A Reexamination of the Robinson Annelation of 2-Methylcyclohexanone with 3-Penten-2-one and 4-Phenyl-3-buten-2-one[1]

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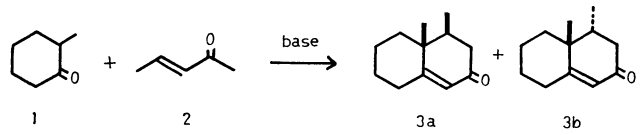
The reported Robinson annelation of 2-methylcyclohexanone with 3-penten-2-one has been reexamined. In contrast to the previous result, it was found that the reaction product was not only obtained in a low yield, but also the solvent-depending stereoselectivity in the formation of *cis*-4,4a-dimethyl-4,4a,5,6,7,8-hexahydronaphthalen-2(3*H*)-one (**3a**) and its *trans* isomer (**3b**) was considerably lower than that reported. As expected, regioisomers, 4β,8α-dimethyl-4,4aβ,5,6,7,8-hexahydronaphthalen-2(3*H*)-one and 4β,8β-dimethyl-4,4aα,5,6,7,8-hexahydronaphthalen-2(3*H*)-one, were also formed in the annelation. A similar tendency was observed in the reaction with 4-phenyl-3-penten-2-one. The annelation products, **3a**, **3b**, *cis*-4-phenyl-4a-methyl-4,4a,5,6,7,8-hexahydronaphthalen-2(3*H*)-one, and *trans*-4-phenyl-4a-methyl-4,4a,5,6,7,8-hexahydronaphthalen-2(3*H*)-one, were also synthesized by an alternative route.

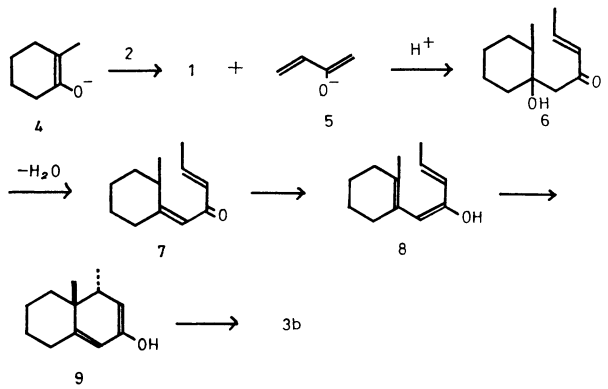
The Robinson annelation has most widely been employed as a useful method of synthesizing *cis*-1,8a-dimethyldecalins, the fundamental structures of eremophilanoids.

Scanio and Starrett[2] recently reported that *cis*-dimethyloctalone (**3a**) in an isomeric purity exceeding 95% was produced by the Robinson annelation of 2-methylcyclohexanone (**1**) with 3-penten-2-one (**2**) in dioxane, while change of the solvent to dimethyl sulfoxide dramatically altered the ratio of the diastereomers to give *trans*-dimethyloctalone (**3b**) in a high isomeric purity (over 95%) (Scheme 1). They also proposed a reaction mechanism (Scheme 2) for the predominant formation of the *trans*-isomer **3b** in dimethyl sulfoxide; the enolate, **4**, of 2-methylcyclohexanone (**1**) gives the 1,3-butadien-2-olate anion (**5**) by proton exchange, and the latter attacks the regenerated ketone, **1**, to yield olefinic alcohol, **6**. Under these reaction conditions, **6** is dehydrated to crossed dienone **7**, and its enol form, **8**, thermally cyclizes in a disrotatory manner to yield **9** predominantly.

To test their hypothesis concerning this unusual Robinson annelation in dimethyl sulfoxide, we reexamined their reaction of **1** and **2**, and also that of **1** and 4-phenyl-3-buten-2-one (**11**) for comparison.

