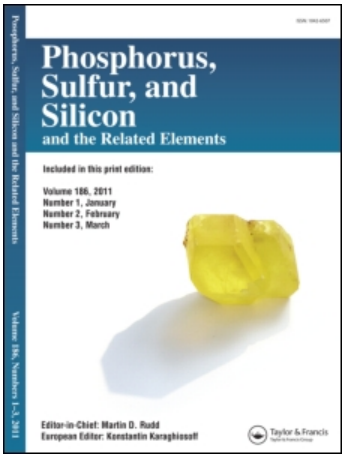

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CHLOROSULFONATION OF 3-(ARYLIDENE) D-CAMPHORS

Richard J. Cremlyn[a]; Helio T. Prates[a]
[a] Division of Chemical Sciences, The University of Hertfordshire, Hatfield, Herts, England

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CHLOROSULFONATION OF 3-(ARYLIDENE) D-CAMPHORS

RICHARD J. CREMLYN and HELIO T. PRATES
Division of Chemical Sciences, The University of Hertfordshire, Hatfield, Herts AL10 9AB, England

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The preparation of 3-(arylidene) camphors (3–8) from benzaldehyde, *o*-, *m*- and *p*-anisaldehyde, *p*-nitrobenzaldehyde and thiophen-2-carboxaldehyde is discussed. The arylidenes (3–6, 8) reacted with chlorosulfonic acid-thionyl chloride to give the sulfonyl chlorides (9, 27, 32, 42).

In contrast, the *m*-methoxybenzylidene derivative (5) on similar treatment with chlorosulfonic acid afforded the 4′, 6′-disulfonyl chloride (37). The sulfonyl chlorides were converted into 29 sulfonamides, 2 hydrazides (23, 47) and 4 hydrazones (24–26, 48) for biological screening as candidate pesticides and pharmaceutical agents.

The spectral data of the compounds are briefly discussed and the configuration of the benzylidene derivatives have been assigned.

Key words: 3-Arylidenecamphors; chlorosulfonation; sulfonamides; pesticides.

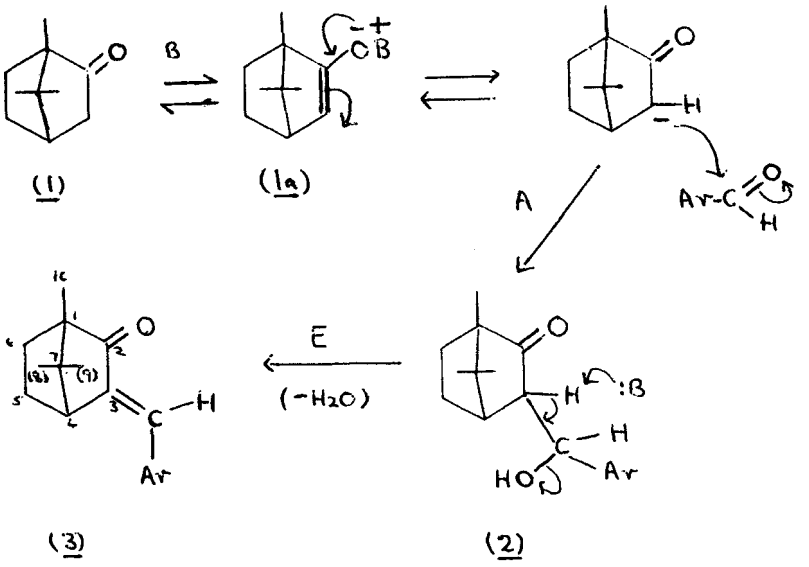
INTRODUCTION

The work described in this paper represents an extension of our previous studies into the chlorosulfonation of various types of benzylidene derivatives, e.g., chalcones[1,2]; cinnamide[3]; mono- and di-benzylideneacetone[4,5]; benzylidenepinacolone[6]; 5-benzylidene-hydantoins[7] and barbiturates.[8]

In these compounds, it was found that the benzylidene moiety provides a reactive site for sulfonation as a result of electron-release from the Π-electrons of the alkylidene double bond. The chlorosulfonation of 3-benzylidenecamphor has not been reported and would be expected to occur readily and preferentially in the *para*-position with respect to the alkylidene double bond.

Benzylidene derivatives of simple alicyclic ketones such as cyclohexanone are generally readily obtained at room temperature or by warming the appropriate ketone with an ethanolic solution of benzaldehyde in the presence of aqueous sodium hydroxide.[9–11] However, this procedure completely failed with camphor. 3-Benzyldene d-camphor (3) was first prepared by Haller[12] by refluxing d-camphor (1) with sodium (18 hours), followed by treatment with redistilled benzaldehyde at 60°C (4 hours). An essentially similar procedure was later reported by Richer and Rossi.[13] In this work, the intermediate keto-alcohol (2) was not isolated and 3-benzylidene d-camphor (3) crystallised out from a complex mixture of products after evaporation and addition of absolute ethanol. The corresponding derivative of dl-camphor was an oil and therefore could not be isolated in a pure form by this procedure.

The mechanism for the formation of the 3-arylidenecamphors (Scheme I) occurs *via* the intermediate enolate anion (1a), which subsequently undergoes an addition-



(B = base used)

SCHEME I

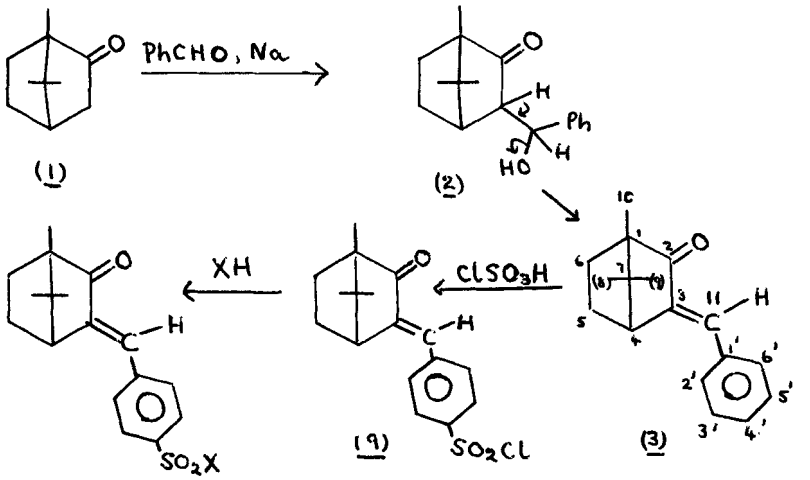
elimination (A–E) reaction with the arylaldehyde to yield the arylidene derivative (3).

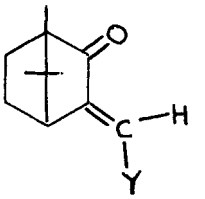
The rigidity of the structure of the camphor molecule imposed by the geminal dimethyl bridge bond probably causes resistance to the formation of the enolate anion and may account for the fact that benzylidene formation is so much more difficult than with simple, more flexible, alicyclic ketones like cyclohexanone.[10]

Condensation of benzaldehyde with the lithium enolate of d-camphor is reported[14] to give the keto-alcohol (2) derived from the benzaldehyde bonding to the *exo* face of the camphor molecule. The stereochemical configuration of arylidenecamphors has been determined by NMR spectroscopy and UV studies[15] to be as shown in 3 (Chart 1) in which steric interaction between the 4 and 2′ hydrogens causes the phenyl ring to be pushed slightly out of coplanarity with the alkylidene double bond. In the present work, this stereochemistry was confirmed by NOE NMR spectroscopy.

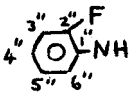
RESULTS AND DISCUSSION

We repeated the literature synthesis of benzylidene-d-camphor (3).[12,13] In our hands, the maximum yield of isolated product was 37%, the reported yields of 50–70% could not be realised. The use of toluene (18 hours), xylene (1 hour) or ether (4 hours) afforded lower yields of (3) (29, 11 and 22%, respectively). When all the reagents were heated together in benzene, none of the pure derivative (3) was obtained.





