Changes in the Photochemistry of Tropone or 2-Methoxytropone on Complexation with Acids

Marino Cavazza,*[a] Maurizio Zandomeneghi,*[a] and Francesco Pietra*[b]

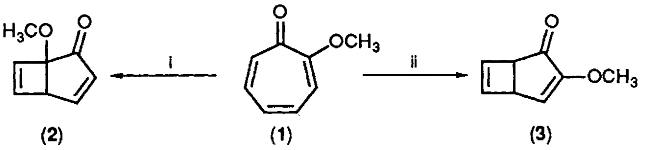
[a] *Dipartimento di Chimica e Chimica Industriale, Università di Pisa, 56100 Pisa, Italy*
[b] *Istituto di Chimica, Università di Trento, 38050 Povo-Trento, Italy*

On addition of either $BF_3 \cdot Et_2O$ or H_2SO_4 the valence photoisomerization of 2-methoxytropone (**1**) in CH_3CN is diverted from 1-methoxy- (**2**) to 3-methoxybicyclo[3.2.0]hepta-3,6-dien-2-one (**3**) as products whereas with tropone there is a change from photodimerization to valence isomerization to give cleanly bicyclo[3.2.0]hepta-3,6-dien-2-one (**5**).

The changes induced by added acids on the course of photochemical reactions of carbon compounds has recently aroused much interest. For α,β-unsaturated carbonyl compounds this includes changes in either the *Z*:*E* ratio in photoisomerizations,[1a] or the head-to-tail regiochemistry in photodimerizations,[1b] while extensive backbone rearrangements are also known.[1c]

We report preliminary results with troponoids. On irradiation with UV light in either organic solvents or acidic or neutral water, 2-methoxytropone (**1**) undergoes valence isomerization to give 1-methoxybicyclo[3.2.0]hepta-3,6-dien-2-one,[2]† (**2**) (Scheme 1) while tropone (**4**) either undergoes [6 + 2], [6 + 4], and [4 + 2] photodimerizations in organic solvents[3] (Scheme 2) or gives a 1:1 mixture of bicyclo[3.2.0]hepta-3,6-dien-2-one (**5**) and a norbornenone derivative in neat FSO_3H at −75 °C, which were only spectroscopically observed *in situ* as protonated species.[4] We show now that on complexation with acids in CH_3CN the photochemistry of tropone shifts from dimerizations to valence photoisomerization giving a single product (Scheme 2), while with 2-methoxytropone there is a change in the course of the valence photoisomerization from product (**2**) to (**3**).

Thus, irradiation with an immersion 125 W Pyrex-filtered medium-pressure Hg lamp of a solution of 0.58 mmol of tropone–boron trifluoride monohydrate adduct[5] in CH_3CN (130 ml) for 30 min up to 80% conversion, followed by evaporation and silica-gel TLC with 3:2 Et_2O/petroleum ether, gave bicyclo[3.2.0]hepta-3,6-dien-2-one[6] (**5**) (0.27 mmol, 59%, R_F 0.5). A similar irradiation with 0.8 mmol of 2-methoxytropone–boron trifluoride adduct[5] for 120 min, up to 54% conversion and silica-gel TLC with Et_2O, gave 3-methoxybicyclo[3.2.0]hepta-3,6-dien-2-one[7] (**3**) (0.3 mmol, 67%, R_F 0.6). Similar results were obtained on irradiation of solutions of either tropone (**4**) or 2-methoxytropone (**1**) in CH_3CN on addition of a slightly higher than the equimolar amount of $BF_3 \cdot Et_2O$; we have also found that H_2SO_4 in CH_3CN has the same effect as BF_3, although a higher acid to troponoid concentration ratio was required in order to obtain effects comparable to added BF_3.

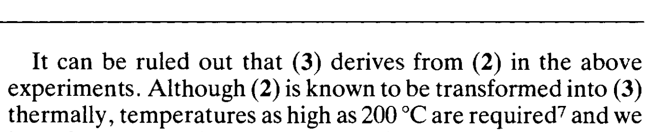


Scheme 1. *Reagents and conditions:* i, CH_3CN, *hv*; ii, CH_3CN/BF_3 or CH_3CN/H^+, *hv*.

It can be ruled out that (**3**) derives from (**2**) in the above experiments. Although (**2**) is known to be transformed into (**3**) thermally, temperatures as high as 200 °C are required[7] and we have found that photochemically this transformation cannot be induced even in the presence of BF_3.

The quantum yields for the (**1**) to (**3**) (Scheme 1) and (**4**) to (**5**) (Scheme 2) processes are of the same order of magnitude as for the (**1**) to (**2**) process (Scheme 1), which was determined to be 0.05. Thus, the quantum yield for the (**4**) to (**5**) valence isomerization has a dramatically higher yield than the photodimerizations of (**4**) (Scheme 2) as shown in parallel experiments in which by using a merry-go-round apparatus, tropone was recovered unchanged from irradiation in non-acidic CH_3CN solutions, while 30% of the tropone·BF_3 adduct was converted into (**5**).

