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The *endo*- and *exo*-1,7,7-Trimethylbicyclo-[2.2.1]heptan-2-amines (Bornan-2-amines) and Their Acetamides

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Abstract

Melting points provide a poor method for differentiation between the *exo* and *endo* *N*-(bornan-2-yl)-acetamides, and have led to errors by previous workers. Spectral differences leading to unambiguous assignment are discussed in this paper. Trapping of the bornan-2-yl carbenium ion with acetonitrile leads to *exo* products.

Introduction

During attempts[1] to obtain unrearranged *endo*-3-chlorocamphane (1) from *endo* alcohol (2) by use of phosphorus pentachloride, we had occasion to vary the solvent polarity. In acetonitrile a lower yield of the rearranged *exo* chloride (3) was obtained, together with up to 40% of an intermediate by-product, possibly (4), which on hydrolysis during workup gave the amide (5). A literature survey indicated some confusion concerning the stereochemistry at C2 of the *N*-(bornan-2-yl)acetamides (5) and (10), and these misunderstandings are reviewed in this paper.

Discussion and Results

The literature shows that the *exo* acetamide (5) and the *endo* isomer (10) have similar melting points [(1*R*,2*R*,4*R*)-isomer (5): m.p. 143–144°, $[\alpha]_D$ −19°.[2,3] Racemate (5): m.p. 141–143°.[4,5] Compound (5) of unknown optical activity: m.p. 134–135°,[6] 144°,[7] 142–143°.[8] (1*R*,2*S*,4*R*)-isomer (10): m.p. 145–145·5°, $[\alpha]_D$ −43°.[2,9] Racemate (10): m.p. 137·5–140°[10]]. The problem is compounded in that products (5) and (10)

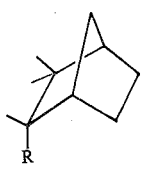
[1] Brecknell, D. J., Carman, R. M., and Greenfield, K. L., *Aust. J. Chem.*, 1984, **37**, 1075.
[2] Forster, M. O., *J. Chem. Soc.*, 1898, **73**, 386.
[3] Forster, M. O., and Hart-Smith, J., *J. Chem. Soc.*, 1900, **77**, 1152.
[4] Roberts, C. W., and Maskaleris, M. L., *J. Org. Chem.*, 1959, **24**, 926.
[5] Ritter, J. J., and Minieri, P. P., *J. Am. Chem. Soc.*, 1948, **70**, 4045.
[6] Takeuchi, K., Nojima, M., and Tokura, N., *J. Chem. Soc., Perkin Trans. 1*, 1976, 2205.
[7] Maki, Y., Ozeki, K., and Suzuki, M., *Chem. Pharm. Bull.*, 1975, **23**, 1619.
[8] Kitagawa, N., Nojima, M., and Tokura, N., *J. Chem. Soc., Perkin Trans. 1*, 1975, 2369.
[9] Frankland, P. F., and Barrow, F., *J. Chem. Soc.*, 1909, **95**, 2017.
[10] Barton, D. H. R., Magnus, P. D., Garbarino, J. A., and Young, R. N., *J. Chem. Soc., Perkin Trans. 1*, 1974, 2101.

0004-9425/84/081785$02.00

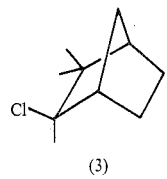
are often derived from carbenium ion pathways where optical purity is not necessarily retained. Despite this, several groups of workers have appeared to use melting points in this series to assign the C2 configuration.

To confirm the *exo* C2 configuration of the acetamide (5) obtained from the reaction of alcohol (2) with phosphorus pentachloride in acetonitrile, we now report the preparation of both the *exo* and *endo* acetamides.

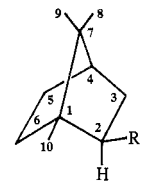
The oxime of (+)-camphor (14) was reduced with sodium in ethanol to give a mixture of the amine hydrochlorides (*endo*/*exo*; 72 : 28). Recrystallization from aqueous acid led to *endo*-bornan-2-amine (11) which was readily acetylated to compound (10).



