34329-47-0; **9b**, 932-03-6; **9c**, 61967-57-5; **9d**, 61967-59-7; *cis*-**9e**, 61967-58-6; *trans*-**9e**, 62014-82-8; **10a**, 61967-60-0; **10b**, 61967-61-1; **10c**, 61967-62-2; **10d**, 61967-63-3; **10e**, 61967-64-4; **11a**, 61967-50-8; **11b**, 55506-28-0; **11c**, 25127-83-7; **11d**, 61967-51-9; **11e**, 62057-82-3; **12d**, 61967-52-0; **12e**, 61967-53-1; acetylene, 74-86-2; cyclododecanone, 830-13-7; cyclooctanone, 502-49-8; cycloheptanone, 502-42-1; ethylidenecyclododecane, 56888-86-9.

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(10) A 6 ft × 0.25 in. column packed with 10% Dow 710 silicone oil on 60/80 mesh Chromosorb W was employed for this analysis.
(11) A 6 ft × 0.25 in. column packed with 15% Carbowax 20M/NaOH on 60/80 mesh Chromosorb W was employed for this analysis.
(12) The trans isomer was identified by coinjection with an authentic sample.
(13) A 6 ft × 0.25 in. column packed with 15% SF-96 silicone oil on 60/80 mesh Chromosorb W was employed for this analysis.
(14) A 6 ft × 0.25 in. column packed with 15% Carbowax 20M on 60/80 mesh Chromosorb W was employed for this analysis.
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Chlorocarbonylbis(triphenylphosphine)iridium-Catalyzed Isomerization, Isoaromatization, and Disproportionation of Some Cycloalkanones Having Exocyclic Double Bonds

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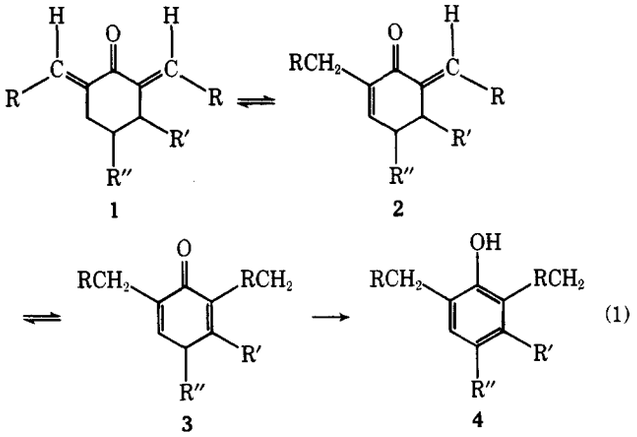
Chlorocarbonylbis(triphenylphosphine)iridium has been shown to be an efficient catalyst at 250 °C for isoaromatization of 2,6-diarylidenecyclohexanones. A stepwise migration of the exocyclic double bonds takes place followed by thermal tautomerization of the cyclohexa-2,5-dienone system. 2-Arylidene-1-tetralones undergo similar transformations to the corresponding naphthols. 2,7-Dibenzylidenecycloheptanone, which cannot form an aromatic system without loss of H_2, exhibits only *E–Z* isomerization. 3,7-Dibenzylidenecycloheptane-1,2-dione is partly converted into 3,7-dibenzyltropolone, and partly disproportionates to dibenzylcycloheptanedione and to polymer precursor. Unsaturated cyclopentanones react to give disproportionation products along with double bond migration into the five-membered ring.

2-Benzylphenols and naphthols have been known for many years to possess specific bacteriostatic and fungistatic activities.[1] They are, however, of little practical value since most of their present syntheses are inefficient and low yielding processes. Direct benzylation of phenols give, in general, mixtures of isomers.[2] Isomerization of benzylidenecyclohexanones[3-7] by acids (PPA, HOAc–HBr) is often accompanied by skeletal rearrangements[8] and ring expansion,[9] whereas heterogeneous transition metal catalysts (Ni, Pd/C, PtO_2)[10] frequently cause oxygen extrusion[11] or, in alcoholic media, result in transfer hydrogenation of the carbon–carbon double bonds.[12]

In a preliminary communication[13] we reported that isoaromatization of 2,6-dibenzylidenecyclohexanones to 2,6-dibenzylphenols can be accomplished in excellent yields by the versatile iridium catalyst, $IrCl(CO)(PPh_3)_2$. We have now extended this study to include further arylidenecyclohexanones, as well as some derivatives of α-tetralone, cyclopentanone, cycloheptanone, and cycloheptanedione.

Isomerization of Diarylidenecyclohexanones. As described in the Experimental Section, (*E,E*)-2,6-dibenzylidenecyclohexanone (**1**, R = C_6H_5; R′ = R″ = H) is converted to 2,6-dibenzylphenol (**4**, R = C_6H_5; R′ = R″ = H) simply by heating the ketone and the catalyst (a high boiling solvent may be used) for 1.5–2 h at 230–250 °C. The reaction is stepwise (vide infra) as shown in eq 1.



(1)

The catalysis proceeds equally well (though at different rates) when the phenyl moieties in **1**, R = C_6H_5; R′ = R″ = H, are exchanged by substituted aryl groups, provided the substituents neither coordinate irreversibly to the catalyst (as does NO_2) nor extend serious steric effects (e.g., ortho substituents).

A summary of some representative experiments using $IrCl(CO)(PPh_3)_2$ as catalyst is given in Table I.

The application of some other typical catalysts, viz., $RhCl_3 \cdot 3H_2O$, $RhCl(PPh_3)_3$, and $RuCl_2(PPh_3)_3$, gives less satisfactory results.

The stepwise nature of reaction 1 follows directly from its kinetic curves (Figure 1).[14] While the equilibration of **1** and **2** and of **2** and **3** is assisted by the iridium catalyst, the tau-

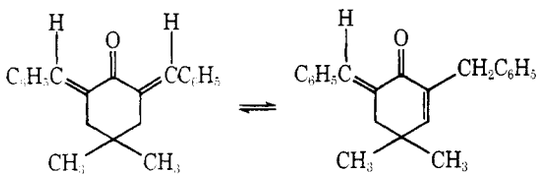
Table I. Isoaromatization of Bis(arylmethylene)cyclohexanones (1) by $IrCl(CO)(PPh_3)_2$ at 250 °C[a]

Registry no.	Expt	R	R′	R″	Solvent	Reaction time, h	Yield, %
42052-61-9	1	C_6H_5	H	H	Ph_2O	2.5	98
	2	C_6H_5	H	H	none	2	76
62085-69-2	3	C_6H_5	CH_3	H	Ph_2O	2.5	87
	4	C_6H_5	CH_3	H	none	2.2	78
42792-77-8	5	C_6H_5	H	$C(CH_3)_3$	Ph_2O	2	92
42792-79-0	6	4-$CH_3C_6H_4$	H	H	Ph_2O	0.5	97
62085-70-5	7	2-$CH_3OC_6H_4$	H	H	Ph_2O	15	52
62085-71-6	8	4-$CH_3OC_6H_4$	H	H	Ph_2O	0.3	98
62085-72-7	9	2-ClC_6H_4	H	H	Ph_2O	24	<1
62085-73-8	10	3-ClC_6H_4	H	H	Ph_2O	4	90
42792-80-3	11	4-ClC_6H_4	H	H	Ph_2O	3.5	98
62085-74-9	12	4-FC_6H_4	H	H	Ph_2O	4	85
62085-75-0	13	2-Furyl	H	H	Ph_2O	2	98
62085-76-1	14	1-$C_{10}H_7$	H	H	Ph_2O	24	0
62085-77-2	15	2-$C_{10}H_7$	H	H	Ph_2O	15	95

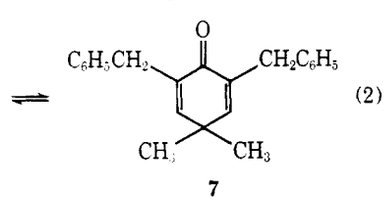
[a] Except in expt 2 and 4, the reaction mixture consisted of 2×10^{-3} mol of ketone, 1.28×10^{-5} mol of catalyst, and 1 mL of diphenyl ether. The yields in these experiments were determined by GLC (5% SE-30 on Chromosorb W). In expt 2 and 4, 3.65×10^{-2} mol of ketone and 1.28×10^{-4} mol of catalyst were reacted and the product was isolated by distillation.

tomerization 3 → 4 is not. It is merely a thermal rearrangement.[15] In this concern it is noteworthy that $IrCl(CO)(PPh_3)_2$, as well as $RhCl(PPh_3)_3$ and $RuCl_2(PPh_3)_3$, are also inactive in other keto to enol transformations such as in anthrone and 2-acetyl-1-tetralone.[16]

2-Benzyl-6-benzylidenecyclohex-2-enone (**2**, R = C_6H_5; R′ = R″ = H) and the substituted analogues are fairly stable. They can be isolated from the reaction mixtures of the uncompleted catalyses by preparative GLC. Diene **3**, R = C_6H_5; R′ = R″ = H, however, is labile. It isomerizes in part and cannot be obtained by this method free of phenol **4**. A stable diene of type **3**, viz., 2,6-dibenzyl-4,4-dimethylcyclohexa-2,5-dienone (**7**), is formed when the two hydrogen atoms in **3**, R = C_6H_5; R′ = R″ = H, are substituted by methyl groups. Upon blocking the final enolization step, **5** gives at 230 °C (without a solvent) an equilibrium mixture of 94.1% **5**, 1,8% **6**, and 4.1% **7**. In diphenyl ether (250 °C) **6** and **7** accumulate in substantial amounts (yields of **5**, **6**, and **7** 1.5, 18, and 74%, respectively). From this mixture **6** and **7** were isolated.



