Preparation of Bicyclic Enamines and Their Reaction with Sulfene

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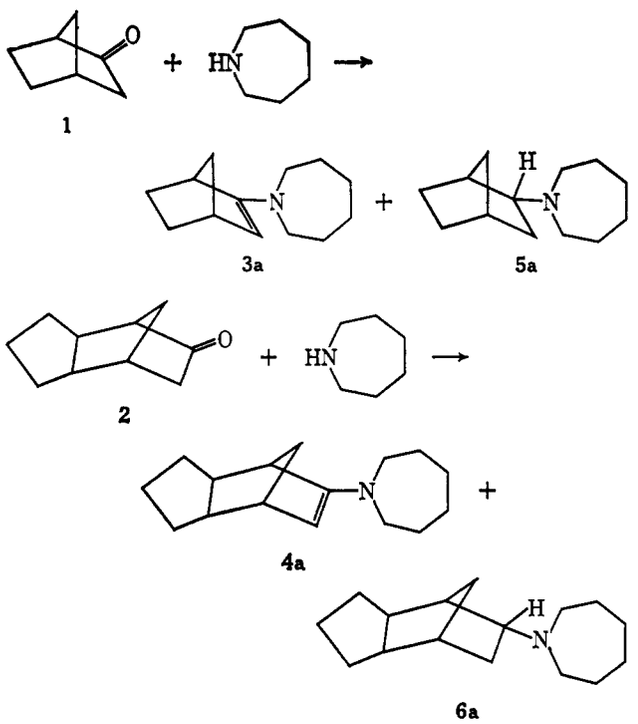
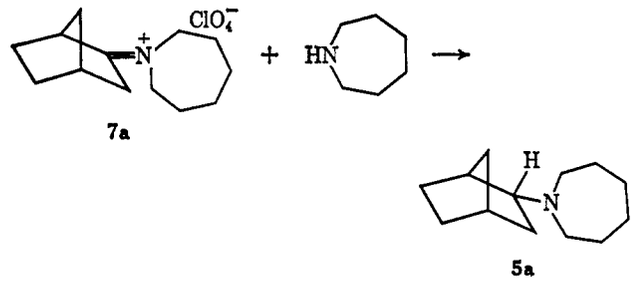
The uncatalyzed reactions of norbornanone and *exo*-tricyclo[5.2.1.$0^{2,6}$]decan-8-one with a variety of secondary amines have been studied and have been found to yield, in addition to the expected enamines, small amounts of the corresponding saturated amines. The α,β-unsaturated amines form ternary iminium salts with strong acid and are readily reduced with 90% formic acid. Addition of sulfene afforded, in stereoselective fashion, single cycloadducts which are probably the result of *exo* addition.

Recently, it was reported that the *p*-toluenesulfonic acid catalyzed reactions of norbornanone (1) and *exo*-tricyclo[5.2.1.$0^{2,6}$] decan-8-one (2) with hexamethylenimine in refluxing xylene produce, in each case, a mixture of the corresponding enamines **3a** and **4a** and the saturated amines **5a** and **6a**. In addition, the authors report that the *p*-toluenesulfonic acid catalyzed reaction of norbornanone (1) with morpholine produces enamine **3b** and no saturated amine, and that the reaction of norbornanone (1) with hexamethylenimine in the absence of added catalyst gives **3a** and no saturated amine.[1-3]



