

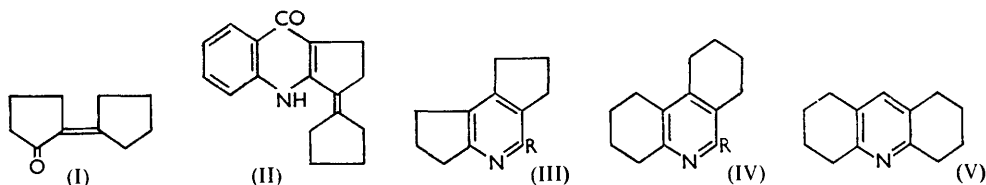
**797.** *High-temperature (300—350°) Reactions of cyclopentanone and Some of its Derivatives with Ammonia and Aliphatic Amines.*

By O. B. EDGAR and DAVID H. JOHNSON.

The products obtained when *cyclopentanone* is heated at 300° under autogenous pressure with anhydrous ammonia or with aliphatic amines have been found to be complex mixtures in which alkylated *cyclopentanones* and pyridine bases, *e.g.*, 6-alkyl-2:3-4:5- or 4-alkyl-2:3-5:6-dicyclopentenopyridines, predominate. Similar products arise in the vapour phase at 350° under base-catalysis.

THE studies now reported form part of a comprehensive investigation undertaken in 1952—1956 into the mode of thermal decomposition of Nylon 66 polymer.<sup>1,2</sup>

Although the condensation of saturated and  $\alpha\beta$ -unsaturated aldehydes and ketones with ammonia and its derivatives, which leads to substituted pyridines, is one of the oldest of synthetical procedures,<sup>3,4</sup> studied particularly by Tschitschibabin and his associates,<sup>5</sup> little information has been available concerning the reactions of cyclic ketones with such bases. Blount and Plant<sup>6</sup> have shown that, unlike *cyclohexanone*, *suberone*, and *perhydroindan-1-one* which behave normally in the Tiedtke condensation<sup>7</sup> with anthranilic acid, *cyclopentanone*, the ketone which is of special interest in matters relating to the thermal stability of Nylon 66 polymer, undergoes self-condensation to 2-*cyclopentylidene-cyclopentanone* (I) before ring-closure to the quinolone (II). From the products of reaction of *cyclopentanone* with acetaldehyde and ammonia, Tschitschibabin<sup>8</sup> isolated 6-methyl-



2:3-4:5-dicyclopentenopyridine (III; R = Me); he also studied the reactions between *cyclohexanone* and aldehydes and ammonia and showed,<sup>9</sup> for example, that *cyclohexanone*, formaldehyde, and ammonia yield a mixture containing the octahydrophenanthridine (IV; R = H) and octahydroacridine (V), with the former predominant. Patent literature<sup>10</sup> contemporaneous with the present investigation describes the production of polycyclic bases from the condensation of anhydrous ammonia with *cyclopentanone* and *cyclohexanone* severally, under autogenous pressure at temperatures below 200°. The constants quoted for these substances, which appear to be of indefinite structure and are claimed to possess certain fungicidal and insecticidal activity, show considerable differences from those of our materials isolated from reactions at higher temperatures (300—350°).

We found that when *cyclopentanone* was heated at 300° under autogenous pressure with 1.2 mol. of anhydrous ammonia, the volatile neutral products (5—6% by wt.) contained 2-*cyclopentylidene-cyclopentanone* (I), 2-*cyclopentyl-cyclopentanone* (VI), and a trace of a crystalline amide, possibly  $\delta$ -*cyclopent-1-enylvaleramide* (VII; R = NH<sub>2</sub>).

<sup>1</sup> Goodman, *J. Polymer Sci.*, 1954, **13**, 175.

<sup>2</sup> *Idem, ibid.*, 1955, **17**, 587; Ph.D. Thesis, London, 1957.

<sup>3</sup> Hübner and Geuther, *Annalen*, 1860, **114**, 35.

<sup>4</sup> Baeyer, *Ber.*, 1869, **2**, 398; *Annalen*, 1870, **155**, 281, 294.

<sup>5</sup> For collected references see Tschitschibabin, "Traité de Chimie Organique," Masson, Paris, 1953, Vol. XX, p. 57.

<sup>6</sup> Blount and Plant, *J.*, 1937, 376.

<sup>7</sup> Tiedtke, *Ber.*, 1909, **42**, 621.

<sup>8</sup> Tschitschibabin, *Bull. Soc. chim. France*, 1939, **6**, 522.

<sup>9</sup> Tschitschibabin and Barkovsky, *Compt. rend.*, 1941, **212**, 914.

<sup>10</sup> U.S.P. 2,692,268/1954; 2,693,491/1954.

The major component of the basic products (22—23% by wt.) was a liquid tertiary base  $C_{15}H_{21}N$  containing no active hydrogen and giving a crystalline chloroplatinate but no other satisfactory derivatives. The ultraviolet absorption (Fig. 1) was consistent with the presence of a vinylic amine system,<sup>11</sup> *e.g.*, as in pyridine bases,<sup>12</sup> and, in particular, was closely similar to that of the pyridine derivative (III;  $R = Pr^n$ ) described by Goodman.<sup>2</sup> The infrared spectrum of our base  $C_{15}H_{21}N$  and of Goodman's compound were also similar, *e.g.*, bands at 1605 and 1585  $cm^{-1}$  indicating a heterocyclic nucleus, whereas absence of bands in the 3500—3300 and the 3100—3000  $cm^{-1}$  region indicated absence of  $-NH-$  and aromatic C-H groups. Further, the mass-spectral breakdown pattern of the two bases was analogous. Thus the spectral characteristics suggest that our base  $C_{15}H_{21}N$  is 6-*n*-butyl-2:3:4:5-dicyclopentenopyridine (III;  $R = Bu^n$ ), and in keeping with this its chemical properties paralleled closely those of the lower homologue (III;  $R = Pr^n$ ). When

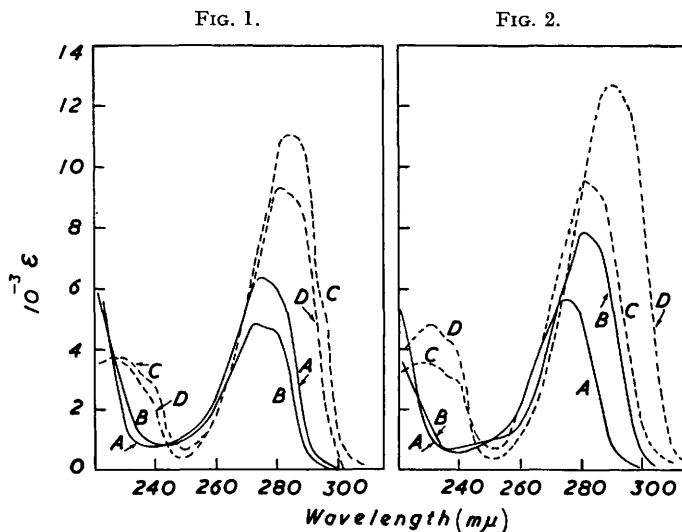
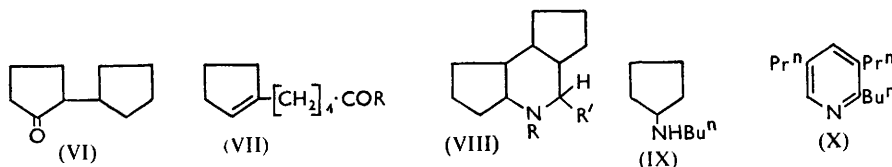


FIG. 1. 6-*n*-Butyl-2:3:4:5-dicyclopentenopyridine (A) in MeOH, (C) in conc. HCl.  
1:2:3:4:5:6:7:8-Octahydro-9-*n*-pentylphenanthridine (B) in MeOH, (D) in conc. HCl.  
FIG. 2. 2-*n*-Propyl-3:4:5:6-dicyclopentenopyridine (A) in MeOH, (C) in conc. HCl.  
4-*n*-Propyl-2:3:5:6-dicyclopentenopyridine (B) in MeOH, (D) in conc. HCl.

freshly isolated, our base (III;  $R = Bu^n$ ) gave a red colour with alcoholic 1:3:5-trinitrobenzene; and with cold aqueous potassium permanganate yielded valeric, butyric, propionic, and acetic acid; the non-volatile, acidic oxidation product, giving a positive Skraup colour reaction with aqueous ferrous sulphate and having ultraviolet absorption similar to those of simple alkylpyridinecarboxylic acids,<sup>13</sup> furnished, upon decarboxylation, a mixture of pyridine and its simple homologues. Like the lower homologue (III;  $R = Pr^n$ ), the



$C_{15}H_{21}N$  base was extremely resistant to catalytic hydrogenation; however, reduction with sodium in boiling ethanol readily afforded a secondary base  $C_{15}H_{27}N$  (VIII;  $R = H$ ,

<sup>11</sup> Bowden, Braude, Jones, and Weedon, *J.*, 1946, 45.

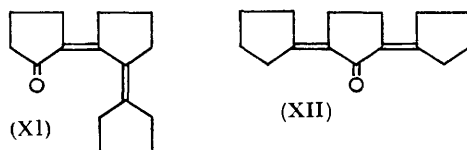
<sup>12</sup> Swain, Eisner, Woodward, and Brice, *J. Amer. Chem. Soc.*, 1949, **71**, 1341.

<sup>13</sup> Plattner, Keller, and Boller, *Helv. Chim. Acta*, 1954, **37**, 1379.

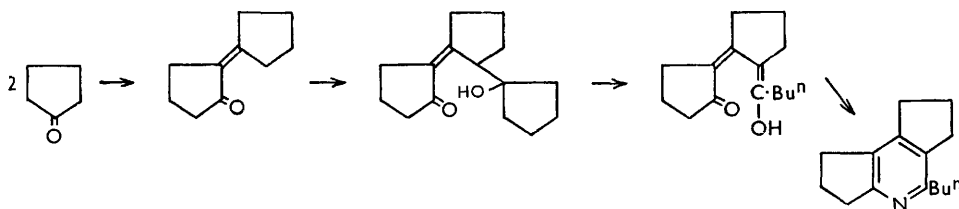
$R' = Bu^n$ ) in which the original chromophore had been eliminated. This piperidine, which formed a chloroplatinate of indefinite composition, had an infrared spectrum very similar to that of *N-n*-butylcyclopentylamine (IX); in particular, a strong band at  $1140\text{ cm.}^{-1}$  appears to be characteristic of this class of compound. The *N*-methyl derivative (VIII;  $R = Me$ ,  $R' = Bu^n$ ) prepared from the reduction product (VIII;  $R = H$ ,  $R' = Bu^n$ ) by formaldehyde-formic acid was highly unstable, readily losing a basic gas (methylamine?) and leaving an intractable gum.

6-*n*-Butyl-2 : 3-4 : 5-dicyclopentenopyridine was synthesised by the Tschitschibabin reaction<sup>8</sup> used by Goodman<sup>2</sup> for the preparation of the analogue (III;  $R = Pr^n$ ). Our compound was produced in low yield from 2-cyclopentylidene-cyclopentanone (I), valeraldehyde-ammonia, and ammonium acetate at  $180^\circ$ , together with (probably) 2-*n*-butyl-3 : 5-di-*n*-propylpyridine (X) arising by condensation of valeraldehyde and ammonia. Our compound (III;  $R = Bu^n$ ) was also the principal basic product (12% yield) in a reaction at  $250^\circ$  between 2-(2'-cyclopentylidene-cyclopentylidene)cyclopentanone (XI) and ammonia in dioxan containing water (1 mol.) (in the absence of solvent and water, these reactants at  $300^\circ$  furnished little base).

The formation of the tricyclic product (III;  $R = Bu^n$ ) from cyclopentanone and ammonia entails condensation between three molecules of the ketone and one of ammonia, one of the  $C_5$  rings opening; and in view of the rapidity with which cyclopentanone self-condenses under base-catalysed conditions, formation of the ketone (XI) or its equivalent



probably is an initial step. The fact that water appears to be essential in pyridine production from (XI) and ammonia suggests that a partial reversal of the aldol condensation is invoked at some stage—it is well established<sup>14</sup> that under conditions necessary for pyridine formation such reversals constitute one of the chief limitations of the Tschitschibabin pyridine synthesis and explain the formation of mixtures in many instances. Reversed aldol condensations seem to be involved in the production of valeric and  $\delta$ -cyclopent-1-enylvaleric (VII;  $R = OH$ ) acid when the ketone (XI) is fused with potassium hydroxide at  $260\text{--}280^\circ$ , one of the reactions investigated by Mleziva<sup>15</sup> in proving structure (XI) for the tricyclic self-condensation product of cyclopentanone, rather than the symmetrical structure (XII) previously accepted.<sup>16</sup> Since 2-cyclopentylidene-cyclopentanone (I) on caustic fusion yielded only the acid (VII;  $R = OH$ ), the valeric acid



obtained from (XI) appears to originate from ring c, and, by analogy, the linear side-chain of the tricyclic base (III;  $R = Bu^n$ ) originates from a similar source. The intramolecular

<sup>14</sup> Frank and Seven, *J. Amer. Chem. Soc.*, 1949, **71**, 2629.

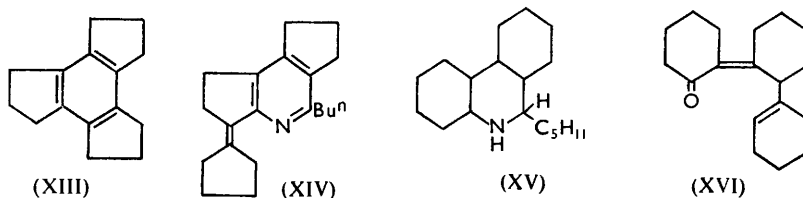
<sup>15</sup> Mleziva, *Coll. Czech. Chem. Comm.*, 1954, **19**, 517.

<sup>16</sup> Wallach, *Ber.*, 1896, **29**, 2963; Goheen, *J. Amer. Chem. Soc.*, 1941, **63**, 744; Rosenfelder and Ginsburg, *J.*, 1954, 2957.

hydrogen-transfer required after the intermediate formation of (XI) or its partially-alldised equivalent probably occurs under the stimulus of aromatisation, as annexed.

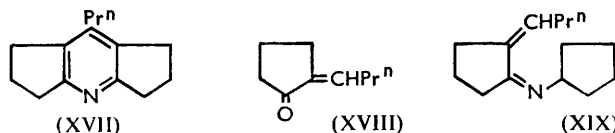
When *cyclopentanone* (1.26 mol.) reacted with anhydrous ammonia (1 mol.) at 300°, the neutral products contained the ketones (I) and (XI), and *tricyclopentenobenzene* (XIII), all self-condensation products of *cyclopentanone*. Whilst producing the base (III; R = Bu<sup>n</sup>), this reaction also yielded a tertiary base C<sub>20</sub>H<sub>27</sub>N, which in addition to showing pyridine absorption maxima at 273 mμ (in MeOH) and at 284 mμ (in conc. HCl), had ultraviolet absorption at longer wavelengths [ $\lambda_{\text{inflex.}}$  310 mμ (in MeOH),  $\lambda_{\text{max.}}$  323—325 mμ (in conc. HCl)]. Catalytic hydrogenation completely removed this high wavelength absorption, whilst the principal pyridine absorption in the 275 mμ region was unaffected. Structures of type (XIV) in which a *cyclopentylidene* system is conjugated with the pyridine nucleus seem likely.

