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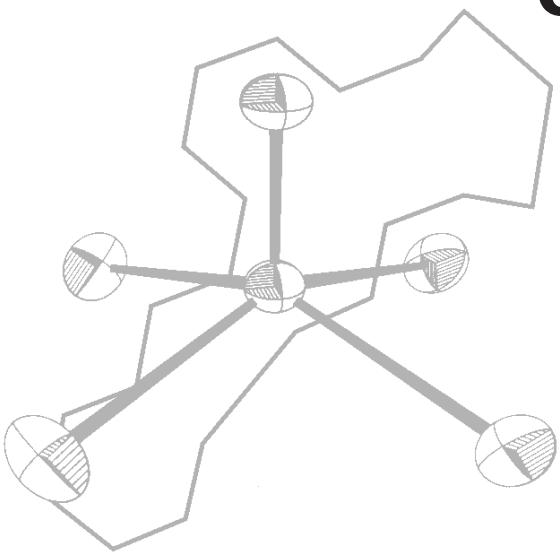

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Competing Radical- and Anion-Mediated Pathways in the Reduction of Bridgehead Tosylates with Lithium Aluminium Hydride

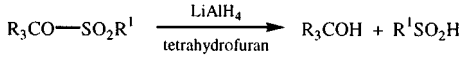
Ernest W. Della[A,B] *and Wit K. Janowski*[A]

[A] Department of Chemistry, Flinders University, Bedford Park, S.A. 5042.
[B] To whom correspondence should be addressed.

Reaction of norborn-1-yl tosylate with lithium aluminium hydride in boiling tetrahydrofuran affords a mixture of norbornan-1-ol accompanied by the ring-opened products 4-methylcyclohexanol and 3-ethylcyclopentanol as their *cis*/*trans* isomers, as well as *p*-thiocresol and *p*-tolyl disulfide. Evidence strongly suggests that the reaction is mediated by the norborn-1-yloxy radical rather than the norborn-1-yloxy anion. The process is initiated by very slow acyl oxygen fission of the norbornyl tosylate, followed by reduction of the derived *p*-toluenesulfinate ion to give the *p*-thiocresoxide anion. Transfer of an electron from the latter to the substrate and decomposition of the derived norborn-1-yl tosylate radical anion leads to the norborn-1-yloxy radical which, upon ring opening, generates the monocyclic alcohols via the corresponding ketones. It is noteworthy that, when norborn-1-yl mesylate is exposed to lithium aluminium hydride, it yields norbornan-1-ol exclusively. In the absence of an efficient electron-transfer agent, the mechanism of reaction of norborn-1-yl mesylate is suggested to involve acyl oxygen fission only.

Introduction

Acyl oxygen fission is an important pathway in the reaction of hindered sulfonate esters with lithium aluminium hydride[1–6] (Scheme 1), and there is strong evidence to suggest that the cleavage of tosylates, for example, occurs by an ionic mechanism involving nucleophilic attack of the aluminium hydride ion on sulfur.



Scheme 1

We have reported[7] that reduction of tricyclo-[3.2.1.$0^{3,6}$]oct-6-yl tosylate (1) with lithium aluminium hydride in boiling tetrahydrofuran gives a mixture of the corresponding alcohol (2) together with *endo*-bicyclo[3.2.1]octan-6-ol (3). Superficially, this transformation can be imagined to proceed on the basis of acyl oxygen fission of the substrate (1) to give the alkoxide (4), some of which survives intact to yield the tricyclic alcohol (2), while the remainder undergoes ring opening affording (3) via the ketone (5). In practice, however, we found that the alcohol (2) could be recovered unchanged when exposed to the reaction conditions, a result demonstrating that the derived ion (4) does not rearrange even though, as a cyclobutenoxide anion, it was expected to ring open readily.[8]

An alternative mechanism of reduction was clearly operating, and the available evidence at the time pointed to the intermediacy of the alkoxy radical (6). Rearrangement of (6) would lead to the radical (7) which gives alcohol (3) on abstraction of a hydrogen atom from tetrahydrofuran.

