Bicyclic Enamines. II. The Reaction of Norbornanones with Secondary Amines[1,2]

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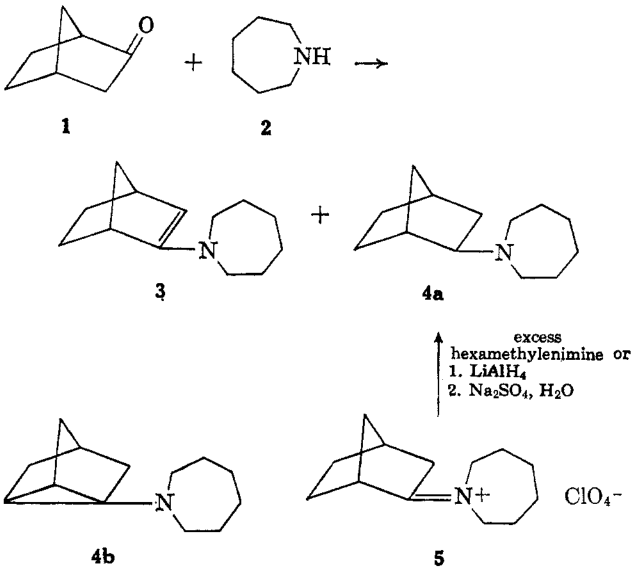
Synthesis of bicyclic enamines by the normal route of treating a ketone or aldehyde with a secondary amine is complicated in the case of hexamethylenimine because of the reductive power of this amine toward enamines. Evidence is presented showing that hexamethylenimine reduces both bicyclic and other enamines to saturated amines. This is in marked contrast to the observation that 98% formic acid does not readily reduce bicyclic enamines. The cyclopropane ring of tricyclenone is found to rupture quite readily in the presence of secondary amines. The first reported synthesis of a tricyclenamine along with evidence for its structure is also noted.

The formation of enamines from bicyclic ketones such as norbornanones would seem to be of great interest because of the significant number of rearrangements observed with reactions in this series and because of the theoretical implications arising from these reactions.[3] The formation of the ternary iminium salts of these ketones could also be of considerable significance since many of these rearrangements are cationic in nature. One of the most useful synthetic routes for making enamines consists of the reaction between a secondary amine and a ketone or an aldehyde.[4-7] Formation of a ternary iminium salt can be accomplished by the addition of a strong acid to an enamine in which the proton adds to the β-carbon atom,[8] unless protonation at the β-carbon atom is sterically prohibited, in which case N-protonation takes place.[8,9] Ternary iminium salts can also be produced directly by allowing secondary amine salts to react with ketones or aldehydes.[10]

Contrary to a previous report,[1] the reaction between norcamphor (**1**) and hexamethylenimine (**2**) in refluxing xylene produces *two* isolable products in approximately equal amounts, namely 2-N-hexamethyleniminobicyclo[2.2.1]hept-2-ene (**3**) and 2-N-hexamethyleniminobicyclo[2.2.1]heptane (**4a**). The protonation of this product mixture does *not* result in the formation of a nortricyclenamine salt as previously reported,[1] but rather the salt of saturated amine **4a** was formed and mistakenly identified as the nortricyclenamine salt. This was due to many similarities in their expected physical and chemical properties. The presence of a maximum in the infrared spectrum of the product mixture at 1685 cm.$^{-1}$ ($>C{=}C<^{N}$) indicated the presence of **3**. Basic hydrolysis of the product mixture destroyed enamine **3** and made possible the isolation of pure **4**. This product was shown not to be an enamine by the absence of maxima in the 1500–1800-cm.$^{-1}$ region in its infrared spectrum, and the n.m.r. spectra of **4** and its perchlorate salt do not show signals downfield from τ 6, indicating the absence of any vinyl hydrogens. The infrared spectrum of the perchlorate salt of **4** exhibited a maximum at 3150 cm.$^{-1}$ due to $>\overset{+}{N}H$ stretch. This observation cannot be accommodated by enamine **3** since the infrared spectrum of the pure perchlorate salt of **3**, N-2-bicyclo[2.2.1]heptylidenehexamethyleniminium perchlorate (**5**), which was produced by allowing norcamphor to react with hexamethyleniminium perchlorate,[10] showed a strong maximum at 1680 cm.$^{-1}$ caused by $>C{=}N<^{+}$ grouping but no band assignable to $>\overset{+}{N}H$. An alternate possibility for the structure of this product beside **4a** is the substituted nortricyclene **4b**. This possibility was eliminated; structure **4a** was assigned on the basis of the following near-infrared, infrared, n.m.r., mass spectral, and chemical evidence. The near-infrared spectrum showed no maxima in the 1600–1700-mμ region as would be expected of a nortricyclene such as **4a**,[11] and the infrared spectrum of **4** showed no maximum in the 3000–3200-cm.$^{-1}$ region, a region where a typical nortricyclene band appears.[12,13] Reduction of perchlorate salt **5** with lithium aluminum hydride produced a compound in a 79% yield which was shown to be identical with **4** by identity of near-infrared, infrared, n.m.r., and mass spectra as well as



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[1] For the first article in the series, see A. G. Cook, *J. Am. Chem. Soc.*, **85**, 648 (1963).

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

[3] For a good review of these reactions, see J. A. Berson, "Molecular Rearrangements," Vol. 1, P. deMayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p. 111.

[4] C. Mannich and H. Davidsen, *Chem. Ber.*, **69**, 2106 (1936).

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[6] G. Stork, A. Brizzolara, H. Landesmann, J. Szmuszkovicz, and R. Terrell, *ibid.*, **85**, 207 (1963).

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[9] C. A. Grob, A. Kaiser, and E. Renk, *Chem. Ind.* (London), 598 (1957).

[10] N. J. Leonard and J. V. Paukstelis, *J. Org. Chem.*, **28**, 3021 (1963).

[11] P. G. Gassman and W. M. Hooker, *J. Am. Chem. Soc.*, **87**, 1079 (1965).

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[13] G. E. Pollard, *Spectrochim. Acta*, **18**, 837 (1962).

