Studies in the Norbornene Series. Part II.[1] Synthesis and Reactions of Some Norbornanes carrying Fused Heterocycles

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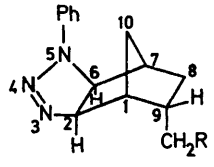
Some norbornanes carrying fused heterocycles have been synthesised by 1,3-dipolar additions to substituted norbornenes. Attempts to prepare heterocycles by reactions of electrophilic reagents with the strained double bond in norbornenes were unsuccessful owing to the occurrence of rearrangements. In the reaction of iodine with 5-*endo*-aminomethylnorborn-2-ene, rearrangement may be prevented by prior nucleophilic attack of the amine group on the cation intermediate to give a 5-azatricyclo[4.2.1.$0^{3,7}$]nonane (32).

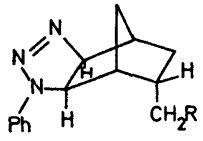
SYNTHESES of heterocycles starting from norbornene derivatives have been studied in order to prepare compounds of possible medicinal interest. Two types of reaction have been examined: (*a*) concerted cycloadditions, and (*b*) electrophilic additions involving carbonium ion intermediates.

Concerted Cycloadditions.—These reactions readily give heterocyclic adducts of norbornene;[2] the strained double bond undergoes, without rearrangements, addition to 1,3-dipolar reagents such as azides [2] and nitrilimines.[2a] Thus, phenyl azide reacts with the appropriate norbornene compounds to form the triazoline derivatives (1)—(5) at room temperature.

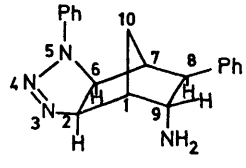
The structures of the triazolines (1)—(3) were assigned from consideration of their n.m.r. spectra and application of the nuclear Overhauser effect (NOE).[1,3,4] The isomeric triazolines (6)—(8) were not obtained. The n.m.r. spectrum alone does not differentiate between, for example, structures (1) and (6), but the rigid nature of



(1) R = CN
(2) R = NH_2
(3) R = OH



(6) R = CN
(7) R = NH_2
(8) R = OH



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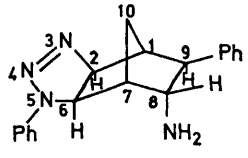


(5)

the tricyclic ring system enables the NOE experiments to locate the *endo*-substituent, the hydrogen atoms, and

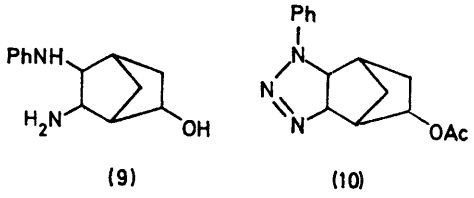
[1] Part I, D. Barraclough, J. S. Oakland, and F. Scheinmann, *J.C.S. Perkin, I* 1972, 1500.

[2] (*a*) R. Huisgen, *Angew. Chem. Internat. Edn.*, 1963, **2**, 565 and references therein; (*b*) R. S. McDaniel and A. C. Oehlschlager, *Tetrahedron*, 1969, **25**, 1381; (*c*) R. L. Hale and L. H. Zalkow, *ibid.*, p. 1393; (*d*) A. C. Oehlschlager, R. S. McDaniel, A. Thakore, P. Tillman, and L. H. Zalkow, *Canad. J. Chem.*, 1969, **47**, 4367; (*e*) J. D. Hobson and J. R. Malpass, *J. Chem. Soc.*, 1970, 1935; (*f*) K. Alder and E. Windemuth, *Chem. Ber.*, 1939, **71B**, 1938; (*g*) K. Alder and G. Stein, *Annalen*, 1931, **485**, 211, 223; 1933, **501**, 1.

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

[4] F. Scheinmann, D. Barraclough, and J. S. Oakland, *Chem. Comm.*, 1970, 1544.

the phenyl group relative to one another. The C-2 and C-6 protons appear in the n.m.r. spectrum as a single AB quartet, indicating *exo*-addition of the azide [5] and hence only one orientation of the phenyl group.[6] The details of the NOE experiments have already been described [1,4] and the structure of the amine (2) has been substantiated by use of the paramagnetic shift reagent tris(dipivaloylmethanato)europium(III) [Eu(dpm)$_3$].[1,7]



(9) (10) (11)