5 ⇌ **6**



7 (2)

Both electronic and steric factors affect reaction 1. In experiments with 1 in diphenyl ether at 250 °C, for which R′ = R″ = H and R represents (a) 4-$CH_3OC_6H_4$, (b) 4-$CH_3C_6H_4$, (c) C_6H_5, and (d) 4-FC_6H_4 a Hammett σ–ρ relationship is obtained for the initial reaction rates. (The corresponding values for the consumption of **1** are 6.7, 3.3, 1.1, and 0.5% min^{-1}.) The initial rate for **1**, R = 4-ClC_6H_4; R′ = R″ = H, is 0.72% min^{-1}. This value is somewhat higher than expected, owing to the complication involved in the activation of aryl chlorides by $IrCl(CO)(PPh_3)_2$.[17] In the absence of diphenyl ether, however, the order of rates no longer parallels with the order of electronegativities of the substituents. The initial rates for isomerization of the *E,E* series of 2,6-dibenzylidene-, 2,6-bis(*p*-methylbenzylidene)-, 2,6-bis(*p*-methoxybenzylidene)-, 2,6-bis(*m*-chlorobenzylidene)-, 2,6-bis(*p*-chlorobenzylidene)-, and 2,6-bis(*p*-fluorobenzylidene)cyclohexanone are 1.80, 0.73, 0.71, 0.49, 0.47, and 0.21% min^{-1}, respectively (230 °C, substrate to catalyst ratio 100:1). This may imply that the solvent serves in our reaction as hydrogen donor for a Harrod–Chalk type mechanism.[18] In fact the application of deuterium labeled diphenyl ether leads to partially deuterated dibenzylphenols. In the absence of the ether the required hydrogen atom is abstracted either from the substrate itself or, less probably, from the ortho position of the triphenylphosphine ligand of the catalyst.[19]

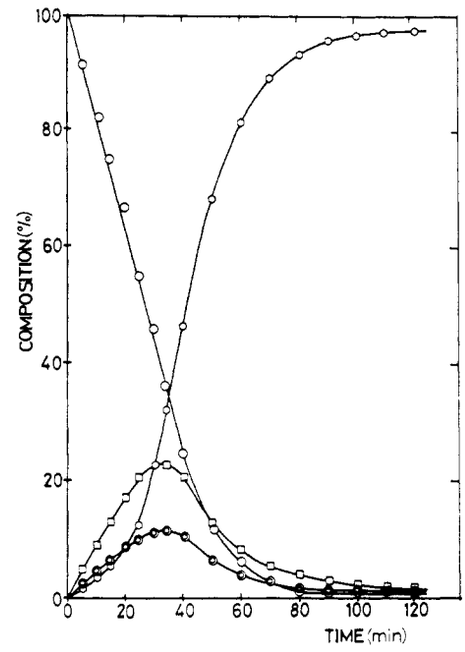


Figure 1. Isoaromatization of (*E,E*)-2,6-dibenzylidenecyclohexanone (2.0 mmol) at 230 °C in the presence of $IrCl(CO)(PPh_3)_2$ (1.28×10^{-2} mmol) under N_2; ○, ketone **1**, R = C_6H_5, R′ = R″ = H; □, **2**, R = C_6H_5, R′ = R″ = H; ◎, **3**, R = C_6H_5, R′ = R″ = H; ○, **4**, R = C_6H_5, R′ = R″ = H.

In contrast to some Rh(I)- and Rh(III)-catalyzed isomerization reactions,[20] the isoaromatization is not affected by

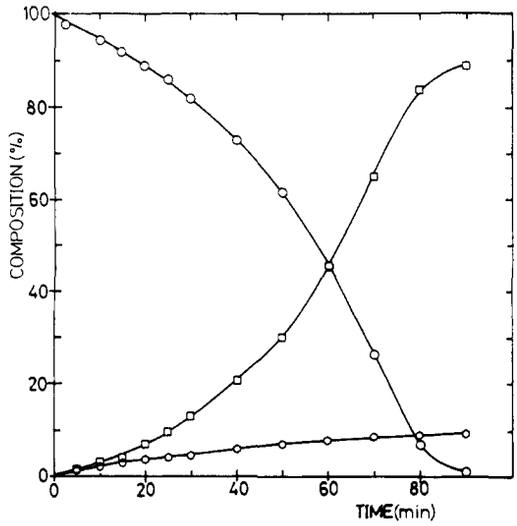


Figure 2. Concentration–time profiles for the reactant and products in $IrCl(CO)(PPh_3)_2$-catalyzed conversion of (*E*)-2-benzylidene-1-tetralone: (○) (**8**, R = R′ = H) into 2-benzyl-1-naphthol (□) (**11**, R = R′ = H) and 2-benzyl-1-tetralone (○). Reaction system: 10^{-3} mol of **8**, 10^{-5} mol of catalyst, 0.5 mL of Ph_2O; 255 °C.

hydrogen chloride. It is thus unlikely that hydrogen chloride transfer (Cramer's mechanism[20]) is of importance to reaction 1.

When the catalyses listed in Table I have been interrupted after a short period, freed from iridium compounds, and analyzed by GLC, 1 mol of PPh_3 per each mole of catalyst could be isolated.[21] However, since neither the liberated phosphine nor that added externally has any significant effect on the reaction rate [as does, e.g., PPh_3 on $RhCl(PPh_3)_3$-catalyzed isomerization[22]], it seems unlikely that $IrCl(CO)(PPh_3)_2$ is activated by reversible dissociation, $IrCl(CO)(PPh_3)_2 \rightleftharpoons$ "$IrCl(CO)(PPh_3)$" + PPh_3.

2-Arylidene-1-tetralones. Isoaromatization of (*E*)-2-benzylidene-1-tetralone (**8**, R = R′ = H) by $IrCl(CO)(PPh_3)_2$ in boiling diphenyl ether gives 2-benzyl-1-naphthol (**11**, R = R′ = H) in high yield. The only by-product is 2-benzyl-1-tetralone (up to 10%) resulting from a slow hydrogen transfer from the solvent to the activated double bond in **8**.[23]

The conversion **8** → **10** proceeds without substantial accumulation of reaction intermediates. The exocyclic double bond migrates into the ring and compound **9**, which is probably formed, either tautomerizes immediately to **11** or undergoes first isomerization to the conjugated species **10**.

A typical reaction curve for the isoaromatization of **8**, R = R′ = H, is shown in Figure 2.

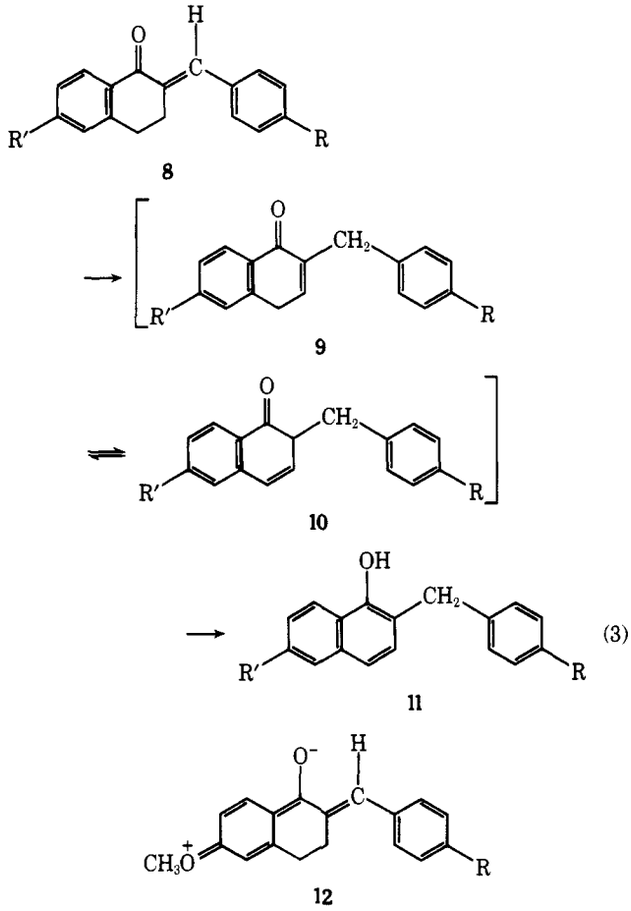
Introduction of CH_3 or Cl into the benzylidene moiety of **8** causes an effect similar to that noted in the diarylidenecyclohexanone series. The electropositive methyl group, which is expected to promote coordination of the carbonyl group and an exocyclic double bond to the iridium atom, enhances the reaction rate, and vice versa, electron-attracting chlorine atoms slow down the catalysis (see Table II). Substitution at C-6 position of the tetralone residue has a similar effect: 6-acetoxy-2-arylidene-1-tetralones react considerably slower than the corresponding unsubstituted 2-arylidene-1-tetralones (Table II). The reactivities of the 6-methoxy derivatives are, however, somewhat lower than expected and are not quite understood. It should be recalled that in the absence of a powerful driving force, $IrCl(CO)(PPh_3)_2$ is a very poor catalyst for exo- to endocyclic double bond migration in some alkylidenecycloalkanes.[24]

