Journal of Organometallic Chemistry, 301 (1986) 247–255
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

ETHOXYACETYLENE: A USEFUL BUILDING BLOCK FOR THE ORGANOCOPPER(I) MEDIATED SYNTHESIS OF 1,4-DIKETONES

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(Received August 5th, 1985)

Summary

Ethoxyacetylene (I) has been converted by organocopper(I) species into (*E*)-2-ethoxy-1-alkenylcopper(I) compounds (II). The adducts II have been shown to be useful intermediates for preparation of 1,4-diketones (VI). Two routes to VI were used: (i) sequential treatment of II with allyl bromide, 3.0 *N* HCl, and $PdCl_2/CuCl$ in DMF/H_2O, and (ii) sequential treatment of II with 2,3-dibromopropene and $Hg(OAc)_2$. A dienone was formed from the first procedure when after the reaction of II with allyl bromide the product was treated first with the $PdCl_2/CuCl$.

Introduction

It has been shown that alkylcopper(I) as well as 1-alkenyl- and aryl-copper(I) compounds add smoothly, regio- and stereo-specifically to the readily available ethoxyacetylene [1,2]. The additions are *cis* processes and yield (*E*)-2-ethoxy-1-alkenylcopper(I) compounds. It is known that 1-alkenylcopper(I) species react with a wide range of electrophiles [3], and thus seemed of interest to investigate the synthetic utility of the adducts mentioned by bringing them in reaction with carbon electrophiles such as allyl bromide and 2,3-dibromopropene, since terminal double bonds and vinylic ethers are well-known masked ketone equivalents. We hoped in this way to find a versatile route to the important class of 1,4-diketones [4]. Such 1,4-diketones are useful starting compounds for the synthesis of cyclopentenones [5]. Cyclopentenone rings occur in many compounds of biological and commercial interest, such as prostaglandines, cyclopentanoid antibiotics, rethrolones, and jasmonoids [6].

It will be shown in the paper that ethoxyacetylene is indeed an attractive starting point for preparation of 1,4-diketones.

