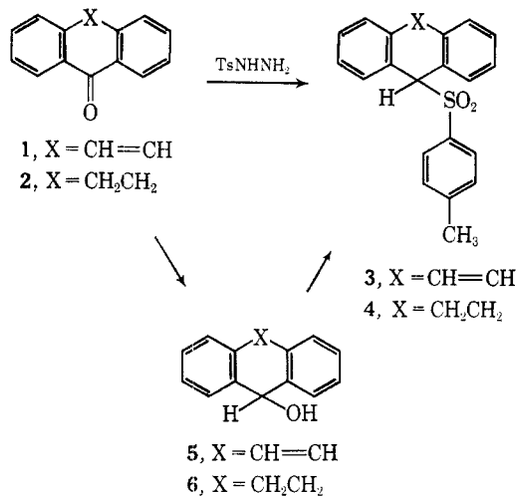

thermal decomposition of tosylhydrazine.[5] This reaction has also been shown to produce *p*-toluenesulfinic acid, the other required reactant. Reaction of alcohol **5**, obtained by reduction of ketone **1**, with *p*-toluenesulfinic acid was shown to produce sulfone **3** under the original reaction conditions. Alcohol **6**, obtained by reduction of ketone **2**, behaved similarly and gave sulfone **4**. In support of this mechanism, it was found that ketone **1** is reduced to alcohol **5** when heated in alcohol with anthracene-9,10-biimine,[6] a source of diimide. The reduction of ketones in this manner may occur when the carbonyl group is sufficiently inert to nucleophilic attack by tosylhydrazine to permit diimide formation by the thermal process.

An alternative mechanism considered was formation of the tosylhydrazone, decomposition to the diazo compound, conversion to the carbonium ion in the protic medium, and sulfone formation with *p*-toluenesulfinic acid. This is ruled out because the tosylhydrazone, prepared from 5,5-dichloro-5H-dibenzo[*a*,*d*]cycloheptene, is recovered unchanged when subjected to these reaction conditions.

Experimental Section[7]

Reaction of 5H-Dibenzo[*a*,*d*]cyclohepten-5-one with Tosylhydrazine.—A mixture of 5.0 g (0.024 mole) of ketone **1**, 7.0 g (0.038 mole) of tosylhydrazine, 100 ml of ethanol, and 1 ml of acetic acid was heated at reflux for 15 hr. The solid that separated was collected and recrystallized from ethanol–chloroform to give 3.4 g (39%) of sulfone **3**, mp 210–211°.

Anal. Calcd for $C_{22}H_{18}O_2S$: C, 76.4; H, 5.2; S, 9.3. Found: C, 76.5; H, 5.3; S, 9.3.

The nmr spectrum (DMSO) had peaks at τ 2.6–2.8 m (aromatic), 3.37 s (olefinic), 4.12 s (benzylic), and 7.93 s (methyl) in an area ratio of 12:2:1:3. The infrared spectrum (KBr) showed strong sulfone bands at 1310 and 1140 cm^{-1}. A mixture melting point with an authentic sample, prepared as described below, was not depressed.

When 5 g (0.024 mole) of 10,11-dihydro-5H-dibenzo[*a*,*d*]cyclohepten-5-one (**2**) was used in place of the unsaturated ketone **1**, 1.1 g (13%) of the corresponding sulfone (**4**) was obtained, mp 187–188°. A mixture melting point with an authentic sample, prepared as described below, was not depressed.

Anal. Calcd for $C_{22}H_{20}O_2S$: C, 75.9; H, 5.8; S, 9.2. Found: C, 75.9; H, 5.9; S, 9.0.

***p*-Tolyl 5H-Dibenzo[*a*,*d*]cyclohepten-5-yl Sulfone (3).**—A 1.0-g (0.0048 mole) portion of 5-hydroxy-5H-dibenzo[*a*,*d*]cycloheptene (**5**) was converted into the chloride by heating the mixture for 5 min with thionyl chloride and removing volatile material under reduced pressure. A suspension of 4 g (0.02 mole) of sodium *p*-toluenesulfinate dihydrate in 50 ml of ethanol was added to the chloride and the mixture was heated for 30 min at reflux before being poured into ice–water. The solid was collected, washed with water, and dried, giving 1.5 g (90%) of sulfone **3**, mp 210–211°.

By using the same procedure, *p*-tolyl 10,11-dihydro-5H-dibenzo[*a*,*d*]cyclohepten-5-yl sulfone (**4**) was prepared from 5-hydroxy-10,11-dihydro-5H-dibenzo[*a*,*d*]cycloheptene (**6**); the yield was 0.4 g (23%), mp 187–188°.

