Trimethylsilyl-Substituted Norbornenes, Norbornanes, and Nortricyclene[1]

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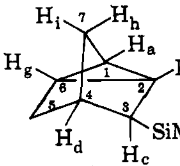
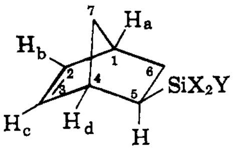
The reaction of vinylsilanes with cyclopentadiene and the addition of silanes to bicycloheptadiene have been explored as routes to 5-trimethylsilylbicyclo[2.2.1]hept-2-enes. Structural and configurational assignments have been made on the basis of infrared and n.m.r. spectra and independent synthesis.

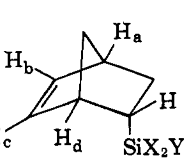
In connection with studies on the chemistry of cyclic compounds substituted by organometallic functions we sought to prepare compounds I, II, and III. The two most obvious routes were addition of silicon hydrides to a double bond of bicycloheptadiene (hydrosilation) and the Diels–Alder reaction between vinylsilanes and cyclopentadiene. The first route has been studied by Petrov, *et al.*, who showed that both norbornenes and nortricyclenes were formed, but they did not attempt to establish the stereochemistry of the products.[3] Wagner and his co-workers[4] have reported the use of the Diels–Alder approach. We have studied each reaction with different silanes and have determined the proportions of I, II, and III formed in each case. Structural assignments were based on infrared and n.m.r. spectral studies and configurations were assigned on the basis of n.m.r. spectra and independent synthesis.



I



II



III

a, X = Y = Cl c, X = Y = CH_3
b, X = Cl; Y = CH_3 d, X = Y = OET

Hydrosilation of Bicycloheptadiene.—Among the catalysts which have been used for the hydrosilation of carbon–carbon multiple bonds are chloroplatinic acid,[5–8] free-radical sources,[5,6,9,10] and platinum on charcoal.[5,9] We have examined the hydrosilation of bicycloheptadiene with methyldichlorosilane and trimethylsilane using chloroplatinic acid as catalyst; with trichlorosilane, methyldichlorosilane, and trimethylsilane using platinum on charcoal; and with trichlorosilane using azobisisobutyronitrile catalysis. The results are summarized in the first six entries of Table I.

The chloroplatinic acid catalyzed hydrosilation of bicycloheptadiene is the first reported case of *endo* addition which produces a norbornenyl product. This is a surprising result in view of the fact that the *exo* side of bicycloheptadiene is the least hindered.[11] This is amply documented by numerous other examples.[12] In each case in which the stereochemistry of the norbornenyl adduct has been determined it has been found that the product was that expected to result from *exo* attack by the initiating electrophile or free radical.[12] The novel stereochemical course of the hydrosilation probably reflects the ability of the *endo* side of the bicycloheptadiene molecule to function as a bidentate ligand.[13] We suggest that the course of hydrosilation catalyzed by chloroplatinic acid procedes to a large extent by a mechanism in which "coordination control" plays an important role. In the present instance a silane–olefin–catalyst complex[8,14] becomes coordinated to the *endo* side of the diene and the reaction proceeds by 2,3-addition to provide the *endo*-norbornene adduct, or by 2,6-addition to provide the nortricyclene. A similar mechanism is indicated in the chloroplatinic acid catalyzed addition of trimethylgermane to norbornadiene which yields 75%

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[3] A. D. Petrov, *et al.*, *Zh. Obshch. Khim.*, **31**, 1199 (1961).

[4] G. H. Wagner, D. L. Bailey, A. N. Pines, M. L. Dunham, and D. B. McIntire, *Ind. Eng. Chem.*, **45**, 367 (1953).

[5] R. A. Benkeser, M. L. Burrous, L. E. Nelson, and J. V. Swisher, *ibid.*, **83**, 4385 (1961).

[6] T. G. Selin and R. West, *ibid.*, **84**, 1856, 1860, 1863 (1962).

[7] A. G. Smith, J. W. Ryan, and J. L. Speir, *J. Org. Chem.*, **27**, 2183 (1962).

[8] J. Saam and J. L. Speier, *J. Am. Chem. Soc.*, **83**, 1351 (1961).

[9] R. A. Benkeser and R. A. Hickner, *ibid.*, **80**, 5298 (1958).

[10] J. L. Speier and J. A. Webster, *J. Org. Chem.*, **21**, 1044 (1956).

[11] J. Meinwald, Y. C. Meinwald, and T. N. Baker, III, *J. Am. Chem. Soc.*, **85**, 2513 (1963).

[12] Powerful dienophiles, such as maleic anhydride [E. F. Ullman, *Chem. Ind.* (London), 1173 (1958)], bis(trifluoromethyl)acetylene [C. G. Krespan, B. C. McKusick, and T. L. Cairns, *J. Am. Chem. Soc.*, **83**, 3428 (1961)], dicyanoacetylene [C. D. Wies, *J. Org. Chem.*, **28**, 74 (1963)], tetracyanoethylene [A. T. Blomquist and Y. C. Meinwald, *J. Am. Chem. Soc.*, **81**, 667 (1959)], and acrylonitrile [G. N. Schrauzer and S. Eichler, *Chem. Ber.*, **95**, 2764 (1962); H. K. Hall, Jr., *J. Org. Chem.*, **25**, 42 (1960)], react *via* 2,6-addition to produce tetracyclo[3.2.1.1^{3,8}.0^{2,4}]nonanes. Dimethyl diazodicarboxylate also reacts to give a 2,6-adduct as well as an olefinic product of undetermined structure [S. J. Cristol, E. L. Allred, and D. L. Wetzel, *ibid.*, **27**, 4058 (1962)]. Under ionic conditions water, methanol, performic acid, hydrogen bromide [G. T. Youngblood, C. D. Trivette, Jr., and P. Wilder, Jr., *ibid.*, **23**, 684 (1958)], bromine [S. Winstein and M. Shatavsky, *J. Am. Chem. Soc.*, **78**, 592 (1956)], iodine [H. W. Johnson, Jr., and P. N. Landerman, *J. Org. Chem.*, **27**, 303 (1962)], and *t*-butyl hydroperoxide [N. A. Milas and P. P. H. L. Otto, *ibid.*, **25**, 2225 (1960)] yield predominantly or exclusively nortricyclene derivatives. Nortricyclenes are also formed upon reaction with boron trichloride, phenylboron dichloride [F. Joy and M. F. Lappert, *Proc. Chem. Soc.*, 353 (1960)], stannic bromide [F. M. Rabel and R. West, *J. Am. Chem. Soc.*, **84**, 4169 (1962)], methylphosphonous dichloride [M. Green, *Proc. Chem. Soc.*, 177 (1963)], and 1-iodoperfluoropropane [N. O. Brace, *J. Org. Chem.*, **27**, 3027 (1962)]. On the other hand, benzyne, tetrafluoroethylene [R. J. Shozda and R. E. Putnam, *ibid.*, **27**, 1557 (1962)], diborane [H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **81**, 5832 (1959)], nickel carbonyl [C. W. Bird, R. C. Cookson, J. Hudec, and R. O. Williams, *J. Chem. Soc.*, 410 (1963)], methylene iodide–zinc–copper couple [H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959)], and triphenylchromium [W. Metlesics, P. J. Wheatley, and J. Zeiss, *ibid.*, **84**, 2327 (1962)] undergo reaction to form norbornenes by predominantly *exo* addition. Nitrosyl chloride [J. Meinwald, Y. C. Meinwald, and T. N. Baker, III, *ibid.*, **85**, 2513 (1963)] adds to norbornene and norbornadiene *via exo–cis* addition. The free-radical additions of thiophenol and *p*-thiocresol produce mixtures of 3-nortricyclyl aryl thio ether and *exo*-5-norbornenyl aryl thio ether [S. J. Cristol, G. D. Brindell, and J. A. Reeder, *ibid.*, **80**, 635 (1958); D. J. Trecker and J. P. Henry, *ibid.*, **85**, 3204 (1963)]. Other free-radical addends yield nortricyclenes exclusively upon reaction with norbornadiene (preceding reference).

