Conversion of Alcohols into Amides by Chlorodiphenylmethylium Hexachloroantimonate in Nitrile Solvents; Some Further Reactions of the Triphenylmethyl Cation

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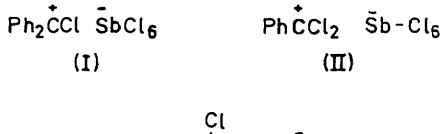
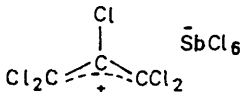
Treatment of alcohols with the cations chlorodiphenylmethylium (I), dichloro(phenyl)methylium (II), and pentachloroallylium (III) in nitrile solvents gives the nitrilium ions derived from the alcohols, which on quenching with water give the corresponding amides. Quenching the nitrilium ions with suitable nucleophiles provides tetrazoles, thioamides, amidines, and amidates. Certain limitations on the oxidations by triphenylmethyl cation reported previously are described.

CHLORO-ANALOGUES of the triphenylmethyl cation have been prepared recently as stable salts by Olah and Svoboda.[1] The salts [chlorodiphenylmethylium (I), dichloro(phenyl)methylium (II), and pentachloroallylium (III) hexachloroantimonates] can be obtained readily, although they are extremely sensitive to moisture and must be handled in a dry atmosphere.

For comparison with earlier work [2] with the triphenylmethyl cation, we have studied the reactions of the cations (I)—(III) with alcohols.[3] At room temperature

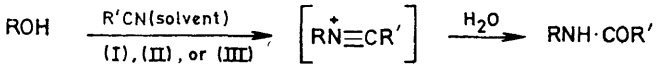


(I) (II)



(III)

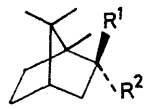
products were obtained in which the alcohol function in the substrate had been replaced by the nucleophilic species in the reaction medium. In nitrile solvents, after aqueous work-up, amides were formed (Scheme 1; Table 1).



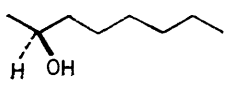
SCHEME 1

Superficially the reaction seems to be a non-protonic analogue of the Ritter reaction.[4] However, there are notable differences. Cholesterol, which does not undergo the simple Ritter reaction,[4] reacts with dichloro(phenyl)methylium (II) in acetonitrile to give 3β-acetamidocholest-5-ene. Also n-decanol reacts with the cations (I) and (II) in acetonitrile to give acetyldecylamine, whereas the Ritter reaction works poorly, if at all, with primary alcohols. Thus the carbonium ion reagents are more widely applicable than the Ritter reaction.

Treatment of (+)-bornan-2-*endo*-ol with the cation (I) in acetonitrile gave the racemic amide (IV; $R^1 = H$, $R^2 = NHAc$), and cholesterol gave exclusively 3β-substituted products. These results suggest a carbonium ion intermediate. Treatment of bornan-2-*endo*-ol (IV; $R^1 = H$, $R^2 = OH$) with the cation (I) in t-butyl cyanide followed by quenching after 5 min resulted in complete conversion into the amide (IV; $R^1 = H$, $R^2 = NH{\cdot}COBu^t$). However, addition of acetonitrile instead of quenching, followed by work-up, gave the two amides (IV; $R^1 = H$, $R^2 = NHAc$ or $NH{\cdot}COBu^t$). Similarly if bornan-2-*endo*-ol (IV; $R^1 = H$, $R^2 = OH$) was treated with the cation (I) in acetonitrile, work-up gave the acetamide (IV; $R^1 = H$, $R^2 = NHAc$),



(IV)



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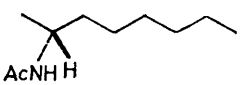


(VI)

whereas quenching with t-butyl cyanide gave the two amides (IV; $R^1 = H$, $R^2 = NHAc$ or $NH{\cdot}COBu^t$). The ratio of the two amides was roughly the same as the molar ratio of the two solvents (MeCN and Bu^tCN). A similar experiment with MeCN and CD_3CN gave the two

[1] G. A. Olah and J. J. Svoboda, *Synthesis*, 1972, 307.
[2] D. H. R. Barton, P. D. Magnus, G. Smith, G. Strecker, and D. Zurr, *J.C.S. Perkin I*, 1972, 542.
[3] D. H. R. Barton, P. D. Magnus, and R. N. Young, *J.C.S. Chem. Comm.*, 1973, 331.
[4] J. J. Ritter and P. P. Minieri, *J. Amer. Chem. Soc.*, 1948, **70**, 4045.

