Stereochemistry of Cyclopropyl Ketones from the Reaction of Dimethylsulphoxonium Methylide with 3-Benzylidenechroman-4-ones

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Stereochemical assignments have been made to the cyclopropyl ketones obtained from 3-benzylidenechroman-4-ones by their reaction with dimethylsulphoxonium methylide. The effect of increasing the steric hindrance at the α-position of the double bond on the course of the reaction has been noted and the predominant formation of one isomer is attributed to the steric effect of a ring carbonyl group having an adjacent anionic centre.

SINCE the original work [1] on the reaction of dimethylsulphoxonium methylide with an enone system, this convenient method for the synthesis of cyclopropyl carbonyl compounds has been extensively studied.[2] Some of this work,[3] including our preliminary note,[4] has dealt with the stereochemistry of the reaction products.

Simple unsaturated *trans*-esters have been found [3b] to react with dimethylsulphoxonium methylide stereospecifically to give *trans*-substituted cyclopropanes. Agami and his co-workers [3c] observed that chalcone and *cis*-3-methylpent-3-en-2-one react similarly. They found, however, that 4-phenylpent-3-en-2-one, 4-phenylbut-3-en-2-one, and 1-phenylbut-2-en-1-one gave mixtures of *trans*- and *cis*-isomers. They suggested that stereospecificity was related to the degree of steric hindrance offered by any substituent on the α-carbon atom of the double bond (*e.g.*, ·CO·C*R*:C:), the brevity of the lifetime of the zwitterionic intermediate (I), and the difficulty of epimerising the 1-position of the cyclopropyl product (II). In connection with this last factor, it has since been shown [5] that the base-catalysed enolisation of cyclopropyl ketones does not occur readily. We have studied the methylide reaction with a series of 3-benzylidenechroman-4-ones (III) and (IV) in which the steric hindrance at the α-carbon atom of the double bond varied and in which epimerisation at C-1 of the cyclopropyl products is impossible.

3-Benzylidenechroman-4-ones.—N.m.r. spectroscopy can give definitive assignments of stereochemistry to *cis*- and *trans*-exocyclic αβ-unsaturated ketones when both isomers are available; the proton *cis* to the carbonyl group is deshielded relative to the corresponding *trans*-proton.[6] Thus the product obtained from the acid-catalysed condensation of chromanone with benzaldehyde, the benzylic proton signal (Table 1) of which occurs at τ 2·13, is *trans*-3-benzylidenechroman-4-one * (IIIa) and the product of photoisomerising this 3-benzylidenechroman-4-one is *cis*-3-benzylidenechroman-4-one (IVa), with a benzylic proton signal at τ 3·08. The protons at the 2-position of the *cis*-isomer are shielded relative to those of the *trans*-isomer owing to the greater distance from the side-chain phenyl group.

The substituted 3-benzylidenechroman-4-ones (IIIb—d) synthesised by acid-catalysed condensation of the corresponding chromanones and aldehydes were, by analogy, also assigned the *trans*-configuration. The condensation of deuteriobenzaldehyde with chromanone gave a mixture of 3-(α-chloro-α-deuteriobenzyl)chromanone (V) and *trans*-3-(1-deuteriobenzylidene)chroman-4-one. The former was readily dehydrochlorinated to the latter by aqueous ethanolic sodium hydroxide.

TABLE 1

N.m.r. spectra of 3-benzylidenechroman-4-ones (τ values; *J* in Hz)

	H_β	2-H	5-H	$J_{2,\beta}$ *	2-Me
(IIIa)	2·13	4·67	1·96	1·8	
[$^2H_\beta$]-(IIIa)		4·67	1·96		
(IVa)	3·08	5·03	2·00	1·2	
(IIIb)	2·18	4·65	1·98	1·6	
(IIIc)	2·01	4·56	1·92	1·6	
(IIId)	2·08	4·58	1·97	1·5	
(IIIe)	2·36	4·25	2·04	1·3	8·42
(IIIf)	2·33	4·15	1·98	1·3	8·37
(IIIg)	2·28	4·20	2·05	1·3	8·42
(IVg)	3·12	4·87	2·12	1·4	8·40
(IIIh)	2·27	4·06	2·02	1·3	8·37
(IIIi) †	1·99	3·34	2·08		
(IVi) †	3·29	3·90	2·08		

* The size (M. Barfield and B. Chakrabarti, *Chem. Rev.*, 1969, **69**, 757) of the allylic coupling constants might be used to assign conformation at the 2-position but, because these coupling constants are not much greater than the experimental error (approx. ±0·8 Hz), this has not been attempted. † Ref. 7.

The 2-methyl-3-benzylidenechroman-4-ones (IIIe—h), products of acid-catalysed condensation reactions, have also been assigned *trans*-configurations by analogy and also in view of the fact that photoisomerisation of the 6-chloro-2′-methyl compound (IIIg) (benzylic proton signal at τ 2·28) gave a mixture of isomers in which the major component showed a benzylic proton signal at τ 3·12; this was obviously the *cis*-isomer. Dreiding

* In this paper, stereochemical prefixes refer, firstly, to the relative configurations of the side-chain phenyl ring and the carbonyl group and, secondly, to those of the 2-substituent and the cyclopropane methylene group.

