

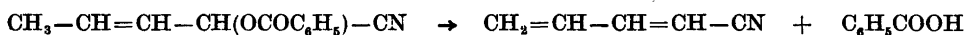
Thermal Rearrangement of Esters of Cyanohydrins of α,β -Unsaturated Aldehydes

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Cyanohydrin benzoates of acrolein, crotonaldehyde, and cinnamaldehyde were shown to undergo thermal rearrangement to γ -hydroxy-crotononitrile benzoates. Evidence of a cyclic mechanism for this reaction is presented. The formation of 1-cyano-1,3-butadiene from crotonaldehyde cyanohydrin benzoate is shown to be a two stage process in which rearrangement precedes elimination.

Pyrolysis of the benzoate of crotonaldehyde cyanohydrin has been reported by Snyder *et al.*¹ to yield a mixture of *cis* and *trans* 1-cyano-1,3-butadiene:



The generally accepted mechanism for the pyrolytic ester elimination involves a synchronous electron shift within a 6-membered ring, the ester carbonyl oxygen attacking the β hydrogen atom as shown in Fig. 1 a. Since according to this mechanism the hydrogen to be eliminated should be one at a β -position to the benzoyloxy group, it must be assumed that a rearrangement takes place also. In the present investigation evidence is offered, that this rearrangement occurs very easily at high temperature. The pyrolytic elimination by the cyclic mechanism is then possible, since the methyl hydrogen is now β to the leaving group.

A priori the possibility of an allenic intermediate formed by β -elimination could not be excluded. Since in this case the reaction should not involve the methyl group, it was decided to subject the benzoate of acrolein cyanohydrin to the pyrolysis. When this reaction was carried out at 530° very little benzoic acid was formed, but by distillation of the reaction product a fraction was obtained, which was isomeric with the starting material. Gas chromatography indicated the oil to consist of two components with slightly different retention times. By repeated fractional distillation combined with crystallization of the fractions, two crystalline products with m.p. 45°–46° and 32°–34° were obtained. The higher melting compound showed infra-red absorption bands at 952 cm^{-1} (*trans* $\text{CH}=\text{CH}$), at 1646 cm^{-1} ($\text{C}=\text{C}$) and at 2225 cm^{-1} ($\text{C}\equiv\text{N}$).

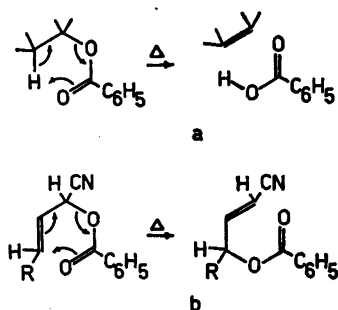


Fig. 1.

This product was *trans*-benzoyloxycrotononitrile, reported m.p.² 44.5°. The other isomer showed no absorption between 900 cm⁻¹ and 1000 cm⁻¹ indicating it to be the *cis* isomer. The yield of crude isomer mixture was 68 % and the ratio *cis/trans* was approximately 1:2. High temperature was essential for the reaction. At temperatures below 400° no γ -benzoyloxycrotononitrile was obtainable and at temperatures of *ca.* 250° a rearrangement of different type took place as will be described in a following paper. Because of the dependency of high temperature and because the starting material has a biallylic structure the rearrangement here described may be related to the Cope rearrangement.³ It may then be presumed to proceed by the cyclic mechanism pictured in Fig. 1 b, R=H, involving the attack of the carbonyl oxygen on carbon as compared to the attack on hydrogen in the elimination reaction, Fig. 1a.

Pyrolysis of esters of methyl vinyl ketone cyanohydrin was performed by Marvel and Brace.⁵ In this case the elimination mechanism Fig. 1 a is competing with the cyclic rearrangement mechanism Fig. 1 b. The rate of rearrangement : elimination was found to be 2:1 for the acetate and *ca.* 6:1 for the benzoate.

The thermal rearrangement was successfully applied also to crotonaldehyde cyanohydrin benzoate, Fig. 1b, R = CH₃. At 200°–300° rearrangement rather than elimination took place, a mixture of *cis* and *trans* γ -methyl- γ -benzoyloxycrotononitrile being obtained in an 80 % yield, the *cis/trans* ratio being *ca.* 1:3. The isomers were separable by analytical gas chromatography, but the separation was only partially successful on a preparative scale. By repeated fractional distillation purified fractions of the isomers were obtained, one consisting of 92 % *trans* isomer and one containing 70 % *cis* isomer.

Since the rearrangement of crotonaldehyde cyanohydrin benzoate was nearly complete within 2 min at 295°, and since the isomer mixture obtained by the reaction could be pyrolysed at 550° to yield *cis* and *trans* 1-cyano-1,3-butadiene, it is justified to assume that rearrangement takes place prior to the ester elimination, when crotonaldehyde cyanohydrin benzoate is pyrolysed.