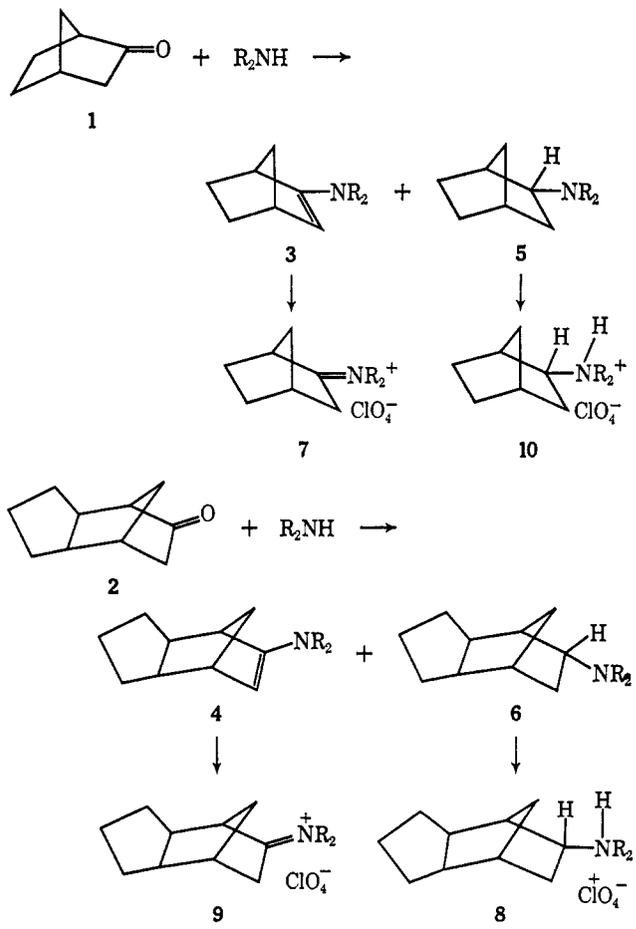
The authors believe that the saturated amines **5a** and **6a** are formed by reduction of the corresponding enamines **3a** and **4a** with hexamethylenimine since they were able to reduce N-2-bicyclo[2.2.1]heptylidenehexamethyleniminium perchlorate (**7a**) to **5a**, in 60% yield,



with an excess of hexamethylenimine.[2,3] In view of the facile reduction of enamine **3a** to saturated amine **5a** with hexamethylenimine, the observation by Cook, *et al.*, that formic acid fails to reduce **3a** and the corresponding pyrrolidine enamine **3c** is surprising.[1,2] Interest in bicyclic and tricyclic enamines as intermediates for other studies led us to investigate the reactions of norbornanone (1) and *exo*-tricyclo[5.2.1.$0^{2,6}$]decan-8-one (2) with a variety of secondary amines, and we report here the results of this investigation.

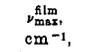
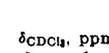
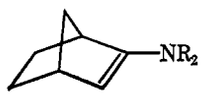
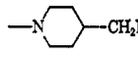
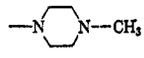
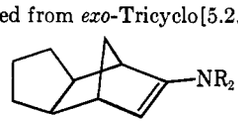
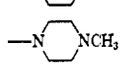
Prolonged reflux of a mixture of norbornanone (1) and excess secondary amine in toluene, in the absence of added catalyst, afforded the bicyclic enamines **3a–f** (Table I, Scheme I). Reaction of *exo*-tricyclo[5.2.1.$0^{2,6}$]dec-

SCHEME I



(1) A. G. Cook, *J. Amer. Chem. Soc.*, **85**, 648 (1963).
(2) A. G. Cook, W. C. Meyer, K. E. Ungrodt, and R. H. Mueller, *J. Org. Chem.*, **31**, 14 (1966).
(3) A. G. Cook and C. R. Schulz, *ibid.*, **32**, 473 (1967).

TABLE I

Compd	$-NR_2$	Reaction solvent	Moles of R_2NH per mole of ketone	Reaction time, days	Yield, %	Yield, % saturated amine	Bp, °C (mm)	ν_{max}^{film}, cm^{-1}, 	δ_{CDCl_3}, ppm[a] 
Enamines Derived from Norbornanone 									
3a		Toluene	1.5	5	48	8	83 (0.5)	1600	4.27 d (J = 3)
3b		Toluene	1.5	14	61	1	91–106 (2)	1600	4.60 d (J = 3)
3c		Benzene	3	14	72	3	66–68 (2)	1600	4.13 d (J = 3)
3d		Toluene	1.5	21	70	2	73–76 (2)	1600	4.48 d (J = 3)
3e		Toluene	1.5	14	65	5	151–157 (2)	1600	4.52 d (J = 3)
3f		Toluene	1.5	13	85	1	62–64 (2)	1600	4.52 d (J = 3)
Enamines Derived from *exo*-Tricyclo[5.2.1.$0^{2,6}$]decan-8-one 									
4a		Toluene	1.5	8	39	7	103–115 (0.2)	1600	4.25 d (J = 3)
4b		Toluene	1.5	21	22	12	114–120 (2)	1600	4.65 d (J = 3)
4c		Toluene	1.5	10	55	0.3	103–107 (0.5)	1600	4.60 d (J = 3)

