Diels-Alder Reactions of 2,4-Cyclohexadienones.* II.**

Stereoselectivity in the Dimerisation of o-Quinols

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Chemical evidence is presented for the steric arrangement at carbon atoms 5 and 9 of o-quinol dimers.

Formation of the phenolic compounds 9 − 11 on treatment of the diacetates of dimers 1 − 3 with ethanolic potassium hydroxide is interpreted as being due to an E2 elimination of acetic acid requiring trans-position of the acetoxy group at C-5 with regard to the hydrogen atom at C-4a.

Furthermore, it is shown that the C-9, C-10 ketol bridge in dimers 1 − 3 is cleaved by periodate, whereas dimers 4 and 5 are stable towards the same oxidant. Considering the accepted mechanism of ketol cleavage by periodate, these results indicate that the hydroxyl group at C-9 is oriented as shown in formulae 1 − 5.

The structural interpretations given in this paper are in harmony with the structures of dimers 1, 2 and 4 earlier established by X-ray crystallography.

Periodate oxidation of 2,6-,[4] 2,5-,[2] and 2,4-dimethylphenol [3] as well as of 2,4,6-trimethylphenol [4] results in the formation of the corresponding 6-hydroxy-6-methyl-2,4-cyclohexadienones ("o-quinols"), which rapidly dimerise by Diels-Alder reaction to give compounds 2 − 5. The parent compound (1)[5] of these methyl homologous dimers has been obtained by acid hydrolysis of 6-acetoxy-6-methyl-2,4-cyclohexadienone which, in turn, was prepared by treatment of o-cresol with lead tetraacetate. In each case, only one of several possible isomers with different structural and steric orientation has been detected, indicating that
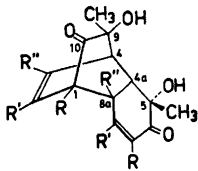
these Diels-Alder dimerisations are regiospecific and stereospecific or at least highly selective in both respects.

As reported in the preceding paper,[2] the structure of the parent dimer (1) was established by the finding that it is reduced by Raney nickel to a product which is also obtained from a dibromo derivative (1, CH₂Br instead of CH₃),[6] the structure of which had been determined by X-ray analysis.[7] After completion of the work described in the present paper (cf. also preliminary communication [1]), X-ray analyses of dimers 2 and 4 were reported; they showed these dimers to be analogous to 1 with regard to both structural orientation and the steric arrangement of the tert. carbinol groups (C-5 and C-9).[8]

Although it seemed rather likely that the o-quinol dimers obtained from 2,5-dimethylphenol and 2,4,6-trimethylphenol, i.e. dimers 3 and 5, would have the same structural and steric characteristics as dimers 1, 2 and 4, experimental confirmation was desirable. The structural orientation of the diene and dienophile moieties in dimer 5 has been clarified earlier from its NMR spectrum.[1,2] Furthermore, this orientation as well as endo configuration of 5 has been established by photochemically induced intramolecular cycloaddition.[9] In the present paper, chemical evidence regarding the stereochemistry of C-atoms 5 and 9 in the o-quinol dimers will be presented.

Steric arrangement at C-5. − In previous work [4] it was shown that the diacetates 6 and 7 of o-quinol dimers 1 and 2 on treatment with ethanolic potassium hydroxide give the phenolic

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* Part XII in the series "Periodate Oxidation of Phenols". Preliminary communication, see Part X.[1]
** Part I, see Ref. 2.

CH₃ OH
R″
R″ OH
R′ R OH
CH₃
R′ O
R

1 R = R′ = R″ = H
2 R = CH₃; R′ = R″ = H
3 R′ = CH₃; R = R″ = H
4 R″ = CH₃; R = R′ = H
5 R = R″ = CH₃; R′ = H
6 = *1*, OAc instead of OH
7 = *2*, OAc instead of OH
8 = *3*, OAc instead of OH

CH₃ OH
CH₃
R′ R OH
R′
R
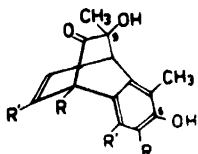
9 R = R′ = H
10 R = CH₃; R′ = H
11 R′ = CH₃; R = H
11a = *11*, OAc instead of 6-OH
11b = *11*, OAc instead of 6-OH and 9-OH

compounds *9* and *10* in addition to the non-acetylated dimers. Similarly, phenol *11* has now been obtained from the diacetate *8* [2] of dimer *3*.

