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REACTIONS OF ACID ANHYDRIDES—II[1]

REACTIONS OF KETONES WITH MIXED SULPHONIC-CARBOXYLIC ANHYDRIDE, ISOPROPENYL ACETATE, AND ACETIC ANHYDRIDE

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Abstract—The reactions of unsymmetrically substituted ketones with trichloroacetyl *p*-toluenesulphonate, isopropenyl acetate and acetic anhydride were investigated.

Trichloroacetyl *p*-toluenesulphonate converted the saturated ketone **2** to the enol tosylate **5** but testosterone acetate **6** to the corresponding dienol trichloroacetate **7b**.

Reaction of the ketones **1, 2** and **10** with isopropenyl acetate or acetic anhydride in the presence of acid led to isomeric enol acetates **3, 4** and **11**. The ratio of the isomeric enol acetates *differed* according to the acid used, when isopropenyl acetate was employed, but was *independent* of the acid, when acetic anhydride was used.

It is suggested that the formation of enol acetates involves addition of either acetic anhydride (when acetic anhydride is used) or mixed anhydride (when isopropenyl acetate or the mixed anhydride is used) to give a *gem* disubstituted intermediate.

RECENTLY we have found[2] that mixed sulphonic-carboxylic anhydrides react with ethers resulting in acylation of the ether O atom, and in the cleavage of C—O bond. The ether cleavage reaction does not require the presence of added Lewis acid.

It appeared to us that mixed anhydrides will react efficiently also with carbonyl groups in the absence of acids.

The mixed anhydride chosen for the reaction with ketones was the previously undescribed trichloroacetic *p*-toluenesulphonic acid anhydride. It was prepared by treatment of *p*-toluenesulphonic acid with a large excess of trichloroacetic anhydride at 125–135° with subsequent distillation of liberated trichloroacetic acid and excess trichloroacetic anhydride. The crystalline residue was identified as trichloroacetyl *p*-toluenesulphonate from its NMR and IR spectra.

Reaction with ethanol cleaved either the bond between oxygen and the trichloroacetyl group, or that between oxygen and the *p*-tosyl group of the mixed anhydride. However, the former bond fission was preferred, resulting in formation of ethyl tosylate and ethyl trichloroacetate in a 1:3 ratio.

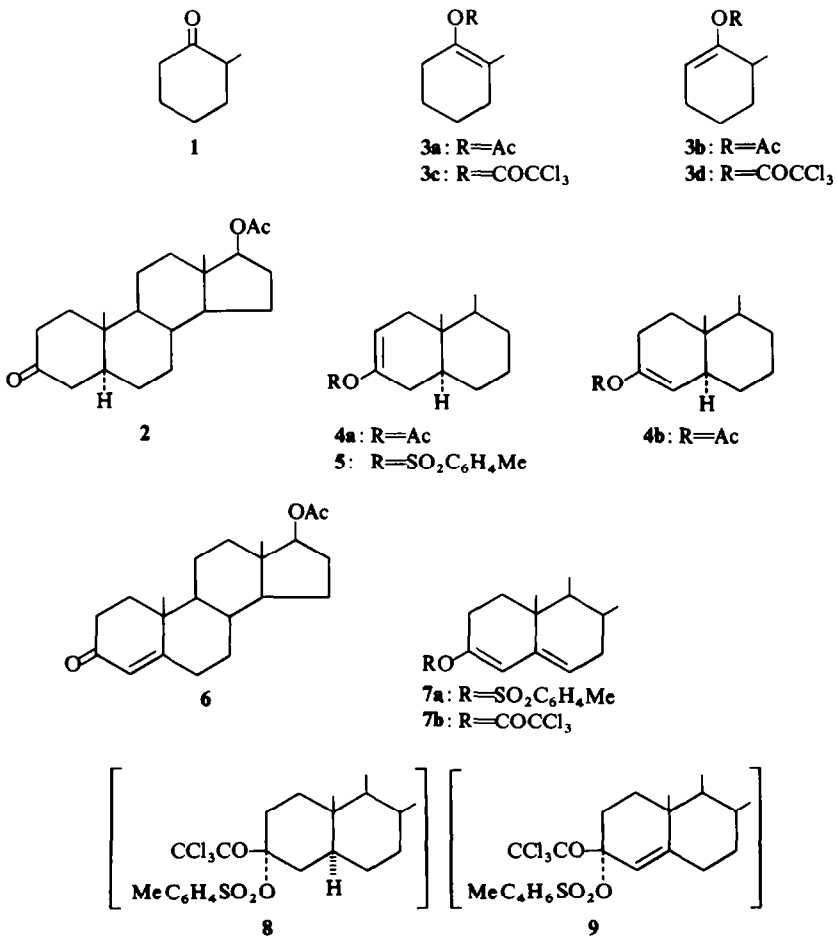
$$MeC_6H_4SO_2OH + (CCl_3CO)_2O \rightarrow MeC_6H_4SO_2OCOCCl_3 + CCl_3COOH$$