TABLE I

PHYSICAL PROPERTIES OF SOME BICYCLIC ENAMINES AND SALTS

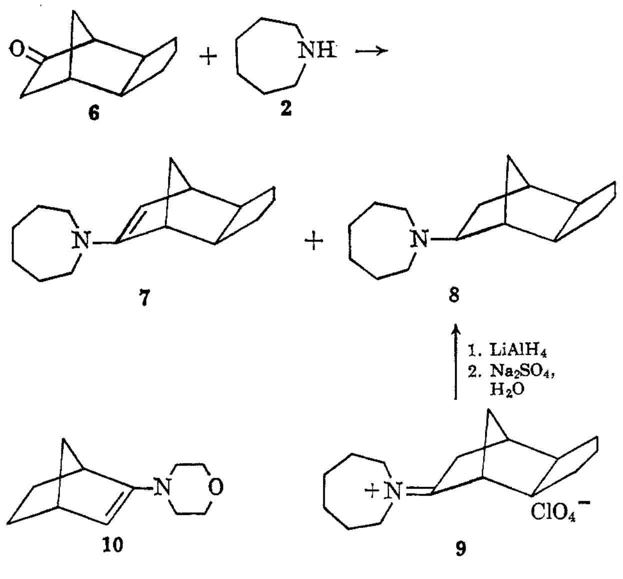
Component reactants to form iminium perchlorate	ν_{max}^{Nujol}, cm.$^{-1}$			Salt m.p., °C.	Recrystn. solvent	Salt formula	C, %		H, %	
	Amine salt[a]	Iminium salt >C=N<$^+$	Free enamine >C=C<N				Calcd.	Found	Calcd.	Found
Norcamphor	1	1680	1685	301.5–302.5 dec.	Ethanol	$C_{13}H_{22}ClNO_4$	53.51	53.73	7.60	7.87[b]
5-Bicyclo[2.2.1]hepten-2-one[c]	1	1680	1685 1660	244–245 dec.	2-Propanol	$C_{13}H_{20}ClNO_4$	53.88	53.81	6.96	7.26
exo-Tricyclo[5.2.1.0^{2,6}]-decan-8-one	1	1680	1685	217.5–219.5	Ethanol	$C_{16}H_{26}ClNO_4$	57.91	58.05	7.90	8.06
Benzonorboranone[d]	1	1680	1685	172–173	Ethanol	$C_{17}H_{22}ClNO_4$	60.08	59.99	6.53	6.73
Tricyclenone	1	1695	...	*e*	...	...	...	...	...	...
Cyclopentanone[f]	1	1672	1630	212–213 dec.	Ethanol	...	...	...	...	...
Norcamphor	2	1690	1685	250–252	Ethanol	$C_{11}H_{18}ClNO_5$	47.23	47.18	6.49	6.59
Norcamphor	3	1700	...	293–294 dec.	Methanol	$C_{13}H_{22}ClNO_4$	51.89	51.89	7.26	7.20
Norcamphor	4	1705	...	228–229	Ethanol	$C_{11}H_{18}ClNO_4$	50.08	49.89	6.88	6.76[g]
Tricyclenone	4	1727	...	*e*	...	...	...	...	...	...
Norcamphor	5	1720	...	154–155	Ethanol	$C_9H_{16}ClNO_4$	45.48	45.22	6.79	6.85
Tricyclenone	5	1723	...	*e*	...	...	...	...	...	...
1-Methyltricyclo-[2.2.1.0^{2,6}]heptan-3-one	5	1723	...	101–103	2-Propanol	$C_{10}H_{16}ClNO_4$	48.11	48.10	6.46	6.40
Bicyclo[2.2.1]heptan-7-one[h]	5	1740	...	193–194	2-Propanol	$C_9H_{16}ClNO_4$	45.48	45.68	6.79	6.97
Norcamphor	6	1725	...	180–181	Ethanol	$C_8H_{14}ClNO_4$	42.98	43.05	6.31	6.60
2-Bicyclo[2.2.1]heptene-5-carboxaldehyde[f]	4	1695	1664	195–197 dec.	2-Propanol	$C_{12}H_{18}ClNO_4$	52.27	52.02	6.58	6.58[i]

[a] 1 = hexamethyleniminium; 2 = morpholinium; 3 = piperidinium; 4 = pyrrolidinium; 5 = dimethylaminium; and 6 = monomethylaminium. [b] *Anal.* Calcd.: N, 4.80. Found: N, 5.04. [c] $\lambda_{max}^{CH_3CN}$ 252 mμ (ε 1400). [d] $\lambda_{max}^{CH_3CN}$ 256 mμ (ε 2700), 271 (1700), and 281 (1500). [e] Obtained as an oil. [f] Salt obtained directly from the enamine. [g] *Anal.* Calcd.: N, 5.31. Found: N, 5.05. [h] P. G. Gassman and P. G. Pape, *J. Org. Chem.*, **29,** 160 (1964). [i] *Anal.* Calcd.: N, 5.08. Found: N, 5.10.

boiling points and refractive indices. The perchlorate salts were also shown to be identical by identity of infrared spectra and physical properties. Structure **4a** has a molecular weight of 193, whereas the substituted nortricyclene structure **4b** has a molecular weight of 191. Mass spectral analysis indicated a molecular weight of 193, further verifying the structural assignment of **4a**.

The question that remained to be answered concerning this reaction is the nature of the reducing agent which produced this saturated bicyclic amine. Refluxing N-2-bicyclo[2.2.1]heptylidenehexamethyleniminium perchlorate (**5**) with an excess of hexamethylenimine produced **4a** in a 60% yield, demonstrating that hexamethylenimine is the reducing agent. The oxidation product formed from hexamethylenimine during the reaction has not been determined yet.

A similar reduction was observed to take place when *exo*-tricyclo[5.2.1.0^{2,6}]decan-8-one (**6**)[14,15] was allowed to react with hexamethylenimine to produce the corresponding enamine (**7**) and saturated amine (**8**) in a 3:7 ratio. The structure of **8** was demonstrated by reducing N-8-*exo*-tricyclo[5.2.1.0^{2,6}]decylidenehexamethyleniminium perchlorate (**9**) with lithium aluminum hydride and finding identical infrared spectra and physical properties. It was found that the reducing property of hexamethylenimine is not restricted to bicyclic enamines. This was illustrated by the reduction of N-cyclopentylidenehexamethyleniminium perchlorate with excess hexamethylenimine to give N-cyclopentylhexamethylenimine in a 27% yield. The latter compound was produced by another route,



namely 98% formic acid reduction of 1-N-hexamethyleniminocyclopentene,[16] and the two products were found to be identical.

Treatment of norcamphor (**1**) with morpholine yields the corresponding enamine **10** as the only isolable product. Most of the iminium salts in Table I were synthesized using the method described by Leonard and Paukstelis[10] of allowing a secondary amine salt to react with a ketone. It was found that the primary amine, methylaminium perchlorate, undergoes a similiar reaction with norcamphor to produce N-2-bicyclo-[2.2.1]hepylidenemethylaminium perchlorate.

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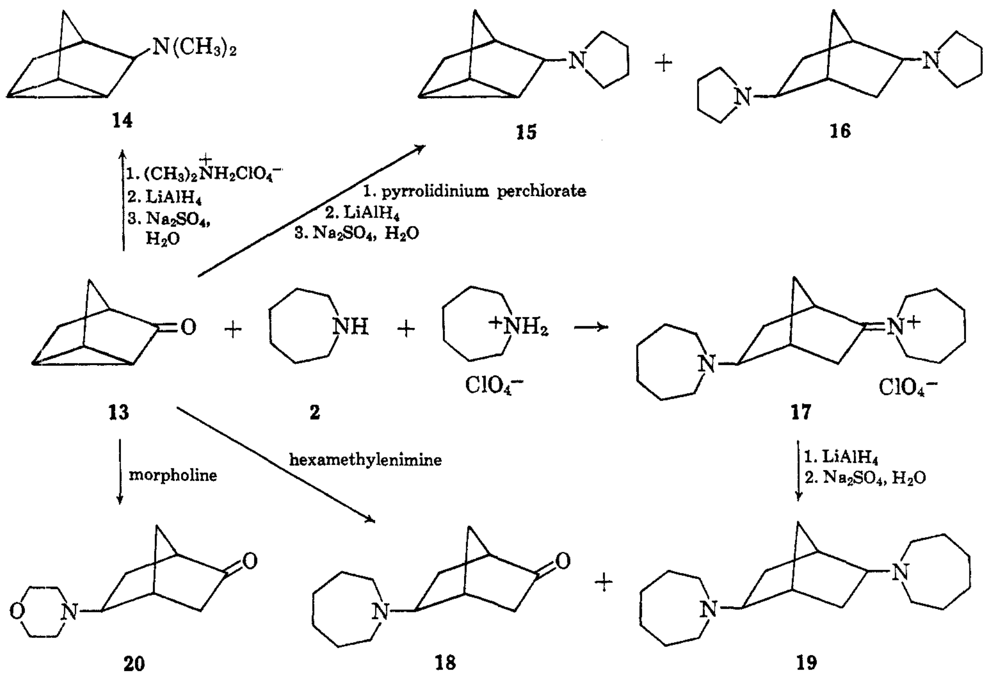
[14] H. A. Bruson and T. W. Riener, *J. Am. Chem. Soc.*, **67,** 723 (1945).