(1) R = Cl
(2) R = OH

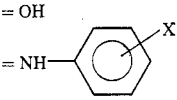


(3)

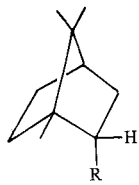


(4) R = N=C(Cl)Me
(5) R = NHCOMe
(6) R = NH_2

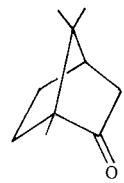
(7) R = Cl
(8) R = OH



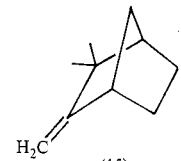
(9) R = NH–



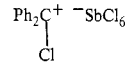
(10) R = NHCOMe
(11) R = NH_2
(12) R = Cl
(13) R = OH



(14)



(15)



(16)

Because others[2,3,11–13] have experienced difficulties in separating pure *exo* amine (6) from the above mixture, the *exo* series was obtained through a Ritter reaction[5] upon camphene (15) in acetonitrile to give the pure racemic *exo* amide (5) which was hydrolysed to *exo* amine (6).

The configuration in the isomeric series can be readily determined by n.m.r. spectroscopy. The chemical shift of C6 is sensitive to the orientation of the C2 substituent,[14,15] and the *endo* isomers (10) and (11) show a large (8–10 ppm) sterically induced upfield shift of C6 relative to the *exo* isomers (5) and (6). In the proton spectra, the C2 proton of the *endo* isomers (*exo* proton) is downfield relative to the *exo* isomers (*endo* proton) (compare δ 4·25 and 3·90 for the amides (10) and (5), and δ 3·06 and 2·71 for the amines (11) and (6) respectively). In the *exo* amine (6)

[11] Pope, W. J., and Read, J., *J. Chem. Soc.*, 1913, **103**, 444.
[12] Goodson, J. A., *J. Chem. Soc.*, 1927, 930.
[13] Heubaum, U., and Noyes, W. A., *J. Am. Chem. Soc.*, 1930, **52**, 5070.
[14] Grutzner, J. B., Jautelat, M., Dence, J. B., Smith, R. A., and Roberts, J. D., *J. Am. Chem. Soc.*, 1970, **92**, 7107.
[15] Lippmaa, E., Pehk, T., Paasivirta, J., Belikova, N., and Plate, A., *Org. Magn. Reson.*, 1970, **2**, 581.

this C 2 proton (dd, J 8·5, 5·5 Hz with some second-order effects) is coupled to the C 3 methylene protons, while H 2 in *endo* amine (11) (ddd, J 11, 4·5, 2 Hz) exhibits an additional long-range W-coupling (2 Hz) to the C 6 *exo* proton. The splittings of the *exo* and *endo* amides (5) and (10) follow a similar pattern, with a further coupling (J 9 Hz) to the amide proton. In pyridine solution the C 2 proton (ddd, J 8,8,8 Hz) of the *exo* amide (5) exhibits equal H 2 *endo*/H 3 *endo* and H 2 *endo*/H 3 *exo* couplings, while no major solvent effect is seen in the H 2 couplings of the *endo* amide (10). The H 2 *endo*/H 3 *exo* coupling of 8 Hz is relatively large, but may be explained[16] if solvation of the *exo* amide group leads to steric interference with the *syn* C 7 methyl, and hence to ring distortion.

These authentic spectra enabled us to confirm that the amide obtained[1] in the phosphorus pentachloride treatment of alcohol (2) in acetonitrile had the *exo* configuration (5). The same amide (5) was also obtained from the reaction of isobornyl chloride (7) in acetonitrile with stannic chloride, with boron trifluoride etherate, or with silver perchlorate. These reactions were performed under anhydrous conditions, when an intermediate could be observed in the n.m.r. tube (δ 0·87, obscured Me; 0·92, 0·96, 2 Me; 3·79, dd, J *c.* 14, 7 Hz; with CD_3CN as both reagent and solvent). This intermediate is considered to be *exo* and is tentatively assigned a structure resembling (4). Hydrolysis of (4) during workup yields amide (5). In the phosphorus pentachloride reaction the intermediate (4) slowly converted into isobornyl chloride (7) on standing (*c.* 3 weeks).

These above results are in agreement with the work of Kitagawa *et al.*[8] who found that the reaction of camphene hydrochloride (3), isobornyl chloride (7) or bornyl chloride (12) with liquid sulfur dioxide–antimony pentachloride in acetonitrile at −70° always gave the *exo* amide (5). Similarly, isoborneol (8) or borneol (13) with sulfuryl chloride in acetonitrile also gave[6] the *exo* amide (5), although the m.p. 134–135° recorded for this product might indicate some contaminant.