$$\downarrow EtOH$$

$$MeC_6H_4SO_2OEt + CCl_3COOEt$$

* Taken in part from the Ph.D. thesis submitted to the Feinberg Graduate School of the Weizmann Institute of Science, Rehovot.

CHART I



Treatment of steroidal ketone **2** with an excess of this mixed anhydride in carbon tetrachloride solution gave the enol tosylate **5** (21%) in addition to dimeric products.[3] On the other hand, treatment of testosterone acetate **6** under the same condition but at room temperature gave the dienol trichloroacetate **7b** and not the dienol tosylate **7a**.

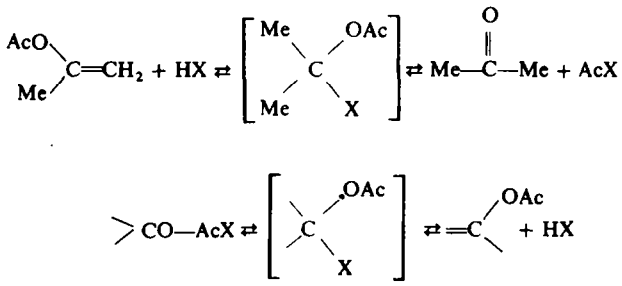
The different behaviour of the ketones **2** and **6** towards this mixed anhydride may be rationalized by assuming stereospecific addition to the CO bond, resulting in *gem* diesters **8** and **9** respectively.* The former diester eliminates in preference the trichloroacetic acid, while the elimination of the tosylic acid from the latter diester is facilitated by the participation of the double bond electrons.

It was proposed by Satchell *et al.*[5] that the active species in enol acylation of ketones with isopropenyl acetates and acids are mixed anhydrides, formed from the two reagents. It was suggested that these mixed anhydrides react with the enolic form of the CO group.[5] However, from the analogy with the reaction of ketones with

* It is noteworthy that another vinylester interchange reaction catalysed by mercury acetate, proceeds via formation of a *gem* diester derivative.[4]

trichloroacetic anhydride,[1] it seemed to us more plausible that the mixed anhydrides attack the keto and not the enol form of the CO group, leading to a *gem* diester. The latter would subsequently eliminate one molecule-of acid resulting in enol acetates. Since isopropenyl acetate, which is itself an enol acetate, is converted to acetone while the reacting ketones are converted to the corresponding enol acetates, analogous pathways and intermediates must be involved in both reactions.

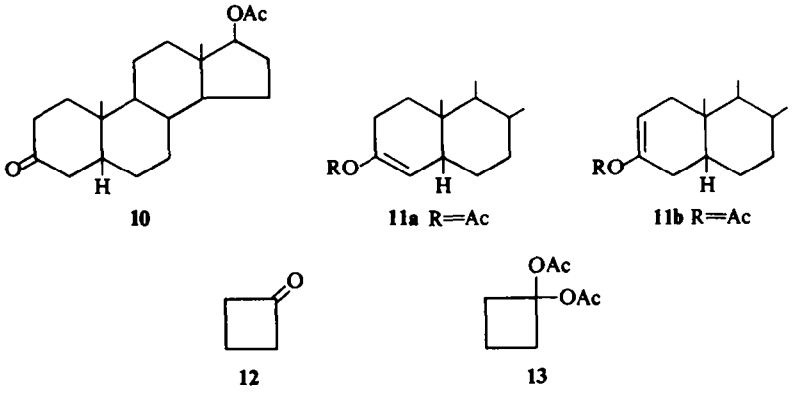
The following scheme is thus proposed for these two reactions,



Accordingly different acid catalysts will result in different *gem* disubstituted intermediates.