X

(10) NH_2
(11) NHEt
(12) NMe_2
(13) NEt_2
(14) pyrrolidino
(15) piperidino
(16) 2,6-dimethylmorpholino
(17) $PhCH_2NH$
(18) PhNH
(19) 
(20) p-F C_6H_4
(21) 2,6-F_2 C_6H_3 NH
(22) p-MeO C_6H_4NH
(23) NH NH_2
(24) NH N=C Me_2
(25) NH N= 
(26) NHN=CH C_6H_4F-p

Y

(4) o-MeO C_6H_4
(5) m-MeO C_6H_4
(6) p-MeO C_6H_4
(7) p-NO_2 C_6H_4
(8) 2-thienyl

CHART 1 3-Aryldenecamphors and the sulfonyl derivatives of 3-benzylidenecamphor.

It was therefore decided to examine the use of the other bases in the reaction of camphor with benzaldehyde to see if the yield of benzylidene camphor (3) could be improved.

The results (Table I) show that the best yields of solid benzylidene camphor (3) were obtained using sodium amide or potassium tert-butoxide in boiling benzene (Experiments 1 and 7, respectively). In the former case, when all the reagents were heated together from the beginning of the experiment, the yield of 3 was reduced to 26%. In Experiments 4 and 8, no pure 3 was isolated, only a complex mixture of products (an oil).

The synthesis of other 3-arylidenecamphors was also investigated using the standard procedure in which camphor was refluxed with sodium in benzene (18 hours) followed by stirring with the appropriate arylaldehyde at 60°C for 4 hours. By this method, *o*-, *m*- and *p*-methoxybenzylidenecamphors (4–6, Chart 1 and Table I) were obtained in yields of 35, 39 and 40%, respectively; *p*-nitrobenzaldehyde and thiophen-2-carboxaldehyde similarly afforded the derivatives (7) and (8) in yields of 45 and 42%.

The results indicated that the reactivity of carbonyl group was not the dominant factor in the formation of the arylidene derivatives otherwise the more reactive *p*-

TABLE I

Influence of different bases on the formation of benzylidene camphor

Expt no.	Base (mol equivs)	Solvent	Period of reflux (hours)	Isolated yield of 3 (%)
1	Sodium amide (1)	Benzene	18	37
2	Sodium amide (1)	Ether	6	32 (26)[a]
3	Sodium methoxide (1)	Benzene	6	23
4	Piperidine (2)	Benzene	32	—
5	Potassium hydroxide (1.5)	Benzyl alcohol	18	13
6	Sodium hydride (1)	Benzene	18	18
7	Potassium tert-butoxide (1)	Benzene	18	37
8	Sodium hydroxide (1.5)	Aqueous ethanol	24	—

[a]When all the reagents were heated together.

TABLE II

Physical data for the 3-arylidene camphors

Comp. No.	Yield (%)	m.p. (°C)	Molecular formula	Microanalysis found (Calc.) % C	H	N	MS (M^+)
3	37	95–97 (lit[13], 97)	$C_{17}H_{20}O$	84.6 (85.0)	8.7 (8.3)	— —	240
4	35	95–97	$C_{18}H_{22}O$	80.2 (80.0)	8.3 (8.1)	— —	270
5	39	oil (bp, 190/2 mm)	$C_{18}H_{22}O$	79.4 (80.0)	8.1 (8.1)	— —	270
6	40	126–127 (lit[13], 124–126)	$C_{18}H_{22}O$	80.3 (80.0)	8.3 (8.1)	— —	270
7	45	288–290	$C_{17}H_{19}NO_3$	70.8 (71.3)	6.9 (6.7)	5.2 (4.9)	285
8	42	50–52	$C_{15}H_{18}OS$	73.5 (73.1)	7.7 (7.4)	— —	246

nitrobenzaldehyde should have given a significantly higher yield of product as compared with the less reactive *p*-methoxybenzaldehyde. In these reactions, the relative stability of the keto-alcohol intermediate, e.g. 2 appears more critical and preliminary studies[16] using computer graphics indicated that there was little difference in potential energy between 2 and 3. This result is probably a reflection of the incomplete coplanarity of the Π-electrons of aryl ring and those of the alkylidene double bond which reduces the resonance stabilisation of 3 as compared with 2.

The chlorosulfonation of 3-benzylidenecamphor (3) was examined; by analogy with previous work on other benzylidene derivatives,[4,5] the reaction was expected to occur under relatively mild conditions leading to *para*-sulfonation.

Initially several experiments were carried out using chlorosulfonic acid (6–10 molar equivalents) at room temperature (1 week), addition to ice afforded low yields (20–30%) of the hydrated sulfonyl chloride. The product appears to be deliquescent and could not be obtained in a pure dry form, the yields were therefore estimated by rapid conversion of the crude sulfonyl chloride into the stable dimethylsulfonamide derivative. It was discovered that the optimum conditions for chlorosulfonation involved treatment with chlorosulfonic acid (6 molar equivalents, 1 week) at room temperature, followed by reaction with excess thionyl chloride (1 day). Addition to ice and neutralisation (aqueous sodium hydrogen carbonate) afforded an estimated 65% yield of the sulfonyl chloride (9).

The chloride (9) was characterised as the sulfonamides (10–22) (Chart 1 and Table III). Treatment of 9 with hydrazine hydrate afforded the sulfonohydrazide (23), which was converted into the hydrazones (24–26). Chlorosulfonation of the methoxybenzylidenecamphors (4–6) and the thienylidenecamphor (8) was successfully carried out using the same procedure as that optimised for the chlorosulfonation of benzylidenecamphor (3).

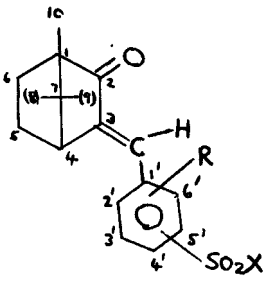
With the *o*- and *p*-methoxy derivatives (4 and 6) it is concluded that sulfonation occurs in the 5′- and 3′-positions, respectively; the orientation is in agreement with previous results[17] obtained for the chlorosulfonation of *o*- and *p*-methoxychalcones. The orientation is controlled by the powerful electron-releasing properties of the methoxy group; this effect is also clearly demonstrated in the *m*-methoxy derivative (5) in which disulfonation occurs in 4′- and 6′-positions which are respectively *ortho* and *para* to the methoxy group. The disulfonation was clearly indicated by the mass spectrum of the dimethylsulfonamide (38) which showed the molecular ion (M^+, 484) for the bis-sulfonamide derivative and the ^1H NMR spectrum showed resonances δ 2, 90, 2.74, 12H) corresponding to the methyl protons of the *two* *N,N*-dimethylsulfamoyl groups. The disulfonation was in agreement with previous studies[17] on the chlorosulfonation of *m*-methoxychalcone as this substrate also afforded the 4,6-disulfonyl chloride.

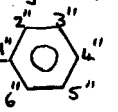
The sulfonyl chlorides (27, 32, 37, 42) were converted into a range of sulfonamides (28–31, 33–36, 38–41, 43–46) (Chart 2 and Table IV). Reaction with hydrazine afforded the hydrazide (47), characterised as the acetone hydrazone (48). The sulfonyl derivatives were required for biological screening as potential pest control and pharmaceutical products. Preliminary results to date against a range of fungi, insect and weed species however did not indicate any compound showing significant pesticidal activity.