TABLE 1

Reactions of the cations (I)—(III) with alcohols

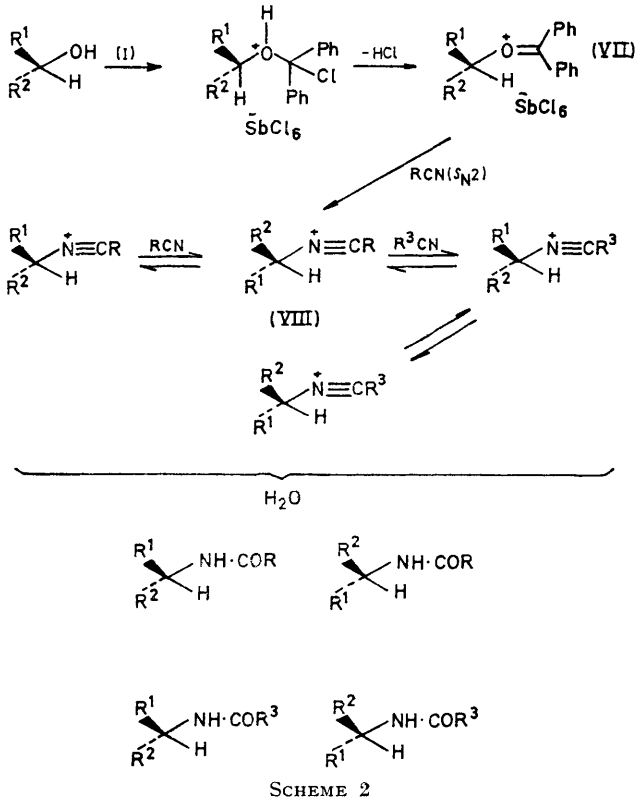
Substrate	Solvent	Cation	Product	Yield (%)
Cholesterol	MeCN	(I) *	*N*-(Cholest-5-en-3β-yl)acetamide [a]	84
	MeCN	(II) †		82
	MeCN	(III) ‡		84
	PhCN	(I)	*N*-(Cholest-5-en-3β-yl)benzamide [b]	65
	CH_2Cl_2	(II)	3β-Chlorocholest-5-ene [c]	74
Cholestanol	MeCN	(II)	*N*-(Cholestan-3α- and 3β-yl)acetamide [c] (1 : 1)	55
(±)-Bornan-2-*endo*-ol	MeCN	(I)	(±)-(IV; R^1 = H, R^2 = NHAc) [d]	70
(+)-Bornan-2-*endo*-ol	MeCN	(I)	(±)-(IV; R^1 = H, R^2 = NHAc) [e]	70
(±)-Bornan-2-*endo*-ol	MeCN	(III)	(±)-(IV; R^1 = H, R^2 = NHAc)	45
(±)-Bornan-2-*endo*-ol	Bu^tCN	(I)	(±)-(IV; R^1 = H, R^2 = NH·$COBu^t$)	55
(±)-Bornan-2-*exo*-ol	MeCN	(I)	(±)-(IV; R^1 = H, R^2 = NHAc)	75
(−)-*trans*-*p*-Menthan-*cis*-3-ol	MeCN	(I)	*N*-(*trans*-*p*-Menthan-*cis*-3-yl)acetamide	87
(−)-*trans*-*p*-Menthan-*cis*-3-ol	MeCN	(III)	*N*-(*trans*-*p*-Menthan-*cis*-3-yl)acetamide	42
(+)-*trans*-*p*-Menthan-*trans*-3-ol	MeCN	(I)	(Dehydration)	
Decan-1-ol	MeCN	(I)	*N*-Decylacetamide	50
Decan-1-ol	MeCN	(II)	*N*-Decylacetamide	*ca.* 60
Decan-1-ol	MeCN	(III)	Very little amide	
(+)-Octan-2-ol (V)	MeCN	(I)	(+)-*N*-(1-Methylheptyl)acetamide (VI)	*ca.* 86
(+)-Butan-2-ol	PhCN		(±)-*N*-(1-Methylpropyl)benzamide	30
3α-Methylcholestan-3β-ol	MeCN	(I)	3α-Chloro-3β-methylcholestane + olefin	*ca.* 80
3β-Methylcholestan-3α-ol	MeCN	(I)	3α-Chloro-3β-methylcholestane + olefin	*ca.* 80

* In reactions with the cation (I) benzophenone is also produced. † In reactions with the cation (II) benzoyl chloride is one of the products. ‡ No products derived from the cation (III) could be isolated.
[a] Ref. 7. [b] Ref. 9. [c] Ref. 10. [d] Ref. 12. [e] Ref. 13.

amides (IV; R^1 = H, R^2 = NHAc or NH·$COCD_3$), also in a ratio roughly equal to the molar proportions of the two solvents. Bornan-2-*exo*-ol (IV; R^1 = OH, R^2 = H) afforded the amide (IV; R^1 = H, R^2 = NHAc) in MeCN.

These experiments demonstrate that there exists an intermediate nitrile–alkyl adduct which can undergo nitrile exchange. Consequently the thermodynamically most stable product is formed. The exchange of nitrile molecules does not appear to involve a discrete carbonium ion, since even in the case of n-decanol nitrile exchange takes place (see Experimental section). The reaction with (±)-butan-2-ol also exhibits nitrile exchange. These results appear to indicate that the exchange proceeds by an S_N2 mechanism. However, (+)-octan-2-ol reacts with the cation (I) in acetonitrile to give the inverted product (+)-*N*-(1-methylheptyl)acetamide (VI) (very little racemisation was detected). This unexpected result may be due to the long hydrocarbon chain folding back on itself in solution, thus screening the intermediate nitrile adduct from further attack. Furthermore *no* nitrile exchange took place when (+)-octan-2-ol was subjected to the same procedure as (±)-butan-2-ol. Since (±)-butan-2-ol undergoes nitrile exchange, the product from (+)-butan-2-ol and benzonitrile is racemic. These results for the cation (I) are best accommodated as shown in Scheme 2. The alcohol reacts with the cation (I) to give an oxonium ion (VII). This would be expected to be a powerful alkylating reagent and is attacked by the nucleophilic solvent RCN to give the ion (VIII). This then equilibrates with RCN or R^3CN to give the more stable ion, and work-up with water gives the more stable amide.

In the case of cholesterol the specific formation of 3β-acetamidocholest-5-ene indicates that the reaction proceeds through the *i*-cholesteryl ion (Scheme 3). The racemisation of (+)-bornan-2-*endo*-ol when treated with the cation (I) in acetonitrile is tentatively rationalised as shown in Scheme 4. The intermediate (IX) can undergo methyl migration *via* a symmetrical inter-

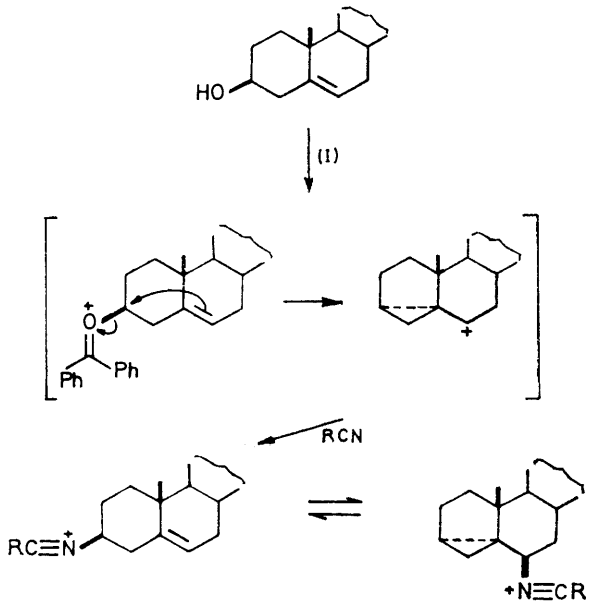


SCHEME 2

mediate thereby causing racemisation. In the case of short-lived carbonium ions in the bornane series, racemisation is generally incomplete.[5] A considerable

