Multiplicity Dependence of Di-π-methane Photochemistry. Regiospecific Formation of Tetramethylvinylcyclopropanes and Chrysanthemic Acid Derivatives

By Peter Baeckström

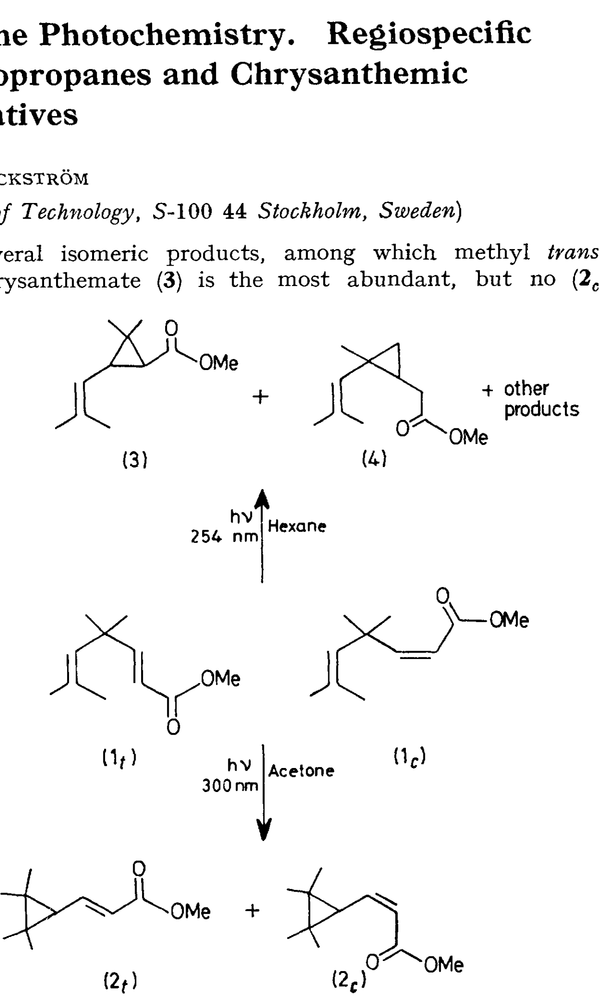
(*Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden*)

Summary Methyl 4,4,6-trimethylhepta-2,5-dienoate and 4,4,6-trimethylhepta-2,5-dienecarbonitrile form chrysanthemic acid derivatives on direct irradiation and tetramethylvinylcyclopropanes on irradiation in acetone.

A VALENCE bond formalism for the di-π-methane rearrangement has been developed by Zimmerman *et al.*[1] It was proposed that a cyclopropyldicarbinyl diradical is formed in the initial step of the reaction, the fate of which depends on structural factors. Thus, regiospecificity is explained by ring opening in the direction of maximum radical stabilisation. Only one reaction performed in the condensed phase is known to violate this rule.[2] Most cyclic di-π-methanes react *via* triplet-excited states. Compounds with at least one of the π-units unconstrained generally react *via* singlet excited states, a reaction which is explained in terms of triplet energy dissipation by *cis–trans*-isomerisation, known as the free-rotor effect.[1,3]

We have investigated the photoreactions of methyl *cis*- and *trans*-4,4,6-trimethylhepta-2,5-dienoate (**1**$_c$,**1**$_t$), which provide the first example of a di-π-methane rearrangement where the ring opening goes in one direction on direct irradiation, and in the other direction when a sensitiser is used. In both cases, rapid *cis–trans*-isomerisation takes place.

Irradiation in acetone and benzene leads to methyl *cis*- and *trans*-3-(2,2,3,3-tetramethyl(cyclopropyl)prop-2-enoate (**2**$_c$, **2**$_t$), in a clean reaction at moderate conversion. Irradiation in hexane,† ether, or dioxan leads to the formation of several isomeric products, among which methyl *trans*-chrysanthemate (**3**) is the most abundant, but no (**2**$_c$)



---

† After the completion of this work a report on the photochemistry of (**1**$_t$) has appeared (M. J. Bullivant and G. Pattenden, *J.C.S. Perkin I*, 1976, 256). The reported results from irradiation in hexane are in good agreement with those obtained by us. On the other hand, we have checked the reaction with acetophenone as a sensitiser and found that the same products as with irradiation in acetone are formed, but at a slower rate.

or (**2**$_t$) was formed. G.l.c. monitoring showed that methyl chrysanthemate increases mainly in the initial part of irradiation during which a rapid build up of (**1**$_c$) occurs. This fact, together with the extensive loss of material as unrecovered products explain why only a 15% chemical yield of methyl chrysanthemate could be achieved. There are strong indications for the formation of (**4**), by the same type of intramolecular hydrogen abstraction as described by Jorgenson.[4]

A preliminary investigation of *cis*- and *trans*-4,4,6-trimethylhepta-2,5-dienecarbonitrile shows that these compounds react in the same way, and circumvent the undesired hydrogen abstraction. On prolonged irradiation in acetone, *cis*- and *trans*-3-(2,2,3,3-tetramethylcyclopropyl)prop-2-enecarbonitrile were formed, and on direct irradiation in hexane, *cis*- and *trans*-chrysanthemic nitrile were formed in good yields.

The patterns obtained in the cases investigated rule out unintended singlet excitation when a sensitiser is used. This shows that vinylcyclopropane formation competes with triplet energy dissipation by the free-rotor effect and which products are formed depends only on relative rates.

(*Received, 2nd April* 1976; *Com.* 342.)

[1] S. S. Hixon, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, 1973, **73**, 531.
[2] M. J. Bullivant and G. Pattenden, *J.C.S. Chem. Comm.*, 1972, 864.
[3] P. S. Mariano and D. G. Watson, *Tetrahedron Letters*, 1975, 3439.
[4] M. J. Jorgenson, *J. Amer. Chem. Soc.*, 1969, **91**, 198.