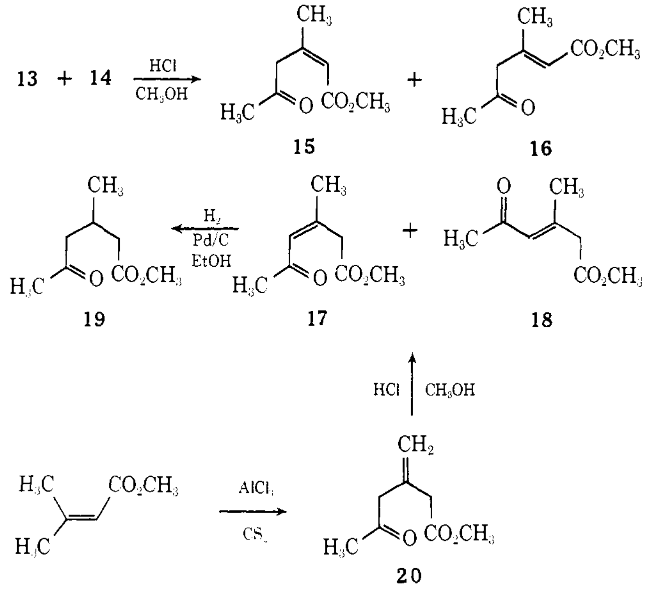
(2 H, s), 3.28 (2 H, s), 3.64 (3 H, s), 4.98 (1 H, m), and 5.04 (1 H, m). Treatment of this product with 1 drop of dilute HCl in methanol (40 ml) overnight at room temperature gave the same mixture (nmr comparison) of esters (**15–18**) obtained by irradiation of 4,6-dimethyl-2-pyrone in methanol (see Scheme II).

Scheme II



It is clear that the photochemical formation of ester products from 4,6-dimethyl-2-pyrone does not involve a ketene intermediate as has been generally assumed. This conclusion raises serious questions whether ketene intermediates are involved in ester-forming reactions of other pyrones and coumarins.

Acknowledgment. This research was supported by Grant No. AM-14624 from the National Institute of Arthritis and Metabolic Disease, U. S. Public Health Service.

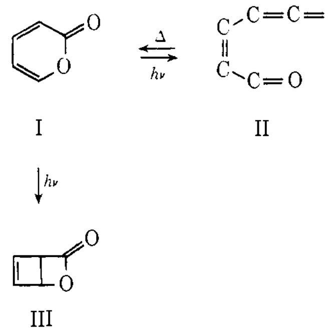
C. L. McIntosh, O. L. Chapman*
Department of Chemistry, Iowa State University
Ames, Iowa 50010

Received July 7, 1972

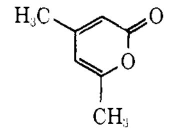
Photochemistry of α-Pyrone in Solid Argon

Sir:

The photochemistry of α-pyrones has been well studied. We present here direct evidence for the mechanism below, where the production of III is a minor photolytic pathway. The back reaction of the ketene to α-pyrone is fast except at cryogenic temperatures.



de Mayo[1,2] first suggested a ketene as a primary product in the photolysis of α-pyrones to explain the production of CH$_3$OCOCH=C(CH$_3$)CH$_2$COCH$_3$ on photolysis of



in methanol. Corey and Streith[3] first produced the bicyclo compound III (bicyclo[2.2.0]pyran-2-one) by photolysis of I in ether at −20°. They suggested it was a direct photoproduct.

Pirkle and McKendry[4] provided further evidence for the existence of the ketene as a direct photoproduct. They showed that the methanolysis product of photo-α-pyrone III was not the methyl ester, implying that III was not a major photoproduct. They photolyzed α-pyrone in a THF–CH$_2$Cl$_2$ glass at 77°K and observed a band near 2140 cm^{-1}. They assigned this band to the ketene II. The ketene band at 2140 cm^{-1} reached a maximum intensity of about 5% of the intensity of the most intense (1765 cm^{-1}) band of α-pyrone after 2 hr of photolysis. They suggested that a steady state was achieved because a thermal back reaction of the ketene II to α-pyrone was occurring.