Kende and MacGregor [10] found that the fluorine-containing analogue of dimer *2* (F instead of OH), when treated with KOH-C₂H₅OH, is converted into the fluorine analogue of phenol *10* (F instead of the *tert.* OH). Assuming this reaction to be due to E2 elimination of hydrogen fluoride from the unbridged ring, these authors concluded that the fluorine atom at C-5 is in a position *trans* to the hydrogen atom at C-4a, the favourable *anti* coplanar orientation of the leaving groups then being easily attained.

By analogy, the formation of phenols *9* − *11* from diacetates *6* − *8* suggested that OAc at C-5 is in a position *trans* to H at C-4a, favouring E2 elimination of HOAc * with concomitant

* This view is supported by results discussed in a recent monograph according to which the *anti* mechanism is greatly preferred to the *syn* mechanism for E2 reactions in six-membered rings (Saunders, Jr., W. H. and Cockerill, A. F. *Mechanism of Elimination Reactions*, Wiley, New York 1973).

aromatisation of the unbridged ring. For the *endo* forms of the corresponding non-acetylated dimers *1* − *3* the steric arrangement at C-5 then could be assumed to be as shown in the formulae given above. As mentioned earlier, this steric orientation as well as *endo* configuration has been finally established for dimers *1* [2,6,7] and *2* [8] by X-ray diffraction.

The base-catalysed elimination of acetic from the unbridged ring of diacetates *6* − *8* may be assumed to be preceded by proton abstraction from C-8a, aromatisation of the resulting enol constituting a driving force for the elimination (*cf.* also Ref. 10). The latter reaction then competes successfully with the hydrolysis of the C-5 acetoxy group.

In the diacetates of dimers *4* and *5*, however, enolisation and aromatisation of the unbridged ring are prevented by the methyl substituent at C-8a. Treatment of these diacetates with KOH-C₂H₅OH simply produces the corresponding dialcohols, no elimination of acetic acid being observed. [3,4]

Steric arrangement at C-9. In the periodate treatment of 2,6- [4] and 2,4-dimethylphenol [3] as well as of 2,4,6-trimethylphenol [4] both the formation of the *o*-quinols and their Diels-Alder dimerisation are fast reactions, consumption of the starting phenols and formation of dimers *2*, *4*, and *5* being complete after reaction times of a few minutes. These dimers contain two ketol groupings and therefore could be expected to consume further periodate undergoing ketol cleavage. In fact, prolonged treatment of 2,6-dimethylphenol with excess sodium metaperiodate or periodic acid produced a monocarboxylic acid (*13*).

Oxidation of 2,5-dimethylphenol with sodium periodate proceeds more slowly than that of the above-mentioned phenols, unchanged starting material still being detectable after reaction times of 1 − 2 h. From the reaction mixtures, dimer *3* as well as its cleavage product (*14*) was isolated. The latter was also obtained on oxidation of 2,5-dimethylphenol with periodic acid.

Acids *13* and *14* also formed when the isolated dimers *2* and *3*, respectively, were oxidised with periodate. Similar oxidation of dimer *1* [5] provided acid *12*.

Periodate as well as periodic acid thus cleaved only one of the two ketol groupings

present in dimers $1-3$. The resulting mono-carboxylic acids remained unchanged even on several hours' treatment with these oxidants.

Assignment of structures $12-14$ is based on spectroscopic evidence. The UV spectra
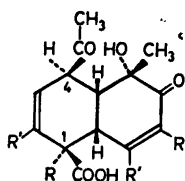
12 R=R'=H
13 R=CH₃ ; R'=H
14 R'=CH₃ ; R=H

of o-quinol dimers $1-5$ in ethanol exhibit a high intensity band with λ_{max} around 210 nm (ε about 10 000),[4] which can be ascribed to charge transfer within the β,γ-unsaturated carbonyl system (2,3-ethylenic bond and C-10 carbonyl group) in the photoexcited state[11] ("photodesmotic band"[12]); cf. also Ref. 6. They further show a comparatively strong absorption band around 310 nm ($\varepsilon = 150 - 330$) involving the $n \rightarrow \pi^*$ absorption of the α,β-unsaturated carbonyl system as well as the characteristically intensified $n \rightarrow \pi^*$ absorption of the β,γ-unsaturated carbonyl system. In the spectra of acids $12-14$, however, the photodesmotic band is lacking, and the $n \rightarrow \pi^*$ bands (λ_{max} 328 nm) due to the α,β-unsaturated carbonyl grouping are of normal intensity ($\varepsilon = 83$, 83, and 100 for 12, 13, and 14, respectively). The $\pi \rightarrow \pi^*$ absorptions of the latter

