vinylamine; but, as mentioned previously, Mulder's method¹⁹ fails when N -methylaniline is substituted for aniline, so that the possibility cannot be tested.

The three homologous anils, (IX), (VI), and (VII), all recombine smoothly and rapidly with anhydrous hydrogen cyanide at room temperature to regenerate the parent anilino-nitriles in almost quantitative yield, a fact which is in line with the efficient synthesis of the anilino-nitrile (XVIII) from its anil (XIX).

EXPERIMENTAL

Apparatus.—Pyrolyses were run in three different reactors, (a) macro, static (Tables 1, 2), (b) semimicro, static (Table 3), and (c) macro, flow. In (a) the pyrolysand (5–15 g.) was heated in a 25-ml. distillation flask, immersed in a bath of Wood's metal on an electric hot-plate controlled thermostatically ($\pm 5^\circ$); the evolved hydrogen cyanide was swept into aqueous 3*N*-sodium hydroxide by a gentle metered current of nitrogen, the cyanide content of the trap being determined periodically. In (b), a smaller flask was used; the pyrolysand was limited to 300 mg., and a micro-burette was used for the analytical titrations, but conditions were otherwise as in (a). In (c), a flow-reactor of the type previously described²³ was used; here the feed-rate was *ca.* 0.25 g./min., and the residence time *ca.* 22 sec.

Analytical Methods.—Ketones,²⁴ aniline, and hydrogen cyanide were determined by standard methods. Anils were identified by acidic hydrolysis to ketone and aniline, and by catalytic hydrogenation to amine (Adams platinum oxide catalyst; $p = 1$ atm.; ethyl acetate as solvent). Aniline was characterised as acetanilide; this and other solid products were identified by mixed m. p. Gas-liquid chromatography, infrared spectrometry, and nuclear magnetic resonance (n.m.r.) spectrometry were applied in some cases.

²² v. Miller and Plöchl, *Ber.*, 1892, **25**, 2056.

²³ Allan, Forman, and Ritchie, *J.*, 1955, 2717.

²⁴ Iddles, Low, Rosen, and Hart, *Ind. Eng. Chem. (Analyt.)*, 1939, **11**, 102.

Preparation of the Anilino-nitriles (I)—(IV).—These were prepared (Mulder's method¹⁹) by gradual addition of anhydrous hydrogen cyanide (50% excess) to an equimolar mixture of aniline and the appropriate ketone at room temperature. The crude products (*ca.* 95%) turned brownish on storage in air, but did not become coloured after recrystallisation. The following were obtained:

1-Anilino-1-cyanocyclobutane (I), needles (70%) (from benzene–light petroleum), m. p. 62–63° (Found: C, 76.9; H, 6.9. C₁₁H₁₃N requires C, 76.7; H, 7.0%).

TABLE 1.

Hydrogen cyanide eliminated (%) from the anilino-nitriles (I)—(IV) and (XVIII).

Macro-reactor; weight of pyrolysand, 15.0 g. [4.5 g. for (I)]; flow-rate of carrier-gas, 0.8 l./hr. [3.0 l./hr. for (I)].

Pyrolysand	(I)		(II)		(III)		(IV)		(XVIII)	
	Temp.	250°	200°	250°	200°	250°	200°	250°	200°	250°
Time (hr.)										
0.5	49.6	26.8	58.6	18.9	62.3	66.1	96.2	96.8	100.4	
1	58.6	38.0	77.5	25.8	71.2	79.6	98.8	99.8		
2	—	47.5	79.6	34.6	79.3	89.7	99.4	100.3		
3	—	—	—	—	83.2	94.2	99.4			
3.5	—	—	—	45.0	—	—	—			
4	—	60.3	—	—	—	—	—			
6	—	64.8	80.2	55.8	—	—	—			
9	—	68.7	—	—	87.8	—	—			
10	—	—	—	64.7	—	—	—			

TABLE 2.

Two-stage elimination of hydrogen cyanide (%) from the anilino-nitrile (II). Temp. raised from 150 to 300° after 96 hr. Macro-reactor; weight of pyrolysand, 5.0 g.; flow rate of carrier-gas, 3.3 l./hr.

