HYDROGENOLYSIS OF ENAMINES—I

REACTION WITH ALUMINIUM HYDRIDE

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Abstract—Enamines react with AlH_3, AlH_2Cl and $AlHCl_2$ to give saturated amines and olefins, products of hydrogenation and hydrogenolysis, respectively. The proportion of the latter is lower with the chlorinated reducing agents. Good yields of olefins are obtained by reaction of AlH_3 with pyrrolidine enamines of acyclic and cyclic ketones. Enamines of α-substituted cyclohexanones are converted to 3-alkylcyclohexenes. Those derived from disubstituted acetaldehydes are only poorly hydrogenolysed as is the dienamine derived from $\Delta_{1,9}$-octalone. 1-N-Pyrrolidinocyclo-octene is unique in giving cyclo-octane in the hydrogenolysis reaction; *trans*-cyclo-octene is the likely intermediate.

THE reactions of enamines with electrophilic reagents have been well explored.[1] Hydrogenation of the enamine double bond has been achieved catalytically[2] and with formic acid[3,4] and sodium borohydride.[5,6] In the latter cases the reaction involves initial protonation (by the solvent in the case of sodium borohydride) followed by hydride ion attack ($\mathbf{1} \rightarrow \mathbf{2}$). LAH which cannot be used in protic solvents is without action on enamines.[1] Diborane and the mixed hydride reagents[7] formed from mixtures of LAH and $AlCl_3$ are electrophilic in character and should, therefore, undergo direct reaction with enamines. Sansoulet and Welvart[8] reacted a number of enamines with aluminium dichlorohydride and obtained the saturated amines. They showed that an adduct **3** was initially formed since hydrolysis with D_2O resulted in incorporation of deuterium at the β-C atom of the amine **4**.
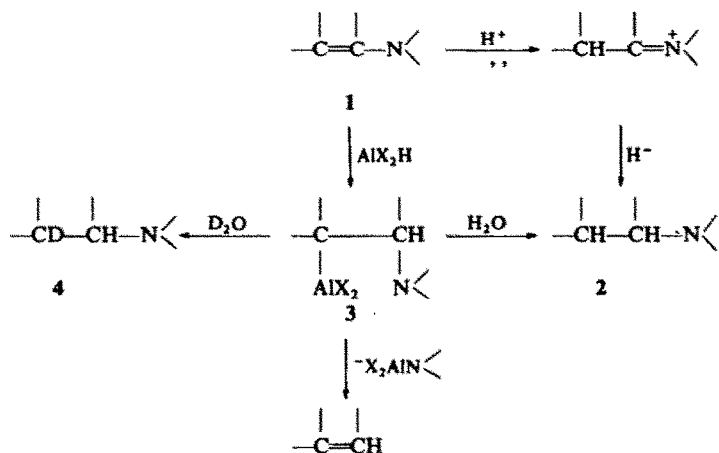
We have investigated more fully the reaction of enamines with the mixed hydrides and have found that in most cases as well as saturated amines, appreciable quantities of olefins are formed. The latter are the products of hydrogenolysis of the enamines resulting from elimination of the aluminium and amine functions from adduct 3. In cases where an enamine was reacted with each of the three reducing agents, viz. $AlCl_2H$, $AlClH_2$ and AlH_3, the proportion of olefin was greatest with AlH_3 and least with $AlCl_2H$ (Table 1). Only in the case of 1-N-pyrrolidinocyclohexene was a good yield of olefin obtained using the chlorohydrides.

TABLE 1. REACTION OF ENAMINES

Enamine (A)	Reagent (B)	Pro			
		Olefin	%	Amine	%
1-N-Pyrrolidino-cyclohexene	$AlHCl_2$[b] AlH_2Cl[c] AlH_3[b]	cyclohexene	75 75 80	N-pyrrolidino-cyclohexane	22 15 13
6-Methyl-1-N-pyrro-lidinocyclohexene	$AlHCl_2$[b] AlH_2Cl[c] AlH_3[b]	3-methylcyclohexene	19 42 85	2-methyl-1-N-pyrro-lidinocyclohexane	81 57 11
6-n-Butyl-1-N-pyrro-lidinocyclohexene	$AlHCl_2$[b] AlH_2Cl[c] AlH_3[b]	3-n-butylcyclohexene	4 13 91	2-n-butyl-1-N-pyrro-lidinocyclohexane	91 74 8
3-N-Pyrrolidino-pent-2-ene	$AlHCl_2$[b] AlH_2Cl[c] AlH_3[b]	pent-2-ene	27 35 81	3-N-pyrrolidino-pentane	66 56 13
4-N-Pyrrolidino-hept-3-ene	$AlHCl_2$[b] AlH_2Cl[c] AlH_3[b]	hept-3-ene	19 30 85	4-N-pyrrolidino-heptane	78 56 9

* Yu. K. Yur'ev and I. K. Korobitsyna, *Zh. Obschei. Khim.* **22**, 852 (1952).
ª Standard reaction conditions: 48 hr in ether under reflux
b B:A = 4.
c B:A = 2.

