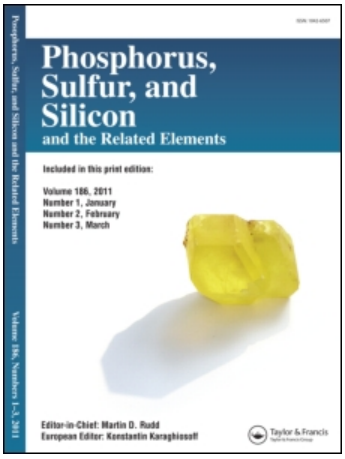

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CHLOROSULFONATION OF 3-(BENZYLIDENE) D-CAMPHOR AND 3-(BENZYLIDENE) ISOPINOCAMPHORONE

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

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CHLOROSULFONATION OF 3-(BENZYLIDENE) D-CAMPHOR AND 3-(BENZYLIDENE) ISOPINOCAMPHORONE

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

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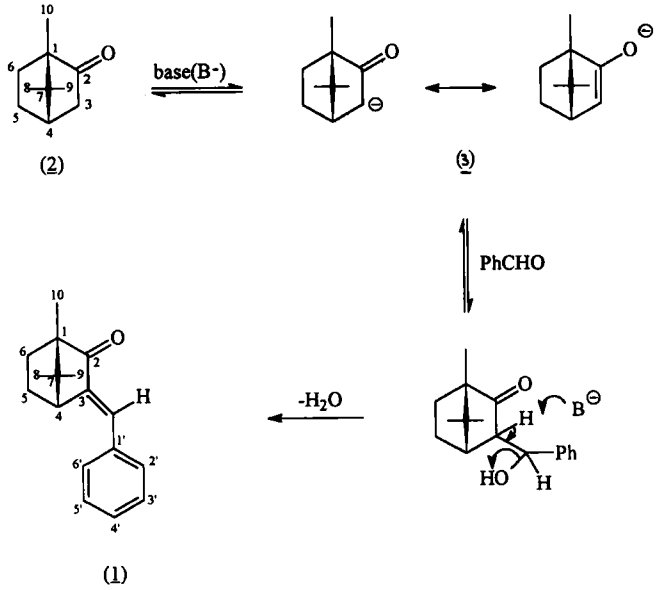
A new improved synthesis of 3-benzylidenecamphor (1) is described; the procedure has also been applied to the conversion of isopinocamphorone (4) into 4-benzylidenepinocamphorone (6a). In the latter reaction, ^{1}H NMR spectral data and X-ray crystallography proved that inversion of the C-2 methyl group had occurred. A mechanism for the base-catalysed interconversion of isopinocamphorone (4) and pinocamphorone (10) is presented. 4-Benzylidene-pinocamphorone (6a) reacted with excess chlorosulfonic acid to yield the *p*-sulfonyl chloride (11) which was characterized by the formation of 6 sulfonamide derivatives. The ^{1}H NMR spectra confirmed that sulfonation occurred in *p*-position of the phenyl ring; the various compounds were required for screening as potential pesticides and pharmaceutical agents.

Key words: 3-Benzylidenecamphor, 4-benzylidenepinocamphorone, X-ray analysis, chlorosulfonation, sulfonamides.

INTRODUCTION

The work described in this paper represents an extension of previous research into the chlorosulfonation of various types of compounds containing the benzylidene group, e.g. chalcones[1]; cinnamide,[2] mono- and di-benzylidene-acetone[3,4]; benzylidene pinacolone[5]; benzylidene-hydantoins[6] and barbiturates[7]; and $\alpha\beta$-unsaturated arylidene ketones.[8] In particular, the work expands that previously reported[9] on the chlorosulfonation of 3-(arylidene) camphors; in the later paper, the preparation of 3-(arylidene) D camphors was extensively studied under a wide range of experimental conditions with only limited success. The optimum yield of 3-benzylidene camphor (1) was comparatively low (37%) and was obtained by refluxing camphor (2) with metallic sodium in benzene for 18 hours before addition of benzaldehyde, as previously described by Richer and Rossi.[10] Our studies[9] suggested that the comparatively low yield of 3-(benzylidene) camphor (1) may be due to the characteristic rigidity of the camphor molecule imposed by the 1,4-*gem*-dimethyl bridge bond so that the formation of the enol intermediate (3) may be thermodynamically unfavourable. Computer graphic studies[9] also indicated little difference in potential energy between the enol (3) and the final benzylidene derivative (1) (Scheme I).