Equimolecular quantities of *cyclohexanone* and anhydrous ammonia under autogenous pressure at 300° furnished a moderate yield (33% of original weight of reactants) of a liquid tertiary base C<sub>18</sub>H<sub>27</sub>N which formed a crystalline chloroplatinate, contained no active hydrogen, and resisted catalytic hydrogenation. Its infrared absorption spectrum had a strong band at 1570 cm.<sup>-1</sup> due to a heterocyclic nucleus, whilst the ultraviolet characteristics (Fig. 1) were those of compounds (III); hence by analogy with the base C<sub>15</sub>H<sub>21</sub>N, the structure (IV; R = *n*-C<sub>5</sub>H<sub>11</sub>) seemed probable. In support of this, permanganate oxidation yielded hexanoic, valeric, butyric, propionic, and acetic acid, whilst decarboxylation of the non-volatile acidic oxidation products gave a mixture of simple alkylbenzenes and pyridines. Sodium-ethanol reduction of the base C<sub>18</sub>H<sub>27</sub>N furnished a secondary amine, presumably the perhydro-compound (XV). The formation of the base (IV; R = *n*-C<sub>5</sub>H<sub>11</sub>) from *cyclohexanone* and ammonia is explicable, by analogy with the *cyclopentanone*-ammonia condensation, on the basis of structure (XVI) established by



Mleziva<sup>17</sup> for the tricyclic self-condensation product of *cyclohexanone*. No attempt has been made during the present studies to confirm structure (IV; R = *n*-C<sub>5</sub>H<sub>11</sub>) by synthesis.

The principal neutral products of lower boiling range (up to 93°/0.3 mm.) from a reaction in which equimolecular amounts of *cyclopentanone* and *n*-butylamine were heated together under autogenous pressure at 300° were 2-*n*-butyl- and 2:5-di-*n*-butyl-*cyclopentanone*; another ketonic product, formed in small amount, had weak ultraviolet absorption at 220—230 mμ, probably associated with 2- or 3-alkyl-*cyclopent-2-enones*.<sup>18</sup> Infrared and ultraviolet spectra of the higher-boiling neutral products (93°/0.3 mm. to 180°/0.15 mm.)



indicated the presence of both saturated and unsaturated *cyclopentanone* derivatives, although no characteristic ketonic derivatives were isolated from these materials. The main constituent of the basic products from the *cyclopentanone*-*n*-butylamine reaction

<sup>17</sup> Mleziva, *Coll. Czech. Chem. Comm.*, 1954, **19**, 505.

<sup>18</sup> Woodward, *J. Amer. Chem. Soc.*, 1941, **63**, 1123; 1942, **64**, 72, 76; Gillam and West, *J.*, 1942, **486**; Acheson and Robinson, *J.*, 1952, 1127.

(a small quantity of di-*n*-butylamine was detected) was a liquid tertiary base  $C_{14}H_{19}N$  which formed a crystalline chloroplatinate. The ultraviolet spectrum of this base, which showed the pyridine-type bathochromic shift of maxima and minima on changing from neutral to acidic solvent,<sup>12</sup> was different from that of the base (III; R = Pr<sup>n</sup>) (see Fig. 2). The infrared spectrum contained a principal band at 1592  $cm^{-1}$  due to a heterocyclic nucleus, whilst  $\bar{N}H$ - and aromatic C-H stretching frequencies were absent; although a number of the infrared bands were found at similar wave-numbers to those in the spectrum of compound (III; R = Pr<sup>n</sup>), there were some intensity differences. The mass spectrum was very similar to that given by the base (III; R = Pr<sup>n</sup>). Thus this product probably has the isomeric structure (XVII). In chemical properties also this base closely resembled the analogue (III; R = Pr<sup>n</sup>): oxidation afforded butyric, propionic, and acetic acid, whilst the non-volatile oxidation product had an ultraviolet spectrum similar to that of analogous material from the isomer (III; R = Pr<sup>n</sup>). Sodium-ethanol reduction yielded the secondary perhydro-compound in which the original pyridine chromophore was destroyed: the infrared spectrum had a band in the 1140  $cm^{-1}$  region characteristic of *N*-substituted cyclopentylamines. It is of interest that a base of molecular weight 215 was detected in the mass spectrum of the cyclopentanone-*n*-butylamine condensation base, although no material corresponding to molecular formula  $C_{15}H_{21}N$  was isolable, probably because of the very small amount present. Such a compound could have been formed by interaction of cyclopentanone with ammonia which was observed to be liberated during the reaction.

Compound (XVII) was synthesised in 11.5% yield from cyclopentylamine and 3 mols. of 2-butyldenecyclopentanone (XVIII) with a catalytic amount of ammonium acetate at 200°. Amongst the neutral products were 2-*n*-butylcyclopentanone (principal component) and 2-cyclopentylidenecyclopentanone (I), whilst there was mass-spectrometric evidence for 2 : 5-di-*n*-butylcyclopentanone and a butylidene- and a di-*n*-butyl-cyclopentylcyclopentanone. In a second synthesis, *N*-(2-butyldenecyclopentylidene)cyclopentylamine (XIX) (1 mol.) [prepared by condensation of the ketone (XVIII) with cyclopentylamine (cf. Norton *et al.*<sup>19</sup>)] and 2-butyldenecyclopentanone (2 mol.) were passed over activated alumina at 350°: the principal products were 2-*n*-butylcyclopentanone and the pyridine (XVII). The structure of the Schiff's base (XIX) was demonstrated by acid hydrolysis to the parent amine and ketone, and by hydrogenation to 2-*n*-butyldicyclopentylamine identical with the base obtained by reductive amination of 2-*n*-butylcyclopentanone with cyclopentylamine.

In an attempt to investigate the materials responsible for the intense colour reaction with *p*-dimethylaminobenzaldehyde, the total neutral material from a reaction between cyclopentanone and *n*-butylamine at 300° was hydrogenated over nickel at 200°/200 atm. The basic material (1.8% yield) isolated from the Ehrlich-negative product, which presumably contained reduction products of pyrrole-type substances, had ultraviolet absorption indicating a high proportion of the pyridine (XVII) which had been inadequately removed in the initial separation or, less probably, was produced by a molecular rearrangement in the presence of the nickel catalyst. Mass spectrometry indicated these reduced bases to be highly complex and since only small amounts were available this problem was not further studied.

After equimolecular amounts of cyclopentanone and di-*n*-butylamine had been heated together under autogenous pressure at 300°, the neutral products of lower boiling-range (up to 88°/0.07 mm.), which had weak ultraviolet absorption in the 240  $m\mu$  region indicative of the presence of a 2 : 3-disubstituted cyclopent-2-enone, were found to contain 2-*n*-butylcyclopentanone and 2-cyclopentylcyclopentanone (VI) as the main constituents. The higher-boiling neutral fractions (88°/0.1 mm. to 180°/0.4 mm.), from which no crystalline ketonic derivatives could be isolated, had infrared spectra indicating the presence of both saturated and unsaturated cyclopentanone compounds, whilst their ultraviolet spectra

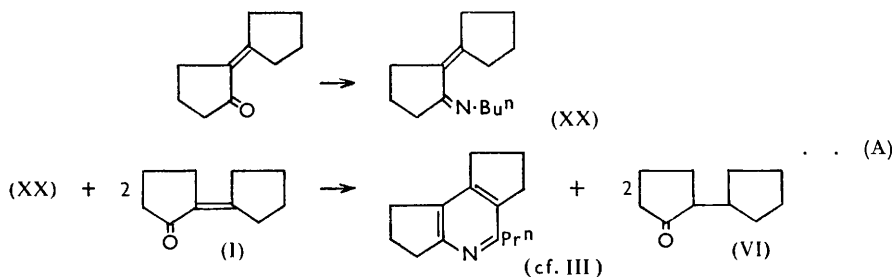
<sup>19</sup> Norton, Haury, Davis, Mitchell, and Ballard, *J. Org. Chem.*, 1954, **19**, 1054.

showed absorption at 228 and 257  $\mu$ , suggesting 2- or 3-substituted *cyclopent-2-enones* and compound (I). The basic reaction products contained much unchanged di-*n*-butylamine together with 4-*n*-propyl-2:3:5:6-dicyclopentenopyridine (XVII). As for the *cyclopentanone-n*-butylamine reaction, mass spectrometry provided some evidence for the presence of  $C_{15}H_{21}N$  base derived from *cyclopentanone* and ammonia, although again, no material of this composition could be isolated.

Reaction between equimolecular amounts of *cyclopentanone* and tri-*n*-butylamine at 300° afforded much unchanged *cyclopentanone* and its self-condensation products 2-*cyclopentylidene**cyclopentanone* (I) and 2-(2'-*cyclopentylidene**cyclopentylidene*)*cyclopentanone* (XI). The basic material isolated was essentially unchanged tri-*n*-butylamine; however, a very small amount of material, b. p. 100—120°/0.4 mm., possessing spectra consistent with the presence of the base (XVII) was obtained.

Fission of a  $Bu^p-N$  link must have occurred during formation of the tricyclic base (XVII) from *cyclopentanone* and *n*-butylamine or di-*n*-butylamine. The mechanism is obscure, but, in that connexion, two further reactions were investigated. *N-cyclopentylidene-n*-butylamine, the expected initial condensation product of *cyclopentanone* and *n*-butylamine, was heated with 3 mol. of *cyclopentanone* at 200° in the presence of ammonium acetate; the principal basic product was the pyridine (XVII), whilst the neutral components contained the *cyclopentanone* derivatives (I), (VI), and (XI), together with *x-n*-butyl- and *x-cyclopentyl-2-cyclopentylidene**cyclopentanone*. The formation of the base (XVII) in this reaction may be consistent with intramolecular rearrangement of the Schiff's base before ring-closure to the heterocyclic system. The neutral products formed from 2-*cyclopentylidene**cyclopentanone* (I) (2 mol.), *n*-butylamine (1 mol.), and a catalytic amount of ammonium acetate at 200° contained *cyclopentanone*, 2-*cyclopentyl**cyclopentanone* (VI), *x-n*-butyl-2-*cyclopentylidene**cyclopentanone*, 2-(2'-*cyclopentylidene**cyclopentylidene*)*cyclopentanone* (XI), and *x-cyclopentyl-2-cyclopentylidene**cyclopentanone*. The presence of *cyclopentanone* and the last two compounds indicates breakdown of 2-*cyclopentylidene**cyclopentanone* (I) into cyclic  $C_5$  units and it is from interaction of these smaller units with *n*-butylamine that the pyridine (XVII), which was produced unexpectedly in this condensation, must have been synthesised.

In connexion with the study of the thermal breakdown of *NN'*-di-*n*-butyladipamide,<sup>1,2</sup> we have investigated also a number of reactions, both catalysed and uncatalysed, between some *cyclopentanone* compounds and *n*-butylamine in the vapour phase. As was first demonstrated by Dr. I. Goodman, lately of these laboratories, no production of carbon



dioxide, alkylated *cyclopentanones*, pyrroles, or  $C_{14}H_{19}N$  bases was observed when an equimolecular mixture of *cyclopentanone* and *n*-butylamine was passed rapidly through a glass tube at 350°; however, *N-cyclopentylidene-n*-butylamine was isolable in moderate yield. We found that an equimolecular mixture of 2-*cyclopentylidene**cyclopentanone* (I) and *n*-butylamine under similar conditions gives a low yield of the resultant Schiff's base (XX) (its structure was proved by hydrolysis and hydrogenation). When, however, a similar reaction mixture was passed over activated alumina at 350°, the crude product, which gave a strong purple-red colour with *p*-dimethylaminobenzaldehyde reagent,

contained some of the Schiff's base (XX), the pyridine (III;  $R = Pr^n$ ), 2-cyclopentylcyclopentanone (VI), and unchanged ketone (I). The formation of these products, and particularly (VI) and (III;  $R = Pr^n$ ) in the approximate molecular ratio of 3:2:1, suggested that a base-catalysed hydrogen-transfer mechanism (cf. Weiss<sup>20</sup>) involving the Schiff's base and 2-cyclopentylidenecyclopentanone (I) may be operative (see annexed scheme). And when reaction (A) was investigated at 350° over activated alumina, the Ehrlich-positive product was shown to contain 2-cyclopentylcyclopentanone (VI) and 6-*n*-propyl-2:3-4:5-dicyclopentenopyridine (III;  $R = Pr^n$ ) in the approximate molecular ratio of 2.5:1, which is in good agreement with the 2:1 stoichiometry considering the difficulty in assessing the true yields.

The vapour-phase reaction between cyclopentanone and *n*-butylamine in the presence of activated alumina at 350° yielded an Ehrlich-positive product containing *N*-cyclopentylidene-*n*-butylamine and the previous products (XX) and (XVII); infrared examination showed the neutral components to be complex but to contain the ketones (I) and (VI) as principal products. In contrast to the uncatalysed vapour-phase reaction, only a trace of unchanged cyclopentanone was recovered.

An abstract of a memoir by Zelinski and Shuikin<sup>21</sup> indicates that cyclopentanone, when passed in the vapour phase over activated alumina at 200°, gives 2-cyclopentylidenecyclopentanone (I) in 41% yield unaccompanied by higher self-condensation products: in our experience 2-cyclopentylidenecyclopentanone prepared by this procedure always contains the tricyclic self-condensation product (XI) of cyclopentanone, even from reaction at temperatures as low as 130° (the b. p. of cyclopentanone). For the preparation of the relatively large quantities of the bicyclic ketone (I) required in this investigation Mleziva's preparation<sup>15</sup> of the tricyclic ketone (XI) from cyclopentanone by the action of potassium hydroxide was suitably modified.

#### EXPERIMENTAL

Ultraviolet absorption spectra were measured on a Cary self-recording spectrophotometer. Infrared spectra were recorded on a Grubb-Parsons double-beam spectrometer (Model S4) with rock-salt optics. Autoclave experiments were conducted in a stainless-steel (18:8:1:1) vessel, of 750 ml. capacity, heated in a metal-bath. Paper chromatograms (Whatman No. 1 paper) of aliphatic acids were run, by the ascending technique, in butan-1-ol saturated with 1.5*N*-aqueous ammonia; spots were located by the conventional ethanolic Bromocresol Green indicator.

cycloPentanone.—Thorpe and Kon's procedure<sup>22</sup> was used for the preparation of large quantities of this ketone, which had b. p. 130—131°,  $n_D^{20}$  1.4365 (Goheen<sup>16</sup> gives b. p. 130.7—130.8°/765 mm.,  $n_D^{20}$  1.43704).

