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ANOMALOUS BEHAVIOUR OF SUBSTITUTED ALLYL BENZENES IN PALLADIUM(II) CATALYSED REACTION

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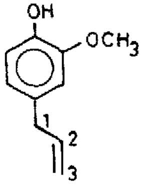
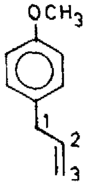
ABSTRACT: The Wacker reaction is one of the finest examples of transition metal promoted nucleophilic addition to olefins. An unusual observation has been made with regard to the normal Wacker process, whereby, the oxidation of eugenol (1) and methyl chavicol (2) does not lead to their respective carbonyl compounds. The reactions leading to the formation of two novel products and their mechanistic aspects are discussed.

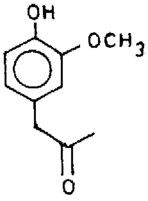
The Wacker reaction is an attractive route to synthesise carbonyl compounds from olefins[1,2]. In our studies on Wacker reaction, two model compounds were chosen, viz., 4-allyl, 2-methoxy phenol (Eugenol)(1) and 4-allyl anisole (Methyl chavicol) (2). Eugenol was subjected to the Wacker reaction in presence of hydrogen peroxide in ethanol medium using the catalytic system comprising of palladium chloride and cupric chloride. The expected product would be the methyl ketone (3).



(1)

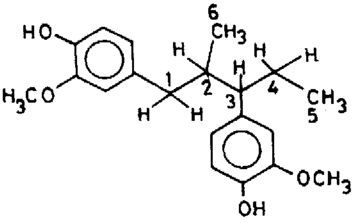


(2)



(3)

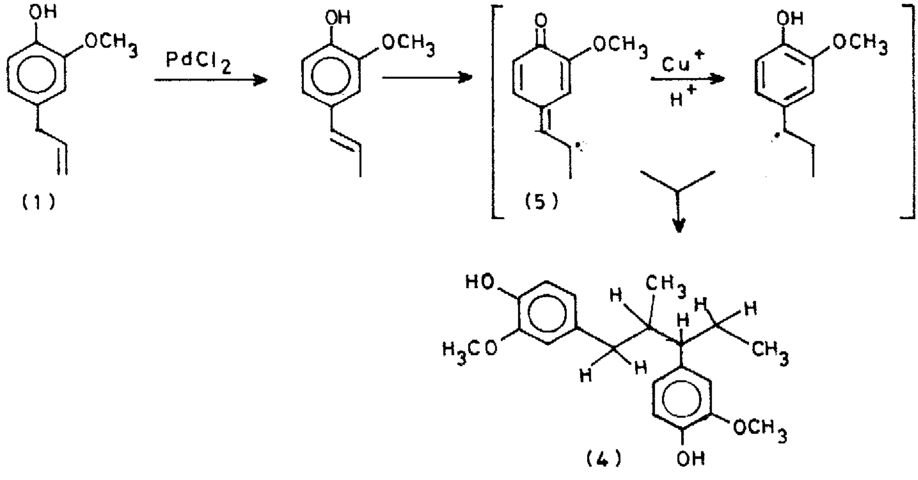
However, the ir spectrum of the product did not indicate a carbonyl functionality. The nmr spectrum indicated the presence of two methoxy groups at δ3.84 and δ3.94 and two exchangable hydroxyl protons at δ5.52. This observation proved that the product was a combination of two eugenol moieties. Two methyl groups, one appearing as a triplet at δ1.0 and the other as a doublet at δ1.02 indicated a dimeric structure for the product. The fact that the two methyls are split differently ruled out a cyclic dimeric structure. The structure (4) namely 2-methyl-1,3-bis(4-hydroxy-3-methoxy phenyl) pentane was found to be compatible with the spectral features[3].



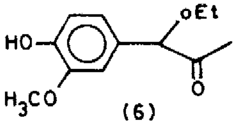
(4)

The structural elucidation was further augmented from the spin decoupling studies (Fig.1). These studies clearly indicated that the C-5 methyl group was coupled to the C-4 methylene protons (C-5 a triplet collapsed to a doublet on irradiation of individual C-4 protons). The C-4 protons were coupled to the benzylic methine proton, C-3. While the C-3, C-4 and C-5 segment was derived from a single eugenol moiety, the other half of the molecule, viz., C-1, C-2 and C-6 originated from a second molecule of eugenol. The connectivity between the two segments was established through the spin decoupling of C-2 methine proton which, on irradiation simplifies the C-3 proton multiplet to a broad singlet. Thus, it emerged that the product arises from the combination of C-2 and C-1 carbons of two eugenol molecules.

