Studies in the Norbornene Series. Part I. Elucidation of the Structure of Norbornene Derivatives by Use of the Nuclear Magnetic Resonance Shift Reagent Trisdipivaloylmethanatoeuropium(III), the Nuclear Overhauser Effect,† and Mass Spectrometry

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An assessment of n.m.r. and mass spectral methods shows that the nuclear Overhauser effect and the shift reagent trisdipivaloylmethanatoeuropium(III) are particularly valuable in assigning the structure and stereochemistry of substituted norbornenes and of norbornanes carrying a fused heterocycle. Mass spectra support the structural assignments.

SYNTHETIC routes to norbornanes containing a fused heterocyclic system have been studied in order to prepare compounds of possible medicinal interest. During this work it was necessary to establish unambiguously the structure and stereochemistry of substituted norbornene derivatives and of norbornanes carrying a fused heterocycle. We now describe some results which establish that use of the nuclear Overhauser effect [1] and the shift reagent trisdipivaloylmethanatoeuropium(III) $[Eu(dpm)_3]$ [2-4] can provide diagnostic structural and stereochemical information in the norbornene series. Mass spectral data support the assignments but alone do not provide any obvious stereochemical information.

Application of the Nuclear Overhauser Effect (*NOE*).—In one approach to the preparation of norbornanes of the types (1) and (2) we employed the method of Alder and Windemuth,[5] which takes advantage of the fact that the strained double bond of bicyclo[2,2,1]heptene systems undergoes ready 1,3-dipolar additions with phenyl azide. Although the reaction between phenyl azide and 5-cyanomethylnorborn-2-ene has been described, no supporting evidence was provided for the stereochemistry of the product. A re-examination of this problem with application of the nuclear Overhauser effect enables us to assign the structure of the phenyl azide–5-cyanomethylnorborn-2-ene adduct as (1a), and a similar analysis shows that the reaction between phenyl azide and 5-aminomethylnorborn-2-ene gives the triazolinonorbornane (1b).

The n.m.r. spectrum of the triazolinonorbornane (1a) shows that the cyanomethyl group is in the *endo*-position, since the signal of the C-8 *endo*-proton (octet at τ 9·15) is at high field. This abnormal shielding is caused by the anisotropy of the bond from C-9 to the *endo*-methylene group.[6] The heterocyclic ring must assume an *exo*-position, because the protons at C-2 and C-6 form an AB system with doublets centred at

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† Preliminary communication, F. Scheinmann, D. Barraclough, and J. S. Oakland, *Chem. Comm.*, 1970, 1544.

[1] F. A. L. Anet and A. J. R. Bourn, *J. Amer. Chem. Soc.*, 1965, **87**, 5250.

[2] K. J. Eisentraut and R. E. Sievers, *J. Amer. Chem. Soc.*, 1965, **87**, 5254; *Inorg. Synth.*, 1968, **11**, 94.

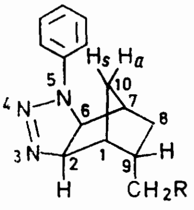
[3] C. C. Hinckley, *J. Amer. Chem. Soc.*, 1969, **91**, 5160.

[4] J. K. M. Sanders and D. H. Williams, *Chem. Comm.*, 1970, 422; *J. Amer. Chem. Soc.*, 1971, **93**, 641.

[5] K. Alder and E. Windemuth, *Chem. Ber.*, 1938, **71***B*, 1939.

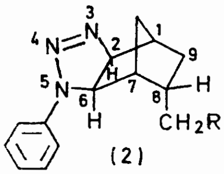
[6] R. G. Foster and M. C. McIvor, *Chem. Comm.*, 1967, 280.

τ 5·35 and 6·30 (J 9·0 Hz). This necessitates these protons assuming *endo*-positions, where there is virtually no coupling to the protons at C-1 and C-7 (dihedral angle *ca.* 90°).



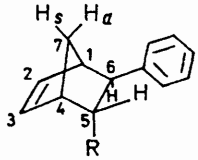
(1)

a; R = CN
b; R = NH2
c; R = OH



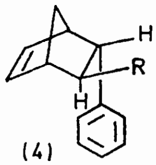
(2)

a: R = CN
b; R = NH2



(3)

a; R = NO2
b; R = NH2



(4)

