Acylation of Olefins by Acetyl Hexachloroantimonate. Selective Formation of β,γ-Unsaturated Ketones under Kinetic Control and Mechanistic Rationale as an Ene Reaction†

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Abstract: The acylation of a variety of olefins including natural products with acetyl hexachloroantimonate in methylene chloride at −50 to −25 °C in the presence of a hindered tertiary amine affords β,γ-unsaturated ketones to the exclusion of any α,β isomers. It is suggested that the deconjugated enone is formed via an ene reaction and that a number of so-called aliphatic Friedel-Crafts reactions have to be reconsidered mechanistically as a function of counterion, reaction medium, temperature, and mode of work up.

Although the acylation of alkenes has been widely studied for more than 80 years[2] and reviewed frequently,[3] the reaction has not yet met with nearly the same success as the remarkably useful Friedel-Crafts acylation of aromatics which was discovered in spring 1877 almost exactly 100 years ago. The comparative failure of aliphatic acylation has been ascribed to the formation of various reactive intermediates arising via electrophilic addition, elimination, and isomerization yielding complex mixtures of products. Nonetheless, the careful observation of optimum reaction conditions and appropriate work up allow reactions that are of synthetic utility. One of these methods appears to involve the use of strongly polarized complexes containing incipient acyl cations[4] as recently reported by Smit and his co-workers.[5]

In this paper we wish to report the acetylation of alkenes, including some natural products, by acetyl hexachloroantimonate ($CH_3C^+O\ SbCl_6^-$).[4a] In particular, we were interested to determine to what extent β,γ-unsaturated ketones might be formed in preference to their α,β isomers under conditions of strict kinetic control.[6,7] To prevent the harmful build up of acid we performed all acetylations in the presence of bases of low nucleophilicity. In general, the reaction was carried out by quickly adding equimolar amounts of the alkene and base to acetyl hexachloroantimonate partially dissolved in dichloromethane at −50 to −25 °C. After less than 1 h the reaction was complete and the products were worked up.

† This paper is dedicated to Professor R. B. Woodward on the occasion of his 60th birthday.

Experimental Section

Acetyl hexachloroantimonate was prepared from acetyl chloride and antimony pentachloride according to the procedure of Olah et al.[4a] The crystalline compound was stored at 0 °C under exclusion of air. Dicyclohexylethylamine and ethyldiisopropylamine were commercially available (British Drug Houses Ltd. and Aldrich Chemical Co., respectively). In the later experiments Hünig base (ethyldiisopropylamine) was preferred to dicyclohexylethylamine as an acid trap, because its hydrochloride can be removed readily from pentane by washing with ice-cold water.

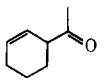
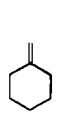
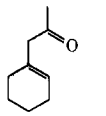
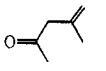
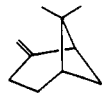
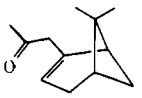
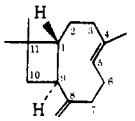
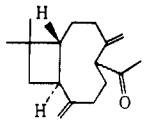
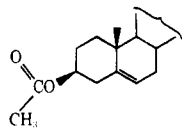
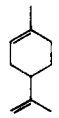
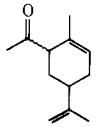
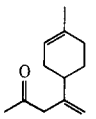
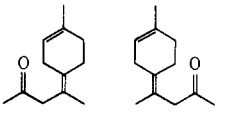
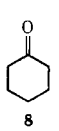
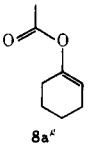
General Procedure. Equimolar amounts of alkene (5 mmol) and dicyclohexylethylamine (5 mmol), each dissolved in 5 mL of CH_2Cl_2, were mixed and quickly added to the partially dissolved acetyl cation complex (5 mmol) in 20 mL of CH_2Cl_2 under vigorous stirring at −50 °C. The temperature was kept at −50 °C for 1 h and in the case of less reactive olefins was gradually raised to −25 °C. After the reaction was completed the dark brown reaction mixture was immediately poured into *n*-pentane (200 mL) containing some water (3 mL) to decompose any remaining acetyl cation complex and shaken for 1 min, the precipitate being removed by filtration. The precipitate was twice washed with *n*-pentane and the combined organic layer was washed with water, dried over Na_2SO_4, and evaporated under reduced pressure to leave an oily product, which was analyzed by GLC; a 30 m dinitrophenyl naphthyl ether capillary column was found to give the best separation. Any remaining starting material and ammonium salt were removed by column chromatography on silica gel (Merck 70-230 mesh) using benzene as an eluent. The ketones formed were then eluted with a mixed solvent (benzene-ethyl acetate). The acetylated products were purified by preparative GLC, preparative TLC (Merck precoated silica gel plates, 2 mm, benzene-ethyl acetate eluent), and in the instance of the reaction with caryophyllene by HPLC. The products were converted into their semicarbazones which were recrystallized to constant mp and analyzed mass spectrometrically.

