

A ground state tri- π -methane rearrangement[†]

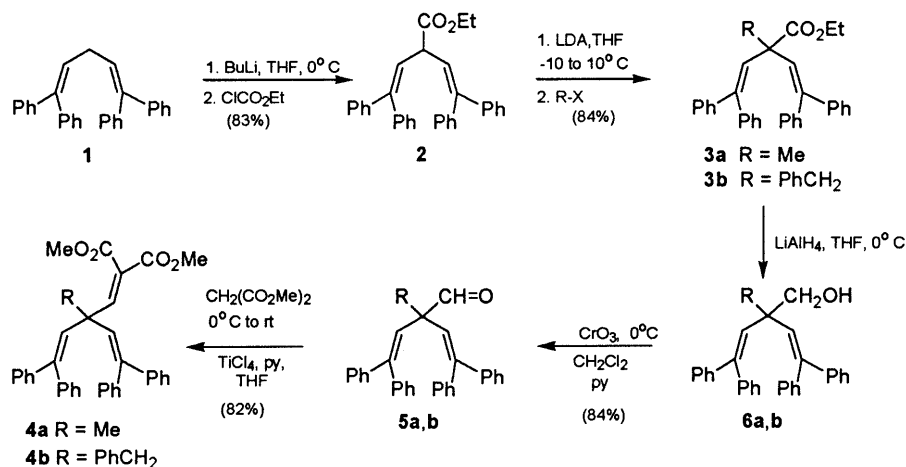
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AbstractAn example of a ground state tri- π -methane rearrangement is described.**1. Introduction**

The di- π -methane rearrangement has been an intensively studied photochemical reaction.² Recently, the tri- π -methane rearrangement has been reported as a reaction which begins with the same initial π - π bonding of the excited state.^{1b} Now we report a curious rearrangement of a tri- π -methane system in the ground state. The reaction mechanism, while reminiscent of the photochemical counterpart, is quite different. The synthesis of the two reactants is outlined in Scheme 1.

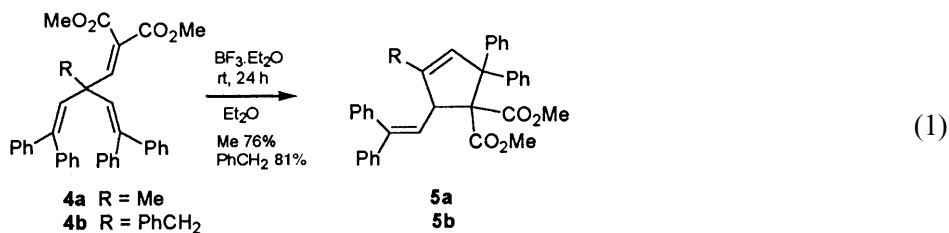
Scheme 1. Synthesis of tri- π -methane reactant

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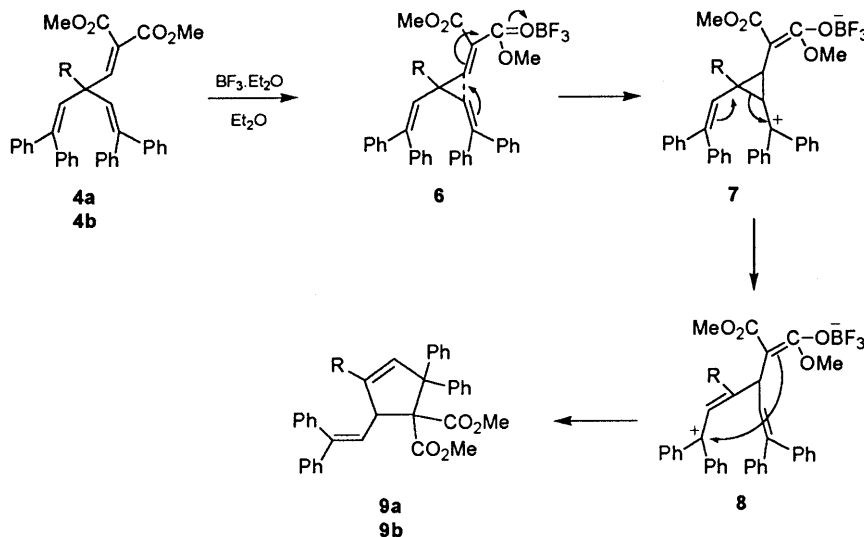
[†] This is Paper 258 of our general series. For Paper 257 see Ref. 1a, for Paper 256 see Ref. 1b

