

## Photochemistry of 2,6-Dimethyl-4-pyrone in Trifluoroethanol

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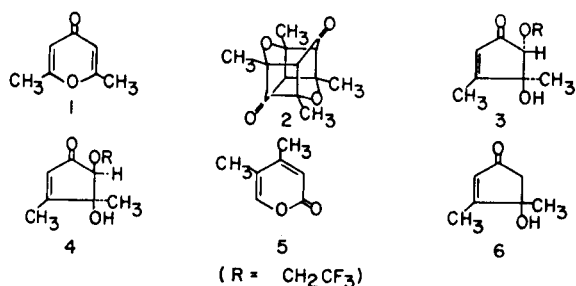
Photolysis of 2,6-dimethyl-4-pyrone (**1**) in trifluoroethanol gave, in addition to the previously observed dimer **2**, three volatile primary photoproducts **3**, **4**, and **5**. Continued irradiation led to the disappearance of the three volatile products with formation of **6**. This secondary photoproduct was shown to arise from **3** and **4** while **5** was converted to non-volatile products.

The formation of **3**, **4**, and **5** can be viewed as arising from an oxybicyclohexenyl zwitterion formed by electrocyclic ring closure of **1**. This zwitterion can thus be trapped by solvent to yield **3** and **4** or rearrange to **5** via and epoxycyclopentenone intermediate. The conversion of **3** and **4** to **6** is explained in terms of a Norrish type II process.

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Sir:

The photodimerization of 2,6-dimethyl-4-pyrone (**1**) in either the solid or solution phase is well documented (1-7). Only in dilute aqueous solution, a condition selected to retard dimerization, was a low yield obtained of a monomeric photoproduct, 4,5-dimethyl-2-furaldehyde (**8**). In view of the dramatic effects of 2,2,2-trifluoroethanol (TFE) on the photochemistry of other 4-pyrones, (9,10), we have investigated the photochemistry of **1** in this highly polar solvent.



We wish to report that irradiation of **1** in TFE gave, in addition to photodimer **2**, the three volatile primary photoproducts **3**, **4**, and **5**. Continued irradiation led to the disappearance of all three primary products with concomitant formation of a single volatile secondary product, **6**, which was also photolabile upon prolonged photolysis.

Irradiation of **1**,  $2.5 \times 10^{-2}$  M in TFE (11), was monitored by gas chromatography (12). After 95 percent conversion of **1**, the accumulated peak areas of the volatile

primary and secondary photoproducts accounted for 70 percent of the loss in the peak area of **1**. Integration of these peak areas indicated yields of **3**, **4**, **5**, and **6** as 43, 3, 7, and 17 percents, respectively. Quantitative nmr analysis (13) of this solution also revealed the presence of 19 percent of photodimer **2**. Although the accuracy of these gc yields suffers from the assumption of equal detector responses, the combined gc and nmr yields demonstrated a good mass accountability in this reaction.

All volatile photoproducts were isolated by preparative gas chromatography. The primary photoproduct of intermediate yield was assigned 2-pyrone structure **5** on the basis of a direct comparison of its chromatographic and spectroscopic properties with an authentic sample of 4,5-dimethyl-2-pyrone (14).

The major primary photoproduct was assigned 4-hydroxycyclopentenone structure **3** on the basis of its spectroscopic properties. Its mass spectrum ( $M^+$  224) clearly revealed the incorporation of a molecule of TFE. In addition, the nmr spectrum in carbon tetrachloride ( $\delta$  1.20, s, 3H; 2.06, d,  $J \sim 1.3$  Hz, 3H; 4.13, s, 1H; 4.02-4.32, m, 2H; 5.90, q,  $J \sim 1.3$  Hz, 1H) verified the presence of a single vinyl hydrogen in the  $\alpha$ -position of an  $\alpha,\beta$ -unsaturated system coupled to the methyl group in the  $\beta$ -position of this moiety. When the spectrum was recorded in DMSO- $d_6$ , the OH absorption (exchangeable with deuterium oxide) was observed as a sharp singlet. This places the OH group at the tertiary C<sub>4</sub> position (15) and allows unambiguous distinction between the proposed structure and its 5-hydroxycyclopentenone isomer. In addition, in this latter solvent, the 2H signal, due to the

