o-Quinone Methides. Part 3.[1] X-Ray Crystal Structure and Reactivity of a Stable o-Quinone Methide in the E-Configuration.

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An X-ray crystal structure determination of 6-(4-methoxybenzylidene)-3,4-methylenedioxycyclohexa-2,4-dienone (2a), allows an E-configuration to be assigned to this stable o-quinone methide. The reactions of (2a) with magnesium phenolates and ethyl vinyl ethers show the same pathway previously observed with unstable o-quinone methides, indirectly confirming the generally preferred E-configuration for these intermediates.

o-Quinone methides[2] (2) are reactive intermediates involved in the chemistry and biochemistry of several phenolic compounds. They are generally obtained through elimination processes from suitable 2-hydroxybenzyl derivatives (1) or by oxidation of o-alkylphenols (3).

(1)   (2)   (3)
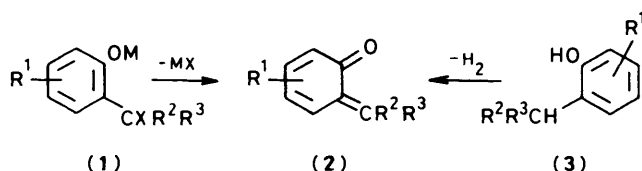
M = H, Metal, etc.   X = OH, NR_3^+, Cl, Br, I, etc.

The high reactivity of o-quinone methides results from the transformation of their high energy quinoid structures into more stable benzenoid products.[3] Since these intermediates are α,β-unsaturated carbonyl compounds, they add nucleophiles to the methide carbon[4] and/or react with dienophiles in Diels–Alder reactions.[1] In the absence of a suitable reagent, the great reactivity of o-quinone methides can lead to di- or trimerization, generally one molecule acting as heterodiene and the other as dienophile,[5] or to intramolecular reactions, as for example isomerization to the alkenyl phenols,[6] cyclizations to chromenes,[7] xanthens,[8] etc.

Our interest in o-quinone methide chemistry arose when we recognized the key role these intermediates play in co-ordinated reactions of phenol salts. In previous papers of this series we have reported indirect evidence for the formation of molecular complexes between these intermediates and phenols or their salts in media of low polarity; these direct the regioselectivity of the phenol functionalization towards an exclusive *ortho* pathway.[9] The hypothesis has also been propounded that formation of these complexes and their subsequent intermolecular reactions are favoured for E-o-quinone methides, whilst intramolecular reactions, leading to rearrangement products, are mainly observed with o-quinone methides constrained in the less stable Z-configuration.[6a]

Further studies on the stereochemistry of cycloaddition reactions between vinyl ethers and o-quinone methides, thermally generated by dehydration of the corresponding 2-hydroxybenzyl alcohols, indirectly confirmed that these intermediates react in the E-configuration.[1] Since there are no literature data on the configuration of these intermediates, and in order to obtain proof that stable o-quinone methides generally exist in the E-configuration we undertook an X-ray structural analysis of 6-(4-methoxybenzylidene)-3,4-methyl-

enedioxycyclohexa-2,4-dienone (2a).[5b] This product obtained by oxidation of the corresponding phenol system, dimerizes rapidly especially in polar solvents. Our first attempts to study the stereochemistry of this product in solution, using ASIS (Aromatic Solvent Induced Shifts), were unsuccessful owing to the presence of the dimer which leads to a very complex n.m.r. spectrum. Recently reported [13]C n.m.r. data

(2a)
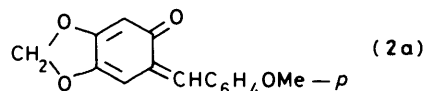
allow no definitive conclusion to be drawn as to the stereochemistry of o-quinone methide intermediates.[10]

We report here both the X-ray crystal and molecular structure of compound (2a) and some of its co-ordinated reactions with magnesium phenolates and cycloaddition processes with vinyl ethers.

Results and Discussion

Structure of Compound (2a).—The o-quinone methide (2a) crystallizes as pale orange prismatic needles in space group $P2_1/n$, with two independent molecules in the cell (Figure 1).

Various parameters connected with molecular geometry are listed in Table 1 and fractional atomic co-ordinates in Table 2.

Bond distances and angles relative to the phenyl rings of the two molecules are not considered because they were refined with constraints in idealized geometry.

