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Palladium(0)-catalyzed isomerization of α,β-epoxy ketones to β-diketones[#]

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Abstract. In the presence of catalytic amounts of tetrakis(triphenylphosphine)palladium(0) and 1,2-bis(diphenylphosphino)ethane, α,β-epoxy ketones isomerize to the corresponding β-diketones in high yields. Both open-chain and cyclic substrates can be used. Possible reaction mechanisms are discussed.

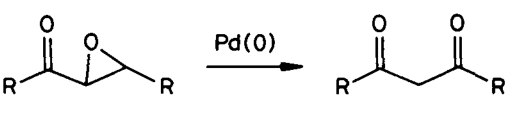
Introduction

β-Diketones have distinct structural properties and high synthetic utility, particularly as building blocks in the construction of carbocyclic and heterocyclic frameworks. Such compounds are usually prepared from the appropriate carbonyl compounds by *Claisen* condensation, *Dieckmann* condensation, *Friedel–Crafts* type reaction *etc.*, under harsh conditions[1]. We here report that the title reaction provides a new entry to β-diketones under entirely neutral, aprotic conditions[2]. The eminent nucleophilicity of Pd(0) species plays a key role in achieving the transformation.

Results and discussion

1. *Palladium-catalyzed isomerization*

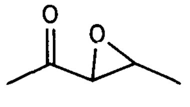
Epoxy ketones exhibit diverse reactivities brought about by the cooperation of the carbonyl and epoxy functions[3]. One of the characteristic features is the high susceptibility towards the nucleophilic opening of the epoxy ring at the α-position[4]. Although the simple epoxides are inert to Pd(0) complexes, α,β-epoxy ketones undergo isomerization, **1** → **2**, under certain catalytic conditions (Eqn. 1).



(1)

1 **2**

We used tetrakis(triphenylphosphine)palladium(0) as a precursor to nucleophilic transition metal species[5,6]. The ease of the catalytic reaction is highly influenced by added tertiary phosphines. The effects were examined by using 3,4-epoxy-2-pentanone (**3**) as substrate in toluene at 140°C. The result is summarized in Table I. In the absence of added auxiliary phosphines, the reaction was sluggish and the desired 2,4-pentanedione (**4**) was obtained in only 11% yield. The yield of product was increased to some extent by addition of triphenylphosphine. However, electron-donating unidentate phosphines did not improve the yield of **4**. Precipitation of palladium black may be the major reason for the failure. When bidentate or tridentate phosphine ligands were added to the reaction system, metal precipitation was avoided, but only 1,2-bis(diphenylphosphino)ethane (DPE), which forms a five-membered chelate complex, gave a reasonable reaction rate and high turnover, affording the β-diketone **4** in good yield (81%). Notably, 1,3- and 1,4-diphosphine ligands, forming six- or seven-membered chelate rings, did not give satisfactory yields. Bis[2-(diphenylphosphino)ethyl]phenylphosphine (TRIPHOS), a typical tridentate ligand, was less effective than DPE.



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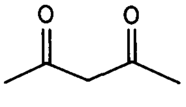

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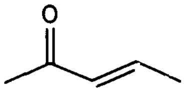

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Aromatic hydrocarbons are the best solvent and in ethereal solvents the reaction was slow. In alcoholic media, the starting material **3** was consumed rapidly but the yield of **4** was low. No noticeable reactions were observed by the reaction of **3** and phosphine ligands in the absence of Pd catalyst. Table II exemplifies the Pd(0)-catalyzed reaction of some α,β-epoxy ketones under the conditions optimized above. A series of open-chain and cyclic substrates isomerize to the corresponding β-diketones in toluene containing 3–14% of the Pd(0) complex and DPE. Five- to seven-membered epoxy ketones react more rapidly than less strained open-chain or medium- to large-ring compounds The presence of a phenyl group at the β-position facilitates

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[#] This paper is dedicated to Professor *G. J. M. van der Kerk* on the occasion of his 75th birthday.

Table I Effects of phosphine ligands and solvents on the Pd(0)-catalyzed reaction of 3,4-epoxy-2-pentanone[a].

Entry	Reaction conditions				Yield[b] (%) of		
	Catalyst system		Solvent	Temp (°C) [time (h)]			
	Pd $(PPh_3)_4$ (mol %)	Additive (mol %)			3	4	5
1	2.9	none	toluene	140 (11)	67	11	0
2	3.0	Bu_3P, 5.9	toluene	140 (11)	84	0	0
3	3.0	$Ph(CH_3)_2P$, 7.6	toluene	140 (11)	98	0	0
4	3.1	$Ph_2(CH_3)P$, 10.3	toluene	140 (11)	69	14	0
5	2.8	$(4\text{-}CH_3OC_6H_4)_3P$, 5.8	toluene	140 (11)	70	14	0
6	5.0	Ph_3P, 5.1	toluene	140 (11)	0	43	4
7	3.0	$Ph_2P(CH_2)_2PPh_2$, 3.0	toluene	140 (11)	0	81	8
8	5.0	$Ph_2P(CH_2)_2PPh_2$, 5.1	benzene	140 (11)	0	77	6
9	4.8	$Ph_2P(CH_2)_2PPh_2$, 4.7	dioxane	140 (11)	0	68	9
10	5.0	$Ph_2P(CH_2)_2PPh_2$, 4.9	THF	140 (11)	0	68	6
11	5.0	$Ph_2P(CH_2)_2PPh_2$, 4.8	methanol	100 (11)	0	15	3
12	5.0	$Ph_2P(CH_2)_2PPh_2$, 4.7	toluene-methanol	100 (11)	0	38	3
13	3.1	$Ph_2P(CH_2)_3PPh_2$, 3.2	toluene	140 (11)	48	32	0
14	2.9	(+)-DIOP[c], 2.8	toluene	140 (11)	63	18	0
15	5.0	$Ph_2P(CH_2)_2PPh(CH_2)_2PPh_2$, 4.9	toluene	140 (11)	0	52	22