We were intrigued by these observations, and pondered whether this might be a widespread phenomenon typical of bridgehead tosylates. In view of the structural similarity between the tosylate (1) and norborn-1-yl tosylate (8) and the ready availability of the latter, we decided to examine the behaviour of the ester (8) under the conditions employed for reduction of the tosylate (1). If, indeed, similar results were observed, it was intended to probe the mechanistic pathway in more detail to determine whether there was any evidence for the suspected radical-mediated process.

Results and Discussion

We have observed that, like the tosylate (1),[7] norborn-1-yl tosylate (8) reacts very slowly with lithium aluminium hydride in boiling tetrahydrofuran requiring 10 days before it is completely consumed. Analysis of the product by gas chromatography–mass spectrometry showed the presence of a 3 : 3 : 1 mixture of three components, which were identified in order of elution from the column as norbornan-1-ol (9) and the *cis*/*trans* mixtures of the isomeric alcohols (10) and (11). These observations contrast with those of Gassman and his associates,[6] who reported that exposure of the tosylate

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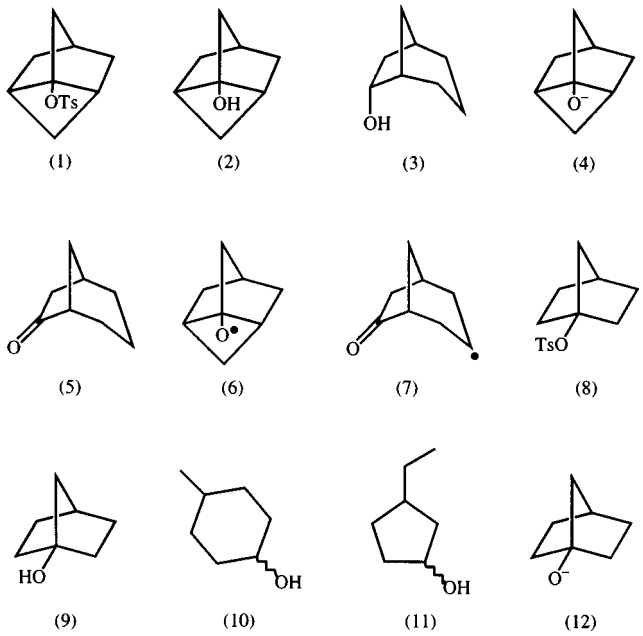
(8) to lithium aluminium hydride in boiling ether gave the corresponding alcohol (9) only; products derived from skeletal rearrangement of the norbornyl system were not detected.



Several additional observations associated with the reaction of tosylate (8) in tetrahydrofuran are noteworthy. First, treatment of norbornan-1-ol (9) with $LiAlH_4$ under the reaction conditions showed that it could be recovered unchanged; this demonstrated that its conjugate base (12) was not the precursor of the ring-opened alcohols (10) and (11). Secondly, analysis of aliquots of the reaction mixture withdrawn during the 10-day period showed that, while the relative proportion of the alcohols (10) and (11) was maintained, the ratio of norbornan-1-ol to the combined mixture of monocyclic alcohols (10)+(11) decreased with time. Thus, for example, a 7 : 5 ratio of (9) to (10)+(11) noted after 6 days decreased to 1 : 1 after 9 days. Thirdly, *p*-thiocresol and *p*-tolyl disulfide were detected among the products, an observation we believe to be the key in providing a rationale for the unusual behaviour of the tosylate (8). Formation of *p*-thiocresol presumably arises from reduction of the *p*-toluenesulfinate anion by $LiAlH_4$, a transformation which has been known[2,9] for some time. Interestingly, addition of *p*-thiocresol at the start of the reaction of tosylate (8) with $LiAlH_4$ caused appreciable enhancement of the rate of reduction, and the reaction was complete within 2 days; furthermore, the ratio of alcohols (9) to (10)+(11) was now 1 : 7 versus the 3 : 4 proportion noted in the absence of added *p*-thiocresol (see Table 1).