The formation of the dimeric product was unusual in view of the fact that Wacker reaction on terminal olefins has been known to yield methyl ketones[4]. The reaction can be rationalised through Scheme I.



The Wacker reaction was also carried out replacing hydrogen peroxide by oxygen in ethanol medium. GLC analysis of the product indicated a mixture of two compounds. The minor product was comparable with vanillin on GLC. Based on the spectral information[5], the product was assigned the structure(6). (Yield - 50%).



(6)

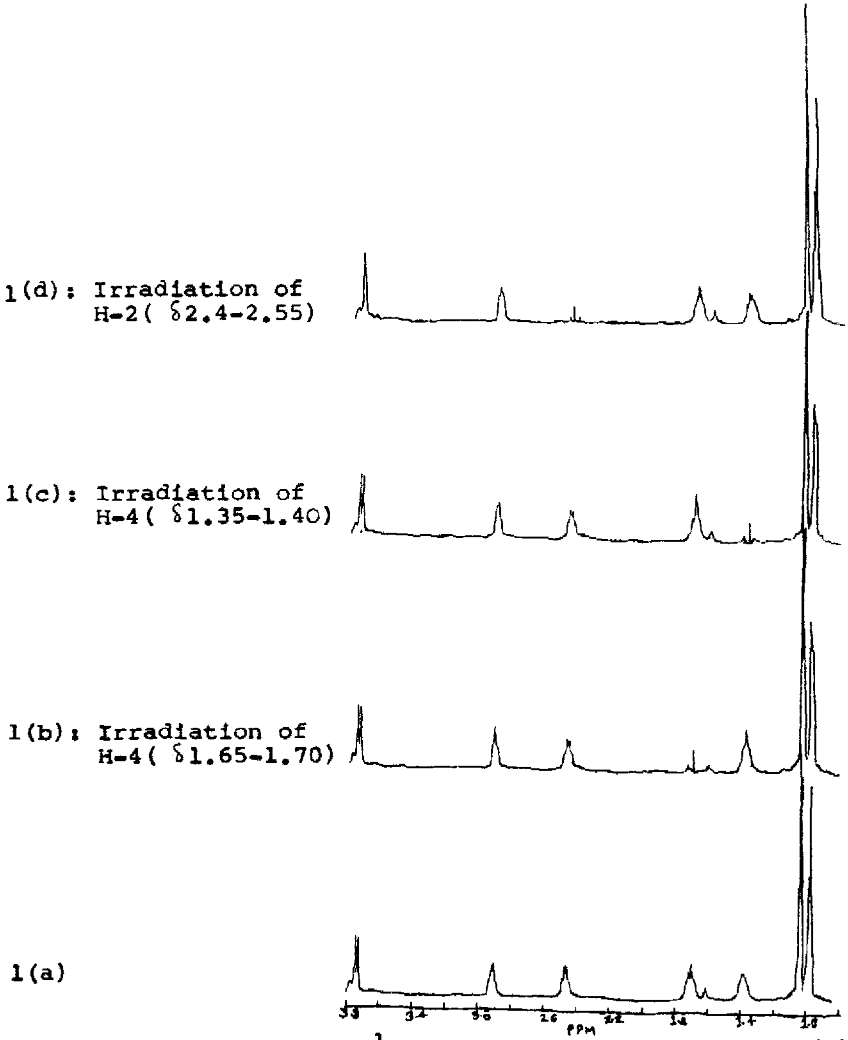
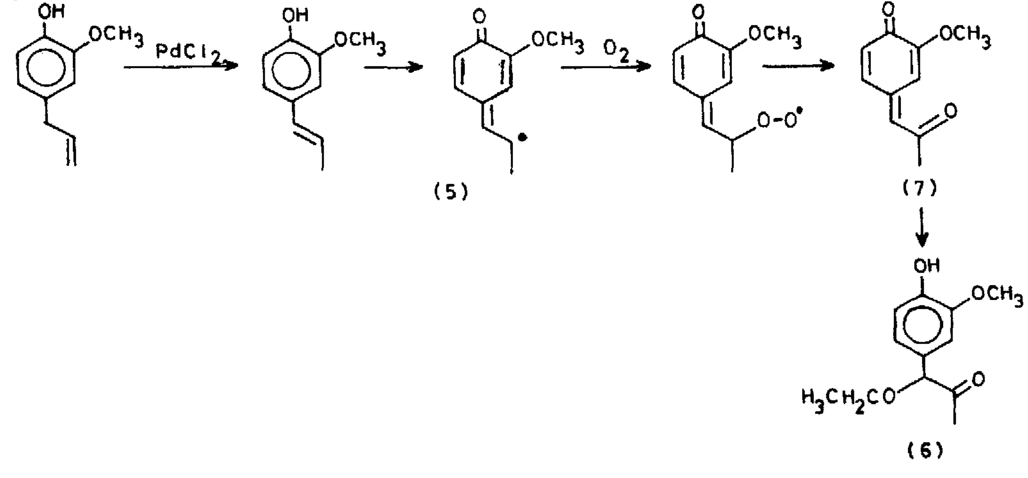