The argument that the low yield of benzylidenecamphor (1) arises from the rigidity of the camphor ring is supported by the fact that the benzylidene derivatives of simple alicyclic ketones, such as cyclohexanone are formed in high yields (≈80%) under mild conditions, by warming the appropriate ketone with an ethanolic solution of benzaldehyde in the presence of aqueous sodium hydroxide.[11] However,

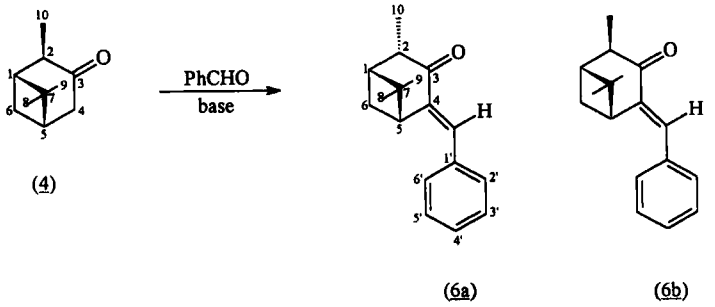


(2) (3) (1)

SCHEME I The mechanism for formation of 3-benzylidenecamphor (1).

this procedure completely failed with camphor; although with isopinocamphorone (4) the benzylidine derivative (6a) was prepared (65%) by refluxing (4) with benzaldehyde in aqueous ethanolic sodium hydroxide for 24 hours.[12] The more facile formation of this derivative is explained by the 1,5-position of the *gem*-dimethyl bridge bond, allowing a greater degree of flexibility around the carbonyl group (Scheme II).

Isopinocamphorone (4) was prepared from α-pinene (5) by treatment with diborane and oxidation as described by Brown and Zweifel[13] to give isopinocamphorol (7). The latter was oxidized to (4) by reaction with chromium trioxide following the procedure of Brown *et al.*[14]



(4) (6a) (6b)

SCHEME II Formation of 4-benzylidenepinocamphorone.

RESULTS AND DISCUSSION

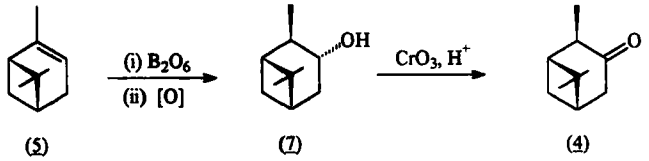
Dryanska and Ivanov[15] claimed the relatively unreactive 2-methylbenzothiazole (8) condensed with benzaldehyde in boiling DMF containing sodium amide (1 hour) to give a high yield (94%) of the benzylidene derivative, namely 2-styryl-benzothiazole (9) (Scheme III).

The condensation afforded only very poor yields using sodium hydroxide in aqueous ethanol. We have successfully repeated the preparation of (9)[16] (91%); it therefore appeared of interest to see if these conditions could be successfully extended to the synthesis of 3-(benzylidene) D-camphor (1). Previous work[9] examined the preparation of (1) using sodium amide in boiling ethanol and ether but afforded low yields (26–37%) of the product. However the use of the polar aprotic solvent DMF may well enhance yields by shifting the equilibrium in favour of the enol and facilitating the final dehydration step (Scheme I).

The experiment proved to be very successful; heating an equimolar mixture of D-camphor (2), benzaldehyde and sodium amide in DMF (50°C, 3 hours) afforded 3-(benzylidenecamphor) (1) (63% yield), as a crystalline solid. The procedure substantially improved the yield with reduced reaction time and removed the need for the tedious purification of the crude oil which was an unsatisfactory feature of the previous synthetic methods.

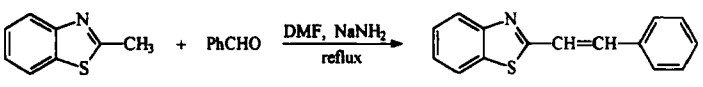
The improved method (sodium amide in DMF 50°C, 3 hours) was also applied to condensation of isopinocamphorone (4) with benzaldehyde to try and enhance the previous 65% yield of the benzylidene derivative (6a) (Scheme II), but there was no improvement in yield although it was obtained with a much shorter reaction time and an easier product isolation. It therefore appeared that the stronger base did not enhance the yield when the substrate permitted comparatively easy enol formation.