a; R = NO2
b; R = NH2

Although both compounds (1a) and (2a) could be formed from the 1,3-dipolar addition reaction, only (1a) was obtained in high yield. However, the n.m.r. spectrum alone does not differentiate between structures (1a) and (2a). The rigid nature of the tricyclic ring system enables the NOE experiments to locate the *endo*-substituent, the hydrogen atoms, and the phenyl group relative to one another. Empirical data [7] suggest that the high-field doublet (τ 6·30) is due to the *endo*-proton at C-6 which is adjacent to the phenyl substituent, and NOE experiments support this assignment. Thus, irradiation at the frequency of the most intense peak in the phenyl region (τ 2·85) causes an increase of 8—9% in the integral of the high-field doublet (Table 1). That the phenyl group is on the opposite side of the molecule to the cyanomethyl, as in structure (1a), was confirmed by irradiation at the frequency of the *endo*-methylene proton signal. An increment of 15% was observed in the integral of the low-field doublet due to the *endo*-proton at C-2. Final proof of structure (1a) was obtained by observing the NOE caused by simultaneous irradiation at the frequencies of the two major peaks due to the C-8 *endo*-proton. This gave rise to approximately 10% enhancement of the integral of the high-field doublet corresponding to the C-6 *endo*-proton (Figure 1). The data are summarised in Table 1.

Since the method depends on the close proximity of the substituents and neighbouring protons, application of the NOE should be generally possible with other norbornanes. Table 2 illustrates NOE experiments on the aminomethyltriazolinonorbornane, which prove the assigned structure (1b).

The results in Tables 1 and 2 could only be obtained when the deuteriochloroform solutions of the triazolinonorbornanes (1a and b) were carefully degassed. It was experimentally easier to obtain similar stereochemical information (when suitable functional groups were present) by use of the pseudo-contact shift reagent Eu(dpm)$_3$.

Application of the Shift Reagent Eu(dpm)$_3$ to Assignment of Stereochemistry.—The structural assignment for the triazolinonorbornane (1b) has now been independently confirmed by n.m.r. studies with the shift reagent Eu(dpm)$_3$. In addition use of this reagent provides information about conformational features and the

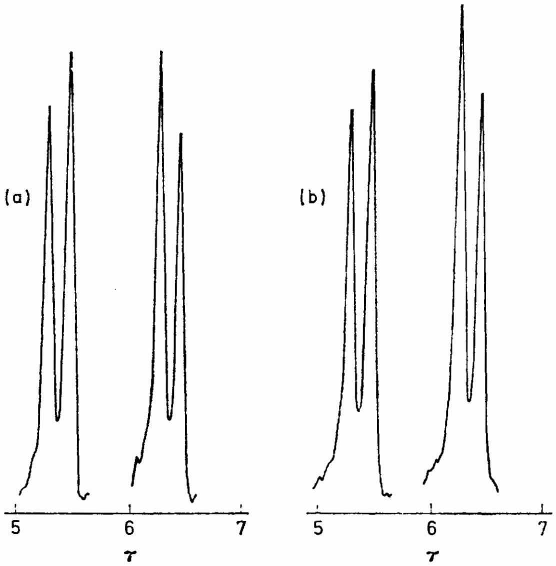


FIGURE 1 NOE experiments on the triazolinonorbornane (1a): (a) AB quartet due to the C-2 and C-6 *endo*-protons with no double irradiation; (b) AB quartet due to the C-2 and C-6 *endo*-protons showing the NOE caused by simultaneous irradiation of the two major peaks due to the C-8 *endo*-proton

TABLE 1

Nuclear Overhauser effect experiments on the triazolinonorbornane (1a)

Signal(s) irradiated	Proton affected	Enhancement (%)
Ph	6-H	8—9
endo-9-CH$_2$	2-H	15
endo-8-H	6-H	10

TABLE 2

NOE experiments on the triazolinonorbornane (1b)

Signal(s) irradiated	Proton affected	Enhancement (%)
Ph	6-H	8
endo-9-CH$_2$	2-H	16
endo-8-H	6-H	9—10

Peak enhancement was deduced by comparing electronically computed integrals of the C-2 and C-6 *endo*-proton signals before and after irradiation. Area measurements of the peaks with a planimeter gave slightly higher values.

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[7] P. Scheiner, *Tetrahedron*, 1967, **24**, 349; R. Huisgen, L. Moebius, G. Mueller, H. Stangl, G. Szeimes, and J. M. Vernon, *Chem. Ber.*, 1965, **98**, 3992.

method is of great value in assigning the stereochemistry of aminonorbornenes.