[5] D. V. Banthorpe, D. G. Morris, and C. A. Bunton, *J. Chem. Soc.* (*B*), 1971, 687.

amount of work has been carried out on the racemisation of camphor and its derivatives under carbonium-ion-forming conditions.[6]



SCHEME 3

Cholesterol did *not* give 3β-acetamidocholest-5-ene when treated with phosphoric trichloride, phosphorus pentachloride, boron trifluoride–ether complex, or dichlorotriphenylphosphorane in acetonitrile. Antimony pentachloride reacted with menthol in acetonitrile to give *N*-menthylacetamide but the reaction was much slower than the cation reaction.

TABLE 2

Reactions of the nitrilium ion intermediates with nucleophiles *

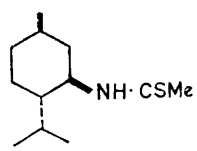
Substrate	Nucleophile	Product	Yield (%)
(−)-*trans*-*p*-Menthan-*cis*-3-ol	$Me_2N{\cdot}CHS$	(X)	33
(−)-*trans*-*p*-Menthan-*cis*-3-ol	$Bu^n_4\overset{+}{N}N_3^-$	(XI)	50
(±)-Bornan-2-*endo*-ol	$Bu^n_4\overset{+}{N}N_3^-$	(XII)	70
Cholesterol	$Bu^n_4\overset{+}{N}N_3^-$	(XIII)	50
Cholesterol	Et_2NH	(XIV)	73
Cholesterol	EtOH	(XV)	75

* In each case a solution of the substrate in acetonitrile was treated with the cation (I) and after a few minutes the mixture was quenched with one of the above nucleophiles. Addition of thiocyanates, isothiocyanates, isocyanides, sulphides, disulphides, or iodide ion gave no useful results.

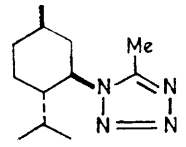
In the case of tertiary alcohols the intermediate nitrilium ion must be less stable than the derived carbonium ion. Capture of this carbonium ion by chloride ion or loss of a proton gives the observed products.

The nitrilium ion intermediates could be quenched by nucleophiles other than water. Table 2 summarises the results obtained. The formation from *p*-menthan-3-ol of the thioacetamide may be rationalised as shown in Scheme 5. The method provides a convenient one-step synthesis of thioamides, tetrazoles, amidines, and amidates from alcohols.

In summary, the cations (I)—(III) are useful reagents for making alkylnitrilium ions from alcohols in nitrile solvents. The nature of the final product is determined by the nucleophile used in the work-up. The reactions are virtually instantaneous at room temperature. The cation (I), which is the preferred reagent since it gives the cleanest reactions, may be used stoicheiometrically; benzophenone is the only by-product.



(X)



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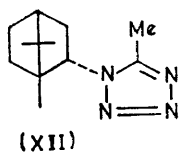

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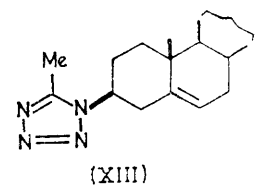

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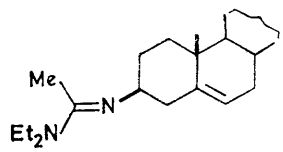

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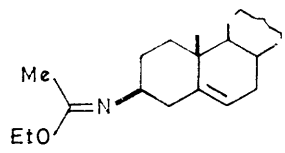

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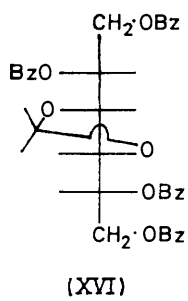

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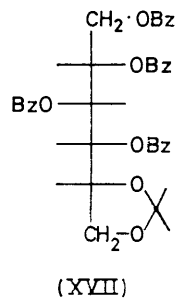

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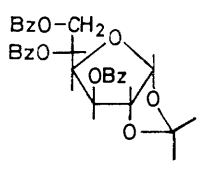
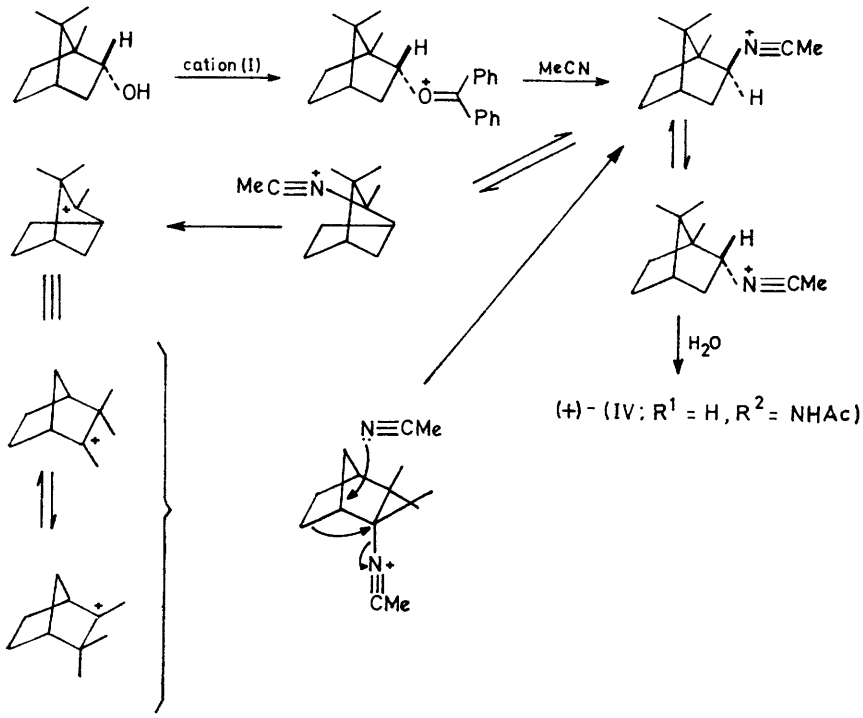