Brown *et al.*[13] observed that inversion of the C-2 methyl group of isopinocamphorone (4) occurred when the compound was treated with sodium methoxide. Prates[17] argued that a similar inversion takes place on formation of the benzylidene derivative, so that it is the derivative (6a) of pinocamphorone that is actually isolated not that of isopinocamphorone (6b) (Scheme II). In support of this argument it was observed that the ^{1}H NMR spectrum of the benzylidene derivative



(5) (7) (4)

SCHEME III Synthesis of isopinocamphorone (4).



(8) (9)

SCHEME IV Formation of 2-styrylbenzothiazole (9).

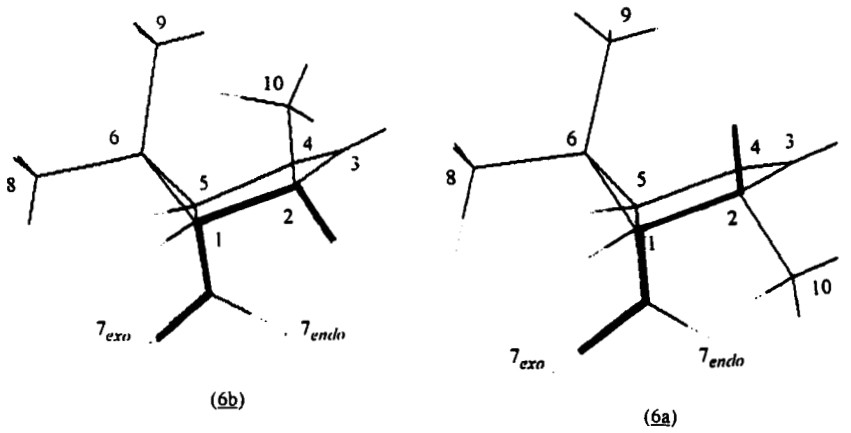


FIGURE 1 Conformations of isopinocamphorone (6b) and pinocamphoronebenzylidene (6a) derivatives.

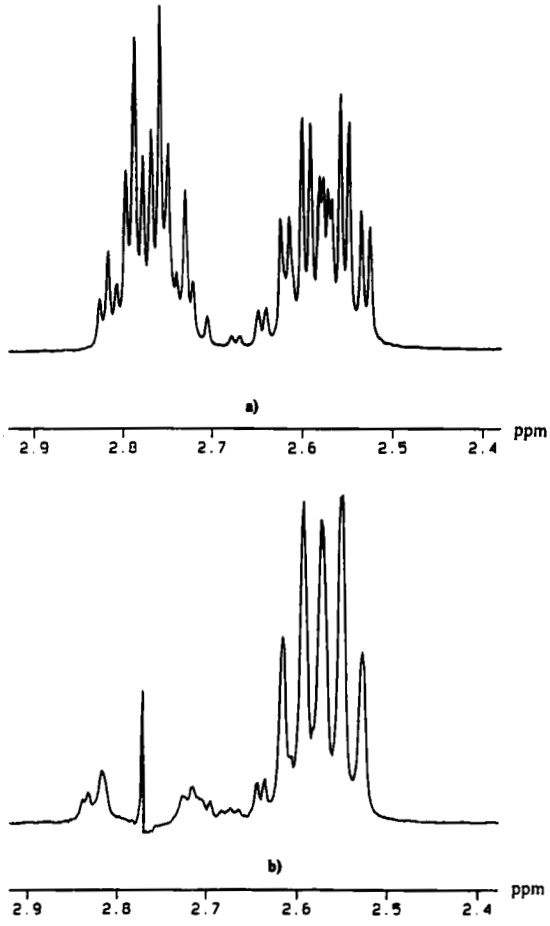


FIGURE 2 The irradiation of the signal at δ2.77 in the NMR spectrum of 4-benzylidenepinocamphorone (6a). a) The normal spectra; b) Irradiation of the signal corresponding to H_2 and simplification of the signal corresponding to H_{7exo}.

