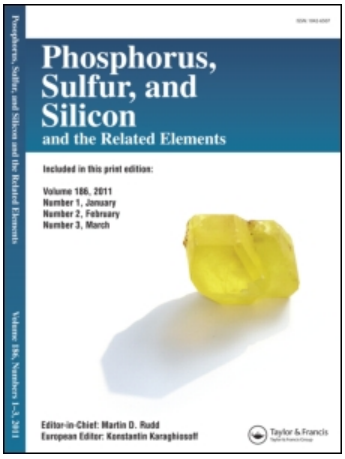

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THE SYNTHESIS AND CHLOROSULFONATION OF SOME DIARYLIDENE AND HETEROARYLIDENE KETONES WITH VARYING ALICYCLIC RING SIZE

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THE SYNTHESIS AND CHLOROSULFONATION OF SOME DIARYLIDENE AND HETEROARYLIDENE KETONES WITH VARYING ALICYCLIC RING SIZE

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A series of diarylidene and heteroarylidene ketones (**1–20**) was prepared using alicyclic ketones ($(CH_2)nC{=}O$ where n = 3 to 7). An improved synthesis of 2,4-dibenzylidenecyclobutanone (**1**) is described and the ease of preparation of the arylidene derivatives is considered in terms of the size of the alicyclic ring. Treatment of 2,5-dibenzylidenecyclopentanone (**2**) with chlorosulfonic acid (10 mole equivalents) afforded the 4,4′-bis-sulfonyl chloride (**23**), reducing the amount of chlorosulfonic acid (6 mole equivalents) produced the corresponding mono-sulfonyl chloride (**24**). Only the respective 4,4′-bis-sulfonyl chlorides (**39, 45, 51**) could be isolated from the diarylidene ketones derived from larger alicyclic rings. Attempted chlorosulfonation of 2,4-dibenzylidene cyclobutanone (**1**) gave a mixture of products which could not be clearly characterised. The sulfonyl chlorides were converted into stable sulfonamides (**25–29, 35, 36, 38, 40–44, 46–48, 52, 54**) by condensation with amines, and selected samples were screened for biological activity as potential insecticides, herbicides and fungicides. The orientation of sulfonation is discussed in relation to stereoelectronic factors and the relevant spectral data.

Key words: Arylidene and heteroarylidene ketones, chlorosulfonation, sulfonamides.

INTRODUCTION

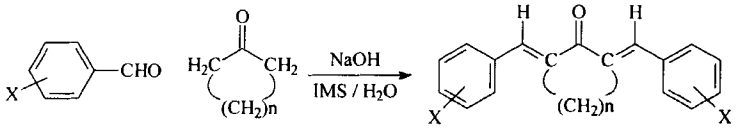
This work forms part of our general programme[1–3] examining the chemistry and the biological evaluation of arylsulfonyl derivatives, in particular the recent studies of the chlorosulfonation of systems containing the α,β-unsaturated carbonyl moiety, such as chalcone,[4,5] benzylidene camphor,[6,7] mono[8,9] and dibenzylideneacetone.[10] Previous results indicated that sulfonation occurred in the 4-position of the benzylidene ring at a rate slower than that for benzene, as anticipated in a phenyl ring containing the —CH═CH—X group, where X is electron-withdrawing moiety. The behaviour on sulfonation is reminiscent of that shown by halogenobenzenes upon electrophilic substitution.[11]

The condensation of cyclopentanone and cyclohexanone, under basic conditions, with a range of arylaldehydes is well documented; the yields of the diarylidene derivatives tend to be high (>80%), and the crystalline products have been widely used in the identification of alicyclic ketones.[12] Considerably less work has been done on the analogous reaction between cyclobutanone and benzaldehyde. Previous workers[13] have reported that 2,4-dibenzylidenecyclobutanones are sensitive to base and are difficult to purify because the normal dibenzylidene derivatives undergo a further intramolecular Michael addition to form dimers. The diarylidene ketones derived from cycloheptanone and cyclooctanone are more difficult to prepare and more forcing conditions need to be employed.[14] The literature contains little expla-

nation of these trends or comparisons of the experimental conditions reported for different substrates.

