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METAL COMPLEXES IN ORGANIC SYNTHESIS—V†

ALKYLATIONS OF PENTANE-2,4-DIONE WITH ALLYLIC ALCOHOLS UNDER PALLADIUM CATALYSIS

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Abstract—Pentane-2,4-dione with allylic alcohols or benzyl alcohol with palladium catalysts gives high yields of C-monoalkylated diketones, arising mainly from reaction at the terminal end of the allyic system for alkyl monosubstituted allyl alcohols. The effect of the catalyst on the alcohols has been evaluated; rearrangements and disproportionations have been observed.

The alkylation of β-dicarbonyl and related compounds with allylic esters and ethers, under catalysis by palladium species is broadly precedented.[1-9] This method has reached maturity in the hands of Trost *et al.* who have studied its scope and applicability to the synthesis of important products and significant structures.[10-25]

It is generally accepted that the reactions go through the intermediacy of a cationic π-allylpalladium complex stabilized by ligands which in general are tertiary phosphines (Scheme 1). The conjugate base of the β-dicarbonyl compound acts normally as the actual nucleophile.[5,8,10-25] In a few cases a catalytic amount of sodium phenoxide has been deemed necessary,[1,2,6] but examples have also been described in which no base was needed.[3,4,7,9]

Products arising from C-alkylation of the β-dicarbonyl compounds are generally obtained. Alkylation on oxygen has been only exceptionally observed.[7,23] Moreover, O→C rearrangement of O-alkylation products has been shown to occur under palladium[7,23] and platinum catalysis.[26]

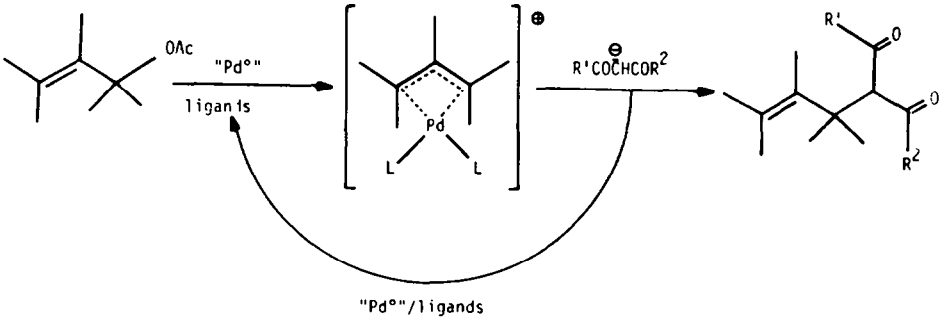
The stereochemical and regioselectivity aspects of this method have been considered, but no easy generalizations have emerged.

In sharp contrast to the attention paid to esters and ethers as substrates, only a few studies have been devoted to the potential applicability of alcohols as starting materials for the allyl transfer to β-dicarbonyl compounds. The adoption of alcohols to react with the active methylene products in the absence of any added base should afford a convenient procedure inasmuch as water would be the only byproduct, a neutral reaction media being secured through the synthetic operation.

Atkins *et al.*[3] described in preliminary form the reaction of allyl alcohol with pentane - 2,4 - dione, which under catalysis by $Pd(acac)_2$ and triphenylphosphine, gave a mixture of the mono- and dialkylated pentane - 2,4 - diones. The reactions of both 2,7 - octadien - 1 - ol and 1,7 - octadien - 3 - ol, under the same conditions, gave also mixtures of the mono- and dialkylated diketones, and alkylation taking place by the terminal carbon atom.[3] The Atkins procedure was also described in the patent literature.[4] While our work was in course the reaction of allyl alcohol with diethyl acetamidomalonate in the presence of palladium acetate/Ph_3P/NaOPh was described.[6] Another allylic alcohol reacts with sodium dimethylmalonate under tetrakis(triphenylphosphine)palladium catalysis,[24] although the corresponding acetate is clearly more active.[24] Ficini and coworkers found that the monoacetate of (*Z*) - 2,5 - dimethyl - 3 - hexene - 2,5 - diol reacts chemoselectively at the acetoxylated carbon atom, with sodium dimethylmalonate again in the presence of tetrakis(triphenylphosphine)palladium.[8]

The little success met by allylic alcohols in transallylation reactions can be related to the poor nucleofugacity of the hydroxyl group but also to their ability to reduce the π-allylpalladium complexes.[10] Further examples of

†For Part IV, see Ref. 30.



Scheme 1.

the scarce operativity of allylic alcohols when compared with esters and ethers in other palladium catalyzed reactions can be additionally found.[27] However, the work of Atkins *et al.*[3,4] seems to deserve more attention. Allylic alcohols have been used as substrates for metal medicated nucleophilic substitutions,[28] e.g. allyl alcohol, (*Z*) - 2 - butene - 1,4 - diol and the structurally related benzyl alcohol and 1-phenylethanol react with amines under palladium catalysis although the intermediacy of the corresponding carbonyl compounds, rather than the π-allylpalladium complexes has been invoked.[29]

Due to our current interest on alkylations under neutral conditions,[30] our attention was drawn to the work of Atkins[3,4] and we considered worthwhile to have a deeper insight on its scope and limitations.

