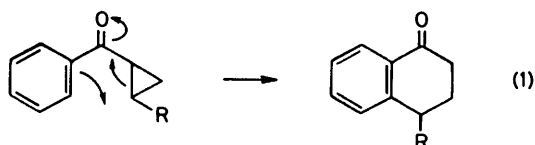


Reactions of Aryl Cyclopropyl Ketones. A New Synthesis of Aryl Tetralones

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Aryl cyclopropyl ketones (2) cyclise to 1-tetralones (3) in the presence of a variety of acid catalysts under mild conditions. Open-chain carbinols (4) are also formed. The ratio of (3) to (4) is dependent on the aryl ring substituents. A cationic mechanism is proposed. Cyclopropyl ketones (1) do not react. Stereoelectronic factors involved in the reactivity of the rigid cyclopropyl ketone (12) are discussed. The reactions of selected phenolic cyclopropyl ketones have been investigated as anionic counterparts to the acid-catalysed reactions. No reaction is observed.

PURSuing our interest in the development of phenol cyclisations,¹ we undertook an investigation of the acid- and the base-catalysed reactions of aryl cyclopropyl ketones.² Specifically our objective was to test the feasibility of the reaction [equation (1)].

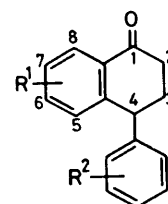
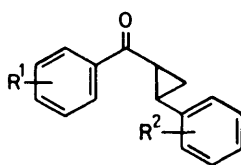
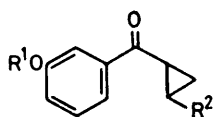


While the acid-catalysed cleavage of cyclopropyl ketones has ample precedent,³ endocyclic⁴ trapping by an aryl group of a formal or incipient carbocation would represent a new application of cyclopropanes and a simple route to 1-tetralones and related lignans.⁵ Base-catalysed reactions are discussed separately below.

Synthesis of Cyclopropyl Ketones.—The cyclopropyl ketones (2c), (2e), and (2g—2l) were readily synthesised from the corresponding chalcones⁶ and dimethylsulphoxonium methylide in hot dimethyl sulphoxide according to the procedure of Corey and Chaykovsky.⁷ However, attempts to synthesise phenolic cyclopropyl ketones such as (2d) and (2f) by the same method failed. The methylated cyclopropyl ketones (2e) and (2g) were

produced exclusively. It is probable that intermediate phenoxide ions formed by proton loss to the methylide were methylated by the so formed trimethylsulphonium salt. Trimethylsulphonium salts are known to act as methylating agents.⁸ This problem was resolved by treating the chalcone with three equivalents of dimethylsulphoxonium methylide in dimethyl sulphoxide at a temperature slightly below ambient for 30 min. None of the methylated products were observed. Subsequently, it was realised that cyclopropanation of the enones and chalcones, described above, was accomplished in excellent yield under these mild conditions. The efficiency of the method was underlined by the synthesis of (1a) from the base-sensitive and readily polymerisable enone precursor.¹

Lewis Acid-catalysed Reactions. Activated aryl cyclopropyl ketones are indeed cyclised under mild conditions to aryltetralones in the presence of Lewis acids (Table 1). Open-chain alcohols (4) are also formed occasionally. For example, cyclopropyl ketone (2l) upon treatment with stannic chloride in benzene at room temperature gave the tetralone (3l) (80%) as a 10 : 90 mixture of *o* : *p* (with respect to the position of alkylation relative to R¹) isomers. This one-pot synthesis constitutes by far the most simple and efficient method for the production of this ketone.⁹ The ketone (2g) also cyclised readily



	(1)	R ¹	R ²
a;		H	H
b;		Me	H
c;		H	Bu ^t
d;		Me	Bu ^t

	(2)	R ¹	R ²
a;		H	3-HO
b;		3-HO	H
c;		3-MeO	H
d;		3-HO	2-HO
e;		3-MeO	2-MeO
f;		3-HO	4-HO
g;		3-MeO	4-MeO
h;		4-MeO	3-MeO
i;		4-MeO	3,4-(MeO) ₂
j;		3,4-(MeO) ₂	3,4-(MeO) ₂
k;		3,4-(MeO) ₂	3,4-CH ₂ O ₂
l;		3,4-CH ₂ O ₂	3,4-(MeO) ₂

	(3)	R ¹	R ²
		H	3-HO
		7-HO	H
		7-MeO	H
		7-HO	2-HO
		7-MeO	2-MeO
		7-HO	4-HO
		7-MeO	4-MeO
		6-MeO	3-MeO
		6-MeO	3,4-(MeO) ₂
		6,7-(MeO) ₂	3,4-(MeO) ₂
		6,7-(MeO) ₂	3,4-CH ₂ O ₂
		6,7-CH ₂ O ₂	3,4-(MeO) ₂