[a] d, doublet; coupling constants (J) in cycles per second.

an-8-one (**2**) with hexamethylenimine, morpholine, and N-methylpiperazine under similar conditions furnished the corresponding tricyclic enamines **4a–c**. In addition to α,β-unsaturated amines, the reactions of **1** and **2** with secondary amine yielded in all cases investigated small amounts of by-product. These by-products were detected by gas–liquid partition chromatography and they showed identical retention times with authentic samples of the corresponding saturated amines prepared by formic acid reduction of the corresponding enamines. On this basis, they have been formulated as such. In seeking further support for our formulation of the by-products as saturated amines, we hydrolyzed the product mixture resulting from the reaction of **2** with morpholine and obtained the saturated amine **6b** which was converted into its perchlorate salt **8b**. This proved to be identical with authentic **8b** made from pure **6b** which had beeh obtained by reduction of enamine **4b** with formic acid.

Bicyclic and tricyclic enamines **3a–f** and **4a–c** are colorless liquids (**4b** and **4c** are solids at 0°) which are extremely sensitive to air and moisture. However, they can be stored for prolonged periods without appreciable decomposition in a nitrogen atomsphere at 0°. The infrared spectra of the α,β-unsaturated amines exhibit a strong C=C stretching band at 1600 cm^{-1} and not at 1685 cm^{-1} as had been reported previously.[2] In our opinion the 1685-cm^{-1} band reported by Cook, *et al.*, for **3a**, **3b**, and **4a** arises from an impurity.[4] The nmr spectra (in $CDCl_3$) show the vinyl hydrogen signal as a doublet; the splitting is presumably due to interaction with the bridgehead hydrogen. With perchloric acid C^{β} protonation occurs to give the ternary iminium salts **7a–e** and **9a–b** (Table II). All of these have been characterized by elemental analyses and by the strong infrared absorption band in the region of 1672–1709 cm^{-1} indicative of $>C{=}\overset{+}{N}<$. In addition, they are identical with respect to melting point and infrared spectra with those prepared by Cook, *et al.*, from the reactions of norbornanone (**1**) and *exo*-tricyclo[5.2.-1.$0^{2,6}$]decan-8-one (**2**) with the corresponding secondary amine perchlorate salts.[2]

In spite of reports to the contrary,[1,2] we find that bicyclic enamines **3a–f** and the tricyclic enamines **4a–c** react vigorously with 90% formic acid[5,6] with evolution of carbon dioxide to afford the saturated amines **5a–f** and **6a–c**, respectively (Table III). Structures **5a–f** and **6a–c** were supported by elemental analyses and infrared and nmr spectra. Gas chromatographic analysis of the saturated amines demonstrated that a single isomer was present, indicating that the reduction is stereospecific. The saturated amines were further characterized by converting them to their perchlorate salts

(4) Dr. Cook kindly furnished us with a copy of the infrared spectrum of the crude product derived from the *p*-toluenesulfonic acid catalyzed reaction of norbornanone with morpholine in refluxing xylene. Comparison of this spectrum with the infrared spectrum of 2-N-morpholinobicyclo[2.2.1]-hept-2-ene prepared by us revealed that, with the exception of minor intensity differences at 1370, 1167, 1147, 1039, and 1030 cm^{-1}, and the presence of additional weak bands at 3278, 1685, 893, and 877 cm^{-1} in Dr. Cook's spectrum, the spectra were identical. We must therefore conclude that the 1685-cm^{-1} band originates from an impurity.

(5) P. L. de Benneville and J. H. Macartney, *J. Amer. Chem. Soc.*, **72**, 3073 (1950).

(6) P. L. de Benneville, U. S. Patent 2,578,787 (1951).