[1] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, 1962, **84**, 867.

[2] For a review see T. Durst, *Adv. Org. Chem.* 1969, **6**, 318.

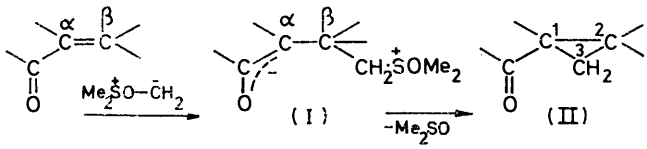
[3] (*a*) T. R. L. Johnson and L. A. Jones, *J. Chem. and Eng. Data*, 1971, **16**, 112; (*b*) S. R. Landor and N. Punja, *J. Chem. Soc.*, 1967, 2495; J. Nozaki, H. Ito, D. Tunemento, and K. Kondo, *Tetrahedron*, 1966, **22**, 141; C. Kasier, B. M. Trost, J. Beeson, and J. Weinstock, *J. Org. Chem.*, 1965, **30**, 3972; (*c*) C. Agami, C. Prevost, and J. Aubouet, *Bull. Soc. chim. France*, 1967, 2299; C. Agami and J. Aubouet, *ibid.*, p. 1391.

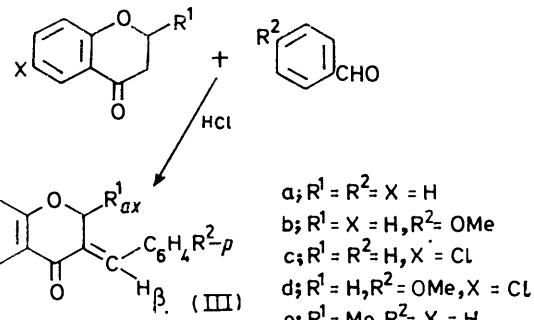
[4] J. A. Donnelly, D. D. Keane, K. G. Marathe, D. C. Meaney, and E. M. Philbin, *Chem. and Ind.*, 1967, 1402.

[5] H. W. Amburn, K. C. Kauffman, and H. Schechter, *J. Amer. Chem. Soc.*, 1969, **91**, 530.

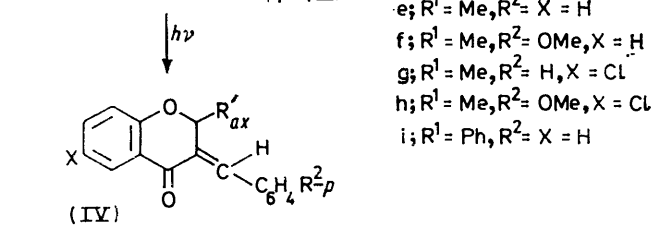
[6] A. Hassner and T. C. Mead, *Tetrahedron*, 1964, **20**, 2201; D. N. Kevill, E. D. Weiler, and N. H. Cromwell, *J. Org. Chem.*, 1964, **29**, 1276.

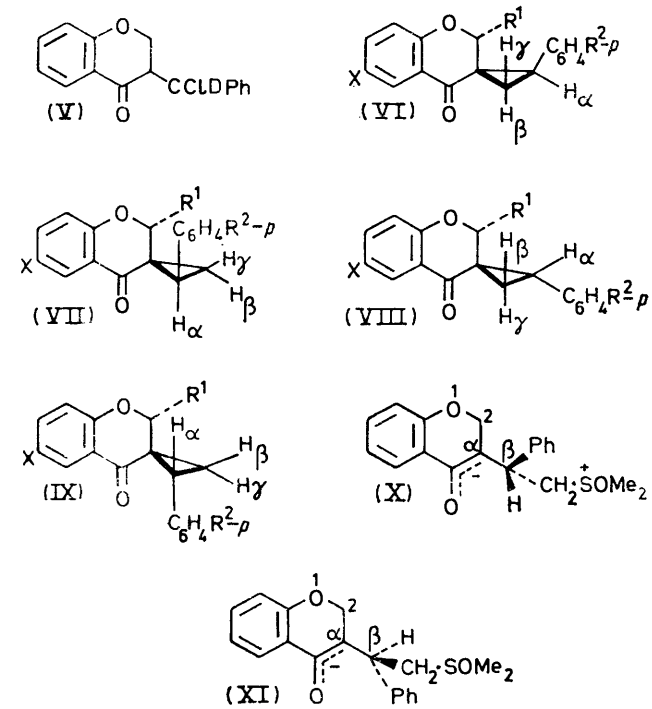
models of *trans*-2-methyl-3-benzylidenechroman-4-ones show that there is severe non-bonded interaction between the 2-methyl substituent and the side-chain





a; $R^1 = R^2 = X = H$
b; $R^1 = X = H, R^2 = OMe$
c; $R^1 = R^2 = H, X = Cl$
d; $R^1 = H, R^2 = OMe, X = Cl$
e; $R^1 = Me, R^2 = X = H$
f; $R^1 = Me, R^2 = OMe, X = H$
g; $R^1 = Me, R^2 = H, X = Cl$
h; $R^1 = Me, R^2 = OMe, X = Cl$
i; $R^1 = Ph, R^2 = X = H$





phenyl group and that the preferred conformation has an axial 2-substituent [as has been demonstrated [7] for *trans*-3-benzylideneflavan-4-one (IIIi)]. The condensation of 2-methylchromanone and benzaldehyde produced 3-(α-chlorobenzyl)-2-methylchroman-4-one as well as *trans*-2-methyl-3-benzylidenechroman-4-one (IIIe). Again, dehydrochlorination of the former to the 3-benzylidenechroman-4-one (IIIe) occurred readily in alkali.

