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A NEW CYCLISATION INVOLVING CYCLOPROPYL KETONES. A SHORT ROUTE TO 1-ARYLTETRALONES.

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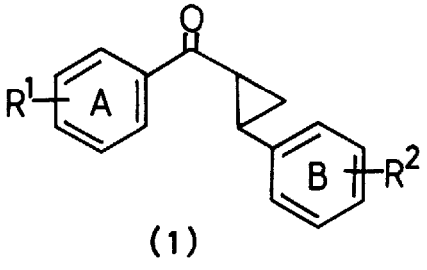
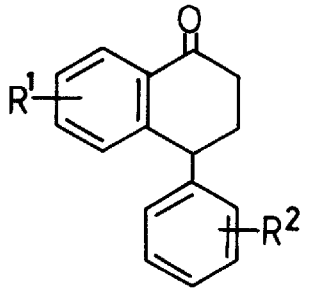
Activated aryl aroylcyclopropanes cyclise with Lewis acids under mild conditions to 1-aryltetralones.

Cyclopropyl ketones are synthetically versatile. Newman[1] noted the formation of 1-arylnaphthalenes when aryl aroyl cyclopropanes were treated with phosphorus pentachloride. When acyl and aroylcyclopropanes are heated in sulphuric acid 3-hydroxyketones are isolated after basic work-up.[2] High temperature treatment of cyclopropylphenylketones resulted in the formation of 1-indanones, amongst other products.[3] Rigid cyclopropyl ketones were employed by Stork[4] for the synthesis of benzodecalones. Non-rigid alkylcyclopropylketones have been used successfully by Grieco.[5]

We now wish to report a new cyclisation of arylaroylcyclopropanes. Our results are outlined (Table). When cyclopropyl ketone (1a) {prepared from the corresponding chalcone by Corey's procedure[6]} was treated with stannic chloride in benzene at room temperature



(1)



(2)

