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2-Acylcyclopentane-1,3-diones

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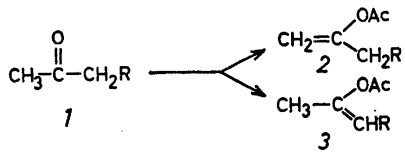
Reaction of 2-acetoxy-3,3-dimethylbut-1-ene with succinic anhydride and aluminium chloride gave small amounts of 2-pivaloylcyclopentane-1,3-dione and 2-acetylcyclopentane-1,3-dione. This result indicates that acyl group interchange occurs in the diacylation of vinyl esters. The mechanistic implications are discussed.

2-Acylcyclopentane-1,3-diones other than the 2-acetyl derivative are therefore best prepared by *C*-acylation of cyclopentane-1,3-dione as exemplified by the preparation of the butyryl and isovaleryl compounds.

Diacylation of isopropenyl acetate with carboxylic anhydrides or acyl chlorides in the presence of aluminium chloride affords a general method for the preparation of 2-acetyl-1,3-diketones which is particularly useful for preparation of 2-acetylcyclopentane-1,3-diones.[1–3] A corresponding diacylation of vinyl acetate has been used for the preparation of acyclic β-diketones which are formed *via* labile 2-formyl-1,3-diketones.[4,5]

The present investigation concerns the possibilities of employing other 1-substituted vinyl acetates, $CH_2=C(R)OAc$, for the preparation of 2-acylcyclopentane-1,3-diones. Such enol esters are not readily prepared, however, since acid-catalysed *O*-acetylation of methyl-methylene ketones (*1*) leads to mixtures of enol acetates *2* and *3*. House and Kramar [6] and Smith and Chen [7] have determined the equilibrium proportions of such enol acetates and



found that the proportion of isomer *2* is generally very small. This fact, as well as the practical difficulties in the separation of the isomers exclude this method of preparation. Our interest was therefore provisionally focused on the use of the enol acetate of pinacolone as a model compound.

The reaction between succinic anhydride, 2-acetoxy-3,3-dimethylbut-1-ene (pinacolone enol acetate) and aluminium chloride, however, gave only a very

poor yield of 2-pivaloylcyclopentane-1,3-dione (3 %) accompanied, surprisingly, by some 2-acetylcyclopentane-1,3-dione (3 %). Apparently some transacylation occurred during the reaction.

The transacylation thus observed limits the practical scope of the diacylation to those 1-substituted vinyl esters where the acyl part and the enol part correspond, *i.e.* CH_2=C(R)OCOR′, R = R′, as in isopropenyl acetate. Other such vinyl esters, however, are not readily available. For the preparation of 2-acylcyclopentan-1,3-diones in general, it seems more useful to use an indirect procedure and *C*-acylate cyclopentane-1,3-dione, which is easily obtained by acid hydrolysis of 2-acetylcyclopentane-1,3-dione.[3] The reacylation is conveniently effected with acid anhydrides in the presence of boron trifluoride in analogy with the *C*-acylation of cyclopentane-1,2,4-triones.[8] Thus 2-butyrylcyclopentane-1,3-dione and 2-isovalerylcyclopentane-1,3-dione were prepared with butyric and isovaleric anhydrides, respectively. The formylation of cyclopentane-1,3-dione is a special case and is discussed elsewhere.[9]

The transacylation observed in the attempted diacylation of pinacolone enol acetate may give some information concerning the mechanism of the diacylation reaction. Similar transacylations have been observed in reactions of vinyl acetate with acyl halides [4] and probably account for the formation, in small amounts, of 2-acetylindane-1,3-dione and 2-acetylcyclopentane-1,3-dione in the reactions with phthaloyl chloride and succinyl chloride, respectively.

Plausible pathways to 2-acetylcyclopentane-1,3-dione and related compounds have been discussed in previous papers.[2,3] Thus, in the reaction of succinic anhydride and isopropenyl acetate it is reasonable to assume an initial monoacylation to give an acyl enol acetate, *4*, R = CH_3 (Fig. 1). This reaction may be followed by more or less reversible rearrangements. One may lead to a mixed anhydride of acetic acid and succinylacetone (*5*, R = CH_3) which on cyclisation would afford 2-acetylcyclopentane-1,3-dione with elimination of acetic acid. With maleic anhydrides cyclisation to enol lactones may occur *via* similar intermediates.[2]