chromophores in acids $12-14$ are very similar to those reported[4] for the corresponding dimers $1-3$, their locations being in harmony with the predicted[13] ones. Finally, the $n \rightarrow \pi^*$ absorption of the CO group at C-9 in $12-14$ is partially overlapped by the $\pi \rightarrow \pi^*$ and the $n \rightarrow \pi^*$ bands of the conjugated carbonyl system and gives rise to shoulders at λ_{max} 280, 285, and 295 nm for 12, 13, and 14, respectively.

The UV spectra of the methyl esters prepared from acids $12-14$ were closely similar to those of the free acids.

Thus, UV spectroscopy clearly indicated that of the two ketol groupings present in dimers $1-3$ the 9,10-ketol bridge was cleaved specifically. This finding is corroborated by the following IR spectroscopic data (Table 1).

Cleavage of the 9,10-ketol bridge in dimers $1-3$ gives rise to a non-conjugated carboxylic acid containing an unconjugated keto group as well as the conjugated carbonyl group initially present. Cleavage of the 5,6-hydroxyketone grouping, however, would produce an α,β-unsaturated carboxylic acid containing two non-conjugated keto groups. The locations of the lowest frequency bands of the acids and their methyl esters (Table 1) agree with those expected for α,β-unsaturated keto groups (cf. the corresponding bands for dimers $1-3$) but are below the range typical of α,β-unsaturated COOH (1690−1715 cm⁻¹)[14] and far below the range accepted for α,β-unsaturated esters (1717−1730 cm⁻¹),[14] respectively.

Contrary to dimers $1-3$, dimers 4 and 5 proved to be stable towards periodate. The presence of a methyl substituent at C-8a in

Table 1. Infrared absorption bands (cm⁻¹, KBr) of o-quinol dimers $1-3$, carboxylic acids $12-14$ and methyl esters $12a-14a$.

Substance	CO (C-10)	CO (at C-4)	COOH	COOCH₃	α,β-unsaturated CO
Dimer 1	1723				1679
Acid 12		1733	1700		1682
Ester $12a$		1720		1742	1679
Dimer 2	1723				1680
Acid 13		1720	1695		1672
Ester $13a$		1716		1729	1670
Dimer 3	1724				1662
Acid 14		1728...............1710			1640
Ester $14a$		1720......................1730			1663

the two latter dimers suggests the following explanation for this striking difference in the behaviour of the two groups of dimers.

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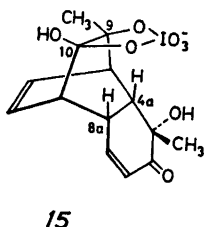
According to Bunton and Shiner,[15] periodate cleavage of α-hydroxy ketones is initiated by nucleophilic attack of periodate oxygen upon the carbonyl group, probably accompanied by co-ordination of the α-hydroxyl group to the periodate, resulting in the formation of a cyclic periodate ester intermediate.[16] Since the stereochemistry of the C-9 carbinol group is established for dimers *1* [2] and *2* [8] (see formulae), and formation of the cyclic intermediate requires approach from the side of the C-9 hydroxyl group, the structure of this intermediate will be as illustrated by formula *15*.

The resistance to periodate of dimers *4* and *5* then suggested that these dimers have the same steric arrangement at C-9 as dimer *1*, the C-9 hydroxyl group being directed towards the C-4a, C-8a linkage.[1] With this arrangement it is easily understood that the methyl group at C-8a in *4* and *5* by steric hindrance prevents the periodate to approach the ketol bridge and to form intermediates of type *15*.* As mentioned earlier, this configuration of C-9 has been confirmed in the case of dimer *4* by X-ray analysis.[8]

16   *17*

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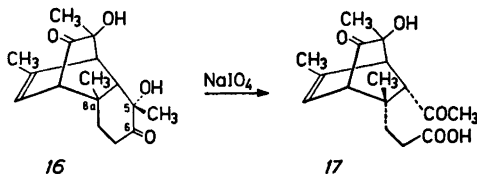
* If the configuration of C-9 would be opposite to that given in formulae *1 — 5*, periodate cleavage would be possible for all dimers. Inspection of Dreiding models indicates that, in this case, the C-10 hydroxyl group of the cyclic intermediate corresponding to *15* would not sterically interfere with the C-8a methyl group.

