The Reaction of 2-Phenyl-2-norbornene with Formaldehyde and Dimethylamine. Additional Evidence for the Occurrence of a 1,5-Hydride Shift during the Aminomethylation of a Strained Bicycloalkene Structure

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Reaction of 2-phenyl-2-norbornene, with formaldehyde and dimethylamine in acetic acid, produced a mixture of compounds best explained by a 1,5-hydride shift in one intermediate step. The compounds in question were *N*-methyl-endo-3-phenyl-exo-2-norbornanemethylamine, *N,N*-dimethyl-endo-3-phenyl-exo-2-norbornanemethylamine, 1,1'-bis(endo-3-phenyl-exo-2-norbornyl)-dimethylamine, 1,1'-bis(endo-3-phenyl-exo-2-norbornyl)trimethylamine and endo-3-phenyl-exo-2-norbornanecarbaldehyde. *N,N*-Dimethyl-1-phenyl-7-nortricyclenemethylamine and *N,N*-dimethyl-3-phenyl-2-norbornene-2-methylamine, formed presumably by the elimination of a proton from the intermediate carbonium ion during the aminomethylation of 2-phenyl-2-norbornene were also identified. In addition, exo-3-dimethylaminomethyl-endo-2-phenyl-exo-2-norbornanol, most likely formed by the addition of water to the same carbonium ion, was found. The normal aminomethylation product of endo-3-phenyl-exo-2-norbornanecarbaldehyde, 2-dimethylaminomethyl-endo-3-phenyl-2-norbornanecarbaldehyde, was identified.

Aminomethylation of an alkene with formaldehyde and a sec. amine usually gives unsaturated amines or saturated amino alcohols.¹ The reaction leading to the unsaturated amine is explained by the assumption that carbonium-immonium-ion I, produced from an amine and formaldehyde, is first added to the double bond, followed by a transfer of a proton from the carbon atom adjacent to the double bond, to the nitrogen atom (Scheme 1).² The tert. amines isolated from the aminomethylation products of norbornene are, however, saturated^{3,4} with the

Scheme 1.

primary products being the sec. amines II and III and the aldehyde IV.⁵ Furthermore, mass spectra of the reaction products of norbornene, formaldehyde and hexadeuteriodimethylamine indicate that deuterium shifts from the dimethyl group of dimethylamine to the norbornene ring.

Scheme 2.

Based on this finding, the intermediate steps in the reaction of norbornene with formaldehyde and dimethylamine must involve the addition of the carbonium-immonium-ion (I) to the double bond and the shift of hydride ion to the norbornane ring (Scheme 2). The similarly derived products formed in a reaction sequence involving a 1,5-hydride shift and subsequent hydrolysis are the amine III and the aldehyde IV. This is readily seen by assuming that in Scheme 2 the ion I is replaced by the ion V. Furthermore, our recent investigation⁵ revealed that the tert. amines, referred to above, which have previously isolated following aminomethylation^{3,4} are Eschweiler-Clarke methylation products produced from the amines II and III.

Since aminomethylation of 2-phenyl-2-norbornene yielded a saturated tert. amine as *N,N*-dimethyl-endo-3-phenyl-exo-2-norbornanemethylamine (VI),⁶ it was of interest to determine if the phenyl substituted products VII, VIII and IX corresponding to the amines II and III and the aldehyde IV as well as X, the methylation product of VIII, are formed during the aminomethylation of 2-phenyl-2-norbornene. 2-Phenyl-2-norbornene was previously aminomethylated using a mol ratio of 1:4:1.5 (2-phenyl-2-norbornene:paraformaldehyde:dimethylamine), with dimethylamine in aqueous solution and the solvent, acetic acid, fortified by

