Tetrahedron Letters,Vol.23,No.36,pp 3723-3724,1982 0040-4039/363723-02$03.00/0
Printed in Great Britain

β-LACTONE AS INTERMEDIATE IN THE PERKIN REACTION CATALYZED BY TERTIARY AMINES

Stefan Kinastowski and Antoni Nowacki
Institute of Physics and Chemistry, Academy of Agriculture,
Wojska Polskiego 75, 60-625 Poznań, Poland

Abstract: The Perkin reaction catalyzed by tertiary amines is found to run not according to the aldol-type condensation mechanism but according to the mechanism in which the first stage is the formation and cycloaddition of ketene, yielding a β-lactone, which cleaves to the unsaturated acid.

Recently we reported the intermediacy of ketene in the Perkin reaction between benzaldehyde and acetic anhydride using triethylamine as catalyst[1]. We proposed that ketene, generated by reaction of acetic anhydride and amine, reacts with benzaldehyde to afford the Perkin product, cinnamic acid. The reaction between ketene and bezaldehyde was studied earlier by Hurd and Williams who suggested that it proceeded via a β-lactone intermediate[2]. However, the latter was not proved.

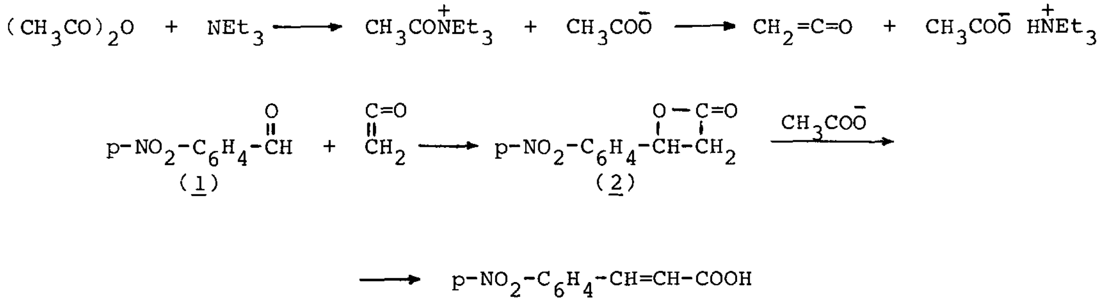
In present paper we provide spectroscopic confirmation of the formation of a β-lactone in the reaction of p-nitrobenzaldehyde with ketene, and demonstrate further that the same species is formed in the Perkin reaction between this aldehyde and acetic anhydride in the presence of triethylamine.

IR Spectroscopy studies of the reaction between prepared ketene and 1 showed a progressive increase and then decay of absorption band at 1830 cm^{-1}. This fact implied that the band was due to an unstable product. The NMR spectrum of the reaction mixture[3], taken at the time when the intensity of the band at 1830 cm^{-1} was at the maximum, confirmed the presence of 2. Thus the hypothesis previously presented by Hurd and Williams was proved, and supported further by the formation of p-nitrocinnamic acid as the final product.

Next, the reaction between 1, acetic anhydride and triethylamine mixed in the proportions 1:15·30 was performed. The reaction proceeded in the absence of solvent at room temperature over several days. Again, in the course of this reaction, a progressive increase and then decay of absorption band at 1830 cm^{-1} was observed demonstrating the intermediacy of 2 under the conditions of the Perkin reaction[4]. (The concentration of 2 under these conditions was unfortunately too low for it to be detected by NMR spectroscopy).

The subsequent experiment showed that prepared 2 mixed with acetic anhydride and triethylamine decomposes at room temperature to p-nitrocinnamic acid after several days[5]. Moreover it was found that decomposition of **2** in dioxane, leading mainly to p-nitrocinnamic acid, is catalyzed exclusively by the acetate anion. On the other hand, amine was found to catalyze the decomposition of **2** to a series of minor products rather than the acid, which is consistent with the observation that the use of excess amine in the Perkin synthesis diminishes the yield of the reaction.

The observations presented above encourage us to propose the following mechanism:



$$(CH_3CO)_2O + NEt_3 \longrightarrow CH_3CO\overset{+}{N}Et_3 + CH_3CO\bar{O} \longrightarrow CH_2{=}C{=}O + CH_3CO\bar{O}\ H\overset{+}{N}Et_3$$

$$\underset{(\mathbf{1})}{p\text{-}NO_2\text{-}C_6H_4\text{-}\overset{O}{\overset{\|}{C}}H} + \overset{C=O}{\overset{\|}{CH_2}} \longrightarrow \underset{(\mathbf{2})}{p\text{-}NO_2\text{-}C_6H_4\text{-}\overset{O\,-\,C=O}{\overset{|\quad\ |}{CH\text{-}CH_2}}} \xrightarrow{CH_3CO\bar{O}}$$

$$\longrightarrow p\text{-}NO_2\text{-}C_6H_4\text{-}CH{=}CH\text{-}COOH$$

The confirmation of the fact that the reaction goes through **2** provides additional support for the ketene mechanism.

Acknowledgment: This research was supported by the Polish Academy of Sciences, MR. I. 12. 1. 1.

References and Notes

1) S. Kinastowski and H. Kasprzyk, Bull. Acad. Polon. Sci. Ser. Chim., 26, 907, (1978).

2) Ch. D. Hurd and J.W. Williams, J. Am. Chem. Soc., 58, 962, (1936).

3) IR ($CHCl_3$). ν_{CO}=1830 cm^{-1}; ^1H-NMR ($CDCl_3$). δ3.4(dd, 1H, J_{gem}=16 Hz, J_{cis}=4.5 Hz) 4.05(dd, 1H, J_{gem}=16 Hz, J_{trans}=5.5 Hz), 5.62(dd, 1H, J_{cis}=4.5 Hz, J_{trans}=5.5 Hz), 7.9(m, 4H, aromatic protons). The data presented are entirely consistent with the literature data available: H.S. Gutowsky, H. Karplus, D.M. Grant, J. Chem. Phys., 31, 1278, (1958).

4) The samples of reaction mixture were analyzed after removal of excessive amine and anhydride and after washing out p-nitrocinnamic acid produced. $CHCl_3$ was used as solwent. After one day at room temperature the 1830 cm^{-1} band vanished completely and p-nitrocinnamic acid was formed.

5) β-(p-nitrophenyl)-β-propiolactone was prepared as described by A. Basler, Ber., 16, 3001, (1883).

(Received in UK 5 July 1982)