Table I. Effect of Bases on the Reaction of Cyclohexene with Acetyl Hexachloroantimonate

No.	Base	[molar ratio]	Product composition, %[a] 1a	1b	Hydrocarbon[b]	Unknown	Unknown[c]
1		1	22.5	8.9	27.2		32.1
2	Tetramethylurea	1	61.2	1.3	29.8	7.7	
3	2,6-Lutidine	1	57.0	1.2	0–0.5	6.2 5.1	30.0
4	2,6-Lutidine	5	75.5	<0.3	3.7	2.6	18.2
5	2,4,6-Collidine	10	80.6	Not detected	3.7	3.2	12.6
6	Triethylamine	10	75.4	Not detected	3.2	5.1	16.7
7	Dicyclohexylethylamine	5	83.3	Not detected	Negligible	Negligible	16.7

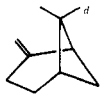
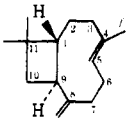
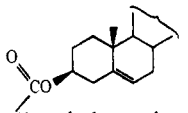
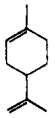
[a] Determined by GLC on a dinitrophenyl naphthyl ether column and taking integrated peak ratios. [b] Most probably dimer. [c] This compound had the longest retention time and its ^1H NMR spectrum showed an acyl singlet as well as complicated broad signals suggestive of a polymer.

Table II. Products of Olefin Acetylation and Their Characterization

No.	Olefin	Products	Yield,[a] %	IR (CCl_4), cm^{-1}	NMR $\delta_{TMS}^{CCl_4}$	Semicarbazone mp, °C	Mass spectrum of semicarbazone
1	 1	 1a	26	1712	2.10 (s, 3 H, CH_3CO), 3.00 (br m, 1 H, CH_3COCH), 5.81 (m, 2 H, olefinic H's)	126–7	181 (M^+), 122, 100, 83, 79, 57
2	 2	 2a	73	1710	2.03 (s, 3 H, CH_3CO), 2.92 (s, 2 H, CH_2COCH_3), 5.52 (br m, 1 H, olefinic H)	122–3	195 (M^+), 136, 100, 83, 79, 57
3	 3	 3a	>90	1712	1.73 (m, 3 H, olefinic CH_3), 2.07 (s, 3 H, CH_3CO), 3.06 (s, 2 H, CH_2COCH_3), 4.80–4.93 (m, 2 H, olefinic H's)	107–8	155 (M^+), 154, 140, 111, 100, 97, 96, 83, 57
4	 4	 4a[b]	10–20	1710	0.83 (s, 3 H, gem CH_3), 1.30 (s, 3 H, gem CH_3), 2.05 (s, 3 H, CH_3CO), 3.00 (s, 2 H, CH_2COCH_3), 5.40 (br m, 1 H, olefinic H)	155–6	235 (M^+), 176, 160, 149, 132, 119, 107, 100, 91, 57
5	 5	 5a[c] (69%) + unknown adduct[d] (31%)	40–50	1710	1.00 (two overlapping s, 6 H, gem CH_3's), 2.01 (s, 3 H, CH_3CO), 4.70–5.20 (m, 4 H, $=CH_2$'s	176–8	303 (M^+), 288, 259, 244, 236, 220, 192, 188, 166, 152, 128, 109, 94
6	 6 cholesteryl acetate	No reaction					
7	 7	 7a[e] (29.7%)  7b (24.8%)  7c + 7d (45.5%) 7c/7d = 19.7:25.8	50–60		**7a:** 1.73 (br s, 3 H, olefinic CH_3), 1.67 (br s, 3 H, olefinic CH_3), 2.13 (s, 3 H, CH_3CO), 4.70 (m, 2 H, $=CH_2$), 5.60 (br m, 1H, olefinic) **7b:** 1.67 (br s, 3 H, olefinic CH_3), 2.07 (s, 3 H, CH_3CO), 3.07 (br s, 2 H, CH_2COCH_3), 4.87–4.97 (m, 2 H, $=CH_2$). **7c + 7d:** 1.67 (m, 6 H, 2 olefinic CH_3's), 2.08 (s, 3 H, CH_3CO), 3.08 (br s, 2 H, CH_2COCH_3), 5.38 (br m, 1 H, olefinic)	**7a:**[f] 178 (M^+), 176, 174, 163, 145, 135, 119, 107, 93, 79, 64 **7b:**[f] 178 (M^+), 176, 163, 161, 145, 135, 120, 119, 105, 95, 93, 79 **7c:**[f] 178 (M^+), 176, 174, 163, 161, 160, 145, 135, 121, 120, 105, 93, 79 **7d:**[f] 178 (M^+), 176, 163, 161, 160, 159, 145, 135, 121, 120 105, 93, 91, 79
8	 8	 8a[g]					