As far as bond distances and angles are concerned the two molecules are very similar, within the limits of the calculated standard deviations. The values of 2.4(1)° for the angle between the planes C(2)–O(1)–C(3)–O(2)–C(4) and C(1)–C(2)–C(4)–C(5)–C(6)–C(7) and that of 1.2(1)° for the corresponding planes C(17)–O(5)–C(18)–O(6)–C(19) and C(16)–C(17)–C(19)–C(20)–C(21)–C(22) in the second molecule show the two fused rings are not coplanar.

The angles between the plane C(7)–C(8)–C(9) and the phenyl ring C(9)–C(14) is 168.1(2)° whereas that of the C(22)–C(23)–C(24) plane with the C(24)–C(29) phenyl ring is 169.7(2)°.

The angle between the aromatic moieties C(1)–C(7) and C(9)–C(14) is 36.3(3)° whereas the corresponding value for the angle between the C(16)–C(22) and C(24)–C(29) nuclei is 33.6(1)°.

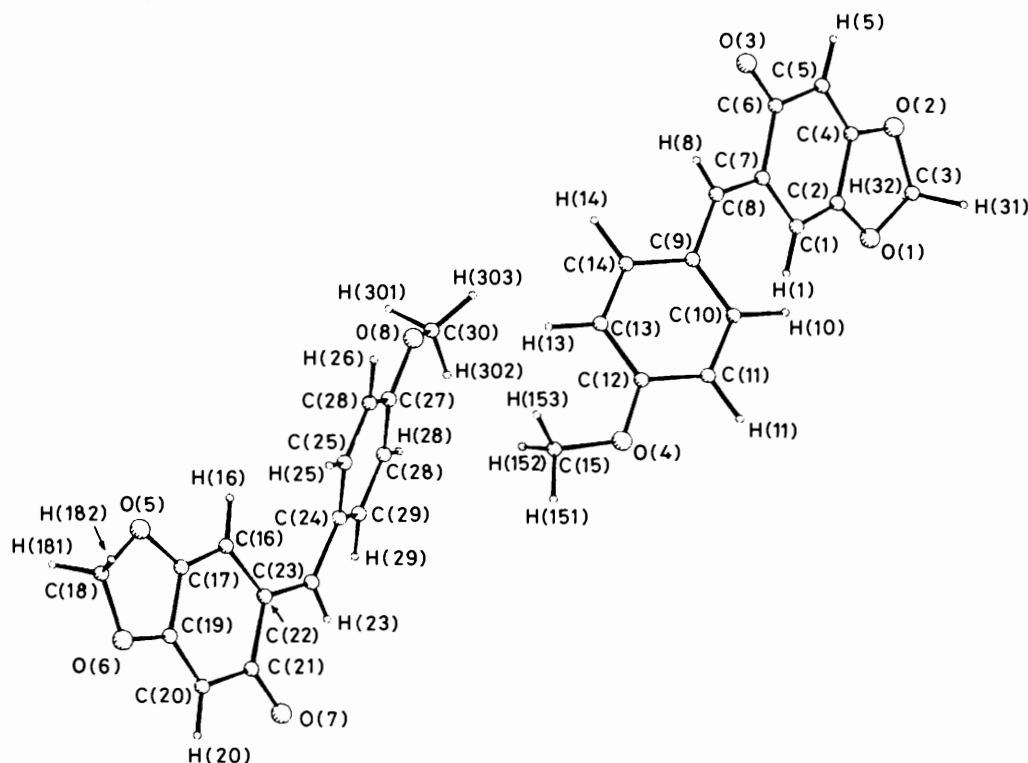The only X-ray crystal and molecular structure of a o-quinone methide reported in the literature is that for 1-

Figure. View of the two crystallographically independent molecular conformations in the crystal structure of (**2a**), with atoms numbered as in the text.

(diphenylmethylene)-1,2-naphthoquinone (**2b**),[11] so that some comparison must be made with the results for *p*-quinone methides.[12] The data confirm[11,12] that the phenyl and cyclohexadienone rings are not coplanar but are tilted in a position which is the best compromise between the maximum of electron delocalization and the minimum of steric interactions.

The values of the two torsion angles $C(7)-C(8)-C(9) = 131.1(3)°$ and $C(22)-C(23)-C(24) = 130.2(3)°$ are different in the two independent molecules and deviate significantly from the ideal value of sp² systems, probably as a result of steric interactions.
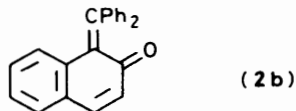
The closest intermolecular contact between non hydrogen atoms is greater than 3.048 Å, indicating no strong intermolecular forces in the lattice.

