*Tetrahedron* Vol. 40, No. 10, pp. 1727 to 1730, 1984
Printed in Great Britain.

0040-4020/84 $3.00 + .00
Pergamon Press Ltd.

# ON THE PYROLYSIS OF ARYL CINNAMATES
## A CONVENIENT ENTRY TO UNSYMMETRICAL STILBENES

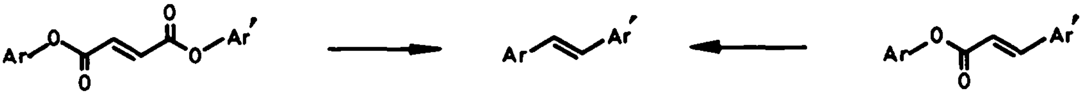
WILAIPORN CHAMCHAANG, NUANPHUN CHANTARASIRI, SOMDEJ CHAONA,
CHACHANAT THEBTARANONTH*, YODHATHAI THEBTARANONTH.

Department of Chemistry, Faculty of Science, Mahidol University,
Rama 6 Road, Bangkok 10400, Thailand.

(*Received in UK* 23 *December* 1983)

Abstract - Symmetrical and unsymmetrical stilbenes can be prepared by pyrolysis of the corresponding aryl cinnamates. The mechanism of product formation is discussed.

The pyrolysis and photolysis of aromatic esters with or without the presence of a Lewis acid catalyst have been widely studied and some of these reactions have proved to be very useful in synthesis. An interesting observation was made by Spatz[1] in 1961 that the aryl fumarates 1 decarboxylated upon refluxing in Dow-Therm to give stilbenes 2, but even more fascinating was the discovery by Anschutz,[2] one century ago, and Skraup[3] in 1927, that stilbenes were produced from the pyrolysis of aryl cinnamates 3.



1 Ar = Ar'

2

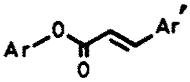
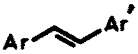
3

In the light that stilbene derivatives are very useful and numerous methods have been developed for their preparations[4] it is surprising that these attractive reactions have not been exploited. Understandably, the pyrolysis of fumarates has limitations, being suitable only for the preparation of symmetrical stilbenes, but, on the other hand, the pyrolysis of cinnamates appears to be a very good entry to unsymmetrical stilbenes, providing that the reaction is general and the product yield reasonable, and scrambling of the aromatic substitution pattern does not occur. Hence we decided to reinvestigate this reaction for more information, and, if possible, for a better understanding of the reaction mechanism.

*Results and Discussion. Pyrolysis of Aryl Cinnamates.*

Aryl cinnamates 3 a-j were prepared and were respectively subjected to pyrolysis in a sealed tube at 320° for 1.5 hr. This condition was found to be optimum for the pyrolysis of phenyl cinnamate 3a and was used throughout this study.

TABLE

| | Aryl cinnamate <u>3</u> | Stilbene <u>2</u><br>% yield (isolated)[+] |
|---|---|---|
| |  |  |
| a. | Ar = Ar' = Ph | 59 |
| b. | Ar = Ph, Ar' = 2-OMe-$C_6H_4$ | 53 |
| c. | Ar = Ph, Ar' = 3-OMe-$C_6H_4$ | 49 |
| d. | Ar = Ph, Ar' = 4-OMe-$C_6H_4$ | 55 |
| e. | Ar = 2-OMe-$C_6H_4$, Ar' = Ph | 51 |
| f. | Ar = 3-OMe-$C_6H_4$, Ar' = Ph | 49 |
| g. | Ar = 4-OMe-$C_6H_4$, Ar' = Ph | 53 |
| h. | Ar = Ar' = 4-OMe-$C_6H_4$ | 46 |
| i. | Ar = 3,5-di OMe-$C_6H_3$, Ar' = 2,4-di OMe-$C_6H_3$ | 17 |
| j. | Ar = β-napthyl, Ar' = 3-OMe-$C_6H_4$ | 47 |

---

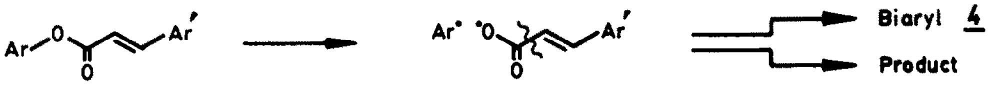
[+] Strongly polar, possibly polymeric material, was not investigated.

Stilbenes were isolated as major products and the results are summarised in Table.

It is apparent from the results obtained that the thermolytic decarboxylation of aryl cinnamates does indeed give rise to stilbenes in reasonable yields with no change in the position of ring substituents. The reaction is thus extremely useful considering the availability of the starting cinnamates and the straight forward technique employed.