The formation of *exo* products is also consistent with the work of Brown[17] who has noted that additions to 7,7-dimethylnorborn-2-enes involving open transition states or intermediates lead to a preference for *exo* attack despite the steric hindrance provided by the C 7 methyl groups. Furthermore, it has recently been established[18] that nucleophilic substitution of the chloride in bornyl chloride (12) by anilines gives the *exo* bornyl aniline (9) as the only substitution product.

In contrast, Barton[10,19] claimed exclusive formation of the *endo* amide (10) in the reaction of either isoborneol (8) or borneol (13) with chlorodiphenylmethylium hexachloroantimonate (16) and acetonitrile at room temperature. While Barton attempted to provide a mechanistic rationalization for this result, his product identification appears to be based only upon m.p. and m.m.p. comparisons, although he does add the blanket cover 'all compounds had n.m.r. data in accord with the assigned structures'. Barton further quotes a literature m.p. of 143°, claiming it to be for the (−)-*endo* acetamide (10), although it actually refers in the original literature[2] to the (−)-*exo* acetamide (5). Consequently, and in view of all the above data indicating preferred *exo* attack, we considered that Barton's product was most likely the *exo*

[16] Flautt, T. J., and Erman, W. F., *J. Am. Chem. Soc.*, 1963, **85**, 3212.
[17] Brown, H. C., Kawakami, J. H., and Liu, K.-T., *J. Am. Chem. Soc.*, 1973, **95**, 2209.
[18] Lysenkov, V. I., Pekhk, T. I., Klyuev, A. Yu., and Zheleznyak, T. L., *J. Org. Chem. USSR*, 1982, **18**, 2309.
[19] Barton, D. H. R., Magnus, P. D., and Young, R. N., *J. Chem. Soc., Chem. Commun.*, 1973, 331.

isomer (5) and have therefore repeated his work as closely as possible. Both isoborneol (8) and borneol (13) with chlorodiphenylmethylium hexachloroantimonate (16) and acetonitrile gave exclusively *exo* amide (5). No evidence for the formation of any *endo* amide (10) could be observed. Isoborneol (8) reacted rapidly (< 5 min) while some unchanged borneol (13) was still evident after 20 min. The rationalizations previously invoked[10] to explain the apparent *endo* product are thus no longer required, and there is now no evidence in the literature to suggest that the 2-bornanyl carbenium ion is trapped by acetonitrile in anything other than an *exo* direction.

Some confusion regarding melting points is also apparent in the paper of Roberts and Maskaleris[4] wherein it is implied that the *exo* amide (5) has a m.p. of 145·5°, whereas the literature quoted refers to the *endo* isomer (10).

We therefore caution against the use of melting points and mixed melting points as criteria by which to assign configuration in this series.

Note Added in Proof

Sir Derek Barton and Dr R. N. Young agree that an error occurred in their original work. Dr Young kindly informs us that his assignment of stereochemistry to the acetamides was by a mixed m.p. comparison with 'authentic' synthetic acetamides whose structures he assigned from Rodd's Chemistry of Carbon Compounds [Vol. II, Alicyclic Compounds, Part C, p. 232, Ed. S. Coffey (Elsevier: Amsterdam 1969)]. However this latter reference has incorrectly reversed the structures portrayed for bornylamine and isobornylamine.

Experimental

General

^{1}H and ^{13}C n.m.r. spectra were recorded upon JEOL JNM PS-100 and JEOL FX-100 spectrometers, and are for $CDCl_3$ solutions unless otherwise stated. G.c.–m.s. data were obtained upon a Hewlett–Packard 5992B instrument containing a 12-m OVl capillary column. Product percentages were obtained from g.c. data by direct integration, and from ^{13}C n.m.r. data by averaging the intensities of all of the peaks.