[13] E. W. Abel, M. A. Bennet, and G. Wilkinson, *J. Chem. Soc.*, 3178 (1959).

[14] J. W. Ryan and J. L. Speier, *J. Am. Chem. Soc.*, **86**, 895 (1964).

TABLE I

DATA ON PREPARATION OF SILYLNORBORNENES AND -NORTRICYCLENES

Silane	Temp., °C.	Catalyst	Yield, %	Product distribution, % I	II	III
$HSiMeCl_2$[a]	50–60	H_2PtCl_6	80	30	6	64
$HSiMeCl_2$[a]	50–60	Pt–C	77	94		6
$HSiCl_3$[a]	35–50	Pt–C	25	100		
$HSiCl_3$[a]	80–100	AIBN	80[b]	53	28	7
$HSiMe_3$[a]	175–200	H_2PtCl_6	45	21	23	56
$HSiMe_3$[a]	175–200	Pt–C	55	12	35	53
$ViSiCl_3$[c]	50–60		68		20	80
$ViSiCl_3$[c,d]	175–200		73		50	50
$ViSiMeCl_2$[c]	50–60		40		27	73
$ViSiMeCl_2$[c,d]	175–200		58		55	45
$ViSi(OEt)_3$[c,d]	175–200		15		65	35

[a] Reaction was carried out with bicycloheptadiene. [b] An unidentified olefinic silane constituted 13% of this reaction mixture. [c] Reaction was carried out with cyclopentadiene; Vi denotes vinyl. [d] The cyclopentadiene was generated *in situ* from the dimer.

endo-norbornene, 15% *exo*-norbornene, and 10% nortricyclene.[15a] The coordinative ability of the diene may also determine the course of addition of certain electrophilic reagents such as tetracyanoethylene[16a] and stannic bromide.[16b]

Intermediate complexes between bicycloheptadiene and metal ions have been invoked to account for the course of reaction in two different ways. Zeiss[17] suggested that phenylation by triphenylchromium involves formation of an *endo* complex with triphenylchromium followed by transfer of a phenyl group to the *exo* side of the complex from another molecule of triphenylchromium. Schrauzer, on the other hand, suggests that the addition of acrylonitrile catalyzed by nickel (II) involves formation of a complex with acrylonitrile and the *endo* side of bicycloheptadiene as ligands followed by direct *endo* 2,6-addition of the nitrile to the diene.[18]

The results obtained in the hydrosilation of norbornadiene catalyzed by platinum on charcoal can be rationalized in terms of predominant or exclusive *endo* attack. "Coordination control" is again indicated in view of the contrasting 97% *exo* addition of methyldichlorosilane to norbornene (see below).

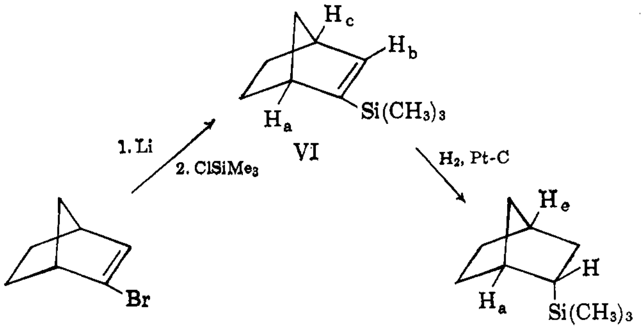
It has been suggested that the active species in chloroplatinic acid catalysis is metallic platinum formed by reduction of the Pt(IV) by the silane.[9] However, in the addition of methyldichlorosilane to bicycloheptadiene at 50–60°, platinum on charcoal and chloroplatinic acid give profoundly different results. The former produces a product mixture which consists of 94% Ib, whereas the latter produces a mixture which contains only 30% Ib. It can therefore be said that there are fundamental differences between the two catalyst systems.

The formation of a significant amount of the *endo* isomer in the free-radical-catalyzed hydrosilation constitutes an exception to the rule that free-radical additions to bicycloheptadiene give only *exo* products.[19] Another exception is the free-radical addition of trimethyltin hydride which gives nearly equal amounts of *endo* and *exo* 2,3-adducts.[15b] These observations suggest that even the attack by organosilyl and organotin radicals may be directed to some extent by coordination involving vacant d-orbitals. The higher polarizability of the organotin radical would account for the higher proportion of *endo* adduct in that case.

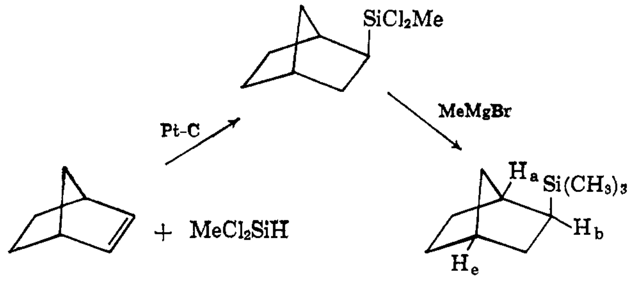
Diels–Alder Reaction between Vinylsilanes and Cyclopentadiene.—Reactions with vinyltrichlorosilane and methyldichlorosilane proceeded according to the rule of Alder and Stein[20] leading to the *endo* adduct as the major product at 50–60°; at 175–200° the distribution of isomers was essentially random. Vinyl triethoxysilane gave only a poor yield of adduct in which the *exo* isomer predominated.