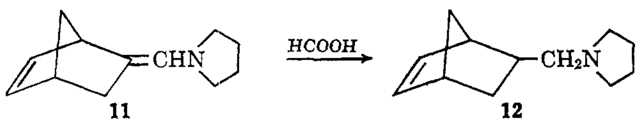
[15] P. D. Bartlett and A. Schneider, *ibid.*, **68,** 6 (1946).

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

CHART I



The reaction of 2-bicyclo[2.2.1]heptene-5-carboxaldehyde[17] with pyrrolidine produced 5-N-pyrrolidylmethylene-2-bicyclo[2.2.1]heptene (**11**) in an 89% yield,[18] probably primarily as the transoid form.[19] Enamine **11** was readily reduced with 98% formic acid[20-22] to produce 5-N-pyrrolidylmethyl-2-bicyclo[2.2.1]heptene (**12**).[23] The carbon–carbon double bond in the bicyclic system was shown to have remained intact by its n.m.r. spectrum. The signal farthest downfield appeared as a doublet with τ 4.47 (J = 3 c.p.s.), and it integrated for two protons, all of which is consistent with an assignment to one vinyl proton on C-2 and C-3, respectively, in compound **12**. However, the enamines obtained from norcamphor (**1**) and hexamethylenimine (**2**) or norcamphor (**1**) and pyrrolidine were not reduced by 98% formic acid as determined by lack of carbon dioxide evolution during the reaction and product analysis. This is rather striking in as much as hexamethylenimine, as previously noted, does reduce bicyclic enamines.



The reaction of tricyclo[2.2.1.0^{2,6}]heptan-3-one (**13**) (tricyclenone)[24-26] with dimethylaminium perchlorate followed by reduction with lithium aluminum hydride resulted in the production of 3-N-dimethylaminotricyclo[2.2.1.0^{2,6}]heptane (**14**) (probably *endo*[27]) in an over-all 55% yield. The infrared spectrum of **14** showed maxima at 3050, 813, and 807 cm.$^{-1}$ which is characteristic of a nortricyclene structure.[13] The near-infrared spectrum indicated a maximum at 1.665 μ (ϵ 0.71, CS$_2$ solvent) also consistent with a nortricyclene structure.[11] The n.m.r. spectrum had a six-proton signal at τ 7.88 [–N(CH_3)$_2$] as its lowest field signal and a signal at τ 9.00 corresponding by integration to three protons as its highest field signal. This latter signal can be assigned to the three cyclopropyl protons at C-1, C-2, and C-6. Comparison of the physical properties and infrared and n.m.r. spectra of **14** with its bicyclic analog, 2-N-dimethylaminobicyclo[2.2.1]heptane, obtained by lithium aluminum hydride reduction of N-2-bicyclo[2.2.1]heptylidenedimethylaminium perchlorate, showed them to be nonidentical. Pyrrolidinium perchlorate failed to react with tricyclenone (**13**) unless catalyzed by a base such as pyrrolidine or pyridine. The optimum yield was obtained with pyridine catalysis. The products obtained after lithium aluminum hydride reduction were 3-N-pyrrolidinotricyclo[2.2.1.0^{2,6}]heptane (**15**) and 2,5-bis(N-pyrrolidino)bicyclo[2.2.1]heptane (**16**) in 2 and 27% yields, respectively (see Chart I).

Treatment of tricyclenone (**13**) with an equimolar mixture of hexamethylenimine (**2**) and its perchlorate salt (treatment with the perchlorate salt alone caused no reaction) resulted in the rupture of cyclopropane ring which was conjugated with the ketone to produce the half-neutralized diamine, N-2(5-N-hexamethyleniminobicyclo[2.2.1]heptylidene)hexamethyleniminium perchlorate (**17**), in a 76% yield. It is interesting to note the stronger basic nature of an enamine compared with the saturated amine as evidenced by the character of this dibasic monoperchlorate salt[28] [$\nu_{\max}^{\text{Nujol}}$ 1680 cm.$^{-1}$ ($>$C$=$N$<$+)]. Reduction of **17** with lithium aluminum hydride yielded the corresponding saturated diamine **19** which, along with the ketoamine **18** and trace of the corresponding enamine, is also the product

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[17] O. Diels and K. Alder, *Ann.*, **460**, 98 (1928).
[18] F. Kasper, *Z. Chem.*, **5**, 153 (1965).
[19] L. A. Paquette, *J. Org. Chem.*, **29**, 2851 (1964).
[20] P. L. deBenneville and J. H. Macartney, *J. Am. Chem. Soc.*, **72**, 3073 (1950).
[21] P. L. deBenneville, U. S. Patent 2,578,787 (1951).
[22] N. J. Leonard and R. R. Sauers, *J. Am. Chem. Soc.*, **79**, 6210 (1957).
[23] W. R. Boehme and J. Nichols, U. S. Patent, 2,846,436 (1958).
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[25] H. Krieger, *Suomen Kemistilehti*, **B32**, 109 (1959).
[26] H. K. Hall, Jr., *J. Am. Chem. Soc.*, **82**, 1209 (1960).
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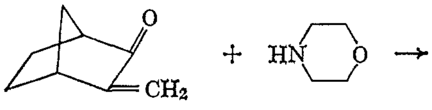
resulting from the reaction between tricyclenone (**13**) and hexamethylenimine (**2**), the latter again acting as a reducing agent. Morpholine, when allowed to react with tricyclenone (**13**), in either equimolar or in twofold excess, produced amino ketone **20** as the only isolated product in 64% yield. The preferential rupture of the conjugated cyclopropane ring in this tricyclic ketone by secondary amines was similar to a reaction observed with an unsaturated, conjugated bicyclic ketone. The reaction of morpholine with 3-methylenebicyclo[2.2.1]heptan-2-one (**21**)[29] in a 2:1 ratio caused 3-N-morpholinomethylbicyclo[2.2.1]heptan-2-one (**22**)[30] to form as the only product isolated (42% yield). It is interesting to compare these observations with those involving monocyclic[31,32] and steroidal[33,34] ketones where dienamines and their iminium salts are formed. When norbornene, nortricyclene,[24] or norbornadiene were treated with morpholine under the same conditions, no reaction took place.