Since our interest was chiefly in the hydrogenolysis reaction AlH_3 was the reagent of choice. The action of this reagent on 1-pyrrolidinocyclohexene was studied in some detail and the results are shown in Table 2. At room temperature no enamine remained after 15 minutes reaction but work up of the reaction mixture at this stage gives only 1-pyrrolidinocyclohexane. With increasing reaction times cyclohexene is formed at the expense of the amine. The elimination reaction giving rise to the olefin is slow compared with the addition reaction and is approximately First Order with respect to the adduct (Fig. 1). The yield of cyclohexene was only slightly lower when a 1:1 ratio of AlH_3 to enamine was used instead of the normal 4:1 ratio. Thus, whilst with an excess of AlH_3 the adduct may be associated with a second molecule of coordinated AlH_3 (5) the latter is not essential to the elimination reaction. When the ratio was reduced to 1:2 only about 50% of the enamine reacted; this shows that

only one of the Al–H bonds of AlH_3 can be utilised in the formation of an adduct so that structure (6) of the R_2AlH type is not possible.

The morpholine enamine of cyclohexanone gave only a slightly lower yield of cyclohexene than the pyrrolidine derivative but the N-methylaniline enamine gave a much lower yield. N-Methylaniline is a weaker base than pyrrolidine or morpholine and should, therefore, be a better leaving group in elimination reactions. That the reverse is found suggests that steric rather than electronic factors determine the facility of elimination from the enamine–aluminium hydride adduct.

WITH $AlHCl_2$, AlH_2Cl AND AlH_3

ducts

| B.p., refractive index, analysis	Picrate (m.p. and analysis)
b.p 62–64°/3 mm, n_D^{20} 1·4824 (lit.* b.p. 65–68°/5 mm)	m.p. 161–162° (lit.* m.p. 163–164°)
b.p. 68–70°/3 mm, n_D^{20} 1·4840 Found: C, 79·0; H, 12·65; N, 8·3 $C_{11}H_{21}N$ requires: C, 79·1; H, 12·7; N, 8·4%	m.p. 129–130° Found: C, 51·3; H, 6·1; N, 14·0 $C_{17}H_{24}N_4O_7$ requires: C, 51·6; H, 6·1; N, 14·1%
b.p. 106–109°/0·5 mm, n_D^{21} 1·4880 Found: C, 80·4; H, 12·7; N, 6·8 $C_{14}H_{27}N$ requires: C, 80·4; H, 13·0; N, 6·7%	m.p. 151–153° Found: C, 55·1; H, 6·95; N, 12·6 $C_{20}H_{30}N_4O_7$ requires: C, 54·8; H, 6·9; N, 12·8%
b.p. 68–70°/19 mm, n_D^{20} 1·4975 Found: C, 76·8; H, 13·3; N, 9·85 $C_9H_{19}N$ requires: C, 76·6; H, 13·5; N, 9·9%	m.p. 96–98° Found: C, 48·7; H, 6·0; N, 15·2 $C_{15}H_{22}N_4O_7$ requires: C, 48·7; H, 6·0; N, 15·1%
b.p. 94–95°/23 mm, n_D^{25} 1·4483 Found: C, 77·95; H, 13·8; N, 8·3 $C_{11}H_{23}N$ requires: C, 78·2; H, 13·7; N, 8·2%	m.p. 108–109° Found: C, 51·1; H, 6·6; N, 14·2 $C_{17}H_{26}N_4O_7$ requires: C, 51·3; H, 6·6; N, 14·1%
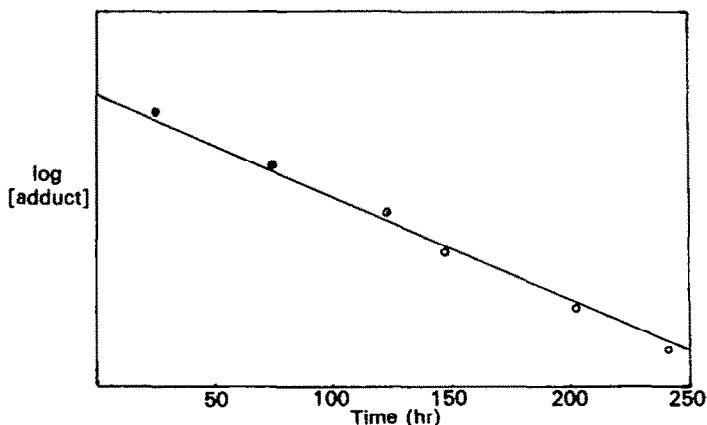
FIG. 1 Decomposition of 1-N-pyrrolidinocyclohexene–AlH_3 adduct in ether at 20°.

For comparison with the cyclohexanone enamines the behaviour of an enacylamine derived from the same ketone was investigated. N-Benzoyl-N-n-butylcyclohex-1-enylamine (**8**) was prepared by the action of benzoyl chloride on cyclohexanonebutylimine (**7**) in the presence of triethylamine and its reaction with aluminium hydride under the usual conditions gave cyclohexene (89 %) and N-butylbenzylamine (80 %).