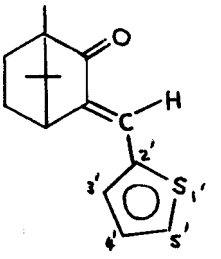
TABLE III

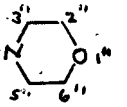
Physical data for the compounds 9-26

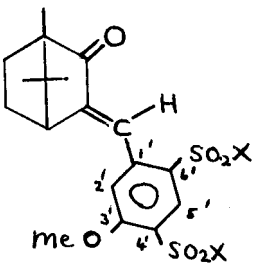
Comp. No.	Yield (%)	m.p. (°C)	Molecular formula	Microanalysis found (Calc.) %			MS (M^+)
				C	H	N	
9	65	121-123	$C_{17}H_{19}ClO_3S$				340,338
10	56	205-207	$C_{17}H_{21}NO_3S$	63.4 (63.9)	6.8 (6.6)	4.2 (4.4)	320
11	60	216-218	$C_{19}H_{25}NO_3S$	65.1 (65.7)	7.2 (7.2)	3.6 (4.0)	347
12	72	144-145	$C_{19}H_{25}NO_3S$	65.7 (65.7)	7.3 (7.2)	4.0 (4.0)	347
13	70	148-150	$C_{21}H_{29}NO_3S$	67.0 (67.2)	7.9 (7.7)	3.9 (3.7)	375
14	82	118-120	$C_{21}H_{27}NO_3S$	67.3 (67.7)	7.2 (7.3)	3.7 (3.8)	374
15	80	123-125	$C_{22}H_{29}NO_3S$	68.6 (68.4)	7.6 (7.5)	3.6 (3.6)	387
16	85	142-143	$C_{23}H_{31}NO_4S$	65.8 (66.2)	7.3 (7.4)	3.3 (3.4)	417
17	69	169-170	$C_{24}H_{27}NO_3S$	70.2 (70.4)	6.7 (6.6)	3.4 (3.4)	410
18	52	204-206	$C_{23}H_{25}NO_3S$	69.5 (69.9)	6.2 (6.3)	3.4 (3.5)	395
19	38	158-160	$C_{23}H_{24}FNO_3S$	66.6 (66.8)	6.0 (5.8)	3.6 (3.4)	413
20	48	182-183	$C_{23}H_{24}F_2NO_3S$	66.3 (66.8)	5.9 (5.8)	3.5 (3.4)	413
21	25	200	$C_{23}H_{23}F_2NO_3S$	63.6 (64.0)	5.3 (5.4)	3.3 (3.2)	431
22	55	104-105	$C_{24}H_{27}NO_4S$	67.3 (67.7)	6.6 (6.4)	3.0 (3.3)	425
23	64	83-85	$C_{17}H_{22}N_2O_3S$	60.6 (61.1)	6.6 (6.6)	8.5 (8.4)	334
24	76	150-152	$C_{20}H_{26}N_2O_3S$	64.5 (64.2)	7.0 (6.9)	7.4 (7.5)	375
25	62	163-164	$C_{22}H_{28}N_2O_3S$	65.5 (66.0)	7.0 (7.0)	6.9 (7.0)	400
26	48	202-204	$C_{24}H_{25}FN_2O_3S$	65.1 (65.4)	5.7 (5.7)	6.3 (6.4)	440



	R	X
(27)	2-OMe	Cl
(28)	"	NMe_2
(29)	"	NEt_2
(30)	"	2,6-dimethylmorpholino
(31)	"	$NHCH_2$ 
(32)	4-OMe	Cl
(33)	"	NH_2
(34)	"	NHEt
(35)	"	$NHCH_2Ph$
(36)	"	NHPh
(47)	"	$NHNH_2$
(48)	"	$NHN{=}CMe_2$



	X
(42)	Cl
(43)	NMe_2
(44)	NEt_2
(45)	
(46)	NHPh



	X
(37)	Cl
(38)	NMe_2
(39)	2,6-dimethylmorpholino
(40)	$NHCH_2Ph$
(41)	o-FC_6H_4NH

CHART 2 Sulfonyl derivatives of 3-arylidenecamphors.

The IR spectra of the arylidenecamphors showed the characteristic absorption bands at approximately 1720, 1640 and 1600–1490 cm^{-1} associated with the C=O, alkyl C=C and aromatic C=C moieties; the sulfonyl derivatives exhibited two additional bands at approximately 1360 and 1180 cm^{-1}.[18]

In the EI mass spectra, the majority of the compounds showed the molecular ions (M^+) including the sulfonyl hydrazides and hydrazones (23–26) (Table III)

TABLE IV

Physical data for the 3-(sulfamoylarylidene) camphors

Comp. No.	Yield (%)	m.p. (°C)	Molecular formula	Microanalysis found (Calc.) % C	H	N	MS (M^+)
27	65	120-122	$C_{18}H_{21}ClO_4S$	55.9 (58.6)	6.0 (5.7)	-	370, 368
28	76	109-110	$C_{20}H_{27}NO_4S$	63.5 (63.7)	7.5 (7.2)	3.5 (3.7)	377
29	78	120-122	$C_{22}H_{31}NO_4S$	65.4 (65.2)	7.8 (7.6)	3.4 (3.5)	405
30	80	179-180	$C_{24}H_{33}NO_5S$	64.2 (64.4)	7.4 (7.4)	3.1 (3.1)	447
31	75	148-150	$C_{25}H_{29}NO_4S$	68.0 (68.3)	6.8 (6.6)	3.1 (3.2)	439
32	50	62-64	$C_{18}H_{21}ClO_4S$	58.1 (58.6)	5.6 (5.7)	- -	370, 368
33	45	112-114	$C_{18}H_{23}NO_4S$	61.5 (61.9)	6.4 (6.7)	3.7 (4.0)	349
34	51	217-218	$C_{20}H_{27}NO_4S$	63.4 (63.6)	7.3 (7.2)	3.6 (3.7)	377
35	62	127-129	$C_{25}H_{29}NO_4S$	68.0 (68.3)	6.6 (6.6)	3.4 (3.2)	439
36	55	170-171	$C_{24}H_{27}NO_4S$	67.4 (67.8)	6.3 (6.3)	3.3 (3.3)	425
37	50	126-130	$C_{18}H_{20}Cl_2O_6S_2$	44.4 (46.2)	4.5 (4.3)		369, 367 [a]
38	62	135-137	$C_{22}H_{32}N_2O_6S_2$	54.0 (54.4)	6.6 (6.6)	5.5 (5.8)	484
39	66	138-140	$C_{30}H_{44}N_2O_8S_2$	57.3 (57.7)	6.7 (7.0)	4.4 (4.5)	510 [b]
40	53	123-125	$C_{32}H_{36}N_2O_6S_2$	62.7 (63.1)	5.7 (5.9)	4.8 (4.6)	438 [c]
41	28	133-135	$C_{30}H_{29}F_2N_2O_6S_2$	57.9 (58.4)	4.5 (4.9)	4.5 (4.5)	506 [b]

TABLE IV (*Continued*)

Comp No.	Yield (%)	m.p. (°C)	Molecular formula	Microanalysis found (Calc.) % C	H	N	MS (M^+)
42	56	110-112	$C_{15}H_{17}ClO_3S_2$	49.5 (52.5)	5.2 (4.9)	-	346, 344
43	73	138-140	$C_{17}H_{23}NO_3S_2$	57.3 (57.8)	6.8 (6.6)	4.0 (4.0)	353
44	80	94-95	$C_{19}H_{27}NO_3S_2$	59.7 (59.8)	7.2 (7.1)	3.5 (3.7)	381
45	77	84-86	$C_{21}H_{29}NO_4S_2$	59.2 (59.6)	6.8 (6.9)	3.2 (3.3)	423
46	46	132-134	$C_{21}H_{23}NO_3S_2$	62.4 (62.8)	5.5 (5.7)	3.7 (3.5)	401
47	50	98-100	$C_{18}H_{24}N_2O_4S$	58.9 (59.3)	6.8 (6.6)	7.2 7.7	364
48	75	173-174	$C_{21}H_{28}N_2O_4S$	62.0 (62.3)	7.0 (7.0)	6.8 16.9)	404

a Highest fragment mass ion observed corresponding to $M^+ - SO_2Cl$
b Highest fragment mass ion observed corresponding to M^+ - amine
c Highest fragment mass ion observed corresponding to $M^+ - SO_2NHCH_2Ph$

and (47–48) (Table IV); this was surprising since the majority of these compounds generally fragment in the mass spectrometer so that the molecular ions were not observed.[19] The UV spectra of the arylidenecamphors in methanol showed a long wavelength absorption band (λ_{max} 294–317 nm, ε_{max} = 11000–22000) associated with the —C(=O)—CH=CH—Ar moiety which was not substantially altered by sulfonation.

