

Note

Method for gas chromatographic acetylation

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(First received April 20th, 1978; revised manuscript received June 28th, 1978)

The gas chromatographic separation of compounds containing hydroxyl groups is difficult because tailing occurs. These difficulties arise with the less volatile C₁₀–C₁₈ fatty alcohols, but can be overcome by the chemical conversion of the hydroxyl group into a more suitable derivative.

According to Drozd¹, the approaches most often used have been silylation and acetylation. Silylation on the micro-scale, which is necessary in gas chromatographic investigations, has been developed satisfactorily.

Several possibilities exist for the preparation of the acetic esters of fatty alcohols. Acetyl chloride^{2,3} and acetic anhydride^{4–6} have been most often for this purpose. Acetylation with a 3–5-fold excess of the acetylating reagent is often carried out in a stream of nitrogen⁴. The catalyst most frequently used is pyridine⁶. The excess of the acetylating reagent and the by-products formed (hydrochloric acid and acetic acid) are removed by subsequent vacuum distillation.

This lengthy process, in which vacuum distillation makes quantitative evaluation difficult, has been eliminated by the method described here, in which a ketene is used for acetylation in an addition reaction without the formation of by-products.

EXPERIMENTAL

The acetates of the even carbon-number fatty alcohols (C₁₀–C₁₈) were prepared by ketenic acetylation of the corresponding alcohols (Condea, Hamburg, G.F.R.). Acetylation was carried out in a ketene reactor (Fig. 1), originally developed for the rapid, quantitative micro-scale acetylation of fatty alcohol ethylene oxide adducts⁷. The ketene was generated from acetone by pyrolysis on a metal wire heated to a dark red colour¹ (1). The unreacted acetone was removed in condensers (2) and a dry-ice–acetone trap (3). Nitrogen was led through the system in order to stir it and to ensure a constant gas flow-rate. The flow-rate was controlled by differential manometers (4). In the acetylation reactor (5) 2 cm³ of alcohol could be acetylated. The reaction mixture was sampled periodically with a Hamilton syringe through a septum. An amount of 1–5 mole of fatty alcohol (depending on the molecular weight) was acetylated for 1–3 min under the given conditions.

Gas chromatographic investigations were carried out with a Model Chrom 31 gas chromatograph equipped with an OH 840 integrator (Chinoin, Nagytétény, Hungary). The acetates of the fatty alcohols were separated on a column of length 1.4

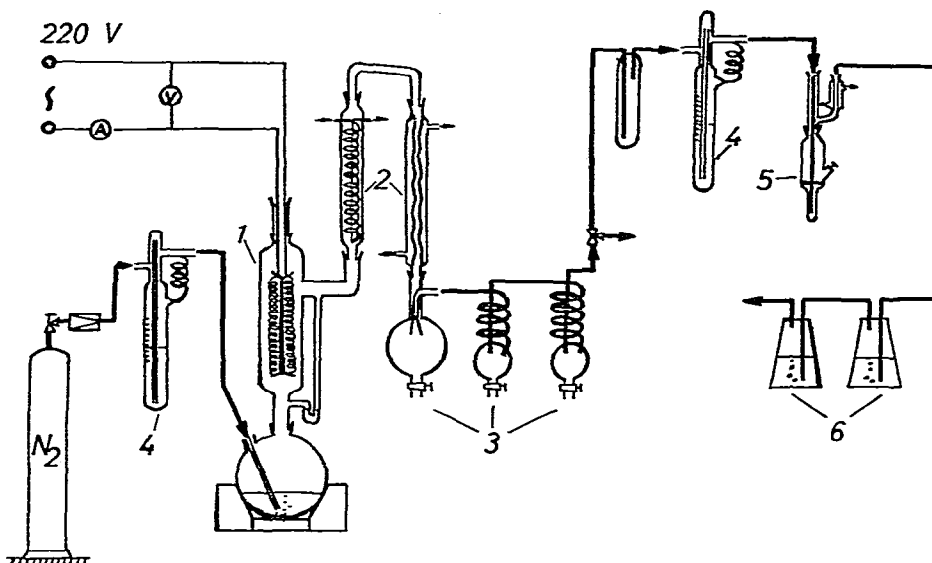


Fig. 1. Apparatus for acetylation. 1 = Ketene generator; 2 = condensers; 3 = acetone separator; 4 = differential manometers; 5 = reactor for acetylation; 6 = gas washing bottles.