### *Nature of the Reaction.*

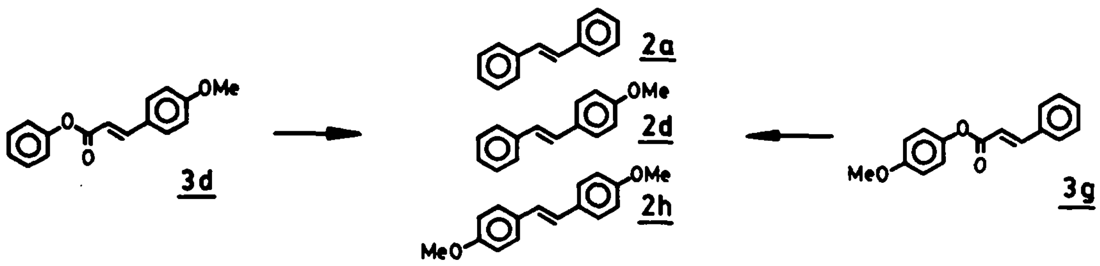
It was expected that if the decarboxylation had proceeded via a radical pathway the biaryl <u>4</u> should be observable. However, no mass ion corresponding to biphenyl could be detected in the crude pyrolysate of cinnamate <u>3a</u>.



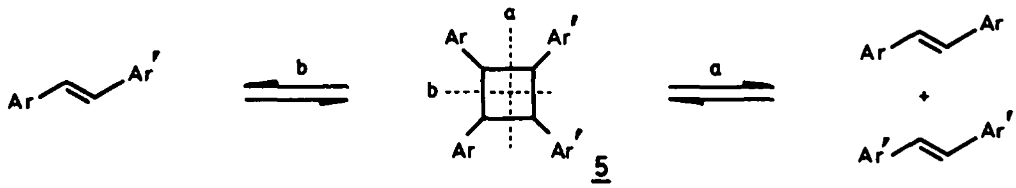
In order to ascertain the intramolecular nature of the reaction an equimolar mixture of <u>3d</u> and <u>3g</u> was heated under the above conditions. Mass spectral analysis of the crude reaction mixture indicated not only the mass ion 210 of the expected stilbene <u>2d</u> (or <u>2g</u>) but also small amounts of the mass ions 180 and 240, belonging, apparently, to products <u>2a</u> and <u>2h</u> respectively. No biaryl ion could be observed. Careful separation of this crude mixture by PLC (silica gel, 4% dichloromethane in hexane) afforded the stilbenes <u>2d</u>, <u>2a</u>, and <u>2h</u> in 52%, 4%, and 5.5% respectively.

These results led us to suspect, at the time, that the reaction was an inter-molecular process. However, further experiments have proved that this is not the case.

Repeated pyrolyses of the pure cinnamates <u>3d</u> and <u>3g</u> and mass spectral examination of each crude pyrolysate at 12 eV showed almost identical data to that obtained from the above experiment (pyrolysis of an equimolar mixture of <u>3d</u> + <u>3g</u>). PLC separation of the products from <u>3d</u> gave stilbenes <u>2a</u>, <u>2d</u>, and <u>2h</u> in 4.5%, 55%, 5.8% while separation of the products from <u>3g</u> yielded the same compounds in 4%,53%, and 6.2% respectively. Although the formation of stilbenes <u>2a</u> and <u>2h</u> was, at first,



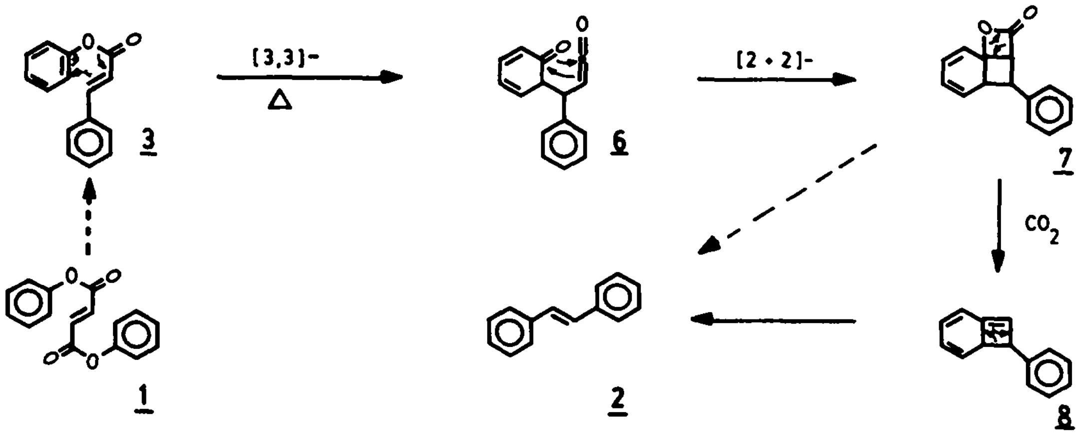
rather puzzling, we have now unambiguously proved that unsymmetrical stilbenes disproportionate, to a certain extent, under the pyrolytic conditions employed. Thus 2a (7%), 2d (71%), and 2h (8%) were obtained when a pure sample of 4-methoxy stilbene 2d was subjected to pyrolysis under these conditions. The disproportionation presumably takes place via a symmetry forbidden 2+2 cyclo-addition reaction to give the cyclobutane 5,[5] which can then revert to the three products as shown.[6]