a catalytic amount of concentrated sulfuric acid. These conditions were changed so that the corresponding molar ratio was 1:1:1, dimethylamine was added as the hydrochloride, and the solvent was acetic acid without sulfuric acid. The previous reaction time of 16 h at reflux temperature, was decreased to 30 min at the same temperature. Dilution of the reaction mixture with an excess of water produced crystals which were collected by filtration and identified as the hydrochloride of VIII. The main product isolated by ether extraction of the acidic filtrate was the aldehyde IX. Neutralization of the acidic filtrate produced a mixture of six amines as indicated by gas chromatography. Three of these compounds were identified as the expected tert. amine VI, sec. amine VII and 2-dimethylaminomethyl-2-norbornanecarbaldehyde (XI). The latter is the conventional aminomethylation product of the aldehyde IX. Considering the results from the corresponding aminomethylation of norbornene,⁵ the three remaining amines were unexpectedly a tricyclic amine XII, an unsaturated amine XIII, and an amino alcohol XIV. The amines XII and XIII are thought to be formed from the intermediate ion XV by the elimination of a proton and the amino alcohol XIV arises from the same ion by hydration (Scheme 3).

Scheme 3.

Since the structure of the tert. amine VI was previously verified⁶ and its IR and NMR spectra were available, it appeared reasonable to identify VII, VIII and IX by converting them to VI. Therefore the aldehyde IX was converted to an oxime, which then was reduced with $LiAlH_4$ to the prim. amine XVI, and thereafter converted by methylation⁷ to VI. The sec. amine VIII was methylated to X, which by Cope elimination⁸ decomposed to a mixture of the known hydrocarbon XVII⁹ and hydroxylamine XVIII. The reduction of XVIII with $LiAlH_4$ in ether produced the sec. amine VII, which by methylation yielded VI. The hydrocarbon XVII was prepared as a reference com-

pound by Cope elimination.⁹ The reactions which are proof for the structure of VII, VIII and XI are shown in Scheme 4. To confirm the structures of XII and XIII, the former was converted by Cope elimination to the tricyclic hydrocarbon XIX and its structure determined by mass and NMR spectra (Fig. 1). The latter (XIII) was hydrogenated to XX, which was converted by the Cope elimination to XVII (Scheme 5). The verification of the structure of XIV is based on comparison of the IR and NMR spectra of the compound prepared in another way.¹⁰

In another experiment with the molar ratio 1:4:2, 2-phenyl-2-norbornene, paraformaldehyde

Scheme 4.

Fig. 1. NMR spectrum of 7-methylene-1-phenylnortricyclene (XIX).

Scheme 5.

and dimethylammonium chloride were heated in acetic acid for 18 hours. Due to the excess of paraformaldehyde and long reaction time, one would expect VII and VIII to methylate to VI and X, respectively, under these conditions. Dilution of the crude reaction mixture with water yielded a compound identified as the hydrochloride of X. Analysis of the other amines indicated that the tert. amine VI was one of the major components. Among the other products were XI, XII and XIII, but gas chromatography indicated that the amino alcohol XIV was not present in the mixture. To ascertain the behavior of XIV during the aminomethylation, it was heated in acetic acid for 20 h. The mixture thus produced contained the same components as found after the aminomethylation of 2-phenyl-2-norbornene and, in addition, 2-phenyl-2-norbornene, therefore one could conclude that the formation of XIV in the amino-

methylation of 2-phenyl-2-norbornene is a reversible reaction.

The results of this investigation indicate that the reaction of 2-phenyl-2-norbornene with formaldehyde and dimethylamine occurs to some extent by a similar intramolecular 1,5-hydride shift as was found to be the case with norbornene.^{4,5} However, a number of other products not formed from norbornene, are produced either by the elimination of a proton from the ion XV or by the addition of water to the ion XV. The 1,5-hydride shift can explain the formation of the amines VII and VIII and the aldehyde IX. VI and VIII are most likely the Eschweiler-Clarke methylation products of the amine VII and VIII, respectively. The amino aldehyde XI seems to be formed by direct aminomethylation of the aldehyde IX. Removal of a proton from the ion XV gives either a tricyclic amine XII or an unsaturated amine

XIII, and the addition of water to XV leads to the amino alcohol XIV.