*Reactions of Compound (**2a**) with Magnesium Phenolates and Vinyl Ethers.*—Having verified the *E*-configuration of this stable *o*-quinone methide we studied its reactivity in two model reactions, in order to compare the results with those previously obtained with less stable intermediates. No reaction was observed at room temperature between (**2a**) and 2-t-butylphenoxymagnesium bromide in toluene and only by warming at 80 C for 24 h was the formation of a product (**4**), which derives from a regiospecific attack of (**2a**) on the *ortho* position of the phenolic nucleus, observed.

This confirms our previous hypothesis of the formation of an 'oriented complex' between (*E*)-*o*-quinone methides and phenolates as a key step for the *ortho*-regioselective functionalization of the latter.
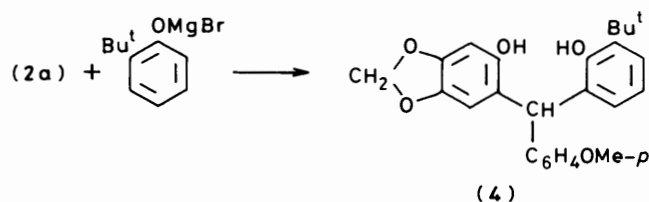
More useful information was obtained from the cycloaddition reactions of (**2a**) with ethyl vinyl ether as (*Z*)- and (*E*)-propenyl ethers, which produce at room temperature (**5**), (**6**), and (**7**) respectively. The structure of these cycloaddition products has been established on the basis of ¹H n.m.r. spectra which were compared with data obtained in a previous study.[1]

Also in this case the relative reactivity ($E > Z$) of the two isomers of propenyl ether follows the order observed in analogous reactions with unstable *o*-quinone methides.[1]

The cycloaddition reactions of (**2a**) seem to be more selective compared with that of *o*-quinone methides thermally generated from 2-hydroxybenzyl alcohols, which usually give a mixture of stereoisomers.

Probably the milder reaction conditions used with the stable compound (**2a**) can account for the higher selectivity observed.

The analogy between data reported in this study with those observed previously suggests that also unstable *o*-quinone methides react probably in the *E*-configuration, which has been established for compound (**2a**).

Experimental

For general directions and analytical instrumentation see ref. 1. Product (**2a**) was prepared by oxidation of 2-(4-methoxybenzyl)-4,5-methylenedioxyphenol (**3a**) according to ref. 5*b* and crystallized from diethyl ether.

Table 1. Relevant interatomic distances (Å), bond (°), and torsion angles (°) with standard deviation in parentheses for compound (2a)

(a) Bond lengths

Molecule 1		Molecule 2	
C(1)–C(2)	1.341(5)	C(16)–C(17)	1.342(5)
C(1)–C(7)	1.464(5)	C(16)–C(22)	1.455(4)
C(2)–O(1)	1.360(5)	C(17)–O(5)	1.368(4)
C(2)–C(4)	1.439(5)	C(17)–C(19)	1.429(3)
O(1)–C(3)	1.414(5)	O(5)–C(18)	1.422(5)
C(3)–O(2)	1.439(5)	C(18)–O(6)	1.439(5)
O(2)–C(4)	1.354(5)	O(6)–C(19)	1.347(5)
C(4)–C(5)	1.353(6)	C(19)–C(20)	1.349(5)
C(5)–C(6)	1.441(6)	C(20)–C(21)	1.459(6)
C(6)–O(3)	1.242(4)	C(21)–O(7)	1.236(4)
C(6)–C(7)	1.510(3)	C(21)–C(22)	1.507(3)
C(7)–C(8)	1.353(5)	C(22)–C(23)	1.362(5)
C(8)–C(9)	1.486(5)	C(23)–C(24)	1.480(5)
C(12)–O(4)	1.370(3)	C(27)–O(8)	1.372(3)
C(15)–O(4)	1.421(5)	C(30)–O(8)	1.429(6)