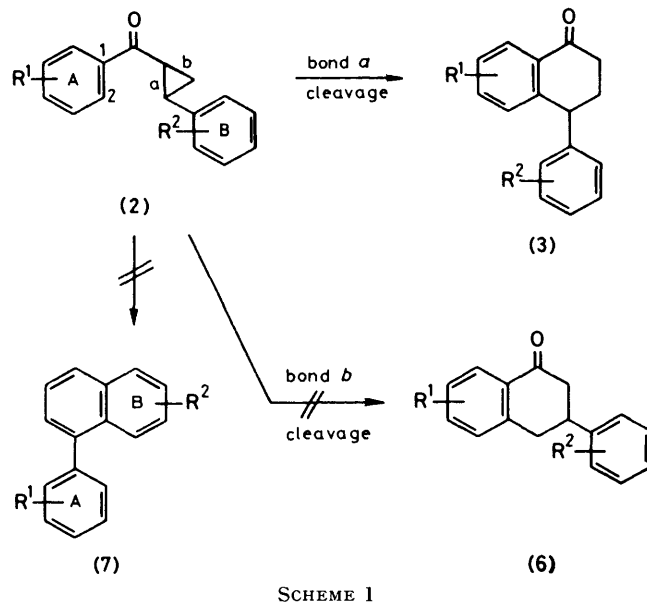
under the same conditions. The structures of the products (3l) and (3g) were readily determined by conversion *via* Clemmensen reduction into the known ¹ tetralins (5a) and (5b).

TABLE I
Lewis acid-catalysed cyclisations of aryl cyclopropyl ketones

Entry	Reactant	Conditions ^a (room temp.)	Yield ^b (%)	
			(3)	<i>o</i> : <i>p</i> ratio (4)
1	(1b) ^c	SnCl ₄ , CH ₂ Cl ₂ , 170 h	0	0
2	(1d) ^c	SnCl ₄ , CH ₂ Cl ₂ , 170 h	0	0
3	(2a)	SnCl ₄ , CH ₂ Cl ₂ , 24 h		68
4	(2c)	SnCl ₄ , CH ₂ Cl ₂ , 24 h	14	12 : 88 ^d
5	(2e)	SnCl ₄ , CH ₂ Cl ₂ , 8 h	75	19 : 81 ^{d,e}
6	(2e)	SnCl ₄ , C ₆ H ₆ , 8 h	80	10 : 90 ^{d,e}
7	(2e)	TFA, CH ₂ Cl ₂ , 8 h	71	8 : 92 ^d
8	(2e)	TFA, (neat), 1 h	60	6 : 94 ^d
9	(2g)	SnCl ₄ , CH ₂ Cl ₂ , 8 h	70	14 : 86 ^{d,e}
10	(2g)	SnCl ₄ , C ₆ H ₆ , 8 h	80	7 : 93 ^{d,e}
11	(2g)	TFA, CH ₂ Cl ₂ , 14 h	50	17 : 83 ^d
12	(2g)	TFA, C ₆ H ₆ , 24 h	60	5 : 95 ^d
13	(2g)	BF ₃ ·Et ₂ O, MeNO ₂ , 5 h	61	12 : 88 ^d
14	(2h)	SnCl ₄ , CH ₂ Cl ₂ , 30 h		41 ^f
15	(2i)	SnCl ₄ , C ₆ H ₆ , 10 h		70
16	(2j)	SnCl ₄ , C ₆ H ₆ , 10 h	15	60
17	(2j)	SnCl ₄ , MeNO ₂ , 20 h	70	
18	(2k)	SnCl ₄ , C ₆ H ₆ , 47 h	35	
19	(2k)	SnCl ₄ , MeNO ₂ , 30 h	72	36
20	(2l)	SnCl ₄ , MeNO ₂ , 35 h	70	

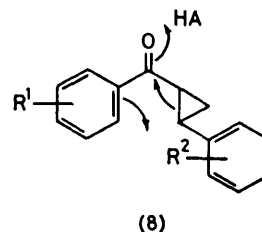
^a Aqueous sodium hydroxide work-up. ^b Isolated pure product (prep. t.l.c.). ^c Recovered unchanged. ^d Determined by ¹H n.m.r. analysis. ^e Determined by g.l.c. analysis. ^f Hemiacetal (9) also isolated (23%) and (2c) recovered (20%). ^g (2h) recovered (41%).

With certain limitations, the results outlined in Table I provide the basis for a general synthesis of 1-aryltetra-ones. A number of acid catalysts are effective (see for example, entries 5, 7, and 13) under mild conditions. The *o/p* cyclisation ratio is influenced by both solvent and catalyst (entries 5–13). It is to be noted ¹⁰ that particularly high *para*-alkylation occurs in trifluoroacetic



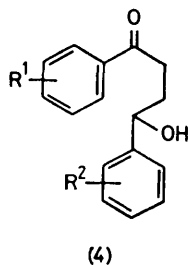
acid (TFA). An interesting variation of reactivity with solvent is noted (compare entry 16 with 18 and 18 with 19) which probably stems from the heterogeneity of reactions in benzene.