The synthetic results indicate that the best route to the silylnortricyclene is the hydrosilation of bicycloheptadiene with trichlorosilane catalyzed by platinum on charcoal. The highest proportion of the *endo*-silylnorbornene IIIb is obtained by hydrosilation of bicycloheptadiene with methyldichlorosilane catalyzed by chloroplatinic acid at 50–60°; whereas, the highest proportion of the *exo*-silylnorbornene IIa results from the free-radical addition of trichlorosilane to the diene at 80–100°.

Configurational Assignments *via* Independent Synthesis.—As a means of establishing configurations of the products of the reactions discussed above, three synthetic schemes, each depending on the well-established rule of *exo* addition,[21] were carried out. Reaction 1 provided authentic *endo*-2-trimethylsilylnorbornane (IV). Catalytic hydrogenation of norbornenes has been shown to proceed predominantly by *exo* addition.[22] It has been suggested that platinum-catalyzed hydrosilation and hydrogenation proceed by analogous mechanisms with the catalyst polarizing the bond involving



IV (1)



V (2)

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(15) Unpublished observations from this laboratory: (a) R. H. Fish; (b) O. R. Kahn and I. J. Tyminski.

(16) (a) A. T. Blomquist and Y. C. Meinwald, *J. Am. Chem. Soc.*, **81**, 667 (1959); (b) F. M. Rabel and R. West, *ibid.*, **84**, 4169 (1962).

(17) W. Metlesics, P. J. Wheatley, and J. Zeiss, *ibid.*, **84**, 2327 (1962).

(18) G. N. Schrauzer and S. Eichler, *Chem. Ber.*, **95**, 2764 (1962).

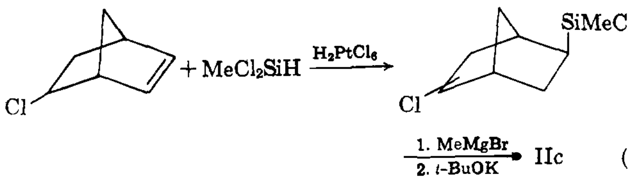
(19) D. J. Trecker and J. P. Henry, *ibid.*, **85**, 3204 (1963).

(20) K. Alder and G. Stein, *Angew. Chem.*, **50**, 514 (1937).

(21) (a) S. J. Cristol, J. R. Douglass, W. C. Firth, Jr., and R. E. Krall, *J. Org. Chem.*, **27**, 2711 (1962); (b) E. J. Corey, R. Harmann, and P. A. Vatakencherry, *J. Am. Chem. Soc.*, **84**, 2611 (1962).

(22) R. L. Burwell, Jr., *Chem. Rev.*, **57**, 895 (1957).

the hydrogen,[23] and supporting evidence has been obtained in the *cis* hydrosilation of acetylenes.[5,9] Accordingly, reaction 2 would be expected to provide *exo*-2-trimethylsilylnorbornane (V). Reaction 3 led to authentic IIc and gave V upon hydrogenation,



(3)

thus confirming the *exo* configuration of the trimethylsilyl group. Authentic IIIc was not prepared independently, and could not be separated from mixtures with IIc. However, hydrogenation of mixtures yielded the corresponding trimethylsilylnorbornanes which could be separated by gas chromatography and characterized individually.

N.m.r. Spectra.—The norbornenyl and nortricyclyl carbon skeletons can be distinguished because of the absorption by the vinyl protons of the former near 6 p.p.m.

The configurational assignments of the norbornenyl isomers were confirmed by n.m.r. spectroscopy. Fraser[24] has observed that protons or proton-bearing substituents of bicyclo[2.2.1]hept-2-enes are shielded by the magnetically anisotropic double bond when in the *endo* 5-position and deshielded when in the *exo* 5-position. Saturation of the double bond removes the effect and the *endo* signals move downfield and the *exo* signals move upfield. These observations apply to the methyl protons of the trimethylsilyl and methyldichlorosilyl groups and even to the methyl and methylene protons of the triethoxysilyl group, which are considerably farther removed from the double bond in the 2,3-position, as can be seen by inspection of Table II. Hydrogenation of IIc and IIIc causes shifts of the trimethylsilyl proton resonances from 0.00 to −0.04 and from −0.10 to 0.00 p.p.m., respectively, as expected.

Table II

Variation of Chemical Shifts as a Function of the Stereochemistry at C-5

Compd.	Assignment	P.p.m.[a]
IIc	$Si(CH_3)_3$	0.00[b]
IIIc		−0.10[b]
IIb	$SiCl_2CH_3$	0.78[b]
IIIb		0.60[b]
IId	CH_3	1.19[c]
	CH_2	3.81[c]
IIId	CH_3	1.14[c]
	CH_2	3.75[c]

[a] Relative to tetramethylsilane. [b] 20% solutions in carbon tetrachloride. [c] Neat.

The vinyl region of the n.m.r. spectrum of 5-*exo*-trimethylsilyl-2-norbornene (IIc) is shown in Fig. 1. This is a pair of typical AB[25] patterns split by 3.0 c.p.s. by coupling with the adjacent bridgehead protons,

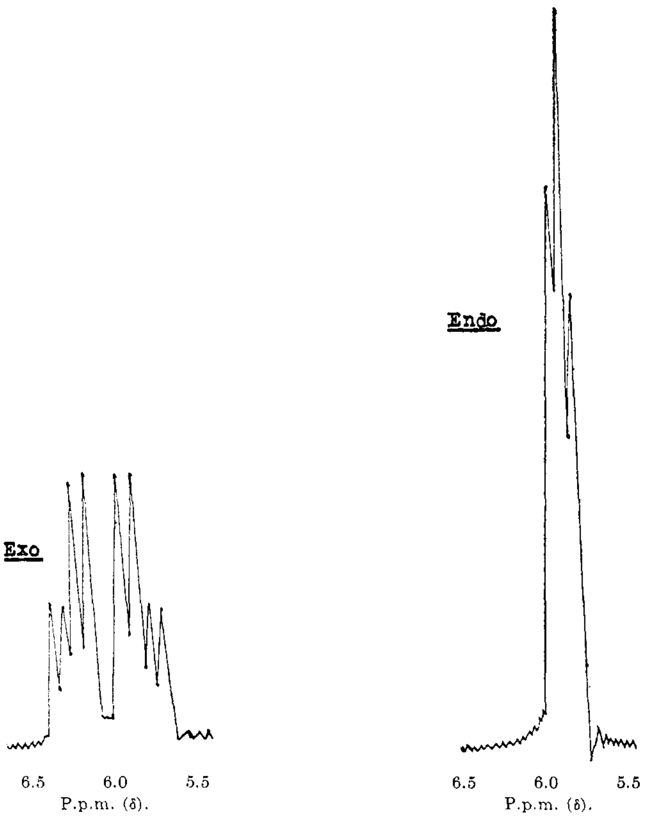


Fig. 1.—The vinyl region in the n.m.r. spectra of bicyclo[2.2.1]hept-2-en-5-yltrimethylsilanes.

with $J_{bc} = 5.5$ c.p.s. and $\delta_{bc} = 15$ c.p.s. The splitting pattern for the *endo* isomer, on the other hand, appears as a triplet as shown in Fig. 1.