(±)-exo-N-(*Bornan-2-yl*)*acetamide* (*5*)

Following the method of Ritter,[5] acetonitrile (1·8 g) was added to a solution of sulfuric acid (conc., 4 g) in acetic acid (glacial, 20 ml) at 20°. Camphene (partly racemic, $[\alpha]_D$ +20°, 6 g) was added and the mixture stirred overnight at below 50°. The product was poured into water, neutralized (Na_2CO_3) and extracted into ether to give racemic amide (5) (6 g), m.p. 143·5–145° (from methanol/water) (lit.[5] 142–143°). ^{1}H n.m.r. δ 0·82, 0·85, 2 s, $(7\text{-Me})_2$; 0·92, s, 1-Me; 1·96, s, acetyl Me; 3·90, ddd, *J* 9, 9, 5 Hz with some second-order effects, H2; 5·85, br d, *J* 9 Hz, NH. ^{1}H n.m.r. δ (C_5D_5N) 0·76, 0·98, 1·01, 3 s, Me; 2·01, s, acetyl Me; 4·25, ddd, *J* 8, 8, 8 Hz, H2. ^{13}C n.m.r. δ 11·64, q, C10; 20·27, 20·30, 2 q, C8 and C9; 23·43, q, acetyl Me; 27·00, t, C5; 35·95, t, C6; 38·85, t, C3; 44·81, d, C4; 46·98, s, C7; 48·47, s, C1; 56·72, d, C2; 169·40, s, acetyl carbonyl. *m/z* 195 (M, 11%), 136 (23), 121 (46), 95 (78), 93 (22), 86 (30), 44 (69), 43 (100), 41 (44).

In another reaction the mixture was stirred for only 3 min, and then worked up as above. ^{13}C n.m.r. analysis revealed two principal components (35 : 65). The minor product was *exo* amide (5) as above; the major product was isobornyl acetate, identical (^{13}C n.m.r.) with an authentic sample.

Other attempted procedures for the synthesis of the *exo* amide (5) included (reactant (0·1 g), 1·03 mol. equiv. of reagent, dry (D_3)acetonitrile (0·7 ml) at room temperature).

(A) Camphene (15) with *p*-toluenesulfonic acid for 1 h gave, after workup, unchanged camphene (9%), amide (5) (70%), and other unidentified compounds (no *endo* amide) (n.m.r., g.c.).

(B) Isobornyl chloride (7) with boron trifluoride etherate for 1 h gave, after workup, unchanged isobornyl chloride (1%), *exo* amide (5) (66%), camphene (6%) and other unidentified compounds (no *endo* amide) (n.m.r., g.l.c.).

(C) Isobornyl chloride (7) with silver perchlorate monohydrate showed, by ^{1}H n.m.r., complete conversion into compound (4)(?) after 2 h (δ (CD_3CN) 0·86, 0·90, 0·94, 3 s, Me; 3·81, dd, J 14, 7 Hz). Addition of water gave immediate hydrolysis to amide (5) (100% by n.m.r.). The amide (5) was isolated and characterized (n.m.r. as for an authentic sample).

(D) Bornyl chloride (12) was unchanged with silver perchlorate monohydrate (24 h).

(E) Isobornyl chloride (7) with stannic chloride (3 drops) was examined by ^{1}H n.m.r. spectroscopy at ambient temperature. The chloride was immediately (< 5 min) converted into an intermediate (δ 0·92, 1·02, 1·12, 3s, Me; 4·38, dd?, J 9, 5 Hz) which changed within 6 h to a second intermediate (4)(?) (δ 0·87, 0·92, 0·94, 3s, Me; 3·83, dd, J 14, 7 Hz) which then remained constant (8 months). Hydrolysis of either of these intermediates gave a similar g.c.–m.s. profile containing *exo* amide (5) (*c.* 75%) with several minor components.

(±)-exo-*Bornan-2-amine* (*6*)

The *exo* amide (5) (5 g) in ethanol (200 ml) and sulfuric acid (10% aq., 200 ml) was refluxed (5 days). Normal workup yielded a yellow oil which crystallized, m.p. 181–183° (sealed capillary) (after sublimation at 40°/1 mm) (lit.[3] 184° for the (−)-isomer). ^{1}H n.m.r. δ 0·82, 0·87, 0·97, 3 s, Me; 1·49, br s, NH_2, exchangeable with D_2O; 2·71, dd, J 8·5, 5·5 Hz, with some second-order effect since the first and third lines from lower field are further broadened. ^{1}H n.m.r. δ (C_6D_6) 0·80, s, 2 Me; 1·08, s, Me; 1·36, br s, NH_2, exchangeable; 2·68, dd, J 8, 5·5 Hz, H2. ^{13}C n.m.r. δ 11·85, q, C10; 20·33, 20·90, 2 q, C8 and C9; 27·25, t, C5; 36·40, t, C6; 40·61, t, C3; 45·01, d, C4; 46·57, s, C7; 48·08, s, C1; 60·43, d, C2. *m/z* 153 (M, 20%), 121 (13), 108 (17), 95 (63), 82 (68), 70 (20), 69 (25), 67 (19), 56 (19), 44 (28), 43 (100), 41 (46).