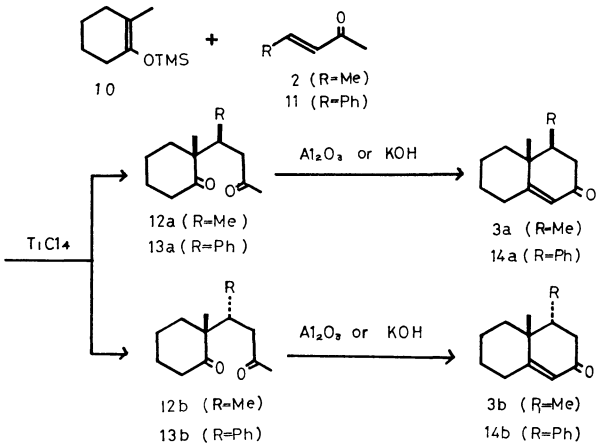


Scheme 1.



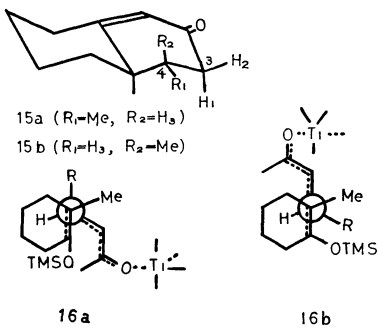
Scheme 2.

In order to obtain authentic samples for the GLC analysis of the annelation products, four octalones, **3a**, **3b**, **14a**, and **14b**, were synthesized by the alternative route shown in Scheme 3, because, contrary to the claim of Scanio and Starrett, these compounds were obtained only in poor yields under similar reaction conditions, as will be discussed later.



Scheme 3.

Silyl enol ether (**10**), prepared from 2-methylcyclohexanone (**1**), was treated with 3-penten-2-one (**2**) (or 4-phenyl-3-buten-2-one (**11**)) in dichloromethane in the presence of titanium tetrachloride,[3] thus giving a mixture of 1,5-diones **12a** and **12b** in a ratio of 25:75 (or **13a** and **13b** in a ratio of 71:29) and in a good yield. These diones were separated by chromatography and then submitted to aldol cyclization to give **3a** and **3b** (or **14a** and **14b**) respectively. The stereochemistry of the octalones thus obtained was assigned by means of ^{1}H NMR.[4] In the lanthanoid-shifted spectra of **3a** using Eu(dpm)$_3$, the signals of the protons on C(3) and C(4) were assigned by a concentration dependence of their chemical shifts on the shift reagent; coupling were confirmed by decoupling experiments, as is shown in Table 1 (cf. the conformational structure **15a**). The large coupling constant (J, 13 Hz) between H(1)- and H(3)-protons



clearly demonstrated a *trans* diaxial disposition of these protons, leading to the *cis*-dimethyloctalone structure **3a**. On the other hand, the **3b** isomer showed a small coupling between these protons (J, 5 Hz), which indicated this compound to be a *trans*-dimethyloctalone, **3b** (*cf.* **15b**). Similar reasoning may also be applicable to **14a** and **14b**.

It is worth a short comment that, in the Lewis acid-promoted Michael addition of **10**, the erythro-threo ratio of the product was reversed, depending on the acceptor used. Considering two preferable conformations, **16a** and **16b**, in the transition states, the R substituent (methyl or phenyl) would control the population of these conformers. When R is methyl, **16b** is more favored than **16a** because the bulkier acetonyl would be disposed between the methyl and cyclohexane methylene groups, yielding the threo isomer, **12a**. Meanwhile, phenyl is bulkier than acetonyl, and the favored conformation in the transition state of the reaction with **11** must be **16a**, which leads to the erythro isomer, **13b**.

With the four authentic octalones, **3a**, **3b**, **14a**, and **14b**, in our hands, we set about the GLC analysis[5] of the Robinson annelation product of **1** with **2** or **11**. The results of the analysis are shown in Table 2.