In another investigation using the deuterated compounds, we will show that the Eschweiler-Clarke methylation of amines VII and VIII under the conditions of aminomethylation gives among the tert. amines VI and X also cleavage products whose existence is explained by the 1,3-hydride shift.¹¹

EXPERIMENTAL

Reaction of 2-phenyl-2-norbornene with formaldehyde and dimethylammonium chloride in acetic acid (the shorter reaction time). 2-Phenyl-2-norbornene (0.2 mol) prepared by dehydration of the alcohol obtained from 2-norbornanone and bromobenzene⁶ by Grignard reaction, paraformaldehyde (6.2 g, equivalent to 0.206 mol formaldehyde) and dimethylammonium chloride (0.2 mol) were heated in acetic acid (60 ml) at 115°C for 30 min. Water (300 ml) and ethyl ether (50 ml) were added to the reaction mixture and the VII-hydrochloride which formed was collected by filtration, recrystallized from ethyl alcohol (yield 11.0 g) and characterized as shown later.

The ether layer from the filtrate was separated and the acetic acid-water layer extracted three times with small amounts of ether. The combined ether solutions containing neutral reaction products were freed of acid by washing with a dilute potassium carbonate solution and water, and then dried with calcium sulphate. The acetic acid-water layer from the filtrate was made alkaline with solid potassium carbonate, the freed amines were extracted by ether and the ether extract dried with anhydrous potassium carbonate.

Evaporation of the ether extract of the neutral solution left a residue of 11.5 g, which was distilled in a vacuum. The first fraction, b.p. 105–115°C/0.05 Torr, yield 8.85 g, contained 13 % biphenyl and 8 % 1-phenylnortricyclene, which were transported as impurities from the starting material, and 79 % endo-3-phenyl-exo-2-norbornanecarbaldehyde (IX) (see the structure interpretation of IX on the following pages). Fraction 2, b.p. 120–220°C/0.05 Torr, yield 1.2 g, was not examined closer.

The ether extract containing free amines, was evaporated until dry and the residue distilled in a vacuum. The fraction boiling at 120–150°C/0.05 Torr, yielded 14.5 g and contained according to gas chromatography 6 % of the tricyclic amine XII, 12 % of the unsaturated amine XIII, 11 % of the tert. amine VI, 36 % of the sec. amine VII, 7 % of the amino aldehyde XI, and 28 % of the amino alcohol XIV. The structure interpretations of these compounds are presented in a separate chapter.

Reaction of 2-phenyl-2-norbornene with an excess of formaldehyde and dimethylammonium chloride in acetic acid (the longer reaction time). 2-Phenyl-2-norbornene (0.25 mol), paraformaldehyde (33 g, equivalent to 1.1 mol formaldehyde) and dimethylammonium chloride (0.5 mol) were heated in acetic acid (170 ml) at 110–120°C for 18 h. Water (1500 ml) and ether (200 ml) were added to the reaction mixture and the X-hydrochloride, which formed, collected by filtration and recrystallized from ethyl alcohol (yield 6.6 g). The neutral products and amines were isolated as described earlier.

The neutral products (15.0 g), which boiled at 120–150°C/0.1 Torr contained endo-3-phenyl-exo-2-norbornanecarbaldehyde (IX) as a main component. Other components in this fraction (more than ten by gas chromatography) were not identified.