We may treat the set comprising the vinyl and bridgehead protons as an A_2X_2 system. In such a case the triplet could arise in either of two ways. In the first, the coupling between the vinyl proton and the nearest bridgehead proton, J, would be of the same magnitude as between the vinyl proton and the allylic bridgehead proton, J'. In this event the separation in the triplet would be $(J + J')/2$ leading to a value of 1.8 c.p.s. for J. However, this value is too small, for a survey of the literature reveals that coupling constants among vinyl and bridgehead protons vary only slightly with rather drastic changes in the stereochemistry, number, and nature of substituents at the 5-, 6-, and 7-positions of the norbornene skeleton.[26–29] Values of J vary between 2.4 and 3.0 c.p.s., vinyl coupling constants J_{bc} vary between 5.0 and 5.8 c.p.s., and the allylic couplings J_{bc} and J_{bd} vary between 0.0 and 1.0 c.p.s. A second, more reasonable, explanation is that the A_2X_2 set is a "deceptively simple spectrum" which can arise, as pointed out by Abraham and Bernstein,[30] if the condition

$$(J - J')^2/(J_{bc} - J_{ad}) \leqslant \Delta\nu_{1/2}$$

where $\Delta\nu_{1/2}$ is the band width at half-height of the component lines and has a value of 0.3 c.p.s. for the Varian A-60 spectrometer, is met. Consistency with previously observed coupling constants and the observed

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[23] L. Goodman, R. M. Silverstein, and J. N. Shoolery, *J. Am. Chem. Soc.*, **78**, 4493 (1956).

[24] R. R. Fraser, *Can. J. Chem.*, **40**, 78 (1962).

[25] K. B. Wiberg and B. J. Nist, "Interpretation of N.M.R. Spectra," W. A. Benjamin, Inc., New York, N. Y., 1962.

[26] O. L. Chapman, *J. Am. Chem. Soc.*, **85**, 2014 (1963).

[27] P. Laszlo and P. von R. Schleyer, *ibid.*, **85**, 2017 (1963).

[28] P. Laszlo and P. von R. Schleyer, Abstracts of Papers, 145th National Meeting of the American Chemical Society, New York, N. Y., 1963, p. 3T.

[29] P. Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.*, **85**, 2709 (1963).

[30] R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 216 (1961).

spectrum results if we assume that $J_{bc} = 5.5$ c.p.s. and $J_{ad} = 0.0$ c.p.s. These values, along with the experimentally observed line separation of 1.8 c.p.s. which equals $(J + J')/2$ and the maximum value of 1.8 c.p.s. for $J - J'$, give $J = 2.7$ c.p.s. and $J' = 0.9$ c.p.s.

The variation in chemical shifts of the bridgehead protons shown in Table III can be interpreted in terms of stereochemical and electronegativity effects of silicon function. In IIIc both protons appear at 2.92 p.p.m. indicating that the trimethylsilyl group exerts a negligible inductive effect. In the *exo* isomer the resonance at 2.72 p.p.m. is assigned to H_d, and the upfield shift is attributed to shielding by the magnetically anisotropic carbon–silicon bond, the angle between the axis of this bond and a line joining its midpoint to H_d being less than 55°.[31] In IIIa and IIIb the greater electronegativity of the chlorosilyl groups causes both of the protons to move downfield owing to inductive deshielding, with the greater effect being felt by the closer H_d. In IIa and IIb this inductive deshielding is just counterbalanced by the magnetic anisotropy effect and both protons have the same chemical shift in each compound. As would be expected, if only the inductive effect operates, the chemical shift of H_a is the same in IIa as in IIIa, and in IIb as in IIIb. Other n.m.r. data are found in Table IV.

TABLE III

CHEMICAL SHIFTS OF BRIDGEHEAD HYDROGENS OF 5-SUBSTITUTED NORBORNENE DERIVATIVES[a,b]

Compd.	H_a	H_d
IIc	2.92	2.72
IIb	3.03	3.03
IIa	3.10	3.10
IIIc	2.92	2.92
IIIb	3.00	3.18
IIIa	3.10	3.27

[a] Probable errors are ±1.0 to ±2.0 cps. Values are given as p.p.m. [b] The samples were run as 20% solutions in carbon tetrachloride with tetramethylsilane as internal reference.

Infrared Spectra.—The spectra of nortricyclenes have a C–H stretching frequency of the cyclopropyl hydrogens at 3070 cm.$^{-1}$ and a characteristic band at 800 cm.$^{-1}$.[32] Nortricyclenes substituted on the cyclopropane ring also have bands near 860 and 780 cm.$^{-1}$ as shown by Hart and Martin.[6] Compound Ia showed a strong absorption at 800 cm.$^{-1}$, and Ic had a strong band at 795 with a shoulder at 802 cm.$^{-1}$. These bands are obscured by an intense band due to the $SiCl_2CH_3$ group around 800 cm.$^{-1}$, in Ib, which is also present in IIb and IIIb. The absence of a band in the spectrum of Ib in the 825–890-cm.$^{-1}$ region indicates that it is not a 1-substituted nortricyclene.[33]

The spectra of all of the norbornenes displayed the carbon–carbon double stretching frequency at 1570 cm.$^{-1}$ [32b,34–36] and the strong sharp C–H in-plane deformation at 1335 cm.$^{-1}$. Compounds IIa, IIIa, IIc, and IIIc have only weak absorbances in the 800–810-cm.$^{-1}$ region.

TABLE IV

N.M.R. SPECTRAL DATA

Chemical[a] shift, p.p.m.	Area (calcd.)	Multiplicity	Coupling constant[b]	Assignment[c]
		Ia		
2.35	1	Multiplet		d
1.63	11	Unsym. doublet	$J_{hi} = 11.5$	h
1.16–1.48	7	Complex		
		Ib		
2.21	1	Multiplet		d
1.10–1.56	8	Complex		
0.72	3	Singlet		$SiCH_3$
		Ic		
1.94	1	Multiplet		d
1.10–1.22	4	Complex		
1.02	3	Singlet		a, b, g
0.62	1	Broad singlet		c
−0.02	9	Singlet		$SiCH_3$
		IIc		
6.13	1	Unsym. quartet	$J_{bc} = 5.5$	b or c
5.87	1	Unsym. quartet	$J_{ab} = J_{cd} = 3.0$	b or c
2.92	1	Broad singlet		a
2.72	1	Broad singlet		d
0.19–1.82	5	Complex		
0.00	9	Singlet		$SiCH_3$
		IIIc		
5.95	2	Triplet	$J_{ab} = J_{cd} \cong 3.0$	b and c
2.92	2	Multiplet		a and d
0.78–2.10	5	Complex		
−0.10	9	Singlet		$SiCH_3$
		IV		
2.31	2	Multiplet		a, e
0.78–1.78	9	Complex		
0.00	9	Singlet		$SiCH_3$
		V		
2.20	2	Broad multiplet		a, e
1.13–1.61	8	Complex		
0.55	1	Unsym. triplet		b
−0.04	9	Singlet		$SiCH_3$
		VI		
6.29	1	Doublet	$J_{bc} = 3.0$	b
2.85–2.93	2	Broad singlet (sh)		a, c
0.83–1.68	6	Complex		
0.06	9	Singlet		$SiCH_3$

[a] Probable errors are −0.05 p.p.m. [b] Given in c.p.s. Probable error is ±0.2 c.p.s. Samples were run as carbon tetrachloride solutions. [c] See structures I–III in text for numbering system.