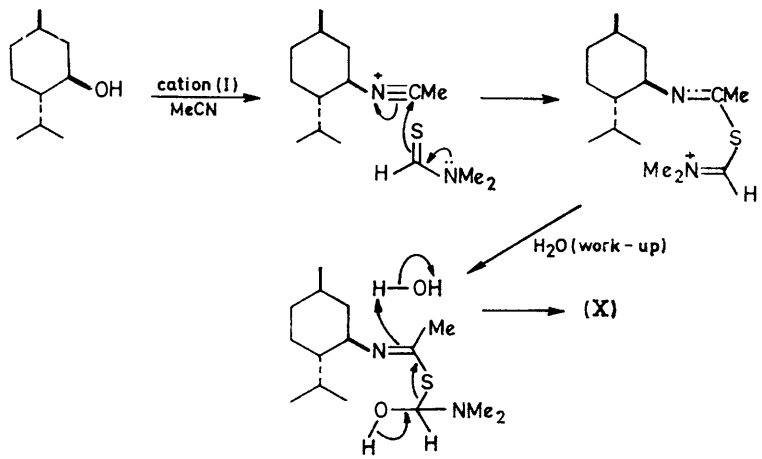
(XVIII)

[6] (*a*) W. R. Vaughan, C. T. Goetschel, M. H. Goodrow, and C. L. Warren, *J. Amer. Chem. Soc.*, 1963, **85**, 2282; (*b*) J. D. Roberts and J. A. Yancey, *ibid.*, 1953, **75**, 3165; (*c*) W. R. Vaughan and R. Perry, *ibid.*, p. 3168; (*d*) W. R. Vaughan and A. M. T. Finch, jun., *ibid.*, 1965, **87**, 5520; (*e*) A. M. Avedikian and A. Kergomard, *Tetrahedron Letters*, 1970, 2315; (*f*) C. A. Bunton, K. Khaleeluddin, and D. Whittaker, *J.C.S. Perkin II*, 1972, 1154.

The reactions of the cations (I)—(III) with 1,2,5,6-tetra-*O*-benzoyl-3,4-*O*-isopropylidene-D-mannitol (XVI) were studied to assess their hydride abstracting properties.[2] No oxidation was observed. We therefore repeated the reaction of the acetal (XVI) with the triphenylmethyl cation. Contrary to our earlier results,[2] no triphenylmethane was produced and the only reaction was a slow conversion into mannitol 1,2,5,6-tetrabenzoate, which on benzoylation gave mannitol hexabenzoate, identical with the compound previously regarded by Dr. Zurr as a ketone. We have, therefore, repeated all the work recorded earlier on ketone acetals. These compounds are indeed converted smoothly into ketones by the triphenylmethyl cation. The two possible mechanisms (A and B) for this reaction are summarised in Scheme 6. With the acetals from ethylene glycol mechanism A is operative and no triphenylmethane is formed. Unless adequate spectroscopic checks are applied it is easy on t.l.c. plates to mistake methyl or ethyl triphenylmethyl ether, formed from adventious traces of methanol or ethanol, for triphenylmethane. If all apparatus is flame-dried and the solvent carefully purified, these misleading impurities can be avoided. With acetals from glycols containing a benzylic hydrogen atom it is mechanism B which operates, as previously reported.

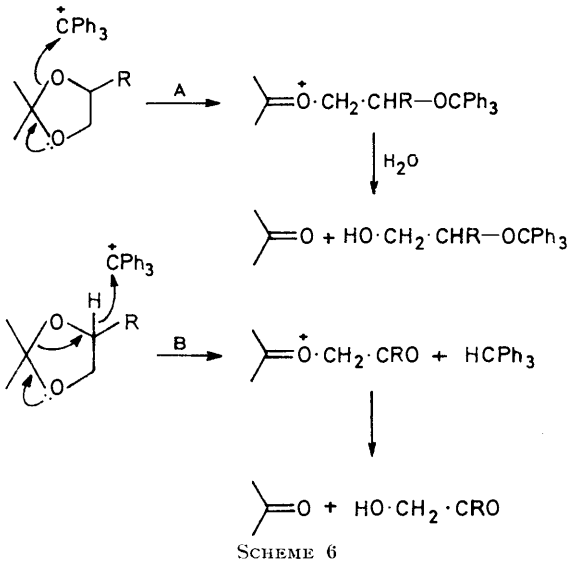


SCHEME 4



SCHEME 5

All our other results, including the conversion of diosgenin into kryptogenin, are correct as reported except for the reactions with the glucose derivatives (XVII) and (XVIII). Here, again, the corresponding glycols were formed slowly on reaction with triphenylmethyl cation and there was, in fact, no dehydrogenation.



SCHEME 6

EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage apparatus. I.r. spectra were measured for solutions in chloroform unless otherwise stated. N.m.r. spectra were measured for solutions in [^{2}H]chloroform with tetramethylsilane as internal standard. All compounds had n.m.r. data in accord with the assigned structures. All solvents were purified and dried by standard techniques before use. Light petroleum refers to the fraction of b.p. 60—80° unless otherwise stated.

Chlorodiphenylmethylium (I) *Hexachloroantimonate.*—The cation (I), prepared [1] from dichlorodiphenylmethane and antimony pentachloride, had m.p. 164—165° (decomp.) [lit.,[1] 166—167° (decomp.)]. Similarly prepared dichloro(phenyl)methylium (II) hexachloroantimonate had m.p. 150—153° (decomp.) [lit.,[1] 152—153° (decomp.)].