The isolated free amines were distilled (b.p. 95–98°C/0.04 Torr, yield 20.6 g) and analyzed by gas chromatography. The distillate contained 8.5 % of the tricyclic amine XII, 15 % of the unsaturated amine XIII, 76 % of the tert. amine VI and 0.5 % of the amino aldehyde XI. *N,N*-Dimethyl-endo-3-phenyl-exo-2-norbornanemethylamine (VI) was isolated by using preparative gas chromatography, and its NMR and IR spectra were compared to the corresponding spectra of VI, which were available from the synthesis of VI by known methods.⁶

Endo-3-phenyl-exo-2-norbornanecarbaldehyde (IX) and its structure interpretation. The aldehyde obtained in the aminomethylation of 2-phenyl-2-norbornene (shorter reaction time) was purified according to Frisch¹² by its bisulphite adduct. From 6 g of the adduct was recovered 3 g of IX, b.p. 111–112°C/0.2 Torr, n_D^{20} 1.5547, $C_{14}H_{16}O$ (200.27). Mass spectrum: M^+ m/e 200 (23 %) with the base peak at m/e 43 (100 %). NMR spectrum (in CCl_4): δ 9.68 (1 H) doublet, $J = 1-2$ cps (formyl proton), 7.18 (5 H) singlet (phenyl protons), 3.60 and 3.50 (1 H) two doublets (C-3 exo-proton), 2.70–2.38 (3 H) a broad signal (C-2 and the bridgehead protons) and 1.77–1.07 ppm (6 H) a broad signal (the other protons). In the IR spectrum (in CCl_4) there was a C=O absorption at 1722 cm^{-1} . The semicarbazone of IX melted at 184–186°C (recrystallized from ethyl alcohol). To further confirm the structure of IX, it was converted to an oxime, which was reduced without purification with $LiAlH_4$ in ether to endo-3-phenyl-exo-2-norbornanemethylamine (XVI). XVI was distilled in a bulb tube oven at 110–113°C/0.02 Torr, $C_{14}H_{18}N$ (201.30). Mass spectrum: M^+ m/e 201 (1 %) with the base peak at m/e 31 (100 %). NMR spectrum (in C_6D_6): δ 7.22 (5 H) a singlet (phenyl protons), 2.60 (1 H) a broad signal having a shoulder (C-3 exo-proton), 2.47 (1 H) a doublet, $J = 7$ cps (methylene protons of the aminomethyl group), 2.30 and 2.12 (2 H) two broad signals (the bridgehead protons), 1.84–1.52 (1 H) three broad signals (C-2 endo proton) and 1.52–0.88 ppm (6 H) the other protons of

the norbornane structure. In the IR spectrum (on film) weak NH_2 absorptions at 3380 and 3470 cm^{-1} were seen. The amine XVI was methylated with formaldehyde in formic acid as described by Cope *et al.*⁷ to a tert. amine, whose NMR and IR spectra were similar to those of the previously mentioned *N,N*-dimethyl-endo-3-phenyl-exo-2-norbornanemethylamine (VI).