TABLE II

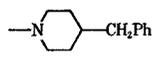
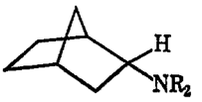
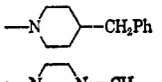
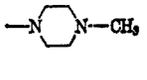
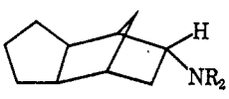
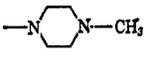
Compd	$-NR_2$	Solvent for crystallisation	Mp, °C	ν_{max}^{KBr}, cm^{-1}, $>C=\overset{+}{N}<$	Formula	Calcd, % C	Calcd, % H	Calcd, % Cl	Calcd, % N	Found, % C	Found, % H	Found, % Cl	Found, % N
Ternary Iminium Salts of Bicyclic Enamines													
7a		Ethanol	302–304 dec	1672	$C_{13}H_{22}ClNO_4$	53.51	7.60	12.15	4.80	53.23	7.73	11.85	4.95
7b		Ethanol	250–253 dec	1694	$C_{11}H_{18}ClNO_5$	47.23	6.49	12.68	5.01	47.07	6.53	12.38	5.15
7c		Ethanol	226–227	1709	$C_{11}H_{18}ClNO_4$	50.10	6.88	13.45	5.31	50.22	6.93	13.59	5.36
7d		Ethanol	293–295 dec	1694	$C_{12}H_{20}ClNO_4$	51.89	7.26	12.77	5.04	51.84	7.34	12.69	5.18
7e		Methanol	172–175	1681	$C_{19}H_{26}ClNO_4$	62.03	7.13	9.64	3.81	61.94	7.32	9.70	3.54
Ternary Iminium Salts of Tricyclic Enamines													
9a		Methanol	210–213	1678	$C_{16}H_{26}ClNO_4$	57.91	7.90	10.68	4.22	57.72	7.80	11.00	4.01
9b		Ethanol	152–154	1694	$C_{14}H_{22}ClNO_5$	52.58	6.94	11.09	4.38	52.20	7.00	11.01	4.48

TABLE III

Compd	-NR₂	Bp, °C (mm)	Yield, %	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
				2-Aminobicyclo[2.2.1]heptanes						
										
5a		88 (1.5)	72	$C_{13}H_{23}N$	80.76	11.99	7.25	80.52	12.12	7.10
5b		70–72 (0.5)	66	$C_{11}H_{19}NO$	72.88	10.57	7.73	73.06	10.56	7.85
5c		64 (0.5)	76	$C_{11}H_{19}N$	79.94	11.59	8.48	79.95	11.33	8.51
5d		79 (1.5)	59	$C_{12}H_{21}N$	80.38	11.81	7.81	80.68	11.73	7.89
5e		183–185 (0.5)	77	$C_{19}H_{27}N$	84.70	10.10	5.20	84.50	10.30	5.12
5f		86–87 (3)	79	$C_{12}H_{22}N_2$	74.17	11.41	14.42	73.87	11.25	14.21
				8-Amino-*exo*-tricyclo[5.2.1.0^{2,6}]decanes						
										
6a		96–97 (1)	74	$C_{16}H_{27}N$	82.34	11.66	6.00	82.48	11.96	5.85
6b		97–98 (1.5)	67	$C_{14}H_{23}NO$	75.97	10.47	6.33	75.70	10.70	6.23
6c		90 (0.5)	77	$C_{15}H_{26}N_2$	76.86	11.18	11.95	77.23	11.18	11.87

10a–f and **8a–c** (Table IV). Leonard and Sauers[7] have shown that the first step in the formic acid reduction of an enamine is the formation of a ternary iminium formate followed by nucleophilic attack of the hydride of the formate anion at the α carbon of the original enamine grouping. In the formic acid reduction of the above bicyclic and tricyclic enamines, attack by the hydride of the formate anion would be expected to take place from the less hindered side of the molecule, the *exo* side, to give the *endo*-amino isomer.[8,9] Comparison of the physical properties of the saturated amines **5a** and **6a** with those of *endo*-2-N-hexamethyleniminobicyclo-[2.2.1]heptane and *endo*-8-N-hexamethylenimino-*exo*-tricyclo[5.2.1.0^{2,6}]decane produced by the lithium aluminum hydride reduction[3] of the iminium salts **7a** and **9a** showed that they were identical. Therefore, saturated amines produced by formic acid reduction of bicyclic and tricyclic enamines are indeed *endo* isomers. Several enamines, **3b**, **3e**, and **3f**, were also reduced catalytically over a 5% palladium-on-carbon catalyst at 50 psi, and it was found that catalytic hydrogenation is also stereospecific and gives rise to the *endo* isomer.