The kinetic curves for the $IrCl(CO)(PPh_3)_2$-catalyzed isoaromatization of the additional eight substituted arylidenetetralones listed in Table II resemble those shown in Figure 2. Induction periods of 40–60 min that precede the *maximum rates are typical for all the tetralones.* (*In the dibenzylidenecyclohexanone series no measurable induction periods have been observed.*)

Table II. Maximum Rates for $IrCl(CO)(PPh_3)_2$-Catalyzed Isoaromatization of 2-Arylidene-1-tetralones (% Consumption of 8 per min)[a]

	R		
R′	CH_3	H	Cl
H	2.07	1.88	0.70
CH_3O	1.75	1.65	0.63
CH_3COO	1.20	0.92	0.20[b]

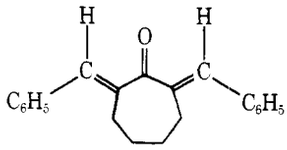
[a] Reaction conditions: 1 mmol of tetralone derivative and 10^{-2} mmol of catalyst in 0.5 mL of diphenyl ether at 255 °C. [b] The reaction seems to stop after 90 min.



(3)

Isomerization of (*E,E*)-2,7-Dibenzylidenecycloheptanone. Leonard et al.[25] reported the conversion of 2,7-dibenzylidenecycloheptanone (**13**) into 16% 2,7-dibenzyltropone (**15**) by 10% Pd/C catalyst in triethylene glycol at 280 °C. The starting ketone, **13**, is assumed to isomerize first to **14** and then, at the elevated temperature, to lose a molecule of hydrogen.

We were, however, unable to duplicate Leonard's experiments. We found instead that Pd/C[26] catalyzes hydrogen transfer from the glycol to **13** to give a mixture of the two isomeric 2,7-dibenzylcycloheptanones (**14**)[27] in almost quantitative yield.[28] Similar transfer hydrogenation is observed when the palladium catalyst is replaced by $IrCl(CO)(PPh_3)_2$ or by some other transition metal complexes.[29] When the reaction is conducted in boiling diphenyl ether or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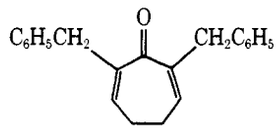
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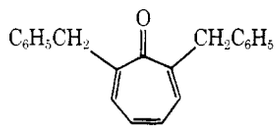
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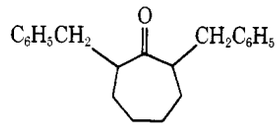

16

in the absence of any solvent, neither double bond migration (to give **14** or **15**) nor transfer hydrogenation takes place. The iridium catalyst promotes merely *Z–E* interconversion of the exocyclic C=C bonds to give an equilibrium mixture of 66% *E,E*, 33% *E,Z*, and <1% *Z,Z* isomer **13**. In fact, the inability of $IrCl(CO)(PPh_3)_2$ to catalyze double bond migration in **13** is not unexpected. In contrast to the two previous systems, in which the conversion of the unsaturated ketones into aromatic phenols (or naphthols) is associated with a substantial gain in energy, there is no such driving force in **13** to cause introduction of exocyclic double bonds into the cycloheptanone ring. It is, however, remarkable that *Z–E* interconversion is *not* observed to any significant extent during isoaromatization of the above (*E,E*)-2,6-diarylidenecyclohexanones (reaction 1) and (*E*)-2-arylidene-1-tetralones (reaction 3); geometric isomerization is quite common in other $IrCl(CO)(PPh_3)_2$-catalyzed transformations of unsaturated systems (see, e.g., ref 24).

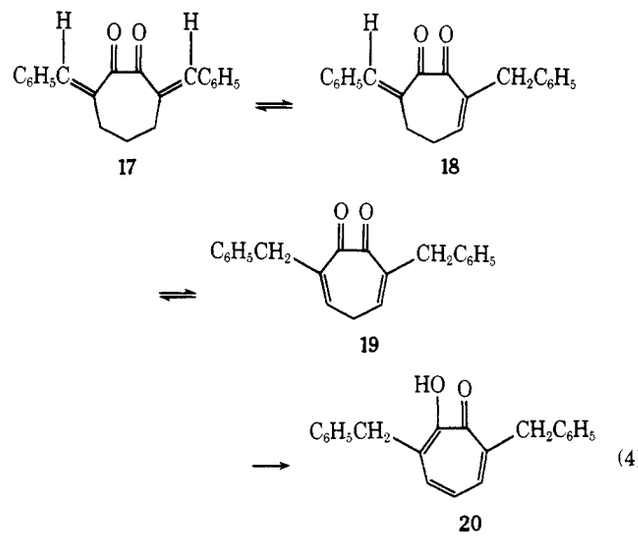
While (*Z,Z*)-**13** is found only in small amounts in the iridium(I)-catalyzed reaction mixture, it can be obtained in 55% yield (together with 40% of the *E,Z* compound) upon irradiation of (*E,E*)-**13** in EtOH for 4 h with a 450-W high-pressure mercury lamp.

The three isomeric 2,7-dibenzylidenecycloheptanones have essentially the same mass spectra;[30] however, their structures could easily be elucidated from their characteristic NMR. The resonances of both vinylic and aromatic protons of (*E,E*)-**13** coincide to give a broad singlet at 7.32 ppm.[31] The corresponding peaks of the *Z,Z* isomer appear at 6.62 and 7.19 ppm. The *E,Z* compound has a vinylic absorption at 6.44 ppm and two aromatic ones centered at 7.15 and 7.31 ppm. The second vinylic peak coincides with the aromatic resonance at 7.31 ppm. (Cf. the NMR of (*E,Z*)-2,5-dibenzylidenecyclopentanone[32].)

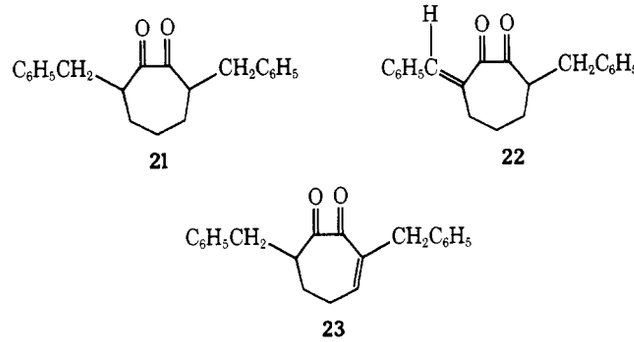
Each of the three isomers can be converted by $IrCl(CO)(PPh_3)_2$ (at 230 °C) into the above equilibrium mixture. The *Z,Z* compound undergoes also thermal isomerization and gives (*E,Z*)-**13** in the absence of the organometallic catalyst.

(*E,E*)-3,7-Dibenzylidenecycloheptane-1,2-dione. Unlike in the previous monoketone, migration of the exocyclic double bonds in **17** may result in formation of a pseudoaromatic compound. The gain in energy associated with the formation of the tropolone structure suffices to drive reaction 4 toward the right.

Continuous analysis of the reaction system by our standard methods (GLC and GLC–MS) proved difficult owing to the low mobility of the tropolone derivative on the GLC columns (see Experimental Section). We have partly overcome this difficulty by silylation of each sample withdrawn from the reaction mixture prior to injection but not without reducing the accuracy of the results. The qualitative results indicate that the features of reaction 4 resemble those of reactions 1 and 3 only in the initial period of the catalysis. As the catalysis proceeds two side reactions, viz., disproportionation[33] and


17 18 19 20 (4)

polymerization, become of importance. In a typical run the starting diketone **17** disappeared completely within 2 h, although the intermediate **18** was consumed only after a further 60 min. By that time the reaction mixture consisted of 40% 3,7-dibenzyltropolone (**20**), 30% 3,7-dibenzylcycloheptane-1,2-dione (**21**), and 30% resinous material. Before completion of the reaction two transient compounds of *m/e* 304 could be identified (not isolated) in the GLC–MS chromatogram. These are presumably the precursors **22** and **23** of the saturated diketone **21**.