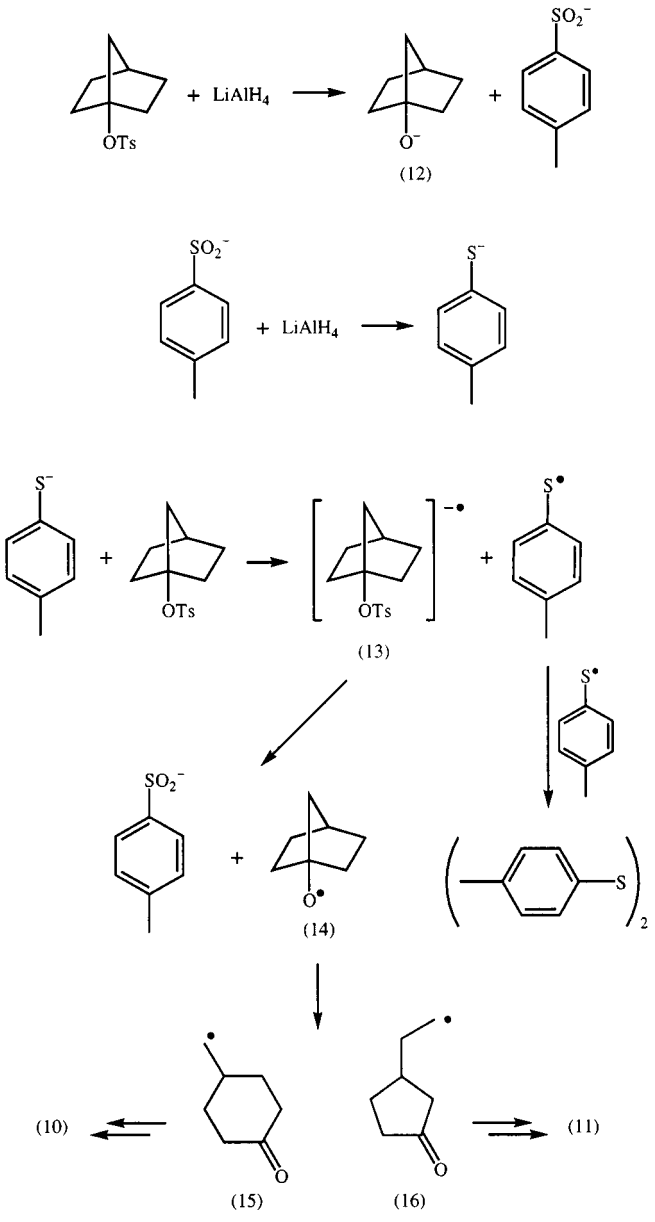
Table 1. Reduction of norborn-1-yl sulfonate esters with $LiAlH_4$ in boiling tetrahydrofuran

Sulfonate ester	Additive used	Reaction time (days)	Product composition (%) SM[A]	(9)	(10)	(11)
Tosylate (8)	none	2	98	2	0	0
	none	6	40	35	19	6
	none	9	20	40	30	10
	none	10	0	41	44	15
	p-thiocresol	2	0	12	66	22
Mesylate (17)	none	1·5	0	100	0	0
	p-thiocresol	1·5	0	100	0	0

[A] Starting material.

On the basis of these observations, we conclude that reduction of norborn-1-yl tosylate (8) occurs stepwise as depicted in Scheme 2. The various steps consist of the following.

(i) The first step consists of slow ionic acyl oxygen fission which delivers the norborn-1-yloxy anion (12) and the *p*-toluenesulfinate anion.



Scheme 2

(ii) This is followed by slow reduction of the latter to the *p*-thiocresoxide ion. In view of the well known one-electron donor properties of the thiophenoxide anion, the following can be suggested.

(iii) Rapid electron transfer from the *p*-thiocresoxide ion to the tosylate (8) then occurs giving the *p*-thiocresoxide radical and the norborn-1-yl tosylate radical anion (13).

(iv) This anion undergoes rapid fragmentation into the *p*-toluenesulfinate ion and the norborn-1-yloxy radical (14).