Time (hr.)	0.5	1	2	4	9	24	48	72	96	96.5	97	99	103	130	
Temp.	← 150°					→ 300°					→				
HCN	20.2	27.7	37.8	47.1	57.4	69.8	78.2	80.1	80.2	87.7	90.6	92.4	92.8	93.2	

TABLE 3.

Hydrogen cyanide eliminated (%) from the anilino-nitriles (I)—(IV) and (XVIII).

Semimicro-reactor; temp., 200°; time, 10 min.; weight of pyrolysand, 300 mg.; flow-rate of carrier-gas, 0.8 l./hr.

	Pyrolysand	(I)	(II)	(III)	(IV)	(XVIII)
Run 1		36.4	66.3	50.8	91.4	96.8
Run 2		38.7	64.2	48.2	92.3	97.0
Mean		37.6	65.3	49.5	91.9	96.9

1-Anilino-1-cyanocyclopentane (II), prisms (86%) (from ethanol), m. p. 56–57° (lit.,⁵ 58°) ϵ_{206} 11,800, ϵ_{243} 12,700, ϵ_{289} 1630 (in ethanol). Repetition of the Plant and Facer⁵ preparation gave only *ca.* 7% yield.

1-Anilino-1-cyanocyclohexane (III), prisms (75%) (from ethanol), m. p. 75° (lit.,²⁵ 76°).

1-Anilino-1-cyanocycloheptane (IV), prisms (78%) (from ethanol), m. p. 85–86° (Found: C, 78.8; H, 8.6; N, 13.3. C₁₄H₁₈N₂ requires C, 78.5; H, 8.5; N, 13.1%).

Pyrolysis of the Anilino-nitriles (I)—(IV).—*Anilino-nitrile (I).* Because of the small quantity available, this was pyrolysed in a semimicro-reactor (300 mg. batches), a micro-burette being used in the analytical titrations (Table 1). In one run on a slightly larger scale (4.5 g.; 250°; N₂ flow, 3.0 l./hr.) the elimination of hydrogen cyanide was 49.6% (0.5 hr.) and 58.6% (1 hr.) (Table 2); distillation of the residue yielded aniline (0.2 g.) and a black high-boiling tar from which no further identifiable material could be isolated.

Anilino-nitrile (II). In a preliminary run (59.0 g.; 230°; 6 hr.; N₂ flow not measured) elimination of hydrogen cyanide was 63.1% (2 hr.) and 64.6% (6 hr.); distillation of the residue

²⁵ v. Walther and Hübner, *J. prakt. Chem.*, 1916, **93**, 119.

yielded aniline (10.0 g.; characterised as acetanilide), a higher fraction with b. p. 75—220°/12 mm., and a residual tar which did not crystallise.

In a second run, compound (II) (40.0 g.) was refluxed at 140—190°(bath)/14 mm., with an alkali trap in the vacuum line; elimination of hydrogen cyanide was 13.3% (1 hr.), 57.3% (2 hr.), and 58.3% (3 hr.). Distillation of the pale yellow residue (33.4 g.), again with an alkali trap, gave further hydrogen cyanide (21.4%) and a liquid (20.3 g.; b. p. 121—124°/7 mm.). Redistilled, this liquid yielded *cyclopentylideneaniline* (IX), b. p. 122°/7 mm., n_D^{20} 1.5648, d_4^{20} 1.0173 (Found: C, 82.7; H, 7.9; N, 8.6. $C_{11}H_{13}N$ requires C, 83.0; H, 8.2; N, 8.8%), as a colourless liquid, becoming brown in contact with air and finally forming a black tar (though more slowly than the other anils studied). Acid hydrolysis of anil (IX) yielded cyclopentanone (94.0, 94.0%) and aniline (99.8, 100.7%); at room temperature, it reacted vigorously with anhydrous hydrogen cyanide, regenerating compound (II) (97.4%) (mixed m. p.). Catalytic hydrogenation of anil (IX) (hydrogen uptake, 95%), followed by fractionation, yielded *N*-cyclopentylaniline (81%), b. p. 139—140°/13 mm. (lit.,²⁶ 137°/12 mm.), n_D^{20} 1.5670, d_4^{20} 1.0084. This amine gave an acetate, m. p. 95—96° (lit.,²⁶ 96°), and showed the Fouque²⁷ colour reaction.