Bond *a* cleavage (Scheme 1) is always observed. The tetralones (6) are not formed. This result points to a carbocation intermediate. A concerted mechanism involving aryl participation as in (8) has been ruled out on steric grounds following an inspection of molecular models. The intermediate (9), perhaps stabilised as the corresponding cyclic oxonium ion ¹¹ (10), is proposed since it provides a consistent rationale for all observed effects.

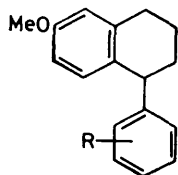


Potential primary [from (1b)] or secondary [from (1d)] carbocations do not provide a sufficient driving force and are probably not formed (entries 1 and 2). It appears therefore that the stability of the potential carbocation dictates the ability and the mode of unsymmetrically substituted cyclopropane ring opening. This theory explains the results of others in related systems.^{3,12}

Aryl substituents are important in this reaction.

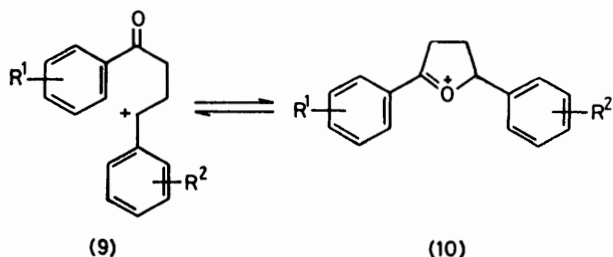


	R ¹	R ²
a;	H	3-HO
b;	3-HO	H
c;	3-MeO	H
d;	3-HO	2-HO
e;	3-MeO	2-MeO
f;	3-HO	4-HO
g;	3-MeO	4-MeO
h;	4-MeO	3-MeO
i;	4-MeO	3,4-(MeO) ₂
j;	3,4-(MeO) ₂	2,4-(MeO) ₂
k;	3,4-(MeO) ₂	3,4-CH ₂ O ₂
l;	3,4-CH ₂ O ₂	3,4-(MeO) ₂



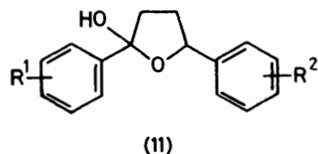
a;	R = 2-MeO
b;	R = 4-MeO

Successful tetralone synthesis is observed only when both ring substituents are suitably activating (see for example entries 5, 9, 17, 19, and 20). When R^2 is incapable of stabilising a benzyl carbocation in the intermediate (9)

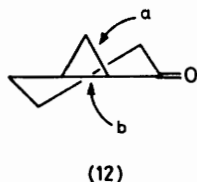


cyclopropane ring opening is slow (see entries 4 and 14). When R^1 does not activate C-2 (see Scheme 1), tetralone ring closure does not occur (see entries, 3, 14, and 15). Instead the carbinol (4) is obtained. Although two separate reaction pathways, one leading to a tetralone the other to a carbinol are consistent with related studies,³ a common intermediate (9) in equilibrium with (10) is sufficient to account for the results.

The hemiacetal (11) was obtained in one experiment (entry 4). A similar observation has been noted previously¹³ in a related system. The hemiacetal is probably formed during basic work-up. It readily reverts to (4) with time and is quite unstable in acid.

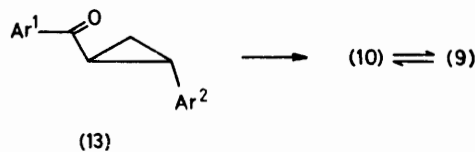


It is of note that 1-arylnaphthalenes (7) (Scheme 1) are not formed even when both aryl rings are equally activated (see entries 9 and 16). This is highlighted by the reactions of (2h) and (2i) (entries 14 and 15) where substitution is such as to favour ring B attack on the carbonyl group. No naphthalene (7) is detectable. This observation contrasts with that of Newman¹⁴ who isolated, as a major product, 1-phenylnaphthalene from the reaction of (2-phenyl)cyclopropyl phenyl ketone with phosphorus pentachloride.



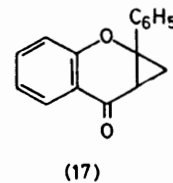
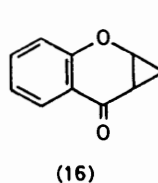
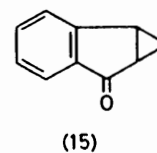
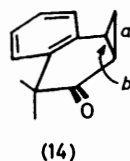
Stereoelectronic Factors.—Since these acid-catalysed reactions are so sensitive to aryl substituent effects, the possibility was considered that stereoelectronic effects might be observable. The orthogonal bond *a* in the bicyclic ketone (12), for example, has been shown¹⁵ to undergo preferential cleavage with hydrogen chloride in chloroform. This result can be explained by greater

overlap by the incipient *p*-orbital in the transition state (mechanism A). However, the data available are confined to reactions conducted in highly nucleophilic media.¹⁶ The mode of cleavage is in addition influenced by the approach¹⁷ and reactivity¹⁸ of the nucleophile.