Differences in the spectra of the *endo* and *exo* isomers consist primarily of weak bands in the fingerprint region. These are distinguished from the other bands listed in the Experimental section by being enclosed in parentheses.

Experimental

General Considerations.—Reagents were used without purification unless otherwise specified. The silanes were purchased from the Union Carbide Company; the norbornene was obtained from the Aldrich Company. The authors are grateful to the Shell Chemical Company for providing a generous quantity of bicycloheptadiene.

The infrared spectra were all taken using a Perkin-Elmer Model 21 spectrometer. The n.m.r. data were recorded using a Varian

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(31) H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957).

(32) (a) G. E. Pollard, *Spectrochim. Acta*, **18**, 837 (1962); (b) J. D. Roberts, E. R. Trumbull, W. Bennet, and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3116 (1950).

(33) H. Hart and R. A. Martin, *J. Org. Chem.*, **24**, 1267 (1959).

(34) H. E. Simmons, *J. Am. Chem. Soc.*, **83**, 1657 (1961).

(35) P. von R. Schleyer, *ibid.*, **80**, 1700 (1958).

(36) C. F. Wilcox, Jr., and R. R. Craig, *ibid.*, **83**, 3866 (1961).

A-60 instrument.[37] The gas–liquid chromatographic (g.l.c.) analyses were carried out using a F & M Model 300 programmed temperature gas chromagraph with helium as the carrier gas at a flow rate of 30 ml./min.

All yields are based on reacted starting material.

Analyses were made by Galbraith Laboratories, Knoxville, Tenn.

Analysis of Product Mixtures.—The reaction mixtures resulting from the use of halosilanes were methylated and the product analysis was carried out on the alkylated silanes. The *exo*- and the *endo*-bicyclo[2.2.1]hept-2-en-5-yltrimethylsilanes always appeared as one peak on gas chromatograms; separation of the isomers remains to be achieved. However, the tricyclo[2.2.1.$0^{2,6}$]hept-3-yltrimethylsilane (Ic) is easily separated from the norbornenes IIc and IIIc using a 4-ft. column of 20% Apiezon L on Chromosorb 60–80 mesh with the temperature programmed at 13°/min. from an injection temperature of 100°. Mixtures consisting of IIc and IIIc only were assayed by measuring the areas under the respective peaks in the n.m.r. spectra due to the protons of the methylsilyl functional group. In mixtures containing all three compounds Ic–IIIc the *exo* to *endo* ratios were determined by inspection of the vinyl region. The downfield half of the symmetrical *exo* multiplet is free of interference by the *endo* triplet; thus measurement of the areas of the vinyl region as diagrammed in Fig. 2 could be used to determine the relative amounts of each. The per cent of *exo* trimethylsilyl norbornene IIc is given by the equation $100 \cdot 2(x)/[(x) + (y)]$.

Positive identification of the products of the Diels–Alder reaction was made by hydrogenating the mixture of IIc and IIIc under conditions identical with those used to hydrogenate bicyclo[2.2.1]hept-2-en-2-yltrimethylsilane. The resulting two saturated isomers were then isolated in quantities sufficient for positive infrared spectral identification by using a copper column 0.25 in. × 17 ft. packed with 20% silicone oil 200 on Chromosorb P. The infrared spectra of the saturated Diels–Alder products were identical with authentic samples of V and IV.

The methylated products from the chloroplatinic acid catalyzed addition of methyldichlorosilane to bicycloheptadiene were separated by careful fractional distillation. Identification of the components was made by infrared spectra and hydrogenation of the unsaturated components. The methylated products from the free-radical reaction were identified by a combination of fractional distillation and g.l.c., n.m.r., and infrared spectra.

Preparation of Platinum-on-Charcoal Catalyst.—The procedure used is identical with that described by Baltzly.[38] Because of the capricious nature of catalysis, the materials used are listed here: (1) chloroplatinic acid prepared by dissolving 3 g. of platinic chloride in 100 ml. of water with 0.02 g. of lead acetate; (2) Norit A produced by Matheson Coleman and Bell; and (3) palladium chloride.

Methylation Procedure for Chlorosilanes.—The chlorosilane was added slowly to a 10% excess of 0.5 *M* methylmagnesium bromide in diethyl ether. After the addition was complete, the reaction mixture was stirred under reflux for 6 hr. and poured into a mixture of saturated aqueous ammonium chloride, ice, and 100 ml. of ether. The ether layer was separated, washed successively with water and saturated aqueous sodium chloride, and dried over magnesium sulfate. The ether was removed at atmospheric pressure and the product was distilled at reduced pressure.

Bicyclo[2.2.1]hept-2-en-2-yltrimethylsilane (VI).—The bicyclo[2.2.1]hept-2-en-2-yl bromide was prepared as described by LeBel.[39]

A suspension of 1.5 g. of lithium sand containing 2% sodium in 25 ml. of anhydrous tetrahydrofuran was placed in a 50-ml. round-bottom flask, equipped with a condenser, drying tube, stirrer, and pressure-equalizing dropping funnel. The system was frequently flushed with nitrogen during the course of the reaction. The reaction flask was chilled to 0° and 8.64 g. (0.053 mole) of bicyclo[2.2.1]hept-2-en-2-yl bromide was added dropwise with rapid stirring. Fifteen minutes after the addition was complete 5.94 g. (0.055 mole) of freshly distilled trimethylchlorosilane was added dropwise. This reaction mixture was stirred for 2 hr. at 0°. It was then poured onto a mixture of saturated aqueous ammonium chloride, ice, and 200 ml. of diethyl ether.

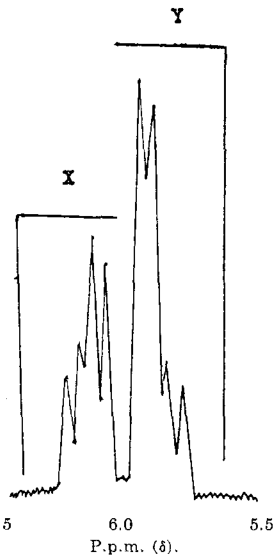

Fig. 2.—Illustrative n.m.r. analysis of a mixture of IIc and IIIc.