In a third run, the macro-reactor (a) was used as specified above. The residue from the 250° run (Table 1), redistilled, yielded (i) 1.8 g., b. p. 76—79°/15 mm., (ii) 1.6 g., b. p. 79—132°/15 mm., (iii) 3.2 g., b. p. 132—135°/15 mm., (iv) 0.9 g., b. p. 135°/15 mm.—184°/4 mm., (v) 1.1 g., b. p. 184—186°/4 mm., and (vi) 2.5 g. of tarry residue. The hydrogen cyanide evolved (Table 1) was 1.7 g. (overall loss, 2.2 g.). Fraction (i) was aniline (48%), fraction (ii) was mainly (IX) (25%), fraction (v) was the complex anil (X) (12%) which yielded aniline and 2-cyclopentylidene-cyclopentanone on acid hydrolysis, as described in detail below.

In a fourth run, compound (II) (5 g.) was pyrolysed at 150° for 96 hr., the temperature being then raised to 300° for a further 24 hr. The results (Table 2) indicate that a cyano-compound is formed during the pyrolysis; it is fairly stable at 150° but breaks down more readily at 300°. The residue was a hard black glassy solid.

The combined residual tars (52 g.) from several pyrolyses of compound (II), redistilled, yielded (i) 12 g., b. p. 160—207°/0.7 mm., and (ii) 8 g., b. p. 207—220°/0.7 mm. Fraction (ii) solidified to a sticky glassy product; on treatment with light petroleum (b. p. 60—80°), it yielded crystalline solid *A* (4.5 g.), m. p. 130—136°, which gave prisms (1.5 g.), m. p. 137—138° (from benzene—light petroleum). More *A* was obtained by pyrolysing (II) (220°; 2 hr.; N_2 flow, 3.0 l./hr.); hydrogen cyanide (53.4%) was evolved, and distillation of the residue gave crude *A* (4.9%), b. p. 211—220°/0.6 mm., which yielded pure *A* (1.3%) on recrystallisation. An improved yield of *A* was obtained by refluxing (ii) (185—215°; 9 hr.; water condenser); hydrogen cyanide (1.4%) was evolved, and fractional distillation to remove (IX) and (X) gave crude *A* (16%), b. p. 212—226°/1 mm., which yielded pure *A* (9.3%) after three recrystallisations. Experiments described below indicate that *A* was most probably 1-anilino-1-cyano-2-(1-cyanocyclopentyl)cyclopentane (XIV); the purest product had b. p. 211—220°/0.6 mm., m. p. 137—138°, ϵ_{207} 14,300, ϵ_{256} 13,100 (in ethanol) [Found: C, 77.6; H, 7.7; N, 15.4; *M* (platinichloride), 287, 290, 283; *M* (Rast), 264. $C_{6n}H_{7n}N_n$ requires C, 77.4; H, 7.6; N, 15.0%; *M* ($n = 3$), 279]. Hydrolysis (conc. hydrochloric acid; 6 hr.), followed by determination of ammonia (semimicro Kjeldahl), showed *M* 277 and 281, on the assumption that the molecule of *A* contains one hydrolysable cyano-group. Heated with aqueous sodium hydroxide, *A* evolves ammonia, and yields a solution containing cyanide ion, resembling in this respect α -anilino-nitriles in general. It dissolves in dilute hydrochloric acid, and is precipitated unchanged by dilute sodium hydroxide; it gives a precipitate with chloroplatinic acid, but shows no obvious reaction with nitrous acid. On methylation (methyl iodide) and degradation, it yields *N*-methylaniline, which indicates the presence of the NHPH group, and this is clearly confirmed by n.m.r. spectrometry in presence of D_2O , the NH group undergoing rapid exchange to form the ND group. Furthermore, n.m.r. spectrometry indicates a structure containing one NHPH group and two cyanocyclopentane residues. On pyrolysis in a semimicro-reactor at 200°, *A* yields only 2% (1 hr.) of hydrogen cyanide, but at 300° the yield rises to 74% (1 hr.), 78% (3 hr.) (calculated on the basis of one labile cyano-group per molecule). The semi-solid pyrolysate, distilled, yields (i) aniline, (ii) a brown viscous liquid, and (iii) a black residual tar. The infrared absorption spectrum of fraction (ii) shows the characteristic band system of the other

²⁶ Loevenich, Utsch, Moldrickx, and Schaefer, *Ber.*, 1929, **62**, 3103.