RESULTS

The Atkins procedure was followed with several alcohols. Thus, an equimolar mixture of the corresponding alcohol and pentane - 2,4 - dione was heated under nitrogen in the absence of solvent and in the presence of 0.01 equiv palladium *bis* - pentano - 2,4 - dionato and 0.03 equiv triphenylphosphine. The molar ratio PPh_3/Pd is appropriate since a maximum of three ligands can be bound to the metal atom in the π-allyl complexes intermediates for the palladium to attain the coordinative saturation. The results are collected in Table 1, from which some conclusions can be drawn.

Alcohols 1–6 can give rise to intermediate complexes monosubstituted at one end of the carbon atoms framework; in these cases the yields are quantitative, alkyl-

$R-CH=CH-CH_2OH$	$R-CHOH-CH=CH_2$	$R-C(CH_3)=CH-CH_2OH$
1 R = H	**3** R = CH_3	**7** R = CH_3
2 R = CH_3	**5** R = *n*-Pr	**8** R = $(CH_2)_3-CH(CH_3)_2$
4 R = *n*-Pr	**6** R = $n-C_5H_{11}$	**9** R = $(CH_2)_2-CH=C(CH_3)_2$

$R-C(CH_3)(OH)CH=CH_2$	$(CH_3CO)_2CH-R$
10 R = $(CH_2)_2-CH=C(CH_3)_2$	**11** R = $CH_2-CH=CH_2$
	12 R = $CH_2CH=CHCH_3$
$(CH_3CO)_2CR_2$	**13** R = $CH(CH_3)CH=CH_2$
	14 R = $CH_2CH=CHCH_2CH_2CH_3$
23 R = $CH_2CH=CH_2$	**15** R = $CH(CH=CH_2)CH_2CH_2CH_3$
24 R = $CH_2CH=CHCH_3$	**16** R = $CH_2CH=CH(CH_2)_4CH_3$
25 R = $CH_2CH=CHCH_2CH_2CH_3$	**17** R = $CH(CH=CH_2)(CH_2)_4CH_3$
26 R = $CH_2CH=CH(CH_2)_4CH_3$	**18** R = $CH_2CH=C(CH_3)_2$
27 2-Acetyl-3,5-dimethyl-phenol	**19** R = $CH_2C(CH_3)=CHCH_3$
	20 R = $CH(CH_3)C(CH_3)=CH_2$
28 3,5-Dimethylphenol	**21** R = $CH_2CH=C(CH_3)(CH_2)_2CH=C(CH_3)_2$
	22 R = $C(CH_3)(CH=CH_2)(CH_2)_2CH=C(CH_3)_2$

Table 1.[a]

ALCOHOL	Ac_2CH-R	Ac_2CR_2	Overall Alkylation Yield	OBSERVATIONS. OTHER PRODUCTS
1	11(70)	23(30)	100	$PdCl_2$(0.5% molar), 8h
(E)-2	(E)-12(37);(Z)-12(11);13(20)	(E,E)-24(23);(E,Z)-24(9);(Z,Z)-24(1)	100	(E)-2 contained 6% of (Z)-2
(Z)-2	(E)-12(48);(Z)-12(13);13(14)	(E,E)-24(17);(E,Z)-24(7);(Z,Z)-24(1)	100	(Z)-2 contained 2.5% of (E)-2
3	(E)-12(41);(Z)-12(11);13(30)	(E,E)-24(12);(E,Z)-24(5);(Z,Z)-24(1)	99	
(E)-4	(E)-14(68);15(5)	(E,E)-25(27)	100	
5	(E)-14(70);15(6)	(E,E)-25(24)	100	
6	(E)-16(66.5);17(8)	(E,E)-26(26)	100	
7	18(58);19(28);20(9)	Two unidentified (5%)	55	See text
8 E:Z/91:9	Four unidentified (20)		20	3,7-Dimethylocta-2,4-diene Other hydrocarbons
(E)-9[b]	(E)-21(86);(Z)-21(14)		36	Na(acac) 100% molar Solvent: acacH at reflux 27, 28, $C_{10}H_{16}$'s, (E)-9
(Z)-9[c]	(E)-21(84);(Z)-21(16)		34	Na(acac) 100% molar Solvent: acacH at reflux 27, 28, $C_{10}H_{16}$'s, (Z)-9
10	(E)-21(84);(Z)-21(16)		17	Na(acac) 100% molar Solvent: acacH at reflux 27, 28, $C_{10}H_{16}$'s, 10, see text

a: The reactions were carried out at about 85-90°C for ca. 17h unless otherwise stated. Reaction times are not optimized. Molar ratios determined by glc. Figures in parentheses are molar percentages of individual products in the crude reaction mixtures.

b: Essentially the same results were obtained with $PdCl_2$ at prolonged reaction times. Under the standard experimental conditions, recovery of starting materials was observed. Use of solvents (dioxane, ethanol, n-butanol, DMSO, DMF, toluene)did not improve the results.

c: Essentially the same results were obtained with $PdCl_2$ at prolonged reaction times. Lower temperatures, excess of (Z)-9, addition of N_2H_4 both without solvent or in EtOH, THF or DMF did not improve the results.