Cyclopropyl Ketones.—The 3-benzylidenechroman-4-ones were converted, in high yields, into cyclopropyl ketones by treatment with dimethylsulphoxonium methylide. As with other benzylideneacetophenone-type compounds,[8] significantly higher yields were obtained by simplifying the original procedure.[9] The products, their proportions, and their n.m.r. spectra are given in Table 2. The Simmons–Smith reaction,[10] believed to be a stereospecific method for the synthesis of cyclopropanes, was carried out on certain 3-benzylidenechroman-4-ones to aid the assignment of configurations to the methylide products. It was found,[11] however, that this reaction was not stereospecific for the less stable member of each geometrically isomeric pair of αβ-unsaturated ketones.

Both *trans*- (IIIa) and *cis*-3-benzylidenechroman-4-one (IVa) gave *trans*-2′-phenylchroman-3-spirocyclopropan-4-one [(VIa) (VIIa)] and, similarly, *trans*- (IIIi) and *cis*-3-benzylideneflavan-4-one (IVi) gave 50 : 50 mixtures of *trans,trans*- (VIi) and *trans,cis*-2,2′-diphenylchroman-3-spirocyclopropan-4-one (VIIi). We were unable to resolve the mixtures obtained from the reactions of dimethylsulphoxonium methylide with the *trans*-2-methyl (IIIe) and *trans*-4′-methoxy-2-methyl (IIIf) derivatives.

The n.m.r. spectra (Table 2) of the cyclopropyl ketones show their stereochemical configurations. There is evidence [12] that the fused benzene ring and the carbonyl group are always coplanar in chromanones and, in the interpretation of the spectra, it has been assumed that this holds for the chromanones discussed here. The arguments used to distinguish between *trans*- and *cis*-isomers and between *trans,trans*-, *trans,cis*-, *cis,trans*-, and *cis,cis*-isomers are exemplified in the following discussion.

A second isomer of 2′-phenylchroman-3-spirocyclopropan-4-one was obtained by photo- or thermal isomerisation of the isomer isolated from the dimethylsulphoxonium methylide reaction. A comparison of the cyclopropyl proton signals (Table 2) of both isomers shows that the former is the *cis*-isomer [(VIIIa) (IXa)] and that the methylide product is the *trans*-isomer

[7] D. D. Keane, K. G. Marathe, W. I. O'Sullivan, E. M. Philbin, R. M. Simons, and P. C. Teague, *J. Org. Chem.*, 1970, 2286.
[8] P. Bennett and J. A. Donnelly, *Chem. and Ind.*, 1969, 783.
[9] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, 1965, **87**, 1353.
[10] H. E. Simmons and R. D. Smith, *J. Amer. Chem. Soc.*, 1959, **81**, 4256.
[11] J. A. Donnelly and P. O'Boyle, *Chem. Comm.*, 1969, 1060.
[12] J. W. Clark-Lewis, L. M. Jackman, and T. M. Spotswood, *Austral. J. Chem.*, 1964, **17**, 632; E. M. Philbin and T. S. Wheeler, *Proc. Chem. Soc.*, 1958, 167; B. L. Shaw and T. H. Simpson, *J. Chem. Soc.*, 1955, 655.

[(VIa) (VIIa)]. Both H_α and H_β of the *trans*-isomer are deshielded (by the carbonyl group) relative to the corresponding protons of the *cis*-isomer; H_γ is relatively shielded. The shielding of the 5-H by the cyclopropyl phenyl ring is also diagnostic for *cis*-isomers.

As regards the *trans*-cyclopropyl ketones (VI) and (VII) with 2-substituents, Dreiding models show that a signal considerably downfield of that of the other *cis*-isomer (and of those of the *trans*-isomers). Apparently, in one of the *cis*-ketones the conformation at the 2-position is changed. Dreiding models show that steric compression between the carbonyl group and the phenyl group on the cyclopropyl ring of the *cis,trans*-ketones (VIII) requires this change to minimise the non-bonded