N-Methyl-endo-3-phenyl-exo-2-norbornanemethylamine (VII) and exo-3-dimethylaminomethyl-endo-2-phenyl-exo-2-norbornanol (XIV). The previously described amine mixture (9.5 g) obtained by aminomethylation of 2-phenyl-2-norbornene (shorter reaction time) and aqueous potassium hydroxide (20 %, 60 ml) were placed in a flask and to this mixture was added gradually *p*-toluenesulphonyl chloride (2.8 g). The contents of the flask were heated for half an hour and the reaction products extracted by ether. The ether solution was extracted with dilute aqueous hydrochloric acid and water, then dried with calcium sulphate. After evaporation of the solvent, the viscous residue (3.4 g) was recrystallized from ethyl alcohol. *N*-Methyl-endo-3-phenyl-exo-2-norbornanemethylamine *p*-toluenesulphonamide, $\text{C}_{22}\text{H}_{23}\text{NSO}_2$ (369.50) mass spectrum M^+ m/e 369, was hydrolyzed according to Snyder *et al.*¹³ by heating in 47 % hydrobromic acid in the presence of phenol. *N*-Methyl-endo-3-phenyl-exo-2-norbornanemethylamine (VII), b.p. 119–121°C/0.03 Torr, n_D^{20} 1.5493, $\text{C}_{16}\text{H}_{21}\text{N}$ (215.33) was obtained in 76 % yield and showed the following spectroscopic properties: mass spectrum m/e 215 (2 %) with the base peak $\text{CH}_3\text{N}^+\text{H}=\text{CH}_2$ at m/e 44 (100 %); NMR spectrum (in C_6D_6): δ 7.22 (5 H) a singlet (phenyl protons), 2.67 (1 H) a multiplet (C-3 exo-proton), 2.50–2.05 (7 H) (in this region the methyl protons appeared as a singlet and the bridgehead and methylene protons of the methylaminomethyl group as a complex signal) and 2.00–1.00 ppm (6 H) the other protons of the norbornane structure. Treatment of VII with formaldehyde in formic acid produced *N,N*-dimethyl-endo-3-phenyl-exo-2-norbornanemethylamine (VI). The unreacted amines extracted by dilute hydrochloric acid, were extracted into ether after addition of solid potassium carbonate. The ether solution was dried with anhydrous potassium carbonate, evaporated and the residue (6.4 g) distilled with collection at 110–150°C/0.1 Torr. The distillate was dissolved in petroleum ether at room temperature, cooled in acetone-dry ice, and the precipitated exo-3-dimethylaminomethyl-endo-2-phenyl-exo-2-norbornanol (XIV) collected. NMR and IR spectra of XIV were comparable to the spectra of the reference compound, prepared by a known method.¹⁰ After five recrystallizations, XIV melted at 65–66°C (reported¹⁰ m.p. 59.5–61.0°).

Endo-3-phenyl-2-dimethylaminomethyl-2-norbornanecarbaldehyde (XI). The aminoaldehyde was isolated from the mixture of amines ob-

tained from aminomethylation of 2-phenyl-2-norbornene (shorter reaction time), by preparative gas chromatography. The reference compound was prepared by heating endo-3-phenyl-exo-2-norbornanecarbaldehyde (IX) (2g), paraformaldehyde (0.3 g) and dimethylammonium chloride (0.85 g) in 3 ml acetic acid for 10 min. The product XI was distilled in a bulb tube oven at 110°C/0.1 Torr yielding 0.15 g. $\text{C}_{17}\text{H}_{23}\text{NO}$ (257.36). Mass spectrum: M^+ m/e 257 with the base peak at m/e 58 (100 %). NMR spectrum (in C_6H_6): δ 9.57 (1 H) a singlet (formyl proton), 7.23 (5 H) a multiplet (phenyl protons), 3.20 (1 H) a doublet, $J=3$ cps (C-3 exo-proton), 2.89 and 2.27 (2 H) $J=13$ cps (the AB-system of methylene protons of the dimethylaminomethyl group), and 2.57–0.50 (14 H) including at 2.48, one of the bridgehead protons as a broad signal and at 2.17 ppm, the methyl protons of dimethylaminomethyl group as a singlet.

Structure evaluation of *N,N*-dimethyl-1-phenyl-7-nortricyclenemethylamine (XII). 7-Methylene-1-phenylnortricycene (XIX). The amine mixture (7 g) obtained by aminomethylation of 2-phenyl-2-norbornene (longer reaction time) was converted with hydrogen peroxide to amine oxides, which were decomposed by heating under reduced pressure. The products were dissolved in ether and purified by removing the unreacted amines from the ether solution with aqueous hydrochloric acid. After drying and removing the ether, the residue was distilled at 124–126°C/8 Torr (2.0 g) yielding two components (14:86), which were isolated by preparative gas chromatography. The main component was endo-3-phenyl-2-methylenenorbornane (XVII) whose mass spectrum confirms the molecular formula of XVII and whose NMR spectrum is identical to that reported for XVII.⁹ The minor component was 7-methylene-1-phenylnortricycene (XIX), $\text{C}_{14}\text{H}_{14}$ (182.25), according to the NMR spectrum (Fig. 1). Mass spectrum: M^+ m/e 182 (100 %).