As mentioned earlier, the *p*-toluenesulfonic acid catalyzed reaction of norbornanone (**1**) with hexamethylenimine is reported as producing a mixture of enamine **3a** and saturated amine **5a** in approximately equal amounts, while the reaction of norbornanone (**1**) with morpholine under similar conditions produces only enamine **3b**.[2,3] Repetition of this latter reaction gave, in our hands, a mixture of enamine **3b** and saturated amine **5b** in a 1:2 ratio. In view of the significantly larger amounts of saturated amine produced in these acid-catalyzed reactions, it would appear that, in spite of the long reaction times involved, the uncatalyzed reaction is the preferred method for the preparation of these and other bicyclic and tricyclic enamines.

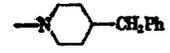
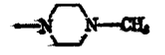
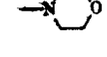
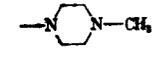
Sulfene chemistry has received a great deal of attention in recent years, and the ability of sulfene to add to electron-rich double bonds has been well documented.[10]

Paquette[11] examined the cycloaddition of sulfene to a variety of enamines derived from 5-norbornene-2-carboxaldehyde and observed that this cycloaddition is stereoselective and gives adducts which are the result of *exo* addition to the enamine double bond. We were interested in preparing the sulfene adducts of the various bicyclic and tricyclic enamines described above; such a study also offered a further opportunity of examining the stereoselectivity of sulfene addition to a bicyclic moiety.

Addition of 1 equiv of methanesulfonyl chloride to an equimolar mixture of the appropriate bicyclic enamine **3a–f** and triethylamine in dioxane or tetrahydrofuran at 5–10° afforded crystalline adducts which have been formulated, on the basis of infrared and nmr spectra and elemental analyses, as the tricyclic aminothietane diox-

(7) N. J. Leonard and R. R. Sauers, *J. Amer. Chem. Soc.*, **79**, 6210 (1957).
(8) S. Beckmann and R. Mezger, *Chem. Ber.*, **89**, 2738 (1956).
(9) For a comprehensive discussion of *exo* and *endo* addition to various norbornane derivatives, see J. A. Berson in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, Chapter 3.
(10) For recent reviews on sulfene chemistry, see T. J. Wallace, *Quart. Rev.* (London), **20**, 67 (1966); G. Opitz, *Angew. Chem. Intern. Ed. Engl.*, **6**, 107 (1967).
(11) L. A. Paquette, *J. Org. Chem.*, **29**, 2851 (1964).

TABLE IV

Compd	–NR_2	Solvent for crystallization	Mp, °C	ν_{max}^{KBr}, cm^{-1}, HNR_2^+	Formula	Calcd, % C	Calcd, % H	Calcd, % Cl	Calcd, % N	Found, % C	Found, % H	Found, % Cl	Found, % N
Perchlorate Salts of 2-Aminobicyclo[2.2.1]heptanes													
10a		Ethanol	303–314 dec	3134[b]	$C_{13}H_{22}ClNO_4$	53.14	8.23	12.07	4.77	53.05	8.43	11.95	4.89
10b		Ethanol	213–214	2439 2564 2631	$C_{11}H_{20}ClNO_5$	46.89	7.16	12.59	4.97	46.71	7.27	12.38	5.08
10c		Ethanol–ether	178–180	2500 2625 2681	$C_{11}H_{20}ClNO_4$	49.71	7.59	13.34	5.27	49.42	7.53	13.27	5.15
10d		Ethanol	270–283 dec	2551 2688	$C_{12}H_{22}ClNO_4$	51.51	7.93	12.67	5.01	51.33	7.81	12.70	4.76
10e		Ethanol	190–193	2584 2688	$C_{19}H_{28}ClNO_4$	61.86	7.65	9.34	3.79	61.86	7.75	9.69	3.44
10f		Methanol	265–271 dec	2469 2564 2667	$C_{12}H_{24}Cl_2N_2O_8$	36.14	6.12	17.94	7.09	36.23	6.21	17.62	7.06
Perchlorate Salts of 8-Amino-*exo*-tricyclo[5.2.1.$0^{2,6}$]decanes													
8a		Methanol	232–234	3125[b]	$C_{16}H_{28}ClNO_4$	57.56	8.45	10.62	4.20	57.30	8.48	10.81	4.24
8b		Ethanol	237–239	3125[b]	$C_{14}H_{24}ClNO_5$	52.25	7.52	11.02	4.35	52.23	7.48	11.01	4.04
8c[a]		Ethanol	243–244 dec	2439 2564 2631	$C_{15}H_{28}Cl_2N_2O_8$	41.39	6.48	16.29	6.44	41.40	6.50	16.08	6.24

[a] Diperchlorate salt. [b] Spectrum obtained in Nujol.