Self-condensation of cycloPentanone.—(a) *In the vapour phase over activated alumina.* cycloPentanone (1574 g.) was allowed to drip during 30 hr. down a vertical column (32 cm. × 2 cm. diam.) of granular activated alumina (4—8 mesh) at 150° ± 10°. Distillation of the dried ( $Na_2SO_4$ ) condensate gave fractions (1) (550 g.) b. p. 128—136°/760 mm., (2) (168 g.) b. p. 36°/22 mm., (3) (441 g.) b. p. 126°/16 mm., (4) (11 g.) b. p. 72—120°/0.14 mm., and (5) (91 g.) b. p. 140—141°/0.14 mm. Fractions (1) and (2) were unchanged cyclopentanone. Fraction (3) was 2-cyclopentylidenecyclopentanone (I), a pale yellow oil,  $n_D^{20}$  1.5218,  $\lambda_{max}$ . 257 m $\mu$  (log  $\epsilon$  4.10 in MeOH) [Wallach<sup>16</sup> gives b. p. 117—119°/12 mm.,  $n_D^{20}$  1.52095; French and Wiley<sup>23</sup> report  $\lambda_{max}$ . 259 m $\mu$  (log  $\epsilon$  4.03 in EtOH)]. The 2:4-dinitrophenylhydrazone of 2-cyclopentylidene-cyclopentanone separated from much methanol or ethyl acetate in maroon needles, m. p. 229—230° (decomp.) (lit.,<sup>24</sup> m. p. 228—229°). The semicarbazone of ketone (I) formed needles, m. p. 205°, from methanol (Wallach<sup>16</sup> records m. p. 200—205°; Kon and Nutland<sup>25</sup> gives m. p. s.

<sup>20</sup> Weiss, *J. Amer. Chem. Soc.*, 1952, **74**, 200.

<sup>21</sup> Zelinski and Shuikin, *J. Russ. Phys. Chem. Soc.*, 1930, **62**, 1343; *Chem. Abs.*, 1931, **25**, 2420.

<sup>22</sup> Thorpe and Kon, *Org. Synth.*, Coll. Vol. I, 2nd edn., p. 192.

<sup>23</sup> French and Wiley, *J. Amer. Chem. Soc.*, 1949, **71**, 3702.

<sup>24</sup> Marvel and Brookes, *ibid.*, 1941, **63**, 2853.

<sup>25</sup> Kon and Nutland, *J.*, 1926, 3106.

223° and 207° respectively for the two forms of this derivative). Fraction (5) was 2-(2'-cyclopentylidenecyclopentylidene)cyclopentanone (XI), which separated from aqueous methanol in massive yellow rhombic plates and from light petroleum (b. p. 60—80°) in long yellow needles, m. p. 80°,  $\lambda_{\max}$ , 301  $\mu$  ( $\log \epsilon$  4.46 in MeOH) [Mleziva<sup>15</sup> gives b. p. 165—183°/5 mm., m. p. 79°,  $\lambda_{\max}$ , 300, 366  $\mu$  ( $\log \epsilon$  4.44, 2.45)]. The C=O absorption was at 1692  $\text{cm}^{-1}$  (Nujol mull).

(b) *In the presence of powdered potassium hydroxide.* cycloPentanone (500 g.) was boiled under reflux in the presence of powdered potassium hydroxide (2.5 g.), and liberated water (55 ml.) was removed (Dean-Stark). The cooled mixture was treated with saturated aqueous sodium chloride (500 ml.), then extracted with ether (8  $\times$  50 ml.). Distillation of the product gave fractions (1) (60 g.) b. p. 40—110°/20 mm. and (2) (213 g.) b. p. 110—136°/20 mm., and a high-boiling residue (119 g.). Fractions (1) and (2) were essentially cyclopentanone and 2-cyclopentylidenecyclopentanone respectively. The crystalline residue had b. p. 141—150°/0.12 mm., and, when recrystallised from aqueous methanol, furnished the ketone (XI) as massive yellow rhombs (103 g.), m. p. 80°.

2-cycloPentylcyclopentanone (VI).—Hydrogen (0.94 mol.) was absorbed when 2-cyclopentylidenecyclopentanone (150 g.) in dioxan (200 ml.) was hydrogenated at 100°/100 atm. over nickel-kieselguhr (15 g.). Distillation of the residue remaining after removal of the catalyst and solvent afforded 2-cyclopentylcyclopentanone (VI) (125 g.), b. p. 120—121°/25.5 mm.,  $n_D^{23}$  1.4768 (Found: C, 78.7; H, 10.6. Calc. for  $\text{C}_{10}\text{H}_{16}\text{O}$ : C, 78.9; H, 10.6%) (lit.: b. p. 117—120°/16 mm.,  $n$  1.4763; <sup>26</sup> b. p. 107—109°/13 mm.,  $n_D^{20}$  1.4772<sup>27</sup>). The C=O absorption band was at 1730  $\text{cm}^{-1}$  (Cherrier<sup>28</sup> gives 1718  $\text{cm}^{-1}$ ). The semicarbazone formed needles, m. p. 208—209°, from methanol (Found: C, 63.7; H, 9.4; N, 19.7. Calc. for  $\text{C}_{11}\text{H}_{19}\text{ON}_3$ : C, 63.1; H, 9.2; N, 20.1%) (lit., m. p. 210°, <sup>21</sup>, <sup>28</sup> 209°<sup>27</sup>). The 2:4-dinitrophenylhydrazone separated from methanol in orange needles, m. p. 158° (Found: C, 58.2; H, 5.8; N, 16.9. Calc. for  $\text{C}_{16}\text{H}_{20}\text{O}_4\text{N}_4$ : C, 57.8; H, 6.1; N, 16.9%) (lit., <sup>29</sup> m. p. 158—159°).

6-n-Butyl-2:3-4:5-dicyclopentenopyridine (III; R = Bu<sup>n</sup>).—(a) *Synthesis from 2-cyclopentylidenecyclopentanone and valeraldehyde-ammonia.* 2-cycloPentylidenecyclopentanone (150 g.), valeraldehyde-ammonia [obtained by passing anhydrous ammonia (19.5 g.) into valeraldehyde (172 g.) at -5° to -10°], and ammonium acetate crystals (10 g.) were heated together under autogenous pressure (max. was 270 lb./sq. in.) at 180°  $\pm$  2° with continuous stirring during 10 hr. The cold product was isolated from the bomb with methanol (100 ml.), ether (500 ml.) was added, and the resulting solution then washed with 2N-sulphuric acid (12  $\times$  100 ml.). After liberation with 40% aqueous sodium hydroxide, the basic product was isolated from this aqueous extract with ether (6  $\times$  100 ml.), and, after solvent had been removed, was treated for 1 hr. with acetic anhydride (105 ml.) containing concentrated sulphuric acid (1 ml.). The cooled mixture was added to water (1000 ml.) and, 2 hr. later, was basified by the careful addition of soda ash and extracted with ether (6  $\times$  100 ml.). After isolation from the ethereal solution with 2N-sulphuric acid, the non-acetylated basic product was distilled and yielded: fractions (1) (19.69 g.) b. p. 92—133°/2.3 mm.; (2) (10.77 g.) b. p. 142—143°/2.3 mm., and (3) (12.55 g.) b. p. 148—150°/2.3 mm.

Fraction (1) was mainly 2-n-butyl-3:5-di-n-propylpyridine (X) (13.02 g.), b. p. 79°/0.07 mm.,  $n_D^{22}$  1.5009 (Found: C, 82.7; H, 11.2; N, 7.0.  $\text{C}_{15}\text{H}_{25}\text{N}$  requires C, 82.1; H, 11.5; N, 6.4%);  $\lambda_{\max}$ , 271  $\mu$  ( $\log \epsilon$  3.72),  $\lambda_{\text{inf}}$ , 279  $\mu$  ( $\log \epsilon$  3.65), and  $\lambda_{\text{min}}$ , 237  $\mu$  ( $\log \epsilon$  2.84 in MeOH);  $\lambda_{\max}$ , 277  $\mu$  ( $\log \epsilon$  3.96),  $\lambda_{\text{inf}}$ , 240  $\mu$  ( $\log \epsilon$  2.93), and  $\lambda_{\text{min}}$ , 246  $\mu$  ( $\log \epsilon$  2.86) in conc. HCl;  $\nu_{\max}$ , 1605m, 1580m, and 1565m (pyridine ring), and at 2933—2865s, 1464—1453s, and 1381  $\text{cm}^{-1}$  ( $\text{CH}_2$  and Me).

Fraction (2) was redistilled; material of b. p. <91°/0.06 mm. was rejected whilst the component (3.27 g.), b. p. 91—96°/0.06 mm.,  $n_D^{22}$  1.5340, was combined with (3). Fractionation of this combined product then gave: (4) (1.28 g.) b. p. 92—94°/0.06 mm.,  $n_D^{22}$  1.5346; (5) (3.29 g.) b. p. 94°/0.06 mm.,  $n_D^{22}$  1.5350; and (6) (9.43 g.) b. p. 94°/0.06 mm.,  $n_D^{22}$  1.5360. Repeated redistillation of fraction (6) afforded 6-n-butyl-2:3-4:5-dicyclopentenopyridine (III; R = Bu<sup>n</sup>), a pale yellow oil (Found: C, 84.0, 83.8; H, 10.1, 10.0; N, 6.5, 7.1.  $\text{C}_{15}\text{H}_{21}\text{N}$  requires C, 83.7; H, 9.8; N, 6.5%);  $\lambda_{\max}$ , 275  $\mu$  ( $\log \epsilon$  3.81),  $\lambda_{\text{min}}$ , 239—240  $\mu$  ( $\log \epsilon$  2.86) in MeOH;  $\lambda_{\max}$ , 227,

<sup>26</sup> Wallach, *Annalen*, 1912, **389**, 179.

<sup>27</sup> Turouva-Pollak, Sosnina, and Treshchova, *Zhur. obshchei Khim.*, 1953, **23**, 1111; *Chem. Abs.*, 1953, **47**, 12207.

<sup>28</sup> Cherrier, *Compt. rend.*, 1947, **225**, 997.

<sup>29</sup> Cordon, Knight, and Cram, *J. Amer. Chem. Soc.*, 1954, **76**, 1646.



284  $m\mu$  ( $\log \epsilon$  3.57, 4.03),  $\lambda_{\text{inf.}}$  237  $m\mu$  ( $\log \epsilon$  3.45), and  $\lambda_{\text{min.}}$  250  $m\mu$  ( $\log \epsilon$  2.78) in conc. HCl;  $\nu_{\text{max.}}$  1605s and 1585s (pyridine ring), and 2959—2841s, 1460s, and 1379ms  $\text{cm.}^{-1}$  ( $\text{CH}_2$  and Me). The mass spectrum was characterised by peaks at mass : charge ratios 215 and 173. The chloroplatinate, orange needles from chloroform—light petroleum (b. p. 60—80°), had m. p. 184° (decomp.) after desolvation at 100° for 18 hr. [Found: C, 42.4; H, 5.3; N, 3.2; Cl, 26.1; Pt (ash), 24.0.  $\text{C}_{30}\text{H}_{44}\text{N}_2\text{Cl}_6\text{Pt}$  requires C, 42.9; H, 5.3; N, 3.3; Cl, 25.3; Pt, 23.2%].

(b) *Synthesis from 2-(2'-cyclopentylidene)cyclopentylidene)cyclopentanone and ammonia.* The ketone (XI) (108 g.) in purified dioxan (120 ml.) containing water (9.0 g.) was heated with anhydrous ammonia (8.5 g.) in an autoclave kept at  $248^\circ \pm 2^\circ$  during 6 hr. (max. pressure was 800 lb./sq. in.); agitation was continuous throughout. Solvent was removed by distillation, and the viscous black residue was dissolved in chloroform (500 ml.), washed with 2N-sulphuric acid ( $6 \times 100$  ml.), and set aside over  $\text{Na}_2\text{SO}_4$ . After being washed with chloroform ( $4 \times 100$  ml.) (these washings were combined with the chloroform solution of neutral reaction products), the acidic extracts were basified and the liberated bases, isolated with ether ( $8 \times 75$  ml.), were distilled and furnished 6-*n*-butyl-2 : 3-4 : 5-dicyclopentenopyridine (13.4 g.), b. p. 112—114°/0.14 mm.,  $n_{\text{D}}^{25}$  1.5366 (Found: C, 83.2, 83.2; H, 9.1, 9.5; N, 6.1, 6.5%). This material had a mass spectrum and ultraviolet and infrared absorption identical with those of the base (III; R = Bu<sup>n</sup>) synthesised by route (a). The chloroplatinate had m. p. and mixed m. p. 182—183° (decomp.) [Found: C, 42.7; H, 5.3; N, 3.4; Cl, 25.7; Pt (ash), 23.0%]. The X-ray powder photographs of the chloroplatinates were identical.

When distilled, the viscous black residue (84.0 g.) which remained after evaporation of the dried chloroform solution of neutral material yielded an oil (0.4 g.), b. p. 100—125°/25 mm., essentially 2-cyclopentylcyclopentanone (semicarbazone, m. p. and mixed m. p. 207°; 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 156°).

6-*n*-Butyl-2 : 3-4 : 5-dicyclopentanopiperidine (VIII; R = H, R' = Bu<sup>n</sup>).—Sodium (6.5 g.) was added in pieces during 2—3 hr. to a solution of the pyridine derivative (III; R = Bu<sup>n</sup>) (3.04 g.) in boiling ethanol (30 ml.). After 18 hours' heating, unchanged sodium was destroyed by ethanol (30 ml.), some of the solvent was distilled off, the residue was poured into water (300 ml.), and the resulting deep-yellow solution was extracted with ether ( $6 \times 50$  ml.). The ethereal extracts were washed with 2N-hydrochloric acid ( $4 \times 50$  ml.), the washings basified with 20% aqueous sodium hydroxide, and the liberated base, isolated with ether, was distilled and yielded 6-*n*-butyl-2 : 3-4 : 5-dicyclopentanopiperidine as a colourless oil (2.58 g.), b. p. 101—102°/0.35 mm.,  $n_{\text{D}}^{25}$  1.4996, which gave a blue colour with sodium nitroprusside—acetaldehyde<sup>30</sup> (Found: C, 81.1; H, 12.1; N, 6.9.  $\text{C}_{15}\text{H}_{27}\text{N}$  requires C, 81.4; H, 12.3; N, 6.3%). Light absorption was not significant at wavelengths greater than 230  $m\mu$ . The infrared spectrum had bands at 3425m and 1149ms (ring -NH-), and at 2985—2195s, 1460s, and 1379ms  $\text{cm.}^{-1}$  ( $\text{CH}_2$  and Me). The mass spectrum contained a series of peaks at mass : charge ratios 221, 206, 192, 178, 164, 150, and 138.

The chloroplatinate of (VIII; R = H, R' = Bu<sup>n</sup>) separated from chloroform—light petroleum (b. p. 60—80°) in orange needles, which, after desolvation at 100°/0.2 mm. during 4 hr., had m. p. 200—201° (decomp. at 203°). This material gave unsatisfactory analyses.