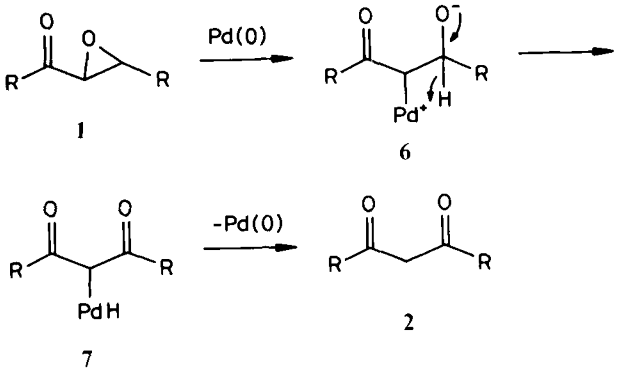
[a] Reaction was carried out under an argon atmosphere. [b] Determined by GIC analysis. [c] (+)-2,3-(Isopropylidenedioxy)-1,4-bis-(diphenylphosphino)butane.

the catalysis, and the reaction of (E)-2,3-epoxy-1,3-diphenyl-1-propanone proceeded smoothly even in the absence of DPE ligand. α-Alkyl substituents, on the other hand, retard the reaction. In some cases, deoxygenation occurs to give the α,β-unsaturated ketones as by-products. Isophorone 2,3-oxide, which has no β-hydrogens, gave isophorone (3,5,5-trimethyl-2-cyclohexenone) as the sole identifiable products[7].

The present isomerization method finds wide applicability. This procedure allows the easy synthesis of unsubstituted, parent 1,3-cyclopentanedione, which is otherwise difficult to prepare[8]. In addition, it has been used for the synthesis of naturally occurring 1-(2,6,6-trimethyl-4-hydroxy-1-cyclohexen-1-yl)-1,3-butanedione[13], which possesses *in vitro* antibiotic activity against *Staphylococcus aureus*[14,15].

2. *Possible mechanisms*

The most probable reaction mechanism is outlined in Eqn. 2. The catalysis is initiated by nucleophilic, back-side attack (S_N2 type)[5,16,17] of Pd(0) species at the epoxy α-carbon to generate the zwitterion **6**.



(2)

Electron release from the negatively charged oxygen to the β-carbon facilitates the movement of the hydrogen to Pd, giving the neutral organopalladium(II) hydride **7**, which in turn undergoes reductive elimination to afford the β-diketone **2** and Pd(0) catalyst. Alternatively, β-metal hydride elimination may occur from **6** to form a 3-ketoenolate anion/HPd cation π-complex[18], which ultimately gives **2** and Pd(0) species by proton transfer[19]. An α-alkyl substituent decelerates the initial nucleophilic reaction of the Pd(0) species by steric hindrance, whereas the β-phenyl substituent electronically stabilizes the transition state of the β-hydrogen movement. Recently, iridium complexes analogous to **7** have been obtained by reaction of a simple epoxide and an Ir(I) phosphine complex[20].

The marked accelerating effect of the added diphosphine, DPE, deserves comment. The reaction system consists of the equilibrating Pd complexes[21] as illustrated by Eqn. 3.

(3)

P = triphenylphosphine
P—P = diphosphine

Thus, the major isomerization catalyst could be the 14-electron, bent dicoordinate species **9**. Not only does DPE act as a supporting ligand, but it also enhances uniquely nucleophilicity of the zerovalent palladium[22]. In this regard, the MO effect would be the most significant (Fig. 1)[23]. As illustrated by **10**, the dicoordinate d^{10} Pd(0) species prefers to have the ligands structurally linear. In this case, the HOMO is of the $d_z{}^2$ type and develops along the P-Pd-P axis. Obviously, this is unfavourable for the bimolecular reaction with epoxides. On the other hand, on going to the five-membered chelate structure **9**, the level of such a MO moves down and the level of the d_{zx}-type MO rises substantially to become the HOMO. This orbital is spatially exposed outside and, consequently, is very appropriate for