Entry 1 indicates the analytical result of the enone fraction of the product obtained from **1** and **2** under the reaction conditions described by the original authors. The combined yield of enones was quite low, and the major products were, rather, the regioisomer, **17a** or **17b**, and the dienone, **18**. These by-products were separated by preparative GLC, and their structures were assigned spectroscopically; the enone showed a carbonyl absorption at 1668 cm^{-1} in the IR spectrum. Two pairs of methyl doublets in the ^1H NMR spectrum demonstrated this compound to be a regioisomer of **3a**; meanwhile, in the lanthanoid-shifted ^1H NMR, its C(3)-methylene protons exhibited a coupling pattern (J, 18 and 12 Hz for H(1) and 18 and 6 Hz for H(2)) which was very similar to that of **3a**. This result supported the idea that the C(4)-methyl in the regioisomeric enone must be equatorial. From these results, we concluded that the **17a** or **17b** stereostructure should be assigned to this compound because this compound was produced under equilibrating con-

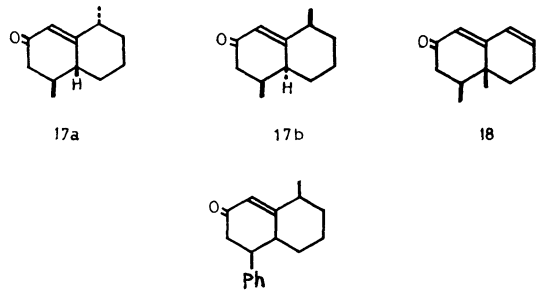


Table 1. Lanthanoid-shifted ^1H NMR of some protons of the octalones[a]

Octalone	Proton	Chemical shift, δ[b]	Coupling pattern and constants, Hz
3a	H_1	5.20	d.d, $J_{1,2}=18$, $J_{1,3}=12$
	H_2	5.44	d.d, $J_{1,2}=18$, $J_{2,3}=6$
	H_3	3.48	d.d, $J_{1,3}=12$, $J_{2,3}=6$
3b	H_1	5.82	d.d, $J_{1,2}=16$, $J_{1,3}=5$
	H_2	5.51	d.d, $J_{1,2}=16$, $J_{2,3}=8$
	H_3	3.36	d.d, $J_{1,3}=5$, $J_{2,3}=8$
14a	H_1	5.18	d.d, $J_{1,2}=18$, $J_{1,3}=16$
	H_2	4.70	d.d, $J_{1,2}=18$, $J_{2,3}=5$
	H_3	4.32	d.d, $J_{1,3}=16$, $J_{2,3}=5$
14b	H_1	4.55	d.d, $J_{1,2}=16$, $J_{1,3}=5$
	H_2	4.79	d.d, $J_{1,2}=16$, $J_{2,3}=9$
	H_3	4.00	d.d, $J_{1,3}=5$, $J_{2,3}=9$

a) $Eu(dpm)_3$ was added to a $CDCl_3$ solution of the substrate in a molar ratio of 1/3. b) Measured at 100 MHz.

Table 2. The robinson annelation of 2-methylcyclohexanone with 3-penten-2-one and 4-phenyl-3-buten-2-one

Entry	Enone	Reaction conditions			Combined yield/%	Ratio of products/%[b]		
		Solvent[a]	Temp/°C	Time/h		*cis*-Enone	*trans*-Enone	By-products identified
1	**2**	A	112—117	100	9	23	7	28(**17**), 40(**18**)
2	**2**	A	112—117	9	14	56	24	20(**17**)
3	**2**	B	75	6	22	25	75	
4	**2**	B	75	3	36	26	74	
5	**11**	A	112—117	6	29	53	15	32(**19a**)
6	**11**	A	112—117	3	36	54	16	30(**19a**)
7	**11**	B	75	6	26	37	34	10(**19a**), 19(**19b**)
8	**11**	B	75	3	26	37	36	8(**19a**), 12(**19b**)

a) A, dioxane; B, dimethyl sulfoxide. b) *Cf.* Ref. 5 for the analytical method.

ditions.