(b) Bond angles

C(2)–C(1)–C(7)	118.0(3)	C(17)–C(16)–C(22)	117.9(2)
C(1)–C(2)–C(4)	123.0(3)	C(16)–C(17)–C(19)	123.2(3)
C(1)–C(2)–O(7)	128.2(3)	C(16)–C(17)–O(5)	127.9(2)
O(1)–C(2)–C(4)	108.7(3)	O(5)–C(17)–C(19)	108.9(3)
C(2)–O(1)–C(3)	107.2(3)	C(17)–O(5)–C(18)	107.5(3)
O(1)–C(3)–O(2)	105.5(3)	O(5)–C(18)–O(6)	106.9(3)
C(3)–O(2)–C(4)	107.1(3)	C(18)–O(6)–C(19)	108.3(3)
C(2)–C(4)–O(2)	108.3(3)	C(17)–C(19)–O(6)	108.4(3)
O(2)–C(4)–C(5)	128.2(4)	O(6)–C(19)–C(20)	128.1(3)
C(2)–C(4)–C(5)	123.5(3)	C(17)–C(19)–C(20)	123.5(3)
C(4)–C(5)–C(6)	117.6(4)	C(19)–C(20)–C(21)	117.9(4)
C(5)–C(6)–C(7)	119.5(3)	C(20)–C(21)–C(22)	118.2(3)
C(5)–C(6)–O(3)	120.1(3)	C(20)–C(21)–O(7)	119.9(3)
O(3)–C(6)–C(7)	120.4(3)	O(7)–C(21)–C(22)	121.9(3)
C(1)–C(7)–C(6)	118.4(3)	C(16)–C(22)–C(21)	119.2(3)
C(6)–C(7)–C(8)	117.3(3)	C(21)–C(22)–C(23)	116.2(3)
C(1)–C(7)–C(8)	124.2(3)	C(16)–C(22)–C(23)	124.5(3)
C(7)–C(8)–C(9)	131.1(3)	C(22)–C(23)–C(24)	130.2(3)
C(8)–C(9)–C(14)	117.2(2)	C(23)–C(24)–C(29)	116.5(2)
C(8)–C(9)–C(10)	122.9(2)	C(23)–C(24)–C(25)	123.4(2)
C(11)–C(12)–O(4)	115.8(2)	C(26)–C(27)–O(8)	115.4(2)
C(13)–C(12)–O(4)	124.8(2)	C(28)–C(27)–O(8)	124.6(2)
C(12)–O(4)–C(15)	118.4(3)	C(27)–O(8)–C(30)	118.0(3)

(c) Torsion angles

C(2)–C(1)–C(7)–C(8)	175.3(3)
O(3)–C(6)–C(7)–C(8)	2.2(5)
C(6)–C(5)–C(4)–O(2)	177.3(4)
C(7)–C(1)–C(2)–O(1)	−174.9(3)
C(4)–C(5)–C(6)–O(3)	−178.2(4)
C(1)–C(7)–C(6)–O(3)	178.1(3)
C(1)–C(7)–C(8)–C(9)	5.2(6)
C(6)–C(7)–C(8)–C(9)	−179.1(3)
C(7)–C(8)–C(9)–C(10)	31.9(5)
C(11)–C(12)–O(4)–C(15)	−178.6(3)
C(17)–C(16)–C(22)–C(23)	179.8(3)
O(7)–C(21)–C(22)–C(23)	0.1(5)
C(21)–C(20)–C(19)–O(6)	179.7(3)
C(22)–C(16)–C(17)–O(5)	−179.3(3)
C(19)–C(20)–C(21)–O(7)	−179.3(4)
C(16)–C(22)–C(21)–O(7)	178.2(3)
C(16)–C(22)–C(23)–C(24)	5.9(6)
C(21)–C(22)–C(23)–C(24)	−176.1(3)
C(22)–C(23)–C(24)–C(25)	29.3(5)
C(26)–C(27)–O(8)–C(30)	177.5(3)

Crystal Data.—$C_{15}H_{12}O_4$, $M = 256.26$ Monoclinic, $a = 10.716(2)$, $b = 22.431(5)$, $c = 10.443(2)$ Å, $\beta = 99.48(3)°$, $U = 2\,475.9(9)$ Å^3, $Z = 8$, $D_c = 1.375$ g cm^{-3}, $F(000) = 1\,072$.