TABLE 2. REACTION OF 1-N-PYRROLIDINOCYCLOHEXENE WITH ALUMINIUM HYDRIDE

|	AlH_3 (moles)	Enamine (moles)	Temperature (°C)	Time (hr)	Cyclohexene %	1-Pyrrolidino-cyclohexane %
1.	0·2	0·05	40[a]	48	80	13
2.	0·05	0·05	40	48	72	19
3.	0·025	0·05	40	48	39	14[b]
4.	0·2	0·05	20	0·1	0	53[c]
5.	0·2	0·05	20	0·25	0	97
6.	0·2	0·05	20	24	4	90
7.	0·2	0·05	20	72	25	[d]
8.	0·2	0·05	20	120	41	[d]
9.	0·2	0·05	20	144	51	[d]
10.	0·2	0·05	20	240	70	[d]

[a] Temperature of refluxing ether solution.
[b] 35 % of recovered cyclohexanone.
[c] 40 % recovered cyclohexanone.
[d] Not determined.

The amide group in **8** is much less effective than a tertiary amine group in conferring strong nucleophilic character to the double bond so that the enacylamine does not directly form an adduct **9** with AlH_3. Instead the amide group is initially reduced and the resulting enamine (**10**) is then able to undergo hydrogenolysis to cyclohexene and N-butylbenzylamine. With LAH reduction of the enacylamine stopped at the enamine which decomposed during the normal isolation procedure to give cyclohexanone and N-benzylbutylamine.

PhCH₂NHBu
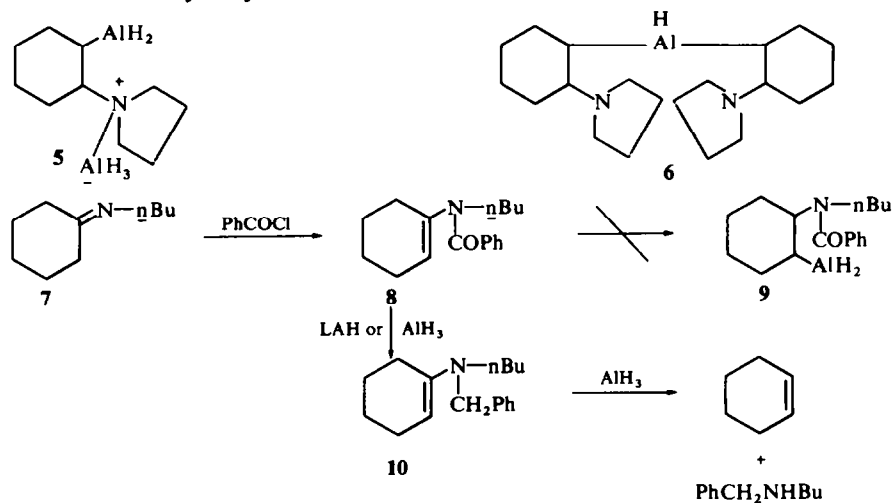
The behaviour of a number of pyrrolidine enamines in reaction with AlH_3 is compared in Table 3. The enamines of unsubstituted cyclic ketones give good yields of cyclo-olefines except cyclo-octanone which is unique in its conversion exclusively to cyclo-octane; no cyclo-octene is formed. The most likely explanation for this result is that the initially. formed olefin undergoes unusually facile reaction with AlH_3 to give an adduct which is hydrolysed to cyclo-octane. Reduction of the reaction time and the hydride:enamine ratio did not allow isolation of the olefin but merely reduced the yield of the saturated hydrocarbon. Thus, addition of AlH_3 to the olefin must be faster than the formation of the latter from the enamine–aluminium hydride adduct.

Olefins normally add AlH_3 only in enclosed systems at elevated temperatures[9] and it is for this reason that they can be isolated from the hydrogenolysis reaction since they are formed in the presence of excess AlH_3. *trans*-Cyclo-octene, however, is known to undergo exceptionally facile addition[10] resulting in release of a large amount of energy from the strained configuration. It seemed likely, therefore, that *trans*-cyclo-octene was stereospecifically formed in the hydrogenolysis of 1-pyrrolidino-cyclo-octene. Confirmation was obtained by independently treating both *cis*- and *trans*-cyclo-octene with AlH_3 under the conditions of the hydrogenolysis reaction. The *cis*-isomer was recovered unchanged but *trans*-cyclo-octene was rapidly converted to an adduct which gave cyclo-octane in the normal acid work-up. The overall sequence is shown in Fig. 2. The enamine also gave cyclo-octane when treated with aluminium monochlorohydride but the yield was much lower (7%) whilst with aluminium dichlorohydride a small amount of *cis*-cyclo-octene was formed and no saturated hydrocarbon. In the latter case *trans*-cyclo-octene may have been initially formed and subsequently isomerized.
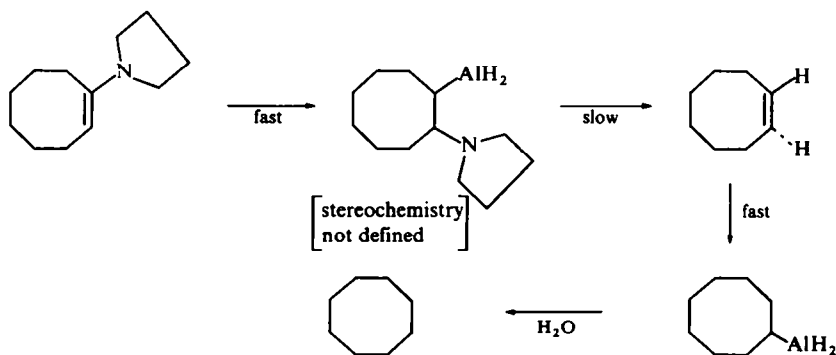

FIG. 2.