Another crystalline by-product showed a carbonyl absorption at 1659 cm^{-1} in the IR spectrum and a strong UV absorption at 239 nm, which indicated an $\alpha,\beta,\gamma,\delta$-unsaturated dienone chromophore. The dehydrogenation of **3a** with chloranil in *t*-butyl alcohol afforded the same dienone. Thus, this dienone is unambiguously shown by the formula **18**. This dienone was probably produced by the air oxidation of **3a** for a long period.

When the reaction time was shortened (Entry 2), the combined yield of the product was slightly raised and the only detectable by-product was the regioisomeric enone **17**.

In the reaction employing dimethyl sulfoxide as the solvent, the ratio of **3a** and **3b** was reversed (Entries 3 and 4), although the stereoselectivity of the reaction was not so high as Scanio and Starrett stated.[2] Unlike the reaction with 3-penten-2-one, no regioisomer was detectable in the reaction in dimethyl sulfoxide.

In the reaction of **1** and **11** employing dioxane as the solvent, the product was a mixture of *cis*- and *trans*-enone (**14a** and **14b**) and the regioisomer **19a**, in which the *cis*-enone **14a** was predominant (Entries 5 and 6). The structure of the regioisomer was supported by a carbonyl absorption at 1661 cm^{-1} in the IR spectrum and a three-proton doublet in the ^1H NMR spectrum. On the other hand, a comparable formation ratio of the *cis*- and *trans*-enones (**14a** and **14b**) was observed in the reaction using dimethyl sulfoxide as the solvent (Entries 7 and 8). Two regioisomers, **19a** and **19b**, were also isolated. The structures of the by-products were confirmed by the IR (1661 cm^{-1}) and ^1H NMR (a three-proton doublet) spectra, which demonstrated that these by-products must both be stereoisomers. However, we have obtained no evidence that allowed us to assign stereostructures to these regioisomers.

In conclusion, we could not observe such high stereoselectivity as was reported by Scanio and Starrett[2] in the Robinson annelation of 2-methylcyclohexanone and 3-penten-2-one, although a change in the formation ratio of the **3a** and **3b** stereoisomers was observed to some extent by replacing the reaction solvent. Accordingly, we are suspicious of the reaction mechanism (Scheme 2) they have proposed for the annelation in dimethyl sulfoxide, for if it will operate, the reaction would proceed much more stereoselectively.

Experimental

All the melting and boiling points are uncorrected. The IR spectra were taken on a Hitachi G-2 or 215 spectrophotometer. The ^1H NMR spectra were recorded on a Hitachi R-22 (90 MHz) or JEOL PS-100 (100 MHz) instrument, using TMS as the internal standard and $CDCl_3$ as the solvent. The recorded chemical shifts are on the δ (ppm) scale. The high resolution mass spectra were recorded on a JEOL JMS-OISC spectrometer. The GLC analysis was performed on a Shimadzu Model 5A instrument using the following columns: A (5% OV-17, 2 m×3 mm) and B (5% SE-30, 2 m×3 mm). The formation ratios of the reaction products were all determined by GLC.[5] The elemental analyses were performed in the microanalytical laboratory of the Chemical Research Institute of Non-Aqueous Solutions, Tohoku University.

2-Methylcyclohexanone (1). The ketone of a reagent grade (Tokyo Kasei Corp.) was distilled, and a fraction boiling at 163.2 °C was utilized.

3-Penten-2-one (2). This enone was prepared according to the method of Lawesson *et al.*[6] A fraction boiling at 52—54 °C/260 mmHg was immediately used.