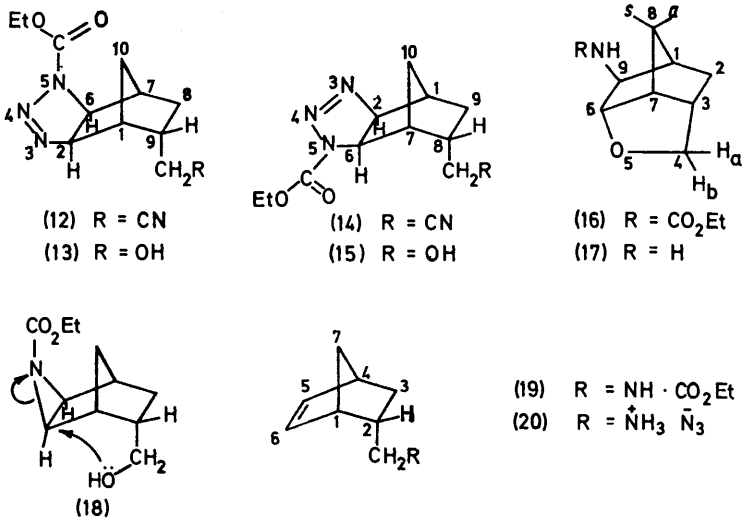
Imidazolinonorbornanes were required for other purposes, and a diamine of the type (9) is a key intermediate. According to Alder *et al.*[8] ' energetic hydrogenation ' of the triazoline (10) with Raney nickel as catalyst gives ammonia and the diamine (9). However, we have been unable to obtain diamines from the hydrogenation of the triazoline derivatives (1)—(3). Thus, in the case of the cyanotriazolinonorbornane (1), no reaction was observed at pressures lower than 100 atm and at temperatures below 150°. The more severe conditions reduced the cyano-group and caused loss of nitrogen from the triazoline ring. Subsequent hydrogenation of the aziridine (or imine) intermediate and attack of the primary amine group on the ethyl acetate solvent gave the norbornane (11).

In the *exo*-addition of phenyl azide to 5-*endo*-amino-6-*exo*-phenylnorborn-2-ene,[1] the two expected adducts (4) and (5) were obtained in the ratio 1 : 1, as shown by the n.m.r. signals of the *endo*-protons at C-2 and C-6 [AB and AM quartets * with doublets (J 9 Hz) centred at τ 4·80, 5·27, 5·57, and 6·16].

The addition of ethyl azidoformate to 5-*endo*-cyanomethylnorborn-2-ene and to the corresponding alcohol gives in each case the two expected *exo*-adducts [(12) and (14), and (13) and (15)] in the ratio 1 : 1·5. This follows from the n.m.r. spectra and in particular from integration of the signals from the *endo* C-2 and C-6 protons (two AB quartets, τ 4·5—6·5). It is not clear in either case which isomer predominates.

The fact that norbornenes react with azides to give only one isomer in some cases [*e.g.* (1)—(3)], whereas at other times mixtures are formed, suggests that steric factors may determine the orientation of attack.

Attempts to separate the adducts (12) and (14) [or (13) and (15)] by chromatography or distillation were unsuccessful owing to the instability of the triazoline ring,[9] even at room temperature. Only one product was isolated in high yield from vacuum fractional distillation of the adducts (13) and (15); this was shown to have structure (16) by its 220 MHz n.m.r. spectrum. The protons at C-6 and C-9 must assume the *trans,exo/endo*-positions because of their relative chemical



* *Cf.* the single AB quartet in the n.m.r. spectrum of the adducts (1)—(3).

[5] R. Huisgen, L. Moebius, G. Mueller, H. Stangl, G. Szeimes, and J. M. Vernon, *Chem. Ber.*, 1965, **98**, 3992.

[6] R. S. McDaniel and A. C. Oehlschlager, *Canad. J. Chem.*, 1970, **48**, 345.

[7] J. K. M. Sanders and D. H. Williams, *Chem. Comm.*, 1970, 422.

[8] K. Alder, H. Krieger, and H. Weiss, *Chem. Ber.*, 1955, **88**, 144.

[9] G. Caronna and S. Palazzo, *Gazzetta*, 1952, **82**, 292 (*Chem. Abs.*, 1953, **47**, 8737h).

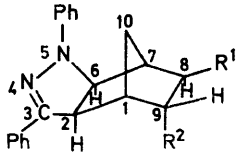
shift values, splitting patterns, and coupling constants. The C-9 proton (τ 6·82br) is necessarily *endo* (no coupling to C-6 or C-1 protons, torsion angles *ca.* 90°). The C-6 *exo*-proton appears as a doublet (J 5 Hz, τ 6·06) since it couples with the bridgehead proton at C-7 (torsion angle *ca.* 35°), but not to the C-9 proton (torsion angle *ca.* 90°). The C-4 proton signals indicate the rigid nature of the tricyclic system; H_a is coupled to H_b but not to the C-3 proton (torsion angle *ca.* 90°) and appears as a doublet (J 8 Hz, τ 6·35). The doublet (J 8 Hz, τ 6·25) for H_b, however, is further split by the C-3 proton into a quartet (J 4 Hz) (torsion angle *ca.* 50°). All other spectroscopic evidence, *e.g.* amide I and II bands at 1710 and 1535 cm^{-1}, and N–H stretch at 3340 and 3450 cm^{-1}, supports the structural assignment.