21 22 23

Aryl- and Alkylmethylenecyclopentanones. The reaction of (*E,E*)-2,5-dibenzylidenecyclopentanone (**24**) and Vaska's catalyst was compared with those of the unsaturated cyclohexanone, cycloheptanone, and cycloheptanedione derivatives. Inspection of the kinetic curves obtained at 230 °C (Figure 3) indicates that **24** was not isomerized over a period of 15 min. Then rapid conversion (19.5% min^{-1}) of **24** into the known 2-benzyl-6-benzylidenecyclopent-2-enone (**25**)[34,35] and polymeric material started. Formation of the semireduced compounds, 2-benzyl-5-benzylidenecyclopentanone (**27**) and

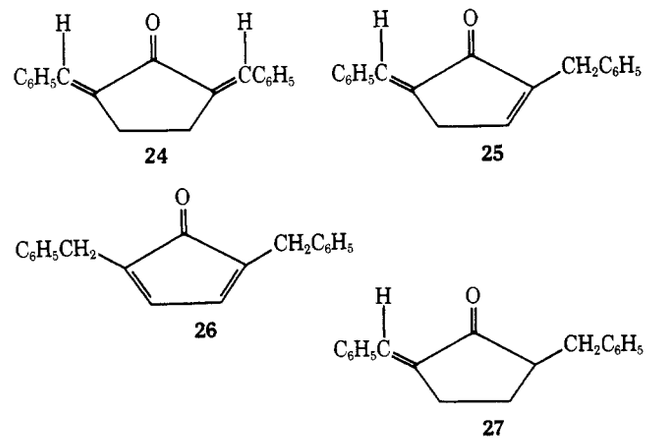

24 25 26 27

Table III. Yields, Melting Points, and NMR Spectra of (*E,E*)-α,α′-Diarylidenecyclohexanones

Compd	Yield, %	Mp, °C	NMR, δ, ppm ($CDCl_3$)	Ref
1, R = C_6H_5; R′ = R″ = H	90	118	1.76 (m, 2), 2.92 (t-d, 4 *J* = 3 and 1 Hz), 7.35 (m, 10), 7.91 (br s, 2)	31, 45
1, R = 2-ClC_6H_4; R′ = R″ = H	47	110	1.80 (m, 2), 2.83 (t-d, 4 *J* = 3 and 1 Hz), 7.33 (m, 8), 7.70 (br s, 2)	46
1, R = 3-ClC_6H_4; R′ = R″ = H	81	106	1.80 (m, 2), 2.90 (t-d, 4 *J* = 3.5 and 1 Hz), 6.78–7.52 (m, 8), 7.73 (br s, 2)	*a*
11, R = 4-ClC_6H_4; R′ = R″ = H	80	147	1.77 (m, 2), 2.85 (t-d, 4 *J* = 3.5 and 1 Hz), 7.40 (AB q, 8), 7.70 (m, 2)	45, 46
1, R = 4-FC_6H_4; R′ = R″ = H	78	155–156	1.75 (q, 2 *J* = 3 Hz), 2.84 (t, 4 *J* = 3 Hz), 6.80–7.52 (m, 8), 7.71 (s, 2)	47
1, R = 4-$CH_3C_6H_4$; R′ = R″ = H	63	169–170	1.78 (m, 2), 2.37 (s, 6), 2.90 (t-d, 4 *J* = 3 and 1 Hz), 7.25 (AB q, 8), 7.77 (s, 2)	48
1, R = C_6H_5; R′ = CH_3; R″ = H	87	126	1.24 (d, 3 *J* = 4 Hz), 1.80 (m, 2), 2.96 (m, 2), 3.43 (m, 1), 7.28 (m, 10), 7.46 (s, 1), 7.63 (br s, 1)	49
1, R = 2-$CH_3OC_6H_4$; R′ = R″ = H	65	139–140	1.90 (m, 2), 2.92 (t-d, 4 *J* = 3 and 1 Hz), 3.91 (s, 6), 6.80–7.55 (m, 8), 7.98 (br s, 2)	*b*
1, R = 4-$CH_3OC_6H_4$; R′ = R″ = H	80	160	1.90 (q, 2 *J* = 3 Hz), 2.93 (t, 4 *J* = 3.5 Hz), 3.82 (s, 6), 7.18 (AB q, 8), 7.72 (br s, 2)	49
1, R = C_6H_5; R′ = H; R″ = $C(CH_3)_3$	40	145	0.95 (s, 9), 2.49 (d, 4 *J* = 6 Hz), 3.12 (d, 1 *J* = 6 Hz), 7.28 (m, 10), 7.63 (m, 2)	50
1, R = 1-$C_{10}H_7$; R′ = R″ = H	52	212[c]	1.60 (m, 2), 2.70 (t, 4 *J* = 3 Hz), 7.25–7.90 (m, 16)	7
1, R = 2-$C_{10}H_7$; R′ = R″ = H	50	150	1.60 (m, 2), 2.70 (t, 4 *J* = 3 Hz), 7.05–7.95 (m, 16)	*d*
1, R = 2-C_5H_3O; R′ = R″ = H	82	148	1.89 (m, 2), 3.18 (t, 4 *J* = 3 Hz), 6.41 (m, 4), 7.36 (br s, 4)	51
5	52	123	0.98 (s, 6), 2.76 (d, 4 *J* = 1.5 Hz), 7.42 (m, 10), 7.82 (br s, 2)	52, 53

[a] Anal. Calcd for $C_{20}H_{16}Cl_2O$: C, 70.0; H, 4.7; Cl, 20.7. Found: C, 69.7; H, 4.7; Cl, 20.7. [b] Anal. Calcd for $C_{22}H_{22}O_3$: C, 79.0; H, 6.6. Found: C, 79.2; H, 6.4. [c] Lit.[7] mp 194–205 °C. [d] Anal. Calcd for $C_{28}H_{22}O$: C, 89.8; H, 5.9. Found: C, 89.5; H, 5.7.

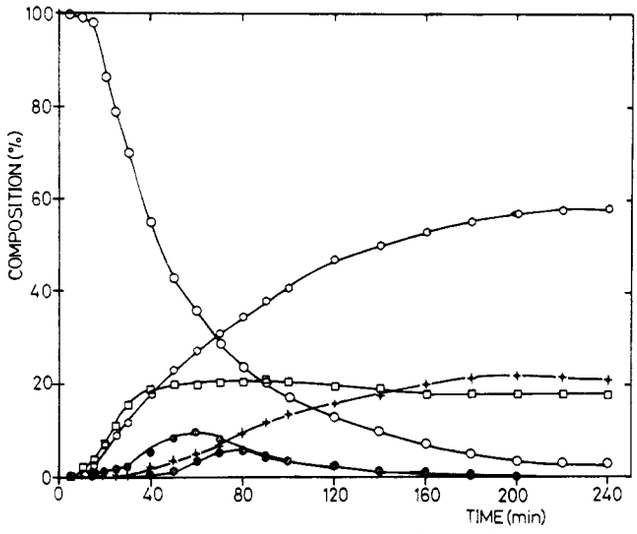
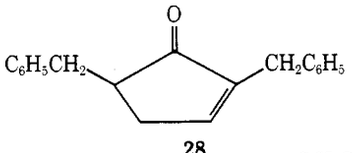
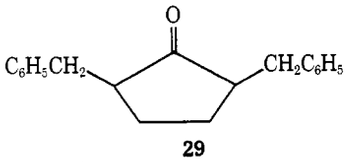


Figure 3. Typical concentration–time profiles for the reactant and products in the catalytic transformation of (*E,E*)-2,5-dibenzylidenecyclopentanone (**24**) (3.66 mmol) by $IrCl(CO)(PPh_3)_2$ (3.87×10^{-2} mmol) at 230 °C. ○, **24**; □, **25**; ✦, **28**; ◍ and ◍, $C_{19}H_{18}O$ isomers; ○, polymers.



28



29

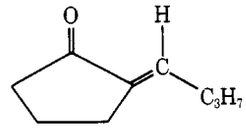
2,6-dibenzylcyclopent-2-enone (**28**),[35] became substantial only some 15 min later, but at rates which soon permit the concentration of **28** to surpass that of **25**.

It is interesting to note that none of the fully hydrogenated ketone **29** of *m/e* 264 was obtained in the catalysis, though it is easily accessible by $RuCl_2(PPh_3)_3$-promoted transfer hydrogenation of **22** in ethylene glycol.[28]

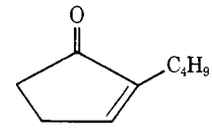
The internal diene **26** did not appear either in the GLC chromatogram. We assume, however, that it is formed as a transient compound and responsible for the formation of part of the polymers. Some support for this assumption could be found in an experiment in which **26** was trapped with benzyne. Diphenyliodonium 2-carboxylate (80 mg) was treated together with 200 mg of **24** and 6 mg of iridium catalyst for 90 min at 230 °C. Mass spectral analysis of the reaction mixture indicated the formation of an adduct of benzyne to **24** (probably rearranged) of *m/e* 336. No peak of this mass appeared in control experiments to which either no catalyst or no diphenyliodonium 2-carboxylate was added.

