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The Diverted Di-π-Methane Rearrangement; Mechanistic and Exploratory Organic Photochemistry[1]

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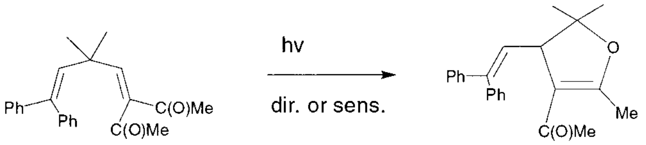
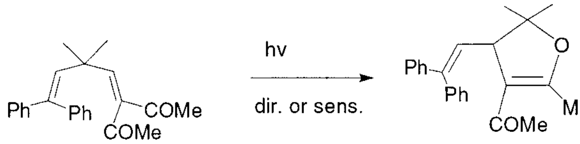
ABSTRACT



An unusual diversion of the di-π-methane rearrangement has been encountered. The reaction is characteristic of di-π-methane systems having one vinyl group bearing one or two carbonyl groups and provides a synthesis of dihydrofurans.

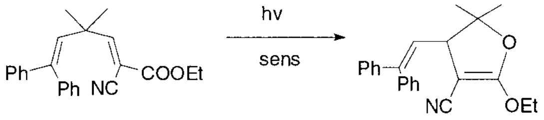
The di-π-methane rearrangement has become a well understood reaction with a large number of examples.[2] Thus it was surprising when we encountered a different reaction course. The photochemical reaction of diene **1** led to an unexpected photoproduct, **2**, rather than the anticipated vinylcyclopropane. We term this a "diverted di-π-methane rearrangement", eq 1.



(1)

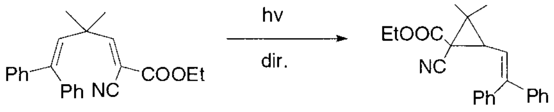
1 **2**

Subsequently, a number of further examples were found for reactants with similar structural features as noted in the following. However, equally interesting was evidence on the reaction multiplicity. Thus, in the irradiation of those systems where intersystem crossing might be anticipated to be less efficient than in the case of ketones, triplet sensitization was necessary for the reaction to proceed in this fashion. The example of cyanoester **3** is depicted in eqs 2 and 3.



(2)

3 **4**



(3)

3 **5**

Indeed, in the case of reactants lacking keto carbonyl groups, such as the cyanoester in eqs 2 and 3, intersystem crossing is anticipated to be slower relative to the rate of rearrangement, and the diverted di-π-methane rearrangement is obtained only upon sensitization.

In the case of the diester **6** where there are two ester carbonyl groups, the diverted di-π-methane photoproduct **8** is obtained along with the normal three-membered ring product, even without sensitization. However, sensitization doubles the relative amount of the diverted photoproduct.

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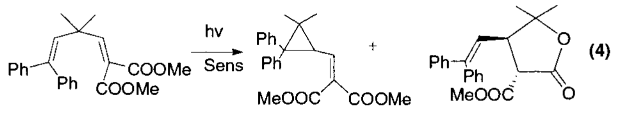
(1) This is paper 265 of our general series. For paper 262 see: Zimmerman, H. E.; Wang, P. *Helv. Chim. Acta* **2001**, *65*, 1342−1346.

(2) Zimmerman, H. E.; Armesto, D. *Chem. Rev.* **1996**, *96*, 3065−3112.

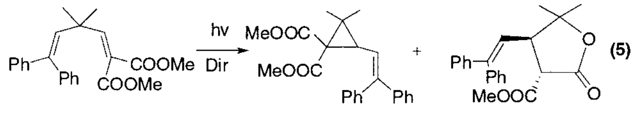
10.1021/ol025564h CCC: $22.00



(4)

6 **7** **8**

RATIO: *1* : *2*



(5)