Structure (16) was confirmed by acidic hydrolysis to give the amine (17) and subsequent n.m.r. analysis with application of the shift reagent $Eu(dpm)_3$. The slopes of the graphs of chemical shift against concentration of $Eu(dpm)_3$ for each proton (obtained by the method of least squares) were plotted on logarithm graph paper, against the vector distance of each proton in the norbornane skeleton from the amino-group. A linear relationship of slope −2·05 exists between these parameters, which confirms structure (17), and provides further justification for the use of the simplified form [1] of the pseudo-contact equation of McConnell and Robertson.[10]

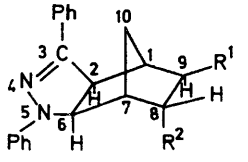
The tricyclic structure (16) is probably formed by intramolecular nucleophilic attack on an aziridine intermediate (18), which may be generated by thermal decomposition of the triazoline.[2d,11]

We did not obtain 1,3-dipolar cycloaddition products from ethyl azidoformate and 5-*endo*-aminomethylnorborn-2-ene. Only the urethane (19) and the azide salt (20), resulting from nucleophilic displacement of the azide group by the primary amine functions, were isolated.

Addition of diphenylnitrilimine, derived from the α-chloro-derivative of benzaldehyde phenylhydrazone and



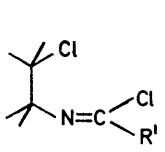
(21) R^1 = H, R^2 = CH_2CN
(22) R^1 = Ph, R^2 = NH_2



(23) R^1 = H, R^2 = CH_2CN
(24) R^1 = Ph, R^2 = NH_2

triethylamine *in situ*,[12] to the appropriate norbornenes gave the pyrazolinonorbornanes (21)—(24). The characteristic pair of AB quartets (τ 5·0—7·0) assigned to the C-2 and C-6 *endo*-protons once again indicated *exo*-addition, and allowed estimation of the relative amounts of the adducts as 1 : 1 in each case.

Electrophilic Attack.—In another approach to the preparation of imidazolinonorbornanes from norbornenes, the method of Beger [13] was followed in which an olefin undergoes electrophilic attack by chlorine in nitrile medium followed by reaction with solvent to give a chloro-imine (25). Subsequent reaction with an imine followed by cyclisation leads to an imidazoline. Indications that the Beger reaction with 5-*endo*-chloromethylnorborn-2-ene did not form a chloro-imine, were first given by the failure of the chlorination products to react with water or primary amines. Likely structures for the three main chlorination products were indicated by spectral analysis.



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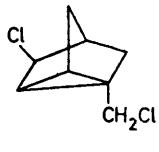

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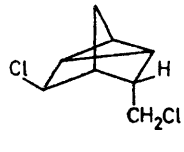

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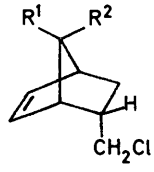
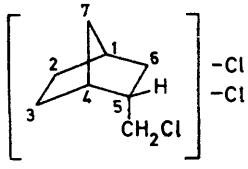


(28) R^1 = H, R^2 = Cl
(29) R^1 = Cl R^2 = H



(30)

The first pure compound obtained by column chromatography is assigned a nortricyclene structure (26) or (27) from the similarity of its i.r. spectrum with that of nortricyclyl chloride,[14] and from the n.m.r. spectral data. We conclude that this component arises from rearrangements of the carbonium ion intermediate by analogy with the pathway suggested by Poutsma.[15] It is not possible to distinguish between structures (26) and (27) without further experimental data, but these studies were discontinued when it was clear that imidazole formation did not occur because rearrangements were favoured.[16] A small amount of an olefinic compound was also isolated from the column. Spectral studies indicated that structures (28) and (29) were possible, (29) being preferred because the n.m.r. spectrum showed no long-range coupling involving the C-7 proton.[17] A further product was shown by mass and i.r. spectra to contain neither a double bond nor a cyclopropane ring;

[10] H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, 1958, **29**, 1361.
[11] G. L'Abbe, *Chem. Rev.*, 1969, **69**, 345 and references therein; P. A. Gembitskii, N. M. Loim, and D. S. Zhuk, *Russ. Chem. Rev.*, 1966, **35**, 105 and references therein.
[12] R. Huisgen, M. Seidel, G. Wallbillich, and H. Knupfer, *Tetrahedron*, 1962, **17**, 3; R. Huisgen, M. Seidel, J. Sauer, J. W. McFarland, and G. Wallbillich, *J. Org. Chem.*, 1959, **24**, 892.
[13] J. Beger, D. Schöde, and J. Vogel, *J. prakt. Chem.*, 1969, **311**, 408.
[14] J. D. Roberts and W. Bennett, *J. Amer. Chem. Soc.*, 1954, **76**, 4623.
[15] M. C. Poutsma, *J. Amer. Chem. Soc.*, 1965, **87**, 4293.
[16] T. G. Traylor, *Accounts Chem. Res.*, 1969, **2**, 152 and references therein.
[17] P. Laszlo and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1964, **86**, 1171.

although its actual structure is as yet unknown, two chlorine atoms must be attached at two of the three positions C-2, C-3, and C-7 in the partial structure (30).