²⁷ Fouque, *Ann. Chim. (France)*, 1921, **15**, 330.

anils studied, and a faint nitrile band; the substance is probably the complex cyano-anil (XIII). Acidic hydrolysis of fraction (ii), however, gives a product which (like the alkaline hydrolysate from *A*) yielded no precipitate with 2,4-dinitrophenylhydrazine; and it is believed that formation of the expected complex ketone derivative is sterically hindered by the bulky 2-(1-cyanocyclopentyl) substituent.

Anilino-nitrile (III). Repetition of the static pyrolysis recorded by Drew and Ritchie⁶ gave closely similar results. Table 1 shows the rate of evolution of hydrogen cyanide under the present more closely controlled conditions. The anil (VI) showed ϵ_{206} 10,900, ϵ_{230} 8550, ϵ_{286} 2130 (in cyclohexane).

A further pyrolysis of (III) (40 g.) in a flow-reactor at *ca.* 500° led to evolution of hydrogen cyanide (21.5%); the sticky yellow solid pyrolysate was extracted with warm light petroleum, filtered, and the filtrate distilled. After removal of solvent, the filtrate yielded (i) 1 g., b. p. 60–100°/2 mm., (ii) 6.5 g., b. p. 106°/2 mm., (iii) 1.3 g., b. p. 106–180°/2 mm., (iv) 1 g., b. p. 180–186°/2 mm., and (v) 2–3 g. of hard yellow glassy residue. Fractions (i)–(iii) contained the anil (VI) and traces of aniline. Fraction (iv), redistilled, yielded 2-cyclohex-1-enylcyclohexylideneaniline (VIII), b. p. 160–170°/1 mm. (lit.,²⁸ 212–214°/18 mm.), acidic hydrolysis of which yielded aniline and 2-cyclohex-1-enylcyclohexanone, characterised as its oxime and semicarbazone (mixed m. p.).

Anilino-nitrile (IV). Distillation of the residue from the 250° run (Table 1) gave *cycloheptylideneaniline* (VII) (85%), b. p. 108–110°/2–3 mm., 152–153°/13 mm., n_D^{20} 1.5568, d_4^{20} 1.0024, ϵ_{207} 13,100, ϵ_{226} 11,050, ϵ_{278} 2130 (in cyclohexane) (Found: C, 83.7; H, 9.5; N, 7.8. $C_{13}H_{17}N$ requires C, 83.4; H, 9.2; N, 7.5%). Acid hydrolysis (cold) regenerated cycloheptanone (94, 94%) and aniline (99, 99%); vigorous reaction (ethereal solution) with anhydrous hydrogen cyanide regenerated compound (IV) (99%) (mixed m. p.); catalytic hydrogenation (hydrogen uptake, 102%), followed by fractionation, yielded *N*-cycloheptylaniline (89%), b. p. 152–154°/13 mm., 168–170°/18 mm. (lit.,²⁶ 156–157°/11 mm.), n_D^{20} 1.5616, d_4^{20} 0.9989. This amine gave an *acetate* as prisms (from ethanol-water), m. p. 52–53° (Found: C, 78.0; H, 9.4; N, 6.4. $C_{15}H_{21}NO_2$ requires C, 77.9; H, 9.2; N, 6.1%), and a *benzoate* as prisms (from light petroleum), m. p. 106–107° (Found: C, 81.9; H, 7.6; N, 5.2. $C_{20}H_{23}NO_2$ requires C, 81.9; H, 7.9; N, 4.8%). The nitroso-derivative of the amine was a non-crystallisable yellow oil, and, unlike the other *N*-cycloalkylanilines studied, the amine did not give the Fouque²⁷ colour reaction.