Table 2. Fractional atomic co-ordinates ($\times 10^4$) for non-hydrogen atoms in compound (2a)

Atom	x	y	z
C(1)	354(3)	6 440(2)	5 252(3)
C(2)	1 121(3)	6 649(1)	4 462(3)
O(1)	1 740(2)	6 337(1)	3 643(2)
C(3)	2 528(4)	6 744(2)	3 119(4)
O(2)	2 176(2)	7 335(1)	3 461(3)
C(4)	1 371(3)	7 274(2)	4 325(3)
C(5)	822(3)	7 708(2)	4 939(4)
C(6)	−51(3)	7 528(1)	5 778(4)
O(3)	−605(3)	7 910(1)	6 338(3)
C(7)	−290(3)	6 873(1)	5 965(3)
C(8)	−1 153(3)	6 727(2)	6 723(3)
C(9)	−1 596(1)	6 137(1)	7 116(2)
C(10)	−817(1)	5 635(1)	7 289(2)
C(11)	−1 291(1)	5 094(1)	7 660(2)
C(12)	−2 545(1)	5 054(1)	7 857(2)
C(13)	−3 324(1)	5 556(1)	7 684(2)
C(14)	−2 850(1)	6 097(1)	7 314(2)
O(4)	−2 906(2)	4 505(1)	8 241(3)
C(15)	−4 178(4)	4 427(2)	8 423(5)
C(16)	−10 351(3)	3 541(1)	9 774(3)
C(17)	−11 189(3)	3 351(1)	10 507(3)
O(5)	−11 975(2)	3 688(1)	11 122(3)
C(18)	−12 696(4)	3 290(2)	11 769(4)
O(6)	−12 289(2)	2 696(1)	11 519(5)
C(19)	−11 402(3)	2 735(1)	10 746(3)
C(20)	−10 794(3)	2 287(2)	10 246(4)
C(21)	−9 868(3)	2 443(1)	9 422(4)
O(7)	−9 301(3)	2 045(1)	8 935(3)
C(22)	−9 625(3)	3 094(1)	9 204(3)
C(23)	−8 746(3)	3 219(2)	8 438(3)
C(24)	−8 234(2)	3 799(1)	8 092(2)
C(25)	−8 138(2)	4 298(1)	8 900(2)
C(26)	−7 674(2)	4 834(1)	8 490(2)
C(27)	−7 307(2)	4 871(1)	7 271(2)
C(28)	−7 403(2)	4 372(1)	6 463(2)
C(29)	−7 866(2)	3 836(1)	6 874(2)
O(8)	−6 854(3)	5 416(1)	6 965(3)
C(30)	−6 511(4)	5 488(2)	5 708(4)

Space group $P2_1/n$ ($P2_1/c$, No. 14), Cu-K_α radiation, $\lambda = 1.541\,78$ Å, μ (Cu-K_α) $= 7.9$ cm^{-1}.

Data Collection and Processing.—A pale orange transparent crystal of dimensions *ca.* $0.2 \times 0.3 \times 0.6$ mm was used; the lattice parameters were refined by least-squares using 25 $(\theta,\chi,\phi)_{hkl}$ measurements taken on a Siemens AED single-crystal diffractometer on-line to a General Automation Jumbo 220 microcomputer.[13]

Intensity data of 7 336 reflections were collected at room temperature with the ω-2θ scan technique and Ni-filtered Cu-K_α radiation, using a scintillation counter with a pulse-height analyser; one standard reflection every 50 was monitored. After the averaging of the 7 336 symmetry-related reflections remained 3 673 independent reflections ($R = 0.015$), 2 417 of which were considered observed [$I > 2\sigma(I)$] and corrected for Lorentz and polarization, but not for absorption effects.

Structure Analysis and Refinement.—The structure was solved by direct methods[14] using normalized structure factors with E 1.2; most of the non-hydrogen atoms came out from one of the E map with the highest figure of merit. Owing to the large number of parameters, the full-matrix least-squares refinement[14] was performed with rigid-body constraints for the C(9)–C(14) and C(24)–C(29) benzene rings allowing anisotropic thermal parameters for all the remaining non-hydrogen atoms.