In the Diels–Alder reaction between cyclopentadiene and *trans*-β-nitrostyrene two adducts are formed,[8] the 5-*endo*-nitro-6-*exo*-phenylnorborn-2-ene (3a) and the 5-*exo*-nitro-6-*endo*-phenylnorborn-2-ene (4a). After fractional distillation of the nitro-compounds and reduction to the amine,[9] followed by fractional distillation of the product, only one isomer of the corresponding 5-amino-6-phenylnorborn-2-ene was isolated. The effect of Eu(dpm)$_3$ on the chemical shifts of the protons can be used to establish the stereochemistry of the 5-amino-group, because the distance of each proton from the shift reagent or the group to which it is complexed bears a logarithmic relationship to the changes in chemical shift produced on addition of the reagent.[10]

This relationship arises from the pseudo-contact interaction equation of McConnell and Robertson,[11] which dominates the paramagnetic shifts in the association of europium complexes with aliphatic systems[12] [equation (1)]. $\Delta\mathrm{Eu}_i$ is the paramagnetic shift induced in proton i, r_i is the distance from the europium ion to the ith proton H_i, θ_i is the angle between the N–Eu axis and the Eu $\cdots$ H_i axis, and k is a constant. In our studies approximations concerning θ_i and r_i have been made which are justified in structural studies because it is difficult to locate the europium atom with precision. The angle dependence term only assumes great importance if a change of sign of $\Delta\mathrm{Eu}_i$ is involved.[13–15] However, if the angle θ_i has a value $0 \longrightarrow 54{\cdot}7°$ or $125{\cdot}3 \longrightarrow 180°$, the $(3\cos^2\theta_i - 1)$ term of equation (1) is positive, resulting in a positive value for $\Delta\mathrm{Eu}_i$ or a shift to lower field, which is usually observed on forming Eu(dpm)$_3$ complexes. In such cases variation in θ_i has been neglected and a simplified form of equation (1) is used which incorporates $(3\cos^2\theta_i - 1)$ in the constant k. A further approximation involves replacing the r_i term by the distance vector R_i, where R_i measures the distance from the co-ordinating nitrogen atom to the ith proton. By ignoring the N–Eu distance and angle θ_i not only is the k term modified but also the power of the distance vector alters and the subsequent graphical analysis leads to equation (2).

$$\Delta\mathrm{Eu}_i = \mathrm{k}(3\cos^2\theta_i - 1)r_i^{-3} \qquad (1)$$

$$\Delta\mathrm{Eu}_i \approx \mathrm{k}/R_i^2 \qquad (2)$$

Equation (2) overcomes the uncertainty and inconsistency in defining the precise location of the co-ordinated europium ion. In the case of lanthanide complexes co-ordinating to the lone pair of oxygen atoms, the oxygen–metal distance may be within the range 1·5—3·5 Å[4,15,16] and Hinckley[3,17,18] prefers yet another value in his analysis of compounds using the dipyridine adduct, Eu(dpm)$_3$py$_2$. Such discrepancies can be ignored in structure elucidation by application of equation (2), and Demarco *et al.*[10] have proved that this relationship provides correct stereochemical information in structural studies on model cyclohexanols and borneols. Our studies now show that application of equation (2) also provides valuable structural information with amino and fused heterocyclic norbornanes.

The logarithmic equivalent of equation (2) is:

$$\log \Delta\mathrm{Eu}_i \approx -2\log R_i + \log \mathrm{k} \qquad (3)$$

and a plot of log $\Delta\mathrm{Eu}_i$ *vs.* log R_i should give a linear graph of slope *ca.* −2.[10,14,19] Thus the addition of increasing amounts of Eu(dpm)$_3$ increasingly resolves the complex n.m.r. spectrum of the aminonorbornene (3b) or (4b) as shown in Figure 2.

The proton assignments are based on observed splitting patterns and the linear dependence of the chemical shift on the concentration of Eu(dpm)$_3$ (Figure 3). The slopes of the latter graphs for each proton (obtained by the method of least squares) were plotted, on logarithm paper, against the vector distance R of each proton in the norbornene skeleton measured from the amino-group. A linear relationship of slope −1·90 exists between these parameters (Figure 4) for the structure with the amino-group in the *endo*-position (3b), but there is no such relationship if we assume that the norbornene has the *exo*-amino-structure (4b). The distance R was measured in Dreiding models of the norbornenes (3b) and (4b). Thus, the *endo*-configuration of the amine (3b) has been precisely established by use of the shift reagent Eu(dpm)$_3$, and use of the approximations given by equation (2) is now further justified in structural work. In addition this work also enables the assignment, in the n.m.r. spectra of (3b), of the 1- and 4-proton signals, which are unresolved prior to the addition of the shift reagent. Similarly it becomes possible to locate the *syn*- and *anti*-protons at C-7 (Figures 2—4).

A recent report by Hinckley *et al.*[18] describes a graphical

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[8] W. E. Noland, B. A. Langager, J. W. Manthey, A. G. Zacchei, D. L. Petrak, and G. L. Eian, *Canad. J. Chem.*, 1967, **45**, 2969.

[9] W. E. Parham, W. T. Hunter, and R. Hanson, *J. Amer. Chem. Soc.*, 1951, **73**, 5068.