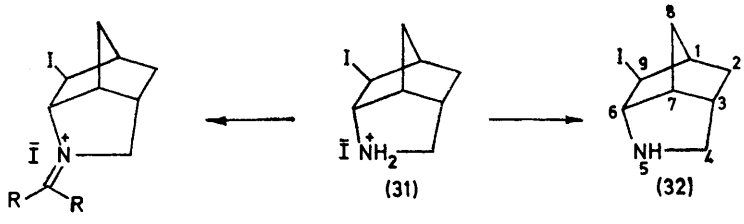
Thus, carbonium ion rearrangement and attack by chloride ion is preferred to nucleophilic attack by the nitrile group of acetonitrile. This explanation is supported by the results of direct chlorination, which yields the same three products and by the work of Poutsma,[15] who obtained *ca.* 90·5% rearrangement products and only *ca.* 9·5% *cis*- and *trans*-addition products in the chlorination of norbornene at 0° in carbon tetrachloride.

We found similar difficulties with other heterocyclic syntheses when electrophilic attack was the first step. For example, the two-step synthesis of imidazoles by Scheinbaum and Dines,[18] involving olefins and nitrosyl fluoroborate in nitrile medium probably proceeds by attack of the nitrosyl ion to form a bridged nitrosyl–olefin complex ion, followed by reaction with the nucleophilic solvent. The addition of nitrosyl fluoroborate (at −12°) to norbornene in acetonitrile results in a complex mixture. The product mixture from a monosubstituted norbornene, *e.g.* 5-*endo*-chloromethylnorborn-2-ene is even more complex. Failure to give an imidazole is probably due to rearrangements of the cation intermediate prior to nucleophilic attack.

Electrophilic addition to a norbornene derivative can, however, be utilised in the synthesis of a heterocycle when a functional group is present which can attack the resulting carbonium ion intermediate.[16,19] Here, internal nucleophilic attack is faster than rearrangement or addition. For example 5-*endo*-aminomethylnorborn-2-ene, when treated with iodine in carbon tetrachloride, presumably generates an iodonium ion intermediate, which undergoes intramolecular attack to give the salt (31). The free amine (32) may be generated by treatment with alkali.

From the salt (31), iminium iodides derived from common ketones can be prepared at room temperature; cyclohexanone and acetone give the iminium salts (33) and (34), respectively. The conventional preparation of such derivatives involves shaking and heating the perchlorate salt of an amine with a ketone.[20] We find, however, that the hydroiodide salts of common amines will perform the reaction adequately.

The iminium salts (33) and (34) have synthetic potential as stable crystalline enamine precursors. Thus the iminium salt (33), on treatment with triethylamine,[21] gives the corresponding enamine, which is converted into 2-acetylcyclohexanone [22] on treatment with acetyl chloride. Iminium salts may also prove generally useful for the preparation and study of acyclic enamines; an investigation of this possibility is in progress.



(33) RR = $[CH_2]_5$
(34) R = Me

EXPERIMENTAL

I.r. spectra, for Nujol mulls unless otherwise stated, were recorded on a Perkin-Elmer 257 grating spectrophotometer. N.m.r. spectra were recorded on Varian HA100 and A60 instruments. Mass spectra were measured on an A.E.I. MS12 single-focusing spectrometer. Accurate mass measurements were performed by the Physico-Chemical Measurements Unit, Harwell. Analytical t.l.c. was carried out on silica gel (Merck; nach Stahl) and aluminium oxide G type E (Merck); column chromatography was performed with Hopkin and Williams silica gel (M.F.C.) and B.D.H. alumina.

Phenyl Azide–Norbornene Adducts.—9-*endo*-Cyanomethyl-5-phenyl-*exo*-3,4,5-triazatricyclo[5.2.1.$0^{2,6}$]dec-3-ene (1), 9-*endo*-aminomethyl-5-phenyl-*exo*-3,4,5-triazatricyclo-[5.2.1.$0^{2,6}$]dec-3-ene (2), and 9-*endo*-hydroxylmethyl-5-phenyl-*exo*-3,4,5-triazatricyclo[5.2.1.$0^{2,6}$]dec-3-ene (3) were prepared as described previously.[1]

9-endo-*Amino*-5,8-exo-*diphenyl*-exo-3,4,5-*triazatricyclo*-[5,2,1,$0^{2,6}$]*dec*-3-*ene* (4) *and* 8-endo-*amino*-5,9-exo-*diphenyl*-exo-3,4,5-*triazatricyclo*[5.2.1.$0^{2,6}$]*dec*-3-*ene* (5). A solution of 5-*endo*-amino-6-*exo*-phenylnorborn-2-ene (1·5 g) in light petroleum (b.p. 60—80°; 10 ml) was added to a solution of phenyl azide (2·0 g) in the same solvent (5 ml). The mixture was stirred at room temperature for 72 h, and the sticky solid which formed was crystallised from chloroform–light petroleum (b.p. 80—100°) to give a 1 : 1 mixture of the adducts (4) and (5) as white plates (1·80 g, 54·8%), m.p. 109°, $\nu_{max.}$ 3340 and 3250 (NH_2) and 1605 and 1500 cm^{-1} (Ph), τ ($CDCl_3$) 2·73 (10H, m, Ph), 4·80 and 5·27 (each 0·5H, d, *endo*-2-H), and 5·57 and 6·16 (each 0·5H, d, *endo*-6-H) (2ABq, *J* 9 Hz), 6·65 [1H, m, *exo*-9 (or 8)-H], 7·3 (2H, m, 1-H and 7-H), 7·8 [1H, m, *endo*-8 (or 9)-H], 8·40 and 8·90 (each 1H, d, 10-H) (ABq, *J* 10 Hz), and 8·60 (2H,