General Procedure for Reactions of the Cations (I)—(III) *with Alcohols* (*Table* 1).—The alcohol in dry solvent was treated with the cation (I), (II), or (III) (transferred from a glove box for weighing) in a dry glove box under dry argon. When the cation had dissolved and the mixture was homogenous the solvent was evaporated off *in vacuo* and the residue dissolved in a small volume of dichloromethane. The mixture was separated by t.l.c. on silica gel (Merck GF 254) or alumina (grade III).

Reactions of Cholesterol.—(i) *With the cation* (I) *in acetonitrile.* Cholesterol (300 mg) in acetonitrile (5 ml), treated with the cation (I) (950 mg), gave 3β-acetamidocholest-5-ene (84%), m.p. 239—241° (from methanol) (lit.,[7] 238—239°), $[\alpha]_D^{23}$ −43·8° (*c* 0·92 in $CHCl_3$) (lit.,[7] $[\alpha]_D$ −41°), mixed m.p. 236—238°. Authentic 3β-acetamidocholest-5-ene was made by treatment of cholesteryl tosylate [8] with liquid ammonia followed by acetylation (Ac_2O–pyridine) of the resulting cholesterylamine.

(ii) *With the cation* (II) *in acetonitrile.* Cholesterol (500 mg) in acetonitrile (10 ml), treated with the cation (II) (950 mg), gave 3β-acetamidocholest-5-ene (82%), identical with an authentic sample. Similarly the cation (III) and cholesterol gave 3β-acetamidocholest-5-ene (84%).

(iii) *With the cation* (I) *in phenyl cyanide.* Cholesterol (500 mg) in phenyl cyanide (2 ml) was treated with the cation (I) (775 mg) and the reaction mixture was chromatographed on alumina. Elution with benzene gave 3β-benzamidocholest-5-ene [9] (65%), m.p. 232—233° (from ethyl acetate) (lit.,[9] 236°), $[\alpha]_D^{22}$ −13·2° (*c* 1·1 in $CHCl_3$), identical with an authentic sample made from cholesterylamine (with PhCOCl–pyridine).

(iv) *With the cation* (II) *in dichloromethane.* Cholesterol (350 mg) in dichloromethane (10 ml) was treated with the cation (II) (455 mg) and the reaction residue was chromatographed on alumina. Elution with light petroleum gave 3β-chlorocholest-5-ene [10] (74%), m.p. 93—94° (from ethanol) (lit.,[10] 96°), $[\alpha]_D^{22}$ −28·3° (*c* 0·5 in $CHCl_3$), identical with an authentic sample.[11]

Reaction of 5α-Cholestan-3β-ol with the Cation (II) *in Acetonitrile.*—Cholestan-3β-ol (215 mg) in acetonitrile (5 ml) and dichloromethane (5 ml) was treated with the cation (II) (1·57 g). Work-up gave a mixture of 3α- and 3β-acetamidocholestane [12] (50%) (1 : 1 by n.m.r.). Crystallisation from methanol gave 3β-acetamidocholestane, m.p. 240—242° (lit.,[12] 243°), $[\alpha]_D^{23}$ +12·6° (*c* 0·8 in $CHCl_3$) (lit.,[12] $[\alpha]_D$ +12°), mixed m.p. 242—244°. Crystallisation of material from the mother liquors from methanol gave 3α-acetamidocholestane, m.p. 210—212° (lit.,[12] m.p. 216°), $[\alpha]_D^{22}$ +34·6° (*c* 0·9 in $CHCl_3$) (lit.,[12] $[\alpha]_D$ +33°), mixed m.p. 211—214°. Authentic 3β-acetamido-5α-cholestane was prepared by lithium aluminium hydride reduction of cholestanone oxime followed by acetylation.[12] The authentic 3α-isomer was prepared by hydrogenation (Adams catalyst in acetic acid) of cholestanone oxime followed by acetylation.[12]

Reactions of (±)-*Bornan*-2-endo-*ol.*—(i) *With the cation* (I) *in acetonitrile.* (±)-Bornan-2-*endo*-ol (230 mg) in acetonitrile (5 ml), treated with the cation (I) (880 mg), gave *N*-(bornan-2-*endo*-yl)acetamide (IV; R^1 = H, R^2 = NHAc) [13] (70%), m.p. 139—141° (from acetone) [lit.[13] for the (−)-isomer, 143°], mixed m.p. with authentic (±)-amide, 136—139°; mixed m.p. with authentic (−)-amide, 120—135°. Authentic samples were made from (±)-camphor oxime.[13]

(ii) *With the cation* (III) *in acetonitrile.* (±)-Bornan-2-*endo*-ol (150 mg), treated with the cation (III) (970 mg) in acetonitrile (5 ml), gave (±)-*N*-(bornan-2-*endo*-yl)acetamide (IV; R^1 = H, R^2 = NHAc) [13] (45%), m.p. 137·5—140° (from acetone), identical with an authentic sample.[13]

(iii) *With the cation* (I) *in t-butyl cyanide.* Bornan-2-*endo*-ol (120 mg) was treated with the cation (I) (422 mg) in t-butyl cyanide (5 ml). Work-up by chromatography and sublimation (55° and 10^{-5} mmHg) gave (±)-N-(*bornan*-2-endo-*yl*)*pivalamide* (IV; R^1 = H, R^2 = NH·COBu^t)

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(55%), m.p. 60—63°, $\nu_{max.}$ (film) 3400 and 1650 cm^{-1}, τ 4·44br (1H, s), 6·1 (1H, m), 7·9—8·5 (7H, m), 8·80 (9H, s), 9·10 (3H, s), and 9·20 (6H, s) (Found: C, 75·8; H, 11·4; N, 5·7. $C_{16}H_{27}NO$ requires C, 75·9; H, 11·5; N, 5·9%).