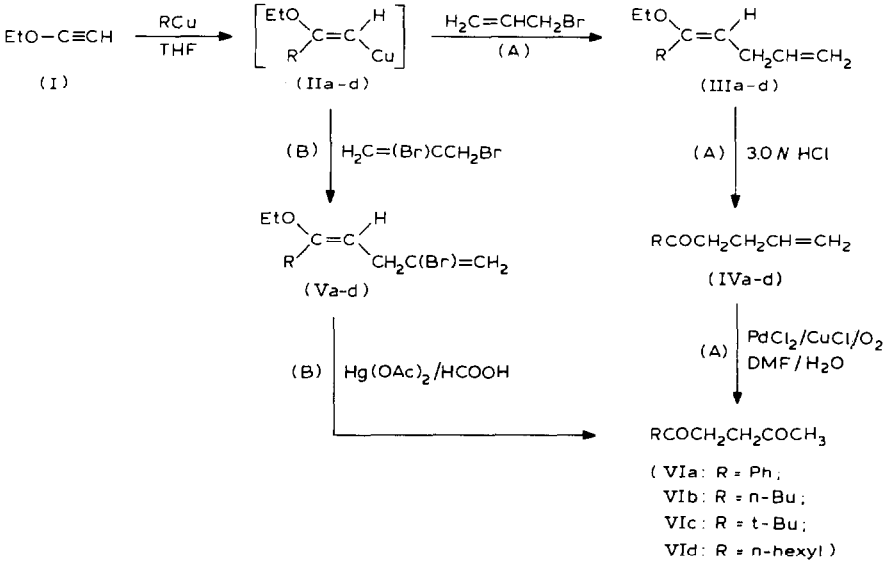
0022-328X/86/$03.50

Results and discussion

The potential route to 1,4-diketones from ethoxyacetylene (I) examined involved sequential treatment of I with organocopper(I) species of the type RCu * and allyl bromide followed by hydrolysis of the vinyl ether function and subjection of the remaining terminal double bond to Wacker oxidation (route A in Scheme 1). This approach is indeed a useful one. Thus, treatment of I with RCu reagents (R = Ph, n-Bu, t-Bu, and n-hexyl) in the solvent tetrahydrofuran (THF) gave the intermediary adducts II, which in turn gave the 5-ethoxy-1,4-alkadienes III in satisfactory yields (55–96%) after reaction with allyl bromide. As shown in Table 1, only for R = t-Bu was the yield of III below 75%; possibly the lower yield for R = t-Bu is due to incomplete reaction of t-BuCu with reagent I [8]. Several attempts to improve the yield from t-BuCu failed. Hexamethylphosphoric triamide (HMPT) was used as a co-solvent for R = n-Bu or n-hexyl, as this improved the yields somewhat. When the group R = Ph or t-Bu, addition of HMPT did not have a beneficial effect.

Hydrolysis of the vinyl ether group of dienes III afforded the enones IV in yields of over 90%. Subsequent oxidation of the terminal double bond using the Wacker reaction [9] gave the 1,4-diketones VI in 64–73% yield.

An alternative route to compounds VI involved the reaction of adducts II with 2,3-dibromopropene followed by hydrolysis of the two double bonds (route B in Scheme 1). The 2-bromo-5-ethoxy-1,4-alkadienes V were obtained in 50–73% yields. Allylation of II (route A) gives better yields, but the advantage of route B is the possibility of hydrolysing both double bonds in one step by treating compounds V



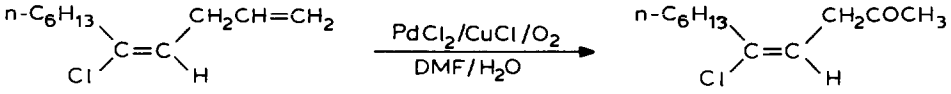
SCHEME 1

* The RCu compounds were prepared in situ from RMgX and cuprous bromide. They do not exist as such, but as oligomers $(RCu)_n$ or, in the presence of HMPT, as bromocuprates [7].

with mercuric acetate, a procedure which gives excellent results (yields 84–89%). With respect to overall yields both routes are about equally satisfactory.

Purification of the 1,4-diketones was easily accomplished by column chromatography on alumina (eluent: n-pentane/Et_2O). Compound VId (R = n-hexyl) can be cyclised by base into dihydrojasmone in over 80% yield [6]; this reaction also proceeded well in our hands.

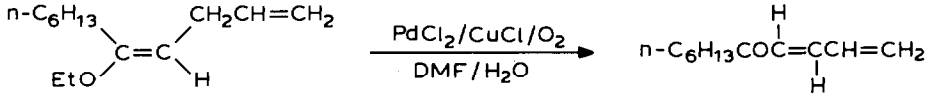
It is of interest to note that for a satisfactory formation of VI the reaction sequence in route A must be that indicated in Scheme 1. In some separate experiments we tried to oxidize first the terminal double bond of IIId by means of the Wacker reaction. This sequence was succesful, for instance, for the conversion of the chloro analogue of IIId, viz. 5-chloro-1,4-undecadiene, into 5-chloro-4-undecen-2-one, a precursor for VId [10] (Scheme 2).



(62%)

SCHEME 2

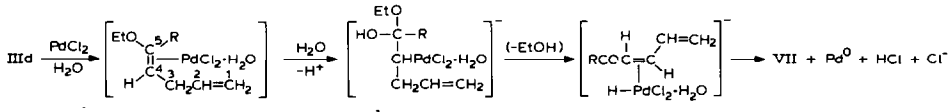
In our systems this alternative sequence failed almost completely. Instead of demasking the terminal double bond of IIId, the Wacker procedure resulted in the formation of (*E*)-1,3-undecadien-5-one (VII) in 25% yield, together with the hydrolysed compound IVd and a small amount of 1,4-diketone VId (Scheme 3). The amount of the interesting dienone VII was increased to 60% by using 25 mol% of $PdCl_2$ instead of the 10 mol% used in the other experiments.