TABLE V

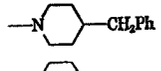
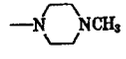
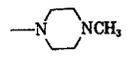
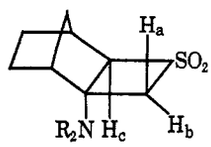
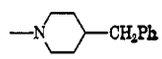
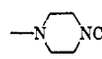
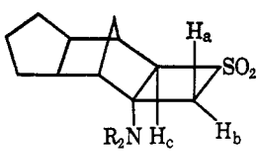
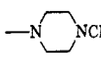
Compd	–NR₂	Yield, %	Mp, °C	Solvent for reaction	Solvent for crystallization	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Calcd, % S	Found, % C	Found, % H	Found, % N	Found, % S
5-Amino-3-thiatricyclo[4.2.1.0^{2,5}]nonane 3,3-Dioxides														
11a		41	99–100	Tetrahydrofuran	Methanol	$C_{14}H_{23}NO_2S$	62.42	8.60	5.20	11.90	62.17	8.75	5.12	11.53
11b		67	161–164	Dioxane	Methanol	$C_{12}H_{19}NO_3S$	56.02	7.44	5.44	12.46	55.81	7.33	5.41	12.46
11c		48	103–106	Tetrahydrofuran	Methanol	$C_{12}H_{19}NO_2S$	59.72	7.93	5.80	13.28	59.46	7.95	5.70	13.22
11d		32	99–101	Dioxane	Methanol	$C_{13}H_{21}NO_2S$	61.14	8.29	5.49	12.55	60.90	8.40	5.46	12.57
11e		50	96–100	Tetrahydrofuran	Methanol	$C_{20}H_{27}NO_2S$	69.52	7.88	4.05	9.28	69.36	7.96	3.99	9.29
11f		54	132–136	Tetrahydrofuran	Methanol	$C_{13}H_{22}N_2O_2S$	57.74	8.20	10.36	11.86	57.66	8.35	10.11	11.63
11-Amino-9-thiatetracyclo[5.4.1.0^{2,6}.0^{8,11}]dodecane 9,9-Dioxides														
12a		29	105–106	Tetrahydrofuran	Petroleum ether (bp 60–70°)	$C_{17}H_{27}NO_2S$	65.98	8.80	4.53	10.36	65.75	8.71	4.45	10.13
12b		61	175–178	Tetrahydrofuran	Methanol	$C_{15}H_{23}NO_3S$	60.58	7.79	4.71	10.78	60.49	7.76	4.63	10.72
12c		47	152–154	Tetrahydrofuran	Cyclohexane	$C_{16}H_{26}N_2O_2S$	61.90	8.44	9.03	10.33	61.81	8.60	9.09	10.31

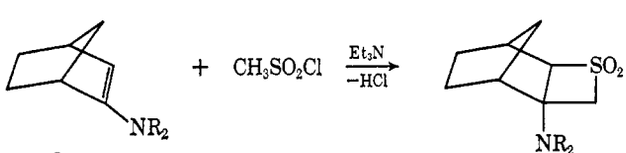
TABLE VI

Nuclear Magnetic Resonance Spectra

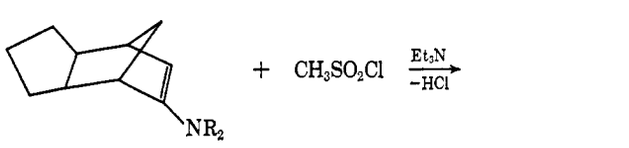
Compd	$-NR_2$	Chemical shifts in δ units[a] H_a	H_b	H_c
				
11a		3.75, J_{AB} = 14	4.13, J_{cb} = 3	3.95 (m), $J_{ac} < 1$
11b		3.64, J_{AB} = 14	4.36, J_{cb} = 3	4.0 (m), J_{ac} = 1
11c		3.66, J_{AB} = 14	4.20, J_{cb} = 3	3.91 (m), J_{ac} = 1
11d		3.53, J_{AB} = 14	4.29, J_{cb} = 3	3.98 (m), J_{ac} = 1
11e		3.48, J_{AB} = 14	4.22, J_{cb} = 3	3.92 (m), $J_{ac} < 1$
11f		3.61, J_{AB} = 14	4.31, J_{cb} = 3	3.96 (m), $J_{ac} < 1$
				
