CHEMISTRY LETTERS, pp. 659-662, 1977. Published by the Chemical Society of Japan

# NOVEL DECARBOXYLATIVE REACTION OF THE SUBSTITUTED CINNAMYL CINNAMATES (STYRACINS) MEDIATED BY TRANSITION METALS

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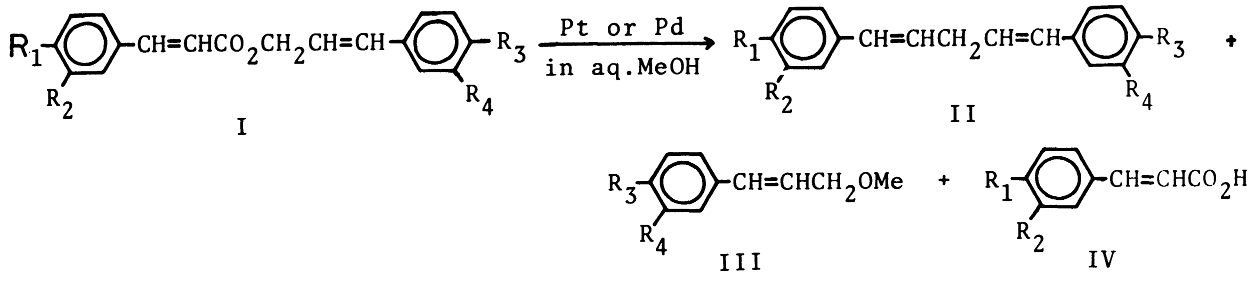
When the substituted cinnamyl cinnamates (I, styracins), which have hydroxyl groups in the phenyl rings, were treated with platinum and palladium catalysts, 1,5-diaryl-1,4-pentadienes (II) were obtained in variable yields up to 34% with other products.

Although the decarbonylations of aldehydes and acid halides catalyzed by transition metals represent very common reactions, such a reaction of esters has been reported only in limited cases.[2)] We delineate in this communication the decarboxylative reaction of cinnamyl cinnamate derivatives (I),[3)] which have hydroxyl groups in the phenyl rings, by the agency of zero valent platinum and palladium in heterogeneous condition. The reaction proceeds with the formal abstraction of carbon dioxide to yield 1,5-diaryl-1,4-pentadiene (II).



When the catalytic oxidation of coniferyl ferulate (Ia) was attempted at the presence of pre-reduced platinum oxide (0.47 molar equiv.) in aqueous methanol solution containing $NaHCO_3$ (10 molar equiv.) at room temperature for 17 hours, 1,5-bis(4-hydroxy-3-methoxyphenyl)-1,4-pentadiene [IIa: IR, no carbonyl absorption; NMR, $\delta$ 3.00(2H, t, J=6 Hz), 3.80(6H, s), 6.00(2H, doublets of t, J=16 and 6 Hz), 6.32(2H, d, J=16 Hz), 6.80 ppm(6H, m)] was obtained in 21% yield along with the recovery of the starting material (4%) and ferulic acid (42%). IIa was further characterized by the derivations to the diacetate ($Ac_2O$-pyridine) and to the tetrahydro compound ($H_2$/Pd-C). The conversion of Ia to IIa was found to occur smoothly under the atmosphere of nitrogen. In order to get insight into the scope and mechanism of this interesting metallo-organic reaction, investigations were made on the effect of the variation in the aryl substituents and the kinds of transition metal. The results, listed in the table, are summarized as follows.[4)]

(i) The presence of the free phenolic hydroxyl groups on both aryl rings is a requisite for the occurrence of the reaction (runs 1-4, 5, and 9).

(ii) The presence of the additional electron releasing group on the aryl rings may favor the reaction (runs 1-4 vs. 5).

(iii) The decarboxylative reactions are competed by the solvolysis in some cases and the methyl ethers (III) are produced (runs 4,5, and 9).