(III d) (VII)

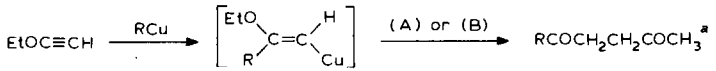
SCHEME 3

The oxidation product VII is probably formed as indicated in Scheme 4. In the first step of the reaction complexation of the vinyl ether double bond with $PdCl_2$ will occur. Generally the Wacker oxidation of terminal double bonds is much more rapid than that of internal double bonds for steric reasons [9]. It is therefore not unexpected that Wacker oxidation of the chloro compound in Scheme 2 should take place at the terminal double bond. In compound IVd, however, the vinyl ether double bond is highly electron rich. Consequently, complexation of the electrophilic transition metal salt with this double bond is more attractive than that with the terminal one. In the next step water will add to the complexed double bond to give, after loss of a proton, an alkylpalladium(II) complex, which loses ethanol to give



SCHEME 4

TABLE 1



RCu	R(EtO)C=CHCH$_2$C(X)=CH$_2$					RCOCH$_2$CH$_2$CH=CH$_2$				RCOCH$_2$CH$_2$COCH$_3$			
	III/V	X	Yield (%) [b]	B.p. (°C/mmHg)	n_D^{20}	IV	Yield (%) [c]	B.p. (°C/mmHg)	n_D^{20}	VI	Yield (%) [d]	B.P. (°C/mmHg)	n_D^{20}
PhCu	IIIa	H	96	38–40/0.001	1.5275	IVa	92	39–40 0.001	1.5325	VIa	65	68–69/0.001	1.5317
	Va	Br	73	54–56/0.001	1.5527						89		
n-BuCu	IIIb	H	76	67–68/15	1.4443	IVb	93	74–75 15	1.4318	VIb	64	70–71/0.2	1.4349
	Vb	Br	57	67–68/0.2	1.4776						89		
t-BuCu	IIIc	H	55	60–62/15	1.4420	IVc	91	63–64 15	1.4298	VIc	66	69–70/0.2	1.4328
	Vc	Br	50	65–66/0.2	1.4742						88		
n-C_6H_{13}Cu	IIId	H	86	60–61/0.2	1.4487	IVd	92	61–64 0.2	1.4388	VId	73	79–81/0.2	[e]
	Vd	Br	65	70–75/0.2	1.4790						84		

[a] Route A: I → II → III (X = H) → IV → VI; route B: I → II → V (X = Br) → VI. [b] Yields refer to compounds purified by column chromatography (neutral alumina; purity 85–95% by GLC and ^{1}H NMR). For the conversion of III and V into IV and VI, respectively, the crude compounds could be used. [c] Yields refer to compounds purified by column chromatography (neutral alumina; purity over 95% by GLC and ^{1}H NMR). For the preparation of VI from IV the crude enones could be used. [d] Yields refer to pure 1,4-diketones (purification by column chromatography over neutral alumina; purity at least 95% by GLC and ^{1}H NMR). [e] M.p. 32.0–33.0°C.

dienone VII after β-H elimination by insertion of Pd^{II} in one of the two C–H bonds at C(3).

This interesting route to (*E*)-dienones is being further explored.

Conclusion

Ethoxyacetylene is a convenient starting compound for preparation of useful 1,4-diketones via (*E*)-2-ethoxy-1-alkenylcopper(I) compounds. The two routes investigated, viz. (i) reaction of the vinylcopper(I) species with allyl bromide, hydrolysis of the vinyl ether group, and Wacker oxidation of the terminal double bond, and (ii) reaction of the vinylcopper(I) species with 2,3-dibromopropene followed by hydrolysis of both double bonds in one step by treatment with mercuric acetate, are of comparable value for obtaining 1,4-diketones as far as overall yields are concerned. The 2,3-dibromopropene route has the advantage that it is shorter, and it is therefore the route of choice in many cases.

Experimental

All reactions with organocopper(I) compounds were performed under dry nitrogen. The products were analysed by GLC, ^1H NMR, IR, and MS spectroscopy. The GLC analyses were carried out with a Pye 104 chromatograph using a SE-33 column (10% on Chromosorb W). ^1H NMR spectra were determined with a Varian EM-390 spectrometer for CCl_4 solutions using Me_4Si as internal standard. Chemical shift values (δ) are given in ppm downfield from Me_4Si. IR spectra were reorded using neat liquids with a Perkin–Elmer 283 Infrared Spectrophotometer. Mass spectra were obtained using a Kratos MS80 spectrometer.