[10] P. V. Demarco, T. K. Elzey, R. B. Lewis, and E. Wenkert, *J. Amer. Chem. Soc.*, 1970, **92**, 5734.

[11] H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, 1958, **29**, 1361.

[12] M. Base, *Progr. N.M.R. Spectroscopy*, 1969, **4**, 335; D. R. Eaton, 'Physical Methods in Advanced Inorganic Chemistry,' ed. H. A. O. Hill and D. Pay, Interscience, New York, 1968, p. 462; B. R. McGarvey, *J. Chem. Phys.*, 1970, **53**, 86 and references therein.

[13] T. H. Siddall, *Chem. Comm.*, 1971, 452; P. H. Mazzocci, H. J. Tamburin, and G. R. Miller, *Tetrahedron Letters*, 1971, 1819; B. L. Shapiro, J. R. Hlubucek, G. R. Sullivan, and L. F. Johnson, *J. Amer. Chem. Soc.*, 1971, **93**, 3281; M. Kishi, K. Tori, T. Komeno, and T. Shingu, *Tetrahedron Letters*, 1971, 3525.

[14] M. R. Willcott, J. F. M. Oth, J. Thio, G. Plinke, and G. Schroder, *Tetrahedron Letters*, 1971, 1579.

[15] S. Farid, A. Ateya, and M. Maggio, *Chem. Comm.*, 1971, 1285.

[16] Z. W. Wolkowski, *Tetrahedron Letters*, 1971, 821, 825; R. R. Fraser and Y. Y. Wigfield, *Chem. Comm.*, 1970, 1471; F. A. Hart, G. P. Moss, and J. Briggs, *ibid.*, p. 1506.

[17] C. C. Hinckley, *J. Org. Chem.*, 1970, **35**, 2834.

[18] C. C. Hinckley, M. R. Klotz, and F. Patil, *J. Amer. Chem. Soc.*, 1971, **93**, 2417.

[19] A. F. Cockerill and D. M. Rackham, *Tetrahedron Letters*, 1970, 5149, 5153.

analysis of paramagnetic shifts for systems having two possible co-ordination sites; we have been able to apply this method in principle to show that in the case of the aminotriazolinonorbornanes [*e.g.* (1b)], where complex formation may occur at any of the four nitrogen atoms present, the primary amino-group is preferentially complexed with Eu(dpm)$_3$. Furthermore, examination of the logarithmic relationship between the influence of Eu(dpm)$_3$ on chemical shift and the distance of a proton from the atom to which the shift reagent is complexed, provides information about the conformation of the primary amino-group. Although Wolkowski and his co-workers[20] have shown that steric, electronic, and basicity factors are important in influencing shifts of protons in different types of amines, supporting experiments were required before confident predictions could be made regarding the site where Eu(dpm)$_3$ is co-ordinated in compounds with more than one site capable of complexing. Since the stereochemistry of the aminotriazolinonorbornane (1b) had already been fully established by NOE experiments, it was selected in order to establish whether preferential complex formation with the lanthanide metal would occur at the primary amino-group. Figure 5 shows that there is a linear relationship between the chemical shift of each proton and the amount of Eu(dpm)$_3$ added. In addition there is a linear relationship of slope −1·92 between the slope of the graphs in Figure 5 and the vector distance of the various protons from the primary amino-group when plotted on logarithm paper (Figure 6). Thus complex formation must take place exclusively with the primary amino-group, since, as Hinckley has shown,[18] substantial association at another site would result in a difference between the measured shift and the straight line of Figure 6, which corresponds to the pseudo-contact contribution from association at the primary amino-group.