The stability of the *trans*-cyclo-olefins compared to the *cis*-isomers increases from 8-membered to 12-membered rings. As in the case of the cyclo-octanone enamine, 1-pyrrolidinocyclododecene would be expected to give the *trans*-olefin in the hydrogenolysis reaction but since this isomer has very little ring strain and is more stable than the *cis*-isomer it should suffer no further transformation. *trans*-Cyclododecene was in fact obtained in good yield after prolonged reaction of the enamine with AlH_3. When a similar reaction was stopped after 10 hours a 60% yield of cyclododecanol was obtained, the remainder of the product being the reduced enamine.

TABLE 3. REACTION OF PYRROLIDINE

Enamine	Hydrocarbon	Amine
1-N-Pyrrolidinocyclopentene	cyclopentene (92 %)	N-pyrrolidinocyclopentane (5 %)
1-N-Pyrrolidinocycloheptene	cycloheptene (85 %)	N-pyrrolidinocycloheptane (14 %)
1-N-Pyrrolidinocyclo-octene	cyclo-octane (85 %)	N-pyrrolidinocyclo-octane (10 %)
1-N-Pyrrolidinocyclododecene[b]	trans cyclododecene (72 %)	N-pyrrolidinocyclododecane (18 %)
2-Ethyl-1-N-pyrrolidinohex-1-ene[c]	2-ethylhex-1-ene (19 %)	2-ethyl-1-N-pyrrolidinohexane (54 %)
N-Pyrrolidinomethylenecyclohexane[d]	methylenecyclohexane (7·5 %) 1-methylcyclohexene (24 %)	N-pyrrolidinomethylcyclohexane (66 %)
1-N-Morpholinocyclohexene	cyclohexene (70 %)	N-morpholinocyclohexane (12 %)
N-Cyclohex-1-enyl-N-methyl-aniline	cyclohexene (52 %)	N-cyclohexyl-N-methylaniline (46 %)
6-Phenyl-1-N-pyrrolidinocyclohexene[d]	—	2-phenyl-1-N-pyrrolidinocyclohexane (72·5 %)

* Yu. K. Yur'ev et al., Zh. Obschei. Khim. 19, 1730 (1949).
† M. Metayer, Bull. Soc. chim. Fr. 1048 (1950).
‡ D. A. Archer and H. Booth, J. Chem. Soc. 322 (1963).

The 12-membered ring is severely puckered and must impede the addition of AlH_3 to the enamine. The secondary alcohol could then be accounted for if during the isolation procedure, ketone formed by hydrolysis of unreacted enamine is reduced by unhydrolysed AlH_3 or by nascent hydrogen.

The pyrrolidine enamines of α-substituted cyclohexanones have the less-substituted olefin structure 11 and are converted in the hydrogenolysis reaction to cyclohexenes substituted in the 3-position (12). Good yields of 3-n-alkylcyclohexenes were obtained but the enamine of 2-phenylcyclohexanone gave no olefin at all. Moreover, in the latter case unreacted enamine was present at the end of the reaction showing that the addition as well as the elimination reaction is slow. The influence of steric factors in these cases will be discussed in a future paper.

ENAMINES WITH ALUMINIUM HYDRIDE

| Amine	Derivative
b.p. 82–84°/15 mm, n_D^{20} 1·4734 (lit.* b.p. 92°/28 mm, n_D^{20} 1·4744)	m.p. 148–149° (picrate) (lit.* m.p. 149–150°)
b.p. 95–97°/5 mm, n_D^{20} 1·4891 Found: C, 78·8; H, 12·4; N, 8·2 $C_{11}H_{21}N$ requires: C, 79·1; H, 12·7; N, 8·4%	m.p. 135–136° (picrate) Found: C, 51·6; H, 5·85; N, 14·1 $C_{17}H_{24}N_4O_7$ requires: C, 51·6; H, 6·1; N, 14·15%
b.p. 80–83°/2 mm, n_D^{20} 1·4937 Found: C, 79·9; H, 13·0; N, 8·0 $C_{12}H_{23}N$ requires: C, 79·6; H, 12·8; N, 7·7%	m.p. 138–141° (picrate) Found: C, 52·6; H, 6·2; N, 13·4 $C_{18}H_{26}N_4O_7$ requires: C, 52·7; H, 6·4; N, 13·7%
b.p. 172–174°/12 mm, n_D^{21} 1·4978 Found: C, 81·4; H, 13·5; N, 5·5 $C_{16}H_{31}N$ requires: C, 81·1; H, 13·2; N, 5·9%	m.p. 112–113° (picrate) Found: C, 56·3; H, 7·2; N, 12·0 $C_{22}H_{34}N_4O_7$ requires: C, 56·7; H, 7·35; N, 12·0%
b.p. 94–96°/14 mm Found: C, 79·1; H, 13·8; N, 7·9 $C_{12}H_{25}N$ requires: C, 78·8; H, 13·8; N, 7·65%	
b.p. 124–126°/14 mm, n_D^{20} 1·5140 Found: C, 79·6; H, 12·85; N, 8·3 $C_{11}H_{21}N$ requires: 79·1; H, 12·7; N, 8·4%	m.p. 138–140° (picrate) Found: C, 51·5; H, 5·9; N, 14·0 $C_{17}H_{24}N_4O_7$ requires: C, 51·6; H, 6·1; N, 14·15%
b.p. 118–120°/14 mm, n_D^{21} 1·4882 (lit.† b.p. 116–117°/13 mm, n_D^{27} 1·4895)	m.p. 202–205° (methiodide) (lit.† m.p. 207°)
b.p. 136–138°/14 mm, n_D^{21} 1·5590 (lit.‡ b.p. 150–152°/14 mm, n_D^{25} 1·5605)	m.p. 95° (picrate) (lit.‡ m.p. 96–97°)
n.p. 178–182°/13 mm, n_D^{23} 1·5480 Found: C, 83·7; H, 10·1; N, 6·0 $C_{16}H_{23}N$ requires: C, 83·9; H, 10·1; N, 6·1%	m.p. 191–193° (picrate) Found: C, 57·55; H, 5·5; N, 12·2 $C_{22}H_{26}N_4O_7$ requires: C, 57·7; H, 5·7; N, 12·2%