2. Ground state tri- π -methane rearrangements

The tri- π -methane systems **4a** and **4b** were found³ to afford five-membered ring products **5a** and **5b** on boron trifluoride catalysis. The structure of **5a** was established by X-ray analysis and that of **5b** derived from NMR which paralleled that of **5a**. This rearrangement is shown in Eq. (1).



The mechanism is quite different from that of the photochemical di- π -methane and tri- π -methane counterparts and is shown in Scheme 2. The boron trifluoride coordination at the carbonyl oxygen leads to a Prins type bonding with the diphenylvinyl moiety to afford zwitterions **7**. This cyclopropylcarbinyl species then undergoes opening of the three-membered ring to afford zwitterion **8**. This much of the mechanism is equivalent to a 1,2-diphenylvinyl shift. However, the mechanism of a 1,2-vinyl shift involves the π system as outlined here rather than being a rearrangement using only the sigma bond to the vinyl group. Finally, bonding of the enolate and diphenylallylic allyl cation moieties of species **8** leads to the final five-membered ring products **9a** and **9b**. We note that the interconversion of species **6**, **7** and **8** may well be reversible but driven forward by the energetics of the final ring closure.



Scheme 2. Mechanism of the BF_3 catalyzed tri- π -methane rearrangement

This is our first example of the reaction. Both the regioselectivity, wherein the diarylviny groups bear different substitution and also the success of five-ring formation where other carbonyl groups are utilized are of interest and presently under investigation.

Acknowledgements

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References

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2. (a) Zimmerman, H. E.; Paufler, R. *J. Am. Chem. Soc.* **1960**, 82, 1514–1515. (b) Zimmerman, H. E.; Grunewald, G. L. *J. Am. Chem. Soc.* **1966** 88, 183–184. (c) Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Sherwin, M. A. *J. Am. Chem. Soc.* **1967**, 89, 3932–3933. For a recent review see Zimmerman, H. E.; Armesto, D. *Chem. Rev.* **1996**, 96, 3065–3112.
3. **Rearrangement detail.** To 28 mg (0.20 mmol) of boron trifluoride etherate in 3 ml of ether was added a 106 mg (0.20 mmol) portion of methyl 2-carbomethoxy-4-methyl-4-(2,2-diphenylvinyl)-6,6-diphenyl-2,5 hexadienoate in 1.0 ml of ether. Stirring for 24 h at room temperature was followed by filtering through silica gel with ether, concentration and chromatography on silica gel with 1:3 ether–hexane. Crystallization from ether–methanol afforded 80 mg (76%) of 1-methyl-3,3-diphenyl-4,4-dicarbomethoxy-5-(2,2-diphenylvinyl)-1-cyclopentene (**30a**) as colorless crystals, mp 175–177°C. Similarly, to 28 mg (0.20 mmol) of boron trifluoride etherate in 3.0 ml of ether was added 121 mg (0.20 mmol) of methyl 2-carbomethoxy-4-benzyl-4-(2,2-diphenylvinyl)-6,6-diphenyl-2,5-hexadienoate in 1.0 ml of ether. After stirring for 24 h at room temperature and workup as in the methyl analog above, crystallization from ether–methanol afforded 98 mg (81%) of 1-benzyl-3,3-diphenyl-4,4-dicarbomethoxy-5-(2,2-diphenylvinyl)-1-cyclopentene (**30b**) as colorless crystals, mp 226–228°C.