6-*n*-Butyl-2 : 3-4 : 5-dicyclopentanopiperidine (1.0 g.) was heated at 100° during 24 hr. with 40% aqueous formaldehyde (5.0 ml.) and formic acid (12.0 ml.), and the mixture then cooled, poured into water (150 ml.), and basified with 2N-sodium hydroxide. Isolated with ether ( $6 \times 50$  ml.), the 1-methyl derivative (VIII; R = Me, R' = Bu<sup>n</sup>) was obtained as a colourless oil (0.77 g.), b. p. 120°/0.5 mm.,  $n_{\text{D}}^{25}$  1.5000, which gave no colour with nitroprusside—acetaldehyde reagent (Found: N, 6.1; N-Me, 12.6.  $\text{C}_{16}\text{H}_{29}\text{N}$  requires N, 5.95; 1N-Me, 12.3%). Satisfactory carbon and hydrogen analyses were not obtained on this material, which rapidly decomposed with the evolution of methylamine (?) and the formation of a tar.

*Oxidation of 6-n-Butyl-2 : 3-4 : 5-dicyclopentenopyridine.*—Finely powdered potassium permanganate (26 g.) was added portionwise during 4 hr. to a stirred suspension of the base (III; R = Bu<sup>n</sup>) (4.0 g.) in water (600 ml.) at 20°; stirring was then continued for a further 48 hr. The precipitated manganese dioxide was collected and washed with water, and the combined filtrate and washings were clarified with sulphur dioxide. The yellow solution was continuously extracted with ether during 16 hr., and the viscous residue (3.75 g.), isolated from the dried ethereal extract, was evaporated at 0.05 mm. from a water-bath (temp. from 20° to

<sup>30</sup> (a) Feigl and Anger, *Mikrochim. Acta*, 1937, 1, 138; (b) Feigl, "Spot Tests," Vol. II. Organic Applications," Elsevier, Amsterdam, 1954, p. 189.

100°). The volatile products (0.49 g.), collected in a trap at  $-80^{\circ}$ , were shown by paper chromatography to be a mixture of valeric, butyric, propionic, and acetic acid, whilst the non-volatile oxidation products (3.16 g.) gave an orange-yellow colour with aqueous ferrous sulphate and had a light absorption max. (in MeOH) at 280 and a min. at 260  $\mu$ .

A solution of the non-volatile oxidation product in water (30 ml.) was made alkaline (Brilliant Yellow) by saturated aqueous barium hydroxide and evaporated. The finely powdered barium salts were mixed with soda-lime (40 g.) and copper bronze (3 g.), and pyrolysed at red-heat. The products of decarboxylation, which steam-distilled from the retort with the water liberated in the reaction, were isolated from the distillate by continuous ether-extraction during 24 hr., and when fractionated gave fractions: (1) (0.65 g.) b. p. 68—100°/36 mm.,  $\lambda_{\max.}$  261, 267  $\mu$  ( $E_{1\text{cm.}}^{1\%}$  200.5, 173),  $\lambda_{\text{inf.}}$  256  $\mu$  ( $E_{1\text{cm.}}^{1\%}$  177),  $\lambda_{\text{min.}}$  266  $\mu$  ( $E_{1\text{cm.}}^{1\%}$  171) (in MeOH); (2) (0.17 g.) b. p. 70—100°/0.08 mm.,  $\lambda_{\max.}$  260, 267  $\mu$  ( $E_{1\text{cm.}}^{1\%}$  247, 243) (in MeOH). Fraction (1) was a mixture of substituted pyridines and benzenes with the former predominant (mass and infrared spectra).

*High-temperature Reactions of cyclopentanone and Related Compounds with Aliphatic Bases under Autogenous Pressure: General Procedure.*—The appropriate ketones and bases were heated (see below) under the conditions summarised in Table 1. After cooling, the product which generally was a dark viscous gum giving an intense purple colour with Ehrlich's *p*-dimethylaminobenzaldehyde reagent, was removed from the autoclave with ether (500 ml.). Two hours later, any aqueous phase was separated and the ethereal solution was extracted with *n*-sulphuric acid (8  $\times$  100 ml.) and set aside over  $\text{Na}_2\text{SO}_4$ . The combined acidic extracts were washed with ether (6  $\times$  50 ml.) (these washings were added to the ethereal solution of non-basic products), basified to Brilliant Yellow with 20% aqueous sodium hydroxide, and extracted with ether for 24 hr. The dried extracts of basic and non-basic materials were then evaporated, and each was examined in detail by the methods described below. In Expt. 2, the crude product was fractionally distilled before chemical separation was effected.

*Reaction of cyclopentanone with Anhydrous Ammonia at 300°* (Table 1; Expt. 1).—(a) *Non-basic products.* Distillation of the crude material gave: (1) (1.46 g.) b. p. 62—70°/0.3 mm.,  $n_D^{25}$  1.4870; (2) (2.84 g.) b. p. 70—102°/0.2 mm.,  $n_D^{25}$  1.5079; (3) (4.00 g.) b. p. 102—140°/0.2 mm., a partly crystalline, pale yellow oil; and a black pitch (12.83 g.). Fractions (1) and (2) were mixtures of 2-cyclopentylcyclopentanone (semicarbazone, m. p. and mixed m. p. 207°; 2 : 4-dinitrophenylhydrazones, m. p. and mixed m. p. 154°) and 2-cyclopentylidenecyclopentanone [2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 229° (decomp.)]; traces of nitrile were also present (infrared spectrum).

Ether (5 ml.) was added to fraction (3) and the crystalline product was filtered off. Recrystallised from much ether, this substance separated in colourless plates (75 mg.), m. p. 114—115° (Found: C, 67.7; H, 9.7; N, 8.0.  $\text{C}_{10}\text{H}_{17}\text{ON}, \frac{1}{2}\text{H}_2\text{O}$  requires C, 68.1; H, 10.3; N, 7.95%.  $\text{C}_{10}\text{H}_{17}\text{ON}$  requires C, 71.8; H, 10.25; N, 8.4%), having infrared absorption bands at

TABLE 1. Condensation of cyclopentanone and related compounds with aliphatic bases under autogenous pressure.

Expt.	Ketone, g. (mole)	Reactants Base, g. (mole)	Max. temp.	Time at max. temp. (hr.)	Max. pressure (lb./sq. in.)	H <sub>2</sub> O layer removed (g.)
1	<i>cyclo</i> Pentanone 125 (1.49)	$\text{NH}_3$ 25 (1.78)	$300^{\circ} \pm 5^{\circ}$	6	1250	24.8
2	<i>cyclo</i> Pentanone 125 (1.49)	$\text{NH}_3$ 20 (1.18)	$300 \pm 5$	6	—	—
3	<i>cyclo</i> Hexanone 130 (1.325)	$\text{NH}_3$ 22.5 (1.325)	$300 \pm 5$	6	820	22.8
4	<i>cyclo</i> Pentanone 84 (1.0)	$\text{NH}_2\text{Bu}$ 73 (1.0)	$300 \pm 5$	6	850	15.0
5	<i>cyclo</i> Pentanone 84 (1.0)	$\text{NHBu}_2$ 129 (1.0)	$300 \pm 5$	6	450	4.8
6	<i>cyclo</i> Pentanone 84 (1.0)	$\text{NBu}_3$ 185 (1.0)	$300 \pm 5$	6	275	3.2
7	<i>cyclo</i> Pentanone 91.5 (1.09)	<i>N-cyclo</i> Pentylidene- <i>n</i> -butylamine 49 (0.352)	$206 \pm 8$	10	$\text{NH}_4\text{OAc}$ cryst. (6.8 g.) added	
8	2- <i>cyclo</i> Pentylidenecyclo- pentanone 185 (1.235)	$\text{NH}_2\text{Bu}$ 30 (0.411)	$200 \pm 5$	10	240	$\text{NH}_4\text{OAc}$ cryst. (10 g.) added

3360, 3180, and 1650  $\text{cm}^{-1}$  ( $-\text{CO}\cdot\text{NH}_2$ ). Fraction (3) (7.3 g. from 2 expts.) in methanol (10 ml.) was hydrolysed during 20 hr. with boiling 40% aqueous potassium hydroxide (10 ml.). Ammonia was evolved, and from the acidified hydrolysate there was isolated an acid, a pale yellow oil (0.41 g.), b. p. 121°/0.1 mm.,  $n_D^{25}$  1.4787 (Found: C, 70.9; H, 10.0. Calc. for  $\text{C}_{10}\text{H}_{16}\text{O}_2$ :

C, 71.4; H, 9.6%) (Mleziva<sup>15</sup> reports b. p. 131—133°/3 mm.,  $n_D^{20}$  1.4662, for  $\delta$ -cyclopent-1-enylvaleric acid).

(b) *Basic products.* When fractionated, the crude material yielded: (4) (25.89 g.) b. p. 121—122°/0.7 mm.,  $n_D^{22}$  1.5368; (5) (3.80 g.) b. p. 125—142°/0.5 mm.,  $n_D^{22}$  1.5385; (6) (4.04 g.) b. p. 162—168°/0.5 mm.,  $n_D^{22}$  1.5442; an involatile pitch (37.0 g.) remained. Fraction (4) was mainly 6-*n*-butyl-2 : 3-4 : 5-dicyclopentenopyridine, b. p. 108—110°/0.1 mm., 120°/0.5 mm.,  $n_D^{22}$  1.5366 [Found: C, 83.5, 83.6, 83.8, 84.2; H, 9.8, 9.1, 9.6, 9.6; N, 6.5, 6.5, 6.9, 7.0; active H, 0.03%; equiv. (potentiometrically), 216.3, 216.4. Calc. for  $C_{15}H_{21}N$ : 1 active H, 0.47%; equiv., 215.3], which gave a chloroplatinate, m. p. and mixed m. p. 182—183° (decomp.) [Found, in sample dried at 100°/0.2 mm.: C, 43.0, 42.9; H, 5.3, 5.0; N, 3.1, 3.4; Cl, 25.5, 26.1; Pt(ash), 23.4%]. The identity of the base was confirmed further by spectra (light, infrared, and mass), by sodium-ethanol reduction to the piperidine (VIII; R = H, R' = Bu<sup>n</sup>), b. p. 92—94°/0.2 mm.,  $n_D^{22}$  1.4999 [Found: C, 81.8; H, 12.1; N, 6.2; active H, 0.43%; equiv. (potentiometrically), 220.3. Calc. for  $C_{15}H_{27}N$ : H, 0.42%; equiv., 221.4] (mass and infrared spectra), and by oxidation with aqueous potassium permanganate.

*Reaction of cycloPentanone (Excess) with Anhydrous Ammonia at 300°.* (Table 1; Expt. 2).—The total product was distilled and yielded: (1) (15.84 g.) b. p. 42°/64 mm.; (2) (10.41 g.) b. p. 123—130°/16 mm.; (3) (24.19 g.) b. p. 126°/0.15 mm. to 131°/0.28 mm.; (4) (4.07 g.) b. p. 148—156°/0.28 mm.; (5) (25.86 g.) b. p. 172—186°/0.35 mm.; an involatile residue (26.01 g.) was left. Fraction (1) was water. Fraction (2) was mainly 2-cyclopentylidene-cyclopentanone [semicarbazone, m. p. and mixed m. p. 204—205°; 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 229—230° (decomp.)]. Fraction (3) was separated into basic and non-basic constituents with ether and *N*-sulphuric acid in the usual way. The basic component yielded 6-*n*-butyl-2 : 3-4 : 5-dicyclopentenopyridine (19.96 g.) [Found: C, 84.2; H, 9.8; N, 7.0%; equiv. (B.D.H. "4.5" indicator), 219.1] (light and infrared spectra); the chloroplatinate, after desolvation at 100°/0.2 mm. for 6 hr., had m. p. and mixed m. p. 182—183° (decomp.). Fractionation of the non-basic component (3.42 g.) of fraction (3) yielded five arbitrary, Ehrlich-positive sub-fractions: (a) (0.50 g.) b. p. 69—79°/0.45 mm.,  $n_D^{22}$  1.5208; (b) (0.62 g.) b. p. 84—86°/0.45 mm.,  $n_D^{22}$  1.5225; (c) (0.23 g.) b. p. 90—104°/0.3 mm.,  $n_D^{22}$  1.5322; (d) (1.15 g.) b. p. 108—120°/0.4 mm.,  $n_D^{22}$  1.5430; (e) (0.68 g.) b. p. 120—130°/0.4 mm.,  $n_D^{22}$  1.5527. (a), (b), and (c) were recombined and gave 2-cyclopentylidene-cyclopentanone [2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 229° (decomp.)]. Sub-fractions (d) and (e) were mixtures containing 2-cyclopentylidene-cyclopentanone, the ketone (XI), and tricyclopentenobenzene (light, infrared, and mass spectra); traces of nitrogenous products were also present.

After recombination, fractions (4) and (5) were separated by the usual procedure into basic and non-basic components. Distillation of the non-basic constituents (5.0 g.) yielded three Ehrlich-positive sub-fractions: (f) (0.42 g.) b. p. 40—136°/0.2 mm.,  $n_D^{22}$  1.5237; (g) (1.68 g.) b. p. 138—150°/0.2 mm.,  $n_D^{22}$  1.5557; (h) (2.26 g.) b. p. 150—164°/0.2 mm.,  $n_D^{22}$  1.5641. Sub-fraction (f) was essentially 2-cyclopentylidene-cyclopentanone [2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 229—230° (decomp.)]. Both sub-fractions (g) and (h) contained, *inter alia*, 2-cyclopentylidene-cyclopentanone, the ketone (XI), and tricyclopentenobenzene; traces of nitrogenous compounds were present also.

The basic components (23.3 g.) of fractions (4) and (5) were distilled and gave two sub-fractions (green-yellow oils): (m) (8.72 g.) b. p. 152°/0.1 mm. to 172°/0.2 mm.,  $n_D^{22}$  1.5482; (n) (5.46 g.) b. p. 172—186°/0.2 mm.,  $n_D^{22}$  1.5779. Sub-fraction (m) (Found: C, 85.2; H, 9.4; N, 5.6. Calc. for  $C_{20}H_{27}N$ : C, 85.35; H, 9.7; N, 5.0%) had  $\lambda_{\max}$ . 273 m $\mu$  ( $E_{1\text{cm}}^{1\%}$  246),  $\lambda_{\text{inf}}$ . 310 m $\mu$  ( $E_{1\text{cm}}^{1\%}$  47.4),  $\lambda_{\text{min}}$ . 235—237 m $\mu$  ( $E_{1\text{cm}}^{1\%}$  83) in MeOH;  $\lambda_{\max}$ . 224—229, 284, and 341—344 m $\mu$  ( $E_{1\text{cm}}^{1\%}$  208, 361, and 89);  $\lambda_{\text{inf}}$ . 237 m $\mu$  ( $E_{1\text{cm}}^{1\%}$  186), and  $\lambda_{\text{min}}$ . 253—255, 323—325 m $\mu$  ( $E_{1\text{cm}}^{1\%}$  93, 71) in conc. HCl. When hydrogenated in the presence of platinum oxide (50 mg.), sub-fraction (m) (534 mg.) absorbed hydrogen (0.75 mol.) and the resulting base (in MeOH) had  $\lambda_{\max}$ . 275 m $\mu$  ( $E_{1\text{cm}}^{1\%}$  225) and  $\lambda_{\text{min}}$ . 239—244 m $\mu$  ( $E_{1\text{cm}}^{1\%}$  40) with absorption in the region above 300 m $\mu$  completely eliminated.