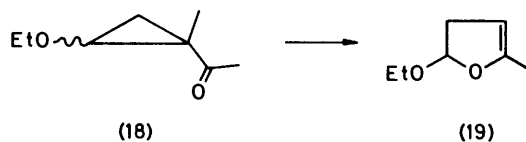
A second mechanism involving concerted carbonyl participation with protonated ring opening (13)¹¹ (mechanism B), must be considered. This route is open to flexible ketones only, not to rigid cyclopropyl ketones. Interestingly, the Stork system,³ where aryl participation has been observed, is rigid.

To initiate a study of stereoelectronic effects, the bicyclic rigid ketone (14) was synthesised by treating the corresponding enone¹⁹ with dimethylsulphoxonium methylide. Cleavage of the orthogonal bond *a* would lead to a primary carbocation. This mode of cleavage is not expected (see entry 1, Table 1). Although less favourably oriented, bond *b*, if cleaved, would lead to the favourable benzyl carbocation. In the event, ketone (14) was stable upon prolonged treatment with stannic chloride under standard conditions. It has been noted by a number of workers²⁰ that ketone (15) is stable towards aluminium chloride. This result indicates that the inability of (14) to open is not the result of the size or stability of the ring being formed. It therefore appears that under these weakly nucleophilic conditions orthogonal cyclopropyl bond cleavage is stereoelectronically preferred and will not occur unless the potential carbocation can be suitably stabilised. This factor can explain the stability of ketones (16)²¹ and (17)²² towards acid.

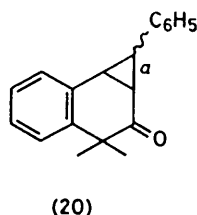


Carbonyl participation and subsequent oxonium ion formation (mechanism B) are not possible with ketones (14)—(17). Unfortunately our results are insufficient to establish unequivocally either mechanism A or B or

determine their relative importance. Nonetheless, the inoperability of both mechanisms offers an explanation for the stabilities of (16)²¹ and (17)²² in acid. The facile acid-catalysed rearrangement of the flexible ketone (18)²³ can be explained by mechanism B.

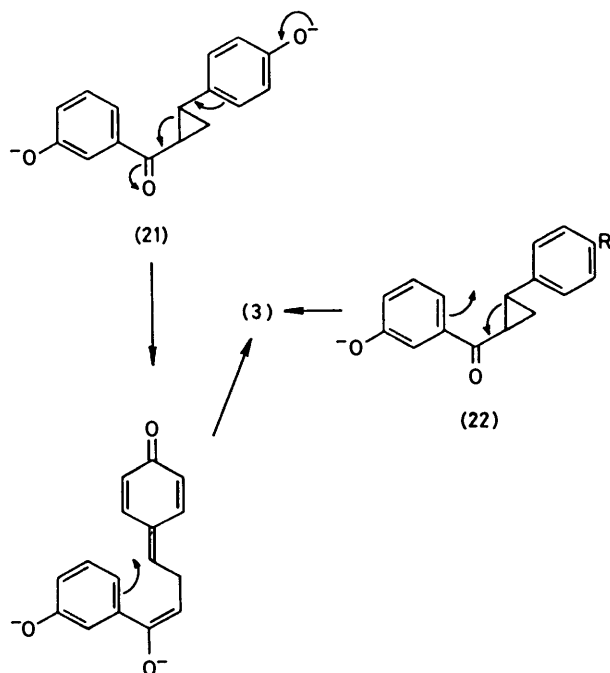


To assess the relative importance of these two mechanisms the model compound (20) was considered, in which the orthogonal bond α is sufficiently activated. Synthesis of (20) was attempted by treating the corresponding enone with tetramethylenesulphonium benzyliide.²⁴ The reaction was unsuccessful.



Further study of the stereoelectronic effects on acid-catalysed cleavage of cyclopropanes is in progress.