Structure evaluation of *N,N*-dimethyl-3-phenyl-2-norbornene-2-methylamine (XIII). *N,N*-Dimethyl-endo-3-phenyl-exo-2-norbornanemethylamine (XX). An aliquot (6.4 g) of the crude amine mixture produced in the aminomethylation (longer reaction time) of 2-phenyl-2-norbornene was hydrogenated in 100 ml methanol with Pd/C as a catalyst. During distillation the products boiled at 115–117°C/0.3 Torr (5.15 g). From this mixture, *N,N*-dimethyl-endo-3-phenyl-endo-2-norbornanemethylamine (XX) (19 mg) was isolated, $\text{C}_{16}\text{H}_{23}\text{N}$ (229.35), purity 98.5 %, m.p. 59–61°C by preparative gas chromatography. Mass spectrum: M^+ m/e 229 with the base peak at m/e 58 (100 %). NMR spectrum (in C_6D_6): δ 7.22 (5 H) a singlet (phenyl protons), 3.10 (1 H) C-3 exo-proton, 2.53–1.20 (17 H) including at 2.01 ppm the methyl protons of the dimethylaminomethyl group as a singlet. To confirm the structure, the sample used for NMR spectrum (17 mg) was decomposed via an amine oxide to a hydrocarbon (8.5 mg),

which was identified as endo-3-phenyl-2-methylenenorbornane (XVII) by its mass spectrum.

1,1'-Bis(endo-3-phenyl-exo-2-norbornyl)dimethylamine (VIII). The slightly water soluble amine hydrochloride produced by aminomethylation of 2-phenyl-2-norbornene (shorter reaction time) was heated with aqueous potassium carbonate (20 %, 150 ml) and the freed amine separated and purified *via* the sulphonamide as described earlier for VII. Hydrolysis of sulphonamide (10 g) yielded 1,1'-bis(endo-3-phenyl-exo-2-norbornyl)dimethylamine (VIII) (6.7 g, 87 %) which was distilled in a bulb tube oven at 225°C/0.02 Torr. $C_{28}H_{38}N$ (385.57), n_D^{20} 1.5773. Mass spectrum: M^+ m/e 385 (1 %) with the base peak at m/e 31 (100 %). NMR spectrum (in C_6D_6): δ 7.20 (10 H) a singlet (phenyl protons) and the other protons 2.80–1.00 (25 H) in this region the *N*-methylene protons show as a doublet ($J=7$ cps) at 2.46 ppm. In the IR spectrum (as film) there is a weak absorption at 3380 cm^{-1} . Methylation of VIII with formaldehyde in formic acid produced 1,1'-bis(endo-3-phenyl-exo-2-norbornyl)trimethylamine (X), whose structure is explained below.