(iv) The solvolytic reactions take place only on the esters (I) which have the free phenolic hydroxyl groups on the aryl rings of the alcoholic moiety (runs 4, 5-7, and 9 vs. 8,10, and 11). The free cinnamic acids (IV) are obtained in substantial amounts on every cases presumably through both base-catalyzed and metal-mediated solvolysis.

(v) The use of $Pt(PPh_3)_4$ as catalyst somewhat lowered the yield of II (run 3).

(vi) Palladium is more liable to cause the solvolysis than platinum (runs 4 and 6 vs. runs 1-3, and 5 respectively).

(vii) The decarboxylative reactions are effected also by palladium metal but in lower yield (run 4 vs. 1-3).

(viii) The reactions seem to proceed intramolecularly (run 9).

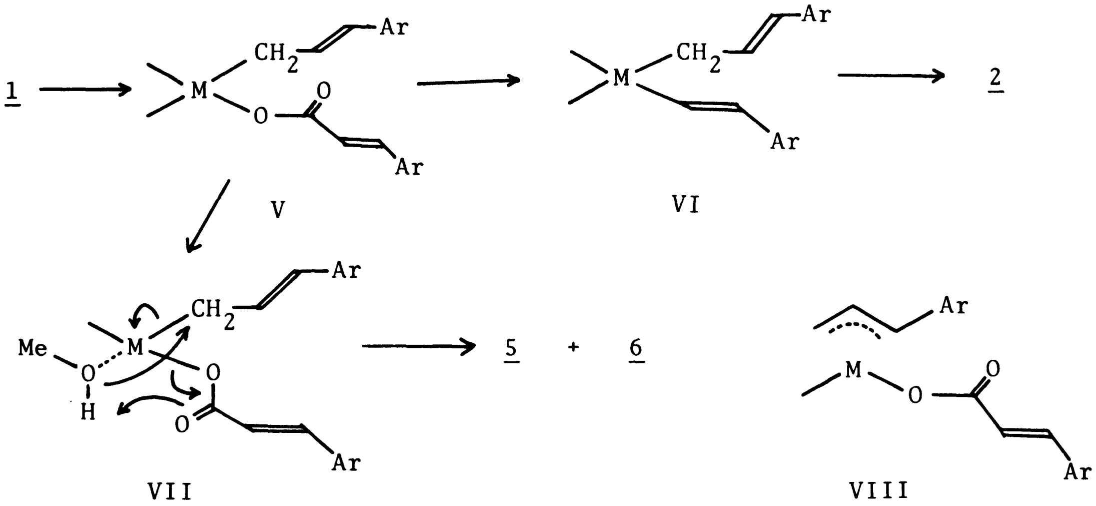
Although the conversion of I to II proceeds only in rather limited cases and with modest yields, the reaction seems to be quite unique. From its heterogeneous nature, the consideration of surface complex with the metal as the reaction intermediate would be the most pertinent. The fact depicted in the above item (i) indicates that the formation of phenolate anions from both aryl groups in I is necessary for the stronger coordination of both alcoholic and carboxylic moiety, and thus for the the progress of the reaction. The presence of the additional electron donating groups offers a further favorable condition. Of the two possible ways of the C-O rapture in the ester linkage, the one at the alkyl side would be preferable, since the other at the carbonyl side, which represents the more common way of the ester cleavage, hardly

TABLE

| Run No. | Substrate I | | | | | Metallic catalyst | Reaction condition* | Yield(%) of products† | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $R_1$ | $R_2$ | $R_3$ | $R_4$ | | | II | III | IV |
| 1. | Ia | OH | OMe | OH | OMe | Pt | a | 21 | - | 42 |
| 2. | Ia | | | | | Pt | b | 34 | - | 54 |
| 3. | Ia | | | | | $Pt(PPh_3)_4$ | b | 14 | - | 65 |
| 4. | Ia | | | | | Pd# | b | 17 | 35 | 53 |
| 5. | Ib | OH | H | OH | H | Pt | a | 6 | 38 | 80 |
| 6. | Ib | | | | | Pd# | b | - | 46 | 85 |
| 7. | Ic | OMe | OMe | OH | OMe | Pt | b | - | 53 | 79 |
| 8. | Id | OH | OMe | OMe | OMe | Pt | b | - | - | ?§ |
| 9. | Ie | OH | H | OH | OMe | Pt | b | 8 | 57 | 74 |
| 10. | If | H | H | H | H | Pt | a | - | - | ?¶ |
| 11. | Ig | OMe | OMe | OMe | OMe | Pt | a | - | - | -§ |