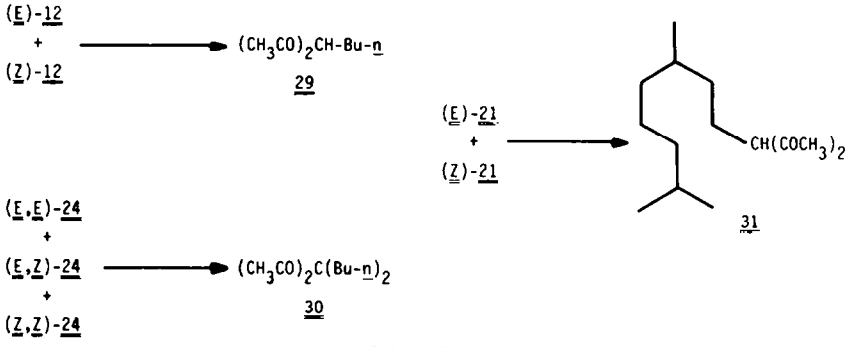
ation at the terminal carbon atom being predominant. The results from isomers (*E*)-**2**, (*Z*)-**2** and **3** are similar, but not exactly the same. Small differences in the molar ratios of final products have been consistently observed through a range of temperatures. On the contrary, the experiments with (*E*)-**4**, **5** and **6** gave the same results. Remarkable differences between both groups of experiments emerge from Table 1. For the butenols runs formation of both lineal substitution products, (*E*)-**12** and (*Z*)-**12** were evident, while no *Z* isomers were detected by glc in two different columns in the crude reaction mixture from (*E*)-**4**, **5** and **6**. Moreover, branched substitution products **15** and **17** (from (*E*)-**4**, **5** and **6**) are formed in a much lower proportionation than its counterpart **13** (from (*E*)-**2**, (*Z*)-**2** and **3**). In all cases reactions with secondary alcohols were much faster. These facts point to highly demanding steric requirements at some point of the reaction pathway.

Full characterization of the products was achieved by isolation of pure samples. Mixtures of (*E*)-**12** and (*Z*)-**12**, and of (*E*, *E*)-**24**, (*E*, *Z*)-**24** and (*Z*, *Z*)-**24** were not resolved, but hydrogenation (10% Pd–C) led to only one product in each case, namely 3 - *n* - butylpentane - 2,4 - dione, **29**, and 3,3 - di - *n* - butylpentane - 2,4 - dione **30** (Scheme 2). Assignment of peaks to the isomers **24** in glc was tentatively carried out by decreasing area percentage criterion, which assigns to (*E*, *E*)-**24** the lowest retention time, like in the case of (*E*)-**12** compared with (*Z*)-**12**.

In order to check the influence of alcohol isomerization on the alkylation reactions, we have treated (*E*)-**2**, (*Z*)-**2** and **3** with the catalytic system at 80° for 17 hr. Isomerizations and disproportions of the butenols are always slower than the pentane - 2,4 - dione alkylations as shown in Table 2. Each of the primary alcohols **2** isomerizes slowly to a mixture containing both of them plus the secondary one, **3**. This can give rise to butanone, in an example of the well-known transition metal mediated isomerization of allylic compounds.[31,32] An intermolecular hydrogen transfer lead to disproportionation, butenone and 2-butanol being the final products.

Returning to the Table 1, the results changed dramatically when alcohols were used which should react through complexes disubstituted at the same end of the carbon atoms framework (**7**–**10**). Operations with **7** were very difficult to reproduce. The highest overall alkylation yields (50–77%) were obtained when a Peligot tube containing Br_2/CCl_4 was fit to the top of the reflux condenser. When a flame-sealed test tube was used the yields decreased to the range 12–49%, and when only a standard reflux condenser was fit to the reaction flask very little reaction took place. Extensive recovery of starting materials was observed in the last two cases. Alkylation under the best conditions gave the expected C-alkylation product **18** as the main β-diketone. However, minor amounts of **19** (undetermined stereochemistry) and **20** were also isolated (Scheme 3). Spectra of pure samples of **18**, **19** and **20** were compared with those previously described.[33] Takahashi *et al.* obtained a mixture of the same **18**, **19** and **20** by aklylation of pentane - 2,4 - dione with isoprene under palladium catalysis.[33] Since we have trapped isoprene in the Peligot tube, it can be assumed that dehydration of **7** to isoprene takes place under our experimental conditions. Indeed, elimination of phenol and acetic acid from allylic phenyl ethers and acetates have been described.[27,34,35]

Similar results were obtained for dihydrogeraniol **8**



Scheme 2.