a: R^1 = 3-OMe; R^2 = 2-OMe

b: R^1 = 3-OMe; R^2 = 4-OMe

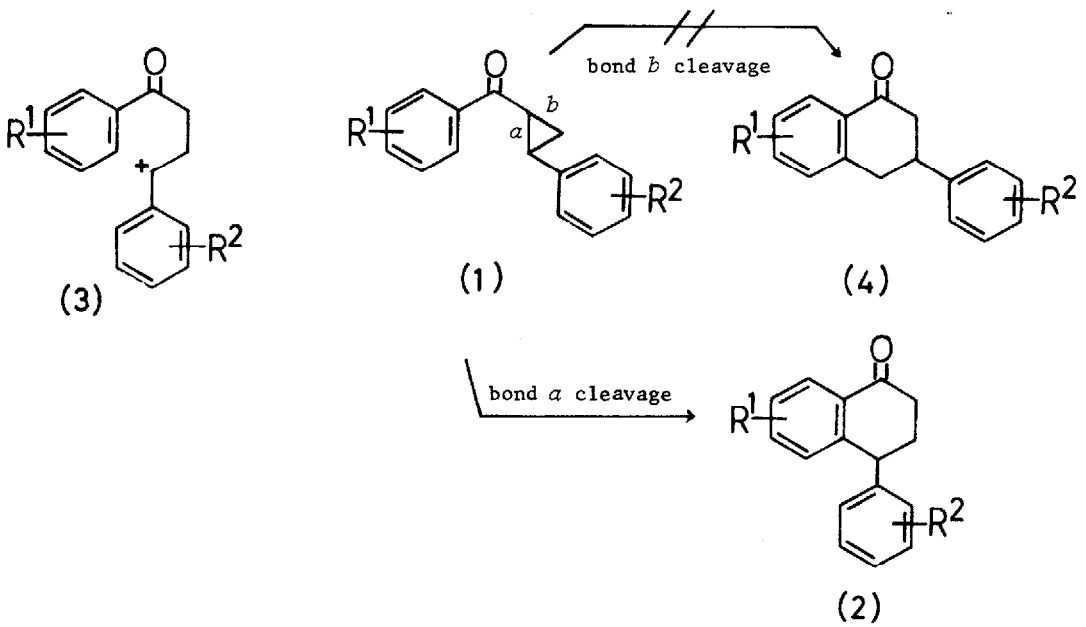
c: R^1 = 3-OMe; R^2 = H

d: R^1 = 4-OMe; R^2 = 3-OMe

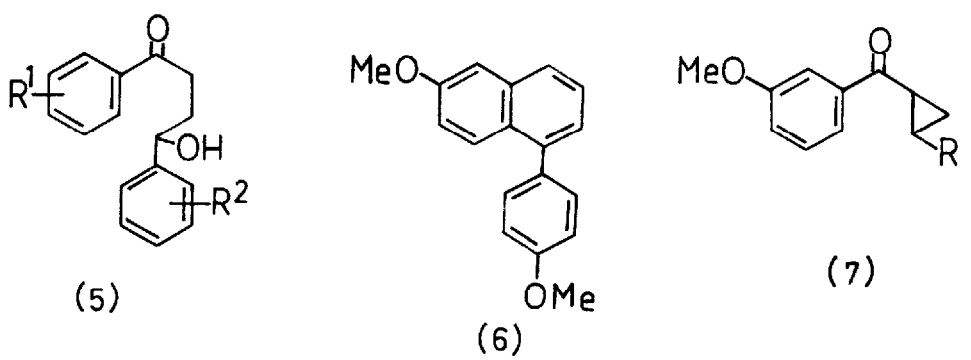
e: R^1 = H; R^2 = 3-OH

the tetralone (2a) (as a 90:10 mixture of *o/p* isomers, see Table) was formed (80% yield). A number of acid catalysts are also effective (entries 1-3, 4-8, Table). The *o/p* cyclisation ratio is influenced by both solvent and catalyst and is consistent with a cationic mechanism. Cyclisation also occurred in the case of (1b) (entries 4-8, Table).

The mode of cyclopropane ring opening also points to a benzylcarbocation intermediate (3) since cleavage of bond *a* is always observed. Tetralone (4) is not formed. Substituent



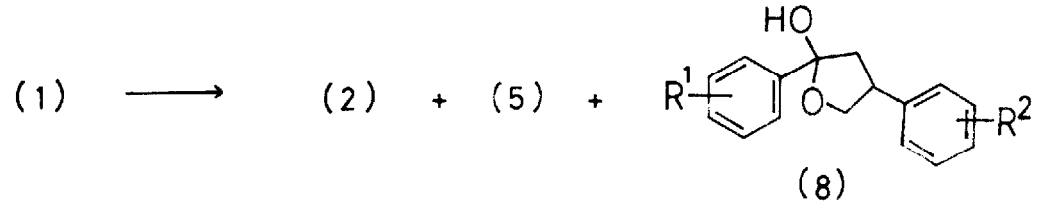
effects are also consistent with the involvement of (3). When R^2 is incapable of stabilising a benzyl carbocation (entries 9, 10, 11, Table) cyclopropane ring opening is slow. When R^1 does not activate ring A at the point of tetralone ring closure (entries 10, 11, Table) cyclisation does not occur. Instead the carbinol (5) is obtained.



It is of note that under these conditions the 1-arylnaphthalene (6) is not formed in the reaction of (1d) (entry 10, Table) even though substitution is such as to favour ring B attack on the carbonyl group.[1] Both substrates (7, R = H) and (7, R = *tert.* butyl) were recovered unchanged when treated for prolonged periods under standard conditions. It appears therefore that the stability of the intermediate carbocation dictates the ability and the course of unsymmetrically substituted cyclopropane ring opening.

Since the starting cyclopropanes are readily prepared,[7] the reaction constitutes a short simple route to substituted tetralones. The application of this reaction to the synthesis of lignans and other natural products is being actively pursued.

TABLE



Entry	Reactant	Conditions[a] (room temp.)	(2) Yield[b]	(2) *o:p* ratio	(5) Yield[b]	(8) Yield[b]
1	1a	$SnCl_4$, CH_2Cl_2 8 h	75	19:81[c]	-	-
2	1a	$SnCl_4$, C_6H_6 8 h	80	10:90[c]	-	-
3	1a	TFA, CH_2Cl_2 14 h	71	8:92[d]	-	-
4	1b	$SnCl_4$, CH_2Cl_2 8 h	70	14:86[c]	-	-
5	1b	$SnCl_4$, C_6H_6 8 h	80	7:93[c]	-	-
6	1b	TFA, CH_2Cl_2 14 h	50	17:83[d]	-	-
7	1b	TFA, C_6H_6 24 h	60	5:95[d]	-	-
8	1b	$BF_3.Et_2O$, CH_3NO_2 5 h	61	12:88[d]	-	-
9	1c	$SnCl_4$, CH_2Cl_2 24 h	14	12:88[d]	31	23[e]
10	1d	$SnCl_4$, C_6H_6 30 h	-	-	41	-
11	1e	$SnCl_4$, CH_2Cl_2 24 h	-	-	68	-

[a]Aqueous sodium hydroxide work-up was used. [b]Isolated yield. [c]Determined by ^1H n.m.r. and g.l.c. [d]Determined by ^1H n.m.r. [e]Mixture of diastereomers.

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7. The same method (ref. 6) was used for the synthesis of each of the substrates. High yields > 90% of the *Trans*-products were always obtained.

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