Since polymerization of **26** can account only for part of the isolated macromolecular product, the remaining part must arise from disproportionation of **24** and, at advanced stages of the catalysis, from the dibenzylcyclopentenone **28** (see Figure 3).

Competition between double bond migration and disproportionation seems to occur generally when methylenecyclopentanone derivatives are subjected to Vaska's catalyst. 2-Butenylidenecyclopentanone (**30**), e.g., yields 2-butylcyclopent-2-enone (**31**) and 2-butylcyclopentanone (**32**) in a ratio 5:4 when 1 mmol is refluxed for 3.5 h with 10^{-2} mmol of catalyst. Prolonged heating causes some deterioration of the cyclopentenone derivative **31**. The facile separation of **31** and **32** on $AgNO_3$-activated Florisil provides thus a convenient route to **31** and to other valuable precursors for jasmone-like plant inhibitors[36] recently synthesized in our department.[37]



30



31

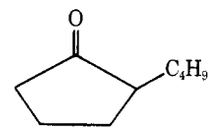


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Table IV. GLC Separation of Starting Material, Reaction Intermediates, and Products of Reaction 1

R	R′	R″	Column and conditions[a]	Retention time, min 1	2	3	4
4-FC_6H_4	H	H	A	11.5	10.0	9.6	8.3
3-ClC_6H_4	H	H	A	16.6	14.4	13.1	10.5
4-ClC_6H_4	H	H	A	16.6	14.4	13.0	9.9
4-$CH_3C_6H_4$	H	H	B	23.2	19.5	18.7	16.5
2-$CH_3OC_6H_4$	H	H	C	14.3	9.7	*b*	6.4
4-$CH_3OC_6H_4$	H	H	B	20.5	17.8	17.1	15.0
2-Furyl	H	H	C	7.5	4.5	*b*	2.7
C_6H_5	CH_3	H	C	3.8	2.5	*b*	2.0
C_6H_5	H	$C(CH_3)_3$	C	5.5	3.5	*b*	2.4

[a] A, 3.16 × 2000 mm stainless steel column packed with 5% OV-101 on 60–80 mesh Chromosorb W, operated between 200 and 285 °C programmed to 6 °C/min, initial hold 1 min, carrier gas (N_2) 30 mL/min, injector and detector temperature 305 °C. B, column as A operated between 200 and 290 °C programmed to 5 °C/min. C, 6.32 × 500 mm copper column packed with 15% SE-30 on 60–80 mesh Chromosorb W, 180 °C, injector and detector 300 °C, carrier gas (He) 50 mL/min. [b] Under these conditions 2 and 3 are not separated.

Experimental Section

General. Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are not correlated. Infrared spectra were measured with either Perkin-Elmer Models 137 or 257 spectrophotometers. Ultraviolet spectra were obtained on a Unicam SP-800 spectrophotometer. Proton magnetic resonance spectra were run using Varian T-60, EM-360, and HA-100 spectrometers. Mass spectra were recorded with a Varian MAT-311 spectrometer or directly from a gas chromatograph using a Varian MAT-111 instrument.[30] Preparative gas-liquid phase chromatography was performed with Aerograph 90-P, Varian 920, and F & M 720 instruments. Analytical GLC was performed with a Packard 4700 (800 series) instrument.

The catalysts $RuCl_2(PPh_3)_3$,[38] $RhCl(PPh_3)_3$,[39] and $IrCl(CO)(PPh_3)_2$[40] were prepared as previously described.

(*E,E*)-α,α′-Diarylidenecyclohexanones[32,41-45] were prepared by the following general procedure. A mixture of 0.2 mol of freshly distilled aldehyde, 9.8 g (0.1 mol) of cyclohexanone, 12 g of NaOH, 100 mL of EtOH, and 50 mL of water was stirred vigorously for 4 h. Water was added and the unsaturated ketone was recrystallized from MeOH. The yields and physical data of the products are given in Table III.[30]

***Z–E* Isomerization of (*E,E*)-2,6-Diarylidenecyclohexanones.** Photoisomerization of the above *E,E* isomers to the corresponding *E,Z* and *Z,Z* compounds was accomplished by irradiation of the methanolic solutions with a Hanovia 450-W UV lamp through quartz essentially as described for (*E*)-2-benzylidenecyclohexanone.[4] The conditions described by George and Roth[32] for (*E,E*)-2,5-dibenzylidenecyclopentanone led to polymers in the cyclohexanone series.

Rearrangement of (*E,E*)-2,6-Diarylidenecyclohexanones to Phenols. A. In a typical experiment a mixture of 10.0 g (3.65×10^{-2} mol) of **1**, R = C_6H_5; R′ = R″ = H, and 100 mg (1.28×10^{-4} mol) of $IrCl(CO)(PPh_3)_2$ was heated under N_2 at 250 °C for 2 h. Distillation afforded 7.6 g (76%) of 2,6-dibenzylphenol: bp 210 °C (3 mm); mp 30 °C;[10] ν_{OH} 3560 cm^{-1}; UV max (EtOH) 280 nm (ε 2000); NMR ($CDCl_3$) δ 3.95 (s, 4), 6.98 ppm (m, 14).

The same result was obtained when the reaction was conducted at ambient atmosphere.

B. A modified reaction tube equipped with gas inlet and outlet was immersed in a thermostat at 250 °C and charged (under N_2) with 500 mg (1.82×10^{-3} mol) of ketone **1**, R = C_6H_5; R′ = R″ = H, 1 mL of freshly chromatographed diphenyl ether (Al_2O_3), and a small amount of n-$C_{28}H_{58}$ (internal standard for GLC analysis). After 20 min, 25 mg (3.2×10^{-5} mol) of $IrCl(CO)(PPh_3)_2$ was added at once. Samples (1–2 μL) were withdrawn and immediately frozen (−20 °C) every 5 min for the first 40 min, and every 10 min thenceforth. GLC analysis was performed on a 3.16 × 2000 mm stainless steel column packed with 5% OV-101 on 60–80 mesh Chromosorb W, operated between 200 and 285 °C programmed to 6 °C/min, initial hold 1 min, carrier gas (N_2) 30 mL/min, injector and detector temperature 305 °C. The compounds having retention times of 8.2, 9.5, 10.0, and 11.6 min proved to be **4**, **3**, **2**, and **1** (R = C_6H_5; R′ = R″ = H), respectively

2-Benzyl-6-benzylidenecyclohex-2-enone (**2**, R = C_6H_5; R′ = R″ = H) was isolated by preparative GLC as a viscous liquid: UV max (MeOH) 290 nm (ε 6850); NMR ($CDCl_3$) δ 1.86–2.96 (m, 4), 3.66 (s, 2), 6.64 (m, 1), 7.24–7.61 ppm (m, 11). Anal. Calcd for $C_{20}H_{18}O$: C, 87.6; H, 6.6. Found: C, 87.7; H, 6.6.

Attempts to isolate phenol-free 2,6-dibenzylcyclohexa-2,5-dienone (**3**, R = C_6H_5; R′ = R″ = H) were unsuccessful. The NMR spectrum of the impure endocyclic diene (that had correct elemental analysis) confirmed, however, the proposed structure: ($CDCl_3$) δ 3.47 (br s, 2 diallylic), 3.70 (br s, 4 benzylic), 6.78 (s, 2 vinylic), 7.20 ppm (m, 10 aromatic).

Substituted 2,6-dibenzylidenecyclohexanones were isomerized to the corresponding phenols[53] and reaction intermediates as described for **1**, R = C_6H_5; R′ = R″ = H. The sequence of peaks in the gas–liquid chromatograms parallels that of the unsubstituted compound as shown in Table IV.

The isoaromatization experiments were repeated in the absence of diphenyl ether at 230 °C. All control experiments without $IrCl(CO)(PPh_3)_2$ gave negative results.

2-Benzyl-6-benzylidene-4,4-dimethylcyclohex-2-enone (6) and 2,6-dibenzyl-4,4-dimethylcyclohexa-2,5-dienone (7) were obtained by heating a mixture of 2×10^{-2} mol of **5**, 10^{-4} mol of $IrCl(CO)(PPh_3)_2$, and 10 mL of Ph_2O for 24 h under N_2 at 250 °C. Separation of the isomers was afforded by a 0.5-m long GLC column packed with 15% SE-30 on 60–80 mesh Chromosorb W operated at 180 °C. The first compound, having retention time 170 s, was **7**: $\nu_{C=O}$ 1675 cm^{-1}; UV max (EtOH) 290 nm (ε 10^4); NMR ($CDCl_3$) δ 1.12 (s, 6), 3.61 (s, 4), 6.57 (s, 2), 7.14–7.26 ppm (m, 10). Anal. Calcd for $C_{22}H_{22}O$: C, 87.4; H, 7.3. Found: C, 87.2; H, 7.1. The intermediate **6**, retention time 270 s; $\nu_{C=O}$ 1680 cm^{-1}; NMR ($CDCl_3$) δ 0.94 (s, 3), 0.97 (s, 3), 2.76 (d, 2 J = 2 Hz), 3.59 (s, 2), 6.38 (s, 1), 7.12–7.66 ppm (m, 11). Anal. Calcd for $C_{22}H_{22}O$: C, 87.4; H, 7.3. Found: C, 87.3; H, 7.0.