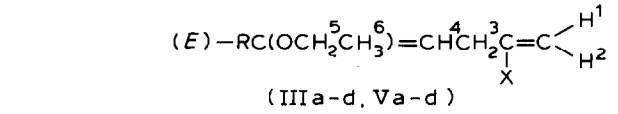
Tetrahydrofuran (THF) was distilled from $LiAlH_4$ before use. Cuprous bromide was obtained by the procedure described by Keller and Wycoff [11]. Lithium bromide was dried at 200°C in high vacuum and used as a 3.0 *M* solution in THF. The molarity of the organomagnesium halide used to synthesize the organocopper(I) compounds was determined by titration [12]. Hexamethylphosphoric triamide (HMPT) was purified as described in ref. 13 and stored under dry nitrogen. Allyl bromide and 2,3-dibromopropene were purchased from Aldrich and distilled before use. Neutral alumina was used for column chromatography after deactivation with water (5% by weight). Ethoxyacetylene was synthesized by standard procedures [13] and stored under dry nitrogen at −20°C.

General procedure for the preparation of the 1,4-dienes III and V

Ethoxyacetylene (I, 0.010 mol) was added at −50°C to a stirred solution of RCu (0.010 mol) in THF (35 ml). (The copper(I) compound had been prepared in situ by stirring RMgX (0.010 mol; X = Cl for R = n-Bu or t-Bu, X = Br for R = Ph and n-hexyl) with the THF soluble complex $LiCuBr_2$ (0.010 mol) for 1 h at −50°C; for R = n-Bu or n-hexyl the RCu solution also contained HMPT (3 ml).) The mixture was then stirred for 1 h at −20°C (R = Ph), 2 h at −20°C (R = n-hexyl), 2.5 h at −25°C (R = n-Bu), or 4 h at 25°C (R = t-Bu). Subsequently, allyl bromide (0.010 mol) was added, together with HMPT (3 ml) when R was t-Bu, in order to produce compounds III. The mixture was stirred for 3 h at −20°C (R = Ph or n-hexyl), for 4 h at 25°C (R = n-Bu), or for 6 h at 25°C (R = t-Bu). To produce compounds V,

2,3-dibromopropene (0.010 mol) was added to the addition product II, together with HMPT (3 ml) when R was Ph and t-Bu, and the mixture was stirred for 4 h at −20°C (R = Ph) or overnight at 25°C in the other cases. The products were isolated by pouring the mixtures into an aqueous NH_4Cl solution (200 ml) containing NaCN (ca. 2 g) and extracting with pentane (3 × 50 ml). The combined extracts were washed with water (6 × 100 ml) to remove THF and dried over $MgSO_4$. The solvent was stripped off in vacuo and the residue purified by column chromatography (eluent, n-pentane). Because of the instability of the products the chromatographic separation was performed within 2 h. Unless otherwise indicated, the purity of the compounds III and V obtained was ca. 95% (by GLC and ^1H NMR). Physical constants and yields are shown in Table 1. Spectroscopic data are as follows.

Compounds



(IIIa-d, Va-d)

IIIa (R = Ph, X = H). ^1H NMR 7.1–7.5 (m, aromatic protons), 5.82 (m, *J* 6.0, 9.5, 17.5 Hz, X), 5.07 (br d, *J* 17.5 Hz, H^1), 4.98 (br d, *J* 9.5 Hz, H^2), 4.70 (t, *J* 8.0 Hz, H^4), 3.73 (q, *J* 7.0 Hz, H^5), 2.78 (m, *J* 6.0, 8.0 Hz, H^3), 1.25 (t, *J* 7.0 Hz, H^6); IR 3080, 3060, 1645, 1600, 1495, 1238, 1128, 910, 770, 700 cm^{-1}; mass spectrum, *m/z* 188 (parent), 105 (base).