(6a) contained an additional coupling (J, 2.5 Hz) associated with the resonances at δ2.77, 2.58 and these were concluded to arise from the *exo* proton at C_7 and the C_2 proton. The observed coupling constant between these protons implies a 'W' conformation of the four σ bonds between the H_7 *exo* and H_2 protons (Figure 1).

Figure 1 clearly shows that long range coupling would only occur if the C-2 methyl group had inverted to give 4-benzylidenepinocamphorone (6a), whereas if the product had been the isopinocamphorone derivative (6b) a 'W' conformation would not be present and the weak coupling between the H_7 *exo* and H_2 protons would not be resolved. To check this suggestion, a homonuclear spin-decoupling experiment was performed to observe the effect of removing either of the resonances at δ2.77 or 2.58 by irradiation with the appropriate Larmor frequency. The close proximity of the two signals meant that some interference beats were observed because of superposition of the two very similar frequencies. Irradiation of the mid-points of the resonance signals (δ2.77, 2.58) resulted in simplification of the spectra (Figure 2 and Table I).

The long range coupling effect (J 2.5 Hz) between the H_2 and H_{7exo} protons clearly implies that the structure of the benzylidene derivative is probably 6a and not 6b and therefore involves inversion of the C-2 methyl group during formation of the derivative. The structure of the product (6a) was unambiguously confirmed by X-ray crystallographic analysis (Figure 3). The inversion occurred because, although the isopinocamphorone molecule (4) can only form a monobenzylidene derivative, an enol (10) can be formed at C-2 which will generate the more thermodynamically stable pinocamphorone nucleus (11) which will reduce steric crowding (Scheme V).

4-Benzylidenecamphorone (6a) reacted with excess chlorosulfonic acid (6 molar equivalents) at room temperature (1 week) followed by treatment with thionyl chloride-DMF (catalyst) to yield the *p*-sulfonyl chloride (12) (Scheme VI).

The optimum conditions required for the chlorosulfonation of 4-benzylidenepinocamphorone (6a) were similar to those previously reported[9] for the analogous reaction with 3-benzylidenecamphor (1). The sulfonyl chloride (12) like the analogous camphor derivative appeared to be deliquescent and could not be isolated

TABLE I

Results of the spin-decoupling experiments with benzylidenepinocamphorone (6a)

Decoupling of the resonance at δ2.77

(a) The resonance due to the H_2 proton removed.
(b) The resonance at δ2.04 due to the H_1 proton simplified to doublet ($J_{2,1}$ 2.5 Hz removed).
(c) The resonance at δ2.58 due to the H_{7exo} proton simplified to a quintet ($J_{2,7exo}$ 2.5 Hz removed).
(d) The resonance at δ1.22 due to the H_{10} proton simplified to a singlet ($J_{2,10}$ 7.5 Hz removed).

Decoupling of the resonance at δ2.58

(e) The resonance due to the H_{7exo} proton removed.
(f) The resonance at δ3.36 (H_5) simplified to a doublet ($J_{5,7exo}$ 5.0 Hz removed).
(g) The resonance at δ2.77 (H_2) simplified to a quartet ($J_{2,7exo}$ 2.5 Hz removed).
(h) The resonance at δ1.34 (H_{7endo}) simplified to a singlet (J_{gem} 10 Hz).

The results (a–d) show that H_2 proton is coupled to H_{7exo}, H_1 and H_{10} protons.
The results (e–h) demonstrate that the H_{7exo} proton is coupled to the H_2, H_5 and H_{7endo} protons.
The overall conclusion is that the H_2 and H_{7exo} protons are coupled by a long range effect.