Also cinnamaldehyde cyanohydrin benzoate undergoes thermal rearrangement, Fig. 1b, R = C₆H₅. When it was heated to 240° for 40 min an 80 % yield of *trans* γ -phenyl- γ -benzoyloxycrotononitrile, m.p. 63°–64°, was isolated.

By gas chromatography was shown that the mother liquor besides *trans* compound contained small amounts of a compound which may be the *cis* isomer. Assignment of structure of the *trans* product was based on the infra-red spectrum which showed a *trans* CH=CH absorption at 966 cm^{-1} .

A characteristic feature of the infra-red spectra of the cyanohydrin esters is the totally quenched C≡N absorption. A strong band at $2220\text{--}2240\text{ cm}^{-1}$ develops as the rearrangement proceeds.

In the three examples investigated the rearrangement goes almost to completion. This indicates a high degree of stabilization gained by conjugation between the carbon-carbon double bond and the carbon-nitrogen triple bond, exceeding even the stabilizing effect of the conjugation between the double bond and the benzene nucleus in the cinnamaldehyde derivative, as well as the hyperconjugation of the methyl group in the crotonaldehyde cyanohydrin ester.

EXPERIMENTAL

Cyanohydrin benzoates. A solution of 1 mole of the unsaturated aldehyde and 1 mole of benzoyl chloride in 200 ml of benzene was kept at -10° , while a solution of 1.3 mole of sodium cyanide in 340 ml of water was added with stirring over a period of 2 h. The mixture was stirred for 2 h at -10° and for one hour at 20° . The benzene layer was washed twice with 200 ml of 5 % sodium carbonate solution, dried with anhydrous magnesium sulphate and distilled *in vacuo*. In this way cyanohydrin benzoates of the following aldehydes were obtained: acrolein, yield 45 %, b.p. $115^\circ/0.8\text{ mm}$, $n_D^{25} = 1.5192$. (Found: C 71.00; H 4.95; N 7.56. Calc. for $C_{11}H_9NO_2$: C 70.55; H 4.86; N 7.48). Crotonaldehyde, yield 94 %, b.p. $125^\circ/1\text{ mm}$ as reported.¹ Mp. 32° . Cinnamaldehyde, yield 80 %, b.p. $180^\circ/0.5\text{ mm}$, m.p. $69^\circ\text{--}71^\circ$, reported⁴ $72^\circ\text{--}73^\circ$.

cis and trans-γ-Benzoyloxycrotononitrile. In an atmosphere of nitrogen a continuous stream of acrolein cyanohydrin benzoate (35 g) was over a period of 2 h led through an 8 mm × 400 mm pyrex tube, heated to 520° . A dark tar (31 g) was obtained which on distillation yielded 18 g of isomer mixture (51 %), b.p. $135^\circ\text{--}42^\circ/0.7\text{ mm}$. By crystallization of the oil from 40 ml of methanol 5.5 g of the *trans* isomer was obtained, m.p. $45^\circ\text{--}46^\circ$, reported² 44.5° . Fractional distillation gave 7.3 g, b.p. $135^\circ\text{--}137^\circ/0.7\text{ mm}$, which on crystallization from 15 ml of methanol yielded 1 g of the *cis* isomer, m.p. $32^\circ\text{--}34^\circ$. (Found: C 70.70; H 4.87; N 7.48. Calc. for $C_{11}H_9NO_2$: C 70.55; H 4.86; N 7.30).

cis and trans γ-Methyl-γ-benzoyloxycrotononitrile. Crotonaldehyde cyanohydrin benzoate (120 g) was heated to 295° for 5 min. On fractionational distillation *in vacuo* 95.5 g of isomer mixture (78 %) was obtained. (Found: C 71.50; H 5.22. Calc. for $C_{15}H_{11}NO_2$: C 71.61; H 4.47). Repeated fractional distillation through a packed column produced the following samples rich in either isomer (as analysed by gas chromatography): 92:8 *trans/cis* mixture, b.p. $135^\circ/0.65\text{ mm}$, $n_D^{25} = 1.5268$ and 70:30 *cis/trans*, b.p. $132^\circ/0.65\text{ mm}$, $n_D^{25} = 1.5248$.

trans-γ-Phenyl-γ-benzoyloxycrotononitrile. Cinnamaldehyde cyanohydrin benzoate (40 g) was heated to 240° for 40 min while kept under 12 mm vacuum. Fractional distillation yielded 38 g oil, b.p. $240^\circ/12\text{ mm}$, which on crystallisation from 60 ml of methanol gave 32 g of the product, m.p. (after recrystallisation) $63^\circ\text{--}64^\circ$. (Found: C 77.30; H 5.08; N 5.36. Calc. for $C_{17}H_{13}NO_2$: C 77.54; H 4.98; N 5.32).

Microanalyses were performed by Mr. Preben Hansen, Microanalytical Division, The Chemical Laboratory, The University of Copenhagen. Infrared Spectra were determined by Mrs. I. G. Krogh Andersen of this Laboratory.

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