We have studied the photochemistry of α-pyrone isolated solid argon at 20°K. The experimental apparatus was similar to that previously described.[5] A sample of α-pyrone was purified by preparative gas chromatography. The sample was held at 0–5°, and the vapor over the sample was deposited onto a cold CsI window at the same time as a large excess of argon. The sample was photolyzed with the 3130-Å group of lines from a medium-pressure Hg arc isolated with a monochromator. The spectrum of pure α-pyrone isolated in argon is shown in Figure 1a. The result of 12 hr of irradiation with 3130-Å light is shown in Figure 1b. The sharp bands at 2140, 1690, 1610, and 980 cm^{-1} had the same relative intensity in several different experiments. They are thus probably due to the same species and are assigned to the ketene II. The small band at 1850 cm^{-1} is assigned to photo-α-pyrone in agreement with Corey and Streith. The broader

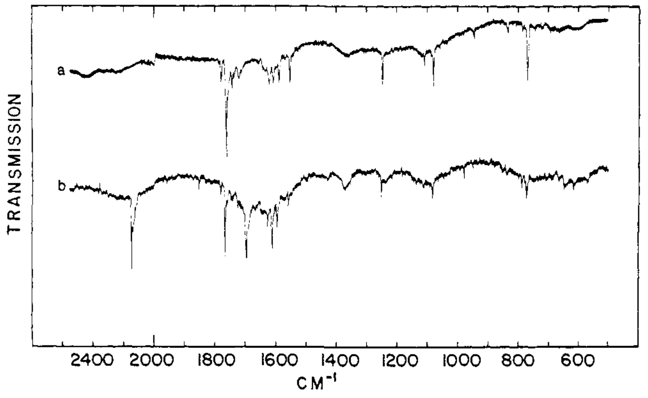


Figure 1. Photolysis of α-pyrone in argon: (a) α-pyrone trapped in argon at 18°K; (b) after 12 hr of photolysis with 3130-Å light.

---

(1) P. de Mayo, *Advan. Org. Chem.*, **2**, 394 (1960).

(2) J. P. Guthrie, C. L. McIntosh, and P. de Mayo, *Can. J. Chem.*, **48**, 237 (1970).

(3) E. J. Corey and J. Streith, *J. Amer. Chem. Soc.*, **86**, 950 (1964).

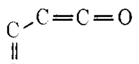
(4) W. H. Pirkle and L. H. McKendry, *ibid.*, **91**, 1179 (1969).

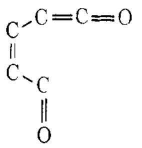
(5) M. L. Lesiecki and J. S. Shirk, *J. Chem. Phys.*, **56**, 4171 (1972).

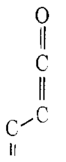
bands with band centers near 1245, 1370, and 1650 cm^{-1} are not as yet identified; they are apparently polymeric species.

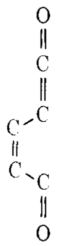
The intensities of the absorptions assigned to the ketene II showed no leveling off after 15 hr of photolysis, indicating that at 20°K the back reaction to α-pyrone is not occurring. The intensity of the band assigned to photo-α-pyrone III was never more than 15% of the intensity of the C=O stretching mode (1690 cm^{-1}) of the ketene II.

High-resolution spectra of the region near 2140 cm^{-1} showed four distinct absorptions. These we assign to the four accessible isomers of the ketene.


A


B


C


D

Presumably ketene A is formed first and rearranges thermally or photochemically to the more stable isomers. Photolysis with 3650-Å light effected interconversion of the isomers without photolysis. The different isomers could also be detected on the carbonyl absorption at 1690 cm^{-1}.

We have shown by direct identification that the ketene II is the principle photoproduct of the photolysis of α-pyrone with 3130-Å light. The lactone III is a minor product. At cryogenic temperatures the thermal back reaction of the ketene to α-pyrone is prevented.

Apparently at more usual temperatures, the thermal back reaction occurs and the ketene is present at a low steady-state concentration. Reaction will occur *via* the ketene if the appropriate reactants are present (*e.g.*, methanol). If the ketene cannot react, the photoproduct will be the less reactive lactone III.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Richard G. S Pong, James S. Shirk*
Department of Chemistry, Illinois Institute of Technology
Chicago, Illinois 60616

Received July 31, 1972

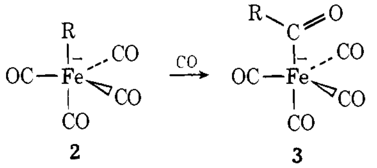
Selective Syntheses of Aliphatic Carboxylic Acids, Esters, and Amides Using Sodium Tetracarbonylferrate(−II)

Sir:

Recently we have shown $Na_2Fe(CO)_4$ (**1**) to be a practical reagent for the preparation of aliphatic aldehydes[1] and unsymmetrical ketones.[2] The significance of these new methods derives from their stereospecificity and their toleration of functional groups. Applications of **1** for the synthesis of carboxylic acids, esters,[3] and amides are described herein.