*1,5-Diketones **12a** and **12b**.* These diketones were prepared according to the method of Mukaiyama *et al.*[3] A solution of $TiCl_4$ (570 mg, 3 mmol) in CH_2Cl_2 (12 ml) was cooled to −78 °C under N_2. Solutions of **2** (303 mg, 3.6 mmol) and **10**[8] (552 mg, 3 mmol) in the same solvent (5.4 and 4.5 ml respectively) were added successively to the above solution with stirring. After stirring for 30 min at −78 °C, the mixture was quenched with aqueous K_2CO_3 (1.05 g in 22 ml of water), and the resultant precipitates were filtered off. The filtrate was extracted with pentane, and the extract was washed with water and brine. After the removal of the solvent, the crude product (553 mg) was distilled in a vacuum to give the main fraction (374 mg; bp 102—126 °C (bath temperature)/1 mmHg††), which consisted of two isomers, **12a** and **12b** (25:75). Because the separation of these isomers by preparative TLC ($AgNO_3$-impregnated silica gel, hexane–AcOEt (5:1)) was incomplete, only one isomer, **12b** was separated in the pure state (21 mg, 13%). In order to separate the isomers completely, preparative GLC (Column B at 140 °C) was utilized. **12a**: R_t 6.7 min (Column B at 140 °C); IR ($CHCl_3$) 1700 cm^{-1}; ^1H NMR 0.86 (3H, d, J=7 Hz), 0.91 (3H, s), and 2.09 (3H, s). **12b**: R_t 7.8 min, IR ($CHCl_3$) 1700 and 1209 cm^{-1}; ^1H NMR 0.73 (3H, d, J=7 Hz), 0.94 (3H, s), and 2.17 (3H, s).

cis-4,4a-Dimethyl-4,4a,5,6,7,8-hexahydronaphthalen-2(3H)-one (3a). A mixture of **12a** (40 mg, 0.2 mmol), active alumina (activity II, 1.6 g), water (1.33 ml), and dioxane (4 ml) was heated at 105—109 °C under reflux for 3 h with stirring under N_2. Then the mixture was filtered, and the crude product (88 mg) was obtained from the filtrate on the removal of the solvent. Pure **3a** (21 mg, 58%) was obtained by preparative TLC repeated four times, using cyclohexane–AcOEt (10:1) as the solvent. IR ($CHCl_3$) 1660 and 1616 cm^{-1}; ^1H NMR 0.95 (3H, d, J=6 Hz), 1.09 (3H, s), and 5.98 (1H, d). The lanthanoid-shifted ^1H NMR spectra were taken as follows: an exact amount of $Eu(dpm)_3$ was added, portion by portion to a solution of **3a** (20 mg) in $CDCl_3$; the spectrum was recorded after each addition until the molar ratio of the substrate and the reagent reached 3:1. The experimental results obtained are shown in Table 1.

trans-4,4a-Dimethyl-4,4a,5,6,7,8-hexahydronaphthalen-2(3H)-one (3b). Pure **3b** (23 mg, 80%) was obtained from **12b** (32 mg, 0.16 mmol) in the same manner as has been described for **3a**. IR ($CHCl_3$) 1660 and 1618 cm^{-1}; ^1H NMR 0.98 (3H, d, J=6 Hz), 1.28 (3H, s), and 5.78 (1H, d). Found: C, 81.04; H, 10.34%. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18%.

*1,5-Diketones **13a** and **13b**.* A solution of freshly distilled $TiCl_4$ (380 mg, 2 mmol) in CH_2Cl_2 (8 ml) was cooled to −78 °C under N_2. A solution of **11**[7] (308 mg, 2.1 mmol) and **10** (450 mg, 2.4 mmol) in the same solvent (3 ml both) were added successively to the above solution with stirring. The mixture was then further stirred at −78 °C for 2.5 h. After quenching with aqueous K_2CO_3 (0.7 g in 15 ml of water), the resultant precipitates were

†† 1 mmHg≈133.322 Pa.