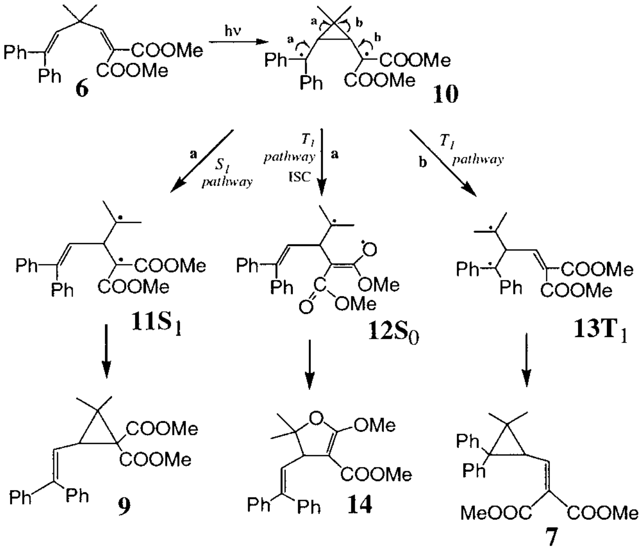
6 **9** **8**

RATIO: *1* : *1*

In direct and sensitized control runs, the di-π-methane cyclopropanes **7** and **9** did not afford the five-membered ring product and thus are not reaction intermediates.

The mechanism of the diverted di-π-methane rearrangement is given in Scheme 1. We note that the cyclopropyldicarbinyl diradical **10** opens regioselectively in formation of the ordinary di-π-methane three-membered ring photoproducts. This regioselective preference as a function of the diradical multiplicity has been observed in a number of our earlier studies.[3] Thus bond *a* fission (leading to photoproduct **9**) is expected to be preferred by the singlet S_1, whereas bond *b* cleavage (leading to **7**) is characteristic of the triplet T_1 of the cyclopropyldicarbinyl diradical **10**. These triplet−singlet differences in reactivity result from exchange integral control.[3]

Scheme 1. Mechanism of the Di-π- and Diverted Di-π-Methane Rearrangements



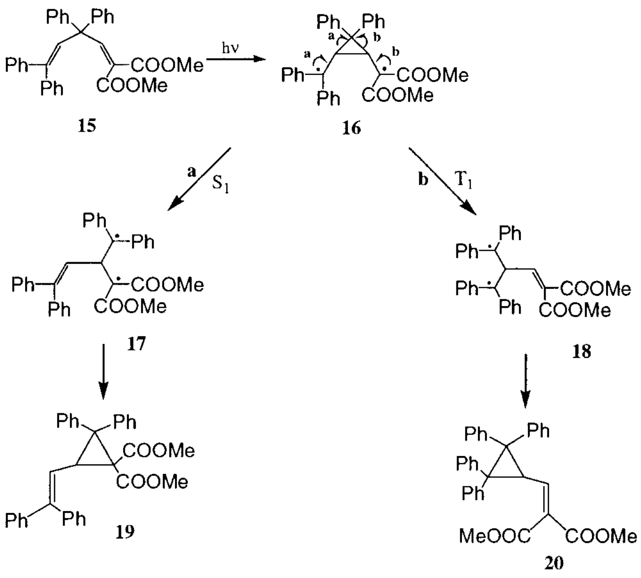
Surprisingly, as noted in Scheme 1, species **14** (the precursor of **8** before hydrolytic workup) is a product that results from fission of bond *a* rather than bond *b* and yet originates from the triplet. Indeed it is the sensitized reactions (i.e., triplet conditions) that afford the diverted di-π-methane products throughout.

Hence we conclude that, in the systems presently under study, there is an anomaly in which the triplet cyclopropyldicarbinyl diradical species partitions differently. The formation of normal di-π-methane products follows the usual regioselectivity with fission of bond *b*, whereas the formation of the diverted di-π-methane products involves the unusual fission of bond *a*.

One possibility is that the less regioselective triplet cyclopropyldicarbinyl diradical **10** ring opening, with dimethyl substitution, merely results from smaller energy differences slightly favoring bond *a* fission. However, additionally there is the point that bond *a* scission leads to the five-membered ring product and not the usual three-ring di-π-methane one.

In earlier studies,[3b] we investigated a similar reactant **15** with phenyl groups at the central carbon rather than the methyls as in the present reactant **6**. In that case the same multiplicity dependent regioselectivity of cyclopropyldicarbinyl ring opening was observed in formation of di-π-methane photoproducts; note Scheme 2. However, no products corresponding to the diverted di-π-methane rearrangement were encountered.