TABLE 2

Synthesis of cyclopropyl ketones

Substrate	Method [a]	Products	Proportions [b]	N.m.r. spectra (τ values; J in Hz) [c]								
				H_α	H_β	H_γ	2-H	5-H	2-Me	$J_{\alpha\beta}$	$J_{\alpha\gamma}$	$J_{\beta\gamma}$
(IIIa) (IVa) [d]	A, B	(IVa) (VIIa)		6·95	8·00	8·60	6·05 5·69	2·08		8·8	7·5	−4·5
[$^2H_\beta$]-(IIIa)	A	[^{2}H-]-(VIa) (VIIa)			7·97	8·57	6·05 5·69	2·08				−4·7
(VIa) (VIIa)	C, D	(VIIIa) (IXa)		7·20	8·76	7·71	6·06 5·23	2·30		8·1	6·6	−5·7
(IIIb)	A	(VIb) (VIIb)		7·07	8·02	8·69	6·13 5·73	2·06		8·4	6·8	−5·0
(IIIc)	A	(VIc) (VIIc)		6·96	8·00	8·58	6·07 5·71	2·10		8·7	7·1	−4·9
(IIId)	A	(VId) (VIId)		7·03	7·98	8·65	6·08 5·68	2·11		9·2	7·0	−4·3
(IIIg) (IVg) [d]	A	(VIg)	12	6·43	8·53	8·13	5·78	2·07	9·02	9·0	7·4	−4·9
		(VIIg)	2	7·23	7·71	8·74	5·96	2·12	8·63	8·5	7·3	−5·0
		(VIIIg)	1	7·01	8·72	7·71	5·01	2·41	8·61	8·5	7·7	−5·7
		(IXg)	1	7·18	8·79	7·67	5·82	2·80	8·58	9·8	7·5	−5·7
(VIg)	C	(VIg)	12									
		(VIIg)	2									
		(VIIIg)	1									
(IIIh)	A	(VIh)		6·55	8·56	8·23	5·93	2·13	9·01	9·5	7·3	−4·6
(IIIi) (IVi)	A	(VIi)	5	6·33	8·43	8·03	4·98	2·08		9·2	6·6	−4·5
		(VIIi)	2	7·13	7·41	8·53	5·09	2·10		8·7	7·0	−4·0
		(VIIIi)	2	7·41	9·07	7·76	4·12	2·28		8·5	7·8	−4·5
		(IXi)	1	7·00	8·55	7·37	4·80	>2·30		8·8	7·8	−4·8
(IIIi) (IVi)	B	(VIi)	1									
		(VIIi)	1									
(VIi)	C	(VIi)	10									
		(VIIi)	10									
		(VIIIi)	1									
		(IXi)	4									

[a] A dimethylsulphoxonium methylide reaction; B Simmons–Smith reaction; C photoisomerisation; D thermal isomerisation. [b] Relative yields of products. [c] Only the significant signals are given. The cyclopropyl multiplets were analysed as ABX systems by our computer program, ANABEX, which was coupled with K. B. Wiberg's three-spin program ('Computer Programming for Chemists', Benjamin, New York, 1965, p. 195) to check the resulting parameters by computing the spectra. The assignment of chemical shifts to H_α, H_β, and H_γ depends on the fact (D. J. Patel, M. E. H. Howden, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1963, **85**, 2218) that $J_{cis} > J_{trans} > J_{gem}$ and was checked by deuteriating the benzylic position of the cyclopropane [(VIa) (VIIa)]. [d] Contaminated by some of its *trans*-isomer. [e] Erroneously assigned the *cis,cis*-configuration in the preliminary note.[4]

these substituents must have the axial conformation to avoid severe non-bonded interaction with the phenyl group on the cyclopropane ring. The *trans,trans*-isomers are best distinguished from the *trans,cis*-isomers by the chemical shifts of the protons *cis* to the carbonyl group, *i.e.* H_α and H_β. The benzylic proton, H_α, is in the plane of the carbonyl group in the *trans,trans*-ketones and its signal at τ 6·33—6·55 occurs downfield of that of the *trans,cis*-ketones (τ 7·13—7·23), the H_α of which is well removed from the carbonyl plane. The reverse is true for H_β and the signal for this proton in the *trans,trans*-isomers (τ 8·43—8·56) occurs upfield of that of H_β for the *trans,cis*-isomers (τ 7·41—7·71).