[a] For standard reaction conditions see Footnote on Table 1.
[b] 96 hr reaction.
[c] 23% unreacted enamine recovered as 2-ethylhexanal
[d] 26% unreacted enamine recovered as 2-phenylcyclohexanone

The behaviour in the hydrogenolysis reaction of three types of acyclic enamine having different substitution patterns was investigated. The enamines of pentan-3-one (13a) and heptan-4-one (13b) were hydrogenolysed in good yield as was the derivative of the straight chain aldehyde octanal (13c) but the enamines of α-branched aldehydes (13d, e) gave much lower yields. The expected olefin 2-ethylhexene (14) was formed from 2-ethyl-1-N-pyrrolidinohexene (13d) but the olefinic material from the enamine (13e) of hexahydrobenzaldehyde was a mixture of the expected product methylenecyclohexane (15) and 1-methylcyclohexene (16) to which it is easily isomerized under acidic conditions.

11   **12**   **15**   **16**

13
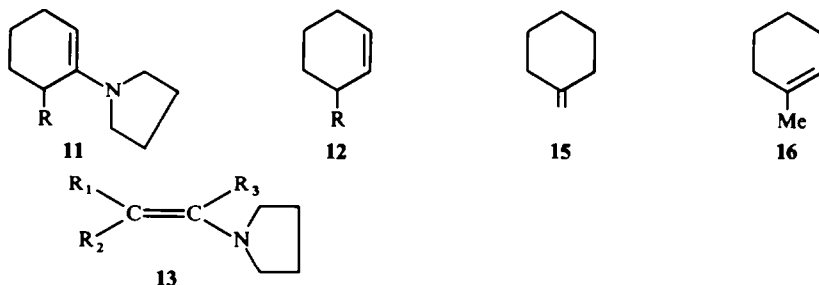
a: $R_1 = Me, R_2 = H, R_3 = Et$
b: $R_1 = Et, R_2 = H, R_3 = nPr$
c: $R_1 = Hexyl, R_2, R_3 = H$
d: $R_1 = nBu, R_2 = Et, R_3 = H$
e: $R_1, R_2 = (CH_2)_5, R_3 = H$

In the case of **13a, b** the enamines are trisubstituted olefins and attack of AlH_3 at the β-C atom is favoured not only by the electronic effect of the amine group but also by the steric effect related to the lower degree of substitution of the β-atom. The α- and β-C atoms are equally substituted in the case of **13c** so that there is no steric preference for attack at either C atom and the electronic effect still controls the reaction. In the other trisubstituted enamines (**13d, e**) the steric and electronic effects are opposed and the possibility of attack of AlH_3 at the stereochemically favoured α-C atom must be considered. Hydroboration of enamine **13d** was shown to give 40% of the β-pyrrolidinoborane (**17**) and 51% of the α-substituted borane (**18**).[11] Protonolysis of **17** gave 2-ethylhexene whereas **18** was converted to the saturated hydrocarbon 3-methylheptane by the path shown in Fig. 3. It is reasonable to expect that the aluminium hydride adduct **19** could behave in a manner analogous to **18**. Since no 3-methylheptane was formed it seems likely that only the β-substituted alane (**20**) is formed but the branching at the β-C atom results in a much slower addition reaction judged by the presence of 23% unreacted enamine at the end of the reaction.
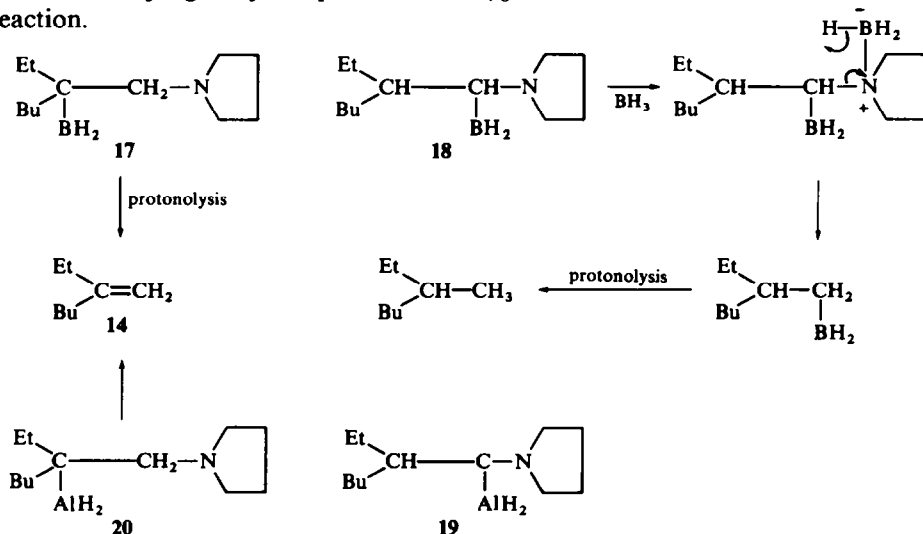