IIIb (R = n-Bu, X = H). ^1H NMR 5.79 (m, *J* 6.0, 9.5, 17.5 Hz, X), 4.99 (br d, *J* 17.5 Hz, H^1), 4.90 (br d, *J* 9.5 Hz, H^2), 4.26 (t, *J* 7.7 Hz, H^4), 3.63 (q, *J* 7.2 Hz, H^5), 2.70 (m, *J* 6.0, 7.7 Hz, H^3), 2.09 (br t, *J* 7.1 Hz, CH_2 of R adjacent to double bond), 1.05–1.68 (overlapping multiplets of two CH_2 groups of R), 1.27 (t, *J* 7.2 Hz, H^6), 0.94 (t, *J* 6.8 Hz, CH_3 of R); IR 3080, 1660, 1640, 1240, 1180, 1112, 910 cm^{-1}; mass spectrum, *m/z* 168 (parent), 83 (base).

IIIc (R = t-Bu, X = H). Purity ca. 85%. ^1H NMR 5.80 (m, *J* 5.8, 9.3, 17.0 Hz, X), 5.00 (br d, *J* 17.0 Hz, H^1), 4.94 (br d, *J* 9.3 Hz, H^2), 4.18 (t, *J* 7.9 Hz, H^4), 3.58 (q, *J* 7.0 Hz, H^5), 2.93 (m, *J* 5.8, 7.0 Hz, H^3), 1.28 (t, *J* 7.0 Hz, H^6), 1.20 (s, R); IR 3080, 1642, 1238, 1150, 908 cm^{-1}; mass spectrum, *m/z* 168 (parent), 83 (base).

IIId (R = n-hexyl, X = H). ^1H NMR 5.80 (m, *J* 5.9, 9.5, 17.5 Hz, X), 5.00 (br d, *J* 17.5 Hz, H^1), 4.90 (br d, *J* 9.5 Hz, H^2), 4.33 (t, *J* 7.9 Hz, H^4), 3.63 (q, *J* 7.0 Hz, H^5), 2.69 (m, *J* 5.9, 7.9 Hz, H^3), 2.10 (br t, *J* 7.0 Hz, CH_2 of R adjacent to double bond), 1.20–1.70 (overlapping multiplets of four CH_2 groups of R), 1.23 (t, *J* 7.0 Hz, H^6), 0.90 (t, *J* 6.0 Hz, CH_3 of R); IR 3080, 1660, 1638, 1235, 1170, 1112, 908 cm^{-1}; mass spectrum, *m/z* 196 (parent), 55 (base).

Va (R = Ph, X = Br). ^1H NMR 7.2–7.5 (m, aromatic protons), 5.63 (br s, H^1), 5.42 (br s, H^2), 4.70 (t, *J* 7.8 Hz, H^4), 3.80 (q, *J* 7.2 Hz, H^5), 3.12 (d, *J* 7.8 Hz, H^3), 1.31 (t, *J* 7.2 Hz, H^6); IR 3080, 3060, 3010, 1650, 1630, 1600, 1495, 1240, 1130, 885, 770, 700 cm^{-1}; mass spectrum, *m/z* 266, 268 (parent for Va with Br^{79} and Br^{81}, respectively), 105 (base).

Vb (R = n-Bu, X = Br). Purity ca. 85%. ^1H NMR 5.63 (br s, H^1), 5.37 (br s, H^2), 4.36 (t, *J* 7.8 Hz, H^4), 3.69 (q, *J* 7.0 Hz, H^5), 3.11 (d, *J* 7.8 Hz, H^3), 2.09 (br t, *J* 7.0 Hz, CH_2 group of R adjacent to double bond), 1.0–1.6 (overlapping multiplets of two CH_2 groups of R), 1.28 (t, *J* 7.0 Hz, H^6), 0.90 (t, *J* 6.5 Hz, CH_3 of R); IR

3100, 3065, 1660, 1630, 1240, 1110, 880 cm^{-1}; mass spectrum, *m/z* 246, 248 (parent for Vb with Br^{79} and Br^{81}, respectively), 97 (base).

