

Phosphorus Pentachloride-Induced Substitution and Fragmentation of A  $\gamma$ -Pyrone

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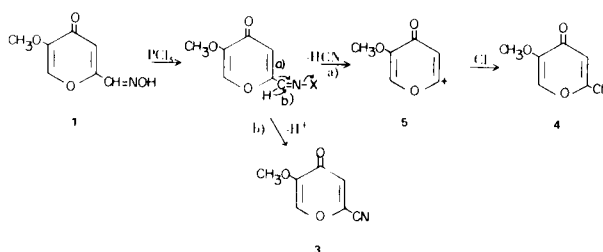
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Sir:

In connection with our studies on the chemistry of  $\gamma$ -pyrones, we wished to accomplish the Beckmann rearrangement of 5-methoxy-4-oxo-4H-pyran-2-carboxaldehyde oxime (**1**) to the corresponding primary amide (**2**) or its dehydration product, 5-methoxy-4-oxo-4H-pyran-2-carbonitrile (**3**). Phosphorus pentachloride is known to be an efficient and mild catalyst for this rearrangement (**1**) and we thus investigated its effect on the oxime (**1**).

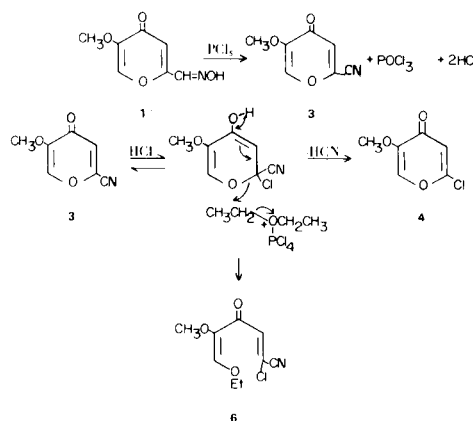
Treatment of (**1**) as a suspension in chloroform at 0° with excess phosphorus pentachloride yielded two products: the first was readily identified as the desired nitrile (**3**) from its ir [ $\nu$  max (potassium bromide) 2250  $\text{cm}^{-1}$ , weak], nmr [deuteriochloroform, 3H, s,  $\delta$  3.79 (OCH<sub>3</sub>), 1H, s, 6.88 (H<sub>3</sub>), and 1H, s, 7.61 (H<sub>6</sub>)], and mass spectra (parent peak,  $m/e$  151.027; calculated for  $^{12}\text{C}_7^{1}\text{H}_5^{14}\text{N}_1^{16}\text{O}_3$  151.027). The nmr spectrum of the second product showed two singlets characteristic of a 2,5-disubstituted  $\gamma$ -pyrone at  $\delta$  7.14 (H<sub>6</sub>) and 6.48 (H<sub>3</sub>) as well as the methoxyl singlet ( $\delta$  3.73), while the presence of chlorine was obvious from the mass spectrum (parent ion cluster at  $m/e$  162, 13.7% and  $m/e$  159.986, 37.2%, due to  $^{12}\text{C}_7^{1}\text{H}_5^{35}\text{Cl}^{16}\text{O}_3$ , calculated 159.993). The second product is thus 2-chloro-5-methoxy-4H-pyran-4-one (**4**). Such a product could be explained by invoking a second-order Beckmann rearrangement (**2**), but we feel that this is unlikely as it would necessitate the intermediacy of the aryl carbonium ion (**5**): the more normal route for this reaction would be proton loss to the nitrile (**3**).



In an effort to clarify the course of the reaction, it was repeated under milder conditions (1): in ether at 0° however, no nitrile or amide could be isolated. Two products were obtained: the chloride (**4**), and a compound

$\text{C}_9\text{H}_{10}\text{ClNO}_3$  ( $m/e$  217, 8.2%, and 215.031, 24.4%,  $^{12}\text{C}_9^1\text{H}_{10}^3\text{Cl}^{14}\text{N}^{16}\text{O}_3$ , calculated 215.035). The usual  $\gamma$ -pyrone absorptions were absent in the ir of this product, and were replaced by sharp absorptions at 1655 and 1600  $\text{cm}^{-1}$  (C=O and C=C of  $\alpha,\beta,\alpha',\beta'$ -unsaturated ketone); also evident were absorptions at 2225 (C≡N) and 655  $\text{cm}^{-1}$  (C-Cl). The presence of signals in the nmr due to an ethoxy group ( $\delta$  3.86, 2H, q; and 1.27, 3H, t) in addition to the expected vinyl ( $\delta$  5.69, 6.19) and methoxyl singlets ( $\delta$  3.86) leads us to suggest that this product is 2-chloro-6-ethoxy-5-methoxy-4-oxo-2,5-hexadienoic acid nitrile (**6**). A possible mechanism for the formation of this compound is given below.

It has been shown that the reaction of nitrile (**3**) in ethanol with dry hydrogen chloride leads only to solvolysis of the nitrile group. No substitution or fragmentation occurs. Further experiments are in hand to clarify the course of the reaction.



## REFERENCES

- (1) C. A. Buehler and D. E. Pearson, Eds., "Survey of Organic Syntheses", John Wiley & Sons, Ltd., New York, N. Y., 1970, pp. 922-923.
- (2) See for example, A. F. Ferris, *J. Org. Chem.*, **25**, 12 (1960).

On page 819 and on page iv, Volume 11, October 1974, the spelling of the senior author's name should be P. M. Carabateas.