1,1'-Bis(endo-3-phenyl-exo-2-norbornyl)trimethylamine (X) and its structure. The slightly water soluble hydrochloride (6.0 g) obtained by aminomethylation of 2-phenyl-2-norbornene (longer reaction time) was freed from its salt with potassium carbonate as described above for VIII and the product 1,1'-bis(endo-3-phenyl-exo-2-norbornyl)trimethylamine (X) distilled in a bulb tube oven at 225°C/0.03 Torr. n_D^{20} 1.5698. $C_{29}H_{37}N$ (399.59). Mass spectrum: M^+ m/e 399 (1 %), $M-171$ (an abstraction of endo-3-phenyl-exo-2-norbornyl radical) m/e 228 (5 %) and the base peak at m/e 58 (100 %). NMR spectrum (in C_6D_6): δ 7.21 (10 H) a singlet (phenyl protons), 2.82–2.48 (2 H) a multiplet (C-3 exoprotons) and 2.37–0.90 ppm (25 H) the other protons as two multiplets. Amine X (0.25 g) was converted with hydrogen peroxide to an amine oxide (yield 0.3 g), which decomposed by heating under reduced pressure to a neutral compound and an amine. These compounds were readily separated by solvent extraction. The neutral product (0.05 g) endo-3-phenyl-2-methylenenorbornane (XVII) was obtained in 25 % yield and its NMR spectrum agreed with that of the reference compound mentioned earlier. The isolated amine was crystallized from petroleum ether to give 0.06 g *N*-methyl-endo-3-phenyl-exo-2-norbornanemethylhydroxylamine (XVIII) in 22 % yield. M.p. 96–98°. $C_{18}H_{21}ON$ (231.33). Mass spectrum: M^+ m/e 231 (3 %), $CH_3N^+(OH)=CH_2$ m/e 231 (3 %) with the base peak at m/e 44 (100 %). NMR spectrum (in C_6D_6): δ 7.26 (5 H) a singlet (phenyl protons), 2.92–2.05 (9 H) a complex signal group, which included a distinct singlet of methyl protons at 2.52 and a broader signal at 1.84–1.05 ppm (7 H). The reduction of XVIII with $LiAlH_4$ in dioxane produced *N*-methyl-endo-3-phenyl-exo-2-norbornanemethylamine (VII), which was

identified by gas chromatography and by its mass spectrum.

Decomposition of exo-3-dimethylaminomethyl-endo-2-phenyl-exo-2-norbornanol (XIV) in acetic acid. The amino alcohol XIV (0.545 g, 2.22 mmol) was heated in acetic acid under reflux for 20 h. To the reaction mixture dilute hydrochloric acid (10 ml) and ether (5 ml) were added, and the crystals which formed separated by filtration, then recrystallized from ethanol (yield 0.063 g). The product was identified by IR spectrum as a mixture of 1,1'-bis(endo-3-phenyl-exo-2-norbornyl)dimethylamine (VIII) and 1,1'-bis(endo-3-phenyl-exo-2-norbornyl)trimethylamine (X) hydrochlorides. From the filtrate the neutral products and amines were isolated by the conventional treatment of solvents. Gas chromatography of the neutral portion (0.17 g) yielded 2-phenyl-2-norbornene (17 %), endo-3-phenyl-exo-2-norbornanecarbaldehyde (IX) (71 %) and three unidentified compounds. 2-Phenyl-2-norbornene and IX were separated by distillation in a bulb tube oven under reduced pressure and their structures were confirmed by IR spectra. Gas chromatography revealed that the amine portion consisted of *N,N*-dimethyl-1-phenyl-7-nortricyclenemethylamine (XII) (2 %), *N,N*-dimethyl-3-phenyl-2-norbornene-2-methylamine (XIII) (7 %), *N,N*-dimethyl-endo-3-phenyl-exo-2-norbornanemethylamine (VI) (17 %), *N*-methyl-endo-3-phenyl-exo-2-norbornanemethylamine (VII) (28 %), the starting material XIV (43 %) and an unidentified amine (3 %).

Apparatus. The gas chromatographic analyses were performed with a Perkin-Elmer chromatograph model F 30 using a two meter long column (10 % Silicone Gum Rubber SE-30 on Chromosorb W) and a flame ionization detector. The analysis was programmed from 170°C to 220°C, the initial time was 5 min, and the heating rate 10 degree/min. An Autoprep model A-700 gas chromatograph manufactured by Wilkens Instrument & Research, Inc., and a 5 m long preparative column (20 % Silicone Gum Rubber SE-30 on Chromosorb W) were used for the chromatographic preparative separations at 210°C with helium as a carrier gas. The instrument was equipped with a hot wire detector. The IR spectra were carried out which a Perkin-Elmer model 457 double beam spectrophotometer, the mass spectra were recorded on a Hitachi Perkin-Elmer RMU 6 E double focusing mass spectrometer, and the NMR spectra on a Varian T 60 spectrometer with tetramethylsilane as the internal standard.

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