trifluoroethoxy methylene group, was more cleanly resolved into a first-order quartet ( $J = 9$  Hz) by reason of its coupling with the three adjacent fluorine atoms. These latter nuclei were likewise clearly visible in the  $^{19}\text{F}$  spectrum as a triplet 31.4 ppm downfield from an external trifluoroacetic acid standard. Catalytic hydrogenation of the major primary photoproduct led to a single volatile product. The carbonyl band at  $1730\text{ cm}^{-1}$  in the photoproduct was shifted to  $1770\text{ cm}^{-1}$  on hydrogenation with concurrent loss of the vinyl hydrogen nmr signal. This provides further verification of the assigned cyclopentenone structure **3**.

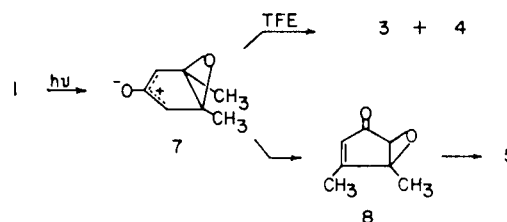
The stereochemistry at  $\text{C}_4$  and  $\text{C}_5$  in **3** was indicated by its infrared spectrum [ $\nu(\text{carbon tetrachloride})$ :  $3640, 3450, 2990, 1730, 1630, 1280, 1160$  and  $1120\text{ cm}^{-1}$ ] which revealed absorption for both free and intermolecularly hydrogen bonded OH at  $3640$  and  $3450\text{ cm}^{-1}$ , respectively. As expected, the relative intensities of these two absorption bands were particularly sensitive to concentration with the broad band at  $3450\text{ cm}^{-1}$  predominating at  $0.2\text{ M}$ , but being essentially negligible compared to the sharp free OH absorption at  $3640\text{ cm}^{-1}$  when the concentration was reduced to  $0.02\text{ M}$ . This observation of strong intermolecular hydrogen bonding is thus consonant with the assigned *trans*-orientation of the OH and  $\text{OCH}_2\text{CF}_3$  groups (16,17).

The minor primary photoproduct was assigned isomeric structure **4**. As anticipated for stereoisomers, the spectroscopic properties of **4** [ $\text{M}^+$ , 224: nmr (DMSO- $d_6$ ):  $\delta$  1.36, s, 3H; 2.01, d,  $J \sim 1.3$  Hz, 3H; 3.83, s, 1H; 4.30, q,  $J = 9$  Hz, 2H; 5.26, s (deuterium oxide exchangeable); 5.87, q,  $J \sim 1.3$  Hz, 1H; ir (carbon tetrachloride):  $\nu$  3640, 3590, 3440, 2990, 1725, 1630, 1275, and  $1165\text{ cm}^{-1}$ ] were very similar to those of **3**. In contrast to these similarities, however, the infrared spectrum of **4** exhibited a sharp signal at  $3590\text{ cm}^{-1}$ , indicative of an intramolecularly hydrogen bonded OH group with a less intense shoulder at  $3630\text{ cm}^{-1}$  for the free OH absorption, and a smaller band at  $3440\text{ cm}^{-1}$  for an intermolecularly hydrogen bonded OH. Furthermore, this portion of the infrared spectrum of **4** was considerably less concentration dependent than the corresponding region of the infrared spectrum of **3**.