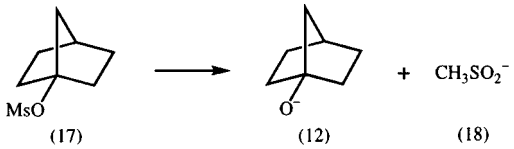
(v) Finally the radical (14) undergoes ring opening yielding the precursor radicals (15) and (16) to the alcohols (10) and (11).

It seems reasonable to assume that *p*-tolyl disulfide, which arises from coupling of *p*-cresylthio radicals, reacts with lithium aluminium hydride to regenerate *p*-thiocresoxide ions.[9,10] Accordingly, as a result of the increase in concentration of *p*-thiocresoxide ions as the reaction of tosylate (8) proceeds, the observed differences in the ratio of norbornan-1-ol (9) and the alcohol mixture (10)+(11) with time can be ascribed to the increasing importance of the single electron transfer channel.

An alternative radical process, in which transfer of an electron from lithium aluminium hydride to the substrate (8) delivers the radical anion (13) directly, seems unlikely; although the intermediacy of radicals has been invoked in the case of $LiAlH_4$ reduction of organohalides,[11] the only case[3] in which electron transfer has been implicated in the corresponding reduction of sulfonate esters appears to be the reduction of 1-tosyloxymethylbicyclo[2.2.2]octanes by lithium aluminium hydride. It is noteworthy that, even in this case, the electron-transfer channel is a very minor component of the total reaction pathway.

If the mechanism depicted in Scheme 2 is correct, then one would not expect the mesylate ester (17) of norbornan-1-ol to behave in a similar way, since there is now no opportunity for production of an efficient single electron transfer reagent such as the *p*-thiocresoxide ion. In accordance with this prediction, we find that treatment of norborn-1-yl mesylate (17) with $LiAlH_4$ under the conditions specified above gives norbornan-1-ol (9) as the only detectable product. Furthermore, the reaction occurs much more rapidly than that of the tosylate (8) and, significantly, addition of the *p*-thiocresoxide ion at the start of the reaction has no observable effect (Table 1).

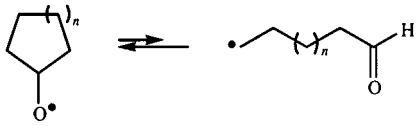
The question arises as to why the norborn-1-yl sulfonate esters (8) and (17) behave differently in (i) their rates of reduction, (ii) the products of their reaction, and (iii) the rate-enhancing effect of added *p*-thiocresol. We believe that a different mechanism of reaction is operating in each case. Reduction of the mesylate (17) is suggested to occur by 'normal' acyl–oxygen fission induced by transfer of hydride from the reagent to the ester and collapse of the intermediate thus formed. This yields the methanesulfinate anion (18) and the norborn-1-yloxy anion (12) which survives the conditions and gives (9) (Scheme 3). This mechanism is consistent with the considerable number of examples[1−5] involving nucleophilic attack at sulfur in sulfonate esters which lead to S–O cleavage. Without the benefit of the aromatic ring to assist in electron capture, the mesylate (17) would be expected to be less amenable than the tosylate (8) to reaction with the *p*-thiocresoxide anion by single electron transfer. Additionally, as Pross[12] has noted, more sterically hindered molecules show greater preference for the single electron transfer route over anionic pathways.



Scheme 3

The different behaviour of the esters (8) and (17) upon reaction with $LiAlH_4$ can be ascribed to the existence of two important features. On the one hand, the greater steric accessibility in (17) would be expected to ensure that its reaction with $LiAlH_4$ proceeds at a much faster rate. At the same time, as suggested above, transfer of an electron from the *p*-thiocresoxide ion should be more effective in the case of the tosylate ester (8); supporting evidence for this is available from electrochemical studies which show that reduction occurs more readily in the case of aryl sulfonate esters relative to alkyl sulfonate esters.[13] Apparently, the poorer electron-acceptor properties of (17) relative to (8) ensure that its mechanism of reduction is not affected by added *p*-thiocresol.