Preparation of the Anilino-nitrile (XVIII).—Benzophenone was converted²² into dichlorodiphenylmethane (87%), 185°/25 mm. which in turn yielded²² α -phenylbenzylideneaniline (XIX) (77%), m. p. 114–115° (lit.,²² 112–113°). With hydrogen cyanide, anil (XIX) gave anilincyanodiphenylmethane (XVIII) (71%), m. p. 144–145° (lit.,²² 146.5°) (overall yield from benzophenone, 47%).

Pyrolysis of the Anilino-nitrile (XVIII).—The pale yellow residue after elimination of hydrogen cyanide (Table 1) was α -phenylbenzylideneaniline (XIX) (mixed m. p.) (98% from run at 200°; 97% from run at 250°).

Preparation of the Anil (IX).—The C_5 -anil was prepared by pyrolysis of compound (III) (see above). In addition, it was synthesised by the Hoch²⁹ method; cyclopentanone was first converted into its diethyl acetal (76%), b. p. 67–69°/24 mm. (lit.,³⁰ 63–65°/20 mm.), which was treated with aniline as described²⁹ for analogous anils, yielding cyclopentylideneaniline (IX) (33%), b. p. 106°/2 mm., 133°/13 mm., n_D^{20} 1.5646.

Pyrolysis of the Anil (IX).—The anil (21.2 g.), heated at 230° for 6 hr., yielded, on distillation, (i) 3.8 g., b. p. 80–83°/17 mm., (ii) 7.2 g., b. p. 83°/17 mm.—178°/3 mm., (iii) 3.5 g., b. p. 178–182°/3 mm., and (iv) 4.8 g. of tarry residue (overall loss, 1.9 g.). Fraction (i) was aniline (6%). Fraction (iii) was (2-cyclopentylidenecyclopentylidene)aniline (X) (23%) (Found: C, 85.9; H, 8.8. $C_{16}H_{16}N$ requires C, 85.3; H, 8.5%), a very viscous pale yellow liquid which crystallised on standing. In contact with air the solid turns brown and forms a black tar, so rapidly that recrystallisation is impracticable. Hydrolysis by 2*N*-hydrochloric acid-ethanol yielded²⁴ 2-cyclopentylidenecyclopentanone (96.5, 96.6%); another portion of compound (X), stirred for 5 min. with 2*N*-hydrochloric acid and freed from ketone by extraction with ether, yielded

²⁸ Reddelien and Meyn, *Ber.*, 1920, **53 B**, 345.

²⁹ Hoch, *Compt. rend.*, 1934, **199**, 1428.

³⁰ Boeseken and Telligen, *Rec. Trav. chim.*, 1938, **57**, 135.

aniline (100.0, 100.8%). The ketone gave an oxime, m. p. 122—123° (lit.,³¹ 122—123°), and a 2,4-dinitrophenylhydrazone as deep red prisms (from glacial acetic acid), m. p. 220° (decomp.) (Found: C, 58.5; H, 5.3; N, 17.0. $C_{16}H_{18}N_4O_4$ requires C, 58.2; H, 5.5; N, 17.0%). A portion of the anil (X) was weighed in an evacuated flask, excess of anhydrous hydrogen cyanide added through a stopcock, unreacted hydrogen cyanide removed by re-evacuation, and the whole re-weighed. In one experiment, the amount of hydrogen cyanide retained was 50% of the theoretical, and in another 81% (both calculated on the assumption that the anil can react with hydrogen cyanide at only one of its double bonds). The addition product, pyrolysed in the flask by heating at 250° in a stream of nitrogen, gave up the whole of the added hydrogen cyanide, thus, 63.2% (0.5 hr.), 74.0% (2 hr.), and 100.5% (23 hr.).

Preparation of the Anil (VI).—The C_6 -anil was prepared by pyrolysis of compound (III) (see above). Careful fractionation yielded an almost colourless product (87%), b. p. 106°/2 mm., n_D^{20} 1.5451, giving only a single peak on gas chromatography. (In contact with air, a portion became yellow within a few hours, and dark orange within a few weeks; gradual concurrent elimination of aniline was demonstrated by periodic chromatography.)