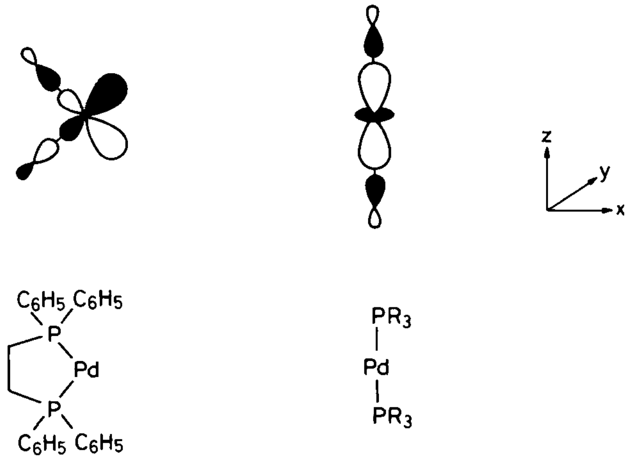
Table II Palladium(0)-catalyzed reaction of α,β-epoxy ketones to give β-diketones[a]

Epoxy ketone		Catalyst		Conditions		Yield[c] (%)
Entry	Weight [mg (mmol)]	Pd $(PPh_3)_4$ (mmol)	DPE[b] (mmol)	Toluene (ml)	Temp (°C) [time (h)]	
	(E)-3,4-epoxy-2-pentanone (**3**)					2,4-pentanedione (**4**)
1	196 (1.96)	0.06	0.06	0.5	140 (11)	81[d]
2	43 (0.43)	0.012	0	0.5	140 (11)	11[d]
	(E)-3,4-epoxy-5-methyl-2--hexanone (**13**)					5-methyl-2,4-hexanedione (**26**)
3	5660 (44)	0.66	0.67	15	140 (60)	80
4	500 (3.9)	0.13	0	3	138 (96)	41
	(E)-4,5-epoxy-6-tridecanone (**14**)					4,6-tridecanedione (**27**)
5	200 (0.94)	0.047	0.047	2	140 (64)	90
	(E)-5,6-epoxy-4-tridecanone (**15**)					4,6-tridecanedione (**27**)
6	247 (1.19)	0.061	0.061	2	140 (90)	90
	(E)-3,4-epoxy-4-phenyl-2--butanone (**16**)					1-phenyl-1,3-butanedione (**28**)
7	75 (0.46)	0.03	0	1.5	80 (6)	63
	(E)-1,2-epoxy-1-phenyl-3--nonanone (**17**)					1-phenyl-1,3-nonanedione (**29**)
	65 (0.28)	0.014	0.014	2	140 (17)	82
8	(E)-2,3-epoxy-1,3-diphenyl-1--propanone (**18**)					1,3-diphenyl-1,3--propanedione (**30**)
9	448 (2)	0.1	0.1	5	90 (18) and 120 (29)	84
10	52 (0.23)	0.03	0	2	80 (14)	94
	(E)-2,3-epoxycyclododecanone (**19**)					1,3-cyclododecanedione (**31**)
11	240 (1.22)	0.12	0.12	2	140 (97)	54
12	95 (0.48)	0.06	0	2	140 (100)	7
	2,3-epoxycyclooctanone (**20**)					1,3-cyclooctanedione (**32**)
13	209 (1.49)	0.074	0.073	1.5	140 (96)	52
	2,3-epoxycycloheptanone (**21**)					1,3-cycloheptanedione (**33**)
14	282 (2.24)	0.093	0.089	2	100 (20)	60
	2,3-epoxycyclohexanone (**22**)					1,3-cyclohexanedione (**34**)
15	109 (0.97)	0.031	0.031	1[e]	80 (24)	62
16	101 (0.9)	0.022	0	4	80 (24)	30
	2,3-epoxycyclopentanone (**23**)					1,3-cyclopentanedione (**35**)
17	30 (0.31)	0.01	0.01	1	80 (2.5)	94
18	70 (0.72)	0.028	0	1[e]	80 (7)	89
19	1220 (12.4)	0.61	0	50	70 (120)	86
	5-isopropyl-2-methyl-2,3--epoxycyclohexanone (**24**)					5-isopropyl-2-methyl-1,3--cyclohexanedione (**36**)
20	127 (0.76)	0.077	0.077	2	140 (66)	18
	2,3-epoxy-3,5,5-trimethylcyclo--hexanone (**25**)					3,5,5-trimethyl-2-cyclohexanone (isophorone) (**37**)
21	308 (2)	0.05	0.05	3	140 (64)	22[f]

[a] Unless otherwise stated, reaction was carried out under argon atmosphere. [b] 1,2-Bis(diphenylphosphino)ethane. [c] After silica-gel column chromatography or distillation. [d] See entries 1 and 7 in Table I. [e] Two-phase reaction in a mixture of toluene and water (50 : 50 v/v). [f] The starting epoxy ketone was recovered in 34%. Yield was determined by GLC analysis.