In order to verify this scheme we have treated unsymmetrically substituted ketones **1**, **2** and **10** with isopropenyl acetate in carbon tetrachloride solution using two different acid catalysts, the sulphuric and perchloric acids. The course of the reaction was followed by recording the NMR spectra of the reaction mixture at varying time intervals.

CHART II



10 **11a** R=Ac **11b** R=Ac

12 **13**

In all these experiments we obtained mixtures of positional double bond isomeric enol acetates. As seen from Table 1 a constant ratio of the two isomers was observed, while the reaction was in progress, whose value however differed according to whether perchloric or sulphuric acid was used. Using sulphuric acid, a "kinetic ratio" of the enol acetates was obtained, the reaction rate being comparatively slow, while using perchloric acid the ratio of the positional double bond isomer is more in favour of the thermodynamically stable isomer, the reaction being faster.

TABLE 1. FORMATION OF ENOL ACETATES FROM KETONES AND ISOPROPENYL ACETATE

Reactant	Reagent	Reaction temperature	Reaction time	Percentage of conversion	Ratio of isomeric enol acetates
2-Methyl-cyclo-hexanone	Isopropenyl acetate, $HClO_4$ in CCl_4[a]	25°C	30 min	50	7:1
1	Isopropenyl acetate, H_2SO_4 in CCl_4[a]	25°C	10 hr	30	4:1
			28 hr	50	4:1
17β-Acetoxy-5α-androstane-3-one	Isopropenyl acetate, $HClO_4$ in CCl_4[a]	25°C	15 min	100	>9:1
	Isopropenyl acetate, H_2SO_4 in CCl_4[a]	25°C	10 hr	50	4:1
			28 hr	100	4:1
2	Isopropenyl acetate, H_2SO_4[b]	102°C	10 min	74	4:1
			20 min	85	4:1
			40 min	100	4:1
			60 min	100	4:1
17β-Acetoxy-5β-androstane-3-one	Isopropenyl acetate, $HClO_4$ in CCl_4[a]	25°C	15 min	100	4:1
	Isopropenyl acetate, H_2SO_4 in CCl_4[a]	25°C	10 hr	50	2:1
			28 hr	100	2:1
10	Isopropenyl acetate, H_2SO_4[b]	102°C	20 min	90	2:1
			40 min	100	2:1
			75 min	100	2:1

Concentration of reactants: [a] 0·5, [b] 0·3 mol/l; concentration of isopropenyl acetate: 2·5 mol/l; concentration of acid catalysts: 0·05 mol/l.

According to the proposed scheme, the *gem* disubstituted intermediates will have the following structures:

The ratio of the isomeric enol acetates will thus be dependent on the nature of the transition states involved in the elimination of acid molecules from these intermediates. This transition state will have a more pronounced carbonium ion character, if perchloric acid is used as catalyst, but less so, if sulphuric or *p*-toluenesulphonic acid is employed. Since a transition state of stronger carbonium ion character is involved in an E_1 type elimination, but of weaker carbonium ion character in an E_2 type elimination, the thermodynamically more stable products are expected to be formed in greater preponderance in the first case.

It was found by Russian workers[6] that the primary products of the reaction of ketones with acetic anhydride in the presence of sulphuric acid are also *gem* diacetates, which could be isolated in a few cases. The latter eliminate acetic acid resulting in the corresponding enol acetates. Analogous *gem* diesters are known to be formed when aldehydes[7] are treated with carboxylic anhydrides. *Gem* diesters have also been obtained from ketones and trichloroacetic anhydride.[1]

However, in contrast to trichloroacetic anhydride, acetic anhydride alone does not react with ketones, the presence of acids being necessary. In order to gain information concerning the role of acid catalysts in these acetylations, we have treated ketones in carbon tetrachloride solutions with acetic anhydride in the presence of two different acids. These reactions were studied by NMR technique. In the presence of perchloric acid cyclohexanone was converted to the extent of 80% into its enol acetate after 20 min. In the presence of sulphuric acid only 10% of conversion was recorded after 10 hr.