[18] M. L. Scheinbaum and M. B. Dines, *Tetrahedron Letters*, 1971, 2205.
[19] A. Factor and T. G. Traylor, *J. Org. Chem.*, 1968, **33**, 2607.
[20] N. J. Leonard and J. V. Paukstelis, *J. Org. Chem.*, 1963, **28**, 3021.
[21] S. Hünig, E. Benzing, and E. Lücke, *Chem. Ber.*, 1957, **90**, 2833; 1958, **91**, 129.
[22] G. Stork, A. Brizzolara, H. Landesman, J. Szumskovicz, and R. Terrell, *J. Amer. Chem. Soc.*, 1963, **85**, 207.

s, NH_2), *m/e* 305 [$C_{19}H_{21}N_4^+$, $(M + 1)^+$] [1] and 276 [$C_{19}H_{20}N_2^+$, $(M - 28)^+$] (Found: C, 74·7; H, 6·5; N, 18·4. Calc. for $C_{19}H_{20}N_4$: C, 75·0; H, 6·6; N, 18·4%).

2-(2-*Acetamidoethyl*)-5(or 6)-*anilinonorbornane* (11).—A solution of 9-*endo*-cyanomethyl-5-phenyl-*exo*-3,4,5-triazatricyclo[5.2.1.$0^{2,6}$]dec-3-ene (1) (1·0 g) in ethyl acetate (100 ml) containing Raney nickel (*ca.* 0·5 g) was hydrogenated in a Baskerville autoclave under various conditions, the reaction being monitored by t.l.c. No reaction was observed until a temperature of 150° and pressure of 100 atm were used. The oily product obtained on removal of the solvent was purified by column chromatography on alumina [elution with chloroform–light petroleum (b.p. 60—80°) (1 : 4)]. The low-melting solid obtained crystallised from benzene–light petroleum (b.p. 80—100°) to give the amide (11) (0·75 g, 66·7%), m.p. 42°, $\nu_{max.}$ 3315 (NH), 1665 (C=O), and 1610 and 1510 cm^{-1} (Ph), τ ($CDCl_3$) 2·90 (2H, m, *meta*-H), 3·30 (3H, m, *ortho*- and *para*-H), 6·75 (4H, m, NH and N·CH_2), 8·03 (3H, s, Ac), and 7·5—9·15 (14H, m) [Found: C, 74·8; H, 8·8%; *M* (mass spec.), 272. Calc. for $C_{17}H_{24}N_2O$: C, 75·0; H, 8·8%; *M*, 272].

Ethyl Azidoformate–Norbornene Adducts.—A solution of ethyl azidoformate (6·0 g) in light petroleum (b.p. 60—80°; 10 ml) was added to a solution of the appropriate norbornene derivative (6·0 g) in the same solvent (10 ml). The solution was stirred for 72 h at room temperature, and the oily product was then separated and dried under vacuum to give the corresponding mixture of adducts (Table 1).

Ethyl N-(5-*Oxatricyclo*[4.2.1.$0^{3,7}$]*nonan*-7-exo-*yl*)*carbamate* (16).—The dried mixture of (13) and (15) (10·0 g) was distilled under vacuum to yield the *carbamate* (16) as a viscous liquid (6·1 g, 69·1%), b.p. 160° at 0·1 mmHg, $\nu_{max.}$ 3340 (NH) and 1710 and 1535 cm^{-1} (amide I and II), τ ($CDCl_3$) 5·00 (1H, d, NH), 5·94 (2H, m, O·CH_2), 6·06 (1H, d, 6-H), 6·25 (1H, q, H_b), 6·35 (1H, d, H_a), 6·82 (1H, s, 9-H), 7·46 (1H, t, 7-H), 7·70 (1H, m, 3-H), 7·90 (1H, s, 1-H), 8·13 (1H, m, *exo*-2-H), 8·35 (1H, d, *syn*-8-H), 8·50 (1H, d, *anti*-8-H), and 8·83 (4H, m, O·CH_2·CH_3 and *endo*-2-H) [Found: C, 62·4; H, 8·4%; *M* (mass spec.), 211. $C_{11}H_{17}NO_3$ requires C, 62·6; H, 8·1%; *M*, 211].

9-exo-*Amino*-5-*oxatricyclo*[4.2.1.$0^{3,7}$]*nonane* (17).—The carbamate (16) (1·0 g) was warmed with 70% w/v sulphuric acid (10 ml). The darkened solution was poured into cold water (100 ml) and basified (NaOH), and the liberated amine was extracted with chloroform (25 ml). The extract was washed four times with water (25 ml), dried, and evaporated to leave a brown liquid. Distillation gave the *amine* (17) as a liquid (0·51 g, 75·9%), b.p. 62° at 0·1 mmHg, $\nu_{max.}$ 3375 and 3300 cm^{-1} (NH_2), τ ($CDCl_3$) 6·28 (2H, m, 6-H and H_b), 6·45 (1H, d, H_a), 7·43 (1H, s, 9-H), 7·48 (1H, m, 7-H), 7·72 (1H, m, 3-H), 8·14 (1H, m, *exo*-2-H), 8·15 (2H, m, 1-H and *syn*-8-H), 8·32 (2H, s, NH_2), 8·55 (1H, d, *anti*-8-H), and 8·98 (1H, m, *endo*-2-H). Results of combustion analyses were unsatisfactory owing to ready formation of the carbonate. Mass measurements are given in Table 2.