[a] For determination of yields see Table III. [b] One minor acetylation product formed in 13% relative to **4a**. [c] The structure of **5a** was elucidated by comparing its ^{13}C NMR spectrum with that of the maleic anhydride adduct of **5** [see A. Nickon, *J. Am. Chem. Soc.*, 77, 1190 (1955)]. The adduct with maleic anhydride showed ^{13}C signals δ 113.9, 118.3 (terminal $=^{13}CH_2$'s), 151.3 (C-4), 156.6 (C-8), whereas the acetylated product **5a** showed the corresponding signals at 113.5, 118.5, 151.3, and 156.9 as well as the $CH_3{}^{13}CO$ signal at 212.5 ppm. Caryophyllene shows significantly different olefinic carbon chemical shifts at 116.3, 128.8, 139.4, and 158.7 ppm. [d] Although this compound could not be isolated, it does not seem to contain olefinic carbon atoms. [e] The best GLC separation of **7a–d** was achieved by using a dinitrophenyl naphthyl ether column. The four isomers are described according to their retention times, **7a** coming off the column first. [f] Mass spectra of **7a–d** determined by combined GLC–MS; **7c + 7d** were also converted into their semicarbazones and shown to give two acetyl singlets in the 100-MHz ^1H NMR spectrum. [g] Identified by comparison with authentic material; it is possible that **8a** is formed via *O*-acetylation of the enol.

Table III. Experimental Details

Reaction	Olefin	g (mmol)	$CH_3C^+OSbCl_6^-$, g (mmol)	Base,[a] g (mmol)	Temp, °C (time, h)	Product, g	Yield, %	Determination of yield
1		0.410 (5.0)	1.885 (5.0)	1.045 (5.0)	−30 ca. −20 (0.5)	0.16	26.0	GLC[b]
2		0.480 (5.0)	1.885 (5.0)	1.045 (5.0)	−50 ca. −30 (0.5)	0.511	73.1	Isolation by column chromatography and distillation
3		0.28 (5.0)	1.885 (5.0)	1.045 (5.0)	−50 ca. −30 (0.5)	0.475	>90[c]	Isolation by distillation
4		0.544 (4.0)	1.508 (4.0)	0.836 (4.0)	−70 ca. −40 (1.0)	0.079[e]	12.9	Isolation by TLC
5		1.428 (7.0)	2.639 (7.0)	1.463 (7.0)	−40 ca. −30 (1.0)	0.804 (mix)	47.4	GLC after column chromatography. Purified by HPLC[g]
6	 cholesteryl acetate	1.712 (4.0)	1.508 (4.0)	0.836 (4.0)	−20 (2–3)	*h*		
7		1.36 (10.0)	3.77 (10.0)	2.09 (10.0)	−30 ca. −20 (0.5)	1.06 (mix)	59.5	GLC after column chromatography. Separated by preparative GLC[i]
8		0.49 (5.0)	1.885 (5.0)	0.505 (5.0)[j]	−20–0	*k*		