FIG. 3.

Enamines derived from αβ-unsaturated ketones where possible have the unshared electron pair of the N atom conjugated with the two double bonds. Thus, the pyrrolidine enamine of $\Delta_{1,9}$-octalone (21) which is prepared by the action of methyl vinyl ketone on 1-N-pyrrolidinocyclohexene[12] has structure 22. From the reaction of this dienamine with AlH_3 a hexahydronaphthalene (39%) and a reduction product (54%) were isolated. Addition of AlH_3 to the dienamine could be 1,2- to give 23 or 1,4- to give 24. From both these adducts elimination can occur to give 1,2,6,7,8,9-hexahydronaphthalene (25). However, the hydrogenolysis product was not 25 but the isomeric 1,2,5,6,7,8-hexahydronaphthalene (26) which was characterized as the tetracyanoethylene adduct and identified by comparison with an authentic sample prepared from $\Delta_{1,9}$-octalone by reduction and dehydration with 3,5-dinitrobenzoyl chloride.[13] (Fig. 4). Isomerization of the initially formed diene must have occurred during the reaction; this would be expected from Carnighan's investigation of the equilibration of hexahydronaphthalenes.[13]

The basic hydrogenation product may have structures 27 or 28 derived from the alternative adducts 23 and 24, respectively. The product was identical with the product of sodium borohydride reduction of the dienamine and by analogy with the borohydride reduction of 3-N-pyrrolidinocholesta-3,5-diene,[5] this product is likely to be 27. The AlH_3 reaction would thus appear to follow the alkylation in giving largely the product of initial 1,2-addition.[14]
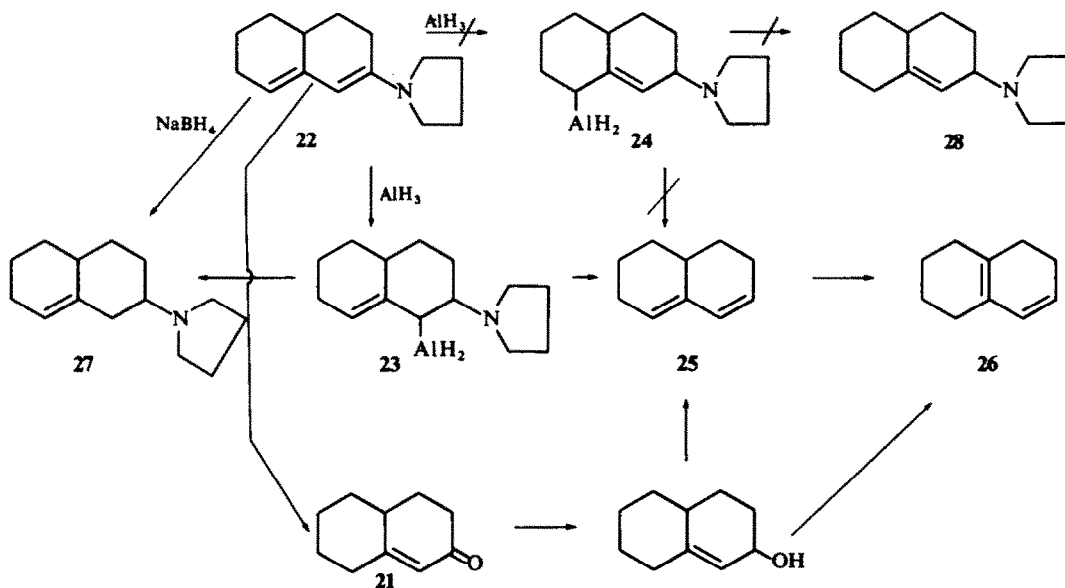
EXPERIMENTAL

All m.ps are uncorrected. GLC was carried out with a Perkin–Elmer Fractometer using silicon oil or polypropylene glycol columns.

Enamines. By the method of Herr and Heyl[15] the following enamines were prepared from the corresponding ketones.