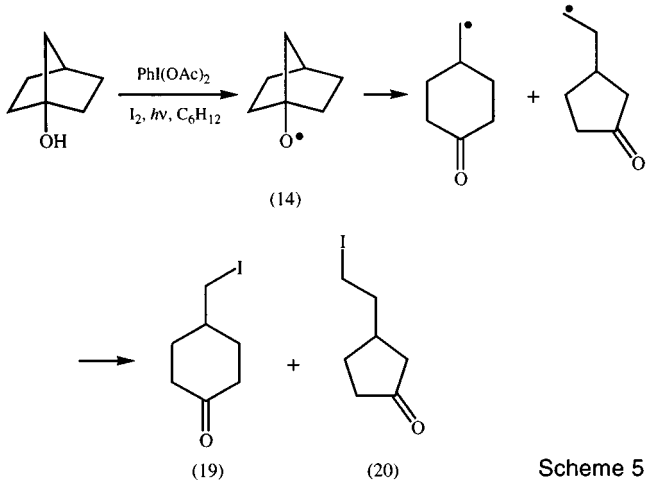
If the implication that the norborn-1-yloxy radical (14) is the intermediate in the reduction of norborn-1-yl tosylate with lithium aluminium hydride is correct, we deemed it appropriate to provide verification that (14) does indeed undergo ring opening readily and irreversibly. For example, the existence of an equilibrium between the cyclic and acyclic isomers below (Scheme 4) is known[14] and, importantly, it favours the former.



Scheme 4

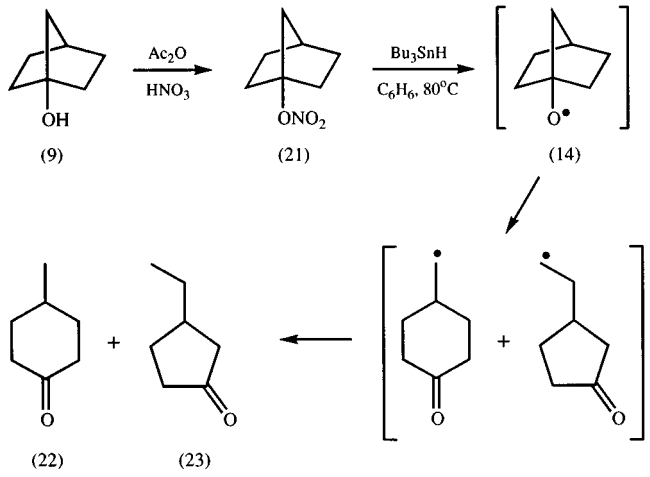
We elected to generate the radical (14) by two independent procedures. In one, treatment of an alcohol under illumination with a mixture of iodobenzene diacetate and iodine in boiling cyclohexane[15] has been shown to yield the corresponding alkoxy radical. Under

these conditions, norbornan-1-ol (9) gave a product which consisted of an 11 : 9 mixture of the isomeric iodo ketones (19) and (20) (Scheme 5). None of the starting alcohol (9) was retained, a result which is to be expected considering that it would be constantly exposed to the reagents.



Scheme 5

In an alternative method, described by Vite and Fraser-Reid,[16] norbornan-1-ol (9) was converted into the nitrate ester (21) and exposed to tributyltin hydride in boiling benzene. This afforded an 8 : 4 : 1 mixture of 4-methylcyclohexanone (22), 3-ethylcyclopentanone (23) and norbornan-1-ol (9) (Scheme 6).



Scheme 6

Thus, in each of the transformations depicted in Schemes 5 and 6, the norborn-1-yloxy radical (14) is seen to undergo ring opening readily.

In summary, it is found that the sulfonate esters (8) and (17) display different behaviour towards lithium aluminium hydride. On the one hand, evidence suggests that reduction of norborn-1-yl tosylate (8) is mediated predominately by the norborn-1-yloxy radical (14), which undergoes ring opening readily. By contrast, the mesylate (17) reacts by acyl oxygen fission to give the norborn-1-yloxy anion (12), which survives the reaction conditions intact.