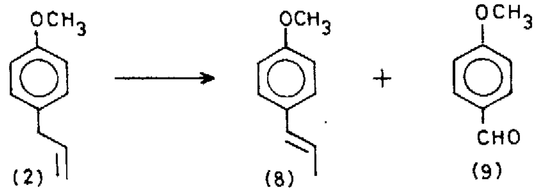
Fig.1 : 500 MHz ^{1}H-nmr part spectrum in $CDCl_3$(a) of compound (4) and its spin-decoupled spectra (b,c,d).

<u>Scheme II</u>



The formation of (6) can be rationalised through Scheme II involving the participation of oxygen as a quencher for the radical species (5) followed by the nucleophilic addition of the solvent ethanol to the quninone methide intermediate (7). Nucleophilic addition of alcohols to quinone methide systems is well documented[6].

The Wacker reaction on 4-allyl anisole (2) using both hydrogen peroxide and oxygen resulted in a major compound identified as anethole (8) and a trace amount of anisaldehyde (9).



(2) (8) (9)

Thus, in case of eugenol, the formation of the products 4 in absence of oxygen and 6 in presence of oxygen can be explained by the stabilisation of the radical intermediate 5 by the p-hydroxy group and its subsequent reaction. The same is not feasible in methyl chavicol.

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References

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The Organic Chemistry of Palladium, London and N.Y., Academic Press (1971).

2. J. Tsuji,
Organic Synthesis with Palladium Compounds, Springer-Verlag Berlin, Heidelberg (1980).

3. Data for compound (4)
m.p. 179-80°C , Yield - 25%
ir($CHCl_3$: ν_{max} cm^{-1} : 3380, 1620, 1450, 1380, 1040
^{1}Hnmr($CDCl_3$,500 MHz) δ:0.95(t,3H), 1.0(d,3H), 1.35-1.40(m,1H),1.65-1.70 (m,1H), 2.40-2.55(q,1H), 2.85-2.95(q,1H), 3.72(d,2H), 3.83(s,3H), 3.90 (s,3H), 5.50(s,1H), 5.52(s,1H), 6.45-6.85(m,6H).
Mass spectrum, m/e : 328(M^+), 298(Base Peak)
Elemental Analysis : $C_{20}H_{26}O_4$ Found : C 72.96, H 7.25
Calculated : C 73.17, H 7.31

4. J. Tsuji, I. Shimizu and K. Yamamoto,
Tetrahedron Letters, 295 (1976).

5. ^{1}Hnmr of compound (6) δ: ($CDCl_3$,100 MHz) : 1.28(t,3H), 2.1(s,13H), 3.4 (q,2H), 3.82(s,3H), 4.72(s,1H), 5.8(s,1H), 6.9-7.0(s,3H).

6. O.L. Chapman , M.R. Engel, J.P. Springer and J.C. Clardy,
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