Attempted Anionic Ring Closures.—We have previously demonstrated that quinone methides can be efficient electrophilic cyclisation initiators.¹ A new methodology for generating quinone methides *via* (21) (Scheme 2) was considered. In addition, a concerted



SCHEME 2

mechanism (22) (Scheme 2) seemed to be a feasible alternative. The basis for this consideration was the enhanced reactivity due to cyclopropane ring strain,²⁵ sensitivity of cyclopropyl ketones to nucleophilic reagents,²⁶ and the well established base-catalysed cleavage of oxycyclopropyl ketones.²⁷

Phenols (1a) and (1c) did not cyclise when treated with sodium hydride in refluxing tetrahydrofuran and were recovered. Attempted closure of the more reactive substrate (2f) also failed. This resistance to cyclisation is attributable to steric strain in the transition state (22). Neither (2b) nor (2d) closed under the above conditions. Since magnesium cations have a marked effect over sodium in enhancing the cyclisations of phenoxide ions,¹ it was disappointing to recover both (2d) and (2f) after treatment with ethylmagnesium bromide in refluxing benzene (48 h). It seems probable that the failure of these reactions is due to the relatively low nucleophilicity of the phenoxide ring. That cleavage of activated cyclopropanes is difficult even with highly reactive nucleophiles, has been emphasised by Danishefsky.²⁶

EXPERIMENTAL

General procedures were as detailed previously.¹ ¹³C N.m.r. spectra were measured on a Jeol FX60 spectrometer in deuteriochloroform.

Synthesis of Cyclopropyl Ketones from Chalcones and Enones with Dimethylsulphoxonium methylide: General Procedure.—To a stirred suspension of trimethylsulphoxonium iodide⁷ (1.1 mmol) in dimethyl sulphoxide (5 ml) at room temperature (20 °C) was added in one portion a dispersion of sodium hydride in mineral oil (1.1 mmol). Upon completion of hydrogen evolution (15–20 min), a solution of the chalcone⁶ or the enone¹ (1 mmol) in dimethyl sulphoxide (4 ml) was added dropwise. The resulting solution was stirred at room temperature for 0.5–1 h (followed by t.l.c.). In the case of hydroxy-compounds, an additional equivalent of ylide per hydroxy-group and a slightly longer reaction time were required. It was then poured into water (100 ml) and extracted with chloroform. The extracts were washed several times with water, dried (Na₂SO₄), and evaporated. In the case of hydroxy-compounds, acidification before extraction with chloroform was also required. Oily products were purified by preparative t.l.c. and crystalline products were purified by recrystallisation. Descriptive and analytical data for cyclopropyl ketones prepared by this procedure are in Table 2.

Lewis Acid-catalysed Cyclisation of Cyclopropyl Ketones: General Procedure.—A solution of the cyclopropyl ketone (1 mmol) in the indicated solvent (*ca.* 10 ml) was treated with the indicated acid catalyst in the following molar ratios: SnCl₄ (1.5 equiv.), TFA (3 equiv.), BF₃·Et₂O (1.5 equiv.) (in the case of entry 8, Table 1, a large excess of TFA was used), at the indicated temperature. The resulting solution (or mixture) was stirred at the given temperature for the time period indicated. It was then poured into cold aqueous sodium hydroxide (5%). The mixture was stirred for *ca.* 5 min and extracted with chloroform. The chloroform extracts were washed with water, dried (brine, sodium sulphate), and evaporated to give an oil. Products were purified by preparative t.l.c. Physical and chemical properties of products are described below.