The ether layer was separated and extracted successively with 50-ml. portions of water and saturated aqueous sodium chloride, and dried over magnesium sulfate. The ether was removed by distillation at atmospheric pressure. Vacuum distillation of the residue yielded 3.0 g. (36%) of VI having b.p. 30° (0.55 mm.), $n^{24}\text{D}$ 1.4630. A gas chromatogram, obtained with a 4-ft. column of 20% Apiezon L on Chromosorb 60–80 mesh, indicated greater than 99% purity; infrared spectrum: $\nu_{\max}$ (film) 3105 (w), 2920, 2850, 1555, 1298, 1248, 1120, 1038, 855, 810, 792, and 750 cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_{18}Si$: C, 72.22; H, 10.91; Si, 16.87. Found: C, 72.15; H, 11.04; Si, 16.61.

Bicyclo[2.2.1]hept-2-yl-*endo*-trimethylsilane (IV).—A sample of 1.75 g. (0.01 mole) of the bicyclo[2.2.1]hept-2-en-2-yltrimethylsilane was added to 10 ml. of ethyl acetate containing 50 mg. of prereduced Adams catalyst. The mixture was hydrogenated at 25 p.s.i. in a Parr hydrogenator for 12 hr. The ethyl acetate was removed and the product was distilled, yielding in excess of 1 g. of the anticipated product; b.p. 31° (0.75 mm.); $n^{24}\text{D}$ 1.4637; infrared spectrum: $\nu_{\max}$ (film) 2965, 2875, 1248, (1191), (1163), 910, 868, 832, (763), 749, and 743 cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_{20}Si$: C, 71.34; H, 11.97; Si, 16.68. Found: C, 71.11; H, 12.07; Si, 16.58.

Bicyclo[2.2.1]hept-2-yl-*exo*-trimethylsilane (V).—A mixture of 20 g. (0.21 mole) of norbornylene, 26.4 g. (0.23 mole) of methyldichlorosilane, and 0.25 g. of the platinum on charcoal was heated at reflux for 2 hr. until the temperature increased to 100°. Distillation of the reaction mixture yielded 24.4 g. (55%) of adduct, b.p. 85.2–87.5° (0.20 mm.).

Methylation in the usual way yielded 11.5 g. (32%) of V, b.p. 34° (1.25 mm.), $n^{24}\text{D}$ 1.4624. G.l.c. of this product using a 17 ft. × 0.25 in. column of 20% paraffin oil on Chromosorb P indicated that it consisted of 97% *exo* isomer V plus 3% *endo* isomer IV. A pure sample collected by g.l.c. provided the following spectral data: $\nu_{\max}$ (film) 2970, 2865, 1248, (1209), (1187), (1147), (1137), 906, 873, 851, 828, 745, and 682 cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_{20}Si$: C, 71.34; H, 11.97; Si, 16.68. Found: C, 71.31; H, 12.04; Si, 16.89.

Bicyclo[2.2.1]hept-2-en-5-yl-*exo*-trimethylsilane (IIc).—The Diels–Alder reaction between vinyl chloride and cyclopentadiene was carried out as described previously.[32b] To 23.5 g. (0.19 mole) of the bicyclo[2.2.1]hept-5-en-2-yl chloride, thus prepared, was added 0.4 ml. of 0.1 *M* ethanolic chloroplatinic acid. This mixture was placed in a 250-ml. flat-bottomed flask equipped with a magnetic stirrer, condenser with a drying tube, and a pressure-equalizing dropping funnel, and 21.2 g. (0.18 mole) of methyldichlorosilane was added dropwise over a 30-min. period as the mixture was refluxed in a nitrogen atmosphere. At this time the solution suddenly turned black and the reaction proceeded vigorously. It was then stirred and heated at 60–70° for 15 min. Distillation yielded 2.8 g. of starting material and 36 g. (92%) of 1:1 adduct, b.p. 104–110° (1.3 mm.).

The usual work-up yielded two fractions: (1) b.p. 63–64° and (2) b.p. 76–79° (1.5 mm.). The first fraction is as yet unidenti-

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[37] Purchase of this instrument was made possible by a grant from the National Science Foundation.

[38] R. Baltzly, *J. Am. Chem. Soc.*, **74**, 4586 (1952).

[39] N. A. LeBel, *ibid.*, **82**, 623 (1960).

fied. The second fraction, 7.0 g. (23%), was used in the next step to prepare the *exo* isomer IIc.

Anal. Calcd. for $C_{10}H_{19}ClSi$: C, 59.22; H, 9.44. Found: C, 59.51; H, 9.63.

The potassium *t*-butoxide solution was prepared by adding 7 g. of potassium metal to 100 ml. of anhydrous *t*-butyl alcohol. As the solution was boiling, 5.5 g. (0.027 mole) of the trimethylsilylchloronorbornane was added quickly. The mixture was stirred and heated under reflux overnight. It was poured into 150 ml. of ice-water and 200 ml. of diethyl ether. The ether layer was separated and washed once with water and once with saturated aqueous sodium chloride. The washings were added to the the aqueous layer which was then extracted with 200 ml. of ether. The ether layer was separated and washed as before. Finally, the aqueous layers were extracted with 100 ml. of pentane. The combined pentane and ether layers were dried over magnesium sulfate, and concentrated at atmospheric pressure. Distillation of the residue yielded two fractions. The first fraction, 0.25 g. (10%), b.p. 34-36.2° (0.75 mm.), proved to be the desired bicyclic olefin IIc along with 10% *endo* isomer IIIc and 20% starting material. The second fraction, 2.5 g., b.p. 63-64° (0.50 mm.), appeared to be starting material in which the number of isomers had been reduced. The identity of this product was established by the hydrogenation to the saturated analog which was then purified by preparative g.l.c. for infrared spectral comparison with authentic bicyclo[2.2.1]hept-2-yl-*exo*-trimethylsilane. The infrared data for IIc were obtained using a sample purified by preparative-scale g.l.c. with a 4-ft. column of 20% Apiezon L on Chromosorb 60-80 mesh: ν_{max} (film) 3140 (vw), 3065 (w), 1569 (w), 1333, 1248, (1196), (1103), (1016), (975), 950, 888, 847, 827, 751, 715, and 684 cm.$^{-1}$.

This same reaction was carried out using the norbornenyl chloride prepared from the reaction of hydrochloric acid with bicycloheptadiene in petroleum ether (b.p. 30-60°) at −70°.[40] Presumably the chlorine would be in the *exo* position. This reaction sequence resulted in a mixture of 73% IIc and 27% IIIc as indicated by n.m.r. and g.l.c.

Anal. Calcd. for $C_{10}H_{18}Si$: C, 72.22; H, 10.91; Si, 16.87. Found: C, 72.03; H, 10.88; Si, 16.75.