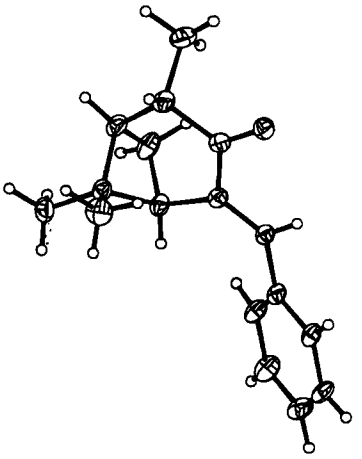
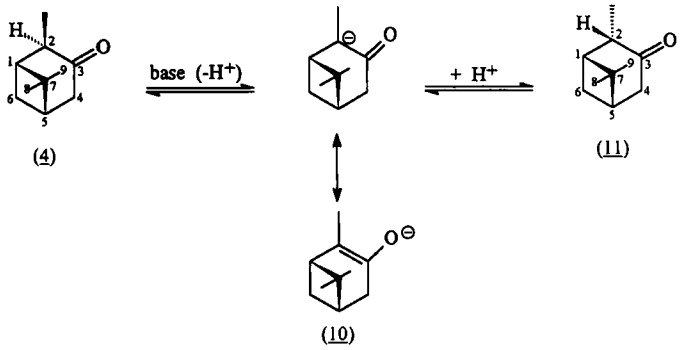
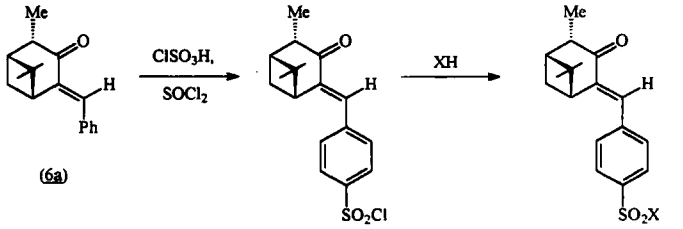


FIGURE 3 The X-ray crystal structure of 4-benzylidenepinocamphorone (6a).



SCHEME V Interconversion of isopinocamphorone(4) and pinocamphorone (11).



SCHEME VI Sulfonyl derivatives of 4-benzylidenepinocamphorone (6a).

in a pure, dry form; the yield was therefore estimated by rapid conversion of the crude product to the stable dimethylsulfonamide derivative (14). The crude sulphonyl chloride (12) was characterized by condensation with ammonia, dimethylamine, diethylamine, morpholine, 2,6-dimethylmorpholine and benzylamine to give the sulfonamides (13–18) (Scheme VI). Chlorosulfonation of 4-benzylidenepinocamphorone (6a) would be expected to occur preferentially in the *para*-position of the phenyl ring due to the electron donating property of the π-electrons of the alkenic double bond as previously noted with 3-benzylidenecamphor (1).[9] The orientation was confirmed by the ^{1}H NMR spectra of the sulfonamide derivatives which showed the aromatic proton resonances (δ7.8, 7.4) as a well-defined AA'BB' pattern. The lower field doublet (δ7.8) is ascribed to H-3' and H-5'-protons which are relatively deshielded by the adjacent electron-withdrawing SO_2X moiety (Scheme VI), compared with the H-2' and H-6' protons (δ7.4).

EXPERIMENTAL

Melting points were determined by a Gallenkamp electric apparatus and are uncorrected. IR spectra were recorded as KBr discs with a Unicam SP 100 spectrometer. NMR spectra were determined with a Bruker AC 250 spectrometer using tetramethylsilane as internal standard and deuterochloroform as solvent unless otherwise stated; resonances indicated by an asterisk were reduced by D_2O treatment.

Mass spectra were measured with a VG micromass V15 spectrometer operating at 70 eV. TLC was carried out using Camlab silica gel plates sensitized to UV 256 nm and cyclohexane-ethyl acetate (2:1) as eluant. The X-ray crystallography was carried out by Professor M. B. Hursthouse (University College of Wales, Cardiff).

3-Benzylidene D-camphor (1) Improved Method

D-Camphor (5.0 g, 0.033 mole) and freshly distilled benzaldehyde (3.5 g, 0.033 mole) were dissolved in DMF (34 ml). Anhydrous sodium amide (1.9 g, 0.049 mole) was added in one portion and the resultant suspension was heated (50°C) on a water-bath for 3 hours. The cooled mixture was poured into cold water (600 ml) and left to crystallise at room temperature overnight. The white solid was collected by vacuum filtration and washed with water until the washings were neutral to litmus. Recrystallization from ethanol afforded the benzylidene derivative (1) as needles (4.9 g, 62%), m.p. 95–97°C (lit.[10] 97°C).

