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THE MULTIPLICITY OF THE REACTIVE
2-PYRONE EXCITED STATES.

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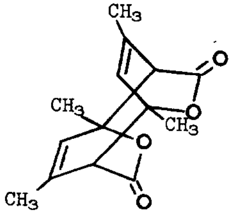
The photochemistry of the 2-pyrone system is rich and varied. Corey (1) has reported that direct irradiation of 2-pyrone (1) affords bicyclo[2.2.0]pyran-2-one (2) while de Mayo (2,3) has found that direct irradiation of 4,6-dimethyl-2-pyrone in methanol affords a ring opened adduct, methyl 4-acetonylcrotonate (3) or, in benzene, affords two 4 + 4 dimers, 4 and 5, and a 2 + 2 dimer, 6, of the type generally encountered in photodimerizations of α,β unsaturated carbonyl compounds (4).



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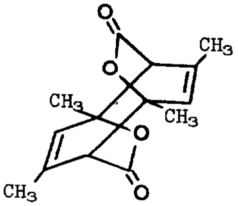

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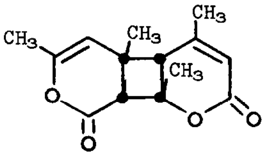

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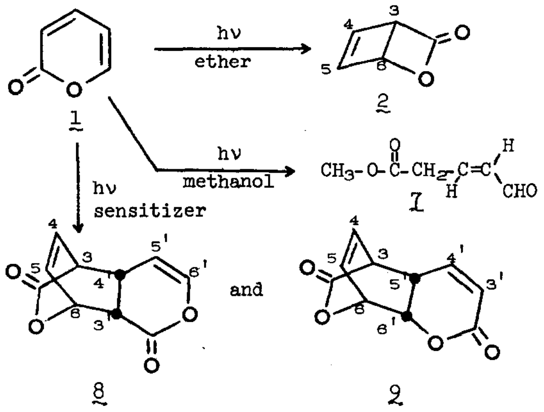
We find that irradiation (Hanovia 450 w medium pressure lamp, Corex filter) of a dilute (4 g/l) solution of 2-pyrone in ether-methanol (90:10) affords an essentially quantitative yield of the ring opened adduct, methyl trans-4-formyl-3-butenoate (7). However, addition of a photosensitizer (acetophenone, 1 g/l) to a similar 2-pyrone solution and irradiation with 3600Å light affords none of the methanol adduct 7 but yields instead approximately equal amounts of two 4 + 2 Diels-Alder-like dimers, 8 and 9. Such 2 + 4 dimers are comparatively rare in photochemistry (4).

Inasmuch as direct irradiation of ethereal 2-pyrone leads either to bicyclolactone 2 (methanol absent) or adduct 7 (methanol present) and neither reaction is slowed by the presence of 0.1M piperylene, it seems highly likely that 2 and 7 arise *via* 2-pyrone singlet excited states. Moreover, the demonstration that the presence of a photosensitizer prevents the formation of 2 and 7 but leads instead to photodimers 8 and 9, products not formed in the absence of the photosensitizer, seems to require that the dimers arise *via* triplet 2-pyrone excited states.



The structure of the somewhat unstable oily adduct 7 follows from its infrared spectrum which shows carbonyl absorption at 5.77 and 5.93μ, from its nmr spectrum which shows resonances at δ9.50(d,1H), 6.96(m, 1H), 6.13(m, 1H), 3.71(s, 3H), and 3.38(q, 2H), and from its elemental composition (Anal. Calcd for $C_6H_8O_3$: C, 56.25; H, 6.25. Found: C, 55.91; H, 6.36). The location of the double bond in 7 is clearly demonstrated by the doublet nature of the aldehydic resonance; the stereochemistry about this double bond follows from the observation of a 16 Hz coupling constant common to the multiplets at δ6.13 and 6.96.

The structures of dimers 8 and 9, separable by preparative tlc [silica gel G, acetone-methylene chloride (1:2)] and crystallizable from cold acetone, follows from their molecular weights (192, mass spectrometric) their elemental compositions (Anal. Calcd for $C_{10}H_8O_4$: C, 62.50; H, 4.17. Found for 8: C, 62.81; H, 4.29. Found for 9: C, 62.38; H, 4.39.), their infrared spectra, which show retention of the lactone rings, and their 100 MHz nmr spectra. In DMSO-d_6, both dimers have nmr spectra which show six well-separated multiplets in area ratios of 3:1:1:1:1:1, the larger multiplet arising from partial overlap of three nonequivalent vinyl protons Since each dimer has eight unique protons, all dimer structures having an element of symmetry can be excluded as possible representations for 8 and 9, thus excluding the majority of the 2 + 2 and all 4 + 4 photodimers which are a priori conceivable.

The infrared spectrum of dimer 8, mp 162°, shows but one lactone carbonyl band, 5.74μ, thus suggesting that neither carbonyl is α,β unsaturated. The 100 MHz nmr spectrum of 8 exhibits multiplets at δ6.68 (3 H), 5.62 (1 H), 5.29 (1 H), 3.60 (1 H), 3.37 (1 H), and 2.76 (1 H). The multiplet at δ6.68 is assigned to H_4, H_5, and H_6', while the other multiplets are assigned to H_6, H_5', H_3, H_3', and H_4' respectively. When **8** is prepared from 2-pyrone-3-*d* (5) the multiplets at δ3.60 and 3.37 disappear; when prepared from 2-pyrone-5-*d* (5) area is lost from the δ6.68 multiplet and the δ5.29 multiplet is lost; when prepared from 2-pyrone-6-*d* (5) area is lost from the 6.68 multiplet and the δ5.62 multiplet disappears. These labeling studies plus double resonance experiments on the deuterated dimers allow confident assignment of the structure of **8** save for the question of whether the carboxyl bridge is *exo* or *endo* to the nonbridged ring.

Dimer **9**, mp 160.5°, has an infrared spectrum showing two lactone absorptions, 5.68 and 5.81μ, suggesting that one carbonyl is conjugated with an α,β double bond. The 100 MHz nmr spectrum of **9** (DMSO-d_6) shows equal area multiplets centered at δ6.87, 6.74, 6.55, 5.99, 5.41, 5.03, 3.68 and 2.98. These multiplets are assigned to H_4', H_4, H_5, H_3', H_6, H_6', H_3, and H_5' respectively. When **9** is prepared from 2-pyrone-3-*d*, the multiplets at δ5.99 and 3.68 are lost; **9** from 2-pyrone-5-*d* has no multiplets at δ6.55 and 2.98; **9** from 2-pyrone-6-*d* has no multiplets at δ5.41 and 5.03. From these labeling studies the structure of **9** is confidently assigned save again for the question as to whether the carboxyl bridge is *exo* or *endo* to the nonbridged ring.

Both dimers are stable toward further irradiation; **8** was shown not photoequilibrate with **9** under reaction conditions. Moreover, while the concentration ratios of the dimers are influenced by solvent choice, the ratios in a given solvent are time invariant and are unaffected by the choice of benzophenone, acetophenone or β-acetonaphthone as the photosensitizer.

Accordingly, dimers **8** and **9** are believed to arise directly from triplet 2-pyrone rather than by rearrangement of other initially formed adducts.*

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*Rigorously, one can only say that any adducts which rearrange to afford dimers **8** and **9** must rearrange so rapidly that adduct concentrations detectable by 100 MHz nmr are never attained.

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