The ^1H NMR spectra showed that the 9- and 10-methyl protons generally resonated as two singlets (δ1.00, 1.03 approximately) at a slightly lower field as compared with the 8-methyl proton resonance which appeared at 0.80. The difference is probably due to the closer proximity of 9- and 10-methyl protons to the deshielding influence of the carbonyl group.

In ^{13}C NMR spectra, the 9- and 10-carbon resonances appeared at δ18 and 20, respectively and the 8-carbon resonance at approximately δ9. The chemical shifts are in good agreement with our previous observations.[20–22]

The stereochemistry of the benzylidenecamphors was determined by a combination of ^{13}C and ^{1}H NMR spectroscopy, the attached proton test, two dimensional (2D) correlations and nuclear overhauser effect (NOE) measurements. In particular, the configurations of the benzylidene—(3) and 2-methoxybenzylidene (4) camphors were confirmed by NOE difference spectroscopy from the 4-H to the 6^1-H proton. In the 2-thienylidenecamphor (8), the structure was confirmed by comparison of the alkylidene carbon resonances with those observed for the *o*-methoxybenzylidene derivative (4).

Camphor is known to undergo sulfonation by treatment with acetic anhydride-sulfuric acid to give the 10-sulfonic acid[23]; while reaction with chlorosulfonic acid (2 molar equivalents) in boiling chloroform afforded the 8-sulfonic acid.[24]

In the present work, it was therefore rather surprising that chlorosulfonation of 3-benzylidene camphor (3) by excess of chlorosulfonic acid occurred entirely in the phenyl ring with no apparent attack on the camphor moiety.

EXPERIMENTAL

Melting points were determined using a Gallenkamp electric apparatus and are uncorrected. IR spectra were recorded as K Br discs with a Unicam SP 100 spectrophotometer. NMR spectra were recorded with Bruker AC 250 spectrometer using tetramethylsilane as internal standard and deuteriochloroform as solvent; resonances indicated by an asterisk were reduced by D_2O treatment. UV spectra were determined with a Perkin Elmer 555 spectrophotometer in methanol solution. Mass spectra were measured with a VG micromass V 15 spectrometer operating at 70 eV. TLC was carried out using Camlab silica gel plates sensitized to UV 256 nm and cyclohexane:ethyl acetate 3:1 as eluant.

3-Benzylidene d-camphor (3) *Method 1*

Small lumps of sodium (5 g, 0.22 mole) were added to a solution of camphor (1) (30 g, 0.20 mole) in anhydrous benzene (300 ml). The mixture was refluxed for 18 hours, cooled to approximately 60°C and transferred to another flask removing any unreacted sodium. Freshly redistilled benzaldehyde (30 ml, 0.28 mole) was added to the solution which was stirred for 4 hours and poured onto water (500 ml). The benzene layer was washed with water (2 × 100 ml); the lower aqueous layer was reextracted with benzene (2 × 100 ml) and the combined benzene layers dried over $MgSO_4$. The desiccant was filtered off and benzene removed under vacuum. The residual oil was triturated with ethanol (a few drops) and left in the freezer (−10°C) overnight to give 3 as colourless crystals (17.5 g, 37%) TLC showed one spot, R_F 0.66.

Method 2

A similar procedure, except that sodium amide was used instead of sodium, afforded the same yield of 3 IR: ν_{max} 1725 (C═O), 1645 (Alk C═C), 1490 (Ar C═C), 700 (ArCH). cm^{-1}. UV: λ_{max} 294 mm (20,090). MS: 240 (M^+), 225,212 (M^+-CO), 197, 169, 158, 149, 141 (M^+-PhCH), 134, 129, 120, 105, 91, 77 (C_6H_5), 69, 55, 41. ^1H NMR (400 MHz): δ7.60-7.4 1 (m, 5H, Ar H), 7.30 (s, 1H, alkenic CH), 3.24 (d, 1H, 4-H; $J_{4,5}$ *exo* 4.0 Hz), 2.38–2.25 (m, 1H, 6-H *exo*), 1.96–1.84 (m, 1H, 5-H *exo*), 1.77–1.57 (m, 2H, 5-H 6-H *endo*), 1.16 (s, 3H, 10-Me), 1.12 (s, 3H, 9-Me), 0.91 (s, 3H, 8-Me). ^{13}C NMR: δ208 (C-2) 142.1 (C-3), 135.6 (C-1^1), 129.7 (C-3^1, 5^1), 128.6 (C-4^1), 128.6 (C2^1, 6^1), 127.45 (C-11), 57.0 (C-1), 49.2 (C-4), 46.6 (C-7), 30.7 (C-6), 26.0 (C-5), 20.5 (C-10), 18.3 (C-9) 9.3 (C-8).

3-(o-Methoxybenzylidene) d-camphor (4) *(Procedure 1)*

TLC showed one spot, R_F 0.75. IR: ν_{max} 1730 (C═O), 1640 (Alk C═C), 1480 (Ar C═C), 1125 (C—O—C), 770 (Ar CH). UV: λ_{max} 290 mm (14, 130). ^1H NMR: δ7.57 (s, 1H, alkenic H), 7.45–6.80 (m, 4H, ArH), 3.85 (s, 3H, OMe) 3.02 (d, 1H, 4-H), 2.23–1.46 (m, 4H, cyclohexyl H), 1.03 (s, 3H, 10-Me), 0.99 (s, 3H, 9-Me), 0.81 (s, 3H, 8-Me).

^{13}C NMR: δ208.1 (C-2), 158.5 (C-2^1), 141.8 (C-3), 130.0 (C-4^1), 129.5 (C-6^1), 124.7 (C-1^1), 122.7 (C-11), 120.2 (C-5^1), 110.8 (C-3^1), 57.2 (C-1), 55.4 (0 $\underline{C}H_3$), 49.1 (C-4), 46.4 (C-7), 30.7 (C-6), 26.0 (C-5) 20.5 (C-10), 18.3 (C-9), 9.3 (C-8).

MS: 270 (M^+), 255, 239 (M^+-OMe), 227, 187, 171, 149, 131, 121, 108 (C_6H_4OMe), 91, 77 (Ph), 55, 41.

3-(m-Methoxybenzylidene)-d-camphor (5) *(Procedure 1)*
TLC showed one spot, R_F 0.76 n_D^{20} 1.4072. IR: ν_{max} 1720 (C=O), 1640 (Alk C=O), 1450 (Ar C=C), 1040 (C—O—C), 780, 690 (ArCH) cm^{-1}. UV: λ_{max} 290 nm (11,000). ^1H NMR: δ7.31–6.89 (m, 4H, ArH), 7.20 (s, 1H, alkenic H), 3.82 (s, 3H, OMe), 3.11 (d, 1H, 4H; $J_{4,5}$ *exo* 4.2 Hz), 2.26–1.50 (m, 4H, cyclohexyl H), 1.03 (s, 3H, 10-Me), 0.99 (s, 3H, 9-Me), 0.80 (s, 3H, 8-Me). ^{13}C NMR: δ208.2 (C-2), 159.7 (C-3^1), 142.4 (C-3), 137.1 (C-1^1), 129.6 (C-5^1), 127.4 (C-11), 122.3 (C-6^1), 115.3 (C-4^1), 114.1 (C-2^1), 57.1 (C-1), 55.2 (O $\underline{C}H_3$), 49.3 (C-4), 46.7 (C-7), 30.7 (C-6), 29.9 (C-5), 20.6, (C-10), 18.3 (C-9), 9.3 (C-8).