Scheme 2. Mechanism in the Tetraphenyl Case



The chief difference in that earlier study was the absence of any three-ring opening of bond *a* from the triplet of the cyclopropyldicarbinyl diradical **16**. Hence intermediate **12** in the present study is a species not encountered previously.

Thus it was of interest to obtain ROHF/6-31G* energies of the triplet diradicals resulting from cyclopropyldicarbinyl ring opening in the tetraphenyl and dimethyldiphenyl cases. These were obtained from Gaussian98[4] computation; note Tables 1 and 2. It is seen that the preferred triplet diradical

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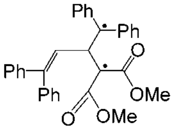
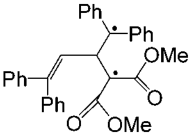
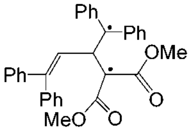
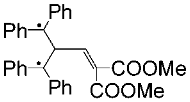
(3) (a) Zimmerman, H. E.; Armesto, D.; Amezua, M. G.; Gannett, T. P.; Johnson, R. P. *J. Am. Chem. Soc.* **1979**, *101*, 6367−6383. (b) Zimmerman, H. E.; Factor, R. E. *Tetrahedron* **1981**, *37*, Supplement 1, 125−141. (c) Zimmerman, H. E.; Cirkva, V. *J. Org. Chem.* **2001**, *66*, 1839−1856.

Table 1. Relative Energies of Triplet Diradicals from Bond *a* and Bond *b* Openings: Tetraphenyl **15**[a]

 **17T-a**	 **17T-b**	 **17T-c**	 **18T**
+11.9 kcal/mole	+2.7 kcal/mole	+4.3 kcal/mole	0.0 kcal/mole

[a] Three conformations of **17T** are included. **18T** is a global mininum.

in the case of the tetraphenyl reactant is species **18**, which has benzhydryl odd-electron centers. Thus the computation is in accord with experimental observation.

In the case of the dimethyl reactant the alternative triplet diradicals, **12T** and **13T**, resulting from cyclopropyldicarbinyl ring opening are within 1 kcal/mol of one another and the diminished regioselectivity encountered is in accord with the computations.

Still, as noted above, the difference between the presently studied dimethyl example and the earlier diphenyl counterpart may be ascribed to an effect other than just relative stability of the diradicals formed in cyclopropyldicarbinyl ring opening. Moreover, the behavior of diradical **12** (note Scheme 1) is suggestive of singlet, rather than triplet, multiplicity; in any case, the triplets do need to intersystem cross to ring close.

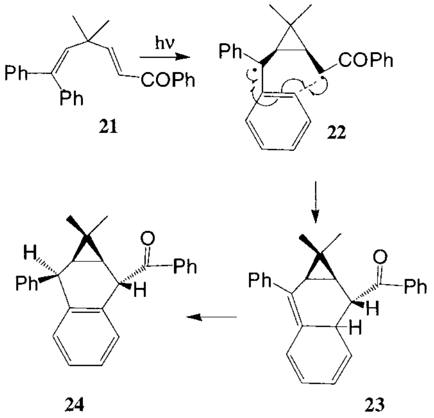
It seems more reasonable that control is by intersystem crossing of T_1 of the dimethyl cyclopropyldicarbinyl diradical **10** to $S_{0.}$ This may occur concomitantly with ring opening and leads directly to species **12** as a ground-state zwitterion rather than to species **12** as a triplet. Actually, intersystem crossing may occur at any point between triplet diradical **10** and ground-state singlet zwitterionic diradical **12**.

This intersystem crossing is enhanced by electron-pair proximity and decreased with separation of electron-pair centers. In the opening of triplet diradical **10** to afford **12**, there is an increased odd-electron density at the carbonyl oxygen that enhances ISC resulting from $p_y-\pi$ interaction.