Camphor Oxime

The oxime of (+)-camphor (14) was prepared in the normal manner, m.p. 117·5–119·5°, $[\alpha]_D$ −41° (*c*, 1·6 in ethanol) (lit.[20] 119°, $[\alpha]_D$ −42·4°). ^{1}H n.m.r. δ 0·81, 0·92, 1·01, 3 s, Me; 9·58, br s, NOH. ^{13}C n.m.r. δ 11·12, q, C10; 18·55, 19·48, 2 q, C8 and C9; 27·26, t, C5; 32·64, 33·11, 2 t, C3 and C6; 43·76, d, C4; 48·26, s, C7; 51·80, s, C1; 169·72, s, C2. *m/z* 167 (M, 23%), 150 (13), 149 (19), 134 (91), 124 (28), 108 (38), 94 (32), 93 (90), 91 (34), 79 (35), 67 (46), 53 (33), 41 (100).

(+)-endo-*Bornan-2-amine* (*11*)

Camphor oxime (11 g) in ethanol (dry, 175 ml) was cautiously treated with sodium (19 g, cut into small pieces) and the reflux continued for 2 h. The solution was cooled and water (175 ml) added. The mixture was reduced to *c.* 175 ml and the precipitate (6·5 g) collected. ^{13}C n.m.r. showed *endo* amine (11) (57%), *exo* amine (6) (23%) and borneol (13) (20%).

The amines were taken into dilute hydrochloric acid, which left the borneol (identical with an authentic sample by ^{1}H and ^{13}C n.m.r.) in ether.

The amine hydrochlorides (72% *endo*/28% *exo*) were recrystallized from hydrochloric acid (2 M) until the optical rotation was constant, $[\alpha]_D$ +19° (*c*, 1·60 in ethanol) (lit.[2] +22·7°), when the amine was liberated with potassium hydroxide solution. Sublimation (70°/760 mm) yielded colourless crystals of *endo* amine (11), m.p. 162·5–164° (sealed capillary), $[\alpha]_D$ +44° (*c*, 2·71 in ethanol) (lit.[2] 163°, $[\alpha]_D$ +45·5°). ^{1}H n.m.r. δ 0·79, 0·88, 0·88, 3 s, Me; 1·46, br s, NH_2, exchangeable; 3·06, ddd, J 11, 4·5, 2 Hz, H2. ^{13}C n.m.r. δ 13·37, q, C10; 18·48, q, C8; 20·39, q, C9; 26·34, t, C6; 28·52, t, C5; 39·73, t, C3; 45·07, d, C4; 48·21, s, C7; 49·09, s, C1; 56·65, d, C2. *m/z* 153 (M, 22%), 121 (14), 108 (16), 95 (66), 93 (20), 82 (71), 70 (20), 69 (25), 67 (20), 44 (30), 43 (100), 42 (20), 41 (46). The mass spectra of amines (11) and (6) were very similar (correlation index of 1·000 when standard Hewlett–Packard software was used) and were not useful for identification purposes.

[20] Bredt, J., and Rosenberg, M., *Justus Liebigs Ann. Chem.*, 1896, **289**, 1.

Amine (11) and amine (6) showed very similar retentions on OV1. Solutions of either compound in carbon disulfide also showed longer retention peaks, increasing in magnitude with time, due to the corresponding isothiocyanate.

(−)-endo-N-(*Bornan-2-yl*)*acetamide* (*10*)