Reaction of (+)-*Bornan with the Cation* (I) *in Acetonitrile.*—(+)-Bornan-2-*endo*-ol (310 mg), treated with the cation (I) (1·26 g) in acetonitrile (5 ml), gave (±)-*N*-(bornan-2-*endo*-yl)acetamide (IV; R^1 = H, R^2 = NHAc) (70%), m.p. m.p. 138—140° (from acetone), identical with an authentic sample.[13]

Reactions of (−)-trans-p-*Menthan*-cis-3-*ol.*—(i) *With the cation* (I) *in acetonitrile.* *p*-Methan-3-ol (156 mg) in acetonitrile (3 ml), treated with the cation (I) (950 mg), gave *N*-(*trans*-*p*-menthan-*cis*-3-yl)acetamide (87%), m.p. 143—145° (from petroleum) (lit.,[14] 145°), $[\alpha]_D^{22}$ −81·8° (*c* 0·9 in $CHCl_3$) (lit.,[14] $[\alpha]_D$ −81·7°); mixed m.p. with authentic sample,[14] 143—145°.

(ii) *With the cation* (III) *in acetonitrile.* *p*-Menthan-3-ol (300 mg) in acetonitrile (3 ml), treated with the cation (III) (1·39 g), gave *N*-(*p*-menthan-3-yl)acetamide (42%), m.p. 143—145° (from light petroleum), identical with an authentic sample.[14]

Reaction of (+)-*Octan*-2-*ol* (V) *with the Cation* (I) *in Acetonitrile.*—(+)-Octan-2-ol {$[\alpha]_D^{21}$ +10·0° (*c* 4·0 in EtOH)} (300 mg) in acetonitrile (2 ml), treated with the cation (I) (1·6 g), gave an oil (86%), b.p. 135° at 0·05 mmHg, $[\alpha]_D^{23}$ +3·23° (*c* 6·9 in $CHCl_3$), $\nu_{max.}$ 3300 and 1645 cm^{-1}, τ 4·40br (1H), 6·05br (1H, m), 8·02 and 8·03 (3H, two s), 8·4—8·8br (10H, s), 8·88 (3H, d), and 9·08 (3H, m). The product mixture (340 mg) was treated with potassium hydroxide (600 mg) in ethylene glycol (1 ml) at 180° for 48 h, then poured into water (20 ml) and extracted with light petroleum. The extract was dried (Na_2SO_4) and evaporated to give an oil (280 mg). A portion (120 mg), with 3,5-dinitrobenzoyl chloride (240 mg) in pyridine (1 ml) for 2 h at room temperature, gave *N*-1-methylheptyl-3,5-dinitrobenzamide (40%), m.p. 139—141° (from dichloromethane–light petroleum), $[\alpha]_D^{24}$ −19·0° (*c* 2·0 in $CHCl_3$), mixed m.p. with the authentic (−)-benzamide, 140—142°.

The above experiment was repeated with (+)-octan-2-ol (300 mg) and the cation (I) (1·8 g) in acetonitrile (3 ml). The mixture was heated to 50° for 10 min, then left at room temperature for 20 h. The *N*-(1-methylheptyl)-3,5-dinitrobenzamide was identical (m.p., mixed m.p., and $[\alpha]_D$) with that previously obtained.

Authentic (−)-*N*-(1-methylheptyl)-3,5-dinitrobenzamide was prepared from (+)-octan-2-ol *via* the tosylate and azide. The intermediate (−)-1-methylheptylamine [15] had b.p. 165° at 760 mmHg, $[\alpha]_D^{25}$ −6·2° (*c* 4·8 in C_6H_6) {lit.,[11] $[\alpha]_D$ −3·70°; values for (+)-isomer are +4·19° and +6·3°}.[16,17] The amine was treated with 3,5-dinitrobenzoyl chloride to yield the *amide*, m.p. 142—142·5° (from dichloromethane–petroleum), $[\alpha]_D^{26}$ −25·1° (*c* 1·1 in $CHCl_3$), $\nu_{max.}$ 3450, 1675, 1530, and 1345 cm^{-1}, τ 0·81 (1H, m), 0·94 (2H, m), 3·40br (1H), 5·80 (1H, m), 8·68 and 8·70 (13H, broad s with overlapping d), and 9·14 (3H, m) (Found: C, 55·7; H, 6·4; N, 12·8. $C_{15}H_{21}N_3O_5$ requires C, 55·7; H, 6·7; N, 13·0%).

Reactions of Decan-1-*ol.*—(i) *With the cation* (I) *in acetonitrile.* Decan-1-ol (149 mg) in acetonitrile (2 ml) was treated with the cation (I) (1·83 g). The mixture was warmed to 40° until all the reagent had dissolved. Work-up gave *N*-decylacetamide (50%), m.p. 39—41° (from light petroleum), mixed m.p. with authentic material 37·5—39·5°.

(ii) *With the cation* (II) *in acetonitrile.* Decan-1-ol (150 mg) in acetonitrile (5 ml), treated with the cation (II) (1·7 g), gave *N*-decylacetamide (113 mg, 60%), m.p. 39—41° (from light petroleum).

(iii) *With the cation* (III) *in acetonitrile.* Decan-1-ol (155 mg) in acetonitrile (3 ml), treated with the cation (III) (700 mg), was unchanged (t.l.c.) after work-up.

N-*Decylacetamide*, prepared from decyl bromide by treatment with phthalimide and acetylation of the resultant amine, had m.p. 38—40° (from light petroleum), τ 4·1br (1H), 6·8 (2H, m), 8·03 (3H, s), 8·75br (16H, s), and 9·15 (3H, m) (Found: C, 72·2; H, 12·4; N, 7·0. $C_{12}H_{25}NO$ requires C, 72·3; H, 12·6; N, 7·0%).