Table 2[a]. (*E*)-**2**, (*Z*)-**2**, **3** $\xrightarrow[80°/17\,hr]{Pd(acac)_2/P\Phi_3}$ Products

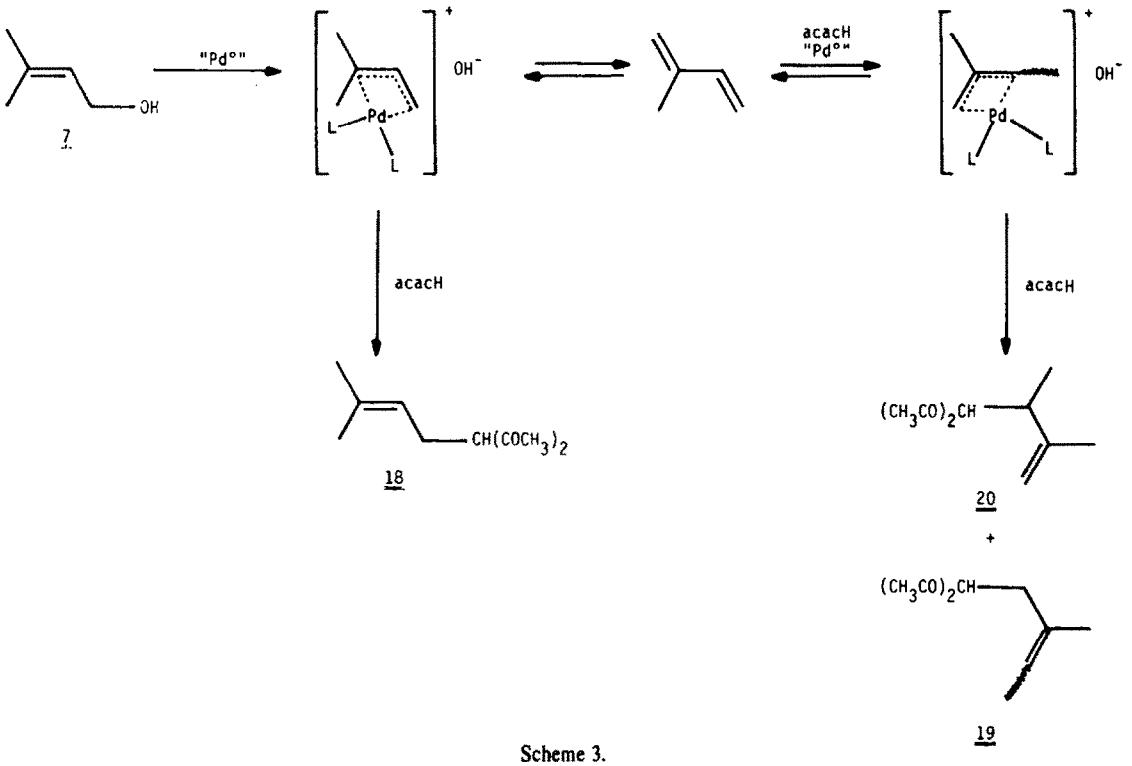
PRODUCTS / ALCOHOL	(E)-2	(Z)-2	3	butanone	butenone	2-butanol	butadiene
(E)-2[b]	80	6	13	-	-	-	-
(Z)-2[c]	7	78	14	-	-	-	-
3[d]	-	-	44	32	12	11	+

[a] Molar ratio 2 or 3/Pd/$P\Phi_3$ of 100:1:3. The final mixtures were analyzed by glc by comparison with authentical specimens.

[b] Containing 6% of (Z)-2.

[c] Containing 2.5% of (E)-2.

[d] Percentages refer to composition of the residual liquid mixtures. Butadiene was trapped with Br_2/CCl_4 and was not evaluated quantitatively.



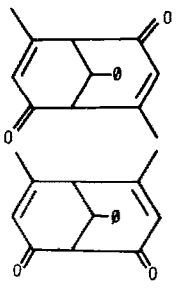
Scheme 3.

from which a mixture of $C_{10}H_{18}$ hydrocarbons and four C-monoalkylation products was formed, which was not studied further.

Although reaction in the absence of added base took place for both **7** and **8**, the presence of an additional double bond at C_6 led to a decreased reactivity. Thus, geraniol (*E*)-**9** did not react at all under the standard Atkins conditions. However, the use of one equivalent of sodium pentane - 2,4 - dionate in pentane - 2,4 - dione as solvent produced a mixture of (*E*)-**21** and (*Z*)-**21** in a 86:14 ratio. Unreacted geraniol was recovered, no isomers being detected; also dehydration hydrocarbons were detected. The phenols **27** and **28** result from condensation of two molecules of the β-diketone in basic conditions.[36] The PMR spectrum of our mixture of isomers **21** was in agreement to one kindly sent to us by Dr. W. Hoffmann, from BASF.[37] Hydrogenation of the mixture gave only product **31**. Similar results were produced by nerol, (*Z*)-**9**, and linalool **10** although the yield was lower in the last case.

At this point we undertook the study of the reactivity of benzyl alcohol, **32**. This was unreactive towards pentane - 2,4 - dione at *ca.* 80°. However, at 140° condensation took place, **33**, the the C-monoalkylated β-diketone **36** and the unsaturated **35** being formed in an overall yield of 50% (Table 3).