Pyrolysis of the Anil (VI).—In the vapour phase (ca. 500°), 6 g. of the anil yielded 5.8 g. of liquid pyrolysate; when distilled, this gave aniline, the complex anil (VIII), and unchanged pyrolysate (gas chromatography) in approximately the same molar proportions (1 : 3 : 16) as in the pyrolysate from anilino-nitrile (III) (see above). Liquid-phase pyrolysis was not performed.

Preparation of the Anil (VII).—The C_7 -anil was prepared by pyrolysis of compound (IV) (see above). Careful fractionation yielded an almost colourless product (86%), b. p. 108—110°/2—3 mm., n_D^{20} 1.5258, changing in contact with air as described above for anil (VI).

Pyrolysis of the Anil (VII).—In the vapour phase (ca. 500°), 10 g. of the anil yielded 9.8 g. of liquid pyrolysate; when distilled, this gave almost exclusively unchanged anil (VII), together with a trace of aniline. Liquid-phase pyrolysis was not performed.

Preparation of Reference Standards.—(2-Cyclohex-1-enylcyclohexylidene)aniline (VIII). Anil (VI) (4.5 g.) was heated at ca. 200° for 5 min. with aniline hydrochloride (0.5 g.); the product, when distilled, yielded (i) 1.4 g., b. p. 180—190°, and (ii) 1.5 g., b. p. 160—170°/1 mm. Fraction (i) was aniline. Fraction (ii) was the anil (VIII) (lit.,^{18,28} b. p. 200—210°/15 mm. and 212—214°/18 mm., respectively), yielding aniline and 2-cyclohex-1-enylcyclohexanone on hydrolysis with 2*N*-hydrochloric acid.

2-Cyclohex-1-enylcyclohexanone. Prepared as described by Edgar and Johnson,¹⁵ the ketone had b. p. 138—140°/12 mm., n_D^{20} 1.5061 (lit.,¹⁶ 137—139°/14 mm., n_D^{20} 1.515; and b. p. 145°/17 mm., n_D^{15} 1.5069), and gave a semicarbazone, m. p. 179—181° (lit.,²⁸ 178—180°; lit.,³² 175—177°), and an oxime, m. p. 142—143° (lit.,³² 146—148°).

Attempted Preparations.—Attempts to prepare the following analogues of compound (III) were unsuccessful, no product being formed after several months: 1-anilino-1-trichloromethylcyclohexane from an equimolar mixture of (i) cyclohexanone, chloroform, and aniline, or (ii) the anil (VI) and chloroform; 1-anilino-1-nitromethylcyclohexane from an equimolar mixture of (i) cyclohexanone, nitromethane, and aniline, or (ii) the anil (VI) and nitromethane; 1-anilino-1-cyano-1,2,3,4-tetrahydronaphthalene from an equimolar mixture of 1-tetralone and aniline, mixed with excess of anhydrous hydrogen cyanide; 1-cyano-1-*N*-methylanilino-cyclohexane from an equimolar mixture of cyclohexanone and *N*-methylaniline, mixed with excess of anhydrous hydrogen cyanide.

Infrared Spectra.—The infrared absorption spectra of the following compounds have been recorded. The anilino-nitrile (II), D.M.S. Index No. 12216. The anils (VIII, X), D.M.S. Index Nos. 9908 and 12215. [The spectrum of the anil (VI) has already been recorded; D.M.S. Index No. 1868.] The product (XIV), D.M.S. Index No. 12217.

The authors thank the D.S.I.R. for the award of Research Studentships (to W. C. B. and A. E. W.), and Imperial Chemical Industries Limited for a grant. For assistance in the study of compound (XIV) they are indebted to Dr. P. Bladon (n.m.r. measurements), Dr. A. Golomb, and Dr. J. McGee.

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³¹ Zelinski and Shuikin, *J. Russ. Phys. Chem. Soc.*, 1930, **62**, 1343.

³² Mannich, *Ber.*, 1907, **40**, 157.