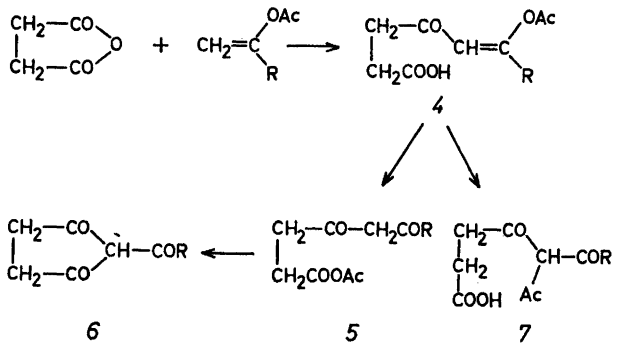


Fig. 1. Simplified scheme for the reaction between succinic anhydride and a 1-substituted vinyl acetate in the presence of aluminium chloride. For convenience aluminium complexes and enolisation (*cf.* Ref. 11) are not indicated.

Other rearrangements could give acyclic triacylmethanes (*e.g.* 7). These seem to be more labile to acidic reagents. The equivalence of the acyl groups and the presumed intermolecular nature of the rearrangements could lead to a considerable scrambling of acyl groups. Cyclisation, however, appears to be favoured with little of the reverse process occurring, and the cyclic products do not seem prone to undergo acyl group exchange; for example 2-acetylcyclopentane-1,3-dione on treatment with mixtures of butyric anhydride and butyric acid and aluminium chloride gave no butyrylcyclopentanedione.[10] This could indicate that the acyl group interchange mainly took place prior to cyclisation.

The acyl group interchange observed in the present work may to some extent be due to decarbonylation of pivaloyl groups, which would possibly shift the equilibria in favour of acetyl compounds.

From the present and previous results it can be concluded that the practical value of the diacylation reaction is largely restricted to the use of isopropenyl acetate and the preparation of 2-acetyl-1,3-diketones where the scrambling of acetyl groups is of no consequence.

EXPERIMENTAL

Melting points were determined on a micro hot stage. Infrared spectra were recorded using *ca.* 0.1 M solutions in 0.1 mm cells or potassium bromide discs on a Perkin Elmer No. 21 or 421 instrument. Ultraviolet spectra were recorded with a Beckman DK 2 spectrophotometer and NMR spectra on a Varian A 60 spectrometer. Reaction mixtures were screened by paper chromatography on paper impregnated with dimethyl sulphoxide[12] with ether, light petroleum (b.p. 40–60°) or di-isopropyl ether as mobile phases, the spots being detected with iron(III) chloride.

2-Acetoxy-3,3-dimethylbut-1-ene (*cf.* Ref. 7). A mixture of pinacolone (1 mole), isopropenyl acetate (2 moles) and *p*-toluenesulphonic acid (2 g) was boiled under reflux overnight. Light petroleum (b.p. 60–70°) was added and then distilled off together with the acetone formed through an efficient Vigreux column at atmospheric pressure. This procedure was repeated twice. The dark mixture was then neutralised with anhydrous sodium acetate, filtered and distilled through an efficient, packed column. The presence of diketen was evident from the IR spectrum and prompted a very cautious distillation. The yield of pure 2-acetoxy-3,3-dimethylbut-1-ene was 43 g (30 %), b.p. 40°/11 mm. The NMR data agree with those reported,[7] the infrared spectrum (pure liquid) shows bands at 1755 (vs) and 1652 cm^{-1} (s) and a shoulder (w) at 1700 cm^{-1}.

Reaction between succinic anhydride and 2-acetoxy-3,3-dimethylbut-1-ene. Succinic anhydride (0.05 mole) and anhydrous aluminium chloride (0.1 mole) were suspended in 1,2-dichloroethane (50 ml) and 2-acetoxy-3,3-dimethylbut-1-ene (0.05 mole) was added fairly rapidly with stirring. The mixture became slightly warmer (25–30°) and was then boiled on a water bath under reflux for 1 h. On cooling a sticky mass separated and the mixture was then added with stirring to hydrochloric acid (125 ml, 2 M) containing crushed ice (125 g). The mixture was stirred until all the material had dissolved. The organic phase was separated and shaken with dilute hydrochloric acid. The combined aqueous phases were extracted with chloroform and then the combined organic phases were extracted with saturated aqueous sodium hydrogen carbonate solution. Acidification and reextraction gave an orange-coloured oil, which according to paper chromatography contained two triketonic compounds. The mixture was chromatographed on silica gel impregnated with dimethyl sulphoxide.[13] Elution with light petroleum gave first 2-pivaloylcyclopentane-1,3-dione as a colourless oil, which was distilled, b.p. 62–63°/0.2 mm; it solidified on standing, m.p. 43.5–45.5° (0.27 g, 3 % yield). (Found: C 65.9; H 7.8. Calc. for $C_{10}H_{14}O_3$: C 65.9; H 7.7). Infrared bands in the carbonyl region (chloroform): 1692, 1590, and 1562 cm^{-1}. Ultraviolet absorption maxima (cyclohexane): 264 nm (ε = 8190) and 223 nm (ε = 12 900). The NMR spectrum (deuterochloroform) showed