The unsymmetrically substituted ketones **1**, **2** and **10** were also subjected to similar reaction conditions. As indicated in Table 2, we have observed initial formation of the "kinetically controlled products" which equilibrated on further treatment with the same reagent to the thermodynamically stable ones. Furthermore, the ratio of isomeric enol acetates formed was constant at identical percentage conversion, and was independent of the acid used. However, the rate of conversion to the enol acetates was found to be higher in the presence of perchloric acid, the stronger of both acids used (Table 2).

TABLE 2. FORMATION OF ENOL ACETATES FROM KETONES AND ACETIC ANHYDRIDE AT ROOM TEMPERATURE

Reactant	Catalyst	Reaction time	Percentage of conversion	Ratio of isomeric enol acetates
2-Methyl-cyclohexanone (**1**)[a]	$HClO_4$	10 min	80	4:1
		15 min	90	5:1
		25 min	92	7:1
		40 min	93	>10:1
1[b]	H_2SO_4	3 hr	68	4:1
		24 hr	90	6:1
17β-Acetoxy-5α-androstane-3-one (**2**)[c]	$HClO_4$	10 min	50	9:1
		3 hr	70	>9:1
		24 hr	70	>20:1
2[d]	H_2SO_4	3 hr	20	9:1
		15 hr	70	>9:1
17β-Acetoxy-5β-androstane-3-one (**10**)[e]	$HClO_4$	10 min	45	3:1
		3 hr	68	4:1
		24 hr	72	>20:1
10[f]	H_2SO_4	2 hr	15	3:1
		15 hr	70	4:1

Concentration of reactant: [a] 0·5, [b] 1·0, [c,d,e,f] 0·5 mol/l; concentration of Ac_2O: [a,d,f] 0·9, [b] 5·0, [c,e] 0·45 mol/l; concentration of the acid catalysts: [a] 0·01, [b] 0·05, [c,e] 0·002, [d,f] 0·02 mol/l.

It is therefore conceivable, that the same reagent, the same pathways and the same intermediates are involved in the reaction of ketones with acetic anhydride in the presence of different acids. The protonated acetic anhydride, which has an increased electrophilic character, is likely to be the effective reagent. Accordingly, the overall rate of formation of the enol acetate should depend on the acidity of the acid catalyst. The protonated acetic anhydride then adds to the ketone in a ter or bimolecular fashion, as suggested for the reaction with trichloroacetic anhydride.[1] The resulting geminal diacetate may eliminate acetic acid to give the enol acetate.

If a *gem* diacetate were the intermediate in the reaction of ketones with acetic anhydride, a labelled carbonyl oxygen would be expected to undergo a reduction in incorporation when converted to the enol acetate. Steroidal ketone **2** labelled with ^{18}O was treated for 30 min at room temperature with acetic anhydride and perchloric acid in carbon tetrachloride. The isolated mixture of enol acetates **4a** and **4b** was found to contain only 28% of the ^{18}O initially present in the starting material **2**. After three hours of reaction the ^{18}O content further decreased to 14%.

These results are in accord with a reversible formation of enol acetate involving a *gem* diacetate as intermediate.

Further support of this mechanism was obtained, when stable 1,1'-bisacetoxycyclobutane (**13**) was isolated from the reaction of cyclobutanone (**12**) with acetic anhydride and perchloric acid in carbon tetrachloride. The stability of this geminal diacetate is likely to be due to the considerable strain present in its elimination product, the enol acetate. The *gem* diacetate **13** readily underwent basic hydrolysis to the parent ketone **12** and gave under electron impact a similar fragmentation to the corresponding geminal bistrichloroacetate.[1]

It is noteworthy that in the reaction of the unsymmetrically substituted ketones **1** and **2** with trichloroacetic anhydride and acid the "kinetically controlled" mixture of the corresponding enol trichloroacetates contained a high proportion of the thermodynamically less stable product. We have already noted[1] that the mixtures of the isomeric enol trichloroacetates derived from the steroidal ketone **2** were obtained in 3:1 ratio. Now we have treated also 2-methylcyclohexanone **1** with trichloroacetic anhydride at 130° and isolated a mixture of **3c** and **3d** also in 3:1 ratio. These results are in accord with our assumption. The transition state involved in the formation of enol trichloroacetates has less carbonium ion character than that involved in the formation of enol acetates, due to the high inductive effect of the trichloromethyl group present in the former, which destablizes the positive charge developing in the transition state.