* a) The substrates **were** allowed to react overnight with 0.4-0.5 equiv. of the metal in $NaHCO_3$-$H_2O$-MeOH. b) The reactions carried out as in a) except that 0.9 equiv. of the metallic catalyst were used. † The products were separated by the chromatography on a silica gel column and the values are the isolated yields based on I. # commercial 'palladium black'. § Most of the starting material was recovered unaltered. ¶ The hydrolysis of the substrate in a large extent was observed.

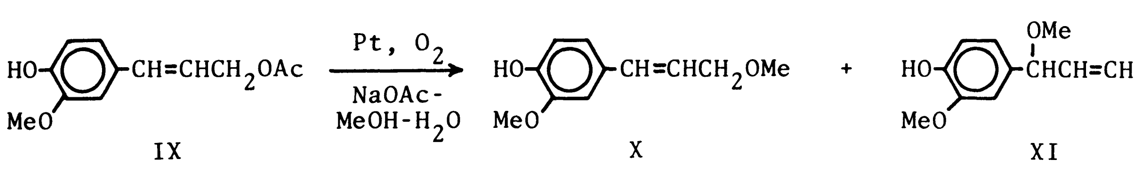
reconcile with the decarboxylation.[5] The reaction of the ester I, in which only the alcoholic part has sufficient coordinating power, leads to the exclusive formation of the solvolysis products as in the run 7.[6] Thus the participation of the π-electron system in the carboxylate moiety to the coordination with the metal would assist the decarboxylation in ester (I) in some way. The observed differences in the product distribution (solvolysis vs. decarboxylative coupling) between platinum- and palladium -catalyzed reactions would be explained from the known greater reactivity of palladium complex over platinum compound.[7] Thus, in the palladium mediated reactions, the intermediate complex is prone to be more easily attacked by the solvent molecule (as in VII) to yield III and IV, while the more abundant electron supply from the metal atom in the more stable platinum complex would tend to accelerate the decarboxylation and to afford the vinyl-allyl complex (VI) which collapses to the final product (II). It may also be possible that the π-allyl complex like VIII intervenes



specially in the reaction with palladium. Further studies are planned to extend the scope of the reaction and to elucidate the mechanism.

## References and Notes

1. Present address: Osaka Municipal Industrial Research Institute, Kita-ku, Osaka 530.
2. Cf. inter alia, T. Tsuji and K. Ohno, Synthesis, 157(1969); H.F. Wetter, ibid., 561(1976).
3. Compounds I are prepared by the reaction of cinnamoyl chlorides with the phenacyl esters of cinnamyl alcohols followed by removal of the protecting group. The details will be published elsewhere.
4. No reaction was observed when Ia was treated with Wilkinson's catalyst, $Rh(PPh_3)_3Cl$, in a mixture of $CH_2Cl_2$-benzene under refluxing.
5. Both types of ester cleavage have been reported on nickel mediated reaction; J. Ishizu, T. Yamamoto and A. Yamamoto, Chemistry Letters, 1091(1976).
6. The similar reaction of coniferyl acetate (IX) results in only methanolysis and two kinds of the product X and XI are obtained in this case; T. Tokoroyama and M. Nakamura, in preparation.



7. F.R. Hartley, "The Chemistry of Platinum and Palladium," p.377ff, Applied Science Publishers, London (1973).

(Received March 22, 1977)