MS: 270 (M^+), 255, 242, 227, 187, 171, 159, 135, 109 (C_6H_4OMe), 95, 77 (Ph), 69, 55, 41.

3-(p-methoxybenzylidene) d-camphor (6) *(Procedure 1)*
IR: TLC showed one spot, R_F 0.73 ν_{max} 1720 (C=O), 1640 (alk C=C), 1500 (ArC=C), 1060 (C—O—C), 820 (ArCH) cm^{-1}. UV: λ_{max} 317 nm (22, 910).

^1H NMR: δ7.44–6.92 (m, 4H, ArH), 7.19 (s, 1H, alkenic H), 3.83 (s, 3H, OMe), 3.10 (d, 1H, 4-H; $J_{4,5}$ *exo* 4.2 Hz), 2.21–1.45 (m, 4H, cyclohexyl H), 1.02 (s, 3H, 10-Me), 0.99, (s, 3H, 9Me), 0.80 (s, 3H, 8-Me).

MS: 270 (M^+), 241 (M^+-CO), 227, 186, 158, 144, 135, 121, 108, (M^+-C_6H_4OMe), 95, 55, 41.

3-(p-Nitrobenzylidene) d-camphor (7)
TLC showed one spot, R_F 0.73. IR: ν_{max} 1720 (C=O), 1640 (Alk C=C), 1600, (Ar C=C), 1520 (NO_2), 850 (ArCH) cm^{-1}. ^1H NMR: δ8.24–7.60 (m, 4H, ArH), 7.30 (s, 1H, alkenic H), 3.10 (d, 1H, 4-H), 2.29–1.50 (m, 4H, cyclohexyl H), 1.06 (s, 3H, 10-Me), 1.03 (s, 3H, 9-Me), 0.81 (s, 3H, 8-Me).

MS: 285 (M^+), 270, 242, 203, 150, 136, 121 (M^+-$C_6H_4NO_2$), 109, 95, 83, 77 (C_6H_5), 69, 55, 43, 41.

3-(2'-Thienylidene) d-camphor (8) *(Method 2)*
TLC showed one spot, R_F 0.78. IR: ν_{max} 1720 (C=O), 1630 (C=C), 710 (thiophen CH) cm^{-1}. ^1H NMR: δ7.42–7.08 (m, 3H, thiophen H), 7.38 (s, 1H, alkenic H), 3.18 (d, 1H, 4-H; $J_{4,5}$ *exo* 4.2 Hz), 2.20–1.41 (m, 4H, cyclohexyl H), 1.02 (s, 6H, 9,10-Me), 0.80 (s, 3H, 8-Me). ^{13}C NMR: δ207.9 (C-2), 139.7 (C-3), 139.4 (C-2^1), 131.9 (C-5^1), 128.4 (C-3^1), 127.7 (C-4^1), 120.4 (C-11), 57.4 (C-1), 49.7 (C-4), 48.6 (C-7), 31.0 (C-6), 25.7 (C-5), 20.6, (C-10), 18.4 (C-9), 9.3 (C-8).

MS: 246 (M^+), 231, 218 (M^+-CO), 203, 175, 163 (M^+-C_4H_3S) 147, 135, 95, 91, 55, 41.

Chlorosulfonation of 3-benzylidenecamphor (3)
3-Benzylidene d-camphor (3) (5.0 g, 0.02 mole) was added to chlorosulfonic acid (8.3 ml, 0.12 mole) at 0°C. The solution was left at room temperature (1 week), then thionyl chloride (3.0 ml, 0.04 mole) and DMF (2 drops) was added to the mixture which was left a further 24 hours. The solution was added to crushed ice, the precipitate was allowed to settle and the liquid decanted off, ice-water (100 ml) was added and the decantation repeated, the solid was neutralised with ice-cold 10% sodium hydrogen carbonate solution, the solid was filtered off, washed with ice-water (100 ml) and air-dried to give hydrated (9). (65% yield, based on conversion to the dimethylamide derivative (12). TLC showed one spot, R_F 0.60; the product appeared to decompose on standing in a vacuum desiccator.

IR: ν_{max} 1735 (C=O), 1650, (alk C=C), 1590 (Ar C=C), 1385, 1175 (SO_2), 680, 660 (ArCH)cm^{-1}.

MS: 340, 338 (M^+), 325, 323, 295, 256, 239 (M^+-SO_2Cl), 211, 155, 149, 128, 106, 83, 55, 41, 36.

Chlorosulfonation of the 3-arylidenecamphors (4–8)
The sulfonyl chlorides (27, 32, 37, 42) were obtained by a similar procedure, except it was not necessary to neutralize the products with sodium hydrogen carbonate. The sulfonyl chlorides could be partially dried in a vacuum desiccator, but appeared to remain as reasonably stable hydrates.

3-(2^1-Methoxybenzylidene) camphor 5^1-sulfonyl chloride (27)
TLC showed one spot, R_F 0.43. IR ν_{max}: 1720 (C=O), 1645 (Alk C=C), 1590 (Ar C=C), 1370, 1170 (SO_2), 1130 (C—O—C), 870, 815 (ArCH) cm^{-1}.

MS: 370, 368 (M^+), 353, 335 (M^+-Cl), 325, 286, 269 (M^+-SO_2Cl), 218, 158, 149, 106, 95, 83, 77, 55, 41, 39.

3-(4^1-Methoxybenzylidene) camphor 3^1-sulfonyl chloride (32)
TLC showed one spot, R_F 0.54. IR: ν_{max} 1725 (C=O), 1640 (Alk C=C), 1600, 1500 (Ar C=C), 1370, 1180, 1060 (C—O—C), 550 (ArCH).

MS: 370, 368 (M^+), 355, 340, 325, 286, 270 (M^+-SO_2Cl), 257, 227, 219, 186, 149, 121, 95, 64, 55, 41, 32.

3-(2¹-Thienylidene) camphor 5¹-sulfonyl chloride (42)
TLC showed one spot, R_F, 0.71. IR: ν_{max} 1735 (C=O), 1640, (Alk C=C), 1500 (Ar C=C), 1380, 1180 (SO_2) 1070 (C—O—C), 800 (ArCH) cm^{-1}.

MS: 346, 344, (M^+), 331, 329, 301, 261, 246 (M^+-SO_2Cl), 203, 175, 163, 149, 134, 121, 106, 95, 83 (C_4H_3S), 77, 64, 55, 41, 36, 32.

Preparation of the sulfonamides (10–22, 28–31, 33–36, 38–41, 42–46)
The appropriate sufonyl chloride (0.005 mole) was treated with a solution of the aliphatic amine (0.015 mole) in ethanol (20 ml) at 0°C. The mixture was left at room temperature for 12 hours and the suspension was poured onto ice-water (100 ml) and acidified (PH 6) with 5M hydrochloric acid. The analogous reactions with aromatic amines were carried out using acetonitrile as solvent. The precipitated sulfonamides were filtered off, washed with water and purified by recrystallisation from ethanol.

Compound 12
IR: ν_{max} 1730 (C=O), 1650 (Alk C=C), 1340, 1160 (SO_2), 730, 710, 700 (ArCH) cm^{-1}.

UV: λ_{max} 292 nm (20, 100).

MS: 347 (M^+), 332 (M^+-Me), 319, 304 (M^+-NMe_2), 278, 239 (M^+-SO_2NME_2), 238, 211, 169, 156, 149, 128, 108, 95, 83, 77, 68, 55, 42.

^{1}H NMR: δ7.80–7.61(m, 4H, ArH, AA¹BB¹ pattern), 7.20 (s, 1H, alkenic H), 3.10 (d, 1H, 4-H *exo*; *J* 4.3 Hz), 2.75 (s, 6H, NMe_2), 2.31–2.17 (m, 1H, 6-H, *exo*), 1.94–1.78 (m, 1H, 5-H *exo*), 1.65–1.47 (m, 2H, 5-H, 6H *endo*), 1.05 (s, 3H, 10-Me) 1.03 (s, 3H, 9-Me), 0.82 (s, 3H, 8-Me).