Reaction of 5-Hydroxy-5H-dibenzo[*a*,*d*]cycloheptene with *p*-Toluenesulfinic Acid.—To a solution of 1.0 g of sodium *p*-toluenesulfinate dihydrate in 25 ml of ethanol and 2 ml of acetic acid was added 0.5 g (0.0024 mole) of 5-hydroxy-5H-dibenzo[*a*,*d*]cycloheptene (**5**). After the solution had been heated at reflux for 30 min, the solid was collected; the yield was 0.70 g (85%), mp 210–211°. A mixture melting point with sulfone **3** was not depressed.

In a similar manner, 5-hydroxy-10,11-dihydro-5H-dibenzo[*a*,*d*]cycloheptene (**6**) gave a 15% yield of *p*-tolyl 10,11-dihydro-5H-dibenzo[*a*,*d*]cyclohepten-5-yl sulfone (**4**), mp 187–188°. A mixture melting point with the authentic sample was not depressed.

Reduction of 5H-dibenzo[*a*,*d*]cyclohepten-5-one with Anthracene-9,10-biimine.—A mixture of 1.0 g (0.050 mole) of ketone **1**, 3.0 g (0.15 mole) of anthracene-9,10-biimine,[6] and 50 ml of ethanol was heated at reflux for 1 hr. After cooling to room temperature, the anthracene was removed by filtration and the filtrate was concentrated and chromatographed on alumina (20 g). Anthracene and starting ketone were removed with benzene, and alcohol **5** was eluted with ethanol; the yield was 0.25 g (25%), mp 118–120°. A mixture melting point was not depressed, and the infrared spectrum was identical with that of an authentic sample.

5H-Dibenzo[*a*,*d*]cyclohepten-5-one *p*-Toluenesulfonylhydrazone.—A 3.7-g (0.02 mole) portion of tosylhydrazine was added to a solution of 5,5-dichloro-5H-dibenzo[*a*,*d*]cycloheptene,[8] obtained from 4.0 g (0.020 mole) of ketone **1**, in 60 ml of acetonitrile. The mixture was stirred overnight and the solid was collected. Additional material was obtained by concentration of the filtrate, and the solid was recrystallized from ethanol–acetonitrile to give 5.2 g (70%) of the tosylhydrazone, mp 213–215° dec (lit.[4] mp 204°). The nmr spectrum is in agreement with the proposed structure.

Anal. Calcd for $C_{22}H_{18}N_2O_2S$: C, 70.6; H, 4.8; N, 7.5; S, 8.6. Found: C, 70.9; H, 4.6; N, 7.7; S, 8.6.

The tosylhydrazone (1.0 g) was recovered quantitatively after treatment for 16 hr at reflux in 20 ml of ethanol containing 0.5 ml of acetic acid.

(5) R. S. Dewey and E. E. vanTamelen, *J. Am. Chem. Soc.*, **83**, 3729 (1961).

(6) E. G. Corey and W. L. Mock, *ibid.*, **84**, 685 (1962).

(7) The nmr spectrum was measured on a Varian Associates Model A-60 spectrometer and the infrared spectrum was measured on a Perkin-Elmer Model 137B spectrometer. Melting points are uncorrected.

(8) J. J. Looker, *J. Org. Chem.*, in press.

Bicyclic Enamines. III. Reduction of Enamines with Secondary Amines[1,2]

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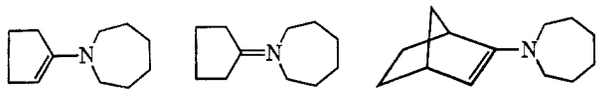
The reduction of enamines derived from both bicyclic and monocyclic ketones by secondary amines has recently been reported.[1] The only secondary amine used in these reductions, however, was hexamethylenimine. The reduction of enamine intermediates by methanolic solutions of either dimethylamine or piperi-

(1) For part II, see A. G. Cook, W. C. Meyer, K. E. Ungrodt, and R. H. Mueller, *J. Org. Chem.*, **31**, 14 (1966).

(2) Support of this work by a grant from the Petroleum Research Fund of the American Chemical Society is gratefully acknowledged.

dine was reported earlier,[3] but the extent and mechanism of the reaction were not studied.