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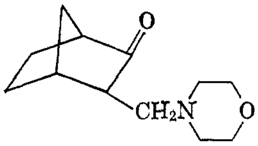

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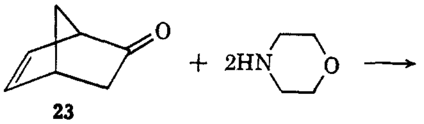
It was seen that it would be of considerable interest to determine what effect a carbon–carbon double bond across the bicyclic ring from a ketone would have on its reaction with a secondary amine. When 5-bicyclo[2.2.1]hepten-2-one (**23**)[35] was allowed to react with morpholine, a solid product, 2,5-bis(N-morpholino)-tricyclo[2.2.1.$0^{2,6}$]heptane (**24**), was obtained in a 23% yield. The structure of *tricyclenamine* **24** was assigned on the basis of elemental analysis and infrared, near-infrared, and n.m.r. spectral analysis. Its infrared spectrum showed maxima at 3070, 860, and 825 cm.$^{-1}$, its near-infrared spectrum displayed a maximum at 1.662 μ (ϵ 0.956, CS$_2$ solvent),[11] and its n.m.r. spectrum has its farthest upfield signal at τ 8.84 (integrated for two protons). All of this data is consistent with the assigned *tricyclenamine* structure **24**. This is the first reported case of the formation of a tricyclenamine. Titration of **24** in an aqueous solution which is 25% methanol and 8 *M* lithium chloride[36] at its half-neutralization point with dilute hydrochloric acid showed pK_a values of 7.37 and 4.68. The former pK_a value was very close to that of N-methylmorpholine[37] and so could be assigned to the morpholine grouping *not* attached to the cyclopropane ring. This assignment was confirmed by titrating amine **25** (prepared by reducing the corresponding ternary iminium borofluoride salt with lithium aluminum hydride) under identical conditions and obtaining a pK_a value of 7.34. Therefore, the 4.68 pK_a value can be assigned to the morpholine on the cyclopropane ring. It would be expected that the nortricyclenamine would be a weaker base because of the electron-attracting power of the cyclopropane ring.[38]



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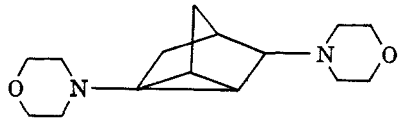

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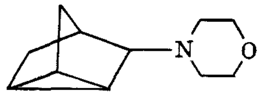

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Experimental Section

The instruments used in this work were the Cary Model 14 spectrophotometer, the Varian Associates Model A-60 spectrometer, and a Perkin-Elmer Model 137 infrared spectrometer. The analyses were carried out by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

1-N-Hexamethyleniminecyclopentene,[17] b.p. 83–85° (1.0 mm.), n^{27}_D 1.5138, ν_{max}^{film} 1630 cm.$^{-1}$, was synthesized from cyclopentanone and hexamethylenimine in the usual manner,[39] 75% yield.

Benzonorbornenone.[40]—A stirred mixture of 22 g. (0.15 mole) of benzonorbornene[41] and 35 g. (0.76 mole) of 98% formic acid was refluxed for 15 hr. The excess formic acid was then removed and the residual oil was distilled to produce 25.3 g. (87%) of benzonorbornenyl formate, b.p. 87–90° (0.6 mm.), n^{31}_D 1.5396, ν_{max}^{film} 1720 cm.$^{-1}$. Oxidation of this formate with chromic acid in acetone[42] produced, after the usual work-up, 12.0 g. (58%) of benzonorbornenone, b.p. 79–81° (0.6 mm.), n^{27}_D 1.5654, ν_{max}^{film} 1750 cm.$^{-1}$.

1-Methyltricyclo[2.2.1.$0^{2,6}$]heptan-3-one.—Oxidation of 20.2 g. (0.13 mole) of 1-methyl-3-tricyclo[2.2.1.$0^{2,6}$]heptyl formate,[43] b.p. 85° (26 mm.), n^{25}_D 1.4600, with chromic acid in acetone[39] yielded, after the usual work-up, 5.3 g. (38%) of colorless liquid product: b.p. 84–85° (24 mm.); n^{28}_D 1.4735; ν_{max}^{film} 3030, 1750, 885, and 830 cm.$^{-1}$. The near-infrared spectrum (0.2 *M* CS$_2$ solution) showed a doublet at 1.649 μ (ϵ 0.41) and 1.652 μ (ϵ 0.46) which is consistent with a nortricyclene structure.[11]

Anal. Calcd. for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.74; H, 8.46.

2-N-Hexamethyleniminobicyclo[2.2.1]heptane (**4a**).—A stirred slurry of 9.78 g. (0.033 mole) of N-2-bicyclo[2.2.1]heptylidenehexamethyleniminium perchlorate (**5**), 7.59 g. (0.2 mole) of lithium aluminum hydride, and 250 ml. of anhydrous ether was refluxed for 18 hr. The hydride was destroyed by addition of a saturated aqueous solution of sodium sulfate. The solution was filtered, solvent was removed, and the residual oil was distilled to give 5.14 g. (79%) of product, b.p. 74.5° (0.4 mm.), n^{23}_D 1.5013. No bands were observed in the infrared spectrum between 1500 and 2500 cm.$^{-1}$. Mass spectral analysis showed the molecular weight to be 193. The n.m.r. spectrum showed no signal downfield from τ 7.0. It showed a strong unassigned

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(30) H. Krieger, *Suomen Kemistilehti*, **B35**, 10 (1962).

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signal (CS$_2$ solvent, 60 Mc.) at 96 c.p.s. and weaker signals at 78, 130, and 149 c.p.s. downfield from a tetramethylsilane reference peak.

Anal. Calcd. for $C_{13}H_{23}N$: C, 80.76; H, 11.99; N, 7.25. Found: C, 80.54; H, 11.83; N, 7.20.

The **perchlorate salt** crystallized from methanol as colorless plates, m.p. 314–315° dec., $\nu_{\max}^{\text{Nujol}}$ 3150 cm.$^{-1}$ ($>\overset{+}{\mathrm{N}}\mathrm{H}$).

Anal. Calcd. for $C_{13}H_{24}ClNO_4$: C, 53.14; H, 8.23. Found: C, 53.13; H, 8.46.

Reaction of Norcamphor with Hexamethylenimine.—A stirred solution of 42.8 g. (0.39 mole) of norcamphor, 38.7 g. (0.39 mole) of hexamethylenimine, a catalytic amount of *p*-toluenesulfonic acid, and 400 ml. of xylene was refluxed (with water being removed by a Dean–Stark trap) under nitrogen for 5 days. At the end of this time the xylene solvent was removed and the residual oil was distilled to give 31.0 g. (0.16 mole, assuming one-half enamine and one-half saturated amine) of a colorless liquid, b.p. 99° (2.5 mm.), $\nu_{\max}^{\text{film}}$ 1685 cm.$^{-1}$, which represents a 41% yield. A total of 13.1 g. (0.045 mole) of recrystallized (from ethanol) perchlorate salt, made from the amine mixture in the usual manner, $\nu_{\max}^{\text{Nujol}}$ 3150 ($>\overset{+}{\mathrm{N}}\mathrm{H}$) and 1680 cm.$^{-1}$ ($>\mathrm{C}{=}\mathrm{N}<^{+}$), was stirred with 200 ml. of 4 *N* sodium hydroxide at 70° for 16 hr. The cooled solution was extracted with ether, the combined extracts were dried over anhydrous magnesium sulfate and filtered, and the solvent was removed. The residual oil was distilled and a total of 4.37 g. (0.023 mole) of colorless liquid product, b.p. 90° (1.65 mm.), $n^{27}\mathrm{D}$ 1.4999, was isolated. Its infrared and n.m.r. spectra were identical with those of saturated amine **4a**, and its mass spectrum likewise indicated a molecular weight of 193. It can be concluded, therefore, that these two amines are identical. The perchlorate salts of the two amines also have identical decomposition points and infrared spectra. It would appear from the amount of saturated amine obtained that the original reaction product mixture was 50% enamine and 50% saturated amine.