(*E*)-2-Benzylidene-1-tetralone (8, R = R′ = H), mp 105–106 °C;[54] **(*E*)-2-(*p*-chlorophenylmethylene)-1-tetralone (8, R = Cl; R′ = H)**, mp 137 °C;[55] and **(*E*)-2-benzylidene-6-methoxytetralone (8, R = H; R′ = OCH_3)**, mp 97–98 °C,[56] were prepared as described in the literature.

(*E*)-2-(*p*-Methylphenylmethylene)-1-tetralone (8, R = CH_3, R′ = H) was obtained by stirring a solution of 7.3 g (0.05 mol) of 1-tetralone and 6 g (0.05 mol) of *p*-tolualdehyde in 50 mL of 4% ethanolic KOH for 2 h. Acidification (AcOH) and dilution with water afforded 11.2 g (90%) of yellow plates: mp 123 °C (from aqueous EtOH); $\nu_{C=O}$ (Nujol) 1650 cm^{-1}; NMR ($CDCl_3$) δ 2.41 (s, 3), 3.04 (m, 4), 7.13–7.57 (m, 7), 7.87 (br s, 1), 8.14 ppm (d-d, 1, $J_{6,8}$ = 2.5 and $J_{7,8}$ = 7 Hz). Anal. Calcd for $C_{18}H_{16}O$: C, 87.1; H, 6.5. Found: C, 87.2; H, 6.2.

(*E*)-2-(*p*-Methylphenylmethylene)-6-methoxy-1-tetralone (8, R = CH_3; R′ = OCH_3) was obtained in the same manner: pale yellow needles, mp 133 °C; $\nu_{C=O}$ (Nujol) 1653 cm^{-1}; NMR ($CDCl_3$) δ 2.40 (s, 3), 3.03 (m, 4), 3.87 (s, 3), 6.70–7.42 (m, 6), 7.82 (t, 1, J = 1.5 Hz), 8.12 ppm (d, 1, $J_{7,8}$ = 8 Hz). Anal. Calcd for $C_{19}H_{18}O_2$: C, 82.0; H, 6.5. Found: C, 82.2, H, 6.5.

(*E*)-2-(*p*-Chlorophenylmethylene)-6-methoxy-1-tetralone (8, R = Cl; R′ = OCH_3) from 6-methoxy-1-tetralone and *p*-chlorobenzaldehyde: pale yellow needles, mp 123 °C; $\nu_{C=O}$ (Nujol) 1645 cm^{-1}; NMR ($CDCl_3$) δ 3.00 (m, 4), 3.88 (s, 3), 6.68–7.42 (m, 6), 7.80 (t, 1, J = 1 Hz), 8.15 ppm (d, 1, $J_{7,8}$ = 8 Hz). Anal. Calcd for $C_{18}H_{15}ClO_2$: C, 72.4; H, 5.0; Cl, 11.9. Found: C, 72.2; H, 5.2; Cl, 12.1.

(*E*)-6-Acetoxy-2-arylidene-1-tetralones. The following general procedure was applied. A mixture of 0.05 mol of 6-hydroxy-1-tetralone (prepared from 6-methoxy-1-tetralone according to Haberland[57]),

Table V. GLC Separation of 2-Arylidene-1-tetralones, 2-Arylmethyl-1-naphthols, and the Corresponding 2-Arylmethyl-1-tetralones

R	R′	Column and conditions[a]	Retention time, min			Registry no.
			8	11	2-Arylmethyl-1-tetralone	
H	H	D	17.5	16.3	14.4	27019-08-5
CH_3	H	E	18.1	16.8	15.0	62085-78-3
Cl	H	F	11.8	10.7	9.5	62085-79-4
H	OCH_3	G	20.7	19.3	17.7	62085-80-7
CH_3	OCH_3	G	23.4	21.3	19.9	62085-81-8
Cl	OCH_3	H	14.1	12.3	12.0	62085-82-9
H	$OCOCH_3$	G	22.1	21.5	19.3	62085-83-0
CH_3	$OCOCH_3$	I	20.7	19.5	17.1	62085-84-1
Cl	$OCOCH_3$	J	18.7	16.0	*b*	

[a] D, 6.32 × 2600 mm glass column packed with 30% SE-30 on Chromosorb W (AW), operated between 190 and 275 °C, programmed to 3 °C/min, initial hold 2 min, injector and detector temperature 300 °C, carrier gas (N_2) 40 mL/min. E, as for D, temperature increase programmed to 4 °C/min. F, 6.32 × 2600 mm glass column 3% SE-30 on Gaschrom Q, operated between 190 and 270 °C, initial hold 1 min, other conditions as for D. G, as E, initial hold 1 min. H, as F, column temperature 200–270 °C. I, as E, column temperature 210–275 °C. J, as D, column temperature 219–285 °C, programmed to 5 °C/min. [b] No reduction product formed.

0.05 mol of the appropriate benzaldehyde, and 50 mL of Triton B (40% in MeOH) was refluxed for 4 h. The reaction mixture was acidified to pH 5 with AcOH and diluted with water. Extraction with $CHCl_3$ and evaporation of the solvent afforded almost pure 2-arylidene-6-hydroxy-1-tetralone. The crude ketone was dissolved in 15 mL of dry pyridine; 10 mL of acetic anhydride was added and the mixture was allowed to stand at room temperature for 24 h. The solvents were evaporated in vacuo and the crystalline residue was recrystallized from aqueous EtOH. The yields of the acetoxytetralone derivatives were 90–92%.

(*E*)-6-Acetoxy-2-benzylidene-1-tetralone (8, R = H; R′ = $OCOCH_3$): mp 109–110 °C; $\nu_{C=O}$ (Nujol) 1752, 1660 cm^{-1}; NMR ($CDCl_3$) δ 2.32 (s, 3), 3.03 (m, 4), 7.03 (s, 1), 6.9–7.4 (m, 6), 7.87 (br s, 1), 8.19 ppm (d, 1, $J_{7,8}$ = 9 Hz). Anal. Calcd for $C_{19}H_{16}O_3$: C, 78.1; H, 5.5. Found: C, 78.1; H, 5.4.

(*E*)-6-Acetoxy-2-(*p*-methylphenylmethylene)-1-tetralone (8, R = CH_3; R′ = $OCOCH_3$): mp 122 °C; $\nu_{C=O}$ (Nujol) 1750, 1655 cm^{-1}; NMR ($CDCl_3$) δ 2.31 (s, 3), 2.39 (s, 3), 3.03 (m, 4), 7.00 (s, 1), 7.05–7.32 (m, 5), 7.83 (br s, 1), 8.14 ppm (d, 1, $J_{7,8}$ = 9 Hz). Anal. Calcd for $C_{20}H_{18}O_3$: C, 78.4; H, 5.9. Found: C, 78.5; H, 6.0.

(*E*)-Acetoxy-2-(*p*-chlorophenylmethylene)-1-tetralone (8, R = Cl; R′ = $OCOCH_3$): mp 142–143 °C; $\nu_{C=O}$ (Nujol) 1755, 1660 cm^{-1}; NMR ($CDCl_3$) δ 2.35 (s, 3), 3.02 (m, 4), 6.85–7.40 (m, 6), 7.80 (s, 1), 8.17 ppm (d, 1, $J_{7,8}$ = 8.5 Hz). Anal. Calcd for $C_{19}H_{15}ClO_3$: C, 69.8; H, 4.6; Cl, 10.9. Found: C, 69.5; H, 4.90; Cl, 11.2.

Isoaromatization of 2-Arylidene-1-tetralones. In a typical example 2.48 g (10^{-2} mol) of 8 (R = CH_3; R′ = H), 7.8 mg (10^{-4} mol) of $IrCl(CO)(PPh_3)_2$, and 5 mL of freshly purified diphenyl ether was gently refluxed (bath temperature 260 °C) for 2 h. The reaction mixture was cooled, diluted with benzene, and chromatographed over silica gel (70–230 mesh). Using benzene as eluent there was obtained 2.01 g (81%) of colorless 11 (R, CH_3; R′ = H): mp 66–67 °C (from cyclohexane); ν_{OH} (Nujol) 3290–3350 cm^{-1}; NMR ($CDCl_3$) δ 2.33 (s, 3), 4.66 (s, 2), 5.20 (s, 1), 7.15–8.22 ppm (m, 10). Anal. Calcd for $C_{18}H_{16}O$: C, 87.1; H, 6.5. Found: C, 86.9; H, 6.3.

Attempts to purify the naphthol derivatives by extraction into aqueous alkali led in general to deterioration of the product.

Reaction rate measurements were followed by GLC analyses. The experimental conditions and retention times are listed in Table V.