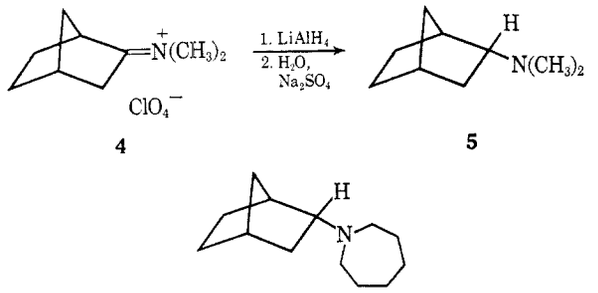
Treatment of 1-N-hexamethyleniminocyclopentene (**1**) with excess hexamethylenimine and *no* acid catalyst resulted in *no* saturated amine being formed. On the other hand, it has been reported that treatment of N-cyclopentylidenehexamethyleniminium perchlorate (**2**) with hexamethylenimine under identical



1 2 3

conditions produces the corresponding saturated amine, N-cyclopentylhexamethylenimine.[1] The reaction of norcamphor with hexamethylenimine and *no* acid catalyst produces enamine **3** in a 20% yield, but *no* saturated amine. A saturated amine is formed along with an enamine when an acid catalyst is present.[1] Therefore the reduction reaction is acid catalyzed.

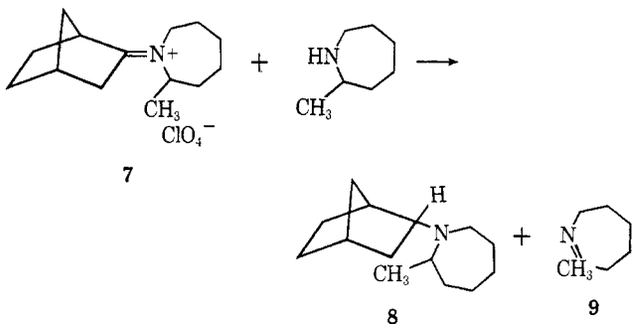
The stereochemical course of this reduction reaction in the case of bicyclic enamines can be deduced from the following argument. Reduction of N-2-bicyclo[2.2.1]heptylidenedimethylaminium perchlorate with lithium aluminum hydride produces saturated amine



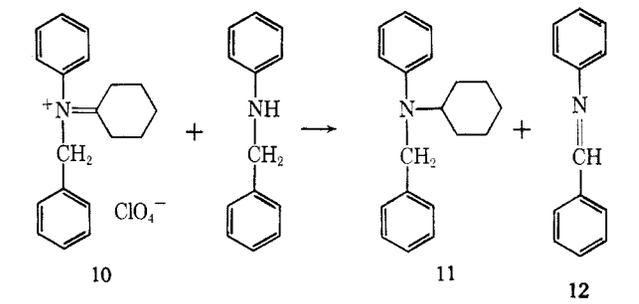
4 5 6

5 in an 85% yield.[1] It would be expected that the stereochemistry of the product obtained from lithium aluminum hydride reduction of a bicyclic iminium salt such as **4** would be *endo* as has been observed in similar reactions where the *exo* side is the least hindered side for hydride attack.[4] This expectation is confirmed by the appearance of a strong band at 795 cm^{-1} in the infrared spectrum of saturated amine **5** and the absence of bands at 820 and 1022 cm^{-1}, all of which identifies compound **5** as *endo*-2-N-dimethylaminobicyclo[2.2.1]-heptane.[5] Since the product obtained by reduction of the iminium perchlorate salt of **3** with excess hexamethylenimine is identical with that obtained by reduction with lithium aluminum hydride,[1] the product must be *endo*-2-N-hexamethyleniminobicyclo[2.2.1]-heptane (**6**). It would appear, therefore, that a hydrogen is added to the less sterically hindered *exo* side of a bicyclic enamine during reduction by a secondary amine also.

The reaction of N-2-bicyclo[2.2.1]heptylidene-2′-methylhexamethyleniminium perchlorate (**7**) with excess 2-methylhexamethylenimine[6] produced, along with saturated amine **8**, Δ^1-2-methylazacycloheptene (**9**) as the oxidation product. Imine **9** was identified by comparison of its infrared spectrum (maximum at 1660 cm^{-1} corresponding to >N=C< stretch) and its gas–liquid partition chromatography retention time with an authentic sample.[7] The corresponding imine oxidation product of unsubstituted hexamethylenimine itself resulting from the reduction of enamine **3** could not be isolated because of its known instability.[7] This undoubtedly accounts for the large amount of dark, intractable residue found upon distillation of the products resulting from this reaction.[1] N-Benzyl-N-cyclohexylideneanilinium perchlorate (**10**) is reduced by N-benzylaniline to yield N-benzyl-N-cyclohexylaniline (**11**) and benzalaniline (**12**). The latter compound was characterized by acid hydrolysis to aniline and benzaldehyde followed by identification of the aniline. Thus a secondary amine is oxidized to an imine by an enamine in this general type of reaction.