Aliphatic halides and tosylates react with **1** to give anionic alkyltetracarbonyliron(0) complexes **2**,[4] a process which can be viewed either as an SN2 displacement at carbon[5] or as an oxidative addition to the d^{10} iron (−II).[6] In the presence of CO, cation-assisted alkyl migration[7] affords anionic acyl complexes **3**.[4]

$Na_2Fe(CO)_4$ + RX ⟶
1



2 **3** (1)

Halogenation of the acyl complexes **3** yields carboxylic acids, esters, and amides (eq 3–5)—apparently through the intermediacy of an acid halide. Oxidation of the acyl complexes **3** with O_2 or NaClO affords carboxylic acids directly (eq 2).

$$\textbf{2}\text{ or }\textbf{3}\xrightarrow{O_2\text{ or NaOCl}}\xrightarrow{H_2O\text{–}H^+}\text{RCOOH}\qquad(2)$$

$$\textbf{2}\text{ or }\textbf{3}\xrightarrow{X_2\text{–}H_2O}\text{RCOOH}\qquad(3)$$

$$\textbf{2}\text{ or }\textbf{3}\xrightarrow{X_2\text{–}R'OH}\text{RCO}_2\text{R}'\qquad(4)$$

$$\textbf{2}\text{ or }\textbf{3}\xrightarrow{X_2\text{–}R'R''NH}\text{RCO}_2\text{NR}'\text{R}''\qquad(5)$$

Surprisingly, halogenation or oxidation (O_2 or NaClO) of the iron alkyls **2** also gives carboxylic acids and acid derivatives (eq 2–5). Either these reagents induce migratory insertion or they trap the unsaturated tetracoordinate acyl intermediate proposed in the migratory insertion mechanism.[7,8]

The scope of these procedures is illustrated in Tables I and II.[9] Using primary aliphatic halides and tosylates all of the routes to esters, amides, and acids (eq 2–5) give nearly quantitative yields by gc; however, isolated yields are about 80%. Secondary substrates are less satisfactory due to competing olefin-forming elimination reactions. These eliminations are minimized in THF, a solvent most compatible with the acyl

---

[1] M. P. Cooke, *J. Amer. Chem. Soc.*, **92**, 6080 (1970).

[2] J. P. Collman, S. R. Winter, and D. R. Clark, *ibid.*, **94**, 1788 (1972).

[3] Esters have been prepared by related methods: Y. Takegami, Y. Watanabe, H. Masada, and I. Kanaya, *Bull. Chem. Soc. Jap.*, **40**, 1456 (1967); H. Masada, M. Mizuno, S. Suza, Y. Watanabe, and Y. Takegami, *ibid.*, **43**, 3824 (1970).

[4] Examples of both the alkyl, **2**, and the acyl, **3**, complexes have been isolated and thoroughly characterized: W. O. Siegl and J. P. Collman, *J. Amer. Chem. Soc.*, **94**, 2516 (1972).

[5] Kinetic studies have shown the rate law for the alkylation in THF to be $-d[RX]/dt = k_2[RX][Na_2Fe(CO)_4]$: J. N. Cawse and J. P. Collman, unpublished results.

[6] J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968).

[7] J. P. Collman, J. N. Cawse, and J. I. Brauman, *J. Amer. Chem. Soc.*, **94**, 5905 (1972).

[8] This intermediate, $Na(RCO)Fe(CO)_3^-$, was suggested as the active species in our ketone synthesis by J. Halpern, 14th International Congress on Coordination Chemistry, Toronto, Can., June 22, 1972.

[9] Procedures for preparing the alkyl, **2**, and acyl, **3**, complexes are given in ref 2. In method 2, O_2 was bubbled into a solution of 10 mmol of the alkyl or acyl for 1 hr, 70 ml of H_2O was added, and the reaction was stirred for 5 hr. The reaction was then filtered and the aqueous filtrate was extracted (ether). The extractions were dried, the solvent was removed, and the product distilled or recrystallized. In methods 3, 4, and 5 the alkyl or acyl solution was cooled (0° in NMP, −15° in THF or THF-HMPA) and for each millimole of complex, 0.5–1 ml of water, alcohol, or amine was added followed by 10 mmol of I_2 in 5 ml of THF. After stirring 0.5 hr at −15° and 0.5–12 hr at 25°, the mixture was diluted with ether, washed with $NaHSO_3$ solution and water, and dried, the solvent removed, and the residue distilled or purified by chromatography.