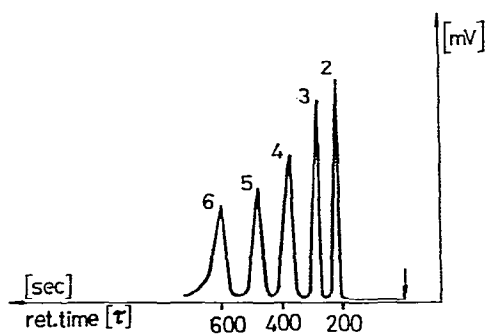
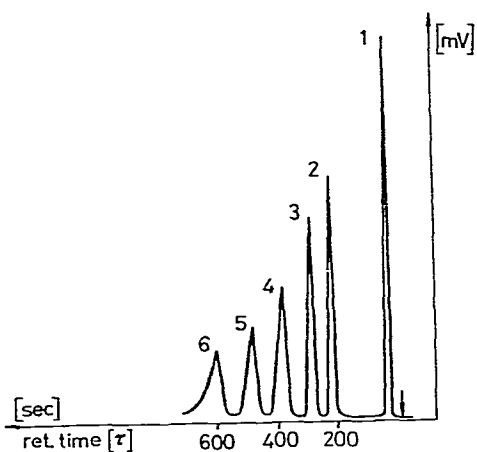


Fig. 2. Characteristic gas chromatograms of fatty alcohols acetylated with acetic anhydride (above) and ketene (below). 10% Apiezon L on Chromosorb WAW DMCS (60-80 mesh). Peaks: 1 = acetic acid and/or acetic anhydride; 2 = decyl acetate; 3 = dodecyl acetate; 4 = tetradecyl acetate; 5 = hexadecyl acetate; 6 = octadecyl acetate.

m and I.D. 6 mm, filled with 10% SE-301 (Carlo Erba, Milan, Italy) or with 10% Apiezon L (Carlo Erba) on Chromosorb W AW DMCS (60–80 mesh) (Merck, Darmstadt, G.F.R.) using a flame-ionization detector.

The operating conditions were as follows: column temperature, increased from 150 to 270° at a rate of 8°/min; temperature of evaporator, 290°; nitrogen flow-rate 50 cm³/min; air flow-rate, 950 cm³/min; and amount of sample, 2 μl.

RESULTS AND DISCUSSION

A mixture of even-carbon-number C₁₀–C₁₈ fatty alcohols of known composition was acetylated with acetic anhydride according to Gildenberg and Trowbridge⁶ and with ketene according to the process we reported earlier⁷. The product acetylated with acetic anhydride was applied to the chromatographic column after preliminary vacuum distillation, whereas the product acetylated with ketene was applied directly. Fig. 2 shows the gas chromatograms of the products acetylated in the two different ways.

In the chromatogram of the product acetylated with acetic anhydride a peak of acetic acid and/or acetic anhydride appears, making evaluation uncertain.

It can be seen from the relationship between the logarithm of retention time ($\log \tau$) and the number of carbon atoms (Fig. 3) that both SE-301 and Apiezon L give good separations of fatty alcohol acetate homologues.

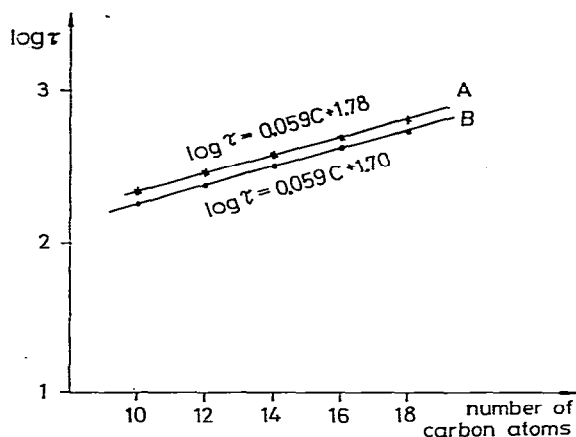


Fig. 3. Dependence of the logarithm of retention time (τ) on the number of carbon atoms in the alkyl group using temperature programming of the column.

The quantitative evaluation of the chromatograms was carried out on the basis of graphs of amount of substance (micrograms) *versus* signal magnitude (pulses counted by the integrator) constructed separately for the single components. The results (Table I) indicate that the less volatile components are enriched in the product acetylated with acetic anhydride.

It can be concluded that for the acetylation required in gas chromatographic separations, ketene, reacting in a rapid, quantitative reaction without the formation

TABLE I

ACETYLATION OF FATTY ALCOHOLS WITH KETENE AND WITH ACETIC ANHYDRIDE

No. of C atoms in the alcohol	Acetate measured by gas chromatography as a percentage of the weight of sample	
	Ketene method	Acetic anhydride method
10	98	93
12	96	92
14	99	95
16	98	99
18	99	99

of by-products, is the most suitable reagent. A further advantage of the proposed acetylation with ketene is that the amount of sample required is an order of magnitude smaller than in procedures described previously.

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