signals at: $\tau = -6.6$ (enolic proton), 8.68 (tert. butyl group) and an A_2B_2 pattern centered at $\tau = 7.35$ (methylene protons). Further elution with di-isopropyl ether gave 2-acetylcyclopentane-1,3-dione (0.22 g, 3 %). Continuous extraction of the aqueous phase with dichloromethane gave a small amount (20 mg) of an acidic compound, m.p. 123–125°, which gave a strong brown colour with iron(III) chloride and probably was a cyclic dioxocarboxylic acid. The infrared spectrum showed broad absorption around 3000 cm^{-1} and bands at 1680, 1625, and 1560 cm^{-1}. (Found: C 54.5; H 5.2. Calc. for $C_7H_8O_4$: C 53.8; H 5.2.).

2-Butyrylcyclopentane-1,3-dione. Cyclopentane-1,3-dione [3] (1 g) was suspended in butyric anhydride (7.3 g), the mixture cooled in ice and saturated with boron trifluoride. The mixture was then left for 3 h at room temperature and then 16 h in a refrigerator. The unchanged anhydride was removed under reduced pressure and the residue boiled with absolute ethanol to decompose the boron complexes; the ethyl borate was removed under reduced pressure. The residue was distilled and the distillate treated with saturated aqueous copper(II) acetate. The copper complex formed was recrystallised from methanol (very soluble), m.p. 254–255° (decomp.). The copper salt was shaken with ether and dilute sulphuric acid, the ether layer separated, dried, and the solvent evaporated leaving an oil (0.57 g, 34 %), which was redistilled, b.p. 64–65°/0.2 mm. The distillate solidified on standing (m.p. 30–32°) and could be recrystallised from light petroleum, m.p. 32–34°. (Found: C 64.3; H 7.2. Calc. for $C_9H_{12}O_3$: C 64.3; H 7.2.) 2-Butyrylcyclopentane-1,3-dione showed IR absorptions (chloroform) at 1695, 1620, and 1580 cm^{-1} and UV maxima (cyclohexane) at 263 nm ($\varepsilon = 7800$) and 220 nm ($\varepsilon = 12\,700$). The NMR spectrum (deuterochloroform) showed the enolic proton signal at $\tau = -4.65$.

2-Isovalerylcyclopentane-1,3-dione. Cyclopentane-1,3-dione (1 g) was suspended in isovaleric anhydride (9.2 g), cooled in ice and saturated with boron trifluoride. The mixture was left at room temperature for 24 h. The excess anhydride was removed under reduced pressure, but the remaining boron complexes were little affected by boiling with ethanol. The residue was distilled and the fraction b.p. 50–110°/0.2 mm collected and treated with copper(II) acetate solution. The precipitate was filtered off, washed with water, dried, and washed with cyclohexane. It melted at about 275° (decomp.). The copper complex was shaken vigorously with dilute sulphuric acid and ether for 48 h as it was only slowly decomposed. The ether solution eventually gave an oil which was distilled to give the pure 2-isovalerylcyclopentane-1,3-dione, b.p. 71°/0.3 mm. This material solidified in the refrigerator, m.p. *ca.* 10–12° (yield 0.22 g, 12 %). (Found: C 65.9; H 7.9. Calc. for $C_{10}H_{14}O_3$: C 65.9; H 7.7.).

The IR spectrum (chloroform) showed bands at 1692, 1617, and 1582 cm^{-1} and the UV spectrum (cyclohexane) at 264 nm ($\varepsilon = 7800$) and 219 nm ($\varepsilon = 612\,900$). The NMR spectrum (deuterochloroform) showed the enolic proton signal at $\tau = -3.72$.

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