Experimental

Spectroscopic and gas chromatographic conditions were as specified previously[7] except that ^{1}H and ^{13}C n.m.r. spectra were recorded on a Varian Gemini 300B MHz spectrometer. Norbornane-1-carboxylic acid was prepared as reported[17] and converted into norbornan-1-ol (9) under prescribed oxidative decarboxylative conditions.[18] 4-Tosyloxymethylcyclohexanone was prepared as described.[19] 4-Methylcyclohexanone (22) (lit. n.m.r.[20]) and *cis*/*trans* 4-methylcyclohexanol (10) were available commercially.

Norborn-1-yl Tosylate (8)

A mixture of norbornan-1-ol (9) (0·34 g, 3·0 mmol) and tosyl chloride (1·19 g, 63 mmol) in pyridine (1·5 ml) was stirred under anhydrous conditions at 50°C for 24 h. The mixture was cooled to 0°C, ice (0·5 g) was then added, and the mixture stirred for 20 min before being treated with saturated sodium hydrogen carbonate (I ml). After stirring was continued for a further 30 min, the mixture was extracted with ether. The ether extracts were washed with cold, dilute hydrochloric acid and then with water, before being dried ($MgSO_4$) and evaporated. The residue was distilled (Kugelrohr: 155°C/0·05 mm) to give norborn-1-yl tosylate (8) as a colourless oil (0·62 g, 78%) which soon solidified, m.p. 28–29°C (lit.[21] 29·2–29·8°C). ^{1}H n.m.r. δ ($CDCl_3$) 1·1–2·2, 11H, m; 2·4, 3H, s; 7·3–7·9, 4H, m. ^{13}C n.m.r. δ ($CDCl_3$) 21·6, 29·6, 32·6, 32·8, 41·8, 94·65, 127·5, 129·6, 136·0, 141·2.

Reduction of Norborn-1-yl Tosylate (8)

(A) *With lithium aluminium hydride*. Norborn-1-yl tosylate (8) (0·3 g, 1·1 mmol) was added to a solution of lithium aluminium hydride (0·3 g, 8 mmol) in anhydrous tetrahydrofuran (25 ml) and the solution heated at reflux under a nitrogen atmosphere. The extent of reaction was monitored by gas chromatographic analysis of aliquots, withdrawn periodically, which showed the presence of four components (8)–(11). The ratio of the alcohol mixture (9) : (10)+(11) was found to decrease with time. The reaction was shown to be complete after 10 days, whereupon it was cooled and worked up by dropwise addition of saturated sodium sulfate. After being dried (Na_2SO_4), the mixture was evaporated to give an oil (0·11 g). Analysis (g.c.–m.s.) showed the product to consist of a 3 : 3 : 1 mixture of norbornan-1-ol (9) together with 4-methylcyclohexanol (10) and 3-ethylcyclopentanol (11), each of which was present as a mixture of *cis* and *trans* epimers. *p*-Thiocresol and *p*-tolyl disulfide were also detected among the products. The identity of each of the constituents was confirmed by comparison of its retention time and mass spectrum with those of an authentic sample.

(B) *With lithium aluminium hydride containing* p-*thiocresol.* *p*-Thiocresol (0·28 g, 2·2 mmol) was added to a similar mixture of the tosylate (8) and lithium aluminium hydride in tetrahydrofuran used above, and the solution heated under the same conditions and monitored as described. The reaction was found to be complete within 2 days. G.c.–m.s. analysis of the product showed the proportion of alcohols (9) to (10)+(11) to be 12 : 88.