1-N-Pyrrolidinocyclopentene (90%) b.p. 85–87°/11 mm, n_D^{20} 1·5149 (lit.[12] b.p. 88–92°/15 mm); 1-N-pyrrolidinocyclohexene (91%) b.p. 70–72°/2 mm, n_D^{20} 1·5222 (lit.[12] b.p. 105–107°/13 mm); 1-N-pyrrolidinocycloheptene (55%) b.p. 121–123°/15 mm, n_D^{20} 1·5179 (lit.[16] b.p. 100–102°/5 mm, n_D^{20} 1·5195);

1-N-pyrrolidinocyclo-octene (64%), b.p. 110–112°/4 mm, n_D^{20} 1·5247 (lit.[16] b.p. 113–114°/5 mm, n_D^{20} 1·5255); 1-N-pyrrolidinocyclododecene (55%), b.p. 126–128°/0·4 mm, n_D^{20} 1·5224 (lit.[17] b.p. 120–125°/0·4 mm, n_D^{20} 1·5237); 1-N-morpholinocyclohexene (67%), b.p. 116–118°/14 mm, n_D^{20} 1·5135 (lit.[12] b.p. 104–106°/ 12 mm); 1-N-methylanilinocyclohexene (70%), b.p. 120–123°/2 mm, n_D^{21} 1·5679 (lit.[12] b.p. 148–153°/12 mm); 3-N-pyrrolidinopent-2-ene (23%), b.p. 73–74°/13 mm, n_D^{20} 1·4861 (lit.[12] b.p. 62–67°/8 mm); 4-N-*pyrrol-idinohept-3-ene* (19%), b.p. 97–99°/17 mm, n_D^{22} 1·4811. (Found: C, 78·85; H, 12·5; N, 8·2. $C_{11}H_{21}N$ requires: C, 79·1; H, 12·7; N, 8·4%); 2-ethyl-1-N-pyrrolidinohex-1-ene (78%), b.p. 71–73°/0·25 mm, n_D^{20} 1·4744 (lit.[18] b.p. 98–99°/10 mm, n_D^{22} 1·4736); N-pyrrolidinomethylenecyclohexane (91%), b.p. 67–69°/0·3 mm, n_D^{20} 1·5130 (lit.[19] b.p. 124°/16 mm). 1-N-pyrrolidino-octene, b.p. 124–125°/15 mm, n_D^{18} 1·5286 (lit.[20] b.p. 127°/10 mm, n_D^{20} 1·5258) was prepared in 78% yield by the method of Mannich and Davidsen.[2]

3,4,5,6,7,10-Hexahydro-2-N-pyrrolidinonaphthalene, b.p. 144–150°/0·2 mm (lit.[12] b.p. 146–150°/3 mm) was prepared in 65% yield by the method of Stork *et al.*[12]

N-*Butyl*-N-*(cyclohex-1-enyl)benzamide*.[cf 21] N-Cyclohexylidinebutylamine [76·5 g; 0·5 mole: prepared in 78% yield by the method of Baltzly and Kauder,[22] b.p. 72–74°/4 mm, n_D^{25} 1·4672 (lit.[22] b.p. 64–65°/2 mm, n_D^{25} 1·4669)] was added to a stirred soln of benzoyl chloride (67·2 g; 0·5 mole) and Et_3N (60·5 g; 0·6 mole) in benzene (150 ml) and the temp was kept below 15°. The mixture was left overnight at room temp and then heated under reflux for 30 min. After removal of the $Et_3N.HCl$, distillation afforded N-*butyl*-N-(*cyclohex-1-enyl)benzamide* (118 g, 92%), b.p. 114–118°/0·25 mm, n_D^{19} 1·5378, v_{max} (CCl_4) 1640 cm^{-1}. (Found: C, 79·4; H, 8·9; N, 5·3. $C_{17}H_{23}NO$ requires: C, 79·7; H, 9·0; N, 5·45%).

1,2,5,6,7,8- *and* 1,2,6,7,8,9-*Hexahydronaphthalenes*. Dehydration of 2-hydroxy-2,3,4,5,6,7,8,10-octahydro-naphthalene by the method of Carnighan[13] gave a mixture of olefins from which 1,2,5,6,7,8-hexahydro-naphthalene (37%) was removed as the tetracyanoethylene adduct, m.p. 151–152° (lit.[13] m.p. 151–153°) and 1,2,6,7,8,9-hexahydronaphthalene (55%), b.p. 87–88°/14 mm, n_D^{20} 1·5157 (Found: C, 89·9; H, 10·4. Calc. for $C_{10}H_{14}$: C, 89·6; H, 10·5%) was obtained by distillation.

Reaction of enamines with aluminium hydride

General procedure. To a stirred soln of LAH (5·7 g; 0·15 mole) in ether (180 ml) a soln of $AlCl_3$ 6·66 g; 0·05 mole) in ether (140 ml) was added. The mixture was left for 1 hr after which the enamine (0·05 mole) in ether (20 ml) was added over 10 min. After 48 hr under reflux the cooled (ice) reaction mixture was cautiously treated with ice-cold 5N HCl (200 ml); in most cases a cold trap (−70°) was attached to the end of the condenser. The ether layer was separated and the aqueous layer was extracted with ether (3 × 75 ml). The dried $(MgSO_4)$ extracts were carefully distilled to obtain the olefin. Alternatively, the latter was identified in the ether soln by comparison (GLC) with an authentic sample and estimated using an internal or external standard.

The aqueous soln was made strongly basic with NaOH (75 g) and was extracted with ether (3 × 100 ml). The washed extracts were dried and evaporated to give the amine reduction product.