Thus, we conclude that the triplet diphenyl cyclopropyldicarbinyl diradical **16** opens to the triplet diradical **18** while the corresponding triplet dimethyl cyclopropyldicarbinyl diradical **10** opens in two competitive ways. Bond *b* fission proceeds in the same way as its diphenyl relative. Additionally there is bond *a* opening and this leads finally to the ground state, S_0, of diradical **12**, a species which is best pictured as a zwitterion. This zwitterion then undergoes ring closure to afford the dihydrofurans **14**.

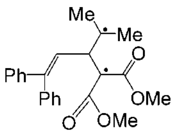
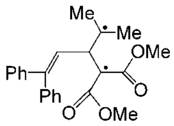
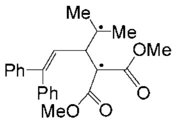
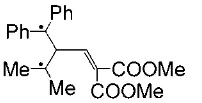
In the case of the direct irradiation of reactant **6**, there is one constraint. There cannot be intersystem crossing of S_1 to T_1 prior to or during ring opening of cyclopropyldicarbinyl diradical **10**, since no bond *b* opening is observed. Thus the ground-state product **9** must be formed by internal conversion of the S_1 excited singlet **11**, perhaps via a conical intersection.[5]

Scheme 3. Photochemical Mechanism of the Benzoyl Reactant **21**



With a single carbonyl substituent as in the benzoyl reactant **21** (Scheme 3) the diverted di-π-methane rearrangement did not occur. Rather an unanticipated product **24** was

Table 2. Relative Energies of Triplet Diradicals from Bond *a* and Bond *b* Openings: DiMethyl-Diphenyl **6**[a]

 **12T-a**	 **12T-b**	 **12T-c**	 **13T**
-1.0 kcal/mole	-1.0 kcal/mole	+0.55 kcal/mole	0.0 kcal/mole

[a] Three conformations of **12T** are included. **13T** is a global minimum.

obtained. As indicated in the mechanism of Scheme 3, the reaction results from cyclization of the cyclopropyldicarbinyl diradical **22**. In virtually all previously studied examples of the di-π-methane rearrangement this intermediate undergoes ring opening more rapidly than competing processes.

In this case, the cyclopropyldicarbinyl diradical is trapped intramolecularly to afford species **23**, which then undergoes tautomerization to afford final product **24**. The stereochemistry at the benzoyl-bearing carbon of **23** is dictated by the product stereochemistry as determined by X-ray.[6]

We are pursuing the reaction to determine its generality and mechanisms as well as computationally to determine the points of maximum spin−orbit coupling and intersystem crossing and the energies of the diradical species involved in the reactions.

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Supporting Information Available: Experimental details and X-ray data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(4) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.6; Gaussian, Inc.: Pittsburgh, PA, 1998.

(5) **Typical Procedure. Preparative Sensitized Irradiation of 1,1-Dimethoxycarbonyl-3,3-dimethyl-5,5-diphenylpentadiene 6.** A solution of 200 mg (0.55 mmol) of 1,1-dimethoxycarbonyl-3,3-dimethyl-5,5-diphenyl-1,4-pentadiene and 8.5 g of acetophenone (70.8 mmol) in 210 mL of benzene was irradiated for 40 min through a 0.20 M cupric sulfate filter, which cuts off below 300 nm. Concentration in vacuo gave a yellow oil that was subjected to bulb-to-bulb distillation (0.05 Torr, 40 °C) to remove acetophenone. The remaining yellow oil was chromatographed on a 4 cm × 70 cm column eluted with 5% ether/hexane. Fraction 1 gave 0.717 g of acetophenone. Fraction 2 gave 10 mg of overlap material. Fraction 3 gave 52 mg of 1,1-dimethyl-2,2-diphenyl-3-(2,2-dimethoxycarbonylvinyl)-cyclopropane **7**, mp 143−144 °C. Fraction 4 gave 110 mg of *trans*-2-methoxycarbonyl-3-(2,2-diphenylvinyl)-4,4-dimethyltetrahydrofuran-2-one **8**, mp 108−109 °C

(6) The structures of compounds **2**, **7**−**9**, and **24** were determined by single-crystal X-ray diffractometry and the remainder by NMR analysis; see Supporting Information for tables and data.