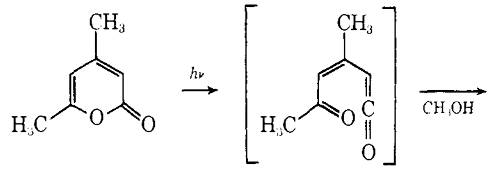
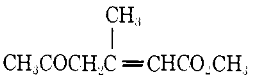
Photochemistry of 4,6-Dimethyl-2-pyrone in Methanol[1]

Sir:

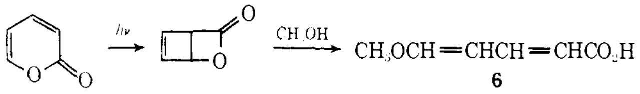
The photochemistry of α-pyrones has received considerable attention since de Mayo first reported irradiation of 4,6-dimethyl-2-pyrone (**1**) in methanol gave methyl 3-acetonylcrotonate (**2**) and suggested that a ketene intermediate (**3**) might be involved.[2-4] Subsequently, Corey reported that irradiation of α-pyrone (**4**) at −20° through Corex gave the bicyclic lactone **5** and suggested that a lactone analogous to **5** might be the precursor of the ester **2**.[5] Pirkle found, however, that methanolysis of **5** gave 5-methoxy-2,4-pentadienoic acid (**6**).[6] Irradiation of α-pyrone at 77°K gives a trace amount of a ketene (2130 cm^{-1}) and warming with methanol gives a small amount (0.3% yield) of methyl *trans*-4-formyl-3-butenoate.[6,7] de Mayo has shown that irradiation of 4-methoxy-6-methyl-2-pyrone (**7**) in benzene or water gives β-methylglutaconic acids and esters (**8** and **9**)[3] presumably formed *via* a polymer of the lactone **10** (Scheme I). Money has found that irradiation of **7** in methanol gives the dimethoxy ortho ester **11** in high yield.[9] An analogous reaction was observed for 4-hydroxy-6-methyl-2-pyrone which gives β-methylglutaconic esters, and a small amount of methyl 3,5-dioxohexanoate.[9] These products were considered to be a consequence of competing reactions involving the lactone path (glutaconic acid derivatives) and the ketene path (methyl 3,5-dioxohexanoate).



1 **2**


$CH_3COCH_2\overset{CH_3}{C}{=}CHCO_2CH_3$

2

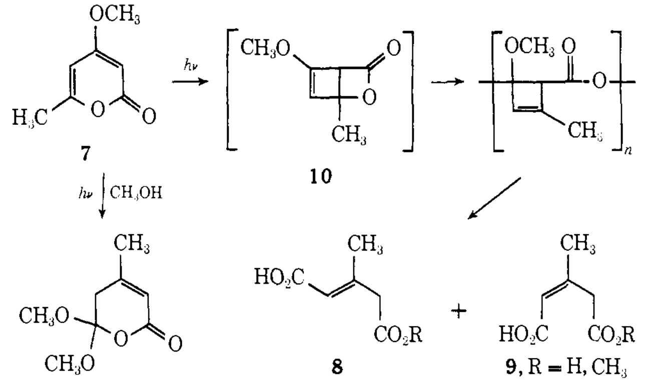


$CH_3OCH{=}CHCH{=}CHCO_2H$

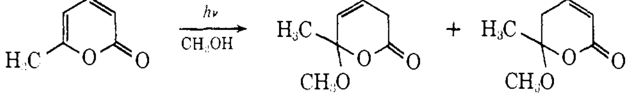
4 **5** **6**

We now wish to record experiments which refute the generally accepted hypothesis that the formation of ester products on irradiation of 4,6-dimethyl-2-pyrone in methanol involves a ketene intermediate. When 4,6-dimethyl-2-pyrone is irradiated in methanol at room temperature the initial products are not esters but two very sensitive, isomeric lactones (**13** and **14**) formed by addition of methanol to the pyrone (**12**). The combined yield is nearly quantitative in all experiments, but the ratio of **13** to **14** varies.[10] Both methanol adducts give parent ions at *m/e* 156. Adduct **13** shows $\nu_{max}^{CCl_4}$ 1750 cm^{-1} and δ^{CCl_4} 1.53 (3 H, s), 1.82 (3 H, s), 2.90 (2 H, m), 3.18 (3 H, s), and 5.45 (1 H, m), and adduct **14** shows $\nu_{max}^{CCl_4}$ 1730 and 1660 cm^{-1} and δ^{CCl_4} 1.53 (3 H, s), 1.95 (3 H, s), 2.44 (1 H, m), 2.49 (1 H, m), 3.29 (3 H, s), and 5.68 (1 H, m). Adduct **13** is very sensitive to heating and reverts rapidly to 4,6-dimethyl-2-pyrone. Both **13** and **14** are extremely sensitive to acid. It is likely that this acid sensitivity is the reason they have not been detected previously. Treatment of a mixture of **13** and **14** (2:3) with a drop of dilute HCl in methanol (40 ml) overnight at room temperature gave a mixture containing approximately equal amounts of the esters **15–18**. The product mixture was not separable. Using the Eu(fod)$_3$ shift reagent the olefinic, methoxy, methyl, and methylene protons of each isomer could be observed in the nmr spectrum of the product mixture. The mixture showed ν_{max} 1745, 1730, 1720, 1700, 1655, and 1630 cm^{-1} and gave a parent ion at *m/e* 156 at room temperature. Catalytic reduction of the mixture (**15–18**) gave **19** (82%), identical with an authentic sample.[11] The identity of the components of the mixture was confirmed by synthesis. The literature contains two reports of the aluminum chloride catalyzed addition of acetyl chloride to methyl β,β-dimethylacrylate in carbon disulfide.[12,13] One report gives the products as **15** and **16**[12] while the other gives the products as **17** and **18**.[13] In our hands, the initial product is **20**. The product showed $\nu_{max}^{CCl_4}$ 1740, 1725, and 1650 cm^{-1}; δ^{CCl_4} 2.12 (3 H, s), 3.10