Reaction of N-2-Bicyclo[2.2.1]heptylidenehexamethyleniminium Perchlorate with Hexamethylenimine.—A stirred mixture of 10.4 g. (0.05 mole) of N-2-bicyclo[2.2.1]heptylidenehexamethyleniminium perchlorate and 45 g. (0.45 mole) of hexamethylenimine was refluxed for 63 hr. It was then stirred with excess 6 *N* sodium hydroxide at 50° for 2 hr. The aqueous layer was separated and extracted with ether. The combined extracts were dried over anhydrous magnesium sulfate and filtered, and the solvent was removed. Distillation of the residual oil produced 6.27 g. (60%) of a colorless liquid product which was shown to be 2-N-hexamethyleniminobicyclo[2.2.1]heptane (**4a**) by comparison of physical properties and infrared spectra.

8-N-Hexamethylenimino-*exo*-tricyclo[5.2.1.0^{2,6}]decane (8).—A stirred slurry of 14.40 g. (0.043 mole) of N-8-*exo*-tricyclo-[5.2.1.0^{2,6}]decylindenehexamethyleniminium perchlorate (**9**), 3.8 g. (0.1 mole) of lithium aluminum hydride, and 150 ml. of anhydrous ether was refluxed for 22 hr. The reaction mixture was worked up with saturated aqueous sodium sulfate in the usual manner. The product was isolated by distillation as a colorless liquid, 4.43 g. (44%), b.p. 107° (0.35 mm.), $n^{28}\mathrm{D}$ 1.5142. The infrared spectrum showed no maxima in the 1500–2500-cm.$^{-1}$ region.

Anal. Calcd. for $C_{16}H_{27}N$: C, 82.33; H, 11.66; N, 6.00. Found: C, 82.15; H, 11.56; N, 5.92.

The **perchlorate salt** separated from ethanol in the form of colorless plates, m.p. 232.5–233.5°, $\nu_{\max}^{\text{Nujol}}$ 3130 cm.$^{-1}$ ($>\overset{+}{\mathrm{N}}\mathrm{H}$).

Anal. Calcd. for $C_{16}H_{28}ClNO_4$: C, 57.56; H, 8.45. Found: C, 57.89; H, 7.99.

Reaction of *exo*-Tricyclo[5.2.1.0^{2,6}]decan-8-one (6) with Hexamethylenimine.—Refluxing a stirred solution of 22.5 g. (0.15 mole) of *exo*-tricyclo[5.2.1.0^{2,6}]decan-8-one,[14,15] 15 g. (0.15 mole) of hexamethylenimine, 200 ml. of xylene, and a catalytic amount of *p*-toluenesulfonic acid for 44 hr. and working up the product in the usual way[35] gave a total of 8.02 g. (23%) of a colorless, liquid product, b.p. 116–117° (0.4 mm.), $\nu_{\max}^{\text{film}}$ 1685 cm.$^{-1}$. A total of 8.82 g. (0.027 mole) of the perchlorate salt of the amine mixture, $\nu_{\max}^{\text{Nujol}}$ 3130 and 1680 cm.$^{-1}$, was hydrolyzed with excess 6 *N* sodium hydroxide at 60° for 6 hr. The solution was extracted with ether, dried, and distilled. A total of 4.25 g. (0.019 mole) of product was obtained, b.p. 112–113° (0.6 mm.), $n^{19}\mathrm{D}$ 1.5162. The infrared spectrum of this product and 8-N-hexamethylenimino-*exo*-tricyclo[5.2.1.0^{2,6}]decane are identical indicating that they are the same compounds. It would appear, therefore, that the original reaction product mixture was 30% enamine and 70% saturated amine.

N-Cyclopentylhexamethylenimine.—To 12.44 g. (0.075 mole) of 1-N-hexamethyleniminecyclopentene[16] in an ice bath was added 3.7 g. (0.085 mole) of 98% formic acid with vigorous evolution of carbon dioxide. The solution was heated to 60° over a period of 40 min. and then worked up in the usual manner.[20] Upon distillation a total of 3.73 g. (30%) of colorless liquid product was obtained, b.p. 125–127° (26 mm.), $n^{26}\mathrm{D}$ 1.4843. The infrared spectrum exhibited no maxima between 1500 and 2500 cm.$^{-1}$.

Reaction of N-Cyclopentylidenehexamethyleniminium Perchlorate with Hexamethylenimine.—A stirred mixture of 6.92 g. (0.026 mole) of N-cyclopentylidenehexamethyleniminium perchlorate and 22 g. (0.22 mole) of hexamethylenimine was refluxed for 20 hr. It was hydrolyzed for 2 hr. with aqueous 6 *N* sodium hydroxide at about 60°. It was separated from the aqueous phase, the aqueous phase was extracted with ether, and the combined nonaqueous solutions were dried over anhydrous magnesium sulfate. The solution was filtered; the solvent was removed and distilled to give 1.18 g. (27%) of colorless liquid product, b.p. 126–128° (30 mm.), $n^{25}\mathrm{D}$ 1.4846. The infrared spectrum was identical with that of N-cyclopentylhexamethylenimine; hence, that is the identity of the product.

2-N-Morpholinobicyclo[2.2.1]hept-2-ene (10).—A stirred solution of 22 g. (0.2 mole) of norcamphor, 17.4 g. (0.2 mole) of morpholine, a catalytic amount of *p*-toluenesulfonic acid, and 200 ml. of xylene was refluxed under nitrogen (water being removed with a Dean–Stark trap) for 25 hr. The reaction mixture was treated in the usual manner[35] to give, upon distillation, 7.1 g. (20%) of colorless liquid product, b.p. 80° (0.15 mm.), $\nu_{\max}^{\text{film}}$ 1685 cm.$^{-1}$.

5-N-Pyrrolidylmethylene-2-bicyclo[2.2.1]heptene (11).[18,19]—A mixture of 20 g. of anhydrous potassium carbonate, 26.3 g. (0.37 mole) of pyrrolidine, and 21.5 g. (0.18 mole) of 2-bicyclo-[2.2.1]heptene-5-carboxaldehyde[17] was kept under nitrogen at ice-bath temperatures for 1 hr. The reaction mixture was filtered and distilled to produce 27.6 g. (89%) of a colorless liquid product, b.p. 75° (0.26 mm.), $n^{23}\mathrm{D}$ 1.5425, $\nu_{\max}^{\text{film}}$ 1664 cm.$^{-1}$ ($>\mathrm{C}{=}\mathrm{C}<^{\mathrm{H}}$).