ØCH$_2$OH **32**
ØCHO **33**
ØCH$_3$ **34**
ØCH = C(COCH$_3$)$_2$ **35**
ØCH$_2$CH(COCH$_3$)$_2$ **36**
ØCOOH **37**
ØCH$_2$OCOCH$_3$ **38**



39

40

Benzaldehyde arises by disproportionation of **32**. Indeed, when **32** was treated with the catalyst, quantitative conversion into a 1:1 mixture of **33** and **34** took place. Such intermolecular hydrogen transfer is not without precedent.[31,38,39]

$$2PhCH_2OH \xrightarrow{Pd(acac)_2/PPh_3} PhCHO + PhCH_3$$

$$PhCHO + (CH_3CO)_2CH_2 \xrightarrow[150°/48\ hr]{Pd(acac)_2/PPh_3} (CH_3CO)_2C = CHPh$$

Next, the reaction of benzaldehyde with pentane - 2,4 - dione gave **35** in 47% yield. The bicyclic compounds **39** and **40**, the former being largely predominant, can be easily formed from **35**.[40] The acetate **38** must be produced by nucleophilic attack of **32** at one carbonyl group of the β-diketone. Ester **38** was isolated in one case, but was always detected in control samples at intermediate reaction times. 3-Benzylpentane - 2,4 - dione can derive from a benzylpalladium complex. This type of complexes has been previously invoked.[41,42] However, hydrogen transfer from benzyl alcohol to the unsaturated diketone **35** can not be ruled out[29,43] (Scheme 4). It is worth mentioning that formation of palladium black was observed in all the reactions leading to oxidation products.

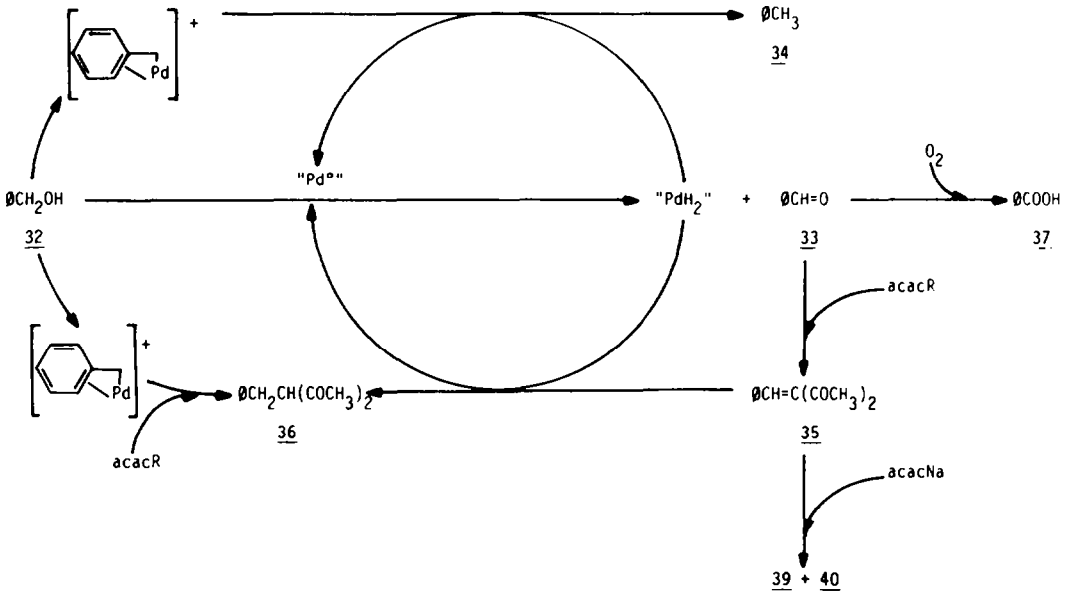
EXPERIMENTAL

IR, PMR and mass spectra were recorded on Perkin–Elmer Infracord 720, Perkin–Elmer R-12 and Hewlett–Packard 5930-A spectrometers respectively. Glc analyses were performed on Hewlett–Packard 5831-A and Perkin–Elmer Sigma-1 instruments with Carbowax 20M (2 meters) and UCW (0.5 meters) columns. Melting points are uncorrected. Alcohols **1**, (*E*)-**2**, **3**–**6**, **9** and **10** were commercially available. Pd(acac)$_2$ was purchased from Johnson Matthey Chemicals Ltd.

Table 3[a]. 32 + $(CH_3CO)_2CHR$ ⟶ Products

R	Oil bath t[a]	Time (h)	Products (%)	Observations
H	80	17	Recovery of starting materials	
H	140	48	33(10), 35(32), 36(8)	b
H	150	72	33(12), 35(33), 37(31)	c
Na	140	24	27, 32(47), 36(8), 38(31)	d
Na	140	72	27, 28, 36(8), 39+40(29)	d

[a] In all the experiments in which R=Na, pentane-2,4-dione was used as solvent.
[b] Both under N_2 or under normal atmosphere the results were similar.
[c] Bubbling O_2
[d] N_2 atmosphere



Scheme 4.

2 - *Butyn* - 1 - *ol*

The method described by Ermilova *et al.* for the synthesis of higher propargylic alcohols was followed.[44] 2 - Butyn - 1 - ol was obtained in 85% yield from the dilithium salt of propargyl alcohol and methyl iodide.