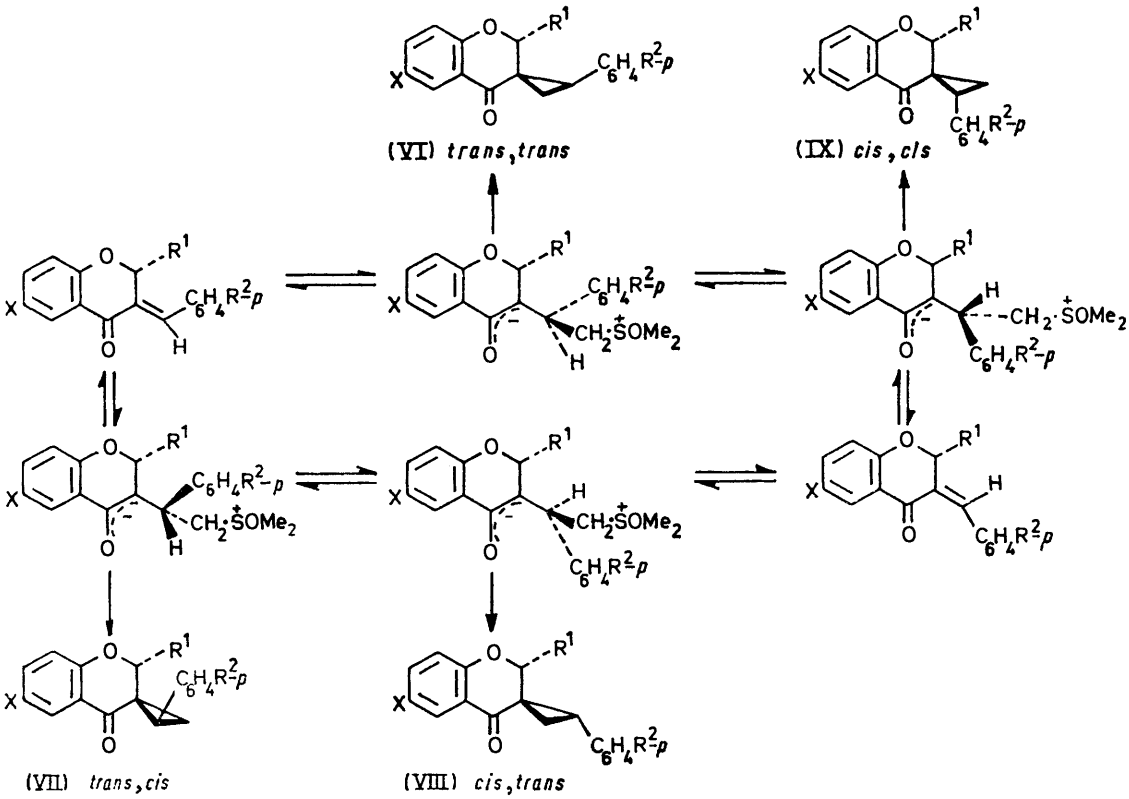
The chemical shift of the 2-proton is the key to distinguishing between the *cis*-isomers, one of which has interaction. Consequently, the equatorial conformation of the 2-proton is changed to axial in the *cis,trans*-isomers, removing this proton from the shielded zone above the cyclopropyl ring and towards the deshielding zone of the fused benzene ring. This conclusion is supported by the similarity of the chemical shifts of the small-ring protons of the *cis*-isomers, particularly those of 6-chloro-2-methyl-2′-phenylchroman-3-spirocyclopropan-4-one [(VIIIg) (IXg)]; change of conformation at the 2-position results in the cyclopropyl protons occupying approximately the same spatial positions relative to the carbonyl group in both *cis*-isomers.

The Dimethylsulphoxonium Methylide Reaction.—*trans*-3-Benzylidenechroman-4-one (IIIa), like the other *trans*-3-benzylidenechroman-4-ones unsubstituted at the 2-

position (IIIb—d), reacted stereospecifically with dimethylsulphoxonium methylide and yielded the *trans*-cyclopropane [(VIa) (VIIa)]. The reaction with *cis*-3-benzylidenechroman-4-one (IVa) was stereoselective and also gave the *trans*-cyclopropane. The preferred conformation of the final transition state of the reaction, therefore, resembles (X) rather than (XI), so that an eclipsing effect between the carbonyl group and the phenyl ring is avoided during the cyclisation as expected. Zimmerman and his co-workers [13] have shown that the coplanarity of the carbonyl group with C-2 and C-β, required for electron delocalisation of the intermediate anion, greatly increases the non-bonded interaction between a carbonyl group and a cisoid β-phenyl ring.

mixture of all four possible cyclopropyl isomers, *trans,trans*- (VIg), *trans,cis*- (VIIg), *cis,trans*- (VIIIg), and *cis,cis*- (IXg), in the ratio 12 : 2 : 1 : 1. *cis*-6-Chloro-2-methyl-3-benzylidenechroman-4-one (IVg) reacted to give the four isomers in exactly the same ratio. *trans*-(IIIi) and *cis*-3-Benzylideneflavan-4-one (IVi) behaved similarly except that the ratio of isomers produced was 5 : 2 : 2 : 1.

So, as shown in the Scheme, the formation of the zwitterionic intermediates is reversible * and the zwitterions are sufficiently long-lived to allow extensive rotation about the exocyclic bond. The preponderance of *trans*-isomers is again attributable to the steric effectiveness of a ring carbonyl group having an adjacent



SCHEME

In addition to this orbital overlap control of the conformation of the ionic intermediate, the fact that the carbonyl group is part of a ring also tends to maintain the coplanarity of this group with C-2 and C-β. In fact, this is probably the major contributor to the steric effectiveness of the carbonyl group in the present system.

trans-6-Chloro-2-methyl-3-benzylidenechroman-4-one (IIIg) with dimethylsulphoxonium methylide afforded a carbanionic centre. This effect favours formation of products which have unhindered carbonyl groups. However its importance diminishes as the group at the α-position of the double bond is increased in size from CH_2 to $CH{\cdot}CH_3$ to CHAr, resulting in a more even distribution of *trans*- and *cis*-isomers. The smaller amounts of *trans,cis*- and *cis,cis*-isomers in the products may reflect a preference [14] by the large methylide

* An alternative explanation, that the initial formation of the zwitterions is irreversible but that the proportion of back- to front-side attack by the methylide on the *trans*-3-benzylidenechroman-4-ones is exactly reversed for *cis*-3-benzylidenechroman-4-ones, is unlikely.

[13] H. E. Zimmerman, L. Singer, and B. S. Thyagarajan, *J. Amer. Chem. Soc.*, 1959, **81**, 108.

[14] G. W. Krakower and H. A. Van Dine, *J. Org. Chem.*, 1966, **31**, 3467.

molecule for the less hindered side of the double bond, *i.e.* the side away from the 2-substituent.