Reaction of (+)-*Butan*-2-*ol with the Cation* (I) *in Phenyl Cyanide.*—(+)-Butan-2-ol (150 mg) (82% optically pure) in phenyl cyanide (500 mg) and chloroform (2 ml), treated with the cation (I) (1·1 g), gave racemic *N*-1-methylpropylbenzamide (30%), m.p. 83—84° (from light petroleum) (lit.,[18] 84—85°).

Reaction of 3β-*Methylcholestan*-3α-*ol with the Cation* (I) *in Acetonitrile.*—3β-Methylcholestan-3α-ol [19] (100 mg) in acetonitrile (2 ml) and chloroform (3 ml) was treated with the cation (I) (500 mg) to give 3α-chloro-3β-methylcholestane (80%), contaminated with some olefin. Crystallisation from acetone gave pure material, m.p. 148—154°, mixed m.p. with an authentic sample [19] 152—157°.

Reaction of 3α-*Methylcholestan*-3β-*ol with the Cation* (I) *in Acetonitrile.*—3α-Methylcholestan-3β-ol (98 mg) in acetonitrile (2 ml) and chloroform (3 ml) was treated with the cation (I) (600 mg) to give 3α-chloro-3β-methylcholestane (80%).

Reactions of (±)-*Bornan*-2-endo-*ol with the Cation* (I) *in t-Butyl Cyanide and Acetonitrile.*—(±)-Bornan-2-*endo*-ol (150 mg) in t-butyl cyanide (2 ml) was treated with the cation (I) (800 mg). A sample (1 ml) of the mixture was worked up to give the amide (IV; R^1 = H, R^2 = NH·$COBu^t$) (50 mg). The remaining mixture was treated with acetonitrile (2 ml) and worked up to give the amides (IV; R^1 = H, R^2 = NHAc) (70 mg) and (IV; R^1 = H, R^2 = NH·$COBu^t$) (20 mg).

(±)-Bornan-2-*endo*-ol (175 mg) in acetonitrile (1·5 ml) was treated with the cation (I) (824 mg). A sample (0·6 ml) of the mixture was worked up to give the amide (IV; R^1 = H, R^2 = NHAc) (*ca.* 30 mg). The remaining mixture was treated with t-butyl cyanide (5 ml) to give, after work-up, the amides (IV; R^1 = H, R^2 = NH·$COBu^t$) (90 mg) and (IV; R^1 = H, R^2 = NHAc) (30 mg).

Reactions of (±)-*Bornan*-2-endo-*ol with the Cation* (I) *in Acetonitrile and* [$^2H_3$]*Acetonitrile.*—(±)-Bornan-2-*endo*-ol (175 mg) in acetonitrile (1 ml) was treated with the cation (I) (804 mg). A sample (0·5 ml) was worked up to give the amide (IV; R^1 = H, R^2 = NHAc) (50 mg). The remaining mixture was treated with [$^2H_3$]acetonitrile (0·5 ml). Work-up gave the amides (IV; R^1 = H, R^2 = NHAc) and (IV; R^1 = H, R^2 = NH·$COCD_3$) which mass spectrometry

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showed to contain 20—24% (IV; $R^1 = H$, $R^2 = NH{\cdot}COCD_3$).

(±)-Bornan-2-*endo*-ol (180 mg) in [$^2H_3$]acetonitrile (1 ml) was treated with the cation (I) (804 mg). A sample (0·7 ml) was worked up to give the amide (IV; $R^1 = H$, $R^2 = NH{\cdot}COCD_3$) (108 mg), M^+ 198 ($C_{12}H_{18}D_3NO$). The remaining mixture was treated with acetonitrile (2 ml). Work-up gave the amides (IV; $R^1 = H$, $R^2 = NHAc$) and (IV; $R^1 = H$, $R^2 = NH{\cdot}COCD_3$), τ 8·01 (2·2H, s, Ac), indicating *ca.* 75% (IV; $R^1 = H$, $R^2 = NHAc$) and 25% (IV; $R^1 = H$, $R^2 = NH{\cdot}COCD_3$).

Reaction of Decan-1-ol with the Cation (I) *in Acetonitrile and* [$^2H_3$]*Acetonitrile.*—Decan-1-ol (105 mg) in [$^2H_3$]acetonitrile (0·5 ml) and chloroform (1·0 ml) was treated with the cation (I) (1·1 g) at 50° for 10 min. A sample (0·75 ml) was worked up to give *N*-decyl[$^2H_3$]acetamide (15 mg), M^+ 202 ($C_{12}H_{22}D_3NO$). The n.m.r. spectrum contained no *N*-acetyl signal.

To the remaining mixture was added acetonitrile (1 ml) and the mixture was warmed to 50° for 10 min. Work-up gave *N*-decylacetamide (28 mg), M^+ 199 and 202 in the ratio 1 : 1, τ 8·03 (1·5H), indicating 50% exchange.

Reaction of (+)-*Octan-2-ol* (V) *with the Cation* (I) *in Acetonitrile and* [$^2H_3$]*Acetonitrile.*—(+)-Octan-2-ol (V) (200 mg) in [$^2H_3$]acetonitrile (0·6 ml) and chloroform (1·0 ml) was treated with the cation (I) (2·08 g) at 80° for 5 min. A sample (1·0 ml) was worked up to give the acetamide (VI) (70 mg), whose n.m.r. spectrum contained no acetyl methyl signal; M^+ 174 ($C_{10}H_{18}D_3NO$). To the remaining mixture was added acetonitrile (3·0 ml), and the mixture was kept at room temperature for 30 min. Work-up gave the acetamide (VI) (140 mg), whose n.m.r. spectrum exhibited a small signal at τ 8·03 (Ac) corresponding to less than 10% nitrile exchange; M^+ 171 and 174 in a ratio indicating less than 3% nitrile exchange.