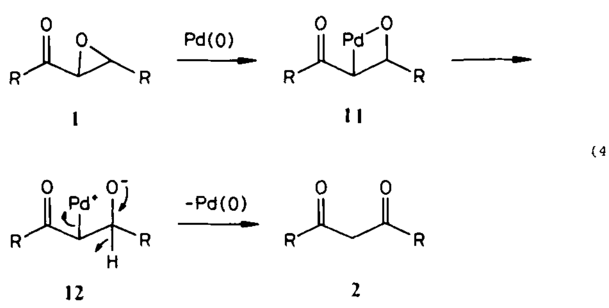
the nucleophilic reaction. A five-membered chelate Pt(0) complex is known to be more reactive than the six-membered analogue[22]. The dicoordinate Pd(0) species, bearing two triphenylphosphine ligands, equilibrates with the bent structure and therefore reacts with epoxides, albeit slowly. However, we cannot dismiss the possibility that the tricoordinate Pd(0) complex of type **8** is the nucleophilic metal species, since TRIPHOS assisted the isomerization of **3** to **4** to some extent (entry 15 in Table I). If this is the case, the **6**→**7** transformation in Eqn. 2 is facilitated by dissociation of one phosphine ligand.

Although the experimental findings are consistent with the mechanism shown in Eqn. 2, a non-metal hydride mechanism is also conceivable. As shown in Eqn. 4, dicoordinate Pd(0) species might undergo front-side insertion into the epoxy C–O bond to generate the palladaoxetane structure **11**. Possible heterolytic bond rupture of the O–Pd bond provides the zwitterion **12**. For geometric reasons, the β-hydrogen is unable to move onto Pd (at least in the cyclic system), but the vicinally located electropositive oxygen and



9 **10**

Fig. 1. Shape of HOMO's of the bent and linear dicoordinate Pd(0) complexes.



electronegative palladium could cooperatively assist the 1,2-hydride shift to give **2** and Pd(0), thus completing the isomerization.

The mechanism of the Pd-catalyzed deoxygenation reaction is not yet clear[24].

Experimental

General

IR spectra were obtained using a JASCO IR A-1 or IR A-3 spectrometer. ^{1}H NMR spectra were obtained using a Varian HA-100, NV-21, a JEOL PMX-60 or a FX-90Q spectrometer with TMS as internal standard. Mass spectra (MS) were recorded using an Hitachi RMU-6C or a JEOL JMSD-10 mass spectrometer with an ionization voltage of 75 eV. High-resolution mass spectra (HRMS) were measured at the Chemical Instrument Center at Nagoya University and Ono Pharmaceutical Co. Analytical GLC was performed on an Hitachi 063 or a NEVA Model 1400 gas chromatograph. Elemental analyses were performed at the Faculty of Engineering of Nagoya University. Bulb-to-bulb distillation was performed using a Büchi Kugelrohrofen. The cited temperatures refer to the oven temperature and are therefore not true boiling points. Melting points were measured on a YANACO micro melting point apparatus and are uncorrected. Silica gel 60 F_{254} precoated plates (E. Merck) of 0.25-mm thickness were used for analytical TLC. The plates were sprayed with a solution of 2% 4-methoxybenzaldehyde in 5% ethanolic sulfuric acid or with a saturated solution of cerium(IV) sulfate in 65% sulfuric acid. They were then heated on a hot plate until the spots became clearly visible. A solution of $FeCl_3$ in methanol was also used as an indicator for the analytical TLC. Column chromatography was conducted by using 70–230 mesh silica gel (E. Merck).

Catalysts and ligands

Tetrakis(triphenylphosphine)palladium(0) was prepared using the standard method as described by *Coulson*[25]. The resulting slightly pale-green yellow crystals were recrystallized from a 3 : 1 mixture of THF and ether at 0°C to give bright yellow crystals. This recrystallization procedure was important for the reproducibility of the reaction. Although the complex can be handled in air for a short period without decomposition, it was stored in a sealed tube under argon to ensure its purity. Tributylphosphine and triphenylphosphine were purchased from Nakarai and used after distillation and recrystallization, respectively. Other phosphine ligands were purchased from Strem and used without any further treatment.

Solvents and materials

Toluene and benzene were purified by distillation from sodium diphenyl ketyl under an argon atmosphere and were stocked in Schlenk tubes under an argon atmosphere. Ethereal solvents were freshly distilled from diphenyl ketyl prior to use. Water used in the reaction was distilled under an argon atmosphere. Starting α,β-epoxy ketones are easily accessible from the corresponding α,β-unsaturated ketones by treatment with basic hydrogen peroxide, tert-butyl hydroperoxide or peracids[26]. Epoxidation of allylic alcohols followed by chromic acid oxidation also gives the substrates[27]. The following epoxy ketones were prepared from the corresponding enones by alkaline hydrogen peroxide oxidation[26]: (E)-3,4-epoxy-2-pentanone (**3**)[28], (E)-3,4-epoxy-5-methyl-2-hexanone (**13**)[28], (E)-3,4-epoxy-4-phenyl-2-butanone (**16**)[29], (E)-2,3-epoxy-1,3-diphenyl-1-propanone (**18**)[29,30], (E)-2,3-epoxycyclododecanone (**19**)[32], 2,3-epoxycyclooctanone (**20**)[33], 2,3-epoxycycloheptanone (**21**)[34], 2,3-epoxycyclohexanone (**22**)[35], 5-isopropyl-2-methyl-2,3-epoxycyclohexanone (**24**)[36], 2,3-epoxy-3,5,5-trimethylcyclohexanone (**25**)[35].