3-Ethylcyclopentanone (23)

A 1·25 M solution of ethyllithium (30 ml, 37·5 mmol) was added dropwise at −60°C under an argon atmosphere to a stirred suspension of copper(I) iodide (5·7 g, 30 mmol) in ether (20 ml). The mixture was stirred for a further 15 min whereupon a solution of cyclopent-2-enone (0·5 g, 6 mmol) in ether (10 ml) was added slowly at −60°C. This temperature

was maintained with stirring for 30 min, after which time the reaction mixture was allowed to warm to room temperature. Hydrolysis was effected by the addition of saturated ammonium chloride (6 ml). The supernatant layer was separated and the aqueous layer extracted with ether (2×15 ml). The combined organic layers were washed with water, then dried ($MgSO_4$) and evaporated. The residual oil was distilled (Kugelrohr: 60°C/0·5 mm) to give 3-ethylcyclopentanone (0·5 g, 76%), b.p. 158°C (lit.[22] 158°C). ν_{max} 1740 cm^{-1} (lit.[23] 1741 cm^{-1}). ^1H n.m.r. δ ($CDCl_3$) 0·95, 3H, t, J 6·0 Hz; 1·15–2·8, 9H, m. ^{13}C n.m.r. δ ($CDCl_3$) 12·0, 28·25, 28·95, 38·3, 38·7, 44·8, 219·5.

cis/trans-*3-Ethylcyclopentanol (11)*

3-Ethylcyclopentanone was treated with lithium aluminium hydride under standard conditions as described.[24] Distillation (Kugelrohr: 55°C/0·5 mm) gave a mixture of *cis/trans*-3-ethylcyclopentanol. ^1H n.m.r. δ ($CDCl_3$) 0·87, 3H, t, J 6·0 Hz; 1·1–2·35, 9H, m; 3·6, 1H, s; 4·1–4·5, 1H, m. ^{13}C n.m.r. δ ($CDCl_3$) 12·9, 28·9 and 29·4, 29·8 and 30·1, 35·0 and 35·1, 39·2 and 40·2, 41·95 and 42·1, 73·5.

Treatment of Norbornan-1-ol (9) with Lithium Aluminium Hydride

The alcohol (9) (0·07 g) was added to a solution of lithium aluminium hydride (0·3 g) in tetrahydrofuran (25 ml) and the mixture heated under reflux for 12 days. Workup as described above gave a product shown to be starting material (9) exclusively.

Norborn-1-yl Mesylate (17)

Methanesulfonyl chloride (0·63 g, 5·5 mmol) was added dropwise to a solution of norbornan-1-ol (9) (0·50 g, 4·5 mmol) in dichloromethane (15 ml) at 0°C. The mixture was stirred at 0°C for 30 min, and then at ambient temperature for 1 h. Workup as outlined above for the tosylate (8) gave an oil which, upon distillation (Kugelrohr: 120°C/0·05 mm), yielded *norborn-1-yl mesylate* (17) (0·7 g, 82%) (Found: C, 50·9; H, 7·2. $C_8H_{14}O_3S$ requires C, 50·5; H, 7·4%). ^1H n.m.r. δ ($CDCl_3$) 1·35–2·2, 11H, m; 3·0, 3H, s. ^{13}C n.m.r. δ ($CDCl_3$) 29·6, C 3,5; 32·7, C 4; 33·1, C 2,6; 41·95, C 7; 94·4, C 1.

Reduction of Norborn-1-yl Mesylate (17)

(A) *With lithium aluminium hydride.* Norborn-1-yl mesylate (17) (0·14 g, 0·7 mmol) was added to a solution of lithium aluminium hydride (0·3 g, 8 mmol) in dry tetrahydrofuran (25 ml) and the mixture heated under reflux and monitored by gas chromatography as before. The reaction was found to be complete within 36 h. Workup in the usual manner gave a product which was found by g.c.–m.s. analysis to consist solely of norbornan-1-ol (9).

(B) *With lithium aluminium hydride containing* p-*thiocresol.* The reaction in (A) was performed with added *p*-thiocresol (0·18 g, 1·8 mmol). Analysis of the product so obtained showed it to consist of norbornan-1-ol (9) exclusively.