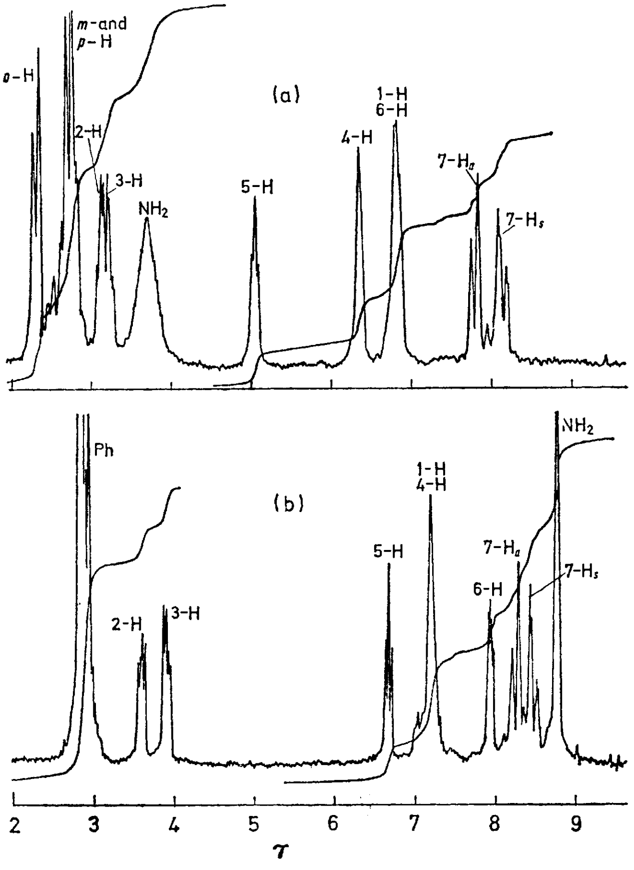

FIGURE 2 N.m.r. spectra of the aminonorbornene (3b) (100 mg) (a) in the presence of Eu(dpm)$_3$ (16·5 mg) in CDCl$_3$, (b) in the absence of Eu(dpm)$_3$

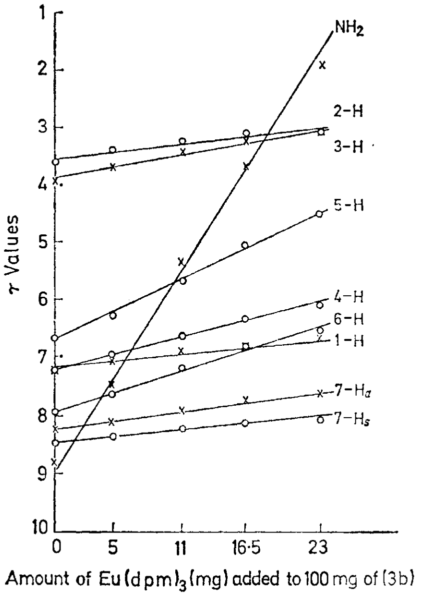

FIGURE 3 Variations in chemical shift (τ) with concentration of Eu(dpm)$_3$ for the aminonorbornene (3b)

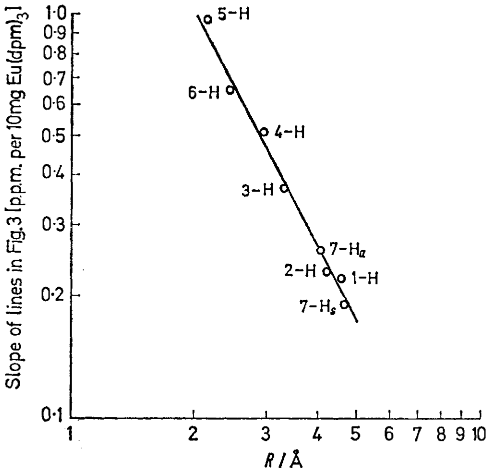

FIGURE 4 Slope of lines in Figure 3 *vs.* R (in Å) (the N ··· H distance) for (3b). The slope of lines in Figure 3 *vs.* R is given instead of ΔEu *vs.* R because the slope embraces several values of ΔEu

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[20] C. Beaute, Z. W. Wolkowski, and N. Thoai, *Tetrahedron Letters*, 1971, 817.

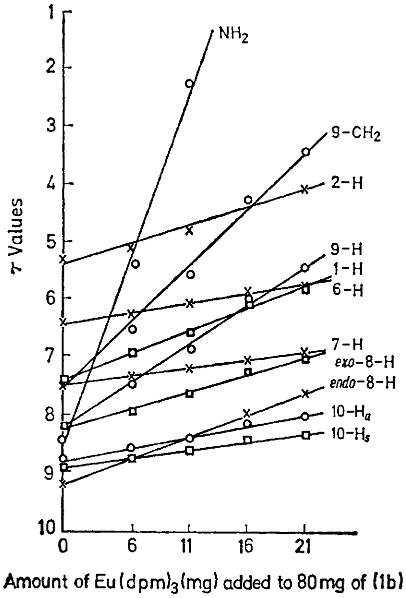


FIGURE 5 Variation in chemical shift (τ) with concentration of Eu(dpm)$_3$ for the triazolinonorbornene (Ib)