TABLE 2
 Aryl cyclopropyl ketones

Compound	Yield (%)	$\nu_{\max}/\text{cm}^{-1}$	Chemical shift (δ)	Found (%) [Requires (%)]
(1b) ^a Oil	85	1 655, 1 580	1.25 (4 H, m, 2 × CH ₂), 2.20 (1 H, m, CH), 3.90 (3 H, s, OMe) and 7.05—7.85 (4 H, m, ArH)	C ₁₁ H ₁₂ O ₂ C, 74.9; H, 6.7 (C, 75.0; H, 6.8)
(1c) M.p. 118—119 °C	70	3 390, 1 650 1 580	0.90 (9 H, s, 3 × Me), 1.45 (3 H, m), 2.5 (1 H, m, COCH), 7.0—7.8 (4 H, m, ArH)	C ₁₄ H ₁₈ O ₂ C, 77.4; H, 8.2 (C, 77.1; H, 8.3)
(1d) ^b Oil	88	1 650, 1 580	0.91 (9 H, 2, 3 × Me), 1.45 (3 H, m), 2.55 (1 H, m, COCH), 3.87 (3 H, s, OMe), 7.05—7.85 (4 H, m, ArH)	C ₁₅ H ₂₀ O ₂ C, 77.2; H, 8.2 (C, 77.5; H, 8.6)
(2a) Oil	70	3 300, 1 650 1 585	1.25—2.0 (2 H, m), 2.85 (2 H, m, COCH + ArCH), 6.75—8.2 (9 H, m, ArH) and 8.5 (1 H, br s, OH)	C ₁₆ H ₁₄ O ₂ C, 80.4; H, 6.0 (C, 80.7; H, 5.9)
(2b) M.p. 102—103.5 °C		3 300, 1 650, 1 600, 1 580	1.40 (1 H, m), 1.81 (1 H, m), 2.70 (2 H, m), 6.70—7.81 (9 H, m, ArH), 8.10 (1 H, br s, OH)	C ₁₆ H ₁₄ O ₂ C, 80.2; H, 6.0 (C, 80.7; H, 5.9)
(2c) Oil	85	1 660, 1 600, 1 580	1.36 (1 H, m), 1.75 (1 H, m), 2.65 (2 H, m), 3.75 (3 H, s, OMe) and 6.70—7.75 (9 H, m, ArH)	C ₁₇ H ₁₆ O ₂ C, 80.9; H, 6.3 (C, 81.0; H, 6.4)
(2d) M.p. 175—177 °C	73	3 300, 1 660 1 600, 1 580	[(CD ₂) ₂ CO] 1.31—2.5 (6 H, m) and 6.61—7.70 (8 H, m, ArH)	C ₁₆ H ₁₄ O ₃ C, 75.2; H, 5.7 (C, 75.6; H, 5.5)
(2f) Oil	69	3 300, 1 650, 1 600, 1 580	[(CD ₂) ₂ CO] 1.41—2.81 (6 H, m) and 6.80—7.81 (8 H, m, ArH)	
(2h) Oil	85	1 660, 1 600, 1 580	1.45 (1 H, m), 1.75 (1 H, m), 2.80 (2 H, m), 3.80 (6 H, s, 2 × OMe), 6.75—7.75 (6 H, m, ArH) and 8.10 (2 H, d, <i>J</i> 10 Hz, ArH)	C ₁₈ H ₁₈ O ₃ C, 76.2; H, 6.1 (C, 76.6; H, 6.4)
(2i) Oil	92	1 650, 1 600 1 580	1.20—2.05 (2 H, m, CH ₂), 2.75 (2 H, m, COCH + ArCH), 3.90 (9 H, s, 3 × OMe), 6.75—7.30 (5 H, m, ArH) and 8.10 (2 H, d, <i>J</i> 10 Hz, ArH)	C ₁₉ H ₂₂ O ₄ C, 73.1; H, 6.2 (C, 73.1; H, 6.4)
(2j) Oil	90	1 655, 1 600, 1 580	1.50 (1 H, m), 1.90 (1 H, m), 2.75 (2 H, m, COCH + ArCH), 3.85 (6 H, s, 2 × OMe), 3.90 (6 H, s, 2 × OMe) and 6.81—7.85 (6 H, m, ArH)	C ₂₀ H ₂₂ O ₅ C, 70.0; H, 6.0 (C, 70.2; H, 6.4)
(2k) Oil	90	1 650, 1 600, 1 585	1.5 (1 H, m), 1.85 (1 H, m), 2.80 (2 H, m, COCH + ArCH), 3.92 (6 H, s, 2 × OMe), 6.01 (2 H, s, O ₂ CH ₂) and 6.7— 7.82 (6 H, m, ArH)	C ₁₉ H ₁₈ O ₅ C, 69.8; H, 5.4 (C, 69.9; H, 5.5)
(2l) Oil	91	1 650, 1 600, 1 585	1.2—2.1 (2 H, m), 2.80 (2 H, m, COCH + ArCH), 3.89 (6 H, s, 2 × OMe) 6.05 (2 H, s, CH ₂ O ₂) and 6.82—7.8 (6 H, ArH)	C ₁₉ H ₁₈ O ₅ C, 70.0; H, 5.3 (C, 69.9; H, 5.5)

^a Synthesised by methylation (methyl iodide, potassium carbonate, refluxing acetone) of (1a).¹ ^b Synthesised by methylation of (1c).

7-Methoxy-4-phenyl-3,4-dihydronaphthalen-1(2H)-one (3c), an oil (Found: C, 80.6; H, 6.2. $C_{17}H_{16}O_2$ requires C, 81.0; H, 6.3%); ν_{\max} 1 670 and 1 600 cm^{-1} ; δ 2.50 (4 H, m, $COCH_2CH_2$), 3.71 (s, OMe of *o*-isomer), 3.89 (s, OMe of *p*-isomer), 4.25 (1 H, m, CH), and 6.79—7.80 (8 H, m, ArH).

7-Methoxy-4-(2-methoxyphenyl)-3,4-dihydronaphthalen-1(2H)-one (3e), an oil (Found: C, 76.5; H, 6.3. $C_{18}H_{18}O_3$ requires C, 76.6; H, 6.4%); ν_{\max} 1 675 and 1 600 cm^{-1} ; δ (CCl_4) 2.35 (4 H, symmetrical m, $2 \times CH_2$), 3.62 and 3.90 ($2 \times s$, $2 \times$ OMe of *o*-isomer), 3.79 and 3.81 ($2 \times s$, $2 \times$ OMe of *p*-isomer), 4.61 (1 H, t, J 6 Hz, CH), and 6.78—7.81 (7 H, m, ArH).