(*E,E*)-2,7-Dibenzylidenecycloheptanone (13) was obtained in 78% yield according to Cornubert et al.:[58] mp 108 °C; $\nu_{C=O}$ (CCl_4) 1675 cm^{-1}; NMR ($CDCl_3$) δ 1.94 (m, 4), 2.66 (m, 4), 7.32 ppm (m, 12).[31]

Isomerization of (*E,E*)-13. A. By Photolysis. A solution of 1.2 g of the above ketone in 300 mL of absolute EtOH was irradiated under N_2 through quartz with a Hanovia 450-W high-pressure mercury lamp. After 4 h the solution was concentrated and separated on a 2-m long column packed with 3% OV-101 on 60–80 mesh Chromosorb W operated between 150 and 285 °C, programmed to a 6 °C increase/min, initial hold 1 min, injector 305 °C, gas flow (N_2) 38 mL/min. The retention times (and yield) for the *E,E*, *E,Z*, and *Z,Z* isomers were 1160 (5%), 1060 (40%), and 997 s (55%), respectively. NMR of *E,Z* isomer ($CDCl_3$) δ 1.91 (m, 4), 2.43 (m, 2), 2.71 (m, 2), 6.44 (s, 1), 7.05–7.40 ppm (m, 11). NMR of *Z,Z* isomer ($CDCl_3$) δ 1.90 (m, 4), 2.70 (m, 4), 6.62 (s, 2), 7.19 ppm (m, 10). The mass spectra of the three isomers proved to be identical (see ref 30), *m/e* 288 ($M^{+\cdot}$).

B. By $IrCl(CO)(PPh_3)_2$. A mixture of 576 mg (2 × 10^{-3} mol) of 13 and 10 mg (1.28 × 10^{-5} mol) of the iridium catalyst was heated under N_2 with the aid of a thermostat at 230 °C. GLC analysis on 3% OV-101 inicated that after 7 min an equilibrium mixture of 66% (*E,E*)-, 33% (*E,Z*)-, and 0.9% (*Z,Z*)-13 resulted. The three isomers were directly compared with the corresponding compounds from the above photolysis. The same results were obtained when 1 mL of Ph_2O was added to the reaction mixture.

On repetition of the reaction with either the *E,Z* or the *Z,Z* compounds (for 30 min) the same mixture of isomers resulted.

Transfer Hydrogenation of 13. Under the exact conditions described by Leonard et al.[25] for the *isomerization–aromatization* of 2,7-diarylidenecycloheptanone, a mixture of 806 mg (2.8 mmol) of **13**, 500 mg of 10% Pd/C,[26] and 25 mL of triethylene glycol was refluxed for 30 min. Column chromatography on alumina afforded 695 mg (85%) of (*E*)- and (*Z*)-2,7-dibenzylcycloheptanone (**16**) identical with a sample prepared from **13** according to Irvine et al.:[27] *m/e* 292 ($M^{+\cdot}$); NMR ($CDCl_4$) δ 1.70 (m, 8), 2.4–3.6 (m, 6), 7.0–7.5 ppm (m, 10). No 2,7-dibenzyltropone (**16**) (prepared for comparison by dehydrobromination of 2,7-dibromobenzylcycloheptanone[25]) was obtained in this and in similar[26] experiments.

(*E,E*)-3,7-Dibenzylidenecycloheptane-1,2-dione (17) was obtained in two steps from cycloheptanone:[59] mp 191–193 °C (from acetone); $\nu_{C=O}$ ($CHCl_3$) 1683 cm^{-1}; NMR ($CDCl_3$) δ 2.14 (m, 2), 2.90 (t, 4 *J* = 3 Hz), 7.40 (s, 10), 7.86 (s, 2); mol wt 302 (mass spectrum).[30]

Isomerization and Disproportionation of 17. Each of 15 reaction tubes was charged with 121 mg (4 × 10^{-4} mol) of **17** and 3 mg (3.9 × 10^{-6} mol) of $IrCl(CO)(PPh_3)_2$ and heated at 230 °C. One tube was removed from the thermostat after 2, 5, 10, 15, 20, 30, 40, 60, 80, 100, 120, 150, 180, 210, and 240 min. Each was treated with 5 mL of dry THF, 2.5 mL of hexamethyldisilazane, and 50 μL of trimethylsilyl chloride, and heated at 55 °C for 30 min. The ammonium chloride was allowed to precipitate. The clear solution was then analyzed on a 2-m long column packed with 3% OV-101 on Chromosorb W, operated between 200 and 285 °C, 6 °C increase/min, initial hold 1 min, injector temperature 300 °C, gas flow 35 mL/min. The peaks observed at the initial stages of the reaction (<100 min) were the starting diketone **17** (retention time 13.6 min), the silylized 3,7-dibenzyltropolone (11.5 min), (*E*)- and (*Z*)-3,7-dibenzylcycloheptane-1,2-dione (**21**) (7.5 and 10.4 min) of *m/e* 306 ($M^{+\cdot}$), and a small peak (12.2 min) of *m/e* 302, presumably **18**, and two of *m/e* 304 (10.9 and 12.8 min) attributed to compounds **22** and **23**. After 2 h the only compounds detectable by GLC were **21** (30%) and the silylized tropolone derivative (40%).

When the reaction mixtures were not silylized **20** was fully absorbed on the GLC column.

Isolation of **20** by extraction of the reaction mixture with $CHCl_3$ followed by fractional crystallization from MeOH was associated with substantial losses. The tropolone proved identical with an authentic sample:[59] IR (CH_3Cl) 2990 and 1605 cm^{-1};[59] mass spectrum (70 eV, 120 °C) *m/e* (rel intensity) 302 (100, M^+), 195, (20), 193 (8), 183 (12), 181 (8), 165 (18), 152 (7), 91 (24).

(*E,E*)-2,5-Dibenzylidenecyclopentanone (24): 90%; mp 190 °C;[31]

$\nu_{C=O}$ (KBr) 1695 cm^{-1}; NMR ($CDCl_3$) δ 3.10 (s, 4), 7.46 (m, 10), 7.60 ppm (m, 2).[31,32]

Catalytic Transformations of 24 by $IrCl(CO)(PPh_3)_2$. As described for **1**, 952 mg (3.7 mmol) of **24**, 30 mg (3.9×10^{-2} mmol) of $IrCl(CO)(PPh_3)_2$, and tetracosane (internal standard) were heated at 230 °C, and samples withdrawn from the reacting mixture. GLC analysis was best carried out on a 6.32 × 2600 mm glass column packed with 3% SE-30 on Chromosorb Q operated between 190 and 255 °C, 4 °C increase/min. The reaction profiles of the products[35] are shown in Figure 3.

The various isomers of 2-benzyl-5-benzylidene- and 2,5-dibenzylcyclopentanone (**27** and **29**, respectively) were prepared by partial and complete transfer hydrogenation of **24** in the presence of $RuCl_2(PPh_3)_3$ and ethylene glycol as described for the reduction of diarylidenecyclohexanones.[13,29]

2-Butylidenecyclopentanone (**30**, 400 mg, 2.90 mmol) reacted with $IrCl(CO)(PPh_3)_2$ (20 mg, 2.58×10^{-2} mmol) at reflux temperature. The products were analyzed on a 2-m long column packed with 10% Carbowax on Chromosorb W operated between 70 and 170 °C, 6 °C increase/min.