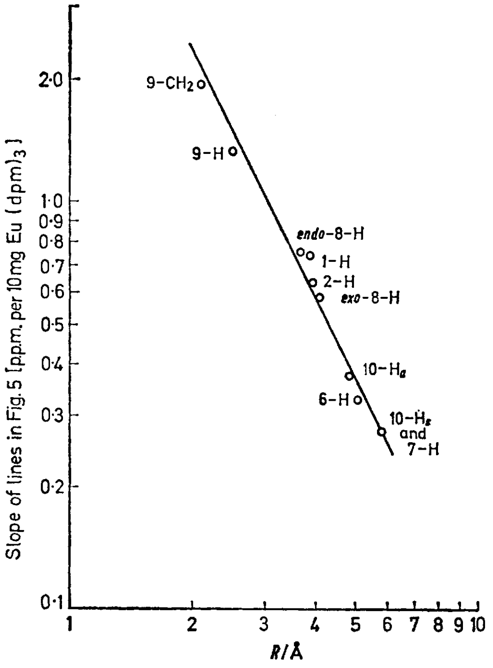
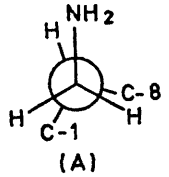
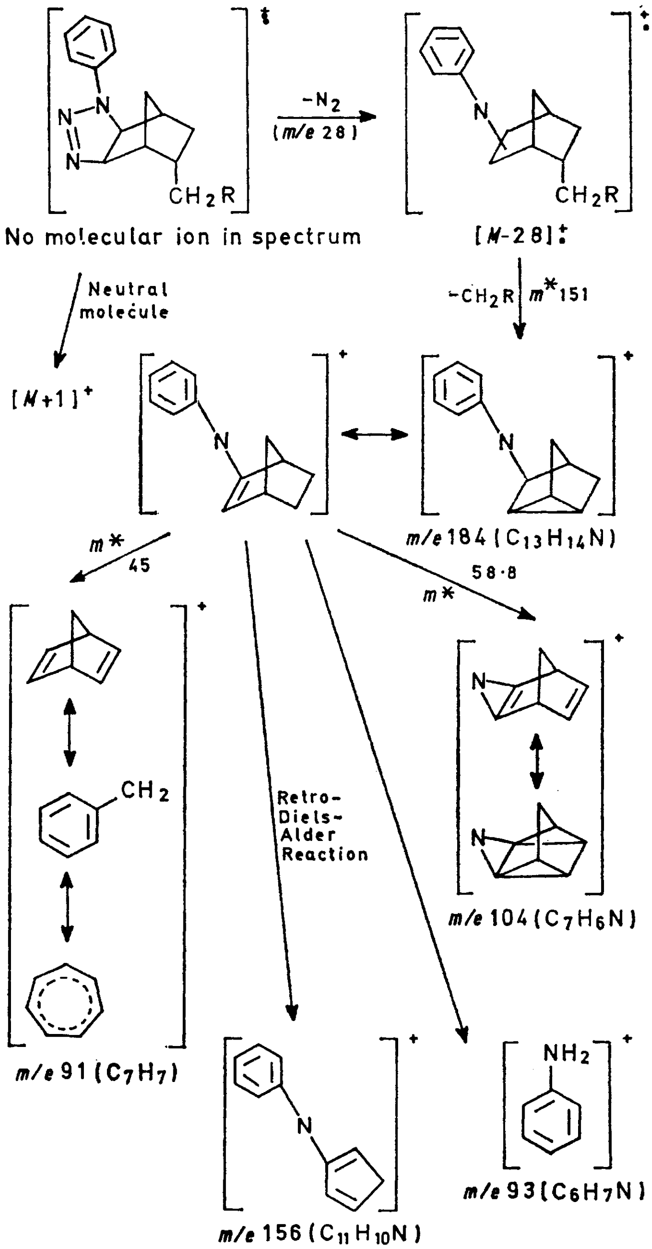


FIGURE 6 Slope of lines in Figure 5 *vs*. *R* in (Å) (the primary amino N · · · H distance) for (1b). The slope of lines in Figure 5 *vs*. *R* is given instead of ΔEu *vs*. *R* because the slope embraces several values of ΔEu

The aminomethyl group of compound (1b) can rotate freely, and to obtain the best linear relationship, *i.e.* Figure 6, it was necessary to measure the vector distance *R* of the various protons in the norbornane system from the nitrogen atom in an almost eclipsed conformation with the hydrogen atom at C-9 [see (A)]. Although eclipsed conformations are usually unfavourable, a Dreiding model of the triazoline (1b) suggests that in this case the eclipsed assignment (A) is reasonable. We have, however, no information as to whether the eclipsed conformation is favourable only after complex formation with Eu(dpm)$_3$. These results, together with



(A)



Accurate mass measurements were obtained for all fragments
R = CN, NH$_2$, or OH

SCHEME

those of Hinckley,[18] Hanson,[21] and Hart[22] suggest that careful use of shift reagents can be extended to compounds containing a number of functional groups and can provide information about conformational features.