The addition of either BF_3 or H^+ also has a profound effect on the UV spectra of our troponoids; Figure 1 shows that the addition of an equimolar amount of $BF_3 \cdot Et_2O$ induces a sharpening of the UV absorption bands of both (**1**) and (**4**)



Scheme 2. *Reagents and conditions:* See Scheme 1.

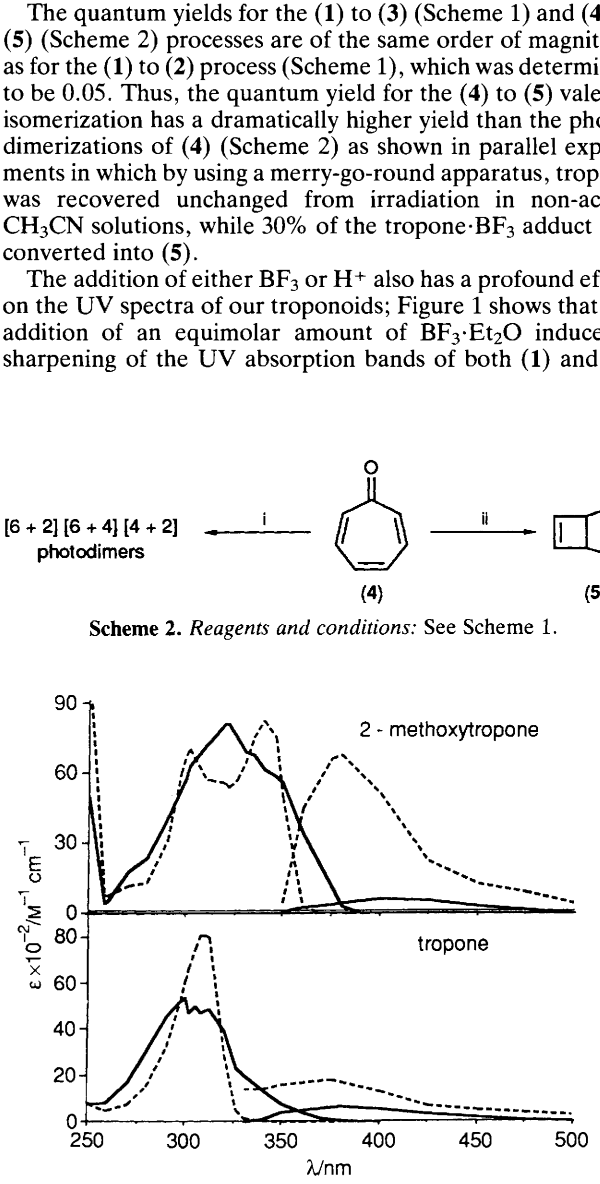


Figure 1. UV absorption spectra (left half) and fluorescence (right half) of either the indicated troponoid in CH_3CN (——) or its 1:1 complex with BF_3 or H^+ (- - -); such complexes were obtained on addition of 1 equiv. of BF_3 or excess H_2SO_4 to the substrate in CH_3CN.

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† Although reaction (**1**) to (**2**) was originally carried out in MeOH,[2] we have now found that the reaction course is the same with CH_3CN as solvent.

whereas the dipolar strength of the transition and the centre of gravity of each band remain unchanged. Figure 1 also shows that the emission spectrum of the BF_3 or H^+ complex is more intense than for the non-complexed troponoid and the Stokes shift is smaller.

These results indicate that for any drastic change in the photochemical reaction course to be observed the substrate must effectively undergo complexation with the acid, which is revealed by a drastic change in the UV absorption.[‡]

Our syntheses above offer notable advantages in terms of yields, economy, and ease of operation with respect to previous methods for (**3**)[7] and (**5**).[6,10]

In view of the current interest in troponoid derivatives as synthons,[11] we are extending the above studies to a wider variety of troponoids and hope to offer mechanistic details in a full paper.

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[‡] For example, tropone, on irradiation in 2 mol dm^{-3} aq. H_2SO_4, where the UV absorption spectrum is not altered with respect to water as solvent, gives photodimers.[8] Addition of $BF_3\cdot Et_2O$ to colchicine in CH_3CN as solvent fails to alter both the photochemical transformation to β-lumicolchicine[9] and the UV absorption spectrum of this alkaloid. Moreover, under conditions of incomplete protonation, at 62% conversion of (**1**), the yields of (**3**) were 17 and 23% for $[H_2SO_4]/[(\mathbf{1})]$ values of 0.5 or 3, respectively. Correspondingly, the yields for (**2**) were 33 and 6%.

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