^{13}C NMR: δ207.6 (C-2), 144.9 (C-4¹), 140.1 (C-3), 135.4 (C-1¹), 130.0 (C-2¹, C-6¹), 128.0, (C-3¹, C-5¹), 125.3 (C-11), 57.2 (C-1), 49.3, (C-4), 46.7 (C-7), 37.9 (N-($\underline{C}H_3)_2$), 30.5 (C-6), 26.0 (C-5), 20.7 (C-10), 18.2, (C-9), 9.2 (C-8).

Compound 19
IR: ν_{max}: 1730 (C=O), 1650, (Alk C=O), 1600, 1500 (Ar C=C), 1340, 1165, (SO_2), 800, 760, 685, 600 (ArCH) cm^{-1}.

MS: 413 (M^+), 398, 384, 357, 303 (M^+-$SO_2NHC_6H_4F$), 239, 149, 128, 110 (NH C_6H_4F), 95, 83, 77, 55, 41.

^{1}H NMR: δ7.82–7.48 (m, 4H, Ar-2¹, 3¹, 5¹, 6¹H, AA¹ BB¹ pattern), 7.20–6.95 (m, 6H, NH alkenic H, fluorobenzene H), 3.02 (d, 1H, 4-H; $J_{4,5}$ *exo* 4.0 Hz), 2.30–1.29 (m, 4H, cyclohexyl H), 1.03 (s, 3H, 10-Me), 1.0 (s, 3H, 9-Me), 0.79, (s, 3H, 8-Me).

^{13}C NMR: δ207.4 (C-2), 160.8, 149.0 (C-2¹¹, $J_{C\text{-}2}$, F 243.2 Hz), 145.5, (C-4¹), 140.7 (C-3), 138.7 (C-1¹), 134.8 (C-1¹¹), 129.9 (C-2¹, C-6¹), 127.5 (C-3¹, C-5¹), 126.6, 126.2, 125.2, 124.9, 123.7 (C-3¹¹, 4¹¹, 5¹¹, 6¹¹ C-11) 115 and 116.0 (C-3¹¹; $J_{C\text{-}3}$, F 19.5 Hz), 57.2 (C-1), 49.3, (C-4), 46.6 (C-7), 30.5 (C-6), 25.9 (C-5), 20.6 (C-10), 18.2 (C-9), 9.2 (C-8).

Compound 28
IR: ν_{max} 1730 (C=O), 1650 (Alk C=C), 1590, 1490 (Ar C=C), 1335, 1165 (SO_2), 1070 (C—O—C), 720 (Ar CH) cm^{-1}.

MS: 377 (M^+), 362 (M^+-Me), 346 (M^+-2 × Me), 334 (M^+- 3 × Me), 294, 270 (M^+-Me, -SO_2Me_2), 239, 185, 158, 149, 120, 95, 83, 77, 55, 44.

^{1}H NMR: δ7.78–7.01 (m, 3H, Ar H), 7.49 (s, 1H, alkenic H), 3.93 (s, 3H, OMe), 2.97 (d, 1H, 4-H), 2.72 (s, 6H, SO_2NMe_2), 2.29–1.47 (m, 4H, cyclohexyl H), 1.03 (s, 3H, 10-Me), 1.0 (s, 3H, 9-Me), 0.83 (s, 3H, 8-Me).

Compound 31
IR: ν_{max} 1715 (C=O), 1640 (Alk C=C), 1590, 1490 (Ar C=C), 1335, 1160 (SO_2), 1060 (C—O—C), 880, 820, 750, 700 (Ar CH) cm^{-1}.

^{1}HNMR: δ7.65–7.21 (m, 8H, ArH), 7.45 (s, 1H, alkenic H), 5.25* (s, 1H, NH), 4.15 (d, 2H, Ph$\underline{CH_2}$), 2.96 (d, 1H, 4-H; $J_{4,5}$ *exo* 4.0 Hz), 2.18–1.45 (m, 4H, cyclohexyl H) 1.01 (s, 3H, 10-Me), 0.99 (s, 3H, 9-Me), 0.79 (s, 3H, 8-Me).

^{13}C NMR: δ207.6 (C-2), 161.3 (C-2¹), 143.0 (C-5¹), 136.4 (C-1¹¹), 131.6, 129.7, 128.6 (C-4¹, 6¹, -2¹¹, -3¹¹, -4¹¹, -5¹¹, -6¹¹), 127.6 (C-3), 125.6 (C-1¹), 120.9 (C-11), 110.0 (C-3¹), 57.3 (C-1), 56.0 (O $\underline{CH_3}$), 49.2 (C-4), 46.6 (C-7), 30.6 (C-6), 26.0 (C-5), 20.6 (C-10), 18.2 (C-9), 9.2 (C-8).

Compound 33
IR: ν_{max} 1710 (C=O), 1645 (Alk C=C), 1600 (Ar C=C), 1340, 1160 (SO_2), 1070 (C—O—C), 930 (ArCH) cm^{-1}.

MS: 349 (M^+), 334, (M^+-NH), 321, 269 (M^+-SO_2NH_2), 238, 200, 149, 108, 95, 83, 55, 43, 41. ^1H NMR: δ8.0–7.0 (m, 4H, ArH and alkenic H), 5.45* (s, 2H, NH_2), 4.04 (s, 3H, OMe), 3.04 (d, 1H, 4-H; $J_{4,5}$ *exo* 4.0 Hz), 2.15–1.26 (m, 4H, cyclohexyl H), 1.0 (s, 6H, 9-Me, 10-Me), 0.76 (s, 3H, 8-Me).

Compound 36
IR: ν_{max} 1725 (C=O), 1640 (Alk C=C), 1600, 1500 (Ar C=C), 1350, 1160 (SO_2), 1065 (C—O—C), 765, 700 (Ar CH) cm^{-1}.

MS: 425 (M^+), 410, 397, 342, 267, 239, 149, 128, 95, 77 (C_6H_5), 65, 55, 43, 41.

^1H NMR: δ8.00–7.00 (m, 9H, ArH and NH) (resonances at δ7.74* reduced by D_2O), 2.96 (d, 1H, 4-H; $J_{4,5}$ *exo* 4.3 Hz), 2.26–1.44 (m, 4H, cyclohexyl H), 1.05 (s, 3H, 10-Me), 1.03 (s, 3H, 9-Me), 0.77 (s, 3H, 8-Me).

^{13}C NMR: δ207.8 (C-2), 156.3 (C-4^1), 142.1 (C-3), 136.8 (C-1^{11}), 136.2 (C-6^1), 131.8 (C-3^1), 129.2 (C-3^{11}, C-5^{11}), 128.3 (C-2^1), 126.5 (C-1^1), 125.3 (C-4^{11}), 125.0 (C-11), 120.8 (C-2^{11}, C-6^{11}), 112.4 (C-5^1), 57.0 (C-1), 56.5 ($O\underline{C}H_3$), 49.0 (C-4), 46.7 (C-7), 30.7 (C-6), 25.7, (C-5), 20.5, (C-10), 18.3 (C-9), 9.2 (C-8).

Compound 38
IR: ν_{max} 1725 (C=O), 1640 (Alk C=C), 1590, 1545 (Ar C=C), 1380, 1160 (SO_2), 1050 (C—O—C), 740, 710 (ArCH) cm^{-1}.

MS: 484 (M^+), 456, 440, (M^+-NMe_2), 405 (M^+-SO_2NMe_2), 376, 294, 269, 83, 55, 44, 41.

^1H NMR: δ8.48 (s, 1H, 5^1-H), 7.78 (s, 1H, 2^1-H), 7.00 (s, 1H, alkenic H), 4.0 (s, 3H, OMe), 2.90 (s, 6H, NMe_2), 2.85 (m, 1H, 4-H), 2.74 (s, 6H, NMe_2), 2.85–1.53 (m, 4H, cyclohexyl H), 1.05 (s, 3H, 10-Me), 1.01 (s, 3H, 9-Me), 0.81 (s, 3H, 8-Me).