TLC: Showed one spot R_F 0.80. (Found: C, 84.8; H, 8.5, $C_{17}H_{20}O$ requires C, 85.0; H, 8.3%).
IR: ϑ_{max} 1700 (C=O), 1640 (ArC=C), 700 (CH deform., monosubstitution) cm^{-1}.
^{1}H NMR: δ 7.5–7.3 (m, 5H, ArH), 7.2 (s, 1H, alkenic H), 3.1 (d, 1H, H-4; *J*, 7.0 Hz), 2.5–1.4 (m. 4H, camphor ring H), 1.05, 1.0 and 0.8 (3 × s, 9H, CH_3).
^{13}C NMR: δ 208.2 (C-12), 142.1 (C-3), 135.7 (C-1'), 129.8 (C-13'), 128.7 (C-2'), 128.6 (C-4'), 127.5 (C-7), 57.1 (C-1), 49.2 (C-4), 46.7 (C-4), 30.7 (C-6), 26.0 (C-5), 20.6 (C-8), 18.3 (C-9), 9.3 (C-10).
MS:m/z 240 (M^+), 239 (M—H) (v. weak 1%), 225 (M—CH_3), 212 (M—CO), 197 (M—CH_3CO), 169 (M—C_2H_4CO), 129 ($C_{10}H_9$), 128 ($C_{10}H_8$), 115 (C_9H_7).

4-Benzylidenepinocamphorone (6a)

Isopinocamphorone (5 g, 0.033 mole) was condensed with benzaldehyde (3.5 g, 0.033 mole) in the presence of sodium amide (1.9 g, 0.049 mole) in DMF (34 ml) under identical conditions to those previously used in the preparation of 3-benzylidenecamphor. A similar work up procedure afforded 4-benzylidenepinocamphorone (6a) (5.0 g, 63%), m.p. 60°C (lit.[12] 58–60°C). TLC showed one spot R_f 0.86. (Found: C, 84.5; H, 8.4. $C_{17}H_{20}O$ requires C, 85.0; H, 8.3%).

IR: ϑ_{max} 1690 (C=O), 1600 (ArC=C) cm^{-1}.
MS: 340, 338 (M^+), 324, 322, 295, 238 (M^+—H—SO_2Cl), 209, 195, 165, 149, 128, 115, 91, 89, 83, 77, 64, 55, 41, 36, 31.

General Procedure for the Preparation of the Sulfonamides (13–18)

4-Benzylidenepinocamphorone *p*-sulfonyl chloride (12, 0.005 mole) was treated with either aqueous (0.88) ammonium hydroxide or a solution of the appropriate amine (0.015 mole) in ethanol (20 ml) at 0°C. The mixture was left at room temperature for 12 hours and the resultant suspension poured onto ice-water (100 ml) and acidified to pH 6 with dilute hydrochloric acid. The precipitate was filtered off with suction, washed with water and purified by recrystallization from ethanol. By this procedure, the following 4-benzylidenepinocamphorone-*p*-sulfonamides were obtained:

Compound 13: (25%), m.p. 105–107°C (Found: C, 63.6; H, 6.4; N, 4.5 $C_{17}H_{21}NO_3S$ requires C, 63.9; H, 6.6; N, 4.4%).

IR: ϑ_{max} 3250, 3200 (NH_2), 2950 (CH), 1690 (C=O), 1620 (ArC=C), 1330, 1160 (SO_2) cm^{-1}.
^{1}H NMR ($(CD_3)_2CO$): δ 7.8–7.4 (m, 4H, ArH, AA'BB' pattern), 7.5 (s, 1H, alkenic H), 6.55* (s, 2H, NH_2), 3.41–2.00 (m, 4H H-1, H-7$_{exo}$, H-2, H-5), 1.45 (s, 3H, 8-Me), 1.37–1.27 (m, 1H, H-7$_{endo}$), 1.16 (d, 3H, 10-Me; J_{Me-H2} 7.4 Hz), 0.96 (s, 3H, 9-Me).
MS: 319 (M^+), 236 (M^+—SO_2NH_2), 208, 196, 168, 155, 128, 83, 55, 45, 41.

Compound 14: (10%), m.p. 80–82°C, TLC showed one spot R_F 0.63. (Found: C, 66.1, H, 6.9, N, 3.8. $C_{19}H_{25}NO_3S$ requires C, 65.7, H, 7.2; N, 4.0%).

IR: ϑ_{max} 1705 (C=O), 1620 (ArC=C), 1355, 1170 (SO_2) cm^{-1}.
^{1}H NMR: δ 7.8–7.4 (m, 4H, ArH, AA'BB' pattern), 7.5 (s, 1H, alkenic H), 3.35–0.95 (m, 14H, pinocamphorone H), 2.7 (s, 6H, NMe_2).