Norborn-1-yl Nitrate (21)

Norbornan-1-ol (0·4 g, 3·5 mmol) was added in small portions to a solution of fuming nitric acid (3 ml) in acetic anhydride (5 ml) cooled in ice and the mixture stirred for 1 h. The mixture was then added to cold (0°C) saturated sodium hydrogen carbonate and extracted with ether, and the combined ether extracts were dried ($MgSO_4$) and evaporated. The residue was chromatographed on silica; elution with hexane afforded the nitrate as a colourless liquid. Distillation (Kugelrohr: 25°C/0·5 mm) yielded *norborn-1-yl nitrate* (21) (0·5 g, 89%) (Found: C, 53·2; H, 7·4; N, 9·1. $C_7H_{11}NO_3$ requires C, 53·5; H, 7·1; N, 8·9%). ^1H n.m.r. δ ($CDCl_3$) 1·35–2·2, 11H, m. ^{13}C n.m.r. δ ($CDCl_3$) 29·8, 31·0, 32·9, 41·2, 95·4.

Reduction of Norborn-1-yl Nitrate (21) with Tributyltin Hydride

A solution of norborn-1-yl nitrate (21) (0·16 g, 1 mmol) and tributyltin hydride (0·58 g, 2 mmol) in benzene (15 ml) was heated under reflux in a nitrogen atmosphere. A solution of α,α-azobis(isobutyronitrile) (0·5 g) in benzene (5 ml) was added to the mixture during the course of reflux. After 48 h the mixture was cooled and evaporated giving an oil which was chromatographed on silica. The fraction that eluted with 1:1 ether/hexane was distilled (Kugelrohr: 50°C/0·5 mm) and shown by g.c.–m.s. analysis to consist of a 2:1 mixture of 4-methylcyclohexanone (22) and 3-ethylcyclopentanone (23), by comparison with authentic samples, together with a trace of norbornan-1-ol (9) (3%).

Reaction of Norbornan-1-ol (9) with Iodobenzene Diacetate and Iodine

A solution of norbornan-1-ol (0·17 g, 1·5 mmol), iodobenzene diacetate (0·26 g, 0·8 mmol) and iodine (0·19 g, 0·75 mmol) in cyclohexane (20 ml) was irradiated (300-W tungsten lamp) while being heated under reflux for 30 min. The mixture was cooled and washed with saturated sodium hydrogen carbonate before being dried ($MgSO_4$) and evaporated. Distillation of the residual oil (Kugelrohr: 90–95°C/0·2 mm) afforded an 11:9 mixture (0·26 g) of 4-iodomethylcyclohexanone (19), which was identified by comparison of its ^1H and ^{13}C n.m.r. spectra with those of the authentic sample below, and a product tentatively identified as 3-(2-iodoethyl)cyclopentanone (20) on the basis of g.c.–m.s. analysis and its ^{13}C n.m.r. spectrum: ($CDCl_3$) δ 4·0, 26·9, 28·6, 38·3, 39·1, 44·0, 218·0.

The product was treated with tributyltin hydride in refluxing benzene under standard conditions and worked up in the usual manner to give an 11:9 mixture of 4-methylcyclohexanone (22) and 3-ethylcyclopentanone (23) whose identities were established by comparison of their ^{13}C n.m.r. spectra with those of authentic materials.

4-Iodomethylcyclohexanone (19)

4-Tosyloxymethylcyclohexanone (5·6 g, 20 mmol) was added to a solution of sodium iodide (12 g, 20 mmol) in 1,2-dimethoxyethane (60 ml) and the mixture stirred at 65°C for 3 h and for a further 16 h at room temperature. Hexane (300 ml) was added and the solution washed with water and saturated sodium sulfate before being dried ($MgSO_4$) and evaporated. The solid residue was recrystallized from hexane to give *4-iodomethylcyclohexanone* (19) (4·3 g, 90%), m.p. 85°C (Found: C, 35·5; H, 4·7. $C_7H_{11}IO$ requires C, 35·2; H, 4·7%). ^1H n.m.r. δ ($CDCl_3$) 1·2–2·5, 9H, m; 3·2, 2H, d, J 6 Hz. ^{13}C n.m.r. δ ($CDCl_3$) 12·3, 32·6, 38·2, 39·9, 210·7.

Acknowledgment

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