The fact that neither the α,β-conjugated ketol group of the o-quinol dimers *1 — 5* nor that present in acids *12 — 14* is cleaved by periodate may be explained by the assumption that in the conjugated system the carbonyl C-atom (C-6) is not sufficiently electropositive to be susceptible to attack by periodate oxygen. Steric hindrance could also be considered at least in the case of the rather rigid dimers but seems less probable in the acids *12 — 14*. The importance of the α,β-conjugation is strongly supported by the finding that the 7,8-dihydro derivative *16* [3] of dimer *4* on treatment with periodate suffers ketol cleavage between C-5 and C-6 to yield monocarboxylic acid *17*. Again, the methyl group at C-8a prevented the 9,10 ketol bridge from being affected.

Conclusions

The results presented above provide chemical evidence for the steric arrangement at carbon atom 5 of o-quinol dimers *1 — 3* as well as at carbon atom 9 of o-quinol dimers *4* and *5*. These assignments are in agreement with the completely established structures of dimers *1*, *2* and *4*.[3,8] It then seems justified to assume that the steric arrangements at C-9 and C-5 of dimers *3* and *5*, respectively, for which there is no direct experimental proof, are analogous to those found in dimers *1*, *2*, and *4*.

In all cases, therefore, the stereochemical orientation at C-5 and C-9 is the same and is certainly due to steric approach control in the dimerisation of the o-quinols, the bulky methyl groups being directed away from the reaction center. The same principle holds true for the formation of dimers from other 2,4-cyclohexadienones containing an asymmetric C-atom in the 6-position. Thus, in the Diels-Alder dimers of spiro(oxirane-2,4-cyclohexadienones)[6,2] the $CH_2 - O$ groupings of the oxirane rings at C-5 and C-9 have been shown to be oriented analogously to the CH_3,OH substituents at the same C-atoms of the o-quinol dimers. Furthermore, dimerisation of the parent o-quinol acetate, 6-acetoxy-6-methyl-2,4-cyclohexadienone, and that of its 2-methyl homologue are known to give the diacetates (*6* and *7*) of compounds *1* and *2*, the latter compounds being the dimerisation products of the corresponding non-acetylated o-quinols.[5,4] Finally, in the halogen containing dimers described by Kende and MacGregor [10] (*2*, F instead of OH) and by Lindgren and Ericsson [17] (*2*, Cl instead

of OH) at least the arrangement at C-5 has been shown to be analogous to that now established for the o-quinol dimers.

From the results discussed in the preceding [2] as well as in the present paper it can be concluded that the Diels-Alder dimerisation of the 2,4-cyclohexadienones hitherto examined proceeds in a uniform fashion with regard to both regiospecificity and stereochemical specificity.

EXPERIMENTAL

UV spectra were recorded on a Cary Model 14 Spectrophotometer; IR and NMR spectra were obtained using Beckman 9A and Varian A-60 instruments, respectively. Chemical shifts are given in δ (ppm) units, TMS being used as internal standard.

1,4-Dihydro-6,9-dihydroxy-2,5,8,9-tetramethyl-[1,4]ethanonaphthalen-10-one (11).* The diacetate 8 [2] of o-quinol dimer 3 [2] (765 mg) was added to a 10 % solution of KOH in ethanol (25 ml), and the mixture was kept under nitrogen for 16 h. Ethanol was removed under vacuum, water being repeatedly added during the distillation. The alkaline aqueous mixture was extracted three times with dichloromethane; the extract gave dimer 3 [2] (13 %). When the aqueous phase was neutralised with CO_2, a crystalline product deposited, m.p. $201-202°$ after recrystallisation from ethanol; yield, 69 %. (Found: C 74.55; H 7.08. Calc. for $C_{16}H_{18}O_3$: C 74.40; H 7.02). UV spectrum (ethanol): λ_{max}, nm (log ε) 208 (4.37) (charge transfer band of β,γ-unsaturated CO system), 280 (3.25), 288 (3.25) (aromatic ring), 314 (2.91) (intensified $n \to \pi^*$ absorption of β,γ-unsaturated CO system). IR (KBr): ν_{max}, cm^{-1} 1513, 1600, 1616 (aromatic ring), 1715 (CO), 3425, 3356 (OH).