*Reaction of cycloHexanone with Anhydrous Ammonia at 300°* (Table 1; Expt. 3).—(a) *Basic products.* When distilled, the total crude basic material (110.5 g.) afforded three fractions, all pale yellow oils; (1) (2.13 g.) b. p. 40—138°/0.10 mm.,  $n_D^{23}$  1.5320; (2) (50.90 g.) b. p. 138—146°/0.10 mm.,  $n_D^{23}$  1.5400; (3) (13.17 g.) b. p. 146—170°/0.10 mm.,  $n_D^{23}$  1.5412; an involatile pitch (42.30 g.) remained.

Fraction (2) was mainly 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydro-9-*n*-pentylphenanthridine (IV);

R =  $n\text{-C}_5\text{H}_{11}$ ), a viscous green-yellow, slightly fluorescent oil, b. p. 142°/0.10 mm.,  $n_D^{23}$  1.5411 [Found: C, 83.9; H, 10.7; N, 5.7; active H, 0.036%; equiv. (potentiometrically), 253.6.  $\text{C}_{18}\text{H}_{27}\text{N}$  requires C, 84.0; H, 10.6; N, 5.4; 1 H, 0.39%; equiv., 257.4];  $\lambda_{\text{max}}$ . 273  $\mu$  (log  $\epsilon$  3.69),  $\lambda_{\text{min}}$ . 242  $\mu$  (log  $\epsilon$  2.91) in MeOH;  $\lambda_{\text{max}}$ . 225—227, 281  $\mu$  (log  $\epsilon$  3.56, 3.97),  $\lambda_{\text{min}}$ . 249  $\mu$  (log  $\epsilon$  2.52) in conc. HCl. The infrared spectrum showed bands at 1570s (pyridine ring), and at 2950—2850s, 1462s, 1442s, and 1380  $\text{cm}^{-1}$  ( $\text{CH}_2$  and Me). The *chloroplatinate* of this base separated from chloroform-light petroleum (b. p. 60—80°) in orange needles, which after desolvation at 100°/0.2 mm. during 16 hr., had m. p. 189—190° (decomp.) [Found: C, 46.6; H, 5.9; N, 2.7; Cl, 22.7; Pt(ash), 21.0.  $\text{C}_{36}\text{H}_{56}\text{N}_2\text{Cl}_6\text{Pt}$  requires C, 46.75; H, 6.1; N, 3.0; Cl, 23.0; Pt, 21.1%]. Reduction of the base (IV; R =  $n\text{-C}_5\text{H}_{11}$ ) (7.5 g.) with sodium (15.0 g.) and ethanol (75 ml.) by the usual procedure furnished *perhydro-9-n-pentylphenanthridine* (XV) (5.72 g.), b. p. 136—138°/0.1 mm.,  $n_D^{23}$  1.5084 (Found: C, 82.2; H, 12.1; N, 5.9.  $\text{C}_{18}\text{H}_{33}\text{N}$  requires C, 82.1; H, 12.6; N, 5.3%), which gave a blue colour with nitroprusside-acetaldehyde reagent.

The base (IV; R =  $n\text{-C}_5\text{H}_{11}$ ) (8.0 g.) in aqueous suspension (700 ml.) with potassium permanganate (55 g.) at room temperature during 6 days gave volatile acids (1.05 g.) shown by paper chromatography to include hexanoic, valeric, butyric, propionic, and acetic acid. The non-volatile oxidation products (6.21 g.), which gave an orange colour with aqueous ferrous sulphate and had  $\lambda_{\text{max}}$ . 284  $\mu$ ,  $\lambda_{\text{min}}$ . 260  $\mu$  (in MeOH), were converted into the mixed barium salts (9.65 g.) and then pyrolysed at red heat with soda-lime (40 g.) and copper bronze (3 g.). Distillation of the decarboxylated material gave: (i) (0.20 g.) b. p. 70—90°/32 mm.,  $\lambda_{\text{max}}$ . 261, 268  $\mu$  ( $E_{1\text{cm}}^{1\%}$ . 176.5, 149),  $\lambda_{\text{inf}}$ . 256, 266  $\mu$  ( $E_{1\text{cm}}^{1\%}$ . 160, 146) in MeOH; (ii) (0.10 g.) b. p. 80—90°/0.1 mm. Fraction (i) had a mass spectrum which indicated the presence of the following benzenes and pyridines:  $\text{C}_6\text{H}_6$ ,  $\text{C}_7\text{H}_8$ ,  $\text{C}_8\text{H}_{10}$ ,  $\text{C}_5\text{H}_5\text{N}$ , and  $\text{C}_6\text{H}_7\text{N}$ ; the peaks due to benzene and its homologues were considerably larger than those due to the accompanying pyridines. The infrared spectrum was similar to that given by analogous mixed bases derived from 6-*n*-butyl-2 : 3-4 : 5-dicyclopentenopyridine.

Fraction (3) had light absorption characteristics very similar to those of the pure base (IV; R =  $n\text{-C}_5\text{H}_{11}$ ) but showed additional weak absorption in the region 300—340  $\mu$ .

(b) *Non-basic products*. Distillation of this material (17.30 g.) afforded: (4) (2.61 g.) b. p. 67°/20 mm.,  $n_D^{23}$  1.4539; (5) (3.24 g.) b. p. 80—120°/0.10 mm.,  $n_D^{23}$  1.4822; both these fractions showed weak light absorption in the range 220—260  $\mu$  but were not studied further.

*N-n-Butylcyclopentylamine* (IX) (with I. GOODMAN).—Hydrogen (0.97 mol.) was absorbed when cyclopentanone (5.01 g.) and *n*-butylamine (4.30 g.), in methanol (20 ml.) containing concentrated hydrochloric acid (0.03 ml.), were hydrogenated in the presence of platinum oxide (94 mg.). After catalyst and solvent had been removed, the residue was distilled and furnished *N-n-butylcyclopentylamine* (IX) (7.52 g.), b. p. 186°,  $n_D^{23}$  1.4460 (Found: C, 76.5; H, 12.9; N, 9.8.  $\text{C}_9\text{H}_{19}\text{N}$  requires C, 76.5; H, 13.6; N, 9.9%), which gave a blue colour with nitroprusside-acetaldehyde reagent, and had characteristic absorption at 1136  $\text{cm}^{-1}$ . The derived *phenylurea* formed needles, m. p. 122°, from aqueous methanol (Found: C, 73.5; H, 8.8; N, 10.4.  $\text{C}_{18}\text{H}_{24}\text{ON}_2$  requires C, 73.8; H, 9.3; N, 10.8%).

*N-cyclopentylidene-n-butylamine*.—(a) *Acid-catalysed liquid-phase synthesis*. When concentrated hydrochloric acid (0.6 ml.) was added to freshly distilled cyclopentanone (84 g.) and *n*-butylamine (73 g.), exothermal reaction occurred. The whole was kept for 80 hr. at 20°. Ether (200 ml.) was added, and the solution was extracted with 2*N*-sulphuric acid (3 × 100 ml.). The basic product, liberated from these washings with alkali and isolated with ether (5 × 75 ml.), was kept at 25°/22 mm. for 30 min. and then distilled. *N-cyclopentylidene-n-butylamine* thus obtained (38.3 g.) had b. p. 91—92°/22 mm.,  $n_D^{23}$  1.4600 (Found: C, 77.8; H, 12.2; N, 10.3.  $\text{C}_9\text{H}_{17}\text{N}$  requires C, 77.6; H, 12.3; N, 10.1%). It resisted hydrolysis with 2*N*-hydrochloric acid but yielded cyclopentanone and *n*-butylamine when boiled with 5*N*-hydrochloric acid during 4 hr. Quantitative gas absorption occurred when *N-cyclopentylidene-n-butylamine* (5.10 g.) in methanol (20 ml.) was hydrogenated over platinum oxide (100 mg.) with the formation of *N-n-butylcyclopentylamine* (IX) (4.51 g.), b. p. 186°,  $n_D^{23}$  1.4468 (phenylurea, m. p. and mixed m. p. 122°).

(b) *Vapour-phase synthesis* (with I. GOODMAN). A mixture of cyclopentanone (42 g.) and *n*-butylamine (36.5 g.) was dropped during 210 min. through a vertical glass tube (32 × 2 cm.) at 350°. Isolation from the dark-coloured, Ehrlich-negative, condensate by a procedure similar to that used in (a) gave *N-cyclopentylidene-n-butylamine* (20.13 g.), b. p. 91—92°/22 mm.,

$n_D^{25}$  1.4604 (Found: C, 77.0; H, 12.3; N, 10.2%) [hydrogenation gave *N-n*-butylcyclopentylamine, b. p. 186°,  $n_D^{22}$  1.4468 (phenylurea derivative, m. p. and mixed m. p. 122°)].

*N-n*-Butyl-2-cyclopentylcyclopentylamine.—Hydrogen (0.93 mol.) was absorbed when a solution of 2-cyclopentylcyclopentanone (5.01 g.) and *n*-butylamine (2.31 g.) in methanol (20 ml.) containing concentrated hydrochloric acid (0.03 ml.) was hydrogenated over platinum oxide (95.5 mg.) during 20 hr. After catalyst and solvent had been removed, the residue, in ether (100 ml.), was shaken with 2*N*-hydrochloric acid (4 × 50 ml.). The basic product (5.20 g.), isolated by ether-extraction of the basified washings, was *N-n*-butyl-2-cyclopentylcyclopentylamine, b. p. 78—80°/0.16 mm.,  $n_D^{22}$  1.4728 (Found: C, 80.8; H, 13.0; N, 6.6.  $C_{14}H_{27}N$  requires C, 80.3; H, 13.0; N, 6.7%), which gave a blue colour with nitroprusside-acetaldehyde reagent. The derived phenylurea formed needles, m. p. 141°, from aqueous methanol (Found: C, 76.4; H, 9.7; N, 8.7.  $C_{21}H_{32}ON_2$  requires C, 76.8; H, 9.8; N, 8.5%). The  $\alpha$ -naphthylthiourea, m. p. 133° (Found: C, 76.3; H, 8.5; N, 6.6; S, 8.2.  $C_{25}H_{34}N_2S$  requires C, 76.1; H, 8.7; N, 7.1; S, 8.1%), crystallised similarly.

*N-n*-Butyl-*N*-2-cyclopentyl- $\alpha$ -cyclopentylacetamide, prepared (1.3 g.) by boiling the foregoing base (1.57 g.) with acetic anhydride (1.5 ml.) and concentrated sulphuric acid (1 drop) for 30 min., had b. p. 130°/0.1 mm.,  $n_D^{22}$  1.4930 (Found: C, 76.8; H, 11.7; N, 6.1.  $C_{16}H_{29}ON$  requires C, 76.4; H, 11.6; N, 5.6%),  $\nu_{max}$ . 2900—2800s, 1650s, 1430s, 1367s, and 1295s  $cm^{-1}$ .

*N*-(2-cyclopentylidene)cyclopentylidene)-*n*-butylamine (XX).—(a) No heat was evolved when concentrated hydrochloric acid (0.3 ml.) was added to 2-cyclopentylidene)cyclopentanone (75 g.) and *n*-butylamine (36.5 g.). After 24 hr. at 20° the initial yellow colour had changed to red and after 5 days at 20° two layers had been formed. After 5 more days at 20°, ether (200 ml.) was added and the solution was shaken with 2*N*-sulphuric acid (4 × 100 ml.). Unchanged 2-cyclopentylidene)cyclopentanone (22.4 g.) was recovered from the dried ethereal solution. The acid washings, when basified and extracted with ether, furnished *N*-(2-cyclopentylidene)cyclopentylidene)-*n*-butylamine (XX), a deep yellow oil (57.6 g.), b. p. 92—94°/0.1 mm.,  $n_D^{23}$  1.5158, which, because of its rapid conversion into a red-brown resin, gave unsatisfactory analyses. When hydrolysed with boiling 5*N*-hydrochloric acid (20 ml.) for 8 hr., this base (1.02 g.) yielded 2-cyclopentylidene)cyclopentanone (0.71 g.) [2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 228—229° (decomp.)], and *n*-butylamine [picrate, m. p. and mixed m. p. 150—151°].

The base (5.03 g.) in methanol (20 ml.) was hydrogenated over platinum oxide (103 mg.), hydrogen (1.96 mol.) being absorbed. The basic product (4.16 g.) was *N-n*-butyl-2-cyclopentylcyclopentylamine, b. p. 77°/0.18 mm.,  $n_D^{23}$  1.4751 (Found: C, 80.2; H, 12.6; N, 6.9%), which gave a phenylurea, m. p. 140° (Found: C, 76.9; H, 9.6; N, 8.2%), and an  $\alpha$ -naphthylthiourea, m. p. 133°, each identical with the authentic compounds.

(b) 2-cyclopentylidene)cyclopentanone (50 g.) and *n*-butylamine (24.3 g.) were mixed and dropped during 6 hr. through a vertical glass tube (32 cm. × 2 cm.) at 400°. The condensate, a brown oil, which contained globules of water and gave no colour with Ehrlich's reagent, was diluted with ether (200 ml.) and separated with dilute acid into basic and non-basic components, the latter being unchanged 2-cyclopentylidene)cyclopentanone (35.83 g.). After removal of excess of *n*-butylamine at 20°/20 mm., the basic products were distilled and gave: (1) (trace) b. p. 70—82°/0.1 mm.,  $n_D^{22}$  1.4778; (2) (5.71 g.) b. p. 86—100°/0.1 mm.,  $n_D^{22}$  1.5005. Fraction (2) was mainly *N*-(2-cyclopentylidene)cyclopentylidene)-*n*-butylamine, b. p. 88—92°/0.2 mm.,  $n_D^{22}$  1.5123, which rapidly resinified (Found: C, 81.0; H, 11.1; N, 5.0.  $C_{14}H_{23}N$  requires C, 81.9; H, 11.3; N, 6.8%). Similar results were observed when a tube packed with glass balls (0.40 cm. diam.) was used to increase contact time.

Hydrogenation of the foregoing Schiff's base (1.095 g.) in methanol (20 ml.) over platinum oxide (56.5 mg.) afforded *N-n*-butyl-2-cyclopentylcyclopentylamine (0.67 g.), b. p. 104—106°/1.6 mm.,  $n_D^{21}$  1.4760 (phenylurea, m. p. and mixed m. p. 137°).

*High-temperature Reaction of cyclopentanone and Related Compounds with Aliphatic Bases in the Vapour Phase over Activated Alumina: General Procedure.*—The appropriate ketones and bases were mixed together at room temperature and dropped down a vertical glass tube (32 cm. × 2 cm. diam.) packed with activated alumina (4—8 mesh), at ~350° (cf. Table 2). The products condensed at the bottom of the reaction chamber, generally as dark viscous oils containing globules of water, which gave intense purple colours with Ehrlich's reagent. Usually a strong odour of amine and hydrocarbon was associated with these products, which were separated into basic and non-basic components with ether and 2*N*-sulphuric acid in the usual way. The dried extracts of these materials were evaporated, and each was examined in detail.