(Z) - 2 - *Buten* - 1 - *ol* (Z) - 2

2 - Butyn - 1 - ol (10.0 g, 0.143 mole) dissolved in methanol (50 ml) was hydrogenated at 2 atm and room temperature in the presence of 10% palladium on barium sulphate (0.4 g) poisoned with freshly distilled quinoline (0.8 g). The solid was filtered off and the filtrate was carefully distilled. (*Z*) - 2 - Buten - 1 - ol (85%) had b.p. 118–120°.

3 - *Methyl* - 2 - *buten* - 1 - *ol* 7

A modification of the method described by H. Eggerer[45] was followed; 3 - methyl - 2 - butenoic acid (50.0 g, 0.5 mole) dissolved in anhydrous ether (250 ml) was added dropwise over 2 h with stirring to lithium aluminium hydride (17.1 g, 0.43 mole) suspended in ether (150 ml). The stirring was then continued for 3 hr. A few drops of ethyl acetate was added (care should be taken not to add a large excess of ethyl acetate. Otherwise the acetate of 7 can be formed). Then, cold water (100 ml) was slowly added and the mixture was extracted with ether. The organic layer was washed with aqueous sodium bicarbonate, dried and evaporated. The residue was distilled. Alcohol 7 (54%) had b.p. 62–4°/18 mmHg.

6 - *Methylheptan* - 2 - *one*

6 - Methyl - 5 - hepten - 2 - one (25.0 g, 0.198 mole) dissolved in ethyl acetate (50 ml) was hydrogenated at 3 atm and room temperature in the presence of 10% Pd/C (250 mg). After the uptake of hydrogen was complete (45 min), the catalyst was filtered off and the solvent evaporated to yield 6 - methylheptan - 2 - one (99%).

Methyl 2,6 - *dimethyl* - 2 - *octenoate*

A mixture of the isomers *E* and *Z* (70:30) was prepared (95%) by the general method of Ogura *et al.*[46] from 6 - methylheptan - 2 - one and dimethyl methoxycarbonylmethylphosphonate. A fraction enriched in the *E* isomer (85:15) was obtained by careful distillation.

Dihydrogeraniol 8

A mixture of *E* and *Z* isomers of methyl 2,6 - dimethyl - 2 - octenoate was reduced by the method of Heilmann and Glenat.[47] A mixture of (*E*)-8 and (*Z*)-8 (ratio 91:9) was obtained by distillation.

Alkylations of pentane - 2,4 - *dione with alcohols* 1–8. *General method*

The liquid reagents were degassed by bubbling dry nitrogen. A mixture of pentane - 2,4 - dione (6.940 g, 69.4 mmole), 3 - buten - 2 - ol, 3, (5.00 g, 69.4 mmole), triphenylphosphine (0.542 g, 2.1 mmole) and $Pd(acac)_2$ (0.212 g, 0.69 mmole) was heated under

nitrogen and with magnetic stirring for 17 hr at 85–90°. The mixture was dissolved in methylene chloride and this solution was passed through a silica gel (10 g) column. The solvent was evaporated, and the residue was analyzed by glc giving the results indicated in Table 1.

The alkylation mixture was distilled at 16 mmHg affording two fractions (b.p. 92–6° and 127–31° respectively). The first fraction containing products **12** and **13** was chromatographed through silica gel with hexane–ether (98:2–96:4). The branched 3 - (1 - methylallyl)pentane - 2,4 - dione, **13**, eluted later. Its spectroscopic constants were as previously described.[33] The mixture of isomers of 3 - (2 - buten - 1 - yl)pentane - 2,4 - dione constitution, **12**, eluted first and could not be resolved. The *E* isomer was evident by comparison with the data already published.[33] A sample of the isomeric mixture (0.198 g, 1.3 mmol) dissolved in ethyl acetate (8 ml) was hydrogenated at atmospheric pressure and room temperature in the presence of 10% Pd–C (0.02 g), for 15 min. The catalyst was filtered off and the solvent was evaporated to afford 3 - *n* - butylpentane - 2,4 - dione, **29**, as the only product (glc). The diketone **29** was compared with authentical sample.[48]

The second fraction of the above distillation consisted of three dialkylation products of constitution **24** (glc, mass spectrum, IR, NMR). A part of this mixture was hydrogenated as above for **12** affording only one product (glc) characterized as 3,3 - di - *n* - butylpentane - 2,4 - dione **30**: IR (film) 2990, 2900, 1710 (sh), 1700, 1460, 1360, 1190, 1120 cm^{-1}. NMR (CCl_4) 0.7–1.6 (m, 14H), 1.7–2.05 (m, 4H), 2.05 (s, 6H). MS *m/e* 213 ($M^+ + 1$, 0.1), 85(38), 72(9), 55(10), 43(100).