Reaction of (±)-*Butan-2-ol with Acetonitrile and* [$^2H_3$]-*Acetonitrile.*—(±)-Butan-2-ol (210 mg) in [$^2H_3$]acetonitrile (0·5 ml) and chloroform (1·5 ml) was treated with the cation (I) (1·58 g). After 5 min a sample (1·0 ml) was withdrawn and worked up to give *N*-(1-methylpropyl)-[$^2H_3$]acetamide (70 mg) as an oil,[20] τ 3·4br (1H), 6·2 (1H, m), 8·6 (2H, q), 8·9 (3H, d), and 9·1 (3H, t), M^+ 118 ($C_6H_{10}D_3NO$). To the remaining mixture was added acetonitrile (1·0 ml). Work-up gave *N*-(1-methylpropyl)-acetamide (140 mg), n.m.r. and mass spectrometry indicating 35% exchange.

N-(trans-p-*Menthan*-cis-3-*yl*)*thioacetamide* (X).—(−)-*trans-p*-Menthan-*cis*-2-ol (310 mg) in acetonitrile (2 ml) was treated with the cation (I). After 5 min dimethylthioformamide (1 ml) was added. Work-up gave the *thioamide* (X) (33%), m.p. 121—121·5° (from light petroleum), $[\alpha]_D^{21}$ −110·4 (*c* 0·97 in $CHCl_3$), $\nu_{max.}$ ($CHCl_3$) 3420, 1390, and 1100 cm^{-1} (Found: C, 67·5; H, 10·6; N, 6·5. $C_{12}H_{23}NS$ requires C, 67·6; H, 10·9; N, 6·6%).

The thioamide (X) was also prepared from *N*-methylacetamide (47 mg) in benzene (2 ml) by treatment with phosphorus pentasulphide (30 mg).

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(−)-1-(trans-p-*Menthan*-cis-3-*yl*)-5-*methyltetrazole* (XI).—(−)-*trans-p*-Menthan-*cis*-3-ol (130 mg) in acetonitrile (2 ml) was treated with the cation (I) (960 mg). After 5 min a solution of tetra-n-butylammonium azide (1·0 g) in chloroform (8·0 mg) was added. Work-up followed by chromatography on alumina gave the *tetrazole* (XI) (50%), m.p. 77—79° (from light petroleum), $[\alpha]_D^{21}$ −56·8° (*c* 0·86 in $CHCl_3$), $\nu_{max.}$ ($CHCl_3$) 1295, 1320, and 1370 cm^{-1} (Found: C, 64·9; H, 10·1; N, 25·0. $C_{12}H_{22}N_4$ requires C, 64·9; H, 10·0; N, 25·2%).

1-(*Bornan*-2-endo-*yl*)-5-*methyltetrazole* (XII).—(±)-Bornan-2-*endo*-ol (165 mg) in acetonitrile (2 ml) was treated with the cation (I) (950 mg). After 2 min tetra-n-butylammonium azide (*ca.* 800 mg) in chloroform (2 ml) was added. Work-up gave the tetrazole (XII) (70%), m.p. 81—82° (from light petroleum) (lit.,[21] 81·5—83·5), mixed m.p. with an authentic sample 80—82°, $\nu_{max.}$ 1302, 1320, 1360, 1395, and 1408 cm^{-1}, τ 3·80 (1H, dd), 7·0—8·7 (7H, m), 7·48 (3H, s), 8·80 (3H, s), 9·10 (3H, s), and 9·40 (3H, s) (Found: C, 65·2; H, 9·1; N, 25·4. Calc. for $C_{12}H_{20}N_4$: C, 65·4; H, 9·2; N, 25·4%).

1-(*Cholest-5-en-3β-yl*)-5-*methyltetrazole* (XIII).—Cholesterol (400 mg) in acetonitrile (2 ml) was treated with the cation (I) (1·2 g). After 2 min tetra-n-butylammonium azide (1·4 g) in chloroform (5 ml) was added. Work-up gave the *tetrazole* (XIII) (50%), m.p. 196—198° (from methanol), $[\alpha]_D^{21}$ −18·1° (*c* 0·95 in $CHCl_3$), $\nu_{max.}$ 1290 and 1315 cm^{-1} (Found: C, 76·9; H, 10·4; N, 12·3. $C_{29}H_{48}N_4$ requires C, 76·9; H, 10·7; N, 12·4%).

N^2-(*Cholest-5-en-3β-yl*)-N^1N^1-*diethylacetamidine* (XIV).—Cholesterol (305 mg) in acetonitrile (2 ml) was treated with the cation (I) (850 mg). After 2 min diethylamine (1 ml) was added. The mixture was diluted with dichloromethane, washed with aqueous 5% potassium hydroxide and saturated aqueous sodium chloride, and dried (Na_2SO_4). Evaporation and chromatography of the residue gave the *amidine* (XIV) (73%), m.p. 132—133° (from methanol), $[\alpha]_D^{21}$ −2·7 (*c* 1·04 in $CHCl_3$), $\nu_{max.}$ 1602 cm^{-1} (Found: C, 81·9; H, 11·9; N, 5·6. $C_{33}H_{58}N_2$ requires C, 82·1; H, 12·1; N, 5·8%).

Ethyl N-(*Cholest-5-en-3β-yl*)*acetimidate* (XV).—Cholesterol (340 mg) in acetonitrile (2 ml) was treated with the cation (I) (920 mg). The mixture was treated with ethanol (2 ml) and worked up to give the *imidate* (XV) (75%), m.p. 140—141° (from ethanol), $[\alpha]_D^{24}$ −15·8° (*c* 1·26 in $CHCl_3$), $\nu_{max.}$ 1665 cm^{-1} (Found: C, 81·7; H, 11·6; N, 2·9. $C_{31}H_{33}NO$ requires C, 81·7; H, 11·7; N, 3·1%).

Reaction of 2,2-*Dimethyl*-4-*phenyl*-1,3-*dioxolan with Triphenylmethyl Cation.*—The dioxolan (178 mg) in dry dichloromethane (5 ml) was treated with triphenylmethyl tetrafluoroborate (2 equiv.) for 5 h. Work-up gave triphenylmethane (147 mg), triphenylmethanol (288 mg), and phenacyl alcohol (85 mg), m.p. 84—85° (lit.,[22] 85·5—86°).

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