Reaction of 2-cycloPentylidenecyclopentanone with *n*-Butylamine in Vapour Phase at 360° over Activated Alumina (Table 2, Expt. 1).—(a) *Basic products*. This material distilled as a yellow oil (11.55 g.), b. p. 30—140°/0.05 mm.,  $n_D^{22}$  1.5029, and when hydrogenated in methanol solution (20 ml.) over platinic oxide (100 mg.) absorbed hydrogen (1016 ml. at N.T.P.) equivalent to the presence of 4.65 g. of the Schiff's base (XX). Distillation of the hydrogenated

TABLE 2. High-temperature reactions of cyclopentanone and related compounds with aliphatic amines in the vapour phase over activated alumina.

Expt.	Reactants Ketone, g. (mole)	Base, g. (mole)	Temp.	Reaction period (min.)
1	2-cycloPentylidenecyclopentanone 75 (0.50)	NH <sub>2</sub> Bu 36.5 (0.50)	360° ± 5°	270
2	2-cycloPentylidenecyclopentanone 47.2 (0.315)	Schiff's base (XX) 32.18 (0.157)	350 ± 10 (in N <sub>2</sub> )	—
3	2-Butylidenecyclopentanone 33.3 (0.241)	Schiff's base (XIX) 24.7 (0.121)	—	180
4	cycloPentanone 84 (1.0)	NH <sub>2</sub> Bu 73 (1.0)	350 ± 5	—

bases afforded: (1) (trace) b. p. 40—70°/0.01 mm.; (2) (4.23 g.) b. p. 70—90°/0.01 mm.,  $n_D^{22}$  1.4811; (3) (5.0 g.) b. p. 90—124°/0.01 mm.,  $n_D^{22}$  1.5078. After recombination, fractions (2) and (3) were treated with acetic anhydride (10 ml.) and concentrated sulphuric acid (2 drops) at 100° for 30 min., and the mixture then cooled and added to water (200 ml.). Two hours later, excess of 2*N*-sodium hydroxide was added and the product, after isolation with ether (5 × 75 ml.), was separated into acetylated and non-acetylated bases with 2*N*-sulphuric acid (4 × 75 ml.) in the usual way. Distillation of the tertiary basic material yielded 6-*n*-propyl-2 : 3-4 : 5-dicyclopentenopyridine (III; R = Pr<sup>n</sup>) (3.54 g., 0.0176 mole), b. p. 104—106°/0.08 mm.,  $n_D^{22}$  1.5370 (Found: C, 83.7; H, 9.7; N, 6.8. Calc. for C<sub>14</sub>H<sub>19</sub>N: C, 83.5; H, 9.5; N, 7.0%), having the light and infrared absorption described by Goodman<sup>2,31</sup> who gives b. p. 104—106°/0.6 mm.,  $n_D^{21}$  1.5405. The mass spectrum confirmed the main constituent as the tertiary base (III; R = Pr<sup>n</sup>); weak peaks at mass : charge ratios 215 (III; R = Bu<sup>n</sup>), 173 (III; R = Me), 159 (III; R = H), 207 (VIII; R = H, R' = Pr<sup>n</sup>), and at 186, 147, and 146 (unidentified), were also present. The chloroplatinate, orange needles from chloroform-light petroleum (b. p. 60—80°), had, after desolvation at 100°/0.1 mm. for 6 hr., m. p. and mixed m. p. 187° (decomp.), and gave an X-ray powder photograph identical with that from the authentic chloroplatinate [Found: C, 41.7; H, 4.8; N, 3.6; Cl, 27.2; Pt(ash), 24.0. Calc. for C<sub>28</sub>H<sub>40</sub>N<sub>2</sub>Cl<sub>6</sub>Pt: C, 41.4; H, 5.0; N, 3.45; Cl, 26.2; Pt, 24.0%].

The acetylated hydrogenated bases were mainly *N*-*n*-butyl-*N*-(2-cyclopentylcyclopentyl)-acetamide (5.65 g.), b. p. 106—114°/0.07 mm.,  $n_D^{22}$  1.4891 (Found: C, 76.5; H, 11.8; N, 5.8. Calc. for C<sub>18</sub>H<sub>29</sub>ON: C, 76.4; H, 11.6; N, 5.6%) (infrared spectrum).

From a second experiment, the hydrogenated basic material [corresponding to fractions (2) and (3) above] (2.0 g.) was warmed with phenyl isocyanate (1.0 g.) in light petroleum (b. p. 60—80°; 15 ml.) for 10 min., then kept at 20° for 4 hr.; the mixture deposited *N*-*n*-butyl-2-cyclopentylcyclopentyl-*N'*-phenylurea, m. p. and mixed m. p. 141° (Found: C, 76.7; H, 9.8; N, 8.6, 8.4. Calc. for C<sub>21</sub>H<sub>32</sub>ON<sub>2</sub>: C, 76.8; H, 9.8; N, 8.5%).

(b) *Non-basic products*. This material, when distilled, gave: (4) (15.70 g.) b. p. 106—128°/17 mm.; (5) (14.08 g.) b. p. 54—128°/0.07 mm.; a viscous involatile residue (4.82 g.) remained. Infrared spectra indicated the major components of these fractions to be 2-cyclopentylcyclopentanone [38% in (4); 17% in (5)] and 2-cyclopentylidenecyclopentanone [19% in (4); 31% in (5)]. Since, however, other unidentified cyclopentanone derivatives with absorption bands overlapping those due to these two ketones were also probably present, analysis by infrared measurement was not accurate. The foregoing figures were arrived at by measurement of the bands at 1275 cm.<sup>-1</sup> in the spectrum of 2-cyclopentylcyclopentanone and at 895 cm.<sup>-1</sup> in that of 2-cyclopentylidenecyclopentanone, and indicated the formation of a total of 8.48 g. (0.0558 mole) of 2-cyclopentylcyclopentanone in the reaction. The molecular ratio of 2-cyclopentylcyclopentanone to base (III; R = Pr<sup>n</sup>) produced in the condensation was therefore 0.0558 : 0.0176 (3.17 : 1).

After filtration through activated alumina, a chloroform solution of the 2 : 4-dinitrophenylhydrazone (0.95 g.) from fraction (4) (0.80 g.) was evaporated and the residue was crystallised

<sup>31</sup> Dr. I. Goodman, personal communication.

from ethyl acetate. Repeated crystallisation (from ethyl acetate) of the dark red crystals which were deposited gave 2-cyclopentylidenecyclopentanone 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 228—229° (decomp.). The residue left after evaporation of the mother-liquors from the original crystallisation was repeatedly crystallised from methanol and yielded 2-cyclopentylcyclopentanone 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 154—155°. The mixed semicarbazones (1.17 g.) from fraction (4) (2.0 g.) furnished the semicarbazone of 2-cyclopentylcyclopentanone, m. p. and mixed m. p. 202°; no pure sample of 2-cyclopentylidenecyclopentanone semicarbazone was isolated from the mother-liquors.

The 2 : 4-dinitrophenylhydrazone (1.03 g.) from fraction (5) (1.00 g.) was filtered in chloroform through activated alumina, and when then repeatedly recrystallised from ethyl acetate gave 2-cyclopentylidenecyclopentanone 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 229° (decomp.). When evaporated, the original mother-liquor yielded a red gum from which no further crystalline derivatives were isolated.

*Reaction of 2-cyclopentylidenecyclopentanone with N-(2-cyclopentylidenecyclopentylidene)-n-butylamine in the Vapour Phase at 350° over Activated Alumina* (Table 2, Expt. 2).—(a) *Basic products*. From this material (6.94 g.), after unchanged Schiff's base had been removed by hydrogenation and subsequent acetylation, the pyridine derivative (III; R = Pr<sup>n</sup>) (3.22 g., 0.0162 mole), b. p. 92—98°/0.07 mm.,  $n_D^{25}$  1.5395 (Found: C, 83.1; H, 9.8; N, 7.3%) (light and infrared spectra), was isolated. The mass spectrum had a major peak at mass : charge ratio 201, and smaller peaks at 229 (III; R = n-C<sub>6</sub>H<sub>11</sub>), 215 (III; R = Bu<sup>n</sup>), 173 (III; R = Me), and 159 (III; R = H), and at 207, 186, and 164 [all derived from the hydrogenated base (VIII; R = H, R' = Pr<sup>n</sup>)]. The chloroplatinate, after desolvation at 100°/0.1 mm. during 8 hr., had m. p. and mixed m. p. 188° (decomp.) and gave an X-ray powder photograph identical with that from authentic salt [Found: C, 41.8; H, 4.1; N, 3.4; Cl, 26.8; Pt(ash), 22.0%].

(b) *Non-basic products*. This material furnished: (1) (10.04 g.) b. p. 60—140°/14 mm.; (2) (8.26 g.) b. p. 90—140°/0.1 mm. Infrared absorption measurements indicated the major components of these fractions to be 2-cyclopentylidenecyclopentanone [45% in (1); 20% in (2)] and 2-cyclopentylcyclopentanone [45% in (1); 30% in (2)]. From fraction (1), 2-cyclopentylcyclopentanone was isolated as the 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 159°, and the semicarbazone, m. p. and mixed m. p. 207—208°, whilst 2-cyclopentylidenecyclopentanone was obtained as the 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 228° (decomp.) from both (1) and (2). The total amount of 2-cyclopentylcyclopentanone from (1) and (2) (from infrared measurements) amounted to 6.17 g. (0.0406 mole); thus the molecular ratio of 2-cyclopentylcyclopentanone to pyridine (III; R = Pr<sup>n</sup>) produced in the reaction was 0.0406 : 0.0162 (2.52 : 1).

*2-n-Butylidenecyclopentanone and 2 : 5-Di-n-butylcyclopentanone*.—Freshly distilled, acid-free n-butyraldehyde (144 g., 2 moles) was added during 6 hr. to a stirred mixture of cyclopentanone (168 g., 2 moles), ether (80 ml.), and 12% aqueous sodium hydroxide (200 ml.) at 10—20°. 60 Min. later the brown, heterogeneous oil was diluted with water (300 ml.), and the whole was made slightly acid (Congo Red) with concentrated hydrochloric acid, and extracted with ether (4 × 200 ml.). The residue (combined material from 4 similar experiments) remaining after evaporation of the dried, ethereal solution was distilled and gave: (1) (158.8 g.) b. p. 30—70°/12 mm.; (2) (618.5 g.) b. p. 90—133°/12 mm.; (3) (81 g.) b. p. 133—160°/12 mm. Fraction (1) was unchanged cyclopentanone. Fraction (2) was boiled under reduced pressure (45 mm.) with anhydrous oxalic acid, and after water (65 ml.) had been removed azeotropically (Dean-Stark), was distilled and furnished a pale yellow oil (515 g.) which upon repeated distillation yielded 2-butylidenecyclopentanone (XVIII), b. p. 90°/12 mm.,  $n_D^{25}$  1.4815 (Found: C, 78.4; H, 10.1. C<sub>9</sub>H<sub>14</sub>O requires C, 78.2; H, 10.2%),  $\lambda_{\max}$ . (in MeOH) 245  $\mu$  (log  $\epsilon$  4.03). The C=O absorption band was at 1724—1709s cm.<sup>-1</sup>. The 2 : 4-dinitrophenylhydrazone separated from ethyl acetate in deep red needles, m. p. 163—164° (Found: C, 57.1; H, 6.1; N, 17.4. C<sub>16</sub>H<sub>18</sub>O<sub>4</sub>N<sub>4</sub> requires C, 56.6; H, 5.7; N, 17.6%). The semicarbazone, needles from aqueous methanol, had m. p. 204° (Found: C, 61.8; H, 8.4; N, 20.9. C<sub>10</sub>H<sub>17</sub>ON<sub>3</sub> requires C, 61.45; H, 8.8; N, 21.5%).

Hydrogenation of 2-butylidenecyclopentanone (10.2 g.) in methanol (150 ml.) over Raney nickel (1.0 g.) afforded 2-n-butylcyclopentanone, b. p. 86°/15 mm.,  $n_D^{25}$  1.4448 (Found: C, 77.1; H, 11.2. Calc. for C<sub>9</sub>H<sub>16</sub>O: C, 77.1; H, 11.5%) (Rapson and Shuttleworth<sup>32</sup> record b. p.

<sup>32</sup> Rapson and Shuttleworth, *J.*, 1940, 640.

89°/10 mm.,  $n_D^{20}$  1.4568). The C=O absorption was at 1727  $\text{cm}^{-1}$ . The 2:4-dinitrophenylhydrazone of this ketone separated from methanol in yellow-orange needles, m. p. 110—111° (Found: C, 56.8; H, 6.2; N, 17.4.  $\text{C}_{15}\text{H}_{20}\text{O}_4\text{N}_4$  requires C, 56.2; H, 6.3; N, 17.6%). The semicarbazone formed rosettes of small prismatic needles, m. p. 197°, from methanol (Found: C, 60.7; H, 9.7; N, 21.2. Calc. for  $\text{C}_{10}\text{H}_{13}\text{ON}_3$ : C, 60.9; H, 9.7; N, 21.3%) (Rapson and Shuttleworth<sup>32</sup> give m. p. 185—186°; Goodman<sup>2,31</sup> found m. p. 188—189°).

Fraction (3) (147.9 g.) and anhydrous oxalic acid (3.0 g.) were boiled under reflux at 42 mm. and liberated water was removed (Dean-Stark). After being washed with 2N-sodium hydrogen carbonate and dried ( $\text{Na}_2\text{SO}_4$ ), an ethereal solution of the residue was evaporated and distilled to give: (4) (26.78 g.) b. p. 104—123°/18 mm.; (5) (17.40 g.) b. p. 123—140°/18 mm.; (6) (65.58 g.) b. p. 140—186°/18 mm.; a high-boiling residue (23.0 g.) remained. From fraction (6), two further fractions, (7) (7.95 g.) b. p. 60—80°/0.07 mm.,  $n_D^{24}$  1.4917, and (8) (53.20 g.) b. p. 80—82°/0.08 mm.,  $n_D^{24}$  1.4980, were obtained. Repeated distillation of sub-fraction (8) gave 2:5-dibutylidencyclopentanone as a lemon-yellow oil (45.0 g.), b. p. 80°/0.08 mm.,  $n_D^{24}$  1.4971 (Found: C, 81.1; H, 10.3.  $\text{C}_{13}\text{H}_{20}\text{O}$  requires C, 81.2; H, 10.5%),  $\lambda_{\text{max}}$ . 251  $\mu$  ( $\log \epsilon$  3.94) (in MeOH). The C=O absorption was at 1684  $\text{cm}^{-1}$ .

Hydrogenation of 2:5-dibutylidencyclopentanone (10.16 g.) in methanol (150 ml.) over Raney nickel (1.0 g.) afforded 2:5-di-*n*-butylcyclopentanone, a colourless oil (8.45 g.), b. p. 140—141°/20 mm.,  $n_D^{23}$  1.4497 (Found: C, 79.5; H, 11.9. Calc. for  $\text{C}_{13}\text{H}_{24}\text{O}$ : C, 79.5; H, 12.3%) (Goodman<sup>2,31</sup> found b. p. 140—142°/13 mm.,  $n_D^{26}$  1.4495). The C=O absorption was at 1718  $\text{cm}^{-1}$ . The semicarbazone separated from aqueous methanol as needles, m. p. 116° (Found: C, 66.5; H, 10.6; N, 16.8. Calc. for  $\text{C}_{14}\text{H}_{27}\text{ON}_3$ : C, 66.4; H, 10.7; N, 16.6%) (Goodman<sup>2,31</sup> found m. p. 116—117°). The 2:4-dinitrophenylhydrazone formed orange needles, m. p. 62—63° (from much methanol) (Found: C, 60.6; H, 7.6; N, 14.3.  $\text{C}_{19}\text{H}_{28}\text{O}_4\text{N}_4$  requires C, 60.6; H, 7.5; N, 14.9%).