The following new products were prepared by the same general method: 3 - ((*E*) - 2 - hexen - 1 - yl)pentane - 2,4 - dione, (*E*) - **14**: IR (film): 2980, 1730, 1700, 1610, 1420, 1360, 980 cm^{-1}. NMR (CCl_4) Enol: 0.9–1.7 (m, 5H), 1.7–2.1 (m, 2H), 2.05 (s, 6H), 2.9 (m, 2H), 5.4 (m, 2H), 16.5 (s, 1H). Keto: 0.9–1.7 (m, 5H), 1.7–2.1 (m, 2H), 2.10 (s, 6H), 2.5 (broad t, J = 7 Hz, 2H), 3.55 (t, J = 7 Hz, 1H), 5.4 (m, 2H). MS *m/e*: 182 (M^+, 13), 139(56), 121(41), 101(18), 97(39), 81(17), 67(20), 55(14), 43(100). 3 - (1 - *n* - Propylallyl)pentane - 2,4 - dione **15**: IR (film): 2980, 1730, 1700, 1420, 1350, 1190, 1150, 990, 910 cm^{-1}. NMR (CCl_4): 0.9–1.6 (m, 7H), 2.00 (s, 3H), 2.10 (s, 3H), 2.6–3.1 (m, 1H), 2.60 (d, J = 10 Hz, 1H), 4.8–5.80 (m, 3H). MS *m/e*: 182 (M^+, 2), 139(53), 112(13), 97(100), 55(18), 43(100). Elemental analysis of a mixture of (*E*)-**14** and **15**: (Found: C, 72.69; H, 10.02; Calc. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95%). 3,3 - di - ((*E*) - 2 - hexen - 1 - yl)pentane - 2,4 - dione, (*E*, *E*) - **25**: IR (film): 3000, 1710(sh), 1700, 1440, 1360, 1180, 970 cm^{-1}. NMR (CCl_4): 0.75–1.6 (m, 10H), 1.6–2.1 (m, 4H), 1.95 (s, 6H), 2.45 (d, J = 6 Hz, 4H), 4.7–5.65 (m, 4H). MS *m/e*: 264 (M^+, 4), 221(75), 181(100), 139(86), 121(40), 109(17), 97(22), 95(26), 81(18), 67(18), 55(18), 43(85). (Found: C, 77.03; H, 10.98; Calc. for $C_{17}H_{28}O_2$: C, 77.22; H, 10.67%). 3 - ((*E*) - 2 - octen - 1 - yl)pentane - 2,4 - dione (*E*) - **16**: IR (film): 2950, 2880, 1720, 1700, 1600, 1420, 1350, 1270, 960 cm^{-1}. NMR (CCl_4) Enol: 0.8–1.6 (m, 9H), 1.8–2.2 (m, 2H), 2.05 (s, 6H), 2.9 (m, 2H), 5.35 (m, 2H), 16.5 (s, 1H). Keto: 0.8–1.6 (m, 9H), 1.8–2.2 (m, 2H), 2.07 (s, 6H), 2.5 (broad deceptive t, J = 8 Hz, 2H), 3.5 (t, J = 8 Hz, 1H), 5.35 (m, 2H). MS *m/e*: 210 (M^+, 1), 43(100). 3 - (1 - *n* - pentylallyl)pentane - 2,4 - dione **17**: IR (film): 2950, 2880, 1700, 1640, 1460, 1420, 1360, 1260, 1190, 1150, 990, 920 cm^{-1}. NMR (CCl_4): 0.7–1.5 (m, 11H), 2.0 (s, 3H), 2.1 (s, 3H), 2.5–3.2 (m, 1H), 3.6 (d, J = 10 Hz, 1H), 4.85–5.9 (m, 3H). MS *m/e*: 210 (M^+, 3), 195(13), 167(72), 153(13), 149(17), 139(74), 111(22), 97(100), 85(10), 81(18), 69(16), 55(10), 43(68). Elemental analysis of a mixture of (*E*)-**16** and **17**. (Found: C, 74.32; H, 10.36; Calc. for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54%). 3,3 - di - ((*E*) - 2 - octen - 1 - yl)pentane - 2,4 - dione (*E*, *E*) - **26**: IR (film): 2950, 2880, 1710 (sh), 1700, 1440, 1360, 1160, 960 cm^{-1}. NMR (CCl_4): 0.7–1.6 (m, 18H), 1.7–2.2 (m, 4H), 2.0 (s, 6H), 2.5 (d, J = 7 Hz, 4H), 4.7–5.7 (m, 4H). MS *m/e*: 320 (M^+, 0.3), 55(15), 43(100). (Found: C, 78.58; H, 10.90; Calc. for $C_{21}H_{36}O_2$: C, 78.70; H, 11.32%).

3 - (3 - methyl - 2 - buten - 1 - yl)pentane - 2,4 - dione, **18**, 3 - (2 - methyl - 2 - buten - 1 - yl)pentane - 2,4 - dione **19** and 3 - (3 - methyl - 3 - buten - 2 - yl)pentane - 2,4 - dione **20**, were separated by repeated column chromatography. Finally, pure samples of all of them could be spectroscopically analyzed. Products **18**[49] and **20**[33] have been previously described in pure form. The spectral data were coincident with the reported data. Product **19** had the following spectroscopic properties: IR (film): 3025, 2960, 2900, 1730, 1700, 1600, 1440, 1280, 1000, 940 cm^{-1}. NMR (CCl_4) Enol: 1.5–1.8 (m, 6H), 2.0 (s, 6H), 2.9 (broad s, 2H), 4.9–5.3 (m, 1H), 16.6 (s, 1H). Keto: 1.5–1.8 (m, 6H), 2.1 (s, 6H), 2.5 (m, 2H), 3.7 (t, J = 7 Hz, 1H), 4.9–5.3 (m, 1H). MS *m/e*: 168 (M^+, 8), 150(37), 135(21), 125(21), 107(32), 93(25), 79(12), 55(12), 43(100).