Compound 15: (25%), m.p. 78–80°. (Found: C, 66.8; H, 7.3; N, 3.7. $C_{21}H_{29}NO_3S$ requires C, 67.2; H, 7.7; N, 3.7%).

IR: ϑ_{max} 2900 (CH), 1700 (C=O), 1620 (ArC=C), 1335, 1200 (SO_2) cm^{-1}.
^{1}H NMR: δ 7.60–7.40 (m, 4H, ArH, AA'BB' pattern), 7.51 ((s, 1H, alkenic H), 3.30–3.20 ((m, 5H, $(NCH_2CH_3)_2$), H-5), 2.85–0.96 (m, 19H, pinocamphorone H and $(NCH_2CH_3)_2$).
^{13}C NMR: δ 203.3 (C-3), 144.0 (C-4'), 139.8 (C-4), 133.8 (C-1'), 129.8 (C-3', C-5', C-2' and C-6'), 127.1 (C-11), 44.8 (C-1 and C-2), 43.5 (C-5), 42.2 (N—($CH_2CH_3)_2$), 41.4 (C-6), 29.1 (C-7), 26.4 (C-8), 21.4 (C-9), 15.4 (C-10), 41.2 ($(NCH_2CH_3)_2$).
MS: 375 (M^+), 332, 292, 264, 195, 168, 156, 141, 136, 128, 115, 83, 72, 55, 44, 41.

Compound 16: (18%), m.p. 98–100°C. TLC showed one spot, R_F 0.56. (Found: C, 65.1; H, 6.6; N, 3.2. $C_{21}H_{27}NO_4S$ requires C, 64.9; H, 6.9; N, 3.4%).

IR: ϑ_{max} 1700 (C=O), 1620 (ArC=C), 1360, 1170 (SO_2) cm^{-1}.
^{1}H NMR ($CDCl_3$): δ 7.8–7.4 (m, 4H, ArH, AA'BB' pattern), 7.5 (s, 1H, alkenic H), 3.8–3.0 (m, 8H, morpholine H), 2.90–0.94 (m, 14H, pinocamphorone H).
^{13}C NMR: δ 203.0 (C-3), 144.2 (C-4'), 140.8 (C-4), 134 (C-1'), 129.8 (C-2'), 129.6 (C-5'), 129.4 (C-6'), 127.9 (C-3'), 66.1 (OCH_2), 46.0 (N—CH_2), 44.8 (C-1 and C-2), 43.4 (C-5), 42.1 (C-6), 29.1 (C-7), 26.4 (C-8), 21.5 (C-9), 15.4 (C-10).
MS: 389 (M^+), 372, 346 (M—CMe_2), 306, 238 (M^+—$SO_2NC_4H_8O$), 86 (C_4H_8NO), 56.

Compound 17: (24%), m.p. 93–95°C. (Found: C, 65.8, H, 7.1; N, 3.2. $C_{23}H_{31}NO_4S$ requires C, 66.2; H, 7.4; N, 3.4%).

IR (KBr): ϑ_{max} 2950 (C—H), 1710 (C=O), 1360, 1165 (SO_2) cm^{-1}.
MS: 417 (M^+), 348, 334, 266, 238 (M^+—$SO_2NC_6H_{12}O$), 196, 168, 156, 128, 114 ($C_6H_{12}NO$), 98, 83, 70, 55, 41.

Compound 18: (18%), m.p. 100–102°C. (Found: C, 70.1; H, 6.4; N, 3.2. $C_{24}H_{27}NO_3S$ requires C, 70.4; 6.6; N, 3.4%).

IR: ϑ_{max} 1620, 1605 (ArC=C), 1340, 1160 (SO_2) cm^{-1}.
^{1}H NMR ($CDCl_3$): δ 8.10* (s, 1H, NH), 7.76–7.10 (m, 9H, ArH), 7.51 (s, 1H, alkenic H), 4.20 (d, 2H, $PhCH_2NH$, $J_{CH_2,NH}$ 6.2 Hz), 3.30–1.75 (m, 5H, alicyclic H), 1.44 (s, 3H, 8-Me), 1.38–1.15 (m, 4H, 10-Me and H-7 *endo*), 0.95 (s, 3H, 9-Me).

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