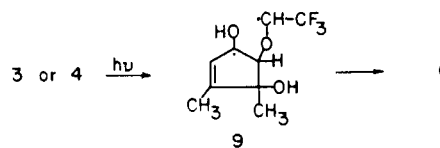
The stereoisomeric relationship between **3** and **4** is also consistent with their photoreactivity. Thus, although photolysis of **5** yielded only very minor volatile products (18), irradiation in TFE of either purified **3** or **4** resulted in the formation of **6** as the only volatile product in an essentially quantitative yield. The mass spectrum of this secondary photoproduct ( $\text{M}^+$  126) suggested that photolysis of either **3** or **4** was accompanied by loss of the trifluoroethoxy group. Similarly, whereas the nmr spectrum of **6** [ $\delta$  (DMSO- $d_6$ ) 1.35, s, 3H; 2.05, d,  $J \sim 1.3$

Hz, 3H; 2.40, s, 2H; 5.30, s, 1H (deuterium oxide exchangeable); 5.70, q,  $J \sim 1.3$  Hz] remained consonant with a 4-hydroxycyclopentenone derivative, the trifluoroethoxy methylene quartet was conspicuously absent in the spectrum of **6**. Furthermore, the  $\text{C}_5$  1H singlet in the spectrum of **3** or **4**, deshielded to  $\delta$  4.10 or 3.83 ppm due to the trifluoroethoxy group, has been replaced in the spectrum of **6** by a 2H singlet upfield at 2.40 ppm.

A plausible mechanism for the formation of **3**, **4**, and **5** involves the intermediacy of zwitterion **7** formed by electrocyclic ring closure, symmetry allowed in the first excited state of **1** (19). 4-Hydroxycyclopentenone



derivatives **3** and **4** accordingly arise by nucleophilic trapping of **7** by TFE (20). The observed relative yields of **3** and **4** thus reflect the sterically preferred approach of the solvent along a line *anti* to the epoxide ring. Alternatively, 2-pyrone **5** could arise from **7** via thermal and/or photochemical rearrangement of epoxycyclopentenone **8** (21,22).



We envision the type II biradical **9** as an intermediate in the conversion of **3** and **4** to **6** (23). Although intramolecular  $\gamma$ -hydrogen abstraction has also been observed as a primary photoprocess in an analogous 5-ethoxycyclopentenone, cyclization of the latter 1,4-diradical was favored over fission of the  $\text{C}_5\text{-O}$  bond (24). In the present 5-trifluoroethoxy cyclopentenone derivatives, the reverse is obviously true since no bicyclic products were observed from the photolysis of either **3** or **4**. With respect to the lability of this bond in the latter cases, it is interesting to note that fission of the  $\text{C}_5\text{-OCH}_2\text{CF}_3$  bond is also the predominant reaction in the 20 eV mass spectrum of either **3** or **4**.

These results show that the effects of TFE solvent on the photochemistry of **1** are quite pronounced. In contrast, irradiation of **1** in methanol solvent has been reported to yield mainly dimers (**7**), and, indeed, we did not observe any gc volatile products from this reaction.

Increasing solvent polarity has been shown to result in a reordering of the low-lying triplet states in certain

carbonyl compounds from  $[n,\pi^*]$  to  $[\pi,\pi^*]$  in nature (25). By analogy, it is tempting to suggest that, in contrast to methanol solvent, photoreactivity of **1** in TFE originates from its  $^3[\pi,\pi^*]$  state. Ishibe and colleagues, however, have shown that **1** emits typical  $[\pi,\pi^*]$  phosphorescence in either methylcyclohexane or ethanol glass with the life-time of the emitting species being insensitive to increased solvent polarity (26). Accordingly, rationalization of the effects of TFE on the photoreactivity of **1** must await the results of additional mechanistic studies.

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- (11) All irradiations were carried out under nitrogen in a water-cooled vycor tube using an 8w 2537 Å low pressure mercury lamp.
- (12) Analysis was performed on a 6' x 1/8" column packed with 2% carbowax 20M-TPA on Chromasorb G. Retentions of **3**, **4**, **5**, and **6** relative to **1** at 140° are 1.80, 0.35, 1.29, and 1.45 respectively.
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