EXPERIMENTAL

The n.m.r. spectra were measured at 60 MHz with a Varian HR60A spectrometer for solutions in deuteriochloroform with tetramethylsilane as internal reference. M.p.s were obtained with a Kofler hot-stage apparatus.

with hydrogen chloride and the precipitate was collected after 24 h. In Method B, the 3-(α-chlorobenzyl)chroman-4-one (0·004 mol) was dissolved in ethanol (100 ml) and sodium hydroxide (0·3 g) in water (15 ml) was added dropwise. The volume of solvent was reduced by evaporation until precipitation occurred. The physical properties of the products are given in Table 3.

The syntheses of *trans*-3-benzylidenechroman-4-one,[15]

TABLE 3

Condensation of chroman-4-ones with aromatic aldehydes

Substrate(s)	Method	Product(s)	M.p. (°C) (solvent) *	Yield (g)	Formula	Analysis (%) † C	H	Cl
6-Chlorochroman-4-one [a] + Benzaldehyde	A	trans-3-*Benzylidene*-6-*chlorochroman*-4-*one* (IIIc)	148—150 (B–P)	10·4	$C_{16}H_{11}ClO_2$	71·1 71·0	3·9 4·1	13·3 13·1
6-Chlorochroman-4-one + 4-Methoxybenzaldehyde	A	trans-6-*Chloro*-3-(4-*methoxybenzylidene*)*chroman*-4-*one* (IIId)	150—152 (B–P)	11·6	$C_{17}H_{13}ClO_3$	68·3 67·9	4·3 4·4	11·7 11·8
Chroman-4-one [b] + α-Deuteriobenzaldehyde [c]	A	3-(α-*Chloro*-α-*deuteriobenzyl*)*chroman*-4-*one* (V)	115—116 (P)	4·3	$C_{16}H_{12}ClDO_2$	69·7 70·2	4·9 5·2	12·9 13·0
		trans-3-(1-*Deuteriobenzylidene*)*chroman*-4-*one*	113—114‡ (P)	1·7				
3-(α-Chloro-α-deuteriobenzyl)chroman-4-one (V)	B	*trans*-3-(1-Deuteriobenzylidene)chroman-4-one	113—114‡ (P)	0·66				
2-Methylchroman-4-one [d] + Benzaldehyde	A	3-(α-*Chlorobenzyl*)-2-*methylchroman*-4-*one*	155—156 (MeOH)	1·6	$C_{17}H_{15}ClO_2$	71·3 71·2	5·5 5·3	12·8 12·4
		trans-3-*Benzylidene*-2-*methylchroman*-4-*one* (IIIe)	58—59 (P′)	4·2	$C_{17}H_{14}O_2$	81·2 81·6	5·9 5·6	
3-(α-Chlorobenzyl)-2-methylchroman-4-one	B	*trans*-3-Benzylidene-2-methylchroman-4-one (IIIe)	58—59	0·68				
2-Methylchroman-4-one + 4-Methoxybenzaldehyde	A	trans-3-(4-*Methoxybenzylidene*)-2-*methylchroman*-4-*one* (IIIf)	101—102 (P)	8·9	$C_{18}H_{16}O_2$	77·5 77·1	6·1 5·8	
6-Chloro-2-methylchroman-4-one [e] + Benzaldehyde	A	trans-3-*Benzylidene*-6-*chloro*-2-*methylchroman*-4-*one* (IIIg)	105—106 (EtOH)	9·8	$C_{17}H_{13}ClO_2$	72·2 71·7	4·6 4·6	12·5 12·5
6-Chloro-2-methylchroman-4-one + 4-Methoxybenzaldehyde	A	trans-6-*Chloro*-3-(4-*methoxybenzylidene*)-2-*methylchroman*-4-*one* (IIIh)	167—168 (Me_2CO)	10·2	$C_{18}H_{15}ClO_3$	68·7 68·7	4·8 4·8	

* B = Benzene, P = light petroleum (b.p. 80—100°), P′ = light petroleum (b.p. 40—60°). † Required values below found values. ‡ Lit., [15] 113° for non-deuteriated analogue.

[a] C. D. Hurd and S. Hayao, *J. Amer. Chem. Soc.*, 1954, **76**, 5065. [b] J. Colonge and A. Guyot, *Bull. Soc. chim. France*, 1958, 325. [c] A. Streitwieser and J. R. Wolfe, *J. Amer. Chem. Soc.*, 1957, **79**, 903. [d] G. W. K. Cavill, F. M. Dean, A. McGookin, B. M. Marshall, and A. Robertson, *J. Chem. Soc.*, 1954, 4573. [e] O. Dann, G. Volz, and O. Huber, *Annalen*, 1954, **587**, 16.