endo-Amine (11) was refluxed (25 min) with acetic anhydride in pyridine to yield, after normal workup, colourless crystals, m.p. 144–146° (after sublimation at 100°/1 mm), $[\alpha]_D$ −41° (*c*, 3·62 in ethanol) (lit.[9] 145·5°, $[\alpha]_D$ −43·5°). ^{1}H n.m.r. δ 0·81, 0·87, 0·94, 3 s, Me; 2·01, s, acetyl Me; 4·25, dddd, *J* 11, 9, 4·5, 2 Hz, H2; 6·37, br d, NH. Irradiation at δ 6·37 collapsed the 4·25 system to a ddd, *J* 11, 4·5, 2 Hz. The 6·37 system slowly exchanged with D_2O and after one week the peak had disappeared while the 4·25 system had collapsed to a ddd, *J* 11, 4·5, 2 Hz. ^{1}H n.m.r. (C_5D_5N) δ 0·82, 0·93, 0·98, 3 s, Me; 2·10, s, acetyl Me; 4·64, dddd, *J* 9, 7, 3·8, 1·7 Hz, H2. ^{13}C n.m.r. δ 13·69, q, C10; 18·66, q, C8; 19·83, q, C9; 23·58, q, acetyl Me; 27·99, t, C6?; 28·34, t, C5?; 37·47, t, C3; 44·93, d, C4; 48·12, s, C7; 49·35, s, C1; 53·76, d, C2; 170·16, s, acetyl carbonyl. *m/z* 195 (M, 19%), 136 (29), 121 (62), 95 (92), 93 (24), 86 (32), 55 (20), 44 (64), 43 (100), 41 (47). The mass spectra of amides (10) and (5) were very similar (correlation index of 0·987 when standard Hewlett–Packard software was used) and were not useful for identification purposes.

Amide (5) ($R_{t,rel}$ 1·00) and amide (10) ($R_{t,rel}$ 1·06) were separable by g.l.c. (OV1 at 125°). The separation was improved in temperature-programmed (80° for 2 min, then 16°/min increase) runs.

Reaction of Alcohol (*2*) *with Phosphorus Pentachloride in Acetonitrile*

Phosphorus pentachloride (0·14 g) and calcium carbonate (powdered, 0·1 g) were stirred (0°, 3 min) in (D_3)acetonitrile (0·7 ml). Alcohol (2) (0·09 g) was added, the mixture stirred (1 min), and then rapidly filtered, dosed with tetramethylsilane and observed by ^{1}H n.m.r. spectroscopy at ambient temperature. No alcohol (2) remained after 20 min. The *exo* chloride (3) rearranged completely within a further 2 h to *exo* chloride (7) and the trideutero compound (4)(?) (up to 40%) (^{1}H n.m.r. (CD_3CN) δ 0·87, Me, obscured under peaks of compound (7); 0·92, 0·96, s, 2 Me; 3·79, dd, *J c.* 14, 7 Hz). Intermediate (4) slowly converted into isobornyl chloride (7) over three weeks.

Hydrolysis of intermediate (4) yielded the trideutero isomer of amide (5) (n.m.r. and g.c. retention). *m/z* 198 (M, $C_{12}H_{18}D_3NO$, 24%), 136 (41), 121 (69), 95 (100), 89 (44), 63 (9), 46 (40), 45 (45), 44 (55).

When the above reaction was repeated in undeuterated acetonitrile, the amide (5) had n.m.r. and mass (M, 195) spectra and g.l.c. retention identical with those from an authentic sample.

Chlorodiphenylmethylium Hexachloroantimonate (*16*) *Reactions*

The alcohol (8) or (13) (0·23 g) in dry acetonitrile (5 ml) was treated with salt (16) (0·89 g) prepared[21] from dichlorodiphenylmethane[22] and antimony pentachloride in a dry glove bag under dry nitrogen at room temperature. The homogeneous mixture was quenched with water (4 ml) (this step is *not* reported in the Experimental section of reference 10, although it is mentioned in the abstract) and extracted with ether. The ether was dried and removed, and the total crude extract examined (^{1}H and ^{13}C n.m.r., g.c.–m.s.).

When isoborneol (8) was treated by this method (room temperature, 5 min), no alcohol remained and the product was essentially pure *exo* amide (5) contaminated with the expected molar equivalent of benzophenone. The *exo* amide (5), m.p. 143–145°, was isolated (t.l.c.) and showed a ^{13}C n.m.r. spectrum identical with that of an authentic sample and clearly different from that of *endo* amide (10).

The reaction with borneol (13) was not as clean. Workup after 20 min provided, besides benzophenone, unchanged borneol (13%), *exo* amide (5) (82%) (g.c. and ^{13}C n.m.r. confirmation), and an unidentified minor product (5%) (*not endo* amide (10)!).

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[21] Olah, G. A., and Svoboda, J. J., *Synthesis*, 1972, 307.
[22] Mackenzie, J. E., *J. Chem. Soc.*, 1896, **69**, 985.