EXPERIMENTAL

All m.ps were taken in capillaries and are uncorrected. UV spectra were determined on a Cary 14 spectrophotometer and the IR spectra on a Perkin–Elmer infracord. The NMR spectra were recorded on a Varian A-60 spectrometer, using tetramethylsilane as internal standard. The mass spectra were measured with an Atlas CH-4 instrument.

Preparation of trichloroacetyl p-toluenesulphonate

Anhydrous *p*-toluenesulphonic acid, 17·2 g, was heated for 1 hr in an oil bath of 130–135° with 92 g trichloroacetic anhydride. The liberated trichloroacetic acid and excess of trichloroacetic anhydride were distilled off under reduced press (0·03 mm) at a bath temp of 40–60° to give trichloroacetyl *p*-toluenesulphonate; IR (CCl_4) 1780 cm^{-1} (anhydride C=O), 1600 cm^{-1} (Ph), 1400 cm^{-1} (OSO_2), 1200 cm^{-1} (OSO_2), 1150 cm^{-1} (C—O—C); NMR (CCl_4) δ 7·67 (q, $4J$ = 8 and 33 c/s, phenyl-H), 2·48 (s, 3, phenyl-CH_3).

Reaction of trichloroacetyl p-toluenesulphonate with ethanol

Trichloroacetyl *p*-toluenesulphonate, 1·08 g, was dissolved in 0·2 ml ethanol and stirred for 2 hr at room temp. The NMR spectrum of the reaction mixture showed signals at δ = 4·42 (q, J = 7 c/s) and δ = 4·08 (q, J = 7 c/s), attributed to the methylene protons of the ethyl trichloroacetate and ethyl tosylate respectively, with relative intensities corresponding to 75% ethyl trichloroacetate and 25% ethyl tosylate. The reaction mixture was poured into 5% $NaHCO_3$ aq, extracted with pentane, washed with water, dried and the pentane evaporated. The residue, 445 mg, contained a mixture of ethyl trichloroacetate (75%) and

ethyl tosylate (25%) (as determined by IR and NMR spectroscopy) IR (neat) 1770 cm^{-1} (trichloroacetoxy C=O), 1600 cm^{-1} (Ph), 1250 cm^{-1} (trichloroacetoxy C—O—C), 1180 cm^{-1} and 1190 cm^{-1} (OSO_2); NMR (CCl_4) δ 7·52 (q, 1 J = 8 and 27 c/s, phenyl-H), 4·42 (q, 1·5, CH_2OCCl_3), 4·08 (q, 0·5, CH_2—OTs), 2·43 (s, 0·75, phenyl—CH_3), 1·42 (t, 2·25, $CH_3CH_2OCCCl_3$), 1·3 (t, 0·75, CH_3CH_2OTs).

Reaction of trichloroacetyl p-toluenesulphonate with 17β-acetoxy-5α-androstan-3-one (2)