Scheme I



7 **10** **11** **8** **9**, R = H, CH$_3$



12 **13** **14**

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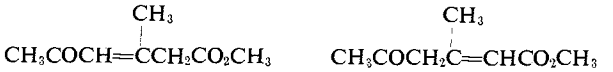
[1] Photochemical Transformations. XLVI. A preliminary account of this work was presented at the 163rd National Meeting of the American Chemical Society, Boston, Mass., April 9–14, 1972.

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

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

[4] The product is given as 3-acetonylcrotonate in the text of ref 2 and 3. The structures shown, however, are i in ref 2 and ii in ref 3. Details of the transformation have not been published.


$CH_3COCH{=}\overset{CH_3}{C}CH_2CO_2CH_3$ $\quad$ $CH_3COCH_2\overset{CH_3}{C}{=}CHCO_2CH_3$

i ii

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

[6] W. H. Pirkle and L. H. McKendry, *ibid.*, **91**, 1179 (1969).

[7] The maximum intensity of the ketene band was 5% of the pyrone carbonyl band.[6] The extinction coefficient of ketene bands in the infrared is unusually large (~1500),[8] *i.e.* about twice that of ordinary carbonyl groups.

[8] Unpublished observation of H. E. Wright.

[9] C. T. Bedford, J. M. Forrester, and T. Money, *Can. J. Chem.*, **48**, 2645 (1970).

[10] The variation seems to be associated with the temperature of the solution during the irradiation and may be due to the thermal destruction of **13**.

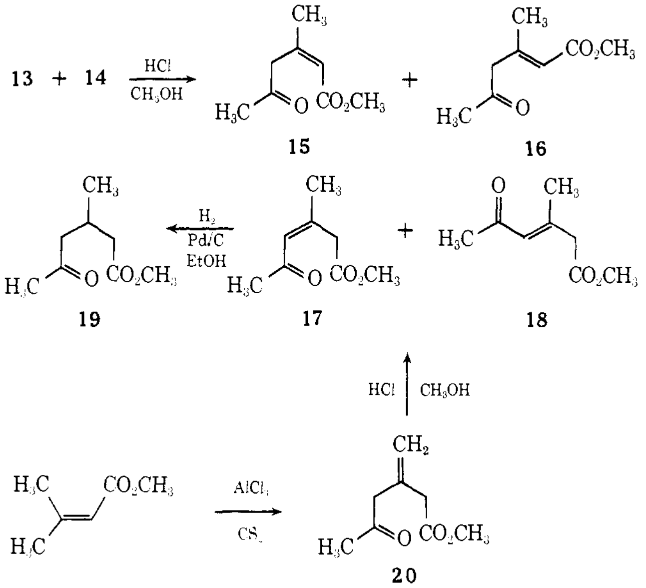
[11] G. S. Marks and N. Polgar, *J. Chem. Soc.*, 3851 (1955).

[12] I. Alkonyi, *Chem. Ber.*, **98**, 3099 (1965).

[13] Farbwerke Hoechst A.G., Belgian Patent 637,170 (1964) (*Chem. Abstr.*, **62**, 7645c (1965)).

(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.

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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.

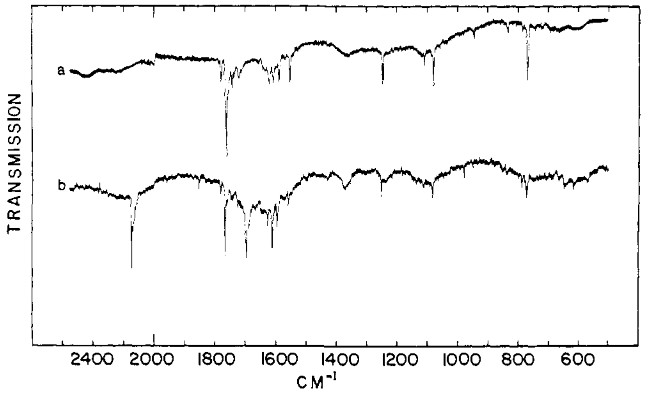
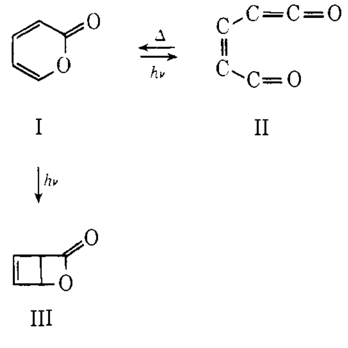
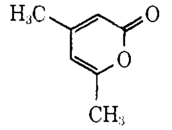


Figure 1. Photolysis of α-pyrone in argon: (a) α-pyrone trapped in argon at 18°K; (b) after 12 hr of photolysis with 3130-Å light.



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

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(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).