Conversion of Alcohols into Amides using Chlorodiphenylmethylium Hexachloroantimonate in Nitrile Solvents

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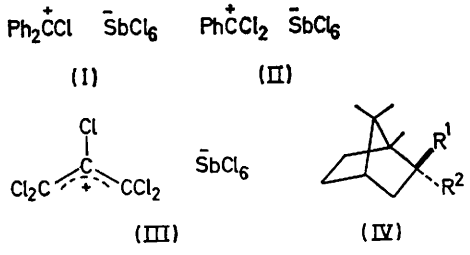
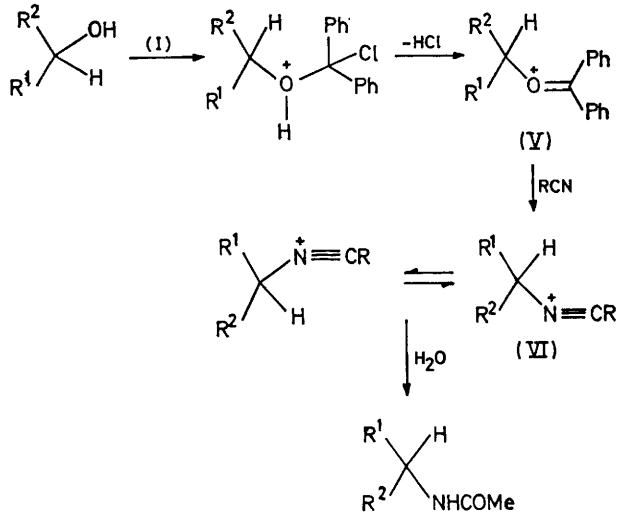
Summary Treatment of alcohols with chlorodiphenylmethylium hexachloroantimonate (I) in nitrile solvents provides a mechanistically interesting method of converting an alcohol into amides under thermodynamic control.

EXTENDING[1] earlier work we have studied the reactions of chlorodiphenylmethylium (I), dichlorophenylmethylium (II), and pentachlorallylium (III) hexachloroantimonates[2] with alcohols in nitrile solvents. The results obtained, after quenching with water are given in the Table. The reactions



listed were all virtually instantaneous (complete on mixing) Cholesterol did *not* give 3β-acetamidocholest-5-ene when treated with phosphorus oxychloride, phosphorus pentachloride, boron trifluoride etherate, or triphenylphosphine dichloride in acetonitrile. The simple Ritter reaction[3] does not work on cholesterol.

Treatment of borneol (IV; $R^1 = H$, $R^2 = OH$) with the cation (I) in t-butyl cyanide, followed by quenching a portion of the reaction after 5 min showed complete conversion into (IV; $R^1 = H$, $R^2 = NHCOBu^t$). However, addition of acetonitrile to the remaining reaction mixture gave (IV; $R^1 = H$, $R^2 = NHCOMe$) and (IV; $R^1 = H$, $R^2 = NHCOBu^t$). Similarly if borneol (IV; $R^1 = H$, $R^2 = OH$) was treated with the cation (I) in acetonitrile, work-up on one portion gave (IV; $R^1 = H$, $R^2 = NHCOMe$),



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while quenching of the remainder with t-butyl cyanide gave (IV; $R^1 = H$, $R^2 = NHCOMe$) and (IV; $R^1 = H$, $R^2 = NHCOBu^t$). The ratio of the two amides is roughly the molar ratio of the two solvents (MeCN and Bu^tCN respectively). A similar experiment with CH_3CN and CD_3CN

TABLE

Substrate	(Solvent)	Cation	Product	Yield
Cholesterol ..	(MeCN)	(II)	3β-Acetamidocholest-5-ene[3]	82%
,, ..	(PhCN)	(I)	3β-Benzamidocholest-5-ene[4]	65%
,, ..	(Me CN)	(III)	3β-Acetamidocholest-5-ene	84%
,, ..	(CH_2Cl_2)	(II)	3β-Chlorocholest-5-ene[5]	74%
Cholestanol ..	(Me CN)	(II)	3α- and 3β-Acetamidocholestane[6] (1 : 1)	55%
(±)-Borneol ..	(MeCN)	(I)	(±)-(IV; R^1 = H, R^2 = NHCOMe)[7]	70%
(+)-Borneol ..	(MeCN)	(I)	(±)-(IV; R^1 = H, R^2 = NHCOMe)[7]	70%
(±)-Borneol ..	(Bu^tCN)	(I)	(±)-(IV; R^1 = H, R^2 = NHCOBu^t)	55%
(±)-Borneol ..	(MeCN)	(III)	(±)-(IV; R^1 = H, R^2 = NHCOMe)	45%
(±)-Isoborneol ..	(MeCN)	(I)	(±)-(IV; R^1 = H, R^2 = NHCOMe)	75%
Menthol ..	(MeCN)	(I)	Acetylmenthylamine	87%
Menthol ..	(MeCN)	(III)	Acetylmenthylamine	42%
Neomenthol ..	(MeCN)	(I)	Dehydration	
n-Decanol ..	(MeCN)	(I)	Acetyl-n-decylamine	50%
n-Decanol ..	(MeCN)	(II)	Acetyl-n-decylamine	*ca.* 60%
n-Decanol ..	(MeCN)	(III)	Very little amide	

[a] All reactions were carried out at room temperature in a glove box with exclusion of oxygen and moisture. In all cases the cation component was added to the reaction mixture last.

gave (IV; R^1 = H, R^2 = NHCOMe) and (IV; R^1 = H, R^2 = $NHCOCD_3$) in a ratio roughly equal to the molar proportions of the two solvents. Isoborneol (IV; R^1 = OH, R^2 = H) afforded the amide (IV; R^1 = H, R^2 = NHCOMe) in CH_3CN.

These results for the cation (I) are best accommodated by the Scheme. The alcohol gives an oxonium ion (V) which is attacked by the nucleophilic solvent RCN to give the ion (VI). This equilibrates by further displacement by RCN or R^1CN to give the more stable ion. Work-up with water gives the more stable amide. In the case of cholesterol, anchimeric assistance to displacement of the leaving group prior to formation of the intermediate (VI) explains the products.

The first reagent (I) produces cleaner reactions with alcohols; the only other product is benzophenone.

All products were characterised by the usual spectral and microanalytical techniques. Known compounds were compared with authentic samples prepared by literature methods.

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