Analogous procedures were used for the reaction of the enamines with aluminium chlorohydride [$AlCl_3$ (0·05 mole): LAH (0·05 mole)] and aluminium dichlorohydride [$AlCl_3$ (0·15 mole): LAH (0·05 mole)].

Reaction of N-butyl-N-(cyclohex-1-enyl)benzamide with aluminium hydride

N-Butyl-N-(cyclohex-1-enyl)benzamide (12·85 g; 0·05 mole) with AlH_3 (from $AlCl_3$ (0·05 mole) and LAH (0·15 mole) as above) in ether gave cyclohexene (3·7 g; 89%) and N-butylbenzylamine (6·5 g; 80%), b.p. 70–74°/1 mm, n_D^{21} 1·5007 (lit.[23] b.p. 77°/1 mm, n_D^{25} 1·4992).

Reaction of N-butyl-N-(cyclohex-1-enyl)benzamide with lithium aluminium hydride

N-Butyl-N-(cyclohex-1-enyl)benzamide (4·34 g; 0·017 mole) dissolved in ether (20 ml) was added to a stirred soln of LAH (2·6 g; 0·069 mole) in ether (50 ml). The mixture was heated under reflux for 30 min, cooled and treated dropwise with 5N HCl (50 ml). After 30 min the ether layer was separated and the aqueous layer was extracted with ether (3 × 25 ml). The combined extracts were dried $(MgSO_4)$ and by GLC the presence of cyclohexanone (0·4 g; 23%) was shown. After basification and re-extraction with ether N-butylbenzylamine (1·86 g; 72%) was obtained.

Reaction of 2-N-pyrrolidino-3,4,5,6,7,10-hexahydronaphthalene with aluminium hydride

2-N-Pyrrolidino-3,4,5,6,7,10-hexahydronaphthalene (10·1 g; 0·05 mole) and AlH_3 (0·2 mole) in ether (240 ml) for 48 hr gave 1,2,5,6,7,8-hexahydronaphthalene (2·58 g; 39%) by comparison with an authentic sample (see above), b.p. 92–93°/15 mm, n_D^{21} 1·5105. (Found: C, 89·8; H, 10·7. Calc. for $C_{10}H_{14}$: C, 89·6;

H, 10·5 %), tetracyanoethylene adduct, m.p. 152–153°. Also formed was 2-N-*pyrrolidino*-1,2,3,4,5,6,7,10-*octahydronaphthalene* (5·5 g; 54 %), b.p. 116–118°/1·3 mm, n_D^{21} 1·5244. (Found: C, 81·5; H, 11·25. $C_{14}H_{23}N$ requires: C, 82·0; H, 11·3 %). The *picrate* was recrystallized from EtOH as yellow needles, m.p. 156–157°. (Found: C, 55·6; H, 6·3; N, 12·5. $C_{20}H_{26}N_4O_7$ requires: C, 55·35; H, 6·0; N, 12·9%). The product formed by reduction at room temp of 2-N-pyrrolidino-3,4,5,6,7,10-hexahydronaphthalene with $NaBH_4$ in EtOH had identical retention time (GLC) and the picrate, m.p. 158°, showed no m.p. depression when mixed with the above picrate.

Reaction of 1-N-*pyrrolidinocyclo-octene with aluminium monochlorohydride*

1-N-Pyrrolidinocyclo-octene (8·95 g; 0·05 mole), LAH (3·8 g; 0·1 mole) and $AlCl_3$ (13·4 g; 0·1 mole) in ether (250 ml) for 48 hr gave cyclo-octane (0·4 g; 7 %) and N-pyrrolidinocyclo-octane (7·5 g; 84 %).

Reaction of 1-N-*pyrrolidinocyclo-octene with aluminium dichlorohydride*

1-N-Pyrrolidinocyclo-octene (8·95 g; 0·05 mole), LAH (1·9 g; 0·05 mole) and $AlCl_3$ (20 g; 0·15 mole) in ether (250 ml) for 48 hr gave cis-cyclo-octene (0·6 g; 11 % GLC), b.p. 147–148°, n_D^{21} 1·4691 and N-pyrrolidinocyclo-octane (7·0 g; 78 %).

Reaction of cyclo-octene with aluminium hydride

trans-Cyclo-octene (5·5 g; 0·05 mole) and AlH_3 (0·2 mole) in ether (250 ml) for 48 hr with the previously described isolation procedure gave cyclo-octane (5·4 g; 98 % by GLC), b.p. 154–156°, n_D^{21} 1·4583 (lit.[24] b.p. 148–149°, n_D^{20} 1·4581). cis-Cyclo-octene was recovered unchanged when subjected to a similar procedure.

Reaction of trans-cyclo-octene with aluminium monochlorohydride*

trans-Cyclo-octene (5·5 g; 0·05 mole) and $AlClH_2$ (0·2 mole) in ether (250 ml) for 48 hr gave cyclo-octane (5·4 g; 98 %).

Reaction of trans-cyclo-octene with aluminium dichlorohydride*

trans-Cyclo-octene (2·73 g; 0·025 mole) and $AlCl_2H$ (0·1 mole) in ether (125 ml) for 48 hr gave cis-cyclo-octene.

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