7-Methoxy-4-(4-methoxyphenyl)-3,4-dihydronaphthalen-1(2H)-one (3g), an oil (Found: C, 76.3; H, 6.2. $C_{18}H_{18}O_3$ requires C, 76.6; H, 6.4%); ν_{\max} 1 665 and 1 600 cm^{-1} ; δ 2.18—2.81 (4 H, m, $COCH_2CH_2$), 3.72 and 3.78 ($2 \times s$, $2 \times$ OMe of *o*-isomer), 3.81 and 3.89 ($2 \times s$, $2 \times$ OMe of *p*-isomer), 4.21 (1 H, t, J 6 Hz, CH), and 6.75—7.75 (7 H, m, ArH).

4-(3,4-Dimethoxyphenyl)-6,7-dimethoxy-3,4-dihydronaphthalen-1(2H)-one (3j), an oil (Found: C, 70.1; H, 6.1. $C_{20}H_{22}O_5$ requires C, 70.2; H, 6.4%); ν_{\max} 1 665 and 1 600 cm^{-1} ; δ 2.61 (4 H, m, $COCH_2CH_2$), 3.80, 3.86, 3.92, and 3.98 (12 H, $4 \times s$, $4 \times$ OMe), 4.25 (1 H, t, J 6 Hz, CH), 6.57 (1 H, s, ArH), 6.82 (3 H, m, ArH), and 7.73 (1 H, s, ArH).

6,7-Dimethoxy-4-(3,4-methylenedioxyphenyl)-3,4-dihydronaphthalen-1(2H)-one (3k), m.p. 129—132 °C (Found: C, 70.0; H, 5.5. $C_{19}H_{18}O_5$ requires C, 69.9; H, 5.5%); ν_{\max} 1 660 and 1 600 cm^{-1} ; δ 2.10—2.85 (4 H, m, $COCH_2CH_2$), 3.82 and 3.99 (6 H, $2 \times s$, $2 \times$ OMe), 4.19 (1 H, m, CH), 6.01 (2 H, s, OCH_2O), 6.50 (1 H, s, ArH), 6.55—7.05 (3 H, m, ArH), and 7.63 (1 H, s, ArH).

4-(3,4-Dimethoxyphenyl)-6,7-methylenedioxy-3,4-dihydronaphthalen-1(2H)-one (3l), m.p. 120—123 °C (Found: C, 68.9; H, 5.3. $C_{19}H_{18}O_5$ requires C, 69.9; H, 5.5%); ν_{\max} 1 660 and 1 600 cm^{-1} ; δ 2.2—2.9 (4 H, m, $COCH_2CH_2$), 3.89 and 3.92 (6 H, $2 \times s$, $2 \times$ OMe), 4.80 (1 H, t, J 6 Hz, CH), 6.08 (2 H, s, OCH_2O), 6.50 (1 H, s, ArH), 6.55—7.10 (3 H, m, ArH), and 7.62 (1 H, s, ArH).

3-Benzoyl-1-(3-hydroxyphenyl)propanol (4a), m.p. 143—145 °C (chloroform-hexane) (Found: C, 74.8; H, 6.1. $C_{16}H_{16}O_3$ requires C, 75.0; H, 6.3%); ν_{\max} 3 340, 1 660, and 1 600 cm^{-1} ; δ [(CD_3) $_2CO$] 2.1 (2 H, m), 2.5 (1 H, br, s, OH), 3.19 (2 H, t, J 7 Hz, $COCH_2$), 4.80 (1 H, m, CH), and 6.81—7.92 (9 H, m, ArH).

3-(3-Methoxybenzoyl)-1-phenylpropanol (4c), an oil (Found: C, 75.4; H, 6.3. $C_{17}H_{18}O_3$ requires C, 75.6; H, 6.6%); ν_{\max} 3 400, 1 665, 1 600, and 1 580 cm^{-1} ; δ 2.25 (2 H, q, J 7 Hz, CH_2), 2.50 (1 H, br, s, OH, replacement + D_2O), 3.12 (2 H, t, J 7 Hz, $COCH_2$), 3.77 (3 H, s, OMe), 4.88 (1 H, t, J 7 Hz, CH), and 7.05—7.75 (9 H, m, ArH).

3-(3,4-Dimethoxybenzoyl)-1-(3,4-dimethoxyphenyl)propanol (4j), an oil (Found: C, 66.5; H, 6.4. $C_{20}H_{24}O_6$ requires C, 66.7; H, 6.7%); ν_{\max} 3 400, 1 670, and 1 600 cm^{-1} ; δ 2.14 (2 H, q, J 7 Hz, CH_2), 3.04 (2 H, t, J 7 Hz, $COCH_2$), 3.93 (6 H, s, $2 \times$ OMe), 4.77 (1 H, m, CH), 6.01 (2 H, s, OCH_2O), and 6.70—7.81 (6 H, m, ArH).