[a] Dicyclohexylethylamine was used. [b] Acetophenone was used as internal reference. [c] The NMR spectrum of crude product did not show any impurity. [d] β-Pinene was purified by fractionation using a spinning band column. [e] The product contains a very minor impurity as mentioned in Table II. Complete purification could be achieved by repeating TLC with sacrifice of yield. When tetramethylurea was used as base, almost no acylation product was formed. [f] Caryophyllene was purified by column chromatography on Merck neutral alumina. [g] A small amount of the product was purified by high-pressure liquid chromatography using *n*-heptane as eluent; complete separation by TLC failed although the mixed solvent system benzene–isopropyl methyl ketone was found to be superior. [h] Any acylated product was found to be negligibly small by TLC and IR. [i] Preparative separation was carried out on a carbowax column, since the DNPNE column cannot be used at temperatures higher than 150 °C. [j] Triethylamine was used as base in this case. This reaction was also examined in the absence of base but did not change at all except proceeding somewhat more slowly. [k] The yield seems poor. Formation of the enol acetate was confirmed by GLC comparison of the reaction mixture and an authentic sample prepared from cyclohexanone and isopropenyl acetate.

Finally, β,γ enones could be identified readily by their characteristic IR and NMR peaks (see Table II).

Results. Table I illustrates the striking effect of added base on the proportion of the two acetylation products, β,γ- and α,β-unsaturated ketones. Whereas the product invariably contains 1-acetylcyclohexene[8] (**1b**), when no acid trap is used, it is clear that the formation of this isomer can be fairly well suppressed in the presence of even a very weak base, tetramethylurea, and eventually totally by bases such as 2,4,6-collidine, triethylamine, and especially ethyldiisopropylamine and dicyclohexylethylamine[9] which provide cleaner reaction products and higher yields than reactions where other bases are used (Table I, No. 7). In Table II, acetylated products obtained from various olefins are listed together with their NMR spectral data and the mass spectral data of the derived semicarbazones. Here again, the presence of hindered tertiary amine cleans up the reaction by allowing primary products to be isolated with minimal isomerization and decomposition. Note also that all reactions listed in Table II have been carried out with equimolar amounts of alkene and acetylating agent. Presumably by using an excess of alkene the yields can be increased further.

IR and GLC analyses of all reaction mixtures revealed clearly that the highly selective formation of β,γ-unsaturated ketones is a general feature of these acetylations regardless of the thermodynamic stability of the product ketones.[10] Acid-catalyzed isomerization studies indicated that under comparable conditions ketones bearing tetrasubstituted and trisubstituted double bonds survived or rearranged much more slowly into α,β-unsaturated ketones than those with disubstituted double bonds.

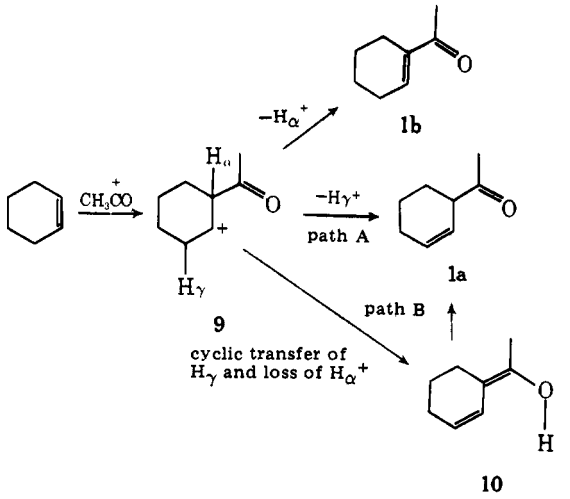
Discussion

The reactivity toward acetylation is dependent on olefin structure as indicated by the results from methylenecyclohexane (**2**) and isobutene (**3**) which are more reactive than cyclohexene[14] (**1**), whereas in caryophyllene (**5**) it is the strained trisubstituted trans double bond which is attacked preferentially. Interestingly, in limonene (**7**) the sterically accessible disubstituted double bond is more reactive by a factor of 2.3 than the internal double bond, although the latter is trisubstituted. In contrast to the reaction with acetyl cation described here, limonene is attacked by singlet oxygen exclusively at the more electron-rich internal double bond.[15] Attempted acetylation of cholesteryl acetate (**6**) with its highly hindered $\Delta^{5,6}$ double bond[16] was not successful and led to recovery of starting material.