Chloroplatinic Acid Catalyzed Reactions. A. Methyldichlorosilane with Bicycloheptadiene.—Because the results obtained in these laboratories are different from those previously reported,[3] the experimental procedure will be described in detail. To a flat-bottomed flask equipped with a magnetic stirrer, pressure-equalizing dropping funnel, and a condenser with a drying tube was added a mixture of 0.5 ml. of 0.1 *M* ethanolic chloroplatinic acid and 18 g. (0.20 mole) of bicycloheptadiene. To this was added dropwise 22.8 g. (0.20 mole) of methyldichlorosilane. The reaction was initiated by heating to 50°, and it then proceeded exothermically. The temperature was maintained at 40-50° by controlling the rate of addition of the silane. After the addition was complete, the reaction mixture was stirred for 1 hr. Distillation yielded one fraction, 32.3 g. (80%), b.p. 56-56.2° (0.35 mm.). The n.m.r. analysis carried out by measuring the areas under the appropriate peak due to the methyl protons of the Si-CH_3 group indicated that the mixture contained 64% of the *endo*-norbornenyl compound IIIb and the remaining 36% consisted of a mixture of the nortricyclene Ib and the *exo*-norbornenylmethyldichlorosilane (IIb). These results were confirmed by methylation of the reaction mixture and separation of the norbornenyl and nortricyclenic products by fractional distillation. Hydrogenation of the norbornenyl fraction and g.l.c. analysis of the resulting saturated products indicated that the *endo* isomer IV was contaminated by 9% V.

B. Trimethylsilane with Bicycloheptadiene.—This reaction was carried out in a sealed ampoule at 175° for 5 hr. A mixture of 2.06 g. (0.022 mole) of bicycloheptadiene and 1.64 g. (0.021 mole) of trimethylsilane with 0.1 ml. of ethanolic chloroplatinic acid yielded 1.3 g. (45%), b.p. 46-47° (1.5 mm.), of the product mixture and 0.8 g. of starting material.

Platinum-on-Charcoal-Catalyzed Reactions. A. Trichlorosilane with Bicycloheptadiene.—A mixture of 45.5 g. (0.49 mole) of bicycloheptadiene, 40.2 g. (0.29 mole) of trichlorosilane, and 0.25 g. of the platinum on charcoal was placed in a round-bottomed flask equipped with a condenser with a drying tube. The mixture was heated at reflux for 4 hr. Distillation yielded 16.6 g. (25%) of Ia: b.p. 48° (0.17 mm.); ν_{max} (film) 3060 (w), 2937, 2860, 1302, 1156, 822, 803, 742, and 672 cm.$^{-1}$. N.m.r. and g.l.c. indicated that only a trace of olefin was present in the product.

Anal. Calcd. for $C_7H_9Cl_3Si$: C, 36.94; H, 3.99; Cl, 46.74; Si, 12.33. Found: C, 37.04; H, 4.15; Cl, 46.51; Si, 12.15.

This material was methylated in the usual way to yield compound Ic: b.p. 81° (18 mm.); $n^{24}D$ 1.4690; ν_{max} (film) 3061 (w), 2950, 2862, 1299, 1248, 1152, 965, 930, 888, 855, 832, 795, 746, and 685 cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_{18}Si$: C, 72.22; H, 10.91; Si, 16.87. Found: C, 71.88; H, 10.80; Si, 17.13.

B. Methyldichlorosilane with Bicycloheptadiene.—A mixture of 18 g. (0.19 mole) of bicycloheptadiene, 0.1 g. of the catalyst,[38] and 22.0 g. (0.19 mole) of methyldichlorosilane was placed in a flask equipped with a magnetic stirrer, and condenser with a drying tube. The reaction mixture was heated at reflux and stirred for 1 hr. until the temperature increased to about 100°. Distillation yielded some starting material and 22.5 g. (77%) of the adduct, b.p. 57.2-57.6° (0.25 mm.). The n.m.r. analysis indicated that this mixture consisted of 92% methyldichlorosilylnortricyclene (Ib) and 8% *endo* compound IIIb. The previous results were substantiated by methylation of the mixture. The infrared spectrum gave the following results: ν_{max} (film) 3062 (w), 2942, 2865, 1299, 1261, 1250, 1152, 964, 928, 824, 805, 785 (vs), 761, and 738 cm.$^{-1}$.

C. Trimethylsilane with Bicycloheptadiene.—A mixture of 3.5 g. (0.04 mole) of bicycloheptadiene, 2.8 g. (0.04 mole) of trimethylsilane, and a catalytic amount of the platinum on charcoal was sealed under nitrogen in a glass ampoule. The ampoule was heated at 175-200° for 5 hr. under autogenous pressure. Distillation of the reaction mixture yielded 0.80 g. of starting material and 3.00 g. (55%), b.p. 46-47° (1.5 mm.), of product.

Free-Radical Reaction of Trichlorosilane with Bicycloheptadiene.—A solution of 19.70 g. (0.214 mole) of freshly redistilled bicycloheptadiene and 28.82 g. (0.213 mole) of trichlorosilane was separated into three equal portions. Each portion was sealed under nitrogen in a glass ampoule with 0.2 g. of azobisisobutyronitrile. The ampoules were then heated at 80-100° for 13 hr. under autogenous pressure. Distillation of the product mixture yielded starting material plus 11.00 g. (75%) of the product, b.p. 70-71° (0.5 mm.).

The methylation of the product was carried out in the usual way in 80% yield.

Diels-Alder Reactions. A. Vinylmethyldichlorosilane and Cyclopentadiene at Low Temperature.—To a flat-bottomed flask equipped with a magnetic stirrer, pressure equalizing dropping funnel, and a condenser with a drying tube was added 84.8 g. (0.6 mole) of methyldichlorovinylsilane. Freshly prepared cyclopentadiene at −70° was added to the silane in 10-ml. portions. After each addition the solution was heated to 50-60° to initiate the reaction. A total of 36 g. (0.54 mole) of cyclopentadiene was used. The reaction mixture was then heated at 50-60° for 1 hr. and distilled yielding 64.1 g. of the methyldichlorovinylsilane and 12 g. (40%) of product.

B. Vinyltrichlorosilane and Cyclopentadiene at Low Temperature.—This reaction was carried out as described above for the methyldichlorovinylsilane. A mixture of 121.2 g. (0.75 mole) of vinyltrichlorosilane and 47 g. (0.74 mole) of cyclopentadiene yielded 115 g. (68%) of the adduct, b.p. 62° (0.75 mm.).