The ratio of the stilbene products from all three experiments (pyrolyses of: 3d + 3g mixture; 3d or 3g singly; 2d) correlate well. These findings indicate that the cross-over products observed in the decarboxylation reaction arise from the initially formed stilbene 2d and not from an intermolecular reaction of the cinnamate.

## *On the Mechanism of Decarboxylation.*

A feasible mechanism for the decarboxylation could involve a (3,3)-sigmatropic rearrangement of the aryl cinnamate 3 to the dienone-ketene 6, followed by a cycloaddition reaction between carbonyl and ketene to give the reactive β-lactone 7,



which could then decarboxylate either directly or via the cyclobutene 8 to the stilbene product 2 as shown.

An inspection of molecular models has confirmed agreeable orbital interactions and structures for the proposed intermediates in the mechanism shown, eventhough our attempts to trap the ketene 6 have not been successful. This mechanism can also explain the formation of stilbenes from fumarates, the pyrolysis of which, in certain cases, have been known to give the corresponding cinnamates and stilbenes.[2,7] In our study, when diphenyl fumarate (1, Ar = Ar' = Ph) and its dimethoxy derivative (1, Ar = Ar' = 4-OMe-$C_6H_4$) were subjected to pyrolysis under the mentioned conditions, stilbene 2a and phenyl cinnamate 3a, and stilbene 2h and cinnamate 3h were isolated respectively.

Although the yields of stilbenes from the pyrolysis of aryl cinnamates are not very high, nevertheless the convenience of the method and the ready availability of the starting materials both combine to make this reaction attractive.
An appropriate choice of aryl cinnamate can thus provide a simple and economical route to the symmetrical and unsymmetrical stilbenes.

## *Experimental*

### *Pyrolysis of Aryl Cinnamates (3): Typical procedure.*

Aryl cinnamates 3 a-j were prepared according to the standard procedure by reacting equimolar quantities of cinnamoyl chlorides with phenols in benzene solutions.

Phenyl cinnamate 3a (500 mg) was placed in a thick wall glass tube which was flushed with nitrogen and sealed. The tube was heated in an oven at 320° for 1.5 hr, then cooled down to -78° before breaking open, to minimize the pressure from the liberated carbon dioxide. The crude product was purified by preparative layer chromatography using silica gel and 2% ethyl acetate in hexane as eluant to obtain pure stilbene 2a (237 mg, 59%).

The physical property data of the stilbenes from these pyrolytic experiments are in agreement with the literature values.

## *Acknowledgement*

We thank the National Research Council of Thailand for support of this work. We also thank Professor M.P.Cava for a very helpful discussion during his recent visit.

## *References*

1. S.M.Spatz, J.Org.Chem., 1961, 26, 4158.
2. R.Anschütz, Ber., 1885, 18, 1945; R.Anschütz, Ber., 1927, 60B, 1320.
3. S.Skraup, E.Beng, Ber., 1927, 60B, 942.
4. K.B.Becker, Synthesis, 1983, 341.
5. This type of reaction is common under photolytic conditions, for example see: N.Yonezawa, T.Yoshida, M.Hasegawa, J.Chem.Soc. Perkin Trans. I, 1983, 1083.
6. 1,2,3,4-Tetraphenylcyclobutane has been reported to split to give stilbene quantitatively upon heating at 300° for 2 hr, see: M.Pailer, U.Müller, Monatsh, 1948, 79, 615.
7. The pyrolysis of phenyl cinnamate was also investigated by Ritchie et.al. (P.E.Reininger, P.D. Ritchie, D.Ferguson, J.Chem.Soc., 1963, 2688) who studied competitive routes of scission of the ester and obtained phenyl acetylene as the mojor product under the conditions employed (500°c).