Monoacetate 11a* was obtained with acetic anhydride-pyridine. M.p. $153-154°$ (ethanol-water). (Found: C 71.84; H 6.65; CH_3CO 13.96. Calc. for $C_{18}H_{20}O_4$: C 71.98; H 6.71; CH_3CO 14.33).

Diacetate 11b* was prepared using Ac_2O-$HClO_4$ in ethyl acetate.[18] M.p. $134-135°$ (ethanol-water). (Found: C 70.02; H 6.38. Calc. for $C_{20}H_{22}O_5$: C 69.98; H 6.39).

4-Acetyl - 1,4,4a,5,6,8a-hexahydro-5-hydroxy-5-methyl-6-oxo-1-naphthalenecarboxylic acid (12).** The solution of o-quinol dimer 1 [5] (200 mg) in acetic acid (25 ml) was mixed with a solution of sodium metaperiodate (0.75 g) in 60 % aqueous acetic acid (25 ml). After 2 h (room temp.) a few drops of ethylene glycol were added to reduce excess periodate, the solvent was removed under vacuum and the residue extracted with dichloromethane. From the

* Experiments carried out by tekn. lic. Ingrid Jansson.

** Experiment carried out by Dr. Britt Berggren.

extract acid 12, m.p. $174-175°$ after recrystallisation from chloroform-hexane, was obtained. (Found: C 63.95; H 6.19. Calc. for $C_{14}H_{16}O_5$: C 63.63; H 6.10). UV (ethanol): λ_{max}, nm (log ε) 224 (4.01), sh 280 (2.08), 328 (1.92). IR (KBr): ν_{max}, cm^{-1}, see Table 1, and 2400 – 3300 (COOH), 3510 (OH). NMR (DMSO-d_6): δ 1.30 (s, 3 H, CH_3), 2.10 (s, 3 H, CH_3CO), 2.88 (2 H, 2 CH), 3.41 (2 H, 2 CH), 5.21 (broad s, 1 H, OH), 5.51, 5.92, 5.94 and 6.73 (doublets, 1 H each, 4 olefinic H).

Methyl ester 12a. Prepared by adding an ethereal solution of diazomethane to a methanolic solution of 12. M.p. $142-143°$ (benzene-hexane). (Found: C 65.0; H 6.7. Calc. for $C_{15}H_{18}O_5$: C 64.7; H 6.5). UV (ethanol): λ_{max}, nm (log ε) 224 (3.99), sh 280 (2.05), 326 (1.92). IR (KBr): ν_{max}, cm^{-1}, see Table 1, and 1622 (C=C), 3480 (OH). NMR spectrum (CDCl$_3$) resembles that of acid 12, but shows an additional signal at δ 3.79 (s, 3 H, ester-CH_3).

4 - Acetyl - 1,4,4a,5,6,8a- hexahydro-5-hydroxy-1,5,7 - trimethyl - 6 - oxo - 1-naphthalenecarboxylic acid (13). An aqueous solution (100 ml) of periodic acid (H$_5$IO$_6$, 41 g, 180 mmol) was added to a solution of 2,6-dimethylphenol (9.15 g, 75 mmol) in water (2250 ml). After 2 h (25°) ethylene glycol (7 g) was added and the solution extracted with six 250 ml portions of chloroform. The combined organic phases were washed with aqueous sodium thiosulphate, dried over anhydrous sodium sulphate and evaporated to dryness. The remaining oil on addition of ethyl ether (10 ml) gave colourless crystals (yield, 54 %, m.p. $180-182°$) which after recrystallisation from ethanol melted at $183-184°$. (Found: C 65.51, H 6.97; equiv. wt. 294. Calc. for $C_{16}H_{20}O_5$: C 65.74; H 6.90; equiv. wt. 292). UV (ethanol): λ_{max}, nm (log ε) 240 (3.87), sh 285 (2.11), 328 (1.92). IR (KBr): ν_{max}, cm^{-1}, see Table 1, and 1630 (C=C), 2300 – 3300 (COOH), 3410 and 3500 (OH). NMR (DMSO-d_6): δ 1.30 and 1.46 (singlets, 3 H each, 2 CH$_3$), 1.76 (t, 3 H, olefinic CH$_3$), 2.10 (s, 3 H, CH_3CO), 2.86 (broad s, 2 H, 2 CH), 3.30 (broad s, 1 H, CH), 5.12 (s, 1 H, OH), 5.50 and 5.74 (doublets, 1 H each, 2 olefinic H), 6.73 (broad s, 1 H, olefinic CH).