Anal. Calcd. for $C_{12}H_{17}N$: C, 82.23; H, 9.78; N, 7.99. Found: C, 82.08; H, 9.76; N, 8.15.

5-N-Pyrrolidylmethyl-2-bicyclo[2.2.1]heptene (12).[23]—To 11.3 g. (0.067 mole) of 5-N-pyrrolidylmethylene-2-bicyclo-[2.2.1]heptene (**12**) in an ice bath was added all at once 7.4 g. (0.16 mole) of 98% formic acid. An exothermic reaction took place with rapid evolution of carbon dioxide. The stirred reaction mixture was kept at 60° for 45 min. It was then basified and extracted with ether, and the combined extracts were dried over anhydrous magnesium sulfate. This was followed by filtration, solvent removal, and distillation to give 7.2 g. (61%) of colorless liquid product, b.p. 75° (1.6 mm.), $n^{25}\mathrm{D}$ 1.5000. The infrared spectrum showed no strong maxima in the 6-μ region compared with that of the starting material which showed a strong maximum in this region. The n.m.r. spectrum (CCl$_4$ solvent, 60 Mc.) showed a signal of τ 4.47 (doublet, $-CH{=}CH-$, J = 3 c.p.s.) along with strong unassigned signals at 47, 73, 95, and 110 c.p.s. as well as a medium signal at 135 c.p.s. downfield from a tetramethylsilane reference peak.

Anal. Calcd. for $C_{12}H_{19}N$: C, 81.29; H, 10.80; N, 7.90. Found: C, 81.29; H, 10.68; N, 7.86.

The **perchlorate salt** separated from 2-propanol–diethyl ether as colorless plates, m.p. 213–214°, $\nu_{\max}^{\text{Nujol}}$ 3150 cm.$^{-1}$ ($>\overset{+}{\mathrm{N}}\mathrm{H}$).

Anal. Calcd. for $C_{12}H_{20}ClNO_4$: C, 51.89; H, 7.26; N, 5.04. Found: C, 52.12; H, 7.32; N, 5.15.

3-N-Dimethylaminotricyclo[2.2.1.0^{2,6}]heptane (14).—A stirred mixture of 6.5 g. (0.06 mole) of tricyclo[2.2.1.0^{2,6}]heptan-3-one,[26] 8.7 g. (0.06 mole) of dimethylaminium perchlorate, and 125 ml. of xylene was refluxed, using a Dean–Stark trap to remove water that was formed, for 12 hr. The xylene was then decanted, and the residual xylene was removed on a rotating evaporator leaving behind a brown viscous oil, impure **N-3-tricyclo[2.2.1.0^{2,6}]heptylidenedimethylaminium perchlorate**, $\nu_{\max}^{\text{film}}$ 1723 ($>\mathrm{C}{=}\mathrm{N}<^{+}$) and 818 (cyclopropyl ring) cm.$^{-1}$. To a stirred mixture of the crude oil product and 125 ml. of anhydrous ether was added 7.6 g. (0.2 mole) of lithium aluminum hydride, and the reaction mixture was refluxed for 36 hr. The mixture was then treated with saturated aqueous sodium sulfate, filtered, and distilled to give 4.61 g. (55%) of colorless liquid product: b.p. 72–73° (26 mm.); $n^{27}\mathrm{D}$ 1.4750; $\nu_{\max}^{\mathrm{film}}$ 3050 (cyclopropyl–hydrogen), 813, and 807 (cyclopropyl ring) cm.$^{-1}$. Its infrared spectrum was not identical with the spectrum of 2-N-dimethylaminobicyclo[2.2.1]heptane. The near-infrared spectrum (0.32 *M* in a CS_2 solution) showed a maximum at 1.665 μ (ϵ 0.71), indicative of a possible nortricyclene structure.[11] The n.m.r. spectrum (CS_2 solvent) exhibited signals at τ 7.88 [$-N(CH_3)_2$] and 9.00 (three cyclopropyl protons).

Anal. Calcd. for $C_9H_{15}N$: C, 78.78; H, 11.02; N, 10.21. Found: C, 79.05; H, 11.11; N, 10.50.

2-N-Dimethylaminobicyclo[2.2.1]heptane.—Refluxing a slurry of 11.9 g. (0.05 mole) of N-2-bicyclo[2.2.1]heptylidenedimethylaminium perchlorate, 7.59 g. (0.2 mole) of lithium aluminum hydride, and 270 ml. of anhydrous ether for 29 hr. and working up the product by using saturated aqueous sodium sulfate in the usual manner resulted in the isolation, upon distillation, of 5.85 g. (84%) of product as a colorless liquid, b.p. 77° (21 mm.), $n^{25}\mathrm{D}$ 1.4670. The conformation of the dimethylamino group is probably *endo*.[27] The infrared spectrum showed no maxima in the 1500–2500-cm.$^{-1}$ region.

Anal. Calcd. for $C_9H_{17}N$: C, 77.63; H, 12.31; N, 10.06. Found: C, 77.64; H, 12.54; N, 10.26.

The **perchlorate salt** crystallized from 2-propanol as colorless plates, m.p. 158–159°, $\nu_{\max}^{\mathrm{Nujol}}$ 3135 cm.$^{-1}$ (>$\overset{+}{\mathrm{N}}$H).

Anal. Calcd. for $C_9H_{18}ClNO_4$: C, 45.09; H, 7.57. Found: C, 45.18; H, 7.73.

Reaction of Tricyclo[2.2.1.0^{2,6}]heptan-3-one (13) with Pyrrolidinium Perchlorate.—An equimolar mixture of **13**[26] and pyrrolidinium perchlorate failed to react in refluxing xylene with a Dean–Stark water trap. However, a reaction did take place when a small amount of pyrrolidine was added to the mixture, but better yields were obtained with pyridine as the basic catalyst. When 10.8 g. (0.1 mole) of **13**, 17.1 g. (0.1 mole) of pyrrolidium perchlorate, 0.8 g. (0.01 mole) of pyridine, and 300 ml. of xylene were refluxed for 19 hr., a dark-colored oil–solid separated from solution. The solvent was removed and the oil was separated from the solid product by filtration. A total of 6.86 g. (32%) of crude solid product, **N-2-(5-N-pyrrolidinium bicyclo[2.2.1]heptylidene)pyrrolidinium diperchlorate**, $\nu_{\max}^{\mathrm{Nujol}}$ 3130 (>$\overset{+}{\mathrm{N}}$H) cm.$^{-1}$, was obtained. The crude oil product, **N-3-tricyclo[2.2.1.0^{2,6}]heptylidenepyrrolidinium perchlorate**, $\nu_{\max}^{\mathrm{film}}$ 1727 cm.$^{-1}$ (>C=N<+), along with the crude solid product, was refluxed with 7.6 g. (0.2 mole) of lithium aluminum hydride in 200 ml. of anhydrous ether for 26 hr. The organic products were isolated from the reaction mixture by treatment with saturated aqueous sodium sulfate, filtration, removal of solvent, and fractional distillation. A total of 0.26 g. (over-all 2% yield) of the first fraction was obtained as a colorless liquid, b.p. 49° (0.5 mm.), $n^{27}\mathrm{D}$ 1.5000. It was identified as **3-N-pyrrolidinotricyclo[2.2.1.0^{2,6}]heptane (15)**, $\nu_{\max}^{\mathrm{film}}$ 3040 (cyclopropyl–hydrogen) and 810 (cyclopropyl ring) cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{17}N$: C, 80.92; H, 10.50; N, 8.58. Found: C, 81.24; H, 10.67; N, 8.29.