Shift Experiments.—The amine (17) (80 mg) was dissolved in [^{2}H]chloroform (1·0 ml) and accurately weighed amounts (*ca.* 0·005 g) of $Eu(dpm)_3$ were added to the solution. Spectra were recorded after each addition. A Dreiding model of structure (17) was used to obtain distances from the co-ordinating nitrogen atom to various protons.

Reaction of Ethyl Azidoformate with 5-endo-*Aminomethylnorborn-2-ene.*—A solution of ethyl azidoformate (11·0 g) in benzene (20 ml) was added dropwise to a solution of 5-*endo*-aminomethylnorborn-2-ene (10·0 g) in benzene (20 ml) with cooling. The solution was stirred at 6° for 0·5 h; the solid which formed was collected and crystallised twice from benzene to give *norborn*-5-*en*-2-endo-*ylmethylammonium azide* (20) as plates (6·0 g, 44·1%), m.p. 130°, $\nu_{max.}$ (KBr) 2980vbr ($\overset{+}{N}H_3$), 2040 (azide), and 1625 cm^{-1} (C=C), n.m.r. spectrum not resolvable owing to broad bands, *m/e* 123 ($C_8H_{13}N$, M^+ of free amine) (Found: C, 57·4; H, 8·2; N, 33·8. $C_8H_{14}N_4$ requires C, 57·8; H, 8·4; N, 33·7%). The solvent was removed from the filtered reaction mixture to give a pale yellow viscous oil, which was purified by column chromatography on alumina [elution with chloroform–benzene (1 : 1·5)] to give *ethyl* N-(*norborn*-5-*en*-2-endo-*ylmethyl*)*carbamate* (19) as a solid (7·2 g, 45·4%), m.p. 44°, $\nu_{max.}$ 3340 (NH), and 1710 and 1535 cm^{-1} (amide I and II), τ ($CDCl_3$) 3·87 (2H, m, 5-H and 6-H), 5·08 (1H, s, NH), 5·83 (2H, q, O·CH_2), 7·12 (5H, m, N·CH_2, 1-H, 4-H, and 2-H), 8·0 (1H, m, *exo*-3-H), 8·76 (3H, t, O·CH_2·CH_3), 8·70 (2H, m, 7-H), 9·42 (1H, m, *endo*-3-H) [Found: C, 68·2; H, 9·1%; *M* (mass spec.), 195. $C_{11}H_{17}NO_2$ requires C, 67·8; H, 8·7%; *M*, 195].

TABLE 1

Ethyl azidoformate–norbornene adducts *

Adduct mixture	Yield	$\nu_{max.}$(film)/cm^{-1}	τ ($CDCl_3$)	*m/e*
(12) + (14)	9·8 g (87·6%)	2355 (C≡N), 1730 (C=O)	5·58 (2H, q, O·CH_2), 8·60 (3H, t, O·CH_2·CH_3), 4·90 (0·4H, d) and 5·14 (0·6H, d), and 5·88 (0·6H, d) and 6·22 (0·4H, d) (2ABq, *J* 9 Hz), 6·7—9·15 (9H, m)	249 [$C_{13}H_{17}N_4O_2^+$, $(M + 1)^+$], 220 [$C_{12}H_{16}N_2O_2^+$, $(M - 28)^+$]
(13) + (15)	10·3g (89·05%)	3450 and 3360 (OH), 1715 (C=O)	5·73 (2H, q, O·CH_2), 8·75 (3H, t, O·CH_2·CH_3), 5·11 (0·4H, d) and 5·44 (0·6H, d) (part of 2ABq, *J* 9 Hz), 6·2—9·15 (11 H, m)	211 [$C_{11}H_{17}NO_3$, $(M - 28)^+$]

* Satisfactory elemental analyses were not obtained owing to instability.

TABLE 2

Mass measurements for the amine (17)

	m/e	
Ion	Found	Calc.
$C_8H_{13}NO$	139·0987	139·0997
$C_8H_{10}O$	122,0733	122·0732
C_7H_9O	109·0660	109·0653
C_5H_8NO	98·0600	98·0606