filtered off. The filtrate was extracted with CH_2Cl_2 and the extract was washed with water and brine. The subsequent removal of the solvent gave the crude product (598 mg). GLC (Column A at 180 °C) indicated two isomers (**13a** and **13b**, 71:29). Without distillation, the crude product was separated by preparative TLC, using hexane–AcOEt (5:1), to afford the respective isomers, **13a** (114 mg, 22%) and **13b** (211 mg, 41%). **13a**: R_t 9.4 min (Column A at 180 °C), IR ($CHCl_3$) 1702 and 1690 cm^{-1}; ^1H NMR 0.99 (3H, s) 1.98 (3H, s), 3.01 (H_1, dd, $J_{1,2}=16$, $J_{1,3}=10$ Hz), 2.48 (H_2, dd, $J_{1,2}=16$, $J_{2,3}=4$ Hz), 3.93 (H_3, dd, $J_{1,3}=10$, $J_{2,3}=4$ Hz) and 7.36 (5H, s). Found: C, 79.36; H, 8.91%. Calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58%. **13b**: R_t 10.1 min, IR ($CHCl_3$) 1701 and 1689 cm^{-1}; ^1H NMR 1.00 (3H, s). 2.03 (3H, s), 2.68 (H_1, dd, $J_{1,2}=16$, $J_{1,3}=4$ Hz), 3.03 (H_2, dd, $J_{1,2}=16$, $J_{2,3}=11$ Hz), 3.83 (H_3, dd, $J_{1,3}=4$, $J_{2,3}=11$ Hz), and 7.35 (5H, s). Found: C, 79.30; H, 8.83%. Calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58%.

cis-*4-Phenyl-4a-methyl-4,4a,5,6,7,8-hexahydronaphthalen-2(3H)-one (14a)*. Aqueous KOH (213 mg in 0.39 ml of water) was added to a mixture of **13a** (128 mg, 0.50 mmol) and ethanol (3 ml) with stirring under N_2. The whole mixture was heated at 90 °C under reflux for 4 h. The mixture was then cooled with ice, and 2% HCl was dropped into the mixture until the solution became pH 4. The resulting solution was extracted with CH_2Cl_2, and the extract washed with water and brine. The subsequent removal of the solvent gave the crude product (187 mg). Preparative TLC, using cyclohexane–AcOEt (4:1) as the solvent, gave the pure enone (90 mg, 76%), which solidified on distillation (bp 123—186 °C (bath temperature)/1 mmHg, mp 70.2—72 °C (recrystallized from pentane–benzene (5:1)); IR ($CHCl_3$) 1662 and 1616 cm^{-1}; ^1H NMR 1.10 (3H, s), 5.98 (1H, d), and 7.44 (5H, m). Found: C, 84.67; H, 8.29%. Calcd for $C_{17}H_{20}O$: C, 84.95; H, 8.39%.

trans-*4-Phenyl-4a-methyl-4,4a,5,6,7,8-hexahydronaphthalen-2-(3H)-one (14b)*. Pure **14b** (109 mg, 73%) was obtained from **13b** (161 mg, 0.63 mmol) in a similar manner. Distillation (bp 101—121 °C (bath temperature)/1 mmHg) of the enone gave a soft mass; mp 48.5—52 °C. No appropriate solvent was found for recrystallization. IR ($CHCl_3$) 1662 and 1614 cm^{-1}; ^1H NMR 1.35 (3H, s), 6.14 (1H, d), and 7.48 (5H, m). Found: C, 84.64; H, 8.29%. Calcd for $C_{17}H_{20}O$: C, 84.95; H, 8.39%.