12a		3.62, J_{AB} = 14	4.05, J_{cb} = 3	3.85 (m), $J_{ac} < 1$
12b		3.54, J_{AB} = 14	4.28, J_{cb} = 3	3.90 (m), J_{ac} = 1
12c		3.54, J_{AB} = 14	4.28, J_{cb} = 3	3.90 (m), J_{ac} = 1

[a] m, multiplet; coupling constants (J) in cycles per second.

ides **11a–f** (Table V). Under similar conditions, the tricyclic enamines **4a–c** reacted with sulfene to yield the corresponding tetracyclic aminothietane dioxides **12a–c**



3 11



4 12

(Table V). Examination of the nmr spectra of the adducts (Table VI) reveals that the nonequivalent methylene hydrogens (H_a, H_b) adjacent to the sulfone group appear as an AB quartet and that each peak of the AB quartet is additionally split into a doublet. The coupling constant (J_{AB} = 14 cps) is in good agreement with the coupling constants expected for geminal protons. The pair of doublets at lower field was assigned to H_b, since H_b is subject to substantial deshielding from the proximate amino group, while H_a is effectively removed from the area of strong deshielding and therefore resonates at higher field. Based on these assignments, the splitting of the pair of AB lines at lower field can be attributed to a *cis*-1,3-transannular interaction with H_c, while the splitting of the upfield pair is due to a *trans*-1,3-transannular interaction of H_a with H_c. The tertiary hydrogen H_c appears as a multiplet which is not well enough resolved to permit a detailed analysis. Furthermore, in view of the complexity of the spectrum at higher field, it has not been possible to establish whether H_c is coupling with a bridgehead or bridge methylene proton of the norbornane system. Consequently, although attack of sulfene from the *exo* side is to be expected,[9] confirmation of *exo* addition based on nmr data has not been possible.

The cycloaddition of sulfene to bicyclic and tricyclic enamines derived from norbornanone (**1**) and *exo*-tricyclo[5.2.1.$0^{2,6}$]decan-8-one (**2**) appears to be stereoselective inasmuch as only single adducts were obtained. However, in view of the low yields of adducts isolated, mention should be made of the possibility that only the major isomer was isolated and that the minor isomer, if indeed any was formed, was lost during work-up.

Experimental Section

All melting points and boiling points are uncorrected, and melting points were taken with a Mel-Temp capillary melting point apparatus. Infrared spectra were determined with Baird-Atomic Models 4-55 and AB-2 and Perkin-Elmer Model 21 spectrometers

with potassium bromide pellets or Nujol mulls of the solids, and neat samples of the liquids. Nmr spectra were obtained from Varian A-60 and HA-100 spectrometers using tetramethylsilane as internal standard and $CDCl_3$ as solvent. Elemental analyses were performed by Union Carbide European Research Associates, Brussels, Belgium. Norbornanone was obtained from Aldrich Chemical Co. *exo*-Tricyclo[5.2.1.$0^{2,6}$]decan-8-one was derived from dicyclopentadiene in three steps, by a procedure similar to that described in the literature.[12,13] Toluene and benzene were dried over sodium. The secondary amines employed were dried over potassium hydroxide and freshly distilled prior to use.

General Procedure for Enamine Formation.—A solution of norbornanone (55 g, 0.5 mol) and secondary amine (1.5 mol) in 300 ml of toluene was refluxed for 14 days, under a 3-ft column packed with glass helices and topped with a water separator. The solution was concentrated *in vacuo*. The residue was distilled through a 6-in. column packed with glass helices at reduced pressure to give the enamine which was analyzed by vapor phase chromatography. The analytical gas chromatography was performed on an F & M Model 720 dual column chromatograph with helium as carrier gas, on a 12 ft × 0.25 in. column of poly(*m*-phenyl ether) (5% suspended on Chromosorb G, DMCS treated), at a flow rate of 60 ml/min, and at a column temperature of 200°. The relative areas of enamine and saturated amine were measured by a disk integrator, and in converting to weight ratios it has been assumed that area per cent = weight per cent. For the analyses of enamines **3e** and **3f** a 5 ft × 0.25 in. column packed with 10% phenyl diethanolamine succinate on Anakrom was used.