2-*n*-Butylidicyclopentylamine.—Hydrogen (1.03 mol.) was absorbed when 2-*n*-butylcyclopentanone (5.0 g.) and cyclopentylamine (3.1 g.) in methanol (20 ml.) containing concentrated hydrochloric acid (0.03 ml.) were reduced over platinum oxide (1.0 g.) during 48 hr. Isolated in the usual manner, 2-*n*-butylidicyclopentylamine was obtained as a colourless oil (5.50 g.), b. p. 78°/0.2 mm.,  $n_D^{23}$  1.4730 (Found: C, 79.7; H, 13.0; N, 6.4.  $\text{C}_{14}\text{H}_{27}\text{N}$  requires C, 80.3; H, 13.0; N, 6.7%). This base did not give a colour reaction with nitroprusside-acetaldehyde reagent, and had infrared bands at 1176ms, 1149ms, and 1124ms  $\text{cm}^{-1}$ . The phenylurea formed needles, m. p. 127—128°, from aqueous methanol (Found: C, 76.2; H, 9.8; N, 8.5.  $\text{C}_{21}\text{H}_{32}\text{ON}_2$  requires C, 76.8; H, 9.8; N, 8.5%).

*N*-(2-Butylidencyclopentylidene)cyclopentylamine (XIX).—A mixture of 2-butylidencyclopentanone (81 g.) and cyclopentylamine (50 g.) was treated with concentrated hydrochloric acid (2 ml.) and kept at 20°. After 15 hr., two layers had formed and after 6 days the heterogeneous product was diluted with ether (300 ml.) and separated by the usual procedure into basic and non-basic components; of these, the latter was unchanged 2-butylidencyclopentanone (31.5 g.). The basic material afforded *N*-(2-butylidencyclopentylidene)cyclopentylamine (XIX), a yellow oil (26.7 g.), b. p. 86—123°/0.3 mm.,  $n_D^{25}$  1.5098, which rapidly resinified; much decomposition attended the distillation and a considerable residue remained. When boiled under reflux with 5N-hydrochloric acid (20 ml.) during 20 hr., this Schiff's base (1.05 g.) yielded 2-butylidencyclopentanone (0.65 g.) (2:4-dinitrophenylhydrazone, m. p. and mixed m. p. 162°) and cyclopentylamine (identified by paper chromatography).

Hydrogenation of this product (XIX) (2.04 g.) in methanol (20 ml.) over platinum oxide (300 mg.) gave 2-*n*-butylidicyclopentylamine (1.36 g.), b. p. 80—81°/0.3 mm.,  $n_D^{25}$  1.4744 (Found: C, 80.2; H, 12.8; N, 6.8%) (infrared spectrum; phenylurea, m. p. and mixed m. p. 127°).

4-*n*-Propyl-2:3:5:6-dicyclopentopyridine (XVII).—(a) From 2-butylidencyclopentanone and cyclopentylamine. cyclopentylamine (35 g., 0.415 mole), 2-butylidencyclopentanone (170.5 g., 1.235 moles), and ammonium acetate crystals (10 g.) were heated together at 200°  $\pm$  5° under autogenous pressure (max. was 175 lb./sq. in.) during 10 hr. After being cooled the product, a dark, Ehrlich-positive, mobile oil was separated with ether and *n*-sulphuric acid into non-basic and basic constituents.

(i) *Non-basic products*. This material was distilled and gave: (1) (9.05 g.) b. p. 40—80°/17 mm.,  $n_D^{23}$  1.4336; (2) (20.30 g.) b. p. 80—90°/15 mm.,  $n_D^{22}$  1.4447; (3) (15.11 g.) b. p. 96—140°/15 mm.,  $n_D^{23}$  1.4700; (4) (3.27 g.) b. p. 140—145°/15 mm. to 80—100°/0.2 mm.,  $n_D^{23}$  1.4791; (5) (2.24 g.) b. p. 100—117°/0.2 mm.,  $n_D^{23}$  1.4935. Fraction (1) was mainly cyclopentanone



[2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 144°; semicarbazone, m. p. and mixed m. p. 217—218° (decomp.)]. Fraction (2) was essentially 2-*n*-butylcyclopentanone (semicarbazone, m. p. and mixed m. p. 197°; 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 112—113°). Fraction (3) had as principal components 2 : 5-di-*n*-butylcyclopentanone and 2-cyclopentylidenecyclopentanone (light and mass spectra). The mass spectrum of fraction (5) showed parent peaks at the following mass : charge ratios: 262 (a dibutylcyclopentylidenecyclopentanone?), 206 (*n*-butylidene-2-cyclopentylcyclopentanone?), and 150 (2-cyclopentylidenecyclopentanone).

(ii) *Basic products.* Distillation of the crude basic products (68.1 g.) yielded: (6) (7.85 g.) b. p. 88—104°/0.2 mm.,  $n_D^{22}$  1.5134; (7) (3.50 g.) b. p. 104—110°/0.2 mm.,  $n_D^{22}$  1.5410; (8) (22.64 g.) b. p. 110—117°/0.35 mm.,  $n_D^{22}$  1.5440; (9) (10.76 g.) b. p. 117—138°/0.35 mm.,  $n_D^{22}$  1.5531. Fractions (7) and (8) were recombined and heated at 100° for 2 hr. with acetic anhydride (25 ml.) and concentrated sulphuric acid (4 drops). The cooled mixture was poured into water (800 ml.) and separated into acetylated and non-acetylated bases by the usual procedure. When distilled, the non-acetylated bases furnished fractions, (10) (13.48 g.) b. p. 106—120°/0.3 mm.,  $n_D^{20}$  1.5434, and (11) (9.62 g.) b. p. 120—140°/0.3 mm.,  $n_D^{20}$  1.5429. Fraction (10) on further distillation yielded two sub-fractions: (12) (9.53 g.) colourless, b. p. 106—112°/0.3 mm.,  $n_D^{21.5}$  1.5429; (13) (3.01 g.) pale yellow, b. p. 112—120°/0.3 mm.,  $n_D^{21.5}$  1.5413; the former was 4-*n*-propyl-2 : 3-5 : 6-dicyclopentenopyridine (XVII) (Found: C, 84.0; H, 9.5; N, 7.0.  $C_{14}H_{19}N$  requires C, 83.5; H, 9.5; N, 7.0%).  $\lambda_{max}$ . 282 m $\mu$  (log  $\epsilon$  3.89),  $\lambda_{min}$ . 237 m $\mu$  (log  $\epsilon$  2.83) in MeOH;  $\lambda_{max}$ . 232, 291 m $\mu$  (log  $\epsilon$  3.62, 4.04),  $\lambda_{inf}$ . 237 m $\mu$  (log  $\epsilon$  3.56),  $\lambda_{min}$ . 251 m $\mu$  (log  $\epsilon$  2.44) in conc. HCl;  $\nu_{max}$ . 1592s (pyridine ring), and 2976—2874s, 1468s, 1437s, and 1391s cm.<sup>-1</sup> (CH<sub>2</sub> and Me). The mass spectrum contained a parent peak at mass : charge ratio 201 and was closely similar to that given by the isomeric pyridine (III; R = Pr<sup>n</sup>). The chloroplatinate, orange needles [from chloroform—light petroleum (b. p. 60—80°)], after drying at 80°/0.2 mm. for 8 hr., had m. p. 192° (decomp.) [Found: C, 42.0; H, 4.7; N, 3.5; Cl, 27.0; Pt(ash), 23.2.  $C_{28}H_{40}N_2Cl_6Pt$  requires C, 41.4; H, 5.0; N, 3.45; Cl, 26.2; Pt, 24.0%].

When reduced with sodium metal (10 g.) in boiling ethanol (60 ml.), the pyridine (XVII) (2.14 g.) afforded 4-*n*-propyl-2 : 3-5 : 6-dicyclopentanopiperidine (1.84 g.), b. p. 96—98°/0.4 mm.,  $n_D^{24}$  1.5020 (Found: C, 81.3; H, 12.3; N, 6.8.  $C_{14}H_{25}N$  requires C, 81.1; H, 12.15; N, 6.8%). which gave a blue colour with nitroprusside—acetaldehyde reagent. Light absorption was not significant at wavelengths greater than 230 m $\mu$ . Infrared bands were at 1134ms (ring —NH—) and 2959—2841s, 1449s, and 1379ms cm.<sup>-1</sup> (CH<sub>2</sub> and Me).

A suspension of 4-*n*-propyl-2 : 3-5 : 6-dicyclopentenopyridine (4.28 g.) in water (500 ml.) was treated at room temperature with potassium permanganate (30 g.) during 48 hr., then worked up as for analogous material derived from the base (III; R = Bu<sup>n</sup>). Paper-chromatography of the volatile acids (0.35 g.) indicated butyric, propionic, and acetic acid. The non-volatile acids, a yellow gum (3.84 g.) which gave a yellow-orange colour with aqueous ferrous sulphate, had light absorption max. at 279 and min. at 261 m $\mu$  in MeOH.

(b) *From 2-butylidenecyclopentanone (XVIII) and N-(2-butylidenecyclopentylidene)cyclopentylamine (XIX) in the vapour phase at 350° over activated alumina* (Table 2, Expt. 3). (i) Unchanged base (XIX) was removed from the basic products (7.80 g.), b. p. 92°/0.3 mm. to 160°/0.4 mm., by hydrogenation and subsequent acetylation, and the residual tertiary bases were distilled. Of the 3 fractions obtained, *viz.*, (1) (0.61 g.) b. p. 102—110°/0.22 mm.,  $n_D^{22}$  1.5395, (2) (3.52 g.) b. p. 112—125°/0.22 mm.,  $n_D^{22}$  1.5380, and (3) (1.12 g.) b. p. 125—163°/0.22 mm.,  $n_D^{22}$  1.5320, fractions (1) and (2) were recombined and redistilled to yield two further fractions: (4) (2.93 g.) b. p. 110—120°/0.3 mm. and (5) (1.20 g.) b. p. >120°/0.3 mm. Fraction (4) was mainly 4-*n*-propyl-2 : 3-5 : 6-dicyclopentenopyridine, b. p. 112—118°/0.5 mm.,  $n_D^{25}$  1.5386 (Found: C, 84.1; H, 9.4; N, 7.2%), having ultraviolet and infrared absorption spectra identical with those of the base synthesised by route (a). The mass spectrum was closely similar to that of the latter material; additional weak peaks at mass : charge ratios 229, 215, 147, 146, and 159 were present. The chloroplatinate, after drying at 80°/0.15 mm. for 8 hr., had m. p. and mixed m. p. 183° (decomp.) [Found: C, 42.0; H, 5.1; N, 3.6; Cl, 26.4; Pt(ash), 23.0%] and gave an X-ray powder photograph identical with that of the derivative synthesised by route (a).

(ii) Distillation of the non-basic products afforded fractions (6) (10.87 g.) b. p. 65—125°/25 mm.,  $n_D^{20}$  1.4559, and (7) (13.84 g.) b. p. 83—162°/0.5 mm.,  $n_D^{22}$  1.4945; a viscous residue (8.43 g.) remained. The infrared spectra indicated the presence, in each, of both saturated and

unsaturated *cyclopentanone* derivatives. Fraction (6) was largely 2-*n*-butyl*cyclopentanone* (semicarbazone, m. p. and mixed m. p. 194°; 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 110—111°).

*Reaction of cyclopentanone with n-Butylamine at 300°* (Table 1; Expt. 4).—(a) *Non-basic products*. Distillation of this component afforded: (1) (1.91 g.) b. p. 65—72°/0.5 mm.,  $n_D^{22}$  1.4562; (2) (20.10 g.) b. p. 78—85°/0.5 mm.,  $n_D^{22}$  1.4529; (3) (11.67 g.) b. p. 85—93°/0.3 mm.,  $n_D^{22}$  1.4611; (4) (22.12 g.) b. p. 93—103°/0.15 mm.,  $n_D^{22}$  1.4830; (5) (10.46 g.) b. p. 103—180°/0.15 mm.,  $n_D^{22}$  1.4911; a viscous residue (12.06 g.) was left. All these materials rapidly darkened on exposure to air and light, and contained traces of nitrogenous compounds.

Fraction (1) was mainly 2-*n*-butyl*cyclopentanone* (semicarbazone, m. p. and mixed m. p. 190°; 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 110°). Fraction (2) was primarily 2 : 5-di-*n*-butyl*cyclopentanone* with smaller amounts of other saturated *cyclopentanone* compounds (infrared spectrum). This fraction (4.0 g.) yielded 2 : 5-di-*n*-butyl*cyclopentanone* semicarbazone (4.5 g.), m. p. and mixed m. p. 122° (Found: C, 66.5; H, 10.5; N, 16.8. Calc. for  $C_{14}H_{27}ON_3$ : C, 66.4; H, 10.7; N, 16.6%). After being boiled with ethanolic 2 : 4-dinitrophenylhydrazine hydrochloride fraction (2) (1.0 g.) deposited, on cooling, a red gum which was dissolved in chloroform and filtered through activated alumina. The solvent was evaporated, the residue was dissolved in methanol; and the bright red prisms (55 mg.) which were deposited after the solution had been kept at 20° for 14 days were collected and recrystallised from methanol. This 2 : 4-dinitrophenylhydrazone (Found: C, 61.0; H, 7.6; N, 13.2%) had m. p. 71—72° which was depressed upon admixture with 2 : 5-di-*n*-butyl*cyclopentanone* 2 : 4-dinitrophenylhydrazone; these two derivatives also gave different X-ray diffraction patterns.

Fraction (3) contained less 2 : 5-di-*n*-butyl*cyclopentanone* and more of the other *cyclopentanone* compounds than fraction (2) (infrared spectrum). This fraction (2.0 g.) yielded 2 : 5-di-*n*-butyl*cyclopentanone* semicarbazone (1.55 g.), m. p. and mixed m. p. 116°; a crystalline 2 : 4-dinitrophenylhydrazone was not isolated.

The infrared spectra of fractions (4) and (5) were very similar and indicated the presence of both saturated and unsaturated *cyclopentanone* compounds.

(b) *Basic products*. When distilled, this component gave fractions: (6) (1.20 g.) b. p. 76—80°/25 mm.,  $n_D^{22}$  1.4232; (7) (2.79 g.) b. p. 80—104°/0.1 mm.,  $n_D^{22}$  1.4832; (8) (10.01 g.) b. p. 104—114°/0.2 mm.,  $n_D^{22}$  1.5214; (9) (14.54 g.) b. p. 114—158°/0.2 mm.,  $n_D^{22}$  1.5309; (10) (1.54 g.) b. p. 158—200°/0.25 mm.,  $n_D^{22}$  1.5350; an involatile pitch (2.04 g.) remained.