TABLE 4

Synthesis of cyclopropyl ketones

Substrate(s)	Product(s)	M.p. (°C) (solvent) *	Yield (g)	Formula	Analysis (%) † C	H	Cl
rans-3-Benzylidenechroman-4-one (IIIa)	trans-2′-*Phenylchroman*-3-*spirocyclopropan*-4-*one* (VIa)	61—62 (MeOH)	2·6	$C_{17}H_{14}O_2$	81·8	5·7	
Mixture (0·5 g) of *trans*- (IIIa) (20%) and *cis*- (IVa) (80%) 3-benzylidenechroman-4-one	*trans*-2′-Phenylchroman-3-spirocyclopropan-4-one (VIa)						
trans-3-(1-Deuteriobenzylidene)chroman-4-one	trans-2′-*Deuterio*-2′-*phenyl*-3-*spirocyclopropan*-4-*one*	61—62 (P)	1·5				
trans-3-(4-Methoxybenzylidene)chroman-4-one (IIIb)	trans-2′-(4-*Methoxyphenyl*)*chroman*-3-*spirocyclopropan*-4-*one* (VIb)	81—82 (P)	2·2	$C_{18}H_{16}O_3$	77·0 77·1	5·8 5·8	
trans-3-Benzylidene-6-chlorochroman-4-one (IIIc)	trans-6-*Chloro*-2′-*phenylchroman*-3-*spirocyclopropan*-4-*one* (VIc)	95—96 (MeOH)	1·9	$C_{17}H_{12}ClO_2$	71·9 72·0	4·6 4·6	
trans-6-Chloro-3-(4-methoxybenzylidene)chroman-4-one (IIId)	trans-6-*Chloro*-2′-(4-*methoxyphenyl*)*chroman*-3-*spirocyclopropan*-4-*one* (VId)	99—101 (MeOH)	2·7	$C_{18}H_{15}ClO_3$	68·8 68·7	4·6 4·8	11·3 11·3
trans-3-Benzylidene-6-chloro-2-methylchroman-4-one (IIIg) or a mixture of *trans*- (31%) and *cis*- (IVg) (60%) 3-benzylidene-6-chloro-2-methylchroman-4-one	trans,cis-6-*Chloro*-2-*methyl*-2′-*phenylchroman*-3-*spirocyclopropan*-4-*one* (VIg)	115 (MeOH)	2·4	$C_{18}H_{15}ClO_2$	72·1 72·4	5·0 5·1	11·6 11·9
	trans,cis-6-*Chloro*-2-*methyl*-2′-*phenylchroman*-3-*spirocyclopropan*-4-*one* (VIIg)	95 (MeOH)	0·4	$C_{18}H_{15}ClO_2$	72·5 72·4	5·0 5·1	
	cis,trans-6-*Chloro*-2-*methyl*-2′-*phenylchroman*-3-*spirocyclopropane*-4-*one* (VIIIg) and *cis,cis*-6-chloro-2-methyl-2′-phenylchroman-3-spirocyclopropan-4-one (IXg)	159 (MeOH)	0·2 *a*	$C_{18}H_{15}ClO_2$	72·1 72·4	5·1 5·1	11·6 11·9
trans-6-Chloro-3-(4-methoxybenzylidene)-2-methylchroman-4-one (IIIh)	trans,trans-6-*Chloro*-2-*methyl*-2′-(4-*methoxyphenyl*)*chroman*-3-*spirocyclopropan*-4-*one* (VIh) [b]	127—128 (MeOH)	0·4	$C_{19}H_{17}ClO_3$	69·5 69·4	5·2 5·2	
trans- (IIIi) or *cis*-(IVi) 3-Benzylideneflavan-4-one	trans,trans-2,2′-*Diphenylchroman*-3-*spirocyclopropan*-4-*one* (VIi),	141—142 (EtOH)	1·9	$C_{23}H_{18}O_2$	84·2 84·6	5·6 5·6	
	trans,cis-2,2′-*Diphenylchroman*-3-*spirocyclopropan*-4-*one* (VIIi),	161—162 (EtOH)	0·8	$C_{23}H_{18}O_2$	84·2 84·6	5·6 5·6	
	cis,trans-2,2′-*Diphenylchroman*-3-*spirocyclopropan*-4-*one* (VIIIi), and *cis,cis*-2,2′-diphenylchroman-3-spirocyclopropan-4-one (IXi)	156—157 (EtOH)	0·8 *c*	$C_{23}H_{18}O_2$	84·4 84·6	5·6 5·6	

* P = Light petroleum (b.p. 40—60°), P′ = light petroleum (b.p. 60—80°). † Required values below found values.

[a] Obtained as a mixture with the *cis,trans*-isomer and shown by n.m.r. spectroscopy to be equal in quantity with this isomer. [b] Purified by crystallisation alone. [c] Obtained as a mixture with the *cis,trans*-isomer and shown by n.m.r. spectroscopy to be one-third of the mixture.

trans-3-*Benzylidenechroman*-4-*ones*.—In Method A, a solution of the chromanone (0·043 mol) and the aromatic aldehyde (0·044 mol) in ethanol (*ca.* 50 ml) was saturated

trans-3-benzylideneflavan-4-one [16] and *trans*-3-(4-methoxybenzylidene)chroman-4-one [16] have been described.

cis-3-*Benzylidenechroman*-4-*ones*.—A solution of *trans*-3-

[15] P. Pfeiffer, K. Grimm, and H. Schmidt, *Annalen*, 1949, **564**, 208.