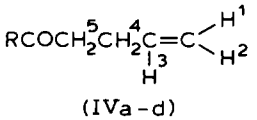
Vc (R = t-Bu, X = Br). Purity ca. 90%. ^1H NMR 5.63 (br s, H^1), 5.40 (br s, H^2), 4.81 (t, *J* 7.5 Hz, H^4), 3.80 (q, *J* 7.2 Hz, H^5), 3.17 (br d, *J* 7.5 Hz, H^4), 1.30 (t, *J* 7.2 Hz, H^6), 1.11 (s, R); IR 3100, 3068, 1658, 1630, 1215, 1108, 883 cm^{-1}; mass spectrum, *m/z* 246, 248 (parent for Vc with Br^{79} and Br^{81}, respectively), 57 (base).

Vd (R = n-hexyl, X = Br). ^1H NMR 5.60 (br s, H^1), 5.35 (br s, H^2), 4.32 (t, *J* 7.5 Hz, H^4), 3.67 (q, *J* 7.0 Hz, H^5), 3.09 (br d, *J* 7.5 Hz, H^3), 2.08 (t, *J* 7.0 Hz, CH_2 of R adjacent to double bond), 1.1–1.7 (overlapping multiplets of four CH_2 groups of R), 1.30 (t, *J* 7.0 Hz, H^6), 0.90 (t, *J* 6.0 Hz, CH_3 of R); IR 3065, 1657, 1628, 1237, 1110, 882 cm^{-1}; mass spectrum, *m/z* 274, 276 (parent for Vd with Br^{79} and Br^{81}, respectively), 125 (base).

General procedure for the preparation of enones IV

Compounds III (0.010 mol) were hydrolysed to enones IV by shaking them vigorously with 3.0 *N* HCl (10 ml) for 0.5 h at 25°C. The enone was isolated by pouring the reaction mixture into water (50 ml) and extracting with a mixture of Et_2O/n-pentane (v/v: 1/1; 3 × 50 ml). The combined extracts were washed with water, dried over $MgSO_4$, and concentrated in vacuo. The products were purified by column chromatography (eluent: n-pentane containing 4% of Et_2O (v/v)). The purities of the enones IV were > 95% (by GLC and ^1H NMR); their physical and spectroscopic data were in good agreement with earlier values [14]. Spectroscopic data are as follows (see for yields and physical constants Table 1).

Compounds



(IVa-d)

IVa (R = Ph). ^1H NMR 7.8–8.0 (m, aromatic *ortho* protons), 7.2–7.5 (m, aromatic *meta* and *para* protons), 5.89 (m, *J* 6.5, 10.0, 17.1 Hz, H^3), 5.02 (br d, *J* 17.1 Hz, H^1), 4.98 (br d, *J* 10.0 Hz, H^2), 2.97 (t. *J* 7.4 Hz, H^5), 2.40 (dt, *J* 6.5, 7.4 Hz, H^4); IR 3080, 3060, 1685, 1640, 1597, 1580, 1450, 1360, 1205, 912, 742, 688 cm^{-1}; mass spectrum, *m/z* 160 (parent), 105 (base).

IVb (R = n-Bu). ^1H NMR 5.80 (m, *J* 6.0, 10.3, 17.5 Hz, H^3), 5.00 (br d, *J* 17.5 Hz, H^1), 4.92 (br d, *J* 10.3 Hz, H^2), 2.1–2.6 (overlapping multiplets, $H^4 + H^5 + CH_2$ group of R adjacent to CO function), 1.1–1.8 (overlapping multiplets, two CH_2 groups of R), 0.90 (t, *J* 7.0 Hz, CH_3 group of R); IR 3080, 1715, 1640, 1410, 1360, 995, 910 cm^{-1}; mass spectrum, *m/z* 140 (parent), 85 (base).

IVc (R = t-Bu). ^1H NMR 5.83 (m, *J* 6.0, 10.0, 17.2 Hz, H^3), 4.99 (br d, *J* 17.2 Hz, H^1), 4.92 (br d, *J* 10.0 Hz, H^2), 2.53 (t, *J* 7.0 Hz, H^5), 2.30 (m, *J* 6.0, 7.0 Hz, H^4), 1.13 (s, R); IR 3080, 1710, 1640, 1480, 1360, 990, 910 cm^{-1}; mass spectrum, *m/z* 140 (parent), 57 (base).