(E)-4,5-Epoxy-6-tridecanone (**14**) was prepared as follows. Hydroalumination of 1-pentyne with diisobutylaluminium hydride (50°C, 6 h) in benzene[37], followed by addition of octanal[38] (0°C; then 25°C for 12 h), gave (E)-4-tridecen-6-ol (44%); R_f 0.33 (5 : 1 hexane/ethyl acetate). IR (neat): 3600–3200, 965 cm^{-1}. ^{1}H NMR δ: 0.8–1.1 (m, 6, 2 CH_3), 1.2–1.7 (br, 15, 7 CH_2 and OH), 2.0 (m, 2, CH_2), 4.05 (br, 1, CHO), 5.40 (dd, 1, J 6 and 15 Hz, vinyl), 5.70 (dt, 1, J 5.5 and 15 Hz, vinyl). Using *Jones'* oxidation (0°C, 4 min) led to (E)-4-tridecen-6-one (74%); R_f 0.63 (5 : 1 hexane/ethyl acetate). IR (neat): 1680, 1630, 980 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.9–1.1 (m, 6, 2 CH_3), 1.2–1.8 (br, 12, 6 CH_2), 2.2–2.5 (m, 2, $CH_2C=$), 2.53 (t, 2, J 7 Hz, CH_2CO), 6.10 (d, 1, J 15 Hz, vinyl), 6.82 (dt, 1, J 7 and 15 Hz, vinyl). Alkaline hydrogen peroxide oxidation under standard conditions (0°C, 2.5 h)[27] in methanol gave **14** (56%); R_f 0.5 (5 : 1 hexane/ethyl acetate). IR (neat): 1715 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 0.8–1.0 (m, 6, 2 CH_3), 1.2–1.7 (br, 14, 7 CH_2), 3.22 (m, 2, CH_2CO), 3.05 (dt, 1, J 2 and 6 Hz, CHO), 2.32 (d, 1, J 2 Hz, CHO). MS (m/z) 212 (M^+). HRMS calcd. for $C_{13}H_{24}O_2$: 212.1776; found: 212.1803.

(E)-5,6-Epoxy-4-tridecanone (**15**) was prepared by a similar reaction sequence to that described above. Hydroalumination (50°C, 5 h) of 1-nonyne, followed by addition of butanal (0°C then 25°C for 45 h), gave (E)-tridecen-4-ol (54%). IR (neat): 3600–3200, 965 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 0.8–1.0 (m, 6, 2 CH_3), 1.2–1.6 (br, 15, 7 CH_2 and OH), 2.0 (br m, 2, $CH_2C=$), 4.05 (br, 1, CHO), 5.42 (dd, 1, J 6 and 15 Hz, vinyl), 5.68 (dt, 1, J 5.5 and 15 Hz, vinyl). *Jones'* oxidation (0°C, 5 min) led to (E)-5-tridecen-4-one. IR (neat): 1680, 1635, 980 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 0.8–1.0 (m, 6, 2 CH_2), 1.2–1.8 (br, 12, 6 CH_2), 2.20 (br m, 2, $CH_2C=$), 2.50 (t, 2, J 7 Hz, CH_2CO), 6.10 (d, 1, J 15 Hz, vinyl), 6.83 (dt, 1, J 6 and 15 Hz, vinyl). Alkaline hydrogen peroxide oxidation (0°C, 0.5 h) gave **15** (68%). IR (neat): 1715 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 0.8–1.0 (m, 6, 2 CH_2), 1.2–1.8 (br, 14, 7 CH_2), 2.1–2.4 (m, 2, CH_2CO), 3.02 (dt, 1, J 2 and 6 Hz, CHO), 3.20 (d, 1, J 2 Hz, CHO). MS (m/z) 212 (M^+). HRMS calcd. for $C_{13}H_{24}O_2$: 212.1776; found: 212.1799.

(E)-1,2-Epoxy-1-phenyl-3-nonanone (**17**) was prepared by condensation of 2-octanone and benzaldehyde with 10% aqueous NaOH (25°C, 12 h) in methanol[39], giving (E)-1-phenyl-1-nonen-3-one (43%); R_f 0.50 (5 : 1 hexane/ethyl acetate). IR ($CHCl_3$); 1685, 1655, 1605, 975 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 0.90 (t, 3, J 6 Hz, CH_3), 1.1–1.8 (br, 8, 4 CH_2), 2.70 (t, 2, J 6.5 Hz, CH_2CO), 6.76 (d, 1, J 16 Hz, vinyl), 7.3–7.7 (m, 6, phenyl and vinyl). This was followed by epoxidation with alkaline hydrogen peroxide[27] (0°C, 2.5 h) in methanol to give **17** (63%); R_f 0.50 (5 : 1 hexane/ethyl acetate); m.p. 51–51.5°C (recrystallization from ether/hexane). IR ($CHCl_3$); 1710 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 0.90 (t, J 6.5 Hz, CH_3), 1.2–1.8 (br, 8, 4 CH_2), 2.4–2.5 (m, 2, CH_2CO), 3.52 (d, 1, J 2.5 Hz, CHO), 3.98 (d, 1, J 2.5 Hz, CHO), 7.2–7.4 (m, 5, phenyl). MS (m/z) 232 (M^+). HRMS calcd. for $C_{15}H_{20}O_2$: 232.1463; found: 232.1465.