Diphenylnitrilimine–Norbornene Adducts.—(a) *Adducts* (21) *and* (23). Triethylamine (3·1 g) was added slowly to a solution of the α-chloro-derivative of benzaldehyde phenylhydrazone (7·0 g) and 5-*endo*-cyanomethylborborn-2-ene (4·0 g) in dry benzene (150 ml). The mixture was stirred at 25° for 24 h, the precipitated triethylamine hydrochloride was filtered off, and the solvent was removed under reduced pressure. The resulting sticky solid was crystallised twice from light petroleum (b.p. 80—100°) to give the adducts (21) and (23) as orange cubes (6·65 g, 67·6%), m.p. 183—185°, $\nu_{max.}$ 2260 (C≡N) and 1605 and 1500 cm^{-1} (Ph), τ ($CDCl_3$) 2·75 (10H, m, Ph), 5·74 (0·5H, d) and 5·98 (0·5H, d, *endo*-2-H), and 6·32 (0·5H, d) and 6·52 (0·5H, d, *endo*-6-H) (2ABq, *J* 9 Hz), 6·8—8·3 (6H, m), 8·55 (1H, d, 10-H) and 8·80 (1H, d, 10-H) (ABq, *J* 9 Hz), and 9·10 [1H, m, *endo*-8 (or 9)-H] [Found: C, 80·8; H, 6·6; N, 12·5%; *M* (mass spec.), 327. Calc. for $C_{22}H_{21}N_3$: C, 80·8; H, 6·4; N, 12·8%; *M*, 327].

(b) *Adducts* (22) *and* (24). Triethylamine (1·1 g) was added to a solution of the α-chloro-derivative of benzaldehyde phenylhydrazone (2·5 g) and 5-*endo*-amino-6-*exo*-phenylnorborn-2-ene (2·0 g) in benzene (50 ml). After stirring for 24 h, filtering, and removing the solvent an oil was obtained which was crystallised twice from benzene–light petroleum (b.p. 80—100°) to give the adducts (22) and (24) as yellow plates (2·6 g, 63·5%), m.p. 121°, $\nu_{max.}$ 3340 and 3280 (NH_2), and 1603 and 1500 cm^{-1} (Ph), τ ($CDCl_3$) 2·72 (15H, m, Ph), 5·10 (0·5H, d) and 5·25 (0·5H, d, *endo*-2-H), and 6·12 (0·5H, d) and 6·22 (0·5H, d, *endo*-6-H) (2ABq, *J* 9 Hz), 8·70 (2H, s, NH_2), and 6·80—8·60 (6H, m) [Found: C, 81·9; H, 6·3; N, 10·9%; *M* (mass spec.), 379. Calc. for $C_{26}H_{25}N_3$: C, 82·3; H, 6·6; N, 11·1%; *M*, 379].

Chlorination of 5-endo-*Chloromethylnorborn-2-ene in the Presence of Methyl Cyanide.*—A solution of 5-*endo*-chloromethylnorborn-2-ene (20·0 g) and methyl cyanide (9·2 g) in carbon tetrachloride (100 ml) was treated with a solution of chlorine (8·0 g) in carbon tetrachloride (85 ml) at −20°. [Alternatively, a solution of 5-*endo*-chloromethylnorborn-2-ene (20·0 g) in methyl cyanide (9·2 g) was treated with dry chlorine gas at −20°.] No precipitation occurred on stirring at −20° for 0·5 h. Half the solution was poured into water at 25° and the resulting suspension was stirred rapidly for 0·25 h, then set aside for 1·5 h. Extraction with ether and removal of the solvent yielded a pale brown liquid. The remaining half of the chlorination solution was treated with n-butylamine (15·0 g) in ether (100 ml). After removal of a small amount of n-butylamine hydrochloride, the solution was evaporated to yield a second brown liquid, which was shown by g.l.c. on polyethylene glycol and t.l.c. on alumina to be identical with the hydrolysis product. Column chromatography on alumina [elution with light petroleum (b.p. 60—80°)] of the reaction mixture (1 g) yielded the dichloronortricyclene derivative (26) or (27) (0·45 g), b.p. 65° at 0·6 mmHg, $\nu_{max.}$ (film) 3080 (cyclopropane) and 810 cm^{-1} (nortricyclene [15]), τ ($CDCl_3$) 5·97 (1H, s, >CHCl), 6·68 (2H, m, CH_2Cl), 7·92 (3H, m), 8·60 (3H, m), and 9·16 (1H, m), *m/e* 176 ($C_8H_{10}Cl_2^+$, M^+), 178, and 180 (Found: C, 54·1; H, 5·7. Calc. for $C_8H_{10}Cl_2$: C, 54·2; H, 5·7%). Further elution yielded the dichloronorbornene derivative (28) or (29) (0·15 g), b.p. 67° at 0·6 mmHg, $\nu_{max.}$ 3075 cm^{-1} (unsat. C–H), τ ($CDCl_3$) 4·00 (2H, s, 2-H and 3-H), 6·10 (1H, s, 7-H), 6·50 (2H, m, CH_2Cl), 7·10 (2H, m), 8·27 (1H, m, *exo*-6-H), 8·61 (1H, m), and 9·16 (1H, m, *endo*-6-H), *m/e* 176 ($C_8H_{10}Cl_2^+$, M^+), 178, and 180 (Found: C, 54·3; H, 5·5. Calc. for $C_8H_{10}Cl_2$: C, 54·2; H, 5·7%). Further elution yielded the trichloronorbornene derivative (30) (0·25 g), b.p. 118° at 0·2 mmHg, $\nu_{max.}$ 725 cm^{-1} (C–Cl), τ ($CDCl_3$) 6·2 (2H, m, >CHCl), 6·72 (2H, m, CH_2Cl), 7·46 (1H, m), 7·60 (1H, m), 7·85 (1H, m), 8·14 (1H, m), 8·62 (2H, m), and 9·16 (1H, m), *m/e* 212 ($C_8H_{11}Cl_3^+$, M^+), 214, 216, and 218 (Found: C, 44·6; H, 5·0. Calc. for $C_8H_{11}Cl_3$: C, 44·9; H, 5·2%).