$Ar = p - MeOC_6H_4$
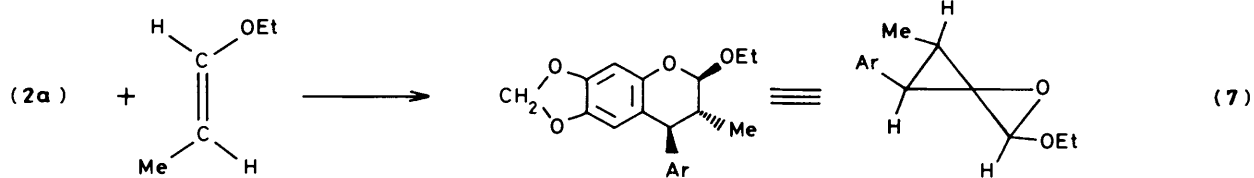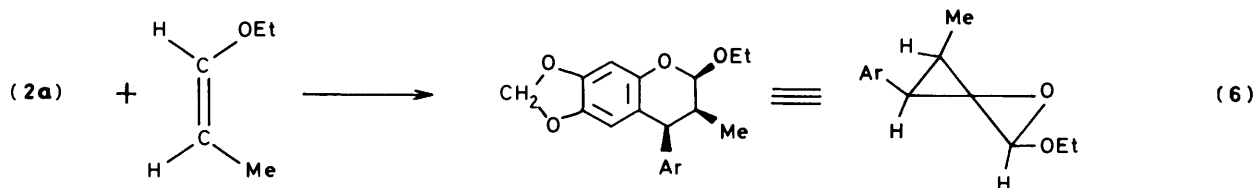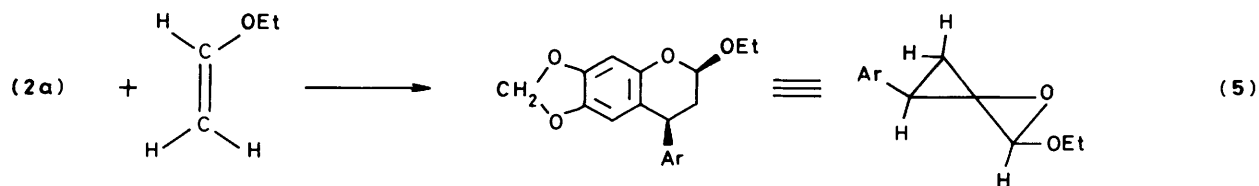
The hydrogen atoms of the benzene rings and of the methyl groups were given idealized geometries, the other ones were refined with isotropic thermal parameters. The final R value for the 2 417 observed reflections was 5.5% (R_w = 6.8; w = $1/\{\sigma^2(F) + 0.3F^2\}$). All calculations were carried out on a CYBER 76 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Casalecchio di Reno, Bologna.

Final atomic co-ordinates with thermal parameters for observed reflections are deposited as Supplementary Publication (SUP. No. 56578 (27 pp.)].* The structure factors are available on request from the Editorial office.

Geometric calculations were performed with the program PARST.[15]

Reaction of Compound (2a) *with* 2-t-*Butylphenoxymagnesium Bromide.*—To a solution of 2-t-butylphenoxymagnesium bromide (1 mmol) in toluene (10 ml) was added (2a) (1 mmol). The mixture was heated at 80 °C for 10 h, quenched with saturated aqueous ammonium chloride, and extracted with diethyl ether. The extracts were dried (Na$_2$SO$_4$), and evaporated and the product (4) purified by preparative t.l.c. using hexane–ethyl acetate (9:1) as eluant.

2-[α-(2-*Hydroxy*-3-*t*-*butylphenyl*)-p-*methoxybenzylidene*]-4,5-*methylenedioxyphenol* (4). It was obtained as a colourless oil in a total yield of 25%, δ$_H$(200 MHz, CDCl$_3$) 7.20 (1 H, dd, J 7.78 and 1.42 Hz, ArH), 7.08 (2 H, d, J 9.21 Hz, ArH), 6.85 (2 H, d, J 9.21 Hz, ArH), 6.85 (2 H, d, J 9.21 Hz, ArH), 6.80 (1 H, t, J 7.78 Hz, ArH), 6.66 (1 H, dd, J 7.78 and 1.42 Hz, ArH), 6.42 (1 H, s, ArH), 6.32 (1 H, s, ArH), 5.87 (2 H, s, CH$_2$), 5.64 (1 H, s, Ar$_3$CH), 5.10 (1 H, s, OH), 5.00 (1 H, s, OH), 3.79 (3 H, s, Me), and 1.39 (9 H, s); m/z 406 (M^+, 1%), 258 (51), 225 (38), 150 (63), and 108 (100) (Found: C, 73.9; H, 6.4. C$_{25}$H$_{26}$O$_5$ requires C, 73.86; H, 6.45%).