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Registry No.—**1** (R = R′ = R″ = H), 62085-85-2; **2** (R = R′ = R″ = H), 62085-86-3; **2** (R = C_6H_5; R′ = R″ = H), 62085-87-4; **2** (R = 4-FC_6H_4; R′ = R″ = H), 62085-88-5; **2** (R = 3-ClC_6H_4; R′ = R″ = H), 62085-89-6; **2** (R = 4-ClC_6H_4; R′ = R″ = H), 62085-50-1; **2** (R = 4-$CH_3C_6H_4$; R′ = R″ = H), 62085-51-2; **2** (R = 2-$CH_3OC_6H_4$; R′ = R″ = H), 62085-52-3; **2** (R = 4-$CH_3OC_6H_4$; R′ = R″ = H), 62085-53-4; **2** (R = 2-furyl; R′ = R″ = H), 62085-54-5; **2** (R = Ph; R′ = CH_3; R″ = H), 62085-55-6; **2** (R = Ph; R′ = H; R″ = $C(CH_3)_3$), 62085-56-7; **3** (R = R′ = R″ = H), 62085-57-8; **3** (R = Ph; R′ = R″ = H), 62085-58-9; **3** (R = 4-FC_6H_4; R′ = R″ = H), 62085-59-0; **3** (R = 3-ClC_6H_4; R′ = R″ = H), 62085-60-3; **3** (R = 4-ClC_6H_4; R′ = R″ = H), 62085-61-4; **3** (R = 4-$CH_3C_6H_4$; R′ = R″ = H), 62085-62-5; **3** (R = 2-$CH_3OC_6H_4$; R′ = R″ = H), 62085-63-6; **3** (R = 4-$CH_3OC_6H_4$; R′ = R″ = H), 62085-64-7; **3** (R = furyl; R′ = R″ = H), 62085-65-8; **3** (R = Ph; R′ = CH_3; R″ = H), 62085-66-9; **3** (R = Ph; R′ = H; R″ = $C(CH_3)_3$), 62085-67-0; **4** (R = R′ = R″ = H), 576-26-1; **4** (R = Ph; R′ = R″ = H), 47157-01-7; **4** (R = 4-FC_6H_4; R′ = R″ = H), 62085-68-1; **4** (R = 3-ClC_6H_4; R′ = R″ = H), 62126-69-6; **4** (R = 4-ClC_6H_4; R′ = R″ = H), 31480-69-0; **4** (R = 4-$CH_3C_6H_4$; R′ = R″ = H), 51866-65-0; **4** (R = 2-$CH_3OC_6H_4$; R′ = R″ = H), 53376-41-3; **4** (R = 4-$CH_3OC_6H_4$; R′ = R″ = H), 53376-42-4; **4** (R = 2-furyl; R′ = R″ = H), 15341-61-4; **4** (R = Rh; R′ = Me; R″ = H), 4732-03-0; **4** (R = Ph; R′ = H; R″ = $C(CH_3)_3$), 53376-43-5; **6**, 62085-34-1; **7**, 53376-46-8; **8** (R = R′ = H), 57558-64-2; **8** (R = Me; R′ = H), 59082-26-7; **8** (R = Cl; R′ = H), 59082-24-5; **8** (R = H; R′ = OMe), 50558-94-6; **8** (R = CH_3; R′ = OMe), 62085-35-2; **8** (R = Cl; R′ = OMe), 62085-36-3; **8** (R = H; R′ = $OCOCH_3$), 62085-37-4; **8** (R = CH_3; R′ = $OCOCH_3$), 62085-38-5; **8** (R = Cl; R′ = $OCOCH_3$), 62085-39-6; **11** (R = R′ = H), 36441-32-4; **11** (R = CH_3; R′ = H), 62085-40-9; **11** (R = Cl; R′ = H), 62085-41-0; **11** (R = H; R′ = OMe), 62085-42-1; **11** (R = CH_3; R′ = OMe), 62085-43-2; **11** (R = Cl; R′ = OMe), 62085-44-3; **11** (R = H; R′ = $OCOCH_3$), 62085-45-4; **11** (R = CH_3; R′ = $OCOCH_3$), 62085-46-5; **11** (R = Cl; R′ = $OCOCH_3$), 62085-47-6; (*E*,*E*)-**13**, 62085-48-7; (*E*,*Z*)-**13**, 62085-49-8; (*Z*,*Z*)-**13**, 62085-25-0; (*Z*)-**16**, 34403-31-1; (*E*)-**16**, 34410-06-5; **17**, 62085-26-1; **18**, 62085-27-2; (*Z*)-**21**, 62085-28-3; (*E*)-**21**, 62085-29-4; **22**, 62085-30-7; **23**, 62085-31-8; **24**, 34611-43-3; **25**, 62085-32-9; **28**, 23923-54-8; $IrCl(CO)(PPh_3)_2$, 14871-41-1; 1-tetralone, 529-34-0; *p*-tolualdehyde, 104-87-0; 6-methoxy-1-tetralone, 1078-19-9; *p*-chlorobenzaldehyde, 104-88-1; 6-hydroxy-1-tetralone, 3470-50-6; cycloheptanone, 502-42-1; trimethylsilyl-3,7-dibenzyltropolone, 62085-33-0.

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Mass Spectrometric Fragmentation of Some Arylidenecycloalkanones

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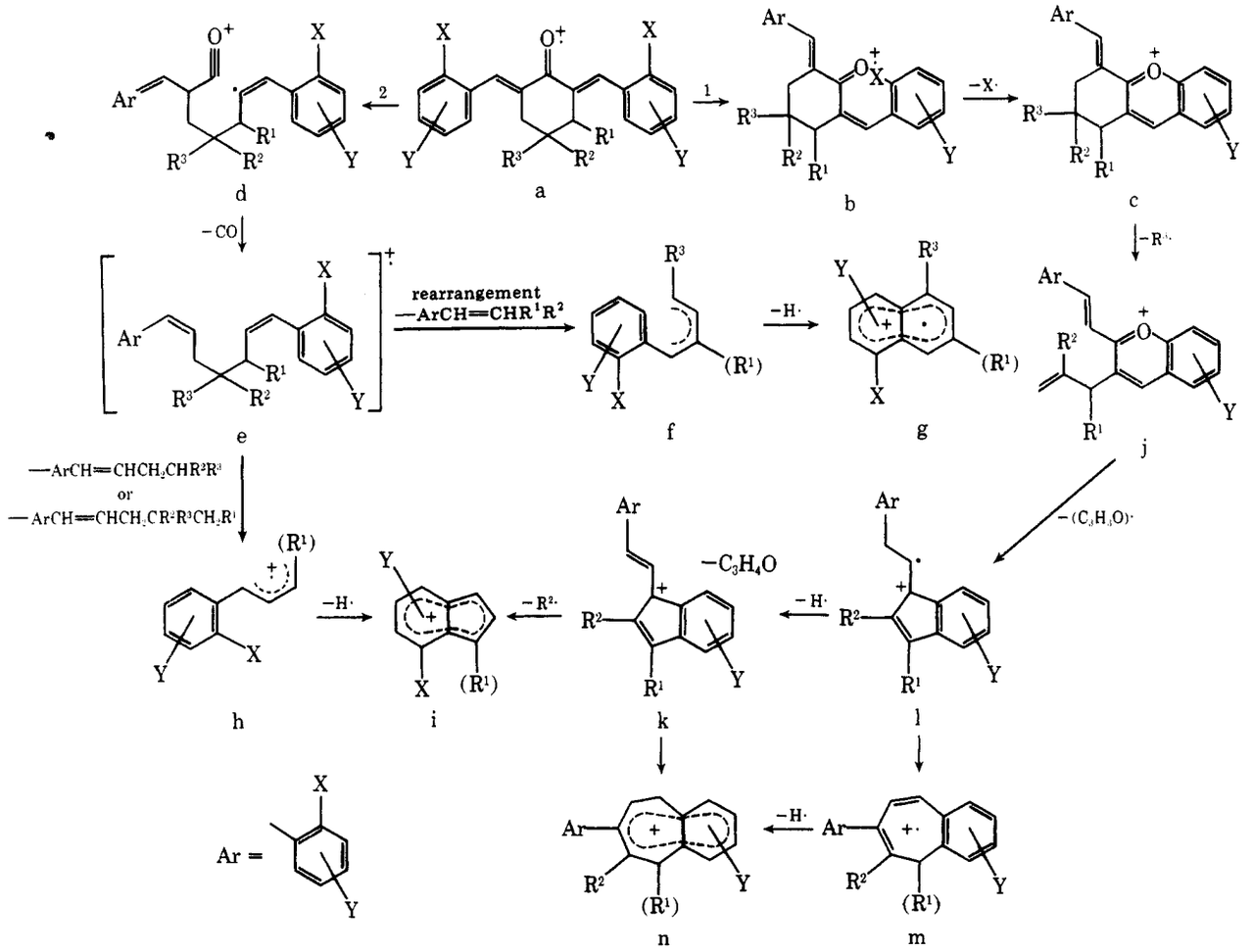
The mass spectra of (*E,E*)-α,α'-dibenzylidenecyclopentanone, -hexanone, -heptanone, and (*E*)-2-benzylidene-1-tetralone are reported. The main feature in these spectra is *E–Z* isomerization of the parent ions followed by production of stable benzopyrilium ions. A competing but less important fragmentation mode involves α-cleavage and CO extrusion as initial steps. The latter route dominates in the mass spectrum of (*E,E*)-3,5-dibenzylidenetetrahydro-4*H*-pyran-4-one. The mass spectrum of (*E,E*)-3,7-dibenzylidenecycloheptane-1,2-dione differs from that of the lower cyclohexanone derivative only by M and M − CO ions. At 70 eV benzopyrilium ion formation is virtually independent of the electronic nature of the benzylidene moieties, but is promoted by electron-donating groups and reduced by electron-attracting substituents attached to the fused aromatic ring in 2-arylidene-1-tetralones.

In the course of our study on $IrCl(CO)(PPh_3)_2$-catalyzed isomerization, isoaromatization, and disproportionation of arylidenecycloalkanones,[1] we found that the mass spectra of these ketones may be utilized not only for unequivocal location of the double bonds, but also as a convenient method for estimation of the exo- to endocyclic C=C bond migration in these systems.

The mass spectrum of (*E,E*)-2,6-dibenzylidenecyclohexanone (1) has been reported previously by Smith, Dimmock, and Turner.[2] The present investigation extends this study to include various substituted diarylidenecyclohexanones and arylidene derivatives of other cyclic structures.

General fragmentation patterns for (*E,E*)-2,6-diarylidenecyclohexanones are suggested in Scheme I, and the

Scheme I[a]



[a] The fragments shown correspond only to the most intense peaks of the 70-eV spectra. Usually no attempts were made to evaluate peaks of relative intensities lower than 5%