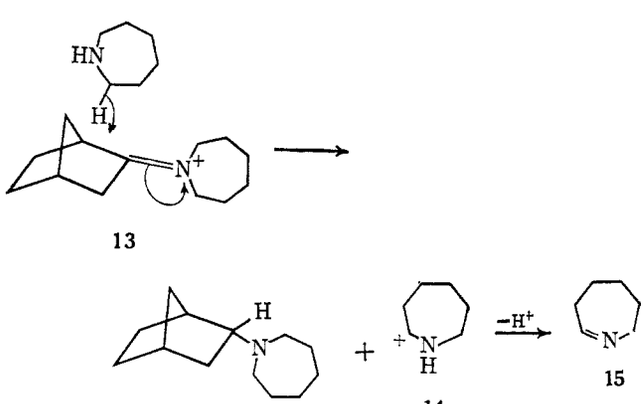


7 8 9



10 11 12

From these data a mechanism can be written for the reaction using the iminium salt of norcamphor and hexamethylenimine (**13**) as an example. A nucleophilic attack of a hydride ion from the α carbon



13 14 15

(3) C. Kaiser, A. Burger, L. Zirngibl, C. S. Davis, and C. L. Zirkle, *J. Org. Chem.*, **27**, 768 (1962).

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(5) A. C. Cope, E. Ciganek, and N. A. LeBel, *J. Am. Chem. Soc.*, **81**, 2799 (1959).

(6) F. F. Blicke and N. J. Doorenbos, *ibid.*, **76**, 2317 (1954).

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TABLE I

YIELDS AND PHYSICAL PROPERTIES OF SATURATED TERTIARY AMINES FROM IMINIUM SALTS

Component ketone to form iminium perchlorate	Secondary amine[a]	Reflux time, hr	Yield, %	Bp, °C (mm)	n^tD	t, °C	Formula	C, % Calcd	C, % Found	H, % Calcd	H, % Found
Norcamphor	1	63	60[b]	...	...	..	...	...	...	...	...
Norcamphor	2	15	25	84–85 (0.5)	1.4838	32	$C_{14}H_{26}ClNO_4$[c]	54.62	54.83	8.51	8.49
Norcamphor	3	46	48	95 (0.5)	1.4681	26	$C_{15}H_{29}N$	80.64	80.91	13.08	13.23
Norcamphor	4	65	62	131 (0.3)	1.5563	28	$C_{16}H_{21}N$	84.52	84.36	9.31	9.35
Cyclohexanone	5	18	28	103–105 (15)	1.4798	26	*d*	...	...	...	...
Cyclohexanone	6	40	0	...	...	..	...	...	...	...	...
Cyclohexanone	7	18	49	193 (0.7)	1.6216	25	...	...	...	...	...
Cyclopentanone	8	88	19	108.5–109 (15)	...	..	*e*	...	...	...	...
Cyclopentanone	1	20	27[b]	...	...	..	...	...	...	...	...

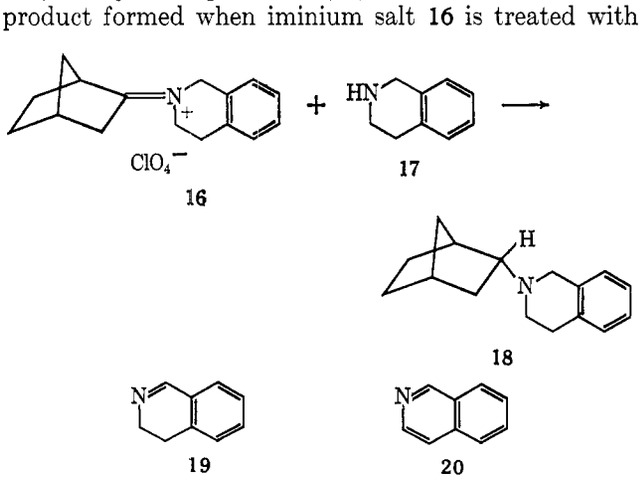
[a] The same secondary amine is used in the iminium salt and as the reducing agent. 1 = hexamethylenimine, 2 = 2-methylhexamethylenimine, 3 = di-*n*-butylamine, 4 = tetrahydroisoquinoline, 5 = pyrrolidine, 6 = morpholine, 7 = N-benzylamine, 8 = piperidine. [b] The physical properties of these amines are described in ref 1. [c] Identified as its perchlorate salt, mp 267–267° dec. [d] Reported previously by J. W. B. Reesor and G. F. Wright [*J. Org. Chem.*, **22**, 375 (1957)] as bp 209–210, n^{20}D 1.4823. Identified by its picrate, mp 165–166° (lit. 166–166.5°). [e] Reported previously by J. I. Jones, *J. Chem. Soc.*, 1392 (1950). Identified by its picrate, mp 171.5–172° (lit. mp 174°).