Studies of Mass Spectral Fragmentation.—The triazolines (1), the stereochemistry of which has been fully elucidated by n.m.r. methods, have interesting diagnostic mass spectra. None of the triazolinonorbornane derivatives so far studied has shown a molecular ion peak. Initially an $[M - 28]^+$ peak was observed (sample injection at 250°; normal sample pressure), but on lowering the temperature of the injection block (150°) and increasing the sample pressure, an $[M + 1]^+$ peak was obtained. The intensity ratio $[M + 1]^+/[M - 28]^+$ was found to vary with sample pressure, indicating a molecule–molecular ion interaction of the type:

$$\mathrm{ABCD}^{+\cdot} + \mathrm{ABCD} \longrightarrow (\mathrm{ABCDABCD})^{+\cdot} \longrightarrow \mathrm{ABCDA}^{+} + \mathrm{BCD}\cdot$$ [23]

The $[M - 28]^+$ peak is due to loss of a nitrogen molecule from the thermally labile triazoline ring. The accurate masses of the major peaks in the spectra of the aminomethyl (1b), cyanomethyl (1a), and hydroxymethyl (1c) triazolines were obtained and these values provide support for the illustrated general fragmentation Scheme for these triazolinonorbornane derivatives. The first fragment lost from the $[M - 28]^+$ ion is CH_2R in all cases ($R = NH_2$, CN, or OH). Thus, the mass spectra of all three triazolines are identical below *m/e* 184. This ion ($C_{13}H_{14}N$) appears to be directly responsible for the ions at *m/e* 91 (C_7H_7), 104 (C_7H_6N), and 93 (C_6H_7N), and the expected retro-Diels–Alder fragment at *m/e* 156 ($C_{11}H_{10}N$). Although no obvious stereochemical information is provided by the mass spectral study, the general structure of the triazolines examined is confirmed. In addition the unusual feature of the molecular ion being replaced by a more stable system, the $[M + 1]^+$ species, is observed.

EXPERIMENTAL

N.m.r. spectra were recorded with a Varian HA 100 instrument. Accurate mass measurements were made by the Physico-Chemical Measurements Unit, Harwell.

Preparation of Phenyl Azide–Norbornene Adducts.—(a) 9-endo-*Cyanomethyl-5-phenyl*-exo-3,4,5-*triazatricyclo*-[5,2,1,0^{2,6}]*dec-3-ene* (1a). The method of Alder and Windemuth[5] yielded the adduct (51·5%), m.p. 174° (lit.,[5] 175°). Mass measurements are given in Table 3.

(b) 9-endo-*Aminomethyl-5-phenyl*-exo-3,4,5-*triazatricyclo*-[5,2,1,0^{2,6}]*dec-3-ene* (1b). A solution of 5-aminomethylnorborn-2-ene (12·5 g.) in light petroleum (b.p. 60—80°; 20 ml) was added to a solution of phenyl azide (12·5 g) in light petroleum (b.p. 60—80°; 20 ml). The solution was stirred for 24 h, after which an oily product had formed. This solidified after stirring for a further 48 h. The product was collected and crystallised twice from light petroleum (b.p. 80—100°) to give the *adduct* (1b) as white cubes (14·3 g, 58·15%), m.p. 90—92°, $\nu_{max.}$ 3390 cm^{-1} (N–H), τ(CDCl$_3$) 5·34 (1H, d, *endo*-2-H) and 6·41 (1H, d, *endo*-6-H) (ABq, *J* 9 Hz), 9·2 (1H, m, *endo*-8-H), 7·1—7·6 (4H, m, 9-CH$_2$, 1H, and 7-H), *ca.* 8·2 (2H, m, 9-H and *exo*-8-H), *ca.* 8·82 (2H, m, 10-H$_2$), 8·46 (2H, s, NH$_2$), and 2·85 (5H, m, Ph) (Found: C, 69·0; H, 7·5; N, 22·7. $C_{14}H_{18}N_4$ requires C, 69·4; H, 7·4; N, 23·1%). Mass measurements are in Table 4.

TABLE 3

Ion	Found	Calc.
$C_{15}H_{17}N_4^+[M + 1]^+$	253·1434	253·1453
$C_{15}H_{16}N_2^+[M - 28]^+$	224·1310	224·1313
$C_{13}H_{14}N^+$	184·1121	184·1126
$C_{11}H_{10}N^+$	156·0813	156·0813
$C_7H_6N^+$	104·0498	104·0500
$C_6H_7N^+$	93·0578	93·0578
$C_7H_7^+$	91·0547	91·0548

TABLE 4

Ion	Found	Calc.
$C_{14}H_{19}N_4[M + 1]^+$	243·1596	243·1610
$C_{14}H_{18}N_2[M - 28]^+$	214·1478	214·1470
$C_{13}H_{14}N^+$	184·1132	184·1126
$C_{11}H_{10}N^+$	156·0819	156·0813
$C_7H_6N^+$	104·0504	104·0500
$C_6H_7N^+$	93·0579	93·0578
$C_7H_7^+$	91·0550	91·0548