The second fraction consisted of 3.16 g. (0.012 mole) of a colorless liquid product, **2,5-bis(N-pyrrolidino)bicyclo[2.2.1]heptane (16)**, b.p. 107–108° (0.25 mm.), $n^{25}\mathrm{D}$ 1.5142, over-all 27% yield. The infrared spectrum showed no bands between 1500 and 2500 cm.$^{-1}$.

Anal. Calcd. for $C_{15}H_{26}N_2$: C, 76.86; H, 11.18; N, 11.96. Found: C, 76.99; H, 11.27; N, 12.16.

N-2-(5-N-Hexamethyleniminobicyclo[2.2.1]heptylidene)hexamethyleniminium Perchlorate (17).—When a solution of hexamethylenimine in ether was neutralized (to congo red indicator) with 1:1 perchloric acid–ethanol, an oil was formed. However, upon partial neutralization (approximately half-neutralized) a white crystalline solid was formed which was essentially the dihexamethylenimine monoperchlorate. A stirred mixture of 19.96 g. (0.067 mole) of this salt, 10.8 g. (0.1 mole) of tricyclo[2.2.1.0^{2,6}]heptan-3-one,[26] and 250 ml. of benzene was refluxed with a Dean–Stark trap for 1.5 hr. A total of 19.70 g. (76%) of solid product was obtained after filtration and recrystallization from ethanol. The product crystallized from ethanol as colorless plates, m.p. 205–206° dec., $\nu_{\max}^{\mathrm{Nujol}}$ 1680 cm.$^{-1}$ (>C=N<+).

Anal. Calcd. for $C_{19}H_{33}ClN_2O_4$: C, 58.67; H, 8.55. Found: C, 58.63; H, 8.50.

The **diperchlorate** separated from methanol as colorless prisms, m.p. 294–295° dec., $\nu_{\max}^{\mathrm{Nujol}}$ 3100 (>$\overset{+}{\mathrm{N}}$H) and 1680 cm.$^{-1}$ (>C=N<+).

Anal. Calcd. for $C_{19}H_{34}Cl_2N_2O_8$: C, 46.63; H, 7.00. Found: C, 46.90; H, 7.03.

2,5-Bis(N-hexamethylenimino)bicyclo[2.2.1]heptane (19).—A total of 19.7 g. (0.0507 mole) of N-2(5-N-hexamethyleniminobicyclo[2.2.1]heptylidene)hexamethyleniminium perchlorate in 300 ml. of anhydrous ether was refluxed for 3 hr. with 11.4 g. (0.3 mole) of lithium aluminum hydride, which was followed by treatment with saturated aqueous sodium sulfate, filtration, and solvent removal. Distillation of the residual oil gave 7.08 g. (47%) of a viscous, colorless liquid product, b.p. 162–163° (0.45 mm.), $n^{33}\mathrm{D}$ 1.5157. The infrared spectrum showed no maxima in the 1500–2500-cm.$^{-1}$ region.

Anal. Calcd. for $C_{19}H_{34}N_2$: C, 78.56; H, 11.80; N, 9.65. Found: C, 78.71; H, 11.75; N, 9.43.

The **diperchlorate** crystallized from methanol as colorless prisms, m.p. 279–281° dec., $\nu_{\max}^{\mathrm{Nujol}}$ 3100 cm.$^{-1}$ (>$\overset{+}{\mathrm{N}}$H).

Anal. Calcd. for $C_{19}H_{36}Cl_2N_2O_8$: C, 46.44; H, 7.38; N, 5.70. Found: C, 46.29; H, 7.37; N, 5.95.

Reaction of Tricyclo[2.2.1.0^{2,6}]heptan-3-one (15) with Hexamethylenimine.—A stirred solution of 19.8 g. (0.2 mole) of hexamethylenimine, 10.8 g. (0.1 mole) of tricyclo[2.2.1.0^{2,6}]-heptan-3-one,[26] a catalytic amount of *p*-toluenesulfonic acid, and 150 ml. of xylene was refluxed (using a Dean–Stark trap to remove water) for 24 hr. Upon distillation two main fractions were isolated. The first fraction distilled as a colorless liquid, b.p. 123–126° (0.45 mm.), $\nu_{\max}^{\mathrm{film}}$ 1750 cm.$^{-1}$ (>C=O), and was identified as **5-N-hexamethyleniminobicyclo[2.2.1]heptan-2-one (18)**. A total of 4.90 g. (24% yield) of this product was obtained. The **perchlorate** salt was prepared in the usual manner, and it crystallized from 2-propanol in the form of colorless prisms, m.p. 254–255° dec., $\nu_{\max}^{\mathrm{Nujol}}$ 3100 (>$\overset{+}{\mathrm{N}}$H) and 1750 cm.$^{-1}$ (>C=O).

Anal. Calcd. for $C_{13}H_{22}ClNO_5$: C, 50.73; H, 7.21. Found: C, 51.01; H, 7.33.

The second fraction appeared as 7.99 g. of a viscous liquid, b.p. 175–180° (0.5 mm.). The infrared spectrum of this crude product exhibited bands at 1750 and 1685 cm.$^{-1}$, indicating some ketone and enamine impurities. The bulk of this fraction, however, was shown to be **2,5-bis(N-hexamethylenimino)bicyclo[2.2.1]heptane (19)** by comparison of the infrared spectrum with that of an authentic sample (see above) and by comparison of the diperchlorate salt with an authentic sample. This represents a crude yield of 28%.

Reaction of Tricyclo[2.2.1.0^{2,6}]heptan-3-one (13) with Morpholine.—A stirred mixture of 26.1 g. (0.3 mole) of morpholine, 10.8 g. (0.1 mole) of tricyclo[2.2.1.0^{2,5}]heptan-3-one,[22] a catalytic amount of *p*-toluenesulfonic acid, and 150 ml. of xylene was refluxed for 48 hr. (using a Dean–Stark trap to remove water). The xylene solvent was removed, and the residual oil was distilled to give 12.52 g. (64%) of colorless liquid product, b.p. 111° (0.5 mm.), $n^{20}\mathrm{D}$ 1.5130, $\nu_{\max}^{\mathrm{film}}$ 1750 cm.$^{-1}$ (>C=O), which was identified as **5-N-morpholinobicyclo[2.2.1]heptan-2-one (20)**.

Anal. Calcd. for $C_{11}H_{17}NO_2$: C, 67.66; H, 8.78; N, 7.17. Found: C, 67.77; H, 9.00; N, 7.40.

Reaction of 3-Methylenebicyclo[2.2.1]heptan-2-one (21) with Morpholine.—After a mixture of 5.22 g. (0.05 mole) of 3-methylenebicyclo[2.2.1]heptan-2-one,[29] 9.14 g. (0.1 mole) of morpholine, a catalytic amount of *p*-toluenesulfonic acid, and 200 ml. of xylene had been refluxed for 24 hr. and the xylene solvent had been removed, a total of 4.0 g. (42% yield) of **3-N-morpholinomethylbicyclo[2.2.1]heptan-2-one (22)** was isolated upon distillation as a colorless liquid, b.p. 134–135.5° (1.8 mm.), $n^{25}\mathrm{D}$ 1.5051 [lit.[30] b.p. 122–124° (0.15 mm.), $n^{20}\mathrm{D}$ 1.5055], $\nu_{\max}^{\mathrm{film}}$ 1750 cm.$^{-1}$ (>C=O).