The Annelation Reaction of 2-Methylcyclohexanone with 3-Penten-2-one. In Dioxane: NaH (178 mg, 3.6 mmol) was suspended in a solution of **1** (345 mg, 3.0 mmol) and dioxane (10 ml), and the mixture was stirred at 112—117 °C for 3 h under N_2. After cooling to room temperature, a solution of **2** (313 mg, 3.7 mmol) in dioxane (4 ml) was added, and the whole mixture was stirred for 9 h at room temperature. After the subsequent addition of a small amount of cold water, the mixture was extracted with pentane. The extract was washed with water and brine, and dried. After the removal of the solvent, the residue (512 mg) was distilled in a vacuum (bp 110—159 °C (bath temperature)/1 mmHg). The distillate (245 mg) was separated by preparative TLC, repeated four times, using cyclohexane–AcOEt (7:1) as the solvent; this gave two main fractions (R_f 4.8, 50 mg, 9% and R_f 5.3, 28 mg, 5%). The polar fraction was shown to be a mixture consisting of **3a** and **3b** (84:16), which was identified with authentic samples by GLC; however, the attempted separation of these isomers by GLC was fruitless. The by-product, **17a** (9 mg; mp 38.5—39 °C), in the less polar fraction was isolated by preparative GLC (Column A at 140 °C) and crystallized on standing, although no appropriate recrystallization solvent was found. IR ($CHCl_3$) 1668 and 1619 cm^{-1}; ^1H NMR 1.07 (3H, d, $J=6$ Hz), 1.16 (3H, d, $J=6$ Hz), and 5.86 (1H, s). Found: M^+ 178.1357. Calcd for $C_{12}H_{18}O$: M^+ 178.1357.

In a similar manner, **1** (337 mg, 3.0 mmol) and **2** (270 mg, 3.2 mmol) were allowed to react in dioxane for 100 h, after which the reaction mixture was worked up as above. A fraction (164 mg) obtained by short-path distillation was chromatographed on a silica-gel column, using hexane–AcOEt (7:1) as the solvent, thus giving an oil (46 mg, 9.0%). The GLC analysis (Column B at 140 °C) of the oil showed two peaks, **17a** (R_t 7.9 min) and **18** (R_t 11.2 min), along with those of **3a** and **3b**. Two by-products were separated by preparative GLC (Column B at 140 °C); **17a** (25 mg) and **18** (13 mg). The former by-product, **17a**, was identified by spectral comparison with the authentic compound. The latter one, **18**, solidified on standing; mp 39.8—42.5 °C; IR ($CHCl_3$) 1659 and 1622 cm^{-1}; ^1H NMR 0.98 (3H, d, $J=7$ Hz), 1.01 (3H, s), 5.72 (1H, s), and 6.21 (2H, br s); UV_{max} (95% EtOH) 239 nm (ε 12122); MS, *m/e* (rel intensity) 176 (M^+, 98), 134 (100), 119 (45), 105 (48), 91 (65).

This dienone was identified by spectral comparison with the authentic compound prepared by the dehydrogenation of **3a** (*vide post*).

In Dimethyl Sulfoxide (DMSO): A suspension of NaH (178 mg, 3.6 mmol) in DMSO (6 ml) was stirred at 75 °C for 30 min. After the addition of a solution of **1** (340 mg, 3 mmol) in DMSO (2 ml) and stirring for 3 h at room temperature, a solution of **2** (307 mg, 3 mmol) in the same solvent (3 ml) was added. The whole mixture was then stirred for 3 h at room temperature. After the subsequent addition of a small amount of ice water, the mixture was extracted with pentane. The extract was washed with water and brine, and dried. The evaporation of the solvent left an oil (373 mg), which was distilled in a vacuum (bp 114—158 °C (bath temperature)/1 mmHg) to give an oil (306 mg). The oil was purified by preparative TLC, repeated three times, using cyclohexane–AcOEt (7:1) as the solvent, to afford the main fraction (R_f 3.3, 193 mg, 36%). The GLC analysis of the fraction with a capillary column showed two peaks, **3a** and **3b** (29:71). Two other unidentified by-products were detected by the GLC (Column A at 140 °C, R_t 3.3 and 3.4 min) of the crude product.