C. High Temperature Diels-Alder Reactions.—The dicyclopentadiene was purified prior to use by passing it through alumina. The mixture containing 1 molar equiv. of the vinylsilane and 0.5 molar equiv. of dicyclopentadiene was sealed in a glass ampoule, the ampoule was then heated to 175-200° for 6 hr., and the contents were distilled. The following results were obtained: (1) a solution of 14.3 g. (0.089 mole) of freshly distilled trichlorovinylsilane and 5.9 g. (0.045 mole) of dicyclopentadiene yielded 13.0 g. (65%) of product on distillation, b.p. 44-45° (0.15 mm.), as well as 2.4 g. of starting material; (2) a solution of 13.2 g. (0.094 mole) of freshly distilled methyldichlorovinylsilane and 6.1 g. (0.046 mole) of dicyclopentadiene yielded 2.0 g. of starting material and 10 g. (58%) of product; (3) a mixture of 6.6 g. (0.050 mole) of dicyclopentadiene and 19 g. (0.10 mole) of triethoxyvinylsilane yielded 1.8 g. of starting material and 3.70 g. (15.5%) of 1:1 adduct (the rest of the material was high boiling); (4) if the temperature of the Diels-Alder reaction was allowed to exceed 230°, then a substantial amount of the 1-substituted nor-

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(40) M. Hanack and W. Kaiser, *Ann.*, **657**, 12 (1962).

tricyclene product was produced. This material was isolated, after methylation, by g.l.c. using an Apiezon L column and identified by infrared and n.m.r. spectra.

Methylation of Triethoxysilylnorbornenes.—A sample of 3.70 g. (0.014 mole) of the triethoxysilylnorbornene was added to 50 ml. of 4.6% methyllithium in diethyl ether. The solution was stirred for 2 days at room temperature. The work-up was carried out in a fashion identical with that used in the methylations with methylmagnesium bromide. Vacuum distillation yielded 1.5 g. (63%) of the product.

The Stereoselective Reaction of Bicyclic Enamines with Sulfene

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The cycloaddition of sulfene to bicyclic enamines derived from 5-norbornene-2-carboxaldehyde and various secondary amines afforded in stereoselective fashion a single substituted thietane dioxide in all but one case. Evidence is presented which demonstrates the configurational features of the adducts. Brief mention is also made of the quaternization of the 3′-substituted spiro[5-norbornene-2,2′-thietane] 1′,1′-dioxides.

This paper reports a study of the reactions of various enamines derived from 5-norbornene-2-carboxaldehyde (I) with methanesulfonyl chloride and triethylamine. Previous work has indicated that such a sulfonyl chloride–tertiary amine combination readily adds to appropriately activated olefins to afford substituted thietane dioxides.[2] More recently, such cycloaddition processes have been shown to proceed *via* sulfene intermediates.[3] The present research was undertaken because it appeared to offer the attractive opportunity to examine the stereoselectivity of sulfene addition to a bicyclic moiety.

5-Norbornene-2-carboxaldehyde (I)[4] readily condenses with a variety of secondary amines in refluxing toluene solution without added catalyst to produce in good yield the related enamines II (see Table I). The α,β-unsaturated amines were colorless liquids which could be stored without change for prolonged periods in a nitrogen atmosphere at 0° or below. Close scrutiny of the enamine structure II will reveal that two isomeric structures are possible in this system, the transoid form IIa and the cisoid counterpart IIb. Comparison of the n.m.r. spectra (in $CDCl_3$) of freshly distilled samples of several of the enamines listed in Table I with those reported by Slomp, MacKellar, and Umbreit[5] for the related *endo*- and *exo*-5-norbornene-2-carboxaldehydes (I) revealed that the transoid form predominated to the extent of 80 to 90% depending on the amine substituent. The ratio of the isomers could be readily determined by integration of the olefinic proton resonance peaks. The triplet pattern (characteristic of the *exo* aldehyde) was assigned to the cisoid form while the two sets of doublets of doublets (characteristic of the *endo* aldehyde) were assigned to the transoid isomer.

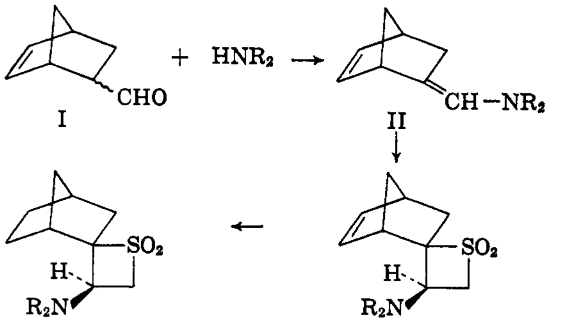
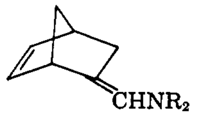
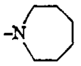
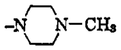
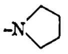
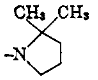
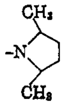
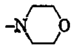
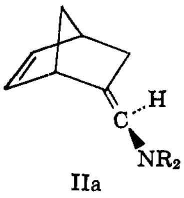


TABLE I

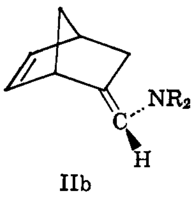
ENAMINES DERIVED FROM 5-NORBORNENE-2-CARBOXALDEHYDE



Compd.	R_2N-	Yield, %	B.p., °C. (mm.)	n_D (°C.)
IIa		85.0	126–129 (11)	1.5318 (26.5)
IIb		52.0	138–144 (16)	1.5355 (25)
IIc		76.5	140–145 (16)	1.5322 (24)
IId		71.5	116–121 (15)	1.5378 (24)
IIe		59.1	94–98 (1)	1.5282 (25)
IIf		64.5	68–70 (0.4)	1.5068 (26)
IIg		81.2	132–135 (14)	1.5346 (23)



IIa



IIb

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[1] Department of Chemistry, The Ohio State University, Columbus 10, Ohio.

[2] G. Stork and I. J. Borowitz, *J. Am. Chem. Soc.*, **84**, 313 (1962); G. Opitz and H. Adolph, *Angew. Chem.*, **74**, 77 (1962); W. E. Truce, J. J. Breiter, D. J. Abraham, and J. R. Norell, *J. Am. Chem. Soc.*, **84**, 303 (1962); W. E. Truce and J. R. Norell, *ibid.*, **85**, 3231 (1963); W. E. Truce, J. R. Norell, J. E. Richman, and J. P. Walsh, *Tetetrahedron Letters*, 1677 (1963); L. A. Paquette, *J. Org. Chem.*, **29**, 2854 (1964).

[3] I. J. Borowitz, *J. Am. Chem. Soc.*, **86**, 1146 (1964); see also J. F. King and T. Durst, *ibid.*, **86**, 287 (1964); W. E. Truce, R. W. Campbell, and J. R. Norell, *ibid.*, **86**, 288 (1964).

[4] Gas chromatographic analysis of this particular commercial sample demonstrated the presence of two major components of which 75% was the *endo* isomer and 25% the *exo* isomer. It is anticipated that either material would give rise to the same mixture of enamines, but we have not elucidated this point.

[5] G. Slomp, F. MacKellar, and G. R. Umbreit, to be published.