General Procedure for Iminium Perchlorate Salt Formation.—A solution of enamine (0.01 mol) in 15 ml of ethanol was treated with a solution of 70% perchloric acid (1.44 g) in 5 ml of ethanol. The salt crystallized from solution during the addition and was recrystallized to constant melting point from ethanol.

General Procedure for Formic Acid Reduction.—90% Formic acid (5.1 g) was added dropwise to the enamine (0.1 mol) at room temperature with vigorous stirring. After a short induction period, the addition was accompanied by a vigorous evolution of carbon dioxide, and the temperature rose to 60° and was maintained at 50–60° by external cooling. After the addition was completed the mixture was stirred and heated at 60–70° for 1–2 hr. The mixture was poured into dilute hydrochloric acid and extracted with ether. The aqueous solution was made basic with sodium hydroxide and extracted with ether. Distillation of the dried ether extract furnished the saturated amine.

General Procedure for the Catalytic Hydrogenation of Bicyclic and Tricyclic Enamines.—A solution of enamine (0.1 mol) in 100 ml of ethanol was hydrogenated over 1.0 g of a 5% Pd/C catalyst in a Parr apparatus at an initial pressure of 50 psi. After hydrogen uptake ceased, the catalyst was removed by filtration. After evaporation of the ethanol the residue was distilled through an 8-in. Vigreux column under reduced pressure to give pure saturated amine.

General Procedure for Perchlorate Salt Formation of Saturated Amines.—A solution of 70% perchloric acid (1.44 g) in 5 ml of ethanol was added dropwise to a solution of saturated amine (0.01 mol) in 10 ml of ethanol. When the addition was completed the salt was precipitated by addition of excess ether and recrystallized from ethanol.

General Procedure for Reaction of Methanesulfonyl Chloride with Bicyclic and Tricyclic Enamines.—A solution of methanesulfonyl chloride (13.8 g, 0.12 mol) in 20 ml of dry purified tetrahydrofuran was added dropwise during 1 hr to a stirred mixture of enamine (0.1 mol) and triethylamine (12.1 g, 0.12 mol) in 100 ml of tetrahydrofuran at 5° under a nitrogen atmosphere. During the addition the temperature was maintained at 5–10° by use of an ice bath. When the addition was completed the mixture was allowed to stand overnight at ambient temperature. The precipitated triethylamine hydrochloride was separated by filtration and washed with tetrahydrofuran and a little ether. The combined filtrates were evaporated under reduced pressure, and the resulting solid or semisolid was purified by crystallization.

Registry No.—**3a**, 20238-04-4; **3b**, 5024-92-0; **3c**, 20238-06-6; **3d**, 20238-07-7; **3e**, 20238-08-8; **3f**, 20238-09-9; **4a**, 20238-33-9; **4b**, 20238-34-0; **4c**, 20238-37-3; **5a**, 20238-38-4; **5b**, 20238-39-5; **5c**, 20238-40-8; **5d**, 20238-41-9; **5e**, 20238-42-0; **5f**, 20238-43-1; **6a**, 20238-44-2; **6b**, 20238-45-3; **6c**, 20238-46-4; **7a**, 5024-72-6; **7b**, 5024-76-0; **7c**, 5024-78-2; **7d**, 5024-77-1; **7e**, 20238-27-1; **8a**, 20290-68-0; **8b**, 20238-47-5; **8c**, 20238-48-6; **9a**, 6200-89-1; **9b**, 20238-50-0; **10a**, 20238-51-1; **10b**, 20238-52-2; **10c**, 20238-53-3; **10d**, 20238-54-4; **10e**, 20238-55-5; **10f**, 20238-56-6; **11a**, 20238-28-2; **11b**, 20238-29-3; **11c**, 20238-30-6; **11d**, 20238-31-7; **11e**, 20238-32-8; **11f**, 20290-67-9; **12a**, 20238-01-1; **12b**, 20238-02-2; **12c**, 20238-03-3.

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(12) H. A. Bruson and T. W. Riener, *J. Amer. Chem. Soc.*, **67**, 723 (1945).
(13) P. D. Bartlett and A. Schneider, *ibid.*, **68**, 6 (1946).