Methyl ester 13a. From 13 and diazomethane. After recrystallisation from benzene-hexane, m.p. $88-89°$. (Found: C 66.68; H 7.29. Calc. for $C_{17}H_{22}O_5$: C 66.64; H 7.23.) UV (ethanol): λ_{max}, nm (log ε) 238 (3.87), sh 285 (2.07), 327 (1.93). IR (KBr): ν_{max}, cm^{-1}, see Table 1, and 1630 (C=C), 3462 (OH). NMR spectrum (CDCl$_3$) resembles that of acid 13, but shows an additional signal at δ 3.75 (s, 3 H, ester-CH_3).

4 - Acetyl - 1,4,4a,5,6,8a -hexahydro-5-hydroxy-2,5,8-trimethyl - 6 - oxo - 1 - naphthalenecarboxylic acid (14). The acid was obtained from 2,5-dimethylphenol and periodic acid, using the procedure described above for acid 13. Yield, 32 %, m.p. $205-206°$. (Found: C 65.65; H 7.01. Equiv. wt. 294. Calc. for $C_{16}H_{20}O_5$: C 65.74; H 6.90. Equiv. wt. 292). UV (ethanol): λ_{max},

nm (log ε) 237 (3.94), sh 295 (2.11), 328 (2.00). IR (KBr): ν_{max}, cm^{-1}, see Table 1, and 1610 (C=C), 2400−3300 (COOH), 3485 (OH). NMR (DMSO-d_6): δ 1.27 (s, 3 H, CH$_3$), 1.89 (s, 6 H, 2 olefinic CH$_3$), 2.09 (s, 3 H, CH$_3$CO), 2.92 and 3.37 (singlets, 2 H each, 4 CH), 5.06 (s, 1 H, OH), 5.35 and 5.84 (broad singlets, 1 H each, 2 olefinic H).

Methyl ester 14a. From *14* and diazomethane, m.p. 135−136° (benzene-hexane). (Found: C 66.44; H 7.25. Calc. for C$_{17}$H$_{22}$O$_5$: C 66.64; H 7.23). UV (ethanol): λ_{max}, nm (log ε) 236 (4.01), sh 287 (2.12), 320 (200). IR (KBr): ν_{max}, cm^{-1}, see Table 1, and 1620 (C=C), 3440 (OH). NMR spectrum (CDCl$_3$) resembles that of acid *14*, but shows an additional signal at δ 3.78 (s, 3 H, ester-CH$_3$).

Periodate oxidation of dimers 2 and 3. The dimers, dissolved in ethanol-water (2:3), were treated with a 2.5-fold excess of NaIO$_4$ for 16 h at room temperature. Chloroform extraction gave the almost pure acids *13* and *14* in yields of 66 and 62 %, respectively, identified by m.p., mixed m.p. and IR spectra.

3-Acetyl-8-hydroxy-2,5-dimethyl-7-oxo-bicyclo-[2.2.2]oct-5-ene-2-propanoic acid (*17*). A solution of NaIO$_4$ (1.28 g, 6 mmol) in 60 % aqueous acetic acid (35 ml) was added to a solution of dihydrodimer *16* ^{3} (0.83 g, 3 mmol) in the same solvent (150 ml). Extraction with dichloromethane (four 100 ml portions) after a reaction time of 18 h (25°) provided a crystalline solid, which was recrystallised from ethyl acetate to give 75 % of *17*, m.p. 193.5−194.5°. (Found: C 65.23; H 7.58. Calc. for C$_{15}$H$_{22}$O$_5$: C 65.29; H 7.53). UV (ethanol): λ_{max}, nm (log ε) sh 210 (3.58) (β,γ-unsat. CO), 308 (2.39) (CO and β,γ-unsat. CO). IR (KBr): ν_{max}, cm^{-1} 1713 (CO and COOH), 2400−3300 (COOH), 3400 (OH). NMR (DMSO-d_6): δ 1.12 and 1.22 (singlets, 3 H each, 2 CH$_3$), 1.94 (d, 3 H, olefinic CH$_3$), 2.15 (s, 3 H, CH$_3$CO), 1.85−3.50 (7 H, 2 CH$_2$ and 3 CH), 5.47 (s, 1 H, OH), 5.64 (d, further split by allylic coupling, 1 H, olefinic H).

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