Ketone 2, 400 mg, was heated for 20 hr with 4·0 g trichloroacetyl *p*-toluenesulphonate in 4 ml CCl_4 at reflux temp. The reaction mixture was then poured into 5% $NaHCO_3$ aq, extracted with ether, and the oily residue was chromatographed on silicagel. Elution with ether–pentane (15:85) gave 25 mg of a dimeric product m.p. 224–226°, followed by 125 mg (21%) of (5), m.p. 168–169° (after crystallization from ether: pentane). IR (KBr) 1730 (acetoxy C=O), 1680 (C=C), 1595 (Ph) 1355, 1195, 1170, 1152 and 1040 cm^{-1} (SO_3): NMR ($CDCl_3$) δ 0·68 (s, 3, CH_3 at C10), 0·77 (s, 3, CH_3 at C13), 2·01 (s, 3, $OCOCH_3$), 2·44 (s, 3, $C_6H_4CH_3$), 4·56 (m, 1, $HCOCOCH_3$), 5·13 (m, 1, C=CH at C2) and 7·51 ppm (q, 4, J = 7 and 24 c/s, Ph). (Found: C, 69·03; H, 7·85. Calcd for $C_{28}H_{38}O_5S$; C, 69·11; H, 7·87%). Further elution with ether–pentane (2:8) yielded 25 mg (7%) of ketone 2, m.p. 157–159°, followed by 30 mg (6%) of another dimeric product, m.p. 184–186°.

Reaction of trichloroacetyl p-toluenesulphonate with testosterone acetate (6)

A soln of 6, 100 mg, in 0·25 ml CCl_4 was treated at 75° with 250 mg mixed anhydride in 0·25 ml CCl_4. The NMR spectra of the reaction mixture was recorded after several time intervals. After ca. 20 hr the signals assisgned to the starting material at δ = 5·65 (s, C=CH) and at 1·21 ppm (s, CH_3 at C10) had disappeared and two new signals in the vinylic region at 5·90 (s, C=C —H at C4) and at 5·50 ppm (m, C=C—H at C5), and one new signal in the Me region (δ = 1·01, s, C19H_3) assigned to the dienol trichloroacetate had appeared. No signals which could have been attributed to 7a were observed. Isolation of the product by extraction with ether and recrystallization gave dienol trichloroacetate, 7b, m.p. 169–173°C, identical with an authentic sample.

Reactions of ketones with isopropenyl acetate

Reactions of ketones with isopropenyl acetate in carbon tetrachloride solution at room temp. The acetylating reagents were prepared from 1·25 ml freshly distilled isopropenyl acetate, 3·75 ml CCl_4 (analar) and either one drop conc H_2SO_4 or one drop 70% aqueous perchloric acid.

The appropriate amount of ketone was placed in an NMR tube and dissolved in 0·5 ml freshly prepared acetylating reagent (with perchloric acid catalysis use of freshly prepared reagent was essential in order to get acetylations). The course of the reaction was followed by recording the NMR spectra of the reaction mixtures after various reaction periods. The product yield was determined by integration of the appropriate signals. TMS was used as external standard. The results are summarized in Table 1.

Reactions of ketones with isopropenyl acetate at reflux temp

Steroidal ketones 2 and 10 (separately), 1·0 g each, were dissolved in 10 ml freshly distilled isopropenyl acetate and 0·008 ml conc. H_2SO_4 was added. The soln was refluxed for various periods under exclusion of water, and then evaporated to dryness in the cold under reduced pressure. The residue was dissolved in $CDCl_3$ and its NMR spectrum recorded. The yield of enol acetates was determined by integration of their respective proton signals.

Reactions of ketones with acetic anhydride

The acetylating reagents were prepared by mixing Ac_2O (4–40 ml, djstilled before use) with 40 ml CCl_4 tetrachloride and addition of conc H_2SO_4 or 70% aqueous perchloric acid.

The appropriate amount of ketone was placed in an NMR tube and dissolved at room temp in 0·5 ml acetylating reagent. The course of the reaction was followed by running the NMR spectra of the reaction mixtures after various reaction periods. The amount of product formed was determined by integration of the appropriate proton signals in the substrates and products.

Reaction of 17β-acetoxy-5α-androstan-3(^{18}O)-one (2) *with acetic anhydride*

(a) Compound 2, 30 mg, (of 14·5% isotopic purity) was treated for 30 min at room temp with 0·2 ml

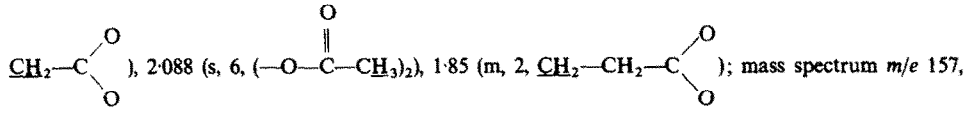
acetylating reagent. (The acetylating reagent was prepared by mixing 4 ml Ac_2O with 40 ml tetrachloride and addition of one drop 70% aqueous perchloric acid).