^{13}C NMR: δ206.2 (C-2), 159.0 (C-3^1), 146.1 (C-3), 142.5 (C-11), 134.1 (C-6^1), 129.5 (C-4^1), 126.5 (C-5^1), 123.8 (C-11), 114.4 (C-2^1), 57.7, (C-1), 56.4 ($O\underline{C}H_3$), 49.3 (C-4), 46.7 (C-7), 37.6, 37.0 (2 × $N(\underline{C}H_3)_2$), 30.3 (C-6), 27.3 (C-5), 20.7 (C-10), 18.2 (C-9), 9.2 (C-8).

Compound 40
IR: ν_{max} 1725 (C=O), 1640 (Alk C=C), 1590, 1550 (Ar C=C), 1380, 1160 (SO_2), 1080, (C—O—C), 750, 700 (ArCH) cm^{-1}.

MS: 438 (M^+-SO_2NHCH_2Ph), 269, (M^+-2 × SO_2NHCH_2Ph), 106, 91 ($PhCH_2$).

^1H NMR: δ8.46 (s, 1H, 5^1-H), 7.75 (s, 1H, 2^1-H), 7.35–6.90 (m, 10H, Ph), 6.75 (s, 1H, alkenic H), 5.50* (s, 2H, N$\underline{H}$), 4.10 (d, 4H, Ph$\underline{C}H_2$), 3.88 (s, 3H, OMe), 2.74 (d, 1H, 4-H; $J_{4,5}$ *exo* 4.2 Hz), 2.23–1.49 (m, 4H, cyclohexyl H), 1.03 (s, 3H, 10-Me), 1.01 (s, 3H, 9-Me), 0.80 (s, 3H, 8-Me).

^{13}C NMR: δ206.9 (C-2), 158.1 (C-3^1), 146.5 (C-3), 136.3, 131.9, 128.6, 128.0 (Ph), 127 (C-5^1), 123.4 (C-11), 113.9 (C-2^1), 57.8 (C-1), 56.6 (OMe), 49.2 (C-4), 47.7 (NH $\underline{C}H_2$ Ph), 46.7 (C-7), 30.4 (C-6), 26.3 (C-5), 20.9 (C-10), 18.2 (C-9), 9.2 (C-8).

Compound 43
IR: ν_{max} 1725 (C=O), 1640 (Alk C=C), 1450 (Ar C=C), 1340, 1160 (SO_2), 720 (ArCH) cm^{-1}.

MS: 353 (M^+), 338 (M^+-Me), 325, 310 (M^+-NMe_2), 270, 245 (M^+-SO_2NMe_2), 217, 149, 134, 108 (SO_2NMe_2), 95, 83, 77, 55, 41.

^1H NMR: δ7.50 (d, 1H, 3^1-H; $J_{31,41}$ 3.9 Hz), 7.30 (s, 1H, alkenic H), 7.25 (d, 1H, 4^1-H); $J_{41,31}$ 3.9 Hz), 3.17 (d, 1H, 4-H); $J_{4,5}$ *exo* 4.2 Hz), 2.80 (s, 6H, SO_2NHe_2), 2.28–1.42 (m, 4H, cyclohexyl H), 1.04 (s, 6H, 9-Me, 10-Me), 0.84 (s, 3H, 8-Me).

^{13}C NMR: δ207.2 (C-2), 145.6 (C-5^1), 143.2 (C-3), 137.6 (C-2^1), 132.3 (C-4^1), 131.3 (C-3^1), 118.8 (C-11), 57.5 (C-1), 50.0 (C-4), 46.8 (C-7), 38.1 (N ($\underline{C}H_3$)$_2$), 30.8 (C-6), 25.7 (C-5), 20.7 (C-10), 18.3 (C-9), 9.3 (C-8).

Compound 45
IR: ν_{max} 1730 (C=O), 1640 (Alk C=C), 1455 (Ar C=C), 1355, 1170 (SO_2), 800, 650 (ArCH) cm^{-1}.

MS: 423 (M^+), 340, 245 (M^+-$SO_2C_6H_{12}NO$), 217, 114 ($C_6H_{12}NO$), 95, 83, 70, 55, 41.

^1H NMR: δ7.50 (d, 1H, 3^1-H; $J_{3,4}$ 3.9 Hz), 7.30 (s, 1H, alkenic H), 7.26 (d, 1H, 4^1-H; J_{413} 3.9 Hz), 3.82–1.43 (m, 10H, cyclohexyl and morpholino H), 3.17 (d, 1H, 4-H; $J_{4,5}$ *exo* 4.3 Hz) 1.23, 1.17 (dd, 6H, morpholino Me), 1.06 (s, 6H, 9-Me, 10-Me), 0.87 (s, 3H, 8-Me).

^{13}C NMR: δ207.1 (C-2), 146.0 (C-5^{1}), 143.4 (C-3), 137.0 (C-2^{1}), 132.6 (C-4^{1}), 131.3 (C-3^{1}), 118.6 (C-11), 71.3, 65.7 (C-2^{11}, -6^{11}), 57.5 (C-1), 50.7, 50.4 (C-3^{11}, 5^{11}), 50.0 (C-4), 46.8 (C-7), 30.8 (C-6), 25.6 (C-5), 20.7 (C-10), 18.7 ($\underline{C}H_3O$), 18.2 (C-9), 17.5 ($\underline{C}H_3$-N), 9.2 (C-8).

Preparation of sulfonohydrazines (23, 47)
The sulfonyl chloride (0.01 mole) was gradually added to ice-cold methanol (30 ml) containing hydrazine hydrate (0.03 mole); the mixture was kept at 0°C during the addition and was then allowed to stand at room temperature (3 hours). The solution was added to ice-water (100 ml); the precipitate was filtered off, washed with ice-cold water and dried in a vacuum desiccator over P_2O_5 to give the hydrazide.

3-(Benzylidene) d-camphor-p-sulfonohydrazide (23)
IR: ν_{max} 3400, 3350 (NH), 1720 (C=O), 1640 (Alk C=C), 1335, 1160 (SO_2), 680, 660 (ArCH) cm^{-1}.

MS: 334 (M^+), 304 (M^+-$NHNH_2$), 289, 272, 240 (M^+-SO_2NHNH_2), 211, 197, 157, 149, 128, 115, 95 ($SO_2N_2H_3$), 83, 55, 43, 41.

^{1}H NMR: δ8.00–7.61 (m, 4H, ArH; AA^{1}BB^1 pattern), 7.23 (s, 1H, alkenic H), 3.60* (br s, 3H, NH, NH_2), 3.10 (s, 1H, 4-H), 2.23–1.30 (m, 4H, cyclohexyl H), 1.04 (s, 6H, 9-Me, 10-Me), 0.87 (s, 3H, 8-Me).

3-(p-Methoxybenzylidene-d-camphor-3^1-sulfonohydrazide (47)
IR: ν_{max} 3300 (NH), 1720 (C=O), 1640 (Alk C=C), 1600, 1500 (Ar C=C), 1330, 1160 (SO_2), 1065 (C—O—C), 840, 720, 700 (ArCH) cm^{-1}.

^{1}H NMR: 8.11–7.50 (m, 2-H, 5-H, 6-H, alkenic H), 4.03 (s, 3H, OMe), 3.10 (d, 1H, 4-H), 2.30–1.27 (m, 4H, cyclohexyl H), 1.03 (s, 6H, 9-Me, 10-Me), 0.90 (s, 3H, 8-Me).

MS: 364 (M^+), 349 (M^+-NH), 334 (M^+-$NHNH_2$), 270 (M^+-SO_2NHNH_2), 227, 186, 121, 64, 41.