3-(4-Methoxybenzoyl)-1-(3-methoxyphenyl)propanol (4h), an oil (Found: C, 71.8; H, 6.5. $C_{18}H_{20}O_4$ requires C, 72.0; H, 6.7); ν_{\max} 3 400, 1 665, and 1 600 cm^{-1} ; δ 2.20 (2 H, q, J 7 Hz, CH_2), 3.03 (2 H, t, J 7 Hz, $COCH_2$), 3.35 (1 H, br, s, OH, replacement + D_2O), 3.77 (3 H, s, OMe), 3.82 (3 H, s, OMe), 4.80 (1 H, t, J 7 Hz, CH), 6.75—7.50 (4 H, m, ArH), and 6.88 and 8.0 (4 H, dd of AB, J 10 Hz, ArH).

1-(3,4-Dimethoxyphenyl)-3-(4-methoxybenzoyl)propanol (4i), m.p. 109—110 °C (Found: C, 68.9; H, 6.8. $C_{19}H_{22}O_5$ requires C, 69.1; H, 6.7%); ν_{\max} 3 400, 1 665, and 1 600 cm^{-1} ; δ 2.25 (2 H, q, J 7 Hz, CH_2), 2.6 (1 H, br, s, OH), 3.08 (2 H, t, J 7 Hz, $COCH_2$), 3.86 (9 H, s, $3 \times$ OMe), 4.78 (1 H, t, J 7 Hz, CH), 6.95 (5 H, m, ArH), and 7.98 (2 H, d, J 8 Hz, ArH).

Clemmensen Reduction of the Tetralones (3e) and (3g).—A mixture of zinc (powder, 1 g), mercuric chloride (100 mg), conc. hydrochloric acid (2 drops), and water (3 ml) was stirred for 5 min. The solution was decanted and to it were added in order as follows: water (8 ml), conc. hydrochloric acid (2 ml), a solution of (3e) (200 mg) in toluene (3 ml), and glacial acetic acid (3 drops). The mixture was heated at reflux for 24 h. The mixture was cooled, diluted with water, and extracted with ether. The ether extracts were washed with water, dried (brine, magnesium sulphate), and evaporated to give a colourless oil of (5a) as the sole product (165 mg, 87%) identical (i.r., n.m.r., t.l.c., and g.l.c.) with the previously prepared specimen.¹

Similar reduction of the tetralone (3g) as described above gave (5b) (85%) identical (n.m.r., t.l.c., and g.l.c.) with the previously known sample.¹

The Cyclopropyl Ketone (14). Treatment of the enone ¹⁹ (348 mg, 2 mmol) in dimethyl sulphoxide (6 ml) with dimethylsulphoxonium methylide, prepared from trimethylsulphoxonium iodide (480 mg, 212 mmol) in dimethyl sulphoxide (8 ml), at room temperature for 1.5 h followed by preparative t.l.c. (ether-light petroleum 1:1) gave (14) as an oil (280 mg, 75%) (Found: C, 83.4; H, 7.1. $C_{13}H_{14}O$ requires C, 83.9; H, 7.5%); ν_{\max} 1 670 and 1 600 cm^{-1} ; δ 0.9—1.8 (2 H, m), 1.46 (6 H, s, $2 \times$ Me), 2.1—2.7 (2 H, m), and 7.35 (4 H, m, ArH); ¹³C δ 20.47, 23.33, 25.99, 29.24, 31.45, 45.16, 126.18; 126.50, 127.41, 127.74, 134.50, 140.93, and 211.36.

Attempted Base-catalysed Cyclisation of (2d).—(a) *Sodium hydride.* To a solution of (2d) (254 mg, 1 mmol) in THF (5 ml) was added sodium hydride (80%, 72 mg, 2.4 mmol) under nitrogen. The mixture was heated at reflux for 24 h. The solution was cooled, acidified with aqueous hydrochloric acid (5%), and extracted with ether. The extracts were washed with water, dried (brine, magnesium sulphate) and the solvent was removed under reduced pressure to give a pale yellow oil (250 mg, 98%) identical with starting material.

Similar treatment of the cyclopropyl ketones (1a), (1c), (2b), and (2f) with sodium hydride in refluxing THF as described above gave only starting material.

(b) *Ethylmagnesium Bromide.* To a solution of (2d) (254 mg, 1 mmol) in ether (6 ml) at room temperature was added ethylmagnesium bromide (2.2 mmol) in ether (5 ml) and the mixture was stirred for 5 min. The ether was removed under reduced pressure. Benzene (20 ml) was added to the reaction mixture which was then heated at reflux. After 2 d, it was cooled and quenched by the addition of saturated aqueous ammonium chloride. The solution was extracted with ethyl acetate and the extract was dried (brine, magnesium sulphate). Removal of the solvent gave an oil identical (i.r., n.m.r., and t.l.c.) with starting material. Methylation of this crude oil gave (2e) which was shown to be identical with the above known sample (n.m.r. and t.l.c.) and no cyclisation was observed. Similar treatment of (2f) with ethylmagnesium bromide gave only starting material.

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