Reaction of 5-Bicyclo[2.2.1]hepten-2-one (23) with Morpholine.—A stirred solution of 9.85 g. (0.113 mole) of 5-bicyclo[2.2.1]hepten-2-one,[35] 20.0 g. (0.23 mole) of morpholine, a catalytic amount of *p*-toluenesulfonic acid, and 200 ml. of xylene was refluxed under a nitrogen atmosphere (using a Dean–Stark trap to remove water) for 24 hr. The xylene solvent was removed and the residual oil was distilled to give 6.80 g. (23%) of **2,5-bis(N-morpholino)tricyclo[2.2.1.0^{2,6}]heptane (24)**, b.p. 170° (1.4 mm.). Upon standing the viscous liquid product changed into a crystalline solid which could be further purified by sublimation (colorless needles): m.p. 79–80°; $\nu_{\max}^{\text{Nujol}}$ 3070 (cyclopropyl–hydrogen), 860, and 825 cm.$^{-1}$ (cyclopropyl ring).[13] The near-infrared spectrum (0.204 *M* CS_2 solution) displayed a maximum at 1.662 μ (ϵ 0.956) which is consistent with a nortricyclene-type structure.[11] The n.m.r. spectrum (in CS_2) shows no signals downfield from τ 6.0 while the signal farthest upfield has a τ value of 8.84 (triplet, cyclopropyl protons, integrated for two protons).

Anal. Calcd. for $C_{15}H_{24}N_2O_2$: C, 68.14; H, 9.15; N, 10.60. Found: C, 68.05; H, 9.41; N, 10.54.

Reaction of 5-Bicyclo[2.2.1]hepten-2-one (23) with Hexamethylenimine.—The reaction between 3.58 g. (0.033 mole) of 5-bicyclo[2.2.1]hepten-2-one[35] and 6.55 g. (0.066 mole) of hexamethylenimine in 75 ml. of xylene was carried out in the same manner as that described above for its reaction with morpholine. Five different products were found to be present upon distillation. Their structures and relative amounts were ascertained by using their infrared spectra and boiling points, and hydrolysis (of enamines) followed by isolation of the hydrolysis products. No nortricyclene-type compound was found among the products. The boiling point range, products isolated, and yields follow: b.p. 83–86° (0.45 mm.), 5-N-hexamethyleniminobicyclo[2.2.1]hept-2-ene (8%) and 2-N-hexamethyleniminobicyclo[2.2.1]hepta-2,5-diene (11%); b.p. 125–130° (0.25 mm.), 5-N-hexamethyleniminobicyclo[2.2.1]heptan-2-one (**18**) (7%); b.p. 163–172° (0.25 mm.), 2,5-bis(N-hexamethylenimino)bicyclo[2.2.1]hept-2-ene (11%) and 2,5-bis(N-hexamethylenimino)bicyclo[2.2.1]heptane (**19**) (10%).

3-N-Morpholinotricyclo[2.2.1.0^{2,6}]heptane (25).—A stirred mixture of 13.0 g. (0.12 mole) of tricyclo[2.2.1.0^{2,6}]heptan-3-one and 10.8 g. (0.12 mole) of morpholinium fluoroborate was refluxed in benzene with a Dean–Stark trap for 48 hr. The crude solid product was isolated by filtration. This solid salt was treated with an excess of lithium aluminum hydride in ether, and the stirred slurry was refluxed for 20 hr. The product was worked up in the usual manner, and upon distillation a total of 8.2 g. (38% yield) of colorless liquid product was obtained: b.p. 91–92° (2.9 mm.); $\nu_{\max}^{\text{film}}$ 3080 (cyclopropyl–hydrogen), 880 (s), 840 (m), and 810 (s, cyclopropane) cm.$^{-1}$. The near-infrared spectrum (0.537 *M* CS_2 solution) showed a maximum at 1.660 μ (ϵ 1.14) which further confirms the nortricyclene-type structure.[11]

Anal. Calcd. for $C_{11}H_{17}NO$: C, 73.71; H, 9.56; N, 7.82. Found: C, 73.92; H, 9.31; N, 7.87.

Nuclear Magnetic Resonance Spectra of the Bornyl and Norbornyl Grignard Reagents[1]

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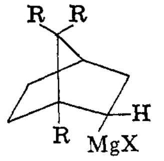
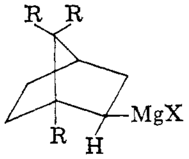
The n.m.r. spectra of the Grignard reagents from bornyl and norbornyl chlorides show that both Grignard reagents consist of a mixture of *exo* and *endo* isomers. The isomers of the bornyl Grignard reagent can be equilibrated by heating; no estimate has yet been obtained of the equilibration rate of the norbornyl isomers.

The Grignard reagents (**1a** and **2a**) from bornyl and isobornyl chlorides have been investigated by Vavon, Riviere, and de Botton.[2] On the basis of product studies (primarily carbonation) under a variety of conditions, they concluded that these Grignard reagents are similar mixtures of the *exo* and *endo* isomers. These appeared to interconvert on heating in xylene and other high-boiling solvents, but to maintain their stereochemical identity at room temperature. Vavon and Thiec[3] concluded that the corresponding lithium compounds are more rapidly equilibrated. Walling and Buckler,[4] in a study primarily concerned with oxygenation of the Grignard reagent from bornyl chloride, confirmed part of the experimental work of Vavon and Riviere. However, since different product mixtures are formed in oxygenation and carbonation, they preferred the interpretation that the "isomerization" of the Grignard reagent by heating might rather involve a change in coordination of the Grignard reagent with change in solvent, which leads to an altered stereochemistry of carbonation.

Sauers[5] investigated the products from carbonation and oxygenation of the Grignard reagent (**1b** and **2b**) from norbornyl bromide. He suggested that his results might best be interpreted if the *exo* and *endo* forms of that Grignard reagent exist in a mobile equilibrium.



1a, R = CH_3
b, R = H



2a, R = CH_3
b, R = H

We have determined the n.m.r. spectra of the bornyl and norbornyl Grignard reagents, the former under a variety of conditions. Both of these consist of a mixture of *exo* and *endo* isomers. The two bornyl isomers are indeed quite slowly interconverted, but we have not obtained unambiguous information about the norbornyl Grignard, except their interconversion is slow enough at about 110° so as not to produce spectral broadening.

Results and Discussion

The α-hydrogen n.m.r. spectra of the norbornyl and bornyl Grignard reagents are reproduced in Figures 1a and b. These reagents were prepared in tetrahydrofuran (THF) from sublimed magnesium. In each case, the spectrum consists of two multiplets. By analogy with the relative chemical shifts and fine structure of other isomeric bicyclo[2.2.1]heptyl pairs, we assign the multiplet at higher field to the *endo* hydrogen of the *exo* isomer.[6] The difference in chemical shift, 0.40 p.p.m. in each case, is in the range previously

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