Reaction of Compound (2a) *with Vinyl Ethers.*—*Method A.* The appropriate vinyl ether (2 mmol) was added to a solution of (2a) (1 mmol) in hexane (20 ml). The reaction mixture was kept at room temperature for 20 h. After this time the reactions mixtures of (2a) with ethyl vinyl ether and (E)-prop-1-enyl ethyl ether were colourless solutions, whilst the reaction mixture of (2a) with (Z)-prop-1-enyl ethyl ether was an intense orange-red. The solvent was removed under reduced pressure and the residue was purified by t.l.c. with hexane–ethyl acetate (8:2, v/v).

Method B. A mixture of (3a) (1 mmol), Ag$_2$O (1.2 mmol), and the appropriate vinyl ether (3 ml) was kept at room temperature for 48 h. The reactions were checked after 4 and 48 h by g.l.c. using eicosane as internal standard. The yield (%) of the product (5), (6) and (7) were 35, 3, 25 after 4 h and 93, 40, 98 after 48 h respectively. The reaction mixtures were filtered, the filtrates evaporated under reduced pressure, and the crude products recrystallized from diethyl ether.

Product (5). Colourless needles, m.p. 114—116 °C (lit.,[5b] 116—117 °C); δ$_H$ (200 MHz, CDCl$_3$) 7.08 (2 H, d, J 8.78 Hz), 6.83 (2 H, d, J 8.78 Hz), 6.42 (1 H, s), 6.15 (1 H, s), 5.80 (2 H, s), 5.16 (1 H, dd, J 2.68 and 8.30 Hz, 2-H), 4.04 (1 H, dd, J 6.20 and 10.94 Hz, 4-H), 4.03 (1 H, dq, J 9.42 and 7.24 Hz), 3.78 (3 H, s), 3.63 (1 H, dq, J 9.42 and 7.24 Hz), 2.32 (1 H, ddd, J 2.68, 6.20 and 13.49 Hz, 3-H), 2.07 (1 H, ddd, J 8.30, 10.94 and 13.49 Hz, 3'-H), and 1.25 (3 H, t, J 7.24 Hz); m/z 328 (24), 282 (32), 255 (100), and 240 (25), 225 (61).

Product (6). Colourless needles, m.p. 108—110 °C, δ$_H$ (200 MHz, CDCl$_3$) 7.08 (2 H, d, J 8.78 Hz), 6.80 (2 H, d, J 8.78 Hz), 6.44 (1 H, s), 6.31 (1 H, s), 5.84 (2 H, s), 5.05 (1 H, d, J 2.20 Hz, 2-H), 4.16 (1 H, d, J 6.84, 4-H), 3.97 (1 H, dq, J 9.62 and 7.08), 3.78 (3 H, s), 3.58 (1 H, dq, J 9.62 and 7.08), 2.28 (1 H, m, J 2.20, 6.84 and 6.84 Hz, 3-H), 1.20 (3 H, t, J 7.08 Hz), and 0.81 (3 H, d, J 6.84); m/z 342 (50), 281 (12), 255 (100), and 225 (58). (Found: C, 70.1; H, 6.5. C$_{20}$H$_{22}$O$_5$ requires C, 70.14; H, 6.48%).

Product (7). Colourless needles, m.p. 122—124 °C, δ$_H$ (200 MHz, CDCl$_3$) 7.04 (2 H, d, J 8.78 Hz), 6.83 (2 H, d, J 8.78 Hz), 6.42 (1 H, s), 6.06 (1 H, s), 5.80 (2 H, s), 4.76 (1 H, d, J 8.06 Hz, 2-

H), 4.06 (1 H, dq, *J* 7.08 and 9.42 Hz), 3.79 (3 H, s), 3.65 (1 H, dq, *J* 7.08 and 9.42), 3.52 (1 H, d, *J* 10.26 Hz, 4-H), 2.05 (1 H, m, *J* 10.26, 6.59, 8.06 Hz, 3-H), 1.27 (3 H, t, *J* 7.08 Hz), and 0.92 (3 H, d, *J* 6.59); m/z 342 (57), 281 (13), 255 (100), 241 (25), and 225 (81) (Found: C, 70.2; H, 6.4. $C_{20}H_{22}O_5$ requires C, 70.14; H, 6.48%).

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