of the secondary amine on the α carbon of the iminium salt results in the production of a saturated tertiary amine and carbonium ion (**14**). Carbonium ion **14** then releases a proton to produce imine **15**.

The reduction of enamines is not limited to the cyclic hexamethylenimine, but the cyclic amines, pyrrolidine, piperidine, and tetrahydroisoquinoline (**17**), are also capable of reducing action. Morpholine does not exhibit this reducing property. The aromatic and aliphatic amines represented by N-benzylaniline and di-*n*-butylamine, respectively, likewise show the ability to reduce enamines. The yields of these reactions along with the physical properties of the saturated amine products are summarized in Table I.

A tertiary amine, N-methylhexamethylenimine,[8] does not show the reducing property toward N-2-bicyclo[2.2.1]heptylidenehexamethyleniminium perchlorate (**13**) that the corresponding secondary amine, hexamethylenimine, does. Thus apparently tertiary amines do not undergo hydride transfer reactions with enamines as they do with the triphenylmethyl carbonium ion.[9]

3,4-Dihydroisoquinoline (**19**) is not the oxidation product formed when iminium salt **16** is treated with



16 17 18 19 20

excess tetrahydroisoquinoline (**17**), but rather isoquinoline (**20**) is formed. This was shown by comparison of the ultraviolet and infrared spectra of this product with that reported for isoquinoline[10] and 3,4-dihydroisoquinoline. It was demonstrated that 3,4-dihydroisoquinoline itself would not reduce enamines by treating iminium salt **16** with 3,4-dihydroisoquinoline (**19**) and finding that no saturated amine **18** was produced. Apparently the isoquinoline is produced in the first reaction by a disproportionation of the 3,4-dihydroisoquinoline produced initially into tetrahydroisoquinoline (**17**) and isoquinoline (**20**). This type of disproportionation reaction with 3,4-dihydroisoquinolines has been observed before.[11]

Experimental Section

The spectra reported in this work were recorded on a Perkin-Elmer Model 137 infrared spectrometer and a Beckman DK-2 spectrometer. The analyses were carried out by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

All of the iminium perchlorate salts were prepared by the method of Leonard and Paukstelis.[12] 2-Methylhexamethylenimine was prepared by the method of Blicke and Doorenbos.[6] N-Methylhexamethylenimine[8] was prepared by treating hexamethylenimine with formic acid and formaldehyde. Δ^1-2-Methylazacycloheptene was produced by the method of Boyer and Canter.[7] 3,4-Dihydroisoquinoline was made by treating the formate of β-phenethylamine with polyphosphoric acid as described by Pratt, Rice, and Luckenbaugh.[13]

General Procedure for Reduction of Enamines with Secondary Amines.—A stirred mixture of an excess of secondary amine and iminium salt was refluxed for a period of time. An excess of 6 *N* hydrochloric acid was added, and the reaction mixture was refluxed for 2 hr. The solution was made strongly basic with 6 *N* sodium hydroxide and extracted several times with diethyl ether. The combined ether extracts were dried over anhydrous magnesium sulfate and filtered, solvent was removed, and the residual oil was distilled through a fractionating column.

Nonacid-Catalyzed Reactions.—No saturated amine product is obtained by treatment of 1-N-hexamethyleniminecyclopentene[14] or 2-N-hexamethyleniminobicyclo[2.2.1]hept-2-ene[1] with excess hexamethylenimine in the manner described above when no acid catalyst is present.

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(11) C. I. Brodrick and W. F. Short, *J. Chem. Soc.*, 2587 (1949).

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(14) M. A. Volodina, V. G. Mishina, A. P. Terent'ev, and G. V. Kiryushkina, *Zh. Obshch. Khim.*, **32**, 1922 (1962).