[16] P. Pfeiffer, E. Breith, and H. Hoyer, *J. prakt. Chem.*, 1931, **129**, 31.

benzylidenechroman-4-one (1·5 g) in benzene (200 ml) was irradiated with u.v. light (Phillips HPK 125 W medium-pressure mercury lamp) for 18·5 h. Removal of the benzene left a yellow oil which was chromatographed on a column of silica gel. cis-3-*Benzylidenechroman-4-one* crystallised from light petroleum (b.p. 40—60°) in yellow needles, m.p. 67—68° (Found: C, 81·2; H, 5·3. $C_{16}H_{12}O_2$ requires C, 81·3; H, 5·1%). Similar irradiation of *trans*-3-benzylidene-6-chloro-2-methylchroman-4-one (IIIg) (3·0 g) in benzene (150 ml) for 8 days gave an oil which reverted to the *trans*-isomer in all attempts to purify it; integration of its n.m.r. spectrum in the range τ 2·0—3·5 showed a *cis*- to *trans*-isomer ratio of 9 : 4. The preparation of *cis*-3-benzylideneflavan-4-one has been previously described.[7]

Cyclopropyl Ketones.—These were generally prepared (without the use of an inert atmosphere) by adding a solution of the 3-benzylidenechroman-4-one (0·014 mol) in dimethyl sulphoxide (50 ml) to a solution of dimethylsulphoxonium methylide [9] (0·015 mol) in dimethyl sulphoxide (20 ml). After 5 min the mixture was added to ice–water and the cyclopropyl ketone(s) extracted into ether. The oil remaining after the ether had been removed was fractionated by preparative layer chromatography (p.l.c.) on silica gel. The details for the individual cyclopropyl ketones are given in Table 4.

The various conditions and results of the reactions of *trans*- and *cis*-3-benzylidenechroman-4-ones with methylene di-iodide and zinc–copper couple have been described [11] elsewhere.

Zinc dust (3·5 g) was added to a hot solution of copper(II) acetate monohydrate (250 mg) in acetic acid (25 ml). The zinc–copper couple was then collected and washed with acetic acid (25 ml) and dry ether (3 × 50 ml). Methylene di-iodide (2 ml) and an ethereal iodine solution (1 mg ml^{-1}; 1 ml) were added to a stirred suspension of the zinc–copper couple in ether (40 ml) and the mixture was refluxed under nitrogen for 30 min. A solution of either *trans*- or *cis*-3-benzylideneflavan-4-one (1 g) in ether (50 ml) and methylene di-iodide (2 ml) was added slowly and refluxing was continued for 5·5 h. The mixture was then filtered. The filtrate was washed with saturated aqueous ammonium chloride solution and water and dried. Removal of the solvent left an oil which was shown by n.m.r. spectroscopy to be a 1 : 1 mixture of *trans,trans*- (VIi) and *trans,cis*- (VIIi) 2,2′-diphenylchroman-3-spirocyclopropan-4-one. The oil crystallised from ethanol to give the former isomer, m.p. 141—142° (10 mg), and the latter, m.p. 161—162° (8 mg).

A solution of *trans*-2′-phenylchroman-3-spirocyclopropan-4-one (VIa) (2·0 g) in benzene (300 ml) was irradiated with a Phillips HPK 125 W medium-pressure lamp for 2 h. Removal of the solvent left a brown oil which was fractionated by p.l.c. on silica gel to give the starting *trans*-isomer (1·35 g) and cis-2′-*phenylchroman*-3-*spirocyclopropan*-4-*one* (VIIIa) as needles (0·35 g) from light petroleum (b.p. 40—60°), m.p. 81—82° (Found: C, 81·7; H, 5·6. $C_{17}H_{14}O_2$ requires C, 81·6; H, 5·6%). Similarly, irradiation of *trans,trans*-2,2′-diphenylchroman-3-spirocyclopropan-4-one (VIi) (2·0 g) gave cis,cis-2,2′-*diphenylchroman*-3-*spirocyclopropan*-4-*one* (IXi) as needles (160 mg) from ethanol, m.p. 148—149° (Found: C, 84·2; H, 5·6. $C_{23}H_{18}O_2$ requires C, 84·6; H, 5·6%), its *trans,trans*-isomer (VIIi) (0·4 g), m.p. 161—162°, and the starting *trans,trans*-isomer (VIi) (0·4 g), m.p. 141—142°. The n.m.r. spectrum of the crude reaction mixture showed that the *cis,trans*-isomer (VIIIi) was also present (*ca.* 3%). U.v. irradiation, as before, of *trans,trans*-6-chloro-2-methyl-2′-phenylchroman-3-spirocyclopropan-4-one (VIg) (2·0 g) gave the starting *trans,trans*-isomer (1·3 g), m.p. 115°, its *trans,cis*-isomer (VIIg) (0·26 g), m.p. 95°, and its *cis,trans*-isomer (VIIIg) (0·11 g), m.p. 159°.

trans-2′-Phenylchroman-3-spirocyclopropan-4-one (VIa) (1·0 g) was heated at 305—310° for 6 min under reduced pressure (14 mmHg). Separation by p.l.c. on silica gel gave the *cis*-isomer (VIIIa) (80 mg), m.p. 81—82°, and the starting *trans*-isomer (460 mg), m.p. 60—61°.

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