Dehydrogenation of 3a with Chloranil. Authentic **18** was obtained by dehydrogenation according to the method of Agnello and Laubach.[10] A mixture of pure **3a** (36 mg, 0.2 mmol), chloranil (149 mg, 0.6 mmol), and *t*-butyl alcohol (5.5 ml) was heated at 80—90 °C for 3.5 h under N_2 with stirring. The reaction mixture was extracted with $CHCl_3$, and the extract was successively washed with water, 5% aqueous NaOH, water, and brine, and dried. After the removal of the solvent, the residue (30 mg) was purified directly by preparative TLC, using hexane–AcOEt (5:1) as the solvent, to give pure **18** (18 mg, 50%) as a soft mass (mp 39—42 °C).

The Annelation of 2-Methylcyclohexanone with 4-Phenyl-3-buten-2-one. In Dioxane: By a similar treatment, a crude product (952 mg) was obtained from **1** (336 mg, 3 mmol) and **11** (438 mg, 3 mmol) by allowing them to react at 112—117 °C for 3 h; subsequent distillation in a vacuum gave a fraction (bp 158—190 °C (bath temperature)/1 mmHg, 439 mg)) which was separated by preparative TLC, repeated twice, using hexane–AcOEt (15:1) as the solvent, to give two fractions (R_f 4.3 and 4.8). The two main compounds in the polar fraction (145 mg, 20%) were **14a** and **14b** (78:22), as identified with an authentic sample by GLC. The less polar fraction (113 mg, 16%) gave **19a** as the main

component upon preparative GLC (Column B at 180 °C, R_t 10.7 min, 9 mg); IR ($CHCl_3$) 1668 and 1619 cm^{-1}; ^1H NMR 1.19 (3H, d, J=7 Hz), 5.90 (1H, br s), and 7.24 (5H, m).

In DMSO: By a similar treatment, a crude product (990 mg) was obtained from **1** (449 mg, 4 mmol) and **11** (584 mg, 4 mmol) by a reaction at room temperature for 6 h. Vacuum distillation afforded a fraction (364 mg; bp 135—200 °C (bath temperature)/1 mmHg) which was subsequently separated by preparative TLC, using hexane–AcOEt (5:1) as the solvent, to give two fractions (R_f 3.5, 165 mg and R_f 4.0, 84 mg). Two enones, **14a** (10 mg) and **14b** (12 mg), were separated from the polar fraction by preparative GLC (Column A at 180 °C). **14a**, R_t 13.4 min; IR ($CHCl_3$) 1658 and 1616 cm^{-1}; ^1H NMR 1.09 (3H, s), 5.86 (1H, br s), and 7.31 (5H, m). **14b**, R_t 11.5 min; IR ($CHCl_3$) 1650 and 1618 cm^{-1}; ^1H NMR 1.33 (3H, s), 2.73 (1H, q, J=5 and 16 Hz), 3.0 and 3.12 (2H, in total), 5.96 (1H, br s), and 7.30 (5H, m). The two main components, **19a** (13 mg) and **19b** (24 mg), were separated from the less polar fraction by preparative GLC (Column A at 180 °C). **19a**, R_t 10.7 min; IR ($CHCl_3$) 1661 and 1601 cm^{-1}; ^1H NMR 1.19 (3H, d, J=7 Hz), 5.96 (1H, s), and 7.33 (5H, m). Found: M^+ 240.1520. Calcd for $C_{17}H_{20}O$: M^+ 240.1513. **19b**, R_t 12.3 min; IR ($CHCl_3$) 1661 and 1619 cm^{-1}; ^1H NMR 1.16 (3H, d, J=6 Hz), 5.79 (1H, s), and 7.36 (5H, m). Found: M^+ 240.1525. Calcd for $C_{17}H_{20}O$: M^+ 240.1513.

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