2,3-Epoxycyclopentanone (**23**) was prepared as follows: To a solution of 2-cyclopentenone (10 g, 0.12 mol) and 35% hydrogen peroxide aqueous solution (27.5 ml, 0.25 mol) in methanol (100 ml) was added slowly at − 50 to − 40°C[40] a 2N NaOH aqueous solution (25 ml) over a period of 40 min in order to maintain the reaction temperature below − 40°C. The mixture was stirred for 50 min at the same temperature. Termination of the reaction was checked by GLC analysis (t_r 6 min, SE-30 on chromosorb W, 0.3 mmφ × 1 m, 1 kg/cm^{-2}, 90°C). The reaction mixture was poured into a NH_4Cl aqueous solution (200 ml) and extracted eight times with CH_2Cl_2 (30 ml each). The combined extracts were washed with satd. NaCl aqueous solution and dried over anhydrous Na_2SO_4. Concentration and distillation under reduced pressure gave **23** (7.43 g, 67%); b.p. 85–87°C/40 mmHg. IR (neat): 1740 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 1.8–2.5 (m, 4, 2 CH_2), 3.18 (d, 1, J 2 Hz, CHO), 3.82 (d, 1, J 2 Hz, COCHO). See the related procedure in ref. 41.

Palladium(0)-catalyzed reaction of α,β-epoxy ketones

Standard procedure. Prior to the introduction of solvents and materials, the reaction vessel (a glass tube or an ampule) was treated with an aqueous solution of ethylenediaminetetraacetic acid disodium salt and dried. In a 50-ml ampule were placed tetrakis(triphenylphosphine)palladium(0)[25] (767 mg, 0.66 mmol) and 1,2-bis(diphenylphosphino)ethane (DPE) (266 mg, 0.67 mmol). The system was then flushed with argon. To this mixture was added toluene (10 ml) through a stainless cannula under a slight argon pressure. A solution of (E)-3,4-epoxy-5-methyl-2-hexanone (**13**) (5.66 g, 44 mmol) in toluene (5 ml), prepared under an argon atmosphere, was then added to the mixture through a cannula under a slight argon pressure. The ampule was then sealed and the mixture heated at 140°C for 60 h. The reaction mixture was cooled to 0°C and the ampule was opened. The mixture was directly subjected to column chromatography on silica gel (50 g) using hexane (100 ml) and then ether (250 ml) as eluents. The ethereal eluent was concentrated and distilled under reduced pressure to give 5-methyl-2,4-hexanedione (**26**) (4.53 g, 80% yield); b.p. 82–84°C/50 mmHg, lit.[42] 160–170°C/760 mmHg; TLC: R_f 0.3 (10 : 1 hexane/ethyl acetate). IR (neat): 3600–2400, 1720, 1650–1550 (br) cm^{-1}. ^1H NMR (CCl_4) δ: 1.10 [d, 1.2, *J* 7 Hz, $C(CH_3)_2$, keto form], 1.14 [d, 4.8, *J* 7 Hz, $C(CH_3)_2$, enol form], 2.00 (s, 2.4, $COCH_3$, enol form), 2.04 (s, 0.6, $COCH_3$, keto form), 2.38 (q, 1, *J* 6 Hz, CH), 3.50 (s, 0.2, CH_2, keto form), 5.40 (s, 0.9, vinyl, enol form), 15.3–15.5 (br, 0.9, OH, enol form).

This compound was readily transformed into the pyrazole derivative. A solution of diketone **26** (57 mg) and hydrazine monohydrate (0.3 ml) in ethanol (1 ml) was stirred at room temperature for 20 min and then refluxed for 10 min. The reaction mixture was extracted twice with ether (10 ml each). The combined ether extracts were dried over $MgSO_4$ and evaporated. The residue was purified by thin-layer chromatography using a 1 : 2 mixture of ethyl acetate and benzene as eluent to give 3-isopropyl-5-methylpyrazole (41 mg, 74% yield). IR ($CHCl_3$): 3460, 3400–2800 (br), 1570 cm^{-1}. ^1H NMR (CCl_4) δ: 1.22 [d, 6, *J* 7 Hz, $C(CH_3)_2$], 2.20 (s, 3, CH_3), 2.90 (heptet, 1, *J* 6 Hz, CH), 5.68 (s, 1, vinyl), 11.96 (s, 1, NH). MS (*m/z*) 124 (M^+).