The reaction mixture was diluted with CCl_4, washed with 5% $NaHCO_3$ aq, then with water, dried and the solvent evaporated. The residue was recrystallized from ether–pentane to give enol acetates **4a** and **4b** (m.p. 166–168°). Mass spectrum *m/e* (rel. intensities of molecular ion peaks) 376 (9), 375 (25), 374 (100). These values correspond to the presence of ca. 4% with ^{18}O labelled enol acetate **4**.

(b) Compound **2**, 30 mg, (of 14·5% isotopic purity) was treated for 3 hours at room temperature with 0·2 ml acetylating reagent. (The acetylating reagent was prepared as described above.) The enol acetates **4** were isolated by extraction and recrystallization from ether pentane, m.p. 166–168°. Mass spectrum *m/e* (rel. intensities of molecular ion peaks) 376 (6–7), 375 (23), 374 (100). These values correspond to the presence of ca. 2% with ^{18}O labelled enol acetates **4**.

Preparation of 1,1-*diacetoxycyclobutane* (**13**)

Cyclobutanone (**12**) 3·0 g, was treated for 2 hr at room temp with 100 ml acetylating reagent. (The reagent was prepared from 100 ml CCl_4, 10 ml Ac_2O and 3 drops 70% aqueous perchloric acid.) The reaction mixture was then diluted with CCl_4, washed with cold 5% $NaHCO_3$ aq, then with water, dried and evaporated. The oily residue was distilled under reduced press to give 2·9 g (40%) of **13**, b.p. 50° (10·5 mm); n_D^{21} 1·4347; UV max (EtOH) 220 mμ (ε 160); IR (neat) 1770 cm^{-1} (ester C=O), 1270 cm^{-1}, 1245 cm^{-1}, 1200 cm^{-1}, 1195 cm^{-1}, 1010 cm^{-1} (ester C—O and O—C—O; NMR ($CDCl_3$) δ 2·68 (4 lines, 4,



), 2·088 (s, 6, (—O—C(=O)—C$\underline{H}_3$)$_2$), 1·85 (m, 2, $\underline{CH}_2$—CH_2—C(=O)—O); mass spectrum *m/e* 157, 144, 130, 113, 112, 102, 84, 70, 42. (Found: C, 56·07; H, 6·86. Calcd. for $C_8H_{12}O_4$: C, 55·80; H, 7·03%).

1-*Trichloroacetoxy*-2-*methylcyclohex*-1-*ene* (**3c**) *and* 1-*trichloroacetoxy*-2-*methylcyclohex*-6-*ene* (**3d**).

Compound **1**, 6·0 g, was treated with *p*-toluenesulphonic acid and trichloroacetic anhydride to give 8·72 g (64%) crude **3c** and **3d**, distillation under reduced pressure gave a mixture of **3c** and **3d**, b.p. 83° (0·1 mm); n_D^{26} 1·4901; NMR ($CDCl_3$) δ 5·5 (m, 0·3, C=C—$\underline{H}$ of **3a**), 2·17 (m), 1·59 (s, 2, C=C—C$\underline{H}_3$ of **3c**), 1·03 (d, J = 7 c/s, 1, C—C$\underline{H}_3$ of **3d**). The ratio of **3c** and **3d** was ca. 3·1 according to the integration. Mass spectrum *m/e* 256, 186, 187, 143, 79. (Found: C, 42·38; H, 4·18. Calcd. for $C_9H_{11}O_2Cl_3$: C, 41·94; H, 4·31%).

Equilibration of **3c** *and* **3d**

A mixture of isomeric enol trichloroacetates **3**, 1·93 g, (containing 70% of enol-ester **3c** and 30% of enol ester **3d**) was heated for 3 hr at 120–130° with 8·5 ml trichloroacetic anhydride in the presence of 850 mg *p*-toluenesulphonic acid. Extraction of the reaction mixture with ether gave pure **3c** as determined by NMR spectroscopy.

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