Preparation of the sulphonohydrazones (24–26, 48)
The sulfonohydrazide (0.005 mole) was reacted with the appropriate aldehyde or ketone (0.005 mole) in methanol (15 ml) at room temperature (1 hour). In the case of the acetone derivatives (24, 48), the sulfonohydrazide was dissolved in acetone as solvent (half hour). Careful addition of ice-water caused the hydrazones to crystallize out from solution.

Acetone 3-(benzylidene) d-camphor-p-sulfonohydrazone (24)
IR: ν_{max} 3440, 1640 (Alk C=C), 1390, 1165 (SO_2), 1060 (C—O—C), 680, 660, 600 (ArCH) cm^{-1}.

MS (CI): 375 (M^+ + 1), 347, 310 (M^+-SO_2), 273, 256, 241, 210.

^{1}H NMR: δ8.05* (s, 1H, NH), 8.00–7.76 (m, 4H, ArH; AA^{1}BB^1 pattern), 7.18 (s, 1H, alkenic H), 3.08 (d, 1H, 4-H), 2.28–1.40 (m, 4H, cyclohexyl H), 1.92, 1.85 (2 × s, 6H, N=CMe_2), 1.02 (s, 6H, 9-Me, 10-Me), 0.80 (s, 3H, 8-Me).

Cyclopentanone 3-(benzylidene) d-camphor-p-sulfonohydrazone (25)
IR: ν_{max} 3200 (NH), 1730 (C=O), 1650 (Alk C=C), 1350, 1170 (SO_2), 680, 670 (ArCH) cm^{-1}.

MS: 400 (M^+), 336 (M^+-SO_2), 240, 157, 97, 67, 55, 41.

^{1}H NMR: δ8.00–7.60 (m, 4H, ArH: AA^{1}BB^1 pattern), 7.22 (s, 1H, alkenic H), 3.10 (d, 1H, 4H), 2.35–1.50 (m, 12H, alicyclic H), 1.03 (s, 6H, 9-Me, 10-Me), 0.81 (s, 3H, 8-Me).

^{13}C NMR: δ207.6 (C-2), 168.8 (C-1^{11}), 144.1 (C-4^{1}), 140.5 (C-3), 130.4 (C-1^{1}), 129.9 (C-2^{1}, 6^{1}), 128.4 (C-3^{1}, 5^{1}), 125.5 (C-11), 57.2 (C-1), 49.4 (C-4), 46.6 (C-7), 33.5 (C-2^{11}), 30.6 (C-6), 28.2 (C-5^{11}), 26.0 (C-5), 24.8 (C-3^{11}), 20.6 (C-10), 18.2 (C-9), 9.23 (C-8).

4-Fluorobenzaldehyde 3-(benzylidene)-d-camphor-p-sulfonohydrazone (26)
IR: ν_{max} 3150 (NH), 1710 (C=O), 1645 (Alk C=C), 1600, 1570 (Ar C=C), 1370, 1170 (SO_2), 780, 720, 670 (ArCH) cm^{-1}.

MS: 440 (M^+), 287, 239 (M^+-$SO_2NHN{=}CHC_6H_4F$), 197, 157, 137 ($C_7H_6FN_2$), 128, 108, 95, 83, 75, 64, 48, 41.

^{1}H NMR: δ11.70* (s, 1H, NH), 8.12–7.20 (m, 8H, ArH), 3.14 (d, 1H, 4-H), 2.70–1.40 (m, 4H, cyclohexyl H), 1.00 (s, 6H, 9-Me, 10-Me), 0.75 (s, 3H, 8-Me).

Acetone 3-(p-methoxybenzylidene) d-camphor-3^1-sulfonohydrazone (48)
IR: ν_{max} 3200 (NH), 1730 (C=O), 1640 (Alk C=C), 1600, 1500 (Ar C=C), 1340, 1170 (SO_2), 1070 (C—O—C), 720 (ArCH) cm^{-1}.

MS: 404 (M^+), 340 (M^+-SO_2), 317, 270, 241, 186, 121 ($SO_2NHN{=}CMe_2$), 95, 71, 64, 55, 41:

^1H NMR: δ8.15–7.04 (m, 3H, ArH), 7.70* (s, 1H, NH), 7.20 (s, 1H, alkenic H), 4.00 (s, 3H, OMe), 3.12 (d, 1H, 4-H), 2.26–1.49 (m, 4H, cyclohexyl H), 1.03 (s, 3H, 10-Me), 1.01 (s, 3H, 9-Me), 0.80 (s, 3H, 8-Me).

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REFERENCES

1. R. J. Cremlyn, F. J. Swinbourne and O. Shode, *J. Chinese Chem. Soc.*, **31,** 383 (1984).
2. R. J. Cremlyn, F. J. Swinbourne and E. Mookerjee, *Indian J. Chem.*, **25B**, 562 (1986).
3. R. J. Cremlyn, O. Obiorah and G. Singh, *Indian J. Chem.*, **25B**, 559 (1986).
4. R. J. Cremlyn, F. J. Swinbourne, P. Fitzgerald, P. Hodges, J. Lapthorne and C. Mizon, *Indian J. Chem.*, **23B**, 1962 (1984).
5. R. J. Cremlyn, F. J. Swinbourne and L. Goodman, *Phosphorus and Sulfur*, **28,** 395 (1986).
6. R. J. Cremlyn, R. J. Swinbourne, P. A. Carter and L. Ellis, *Phosphorus, Sulfur, and Silicon*, **47,** 267 (1990).
7. R. J. Cremlyn, S. Jethwa, G. Joiner and D. White, *Phosphorus and Sulfur*, **36,** 99 (1988).
8. R. J. Cremlyn, J. P. Bassin, F. Ahmad, M. Hastings, I. Hunt and T. Mattu, *Phosphorus, Sulfur and Silicon*, 1992 (in press).
9. R. P. Linstead and B. C. L. Weedon '*A Guide to Qualitative Organic Analysis*' (Butterworths, London 1956), p. 28.
10. Vogel's '*Textbook of Practical Organic Chemistry*,' 5th edn. Longman, Harlow, (1989), p. 1260.
11. W. J. Criddle and G. P. Ellis, '*Spectral and Chemical Characterization of Organic Compounds*'. (Wiley, London 1976), p. 39.
12. A. Haller, *C. R. Acad. Sci. Paris*, **113,** 22 (1891).
13. J. C. Richer and A. Rossi, *Canad. J. Chem.*, **50**, 1376 (1972).
14. R. L. Harlow and S. H. Simonsen, *Cryst. Struct. Comm.*, **5,** 471 (1976).
15. M. M. N. El-Batouti and J. Sotiropoulos, *C. R. Acad. Sci. Paris Ser. C*, **278**, 1109 (1974).
16. R. McGuire, Rhone-Poulenc Ltd, personal communication, 1991.
17. R. J. Cremlyn, F. J. Swinbourne, P. Bassin, D. Dane, K. Higgins, and P. Mitchell, *Phosphorus, Sulfur and Silicon*, **63,** 385 (1991).
18. L. J. Bellamy, '*The Infra-red Spectra of Complex Molecules*' 2nd edn. (Methuen, London, 1958).
19. R. J. Cremlyn, F. J. Swinbourne and O. Shode, *J. Heterocyclic Chem.*, **22,** 1211 (1985).
20. P. D. Stanley, R. J. Cremlyn, J. Nangle and F. J. Swinbourne, *Magn. Reson. in Chem.*, **26,** 14 (1988).
21. R. J. Cremlyn and L. Wu, *Phosphorus and Sulfur*, **39,** 165 (1988).
22. R. J. Cremlyn, M. Bartlett and J. Lloyd, *Phosphorus and Sulfur*, **40,** 91 (1988).
23. P. D. Bartlett and L. H. Knox, *Org. Synthesis*, Coll. Vol. (V), (Wiley, London and New York, 1973), p. 194.
24. R. J. Cremlyn, M. Bartlett and L. Wu, *Phosphorus and Sulfur*, **39,** 173 (1988).