Fraction (6) contained dibutylamine (picrate, m. p. and mixed m. p. 58°). Fraction (7) was a complex mixture containing *cyclopentanone* derivatives (infrared spectrum), amide, and pyridine bases (as (XVII)). Fractions (8) and (9) contained as principal constituent the base (XVII) (spectra).

The total crude basic material (46.5 g.) from a second similar reaction was stirred with 10% aqueous sodium hydroxide (1 l.), and benzenesulphonyl chloride (75 ml.) was added during 2 hr. Next day, the mixture was heated at 70° for 2 hr., then extracted with ether (8 × 100 ml.). From this extract, the tertiary bases were isolated with 2*N*-sulphuric acid in the usual way and were obtained as a yellow oil, essentially 4-*n*-propyl-2 : 3-5 : 6-dicyclopentenopyridine (7.51 g.), b. p. 104—108°/0.25 mm.,  $n_D^{22}$  1.5376 (Found: C, 83.6; H, 9.9; N, 6.7%) [light, infrared, and mass spectra; chloroplatinate, m. p. and mixed m. p. 187° (decomp.); behaviour on oxidation].

*Reaction of cyclopentanone with n-Butylamine in the Vapour Phase at 350° over Activated Alumina* (Table 2, Expt. 4).—(a) *Basic products*. Distillation of the crude bases yielded fractions: (1) (10.06 g.) b. p. 96—104°/32 mm.,  $n_D^{22}$  1.4569; (2) (3.30 g.) b. p. 104—128°/32 mm.,  $n_D^{22}$  1.4625; (3) (1.22 g.) b. p. 42—70°/0.04 mm.,  $n_D^{22}$  1.4639; (4) (16.34 g.) b. p. 70—130°/0.04 mm.,  $n_D^{22}$  1.5019. Of these, only fractions (1) and (4) were examined.

Fraction (1) was *N-cyclopentylidene-n*-butylamine, and when hydrogenated over platinum oxide quantitatively absorbed hydrogen to yield *N-n*-butyl*cyclopentylamine* (phenylurea, m. p. and mixed m. p. 122°). When fraction (4) (16.34 g.) in methanol (40 ml.) was hydrogenated over platinum oxide (500 mg.), hydrogen uptake (1321 ml. at N.T.P.) equivalent to the presence of 6.05 g. of *N*-(2-*cyclopentylidene*-*cyclopentylidene*)-*n*-butylamine took place. The hydrogenation product (13.3 g.), b. p. 40—130°/0.2 mm.,  $n_D^{22}$  1.4929, which gave a blue colour with nitroprusside-aldehyde reagent, was treated with acetic anhydride (15 ml.) containing concentrated sulphuric acid (2 drops) at 100° during 30 min., and then separated into acetylated and non-acetylated components. The acetylated bases contained *N-n*-butyl-*N*-2-*cyclopentylcyclopentylacetamide* (4.35 g.), b. p. 115—122°/0.35 mm.,  $n_D^{22}$  1.4820 (Found: C, 74.5; H, 11.8; N,

7.3. Calc. for  $C_{16}H_{29}ON$ : C, 76.4; H, 11.6; N, 5.6% (infrared spectrum). The non-acetylated basic product was 4-*n*-propyl-2 : 3-5 : 6-dicyclopentenopyridine (4.0 g.), b. p. 98—106°/0.08 mm.,  $n_D^{22}$  1.5367 (Found: C, 83.5; H, 9.6; N, 7.1%) [light, infrared, and mass spectra; chloroplatinate, m. p. and mixed m. p. 186° (decomp.)].

(b) *Non-basic products*. The crude non-basic products (32.4 g.) were distilled and gave six Ehrlich-positive fractions, all of which rapidly darkened upon exposure to air and light: (5) (0.87 g.) b. p. 32—76°/19 mm.,  $n_D^{22}$  1.4284; (6) (2.44 g.) b. p. 80—108°/19 mm.,  $n_D^{22}$  1.4848; (7) (3.00 g.) b. p. 52—106°/0.1 mm.,  $n_D^{22}$  1.4926; (8) (1.05 g.) b. p. 62—84°/0.06 mm.,  $n_D^{22}$  1.4957; (9) (5.60 g.) b. p. 84—96°/0.06 mm.,  $n_D^{22}$  1.5085; (10) (2.30 g.) b. p. 96—128°/0.06 mm.,  $n_D^{22}$  1.5282. Fraction (5) was essentially unchanged cyclopentanone. Infrared spectra showed the other fractions to be complex mixtures, whose principal components were 2-cyclopentylidene- (total 2.09 g.) and 2-cyclopentyl-cyclopentanone (2.03 g.). The ratio of 2-cyclopentylcyclopentanone to 4-*n*-propyl-2 : 3-5 : 6-dicyclopentenopyridine produced was 0.67 : 1 molar.

*Reaction of cyclopentanone with Di-n-butylamine at 300°* (Table 1, Expt. 5).—(a) *Non-basic products*. Distillation of the crude, Ehrlich-positive, material yielded fractions: (1) (0.96 g.) b. p. up to 60°/15 mm.,  $n_D^{22}$  1.4333; (2) (9.89 g.) b. p. 88—96°/15 mm.,  $n_D^{22}$  1.4498; (3) (10.58 g.) b. p. 96—115°/15 mm.,  $n_D^{22}$  1.4697; (4) (2.79 g.) b. p. 62—88°/0.07 mm.,  $n_D^{22}$  1.4721; (5) (6.84 g.) b. p. 88—114°/0.1 mm.,  $n_D^{22}$  1.4760; (6) (12.00 g.) b. p. 114—180°/0.4 mm.,  $n_D^{22}$  1.5038; an involatile pitch (20.42 g.) remained.

Fraction (1) was unchanged cyclopentanone. Fraction (2) was 2-*n*-butylcyclopentanone (infrared spectrum; semicarbazone, m. p. and mixed m. p. 197°; 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 110°). Fractions (3) and (4) each had as major component 2-cyclopentylcyclopentanone (semicarbazone, m. p. and mixed m. p. 202—203°; 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 153°), and minor component 2-*n*-butylcyclopentanone (mass spectrum). Infrared spectra indicated the presence in fractions (5) and (6) of saturated and unsaturated cyclopentanones with the latter predominating.

(b) *Basic products*. Distillation of these products yielded fractions: (7) (86.76 g.) b. p. 160—162°/760 mm.,  $n_D^{22}$  1.4241; (8) (1.83 g.) b. p. 28—76°/0.1 mm.,  $n_D^{22}$  1.4558; (9) (5.76 g.) b. p. 76—102°/0.1 mm.,  $n_D^{22}$  1.5250; (10) (8.44 g.) b. p. 102—142°/0.1 mm.,  $n_D^{22}$  1.5378; a viscous residue (4.64 g.) remained.

Fraction (7) was unchanged di-*n*-butylamine. Fractions (9) and (10) were recombined and heated at 100° with acetic anhydride (15 ml.) and concentrated sulphuric acid (0.5 ml.) during 90 min. Only a trace of acetylated material was produced, whilst the non-acetylated bases were obtained as a colourless oil which was distilled to give materials, (11) (0.62 g.) b. p. 90—98°/0.3 mm.,  $n_D^{23}$  1.5210, and (12) (8.53 g.) b. p. 100—104°/0.3 mm.,  $n_D^{23}$  1.5415. The latter was largely 4-*n*-propyl-2 : 3-5 : 6-dicyclopentenopyridine (7.50 g.), b. p. 100—102°/0.3 mm.,  $n_D^{23}$  1.5420 (Found: C, 83.2; H, 9.4; N, 7.0%) (light, infrared, and mass spectra; behaviour on oxidations).

*Reaction of cyclopentanone with Tri-n-butylamine at 300°* (Table 1, Expt. 6).—(a) *Non-basic products*. This material, which gave only a weak colour reaction with Ehrlich's reagent, was distilled to yield fractions: (1) (21.70 g.) b. p. 60°/65 mm.,  $n_D^{22}$  1.4350; (2) (19.70 g.) b. p. 140—150°/30 mm.,  $n_D^{22}$  1.5042; (3) (8.63 g.) b. p. 120—160°/0.2 mm.,  $n_D^{22}$  1.5289; a viscous residue (3.00 g.) remained.

Fraction (1) was unchanged cyclopentanone. Fraction (2) was mainly 2-cyclopentylidene-cyclopentanone [2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 229° (decomp.)]. The partly crystalline, yellow fraction (3) was a mixture containing the ketone (XI) (m. p. and mixed m. p. 79—80°) and 2-cyclopentylidene-cyclopentanone [2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 229—230° (decomp.)].

(b) *Basic products*. When distilled, this material gave fractions: (4) (179.9 g.) b. p. 210—216°/760 mm.,  $n_D^{22}$  1.4296; (5) (0.39 g.) b. p. up to 100°/0.4 mm.,  $n_D^{22}$  1.4572; (6) (1.18 g.) b. p. 100—120°/0.4 mm.,  $n_D^{22}$  1.5348. Redistillation of fraction (4) afforded unchanged tri-*n*-butylamine. Fraction (6) had ultraviolet and infrared absorption properties indicating the major component to be the pyridine (XVII); additional infrared absorption bands in the region 3350—3200  $cm^{-1}$  suggested the presence of some  $-NH^-$  groupings.

*Reaction of cyclopentanone with N-cyclopentylidene-*n*-butylamine at 200°* (Table 1, Expt. 7).—(a) *Basic products*. This material (76 g.) was heated at 100° for 2 hr. with acetic anhydride (76 ml.) containing concentrated sulphuric acid (0.5 ml.), and then separated into acetylated and non-acetylated components. Distillation of the tertiary bases (63.5 g.) afforded fractions:

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(1) (4.32 g.) b. p. 91—130°/0.2 mm.; (2) (8.30 g.) b. p. 130—146°/0.2 mm.; (3) (4.82 g.) b. p. 146—160°/0.2 mm.; a viscous residue (44.50 g.) remained. Fractions (1) and (2) were recombined and redistilled, to give fractions: (4) (1.23 g.) b. p. 80—99°/0.15 mm.,  $n_D^{22}$  1.4928; (5) (8.93 g.) b. p. 99—108°/0.15 mm.,  $n_D^{22}$  1.5390; (6) (1.47 g.) b. p. 138—148°/0.2 mm.,  $n_D^{22}$  1.5533. Of these, fraction (5) gave 4-*n*-propyl-2 : 3-5 : 6-dicyclopentenopyridine (8.08 g.), b. p. 90°/0.1 mm.,  $n_D^{22}$  1.5407 (Found: C, 83.2; H, 9.6; N, 7.0%) [light and infrared spectra; chloroplatinate m. p. and mixed m. p. 187° (decomp.)].

(b) *Non-basic products*. When distilled, this material (51.5 g.) yielded fractions: (7) (2.08 g.) b. p. 34—80°/22 mm.,  $n_D^{22}$  1.4215; (8) (11.44 g.) b. p. 80—140°/22 mm.,  $n_D^{22}$  1.4859; (9) (12.80 g.) b. p. 100—176°/0.18 mm.,  $n_D^{22}$  1.5255.

Fraction (7) was unchanged cyclopentanone. Fraction (8) was a mixture of 2-cyclopentylcyclopentanone (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 157—158°) and 2-cyclopentylidenecyclopentanone [2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 228—229° (decomp.)]. The mass spectrum of fraction (9) had peaks at mass : charge ratios 218 (weak), 216, 206, 152 (weak), 150, and 84, attributable to *x*-cyclopentyl-2-cyclopentylidenecyclopentanone, 2-(2'-cyclopentylidenecyclopentylidene)cyclopentanone, *x*-butyl-2-cyclopentylidenecyclopentanone, 2-cyclopentylcyclopentanone, 2-cyclopentylidenecyclopentanone, and cyclopentanone respectively; additional peaks of unknown origin were found at mass : charge ratios 249, 251, 265, and 267. This fraction (2.20 g.) yielded *x*-butyl-2-cyclopentylidenecyclopentanone 2 : 4-dinitrophenylhydrazone (?) (1.0 g.), red needles (from ethyl acetate), m. p. 190° (Found: C, 61.3; H, 6.5; N, 14.6. C<sub>20</sub>H<sub>26</sub>O<sub>4</sub>N<sub>4</sub> requires C, 62.2; H, 6.8; N, 14.5%). A satisfactory crystalline semicarbazone could not be isolated from this fraction.

*Reaction of 2-cyclopentylidenecyclopentanone with n-Butylamine at 200°* (Table 1, Expt. 8).—

(a) *Basic products*. This material (77 g.) was treated at 100° during 3 hr. with acetic anhydride (75 ml.) containing concentrated sulphuric acid (0.5 ml.), and then was separated into acetylated and non-acetylated bases. Distillation of the non-acetylated bases afforded fractions: (1) (3.54 g.) b. p. 118—124°/0.4 mm.; (2) (9.08 g.) b. p. 124—138°/0.4 mm.; (3) (3.49 g.) b. p. 140—150°/0.4 mm. Fractions (1) and (2) were recombined and gave 4-*n*-propyl-2 : 3-5 : 6-dicyclopentenopyridine (10.41 g.), b. p. 95°/0.1 mm.,  $n_D^{22}$  1.5405 (Found: C, 83.6; H, 9.0; N, 7.1%) [light and infrared spectra; chloroplatinate, m. p. and mixed m. p. 192° (decomp.)].

(b) *Non-basic products*. When distilled, this material (105.7 g.) yielded fractions: (4) (4.23 g.) b. p. 30—80°/20 mm.,  $n_D^{22}$  1.4290; (5) (25.20 g.) b. p. 90—130°/20 mm.,  $n_D^{22}$  1.4979; (6) (21.58 g.) b. p. 64—126°/0.1 mm.,  $n_D^{22}$  1.5272; (7) (2.09 g.) b. p. 126—140°/0.1 mm.,  $n_D^{22}$  1.5528; a viscous residue (49.6 g.) remained.

Fraction (4) was cyclopentanone [semicarbazone, m. p. and mixed m. p. 217—218° (decomp.); 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 144°]. Fraction (5) was a mixture of 2-cyclopentylcyclopentanone and 2-cyclopentylidenecyclopentanone. The mass spectrum of fraction (6) had parent peaks at mass : charge ratios 218, 216, 206, 152, 150, and 84, due respectively to *x*-cyclopentyl-2-cyclopentylidenecyclopentanone, 2-(2'-cyclopentylidenecyclopentylidene)cyclopentanone, *x*-butyl-2-cyclopentylidenecyclopentanone, 2-cyclopentylcyclopentanone, 2-cyclopentylidenecyclopentanone, and cyclopentanone; other, unidentified, peaks at mass : charge ratios 189, 171, 163, and 161, were found. This fraction yielded *x*-cyclopentyl-2-cyclopentylidenecyclopentanone 2 : 4-dinitrophenylhydrazone (?), scarlet needles (from ethyl acetate), m. p. 210° (Found: C, 63.9; H, 6.3; N, 14.1. C<sub>21</sub>H<sub>26</sub>O<sub>4</sub>N<sub>4</sub> requires C, 63.3; H, 6.6; N, 14.1%). The crystalline fraction (7) was mainly the ketone (XI), m. p. and mixed m. p. 80°.

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