Table II lists the experimental details for the other cases. Unless otherwise stated, the reaction was conducted using a similar procedure. GLC analysis of the experiments shown in Table I was conducted using 5% DEGS on Neopack 1A, 3 mmϕ × 2 m, 75°C, 0.6 Kg/cm^2; 1,3-pentanedione at t_r 5.6 min and 3-penten-2-one at 3.6 min (methyl octanoate as standard material). GLC analysis of entry 21 in Table II was performed using 5% Carbowax 20M on chromosorb WAW, 3 mmϕ × 3 m, 150°C, 1.1 Kg/cm^2; 2,3-epoxy-3,5,5-trimethylcyclohexanone at t_r 3.63 min, 3,5,5-trimethyl-2-cyclohexenone (isophorone, **37**) at t_r 4.3 min (methyl laurate as standard material).

4,6-Tridecanedione (**27**). TLC; R_f 0.39 (1 : 1 benzene/hexane); column chromatography (SiO_2, 13 g), 1 : 1 benzene/hexane as eluent. IR (neat): 3600–2400, 1700, 1640–1560 (br) cm^{-1}. ^1H NMR (CCl_4) δ: 0.87 (t, 3, *J* 7 Hz, CH_3), 0.94 (t, 3, *J* 7 Hz, CH_3), 1.1–1.8 (br, 12, 6 CH_2), 2.20 (t, 4, 2 $COCH_2$), 3.67 (s, 0.1, $COCH_2CO$, keto form), 5.33 (s, 0.95, vinyl, enol form), 15.4–15.8 (br, 0.95, OH, enol form). MS (*m/z*): 212 (M^+), 194, 169, 141, 128, 127, 113. HRMS calcd. for $C_{13}H_{24}O_2$: 212.1776; found: 212.1777. Anal. calcd. for $C_{13}H_{24}O_2$: C 73.53, H 11.39; found: C 73.34, H 11.37%.

1-Phenyl-1,3-butanedione (**28**)[43]. TLC: R_f 0.34 (10 : 1 hexane/ethyl acetate); column chromatography (SiO_2, 10 g), 15 : 1 hexane/ethyl acetate as eluent. IR ($CHCl_3$): 1600 (br) cm^{-1}. ^1H NMR (CCl_4) δ: 2.12 (s, 3, CH_3), 6.08 (s, 1, vinyl, enol form), 7.2–7.9 (m, 5, phenyl).

1-Phenyl-1,3-nonanedione (**29**). TLC: R_f 0.58 (5 : 1 hexane/ethyl acetate); column chromatography (SiO_2, 5 g), 15 : 1 hexane/ethyl acetate as eluent. IR ($CHCl_3$): 3600–2400, 1700–1600 (br) cm^{-1}. ^1H NMR (CCl_4) δ: 0.92 (t, 3, *J* 6 Hz, CH_3), 1.2–2.0 (br, 8, 4 CH_2), 2.34 (t, 2, *J* 7 Hz, $COCH_2$), 3.92 (s, 0.1, $COCH_2CO$, keto form), 6.06 (s, 0.95, vinyl, enol form), 7.2–7.9 (m, 5, phenyl), 15.5–16.5 (br, 0.95, OH, enol form). HRMS calcd. for $C_{15}H_{20}O_2$: 232.1463; found: 232.1434. This compound was readily converted into its pyrazole derivative. A mixture of **29** (75 mg, 0.322 mmol) and hydrazine monohydrate (0.3 ml) in ethanol was stirred at room temperature for 15 min and then heated at 60°C for 1 min. Water (10 ml) was added and extracted three times with ether (10 ml each). Ether extracts were dried over $MgSO_4$ and evaporated. Column chromatography on silica gel (8 g) using a 3 : 1 mixture of hexane and ethyl acetate as eluent gave 3-hexyl-5-phenylpyrazole (63 mg, 85% yield) as crystals; m.p. 71–72°C (recrystallized from ether/hexane); TLC: R_f 0.5 (2 : 1 benzene/ethyl acetate). IR ($CHCl_3$): 3440, 3400–2800, 1605, 1590, 1560 cm^{-1}. ^1H NMR (CCl_4) δ: 0.86 (t, 3, *J* 7 Hz, CH_3), 1.2–1.7 (br, 8, 4 CH_2), 2.50 (t, 2, *J* 7.5 Hz, $CH_2C=$), 6.20 (s, 1, vinyl), 7.1–7.7 (br, 5, phenyl), 11.0–11.6 (br, 1, NH). MS (*m/z*) 228 (M^+). Anal. calcd for $C_{15}H_{20}N_2$: C 78.90, H 8.83, N 12.27; found: C 78.86, H 8.88, N 12.44%.

1,3-Diphenyl-1,3-propanedione (**30**). TLC: R_f 0.57 (5 : 1 hexane/ethyl acetate); column chromatography (SiO_2, 15 g), 20 : 1 benzene/ethyl acetate as eluent. IR ($CHCl_3$); 1650–1500 (br) cm^{-1}. ^1H NMR (CCl_4) δ: 6.74 (s, 1, vinyl, enol form), 7.2–7.5 (m, 6, aromatic), 7.8–8.0 (m, 4, aromatic), 16.80 (br s, 1, OH, enol form). These spectra were identical with those of an authentic commercial sample (Aldrich). Anal. calcd. for $C_{15}H_{12}O_2$: C 80.33, H 5.39; found: C 80.19, H 5.66%.