9-exo-*Iodo*-5-*azatricyclo*[4.2.1.$0^{3,7}$]*nonane* (32).—A solution of iodine (7·0 g) in carbon tetrachloride (200 ml) was added dropwise with stirring to a solution of 5-*endo*-aminomethylnorborn-2-ene (3·0 g) in carbon tetrachloride (10 ml). The yellow solid which formed was crystallised twice from benzene to give the *hydroiodide* (31) as white needles (8·1 g, 88·3%), m.p. 124°, $\nu_{max.}$ 2960 cm^{-1} ($\overset{+}{N}H_2$), τ ($CDCl_3$) 1·8 (2H, s, $\overset{+}{N}H_2$), 5·3 (1H, m, 9-H), 6·4 (1H, m, 6-H), and 6·8—8·8 (9H, m), *m/e* 249 ($C_8H_{12}IN^+$, M^+ of free amine) (Found: C, 25·7; H, 3·6; N, 3·7. $C_8H_{13}I_2N$ requires C, 25·4; H, 3·5; N, 3·7%). A solution of the salt (31) (2 g) in water (40 ml) was treated dropwise with 2N-sodium hydroxide. Extraction with ether yielded a pale yellow oil which crystallised from benzene–light petroleum (b.p. 80—100°) to give the *azatricyclononane* (32) as white plates (1·2 g, 90·8%), m.p. 250° (decomp.), $\nu_{max.}$ 3425 cm^{-1} (NH), τ ($CDCl_3$) 4·0 (1H, s, NH) and 6·0—9·0 (11H, m), *m/e* 249 ($C_8H_{12}IN$, M^+) (Found: C, 38·9; H, 4·7; N, 5·3. $C_8H_{12}IN$ requires C, 38·5; H, 4·8; N, 5·6%).

Iminium Iodides from Reactions of 9-exo-*Iodo*-5-*azatricyclo*[4.2.1.$0^{3,7}$]*nonane Hydroiodide with Cyclohexanone and Acetone.*—A solution of the hydroiodide (31) (2·0 g) in the appropriate ketone (10 ml) was kept at room temperature for 0·5 h. The solid which formed was crystallised from 2-propanol to give the appropriate *iminium salt* [(33) or (34)] (Table 3).*

N-*Isopropylidenepyrrolidinium Iodide.*—Dry hydrogen iodide gas was passed into a solution of pyrrolidine (1·0 g) in diethyl ether (20 ml). The yellow precipitated hydroiodide (2·1 g, 74·9%) was collected, dried, and treated with anhydrous acetone. The pyrrolidine hydroiodide dissolved immediately, but on shaking crystals were precipitated. The product was collected and crystallised from propan-2-ol

TABLE 3

Product	Yield	M.p. (°C) (decomp.)	$\nu_{max.}$/cm^{-1}	*m/e*	Analysis
(33)	2·0 g (82·5%)	200	1655 (C=$\overset{+}{N}$)	329 [$C_{14}H_{20}NI^+$, $(M - HI)^+$]	Found: C, 37·0; H, 4·6; N, 3·0. $C_{14}H_{21}NI_2$ requires C, 36·8; H, 4·6; N, 3·0%
(34)	1·75 g (79·2%)	250	1675 (C=$\overset{+}{N}$)	289 [$C_{11}H_{16}NI^+$, $(M - HI)^+$]	Found, C, 31·7; H, 3·9; N, 3·4. $C_{11}H_{17}NI_2$ requires C, 31·7; H, 4·1; N, 3·4%

* N.m.r. data not obtained owing to insolubility and broadening of peaks.

to give N-*isopropylidenepyrrolidinium iodide* (1·6 g, 66·2%), m.p. 184°, $\nu_{max.}$ 1675 cm^{-1} ($C\overset{+}{=}N$) (Found: C, 35·0; H, 6·0; N, 5·7. $C_7H_{14}NI$ requires C, 35·1; H, 5·9; N, 5·9%).

2-*Acetylcyclohexanone*.—The iminium iodide (33) (1·0 g) was refluxed with triethylamine (0·50 g) in benzene (15 ml) for 48 h, with rapid stirring. The resulting solution was filtered and treated dropwise with acetyl chloride (0·17 g) in benzene (5 ml) at 40° during 0·25 h with stirring. The mixture was kept at 40° for 1 h, then overnight at room temperature and treated with 20% hydrochloric acid (5 ml). The suspension was refluxed for 5 h; the organic layer was washed, dried, and evaporated to leave a yellow liquid which was distilled to give 2-acetylcyclohexanone as a liquid (0·08 g, 26·1%), b.p. 89—93° at 8 mmHg (lit.,[22] 97—104° at 12—14 mmHg), identical with an authentic sample.[22]

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