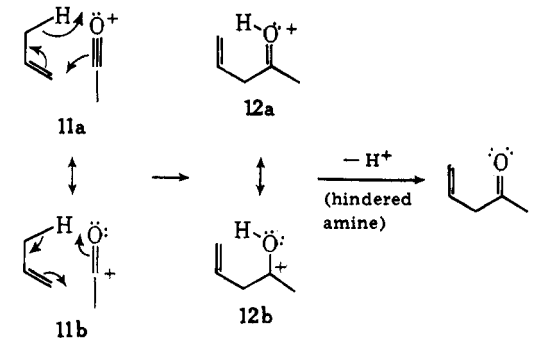
Hitherto, two mechanisms have been invoked to account for the formation of deconjugated enones, viz., electrophilic attack of acetyl cation to give β-ketocarbenium ion **9** as the key intermediate, which was visualized to suffer loss of a γ proton (path A, Scheme I)[5b] or alternatively undergo cyclic transfer of the γ hydrogen to oxygen with simultaneous expulsion of the α proton, yielding dienol **10** and eventually enone **1a** on kinetically controlled reprotonation (path B).[3a,e,17]

As long as a mixture of α,β and β,γ enones is formed, there may be no need to question these mechanistic proposals. However, if a β-ketocarbenium ion analogous to **9** were involved as an intermediate in our conditions, the selective formation of deconjugated enones would be hard to understand, and fragile olefins such as β-pinene (**4**) and caryophyllene (**5**) should afford a host of further products familiar from conventional carbenium ion reactions. In fact, that the bicyclic skeleton of β-pinene survives at all in our conditions is inter-

Scheme I. Olefin Acetylation via a β-Ketocarbenium Ion



Scheme II. Olefin Acetylation via One-Step Transfer of Hydrogen to Oxygen[a]



[a] Note that the reacting atoms (curved arrows) have been projected into a plane. For stereochemical detail see ref 19.

esting, since β-pinene has been polymerized by a wide variety of Lewis acids, even weak ones. Invariably, polymerization also entails opening of the four-membered ring and fragmentation, which provides part of the driving force for the reaction.[18]

We consider that the highly selective formation of β,γ-unsaturated enones can be better rationalized by the following sequence (Scheme II), in which the acetyl cation plays the role of a powerful enophile[19] by abstracting an allylic hydrogen from the olefin in concerted fashion. As has been shown by Olah on the basis of ^{13}C NMR shifts and the strong carbonyl absorption in the IR near 2300 cm^{-1}, the oxonium resonance hybrid **11a** makes the most important contribution to the structure of the acetyl cation,[4b] which is sterically readily accessible and isoelectronic with acetonitrile and methylacetylene, only more electrophilic. Thus, the whole reaction sequence in Scheme II can be formulated via intermediate oxygen cations.

In assessing the scope of our mechanism for rationalizing the course of aliphatic acetylations the following points should be kept in mind. The formation of a β-ketocarbenium ion analogous to **9** is, of course, reasonable in acylations of alkenes such as norbornene[5b] which lack a suitably activated allylic hydrogen. Furthermore, given a more nucleophilic counterion, conventional electrophilic 1,2 additions to the carbon–carbon double bond seem entirely feasible. However, if as in the present instance the acetyl counterion is practically nonnucleophilic, concerted attack with formation of the resonance-stabilized α-hydroxycarbenium ion **12a** ↔ **12b** appears to be energetically most profitable even though a C–H bond has to be broken in the process. In the future, ene reactions of free or long-lived acetyl cations and related species will have to be considered as a general reaction mode and may well join other well-established carbenium ion reactions. It also seems clear that *charged* enophiles[20] involving naked cations, even more so than enophiles activated by Lewis acids,[21] are very reactive and show promise as reagents for the selective functionalization of olefins.[22]

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References and Notes

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