1,3-Cyclododecanedione (**31**)[44]. TLC: R_f 0.50 (5 : 1 hexane/ethyl acetate); preparative TLC conducted three times using 20 : 1 hexane/ethyl acetate as solvent. IR (neat): 3600–3400, 1720–1680 (br), 1620–1580 (br). ^1H NMR (CCl_4) δ: 1.0–2.0 (br, 14, 7 CH_2), 2.50 (t, 4, *J* 6.5 Hz, 2 $COCH_2$), 3.47 (s, 1.5, $COCH_2CO$, keto form), 5.64 (s, 0.25, vinyl, enol form). MS (*m/z*) 196 (M^+). This compound revealed a brown-red colour on spraying with $FeCl_3$ methanolic solution[43].

1,3-Cyclooctanedione (**32**)[44]. TLC: R_f 0.24 (5 : 1 hexane/ethyl acetate); column chromatography (SiO_2, 10 g), 20 : 1 hexane/ethyl acetate as eluent. ^1H NMR (CCl_4) δ: 1.5–2.0 (m, 6, 3 CH_2), 2.3–2.5 (m, 4, 2 $COCH_2$), 3.40 (s, 2, $COCH_2CO$).

1,3-Cycloheptanedione (**33**)[45]. TLC: R_f 0.1 (2 : 1 petroleum ether/ether); column chromatography (SiO_2, 10 g), 5 : 1 hexane/ether as eluent. IR (neat): 1730, 1700 cm^{-1}. ^1H NMR (CCl_4) δ: 1.9–2.2 (m, 4, 2 CH_2), 2.4–3.0 (m, 4, 2 $COCH_2$), 3.45 (s, 2, $COCH_2CO$). MS (*m/z*) 126 (M^+).

1,3-Cyclohexanedione (**34**). 2,3-Epoxycyclohexanone (**22**) (108.7 mg, 0.97 mmol), tetrakis(triphenylphosphine)palladium(0) (35.5 mg, 0.031 mmol), DPE (12.4 mg, 0.031 mmol), toluene (1 ml) and water (1 ml) were placed in an ampule under an argon atmosphere. The mixture was shaken at 80°C for 24 h under an argon atmosphere. The reaction mixture was then filtered and the filtrate extracted five times with water (2 mL each). The combined water extracts were evaporated azeotropically with ethanol under reduced pressure to give **34** (67.7 mg, 62.3% yield); TLC: R_f 0.5 (30 : 1 ethyl acetate/ethanol). IR ($CHCl_3$): 1740 (small), 1720, 1650–1520 cm^{-1}. ^1H NMR (DMSO-d_6) δ: 1.88 (m, 2, CH_2), 2.23 (t, 4, 2 $COCH_2$), 3.65 (br, 0.64, $COCH_2CO$, keto form), 5.22 (s, 0.68, vinyl, enol form). These spectra were identical with those of an authentic commercial sample (Aldrich).

1,3-Cyclopentanedione (**35**). A mixture of tetrakis(triphenylphosphine)palladium(0) (707 mg, 0.61 mmol) and toluene (45 ml) was placed in an ampule. To this was added a solution of 2,3-epoxycyclopentanone (**23**) (1.22 g, 12.4 mmol) in toluene (5 ml) and the vessel was sealed under argon. The mixture was heated with shaking at 70°C for 5 days. The reaction mixture was then opened to air and poured into benzene (50 ml). The remaining solid was dissolved in methanol (10 ml). The combined organic solution was extracted four times with water (50 ml + 30 ml × 3). The combined aqueous extracts were washed twice with benzene (50 ml each) and evaporated under reduced pressure azeotropically with ethanol to give crystalline 1,3-cyclopentanedione (1.05 g, 86% yield). IR (KBr) 3390, 2940, 1655, 1625, 1575 cm^{-1}. ^1H NMR (DMSO-d_6) δ: 2.36 (s, 4, 2 CH_2), 5.10 (s, 1, vinyl, a complete enol form). MS (*m/z*) 98 (M^+). These spectra were identical with those of an authentic commercial sample (Aldrich).

5-Isopropyl-2-methyl-1,3-cyclohexanedione (**36**). Mp 189–190°C; TLC: R_f 0.5 (1 : 1 ethyl acetate/benzene); column chromatography (SiO_2, 20 g), 1 : 4 ethyl acetate/benzene as eluent. IR (neat): 3600–3100, 1735, 1700, 1620 cm^{-1}. ^1H NMR (CD_3OD) δ: 0.93 [d, 6, *J* 6 Hz, $C(CH_3)_2$], 1.63 (s, 3, CH_3), 1.3–2.6 (m, 6, 2 CH_2 and 2 CH), 4.90 (br, s, 1). MS (*m/z*) 168 (M^+). Anal. calcd. for $C_{10}H_{16}O_2$: C 71.45, H 9.29; found: C 71.39, H 9.59%.

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