(c) 9-endo-*Hydroxymethyl-5-phenyl*-exo-3,4,5-*triazatricyclo*[5,2,1,0^{2,6}]*dec-3-ene* (1c). A solution of 5-hydroxymethylnorborn-2-ene (10 g) in light petroleum (b.p. 60—80°; 20 ml) was added to a solution of phenyl azide (10 g) in light petroleum (b.p. 60—80°; 20 ml). The solution was stirred for 72 h, after which an oily product had formed. This was purified by column chromatography on alumina G type E (Merck) [elution with benzene–chloroform (1 : 1)]. The solid obtained crystallised from benzene–light petroleum (b.p. 80—100°) to give the *adduct* (1c) as white needles (10·5 g, 54·4%), m.p. 108°, $\nu_{max.}$ 3380 cm^{-1} (O–H), τ(CDCl$_3$) 5·1 (1H, d, *endo*-2-H) and 6·3 (1H, d, *endo*-6-H) (ABq, *J* 9 Hz), 9·15 (1H, m, *endo*-8-H), 7·0—8·9 (7H, m), 6·3 (2H, m, 9-CH$_2$), and 2·7 (5H, m, Ph) (Found: C, 69·1; H, 7·0; N, 16·9. $C_{14}H_{17}N_3O$ requires C, 69·1; H, 7·0; N, 17·3%). Mass measurements are in Table 5.

TABLE 5

Ion	Found	Calc.
$C_{14}H_{18}N_3O^+[M + 1]^+$	244·1427	244·1450
$C_{14}H_{17}NO^+[M - 28]^+$	215·1310	215·1310
$C_{13}H_{14}N^+$	184·1121	184·1126
$C_{11}H_{10}N^+$	156·0814	156·0813
$C_7H_6N^+$	104·0500	104·0500
$C_6H_7N^+$	93·0578	93·0578
$C_7H_7^+$	91·0547	91·0548

NOE Experiments.—All spectra were obtained by use of a frequency sweep mode, the second r.f. field being obtained by using a Solartron type Co 546·2 audio-generator. The strength of the r.f. field was measured on the oscilloscope incorporated in the instrument. The spectra of all compounds were obtained from filtered and carefully degassed solutions (*ca.* 0·5M) in [^{2}H]chloroform. A small amount of tetramethylsilane was added as an internal lock. The Overhauser effects were measured as area increases by use of either an electronic integrator or a planimeter. The

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[21] I. Fleming, S. W. Hanson, and J. K. M. Sanders, *Tetrahedron Letters*, 1971, 3733.

[22] H. Hart and G. M. Love, *Tetrahedron Letters*, 1971, 625.

[23] K. Biemann, 'Mass Spectrometry Organic Chemical Applications,' McGraw-Hill, New York, 1962, pp. 46—58.

spectra were run with the oscillator at a frequency well away from proton resonance to check that no saturation was occurring. The oscillator frequency was then adjusted to the required frequency to saturate the signals in question and the area was recorded. The oscillator frequency and strength were then adjusted to give a maximum area increase. Finally the irradiating frequency was moved to a value greater than 30 Hz distant from any proton frequency to give a standard area. The area at each frequency was measured at least ten times and after each area had been recorded the system was allowed to return to equilibrium.

Preparation of 5-*Amino*-6-*phenylnorborn*-2-*ene* (3b).—The method of Parham *et al.*[9] was followed. A mixture of isomers of 5-nitro-6-phenylnorborn-2-ene was obtained by treatment of cyclopentadiene with *trans*-β-nitrostyrene.[8] This mixture was reduced to the amine by reduction with iron filings and dil. hydrochloric acid. Only one isomer was obtained by fractional distillation; b.p. 88—90° at 0·15 mmHg (lit.,[9] 90° at 0·1 mmHg).

Preparation of Tris(*dipivaloylmethanato*)*europium*(III).—The method of Eisentraut and Sievers[3] was followed. After recrystallisation from methylcyclohexane, the complex was further purified by sublimation under vacuum; m.p. 189 (lit.,[3] 187—189°).

Downfield Shift Experiments.—5-Amino-6-phenylnorborn-2-ene (3b) and 9-*endo*-aminomethyl-3-phenyl-*exo*-3,4,5-triazatricyclo[5,2,1,$0^{2,6}$]dec-3-ene (1b) (0·1 and 0·08 g, respectively) were each dissolved in [^{2}H]chloroform (1·0 ml) and accurately weighed amounts (*ca.* 0·005 g) of Eu(dpm)$_3$ were added to the solutions. Spectra were recorded after each addition of the europium complex. Dreiding models of structures (3b), (4b), and (1b) were used to obtain distances from the co-ordinating nitrogen atom to various protons.

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