IVd (R = n-hexyl). ^1H NMR 5.80 (m, *J* 6.1, 10.0, 17.4 Hz, H^3), 5.00 (br d, *J* 17.5 Hz, H^1), 4.98 (br d, *J* 10.0 Hz, H^2), 2.1–2.7 (overlapping multiplets, $H^4 + H^5 + CH_2$ group of R adjacent to CO functions), 1.1–1.8 (overlapping multiplets, four CH_2 groups of R), 0.88 (t, *J* 5.5 Hz, CH_3 of R); IR 3080, 1715, 1642, 1470, 1360, 993, 910 cm^{-1}; mass spectrum, *m/z* 168 (parent), 113 (base).

General procedure for the preparation of diketones VI

(a) Wacker oxidation of IV. The conversion of IV (0.010 mol) into VI was carried out by treating IV with $PdCl_2$ (0.001 mol) and CuCl (0.010 mol) in a mixture of DMF/H_2O following the procedure described in ref. 15. The crude products were purified by column chromatography (eluent: n-pentane/Et_2O (1/1 v/v)). The purity of the 1,4-diketones obtained was > 95% (by GLC and ^1H NMR).

(b) Hydrolysis of V (Cf. ref. 16). Mercuric acetate (0.010 mol) was added to a mixture of V (0.010 mol) and formic acid (25 ml) at 0°C and the mixture was stirred for 20 h at 0°C. The 1,4-diketone VI was isolated by adding the mixture to water (50 ml), neutralizing the aqueous layer with sodium bicarbonate, and extracting the product with n-pentane/Et_2O (1/1 v/v; 3 × 50 ml). The combined extracts were washed with water (2 × 25 ml), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified as described under (a); the purity of VI prepared in this way was > 95% (by GLC and ^1H NMR).

Physical constants and spectroscopic data determined for compounds IV agreed well with reported values. Physical constants and yields of the 1,4-diketones are given in Table 1; spectroscopic data are as follows.

Compounds

$RCOCH_3^3CH_2^2COCH_3^1$ (VIa–d)

VIa (R = Ph). ^1H NMR 7.8–8.0 (m, aromatic *ortho* protons), 7.2–7.6 (m, aromatic *meta* and *para* protons), 3.09 (t, *J* 6.5 Hz, H^3), 2.69 (t, *J* 6.5 Hz, H^2), 2.10 (s, H^1); IR 3060, 1713, 1685, 1593, 1580, 1447, 1358, 740, 688 cm^{-1}; mass spectrum, *m/z* 176 (parent), 105 (base).

VIb (R = n-Bu). ^1H NMR 2.75 (br s, $H^2 + H^3$), 2.42 (t, *J* 7.0 Hz, CH_2 group of R adjacent to CO function), 2.13 (s, H^1), 1.1–1.8 (overlapping multiplets, two CH_2 groups of R), 0.90 (t, *J* 7.0 Hz, CH_3 of R); IR 1715, 1362 cm^{-1}; mass spectrum, *m/z* 156 (parent), 99 (base).

IVc (R = t-Bu). ^1H NMR 2.5–2.9 (overlapping multiplets, $H^2 + H^3$), 2.10 (s, H^1), 1.15 (s, R); IR 1720, 1705, 1363 cm^{-1}; mass spectrum, *m/z* 156 (parent), 99 (base).

VId (R = n-hexyl). ^1H NMR 2.60 (s, $H^2 + H^3$), 2.40 (t, *J* 7.0 Hz, CH_2 group of R adjacent to CO function), 2.13 (s, H^1), 1.1–1.8 (overlapping multiplets, four CH_2 groups of R), 0.90 (t, *J* 5.8 Hz, CH_3 of R); IR 1720, 1710, 1363 cm^{-1}; mass spectrum, *m/z* 184 (parent), 114 (base).

The spectroscopic data for dienone VII are in good agreement with those reported by Das and Torssell [17].

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