Reaction of sodium pentane - 2,4 - dionate with terpene alcohols. General method

The liquid reagents were degassed by bubbling dry nitrogen. A mixture of sodium pentane - 2,4 - dionate (2.38 g, 19.5 mmole), geraniol, (*E*)-**9**, (3.00 g, 19.5 mmole), $Pd(acac)_2$ (0.059 g, 0.195 mmole), triphenylphosphine (0.153 g, 0.57 mmole) and pentane - 2,4 - dione (10 ml) was heated at reflux under nitrogen for 17 hr. When cooled the mixture was partitioned between aqueous HCl and methylene chloride. The organic layer was washed with water, dried and evaporated. The residue was analyzed by glc showing the isomers 3 - geranylpentane - 2,4 - dione (*E*) - **21** and 3 - nerylpentane - 2,4 - dione (*Z*) - **21**, as indicated in Table 1. Moreover, the residue was chromatographed on silica gel, the following products being eluted: hydrocarbons, 2 - acetyl - 3,5 - dimethylphenol, **27**, an impure mixture of (*E*)- and (*Z*)-**21**, 3,5 - dimethylphenol, **28**, and finally (*E*)-**9**. The isomers **21** in methanol were treated with an aqueous solution of copper acetate and the mixture was shaked overnight. The precipitated copper complex was filtered, washed with cold methanol and dried. The complex (m.p. 132–134°) (36% overall yield from geraniol) had the following spectroscopic behaviour: IR (KBr): 2960, 2900, 2840, 1575, 1470, 1420, 1400, 1290, 1155, 1100, 1015, 935, 860, 735 cm^{-1}. MS *m/e*: 533 (M^+, 5), 298(14), 229(25), 198(12), 125(13), 109(18), 93(13), 81(11), 69(86), 43(100). (Found: C, 67.49; H, 8.49; Calc. for $C_{30}H_{46}O_4Cu$: C, 67.48; H, 8.68%). The copper complex in methylene chloride was shaked for a few seconds with a concentrated aqueous solution of citric acid. The organic layer was washed with water, dried and evaporated to afford a mixture of the isomers **21**: IR ($CHCl_3$): 3000, 2950, 2875, 1720, 1690, 1600, 1430, 1360 cm^{-1}. NMR (CCl_4) Enol: 1.5–1.7 (m, 9H), 1.9–2.1 (m, 4H), 2.0 (s, 6H), 2.85 (d, J = 7 Hz, 2H), 4.7–5.15 (m, 2H), 16.55 (s, 1H). Keto: 1.5–1.7 (m, 9H), 1.9–2.1 (m, 4H), 2.05 (s, 6H), 2.5 (t, J = 7 Hz, 2H), 3.65 (t, J = 7 Hz, 1H), 4.7–5.15 (m, 2H). MS *m/e*: 236 (M^+, 1), 69(24), 43(100). This spectrum was compared with those of geraniol and nerol resembling to that of the *E* isomer. Also the retention time of (*Z*)-**21** is shorter, as observed by Hoffmann[37] (personal communication). The mixture of isomers **21** was hydrogenated with 10% Pd–C in ethyl acetate at atmospheric pressure and room temperature to afford 3 - (3,7 - dimethyl - 1 - octyl)pentane - 2,4 - dione, **31**, as the only product: IR (CCl_4): 2980, 1730, 1700, 1600, 1460, 1350, 1290, 1160, 940 cm^{-1}. NMR (CCl_4) Enol: 0.8–1.5 (m, 19H), 1.9–2.2 (m, 2H), 2.05 (s, 6H), 16.5 (s, 1H). Keto: 0.8–1.5 (m, 19H), 1.9–2.2 (m, 2H), 2.07 (s, 6H), 3.45 (t, J = 7 Hz, 1H). MS *m/e*: 240 (M^+, 1), 139(23), 71(13), 55(12), 43(100). (Found: C, 74.65; H, 11.33; Calc. for $C_{15}H_{28}O_2$: C, 74.95; H, 11.74%).

Reactions of acacR with benzyl alcohol

The reaction conditions were collected in Table 3. For R = H the same methodology as for reactions with alcohols **1–8** was followed. When R = Na, the one for reactions with **9** and **10** was adopted. The crude reaction mixtures were chromatographed through silica gel. The products were all known and were unequivocally characterized by spectroscopic means with the help of authentic specimens of **36**,[48] **39**[40] and **40**.[40] It must be noted that systematic precipitation of palladium black was observed when oxidation products of benzyl alcohol were formed.

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