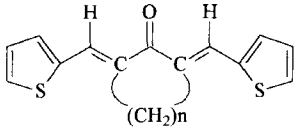
DISCUSSION

The formation of the diarylidene derivatives derived from cyclopentanone and cyclohexanone (**2–10**, Chart 1) occurred using standard aldol reaction conditions[14]; the products were readiy isolated by precipitation from a 2:1 arylaldehyde/ketone mixture after 4 hours at 100°C in 50% ethanolic aqueous sodium hydroxide. In order to maximise yields, the liquid arylaldehydes required washing with sodium carbonate



Compound No.	n	X
1	1	H
2	2	H
3	2	4-OCH_3
4	2	2-Br
5	3	H
6	3	3-OCH_3
7	3	4-OCH_3
8	3	2,6-Cl_2
9	3	2,6-OCH_3
10	3	2,6-F_2
11	4	H
12	4	4-OCH_3
13	4	4-Ph
14	5	H
15	5	4-OCH_3
16	5	4-Ph
17	5	4-NO_2

CHART 1 The synthesis of the diarylidenecycloalkanones.



Compound No.	n
18	1
19	2
20	3

CHART 2 The dithienylidene derivatives of cyclobutanone, cyclopentanone and cyclohexanone.

TABLE I

Physical data of the diarylidene and diheteroarylidene ketones

Compound No	Yield (%)	m.p. ^{0}C	Molecular formula	Microanalysis found (calc.) % C H N	MS(M+)
1	43	189-193 (lit.[13] 193-195)	$C_{18}H_{14}O$	87.7 (87.8), 5.7 (5.7) ------	246
2	92	190-191 (lit.[15] 189)	---------	----------	260
3	84	211-313 (lit.[16] 213-214)	---------	----------	
4	85	168-170	$C_{19}H_{14}Br_2O$	54.5 (54.5), 3.4 (3.3) ------	418
5	88	117-119 (lit.[15] 118-119)	---------	----------	274
6	70	78-80	$C_{22}H_{22}O$	78.7 (79.0), 6.7 (6.6) ------	334
7	73	158-159 (lit.[17] 160)	---------	----------	334
8	85	181-182	$C_{20}H_{14}C_{14}O$	58.1 (58.2), 3.4 (3.4) ------	413⌘
9	63	178-180	$C_{24}H_{26}O_5$	74.2 (73.1), 6.6 (6.6) ------	395⌘
10	69	130-133	$C_{20}H_{14}F_4O$	69.2 (69.4), 4.2 (4.1) ------	346
11	42	102-104 (lit.[18] 107)	---------	----------	288
12	37	118-122	$C_{23}H_{24}O$	78.9 (79.3), 6.8 (6.9) ------	348
13	70	222-226	$C_{33}H_{28}O$	90.1 (90.0), 6.6 (6.4) ------	440
14	33	108-110 (lit.[18] 111)	---------	----------	302
15	24	132-135 (lit.[19] 135-137)	---------	----------	362
16	28	190-193	$C_{22}H_{20}O_5N_2$	67.0 (67.3), 5.2 (5.1), 7.1 (7.1)	392
17	43	168-169	$C_{34}H_{30}O$	89.4 (89.9), 6.5 (.6.6) ------	454
18	42	184-186	$C_{14}H_{10}OS_2$	65.1 (65.1), 3.9 (3.9) -------	258
19	87	224-226 (lit.[15] 226)	$C_{15}H_{12}OS_2$	66.0 (66.2), 4.2 (4.4) -------	272
20	83	158-160 (lit.[15] 156)	$C_{16}H_{14}OS_2$	67.1 (67.1), 5.0 (4.9) -------	286

⌘ $(M+H)^+$ ion observed in the FAB positive ion mass spectrum

TABLE II

Influence of different reaction conditions on the formation of 2, 7-dibenzylidenecycloheptanone (**11**)

Expt. No.	Aldehyde: Ketone	Base	Time (hours)	Temp.	Solvent	Yield (%)	Product
1	2:1	NaOH	4	reflux	50:50 EtOH/H_2O	40	mixture of mono & diarylidene derivatives
2	2:1	NaOH	8	reflux	50:50 EtOH/H_2O	38	mixture of mono & diarylidene derivatives
3	2:1	NaOH	4	reflux	EtOH	42	mainly diarylidene derivative
4	3:1	NaOH	4	reflux	50:50 EtOH/H_2O	39	mixture of mono & diarylidene derivatives
5	2:1	Na	8	reflux	benzene	0	starting materials
6	2:1	Na sand	10	reflux	benzene	0	starting materials
7	2:1	NaOMe	1	reflux	MeOH	32	diarylidene derivative
8	2:1	NaOH	76	R.T.	water	15	mainly monoarylidene derivative
9	2:1	NaOH/ TEBA	3	R.T.	water	22	mainly monoarylidene derivative
10	2:1	$NaNH_2$	3	reflux	DMF	---	decomposed
11	2:1	$NaNH_2$	3	50^{0}C	DMF	53	oil (complex mixture)

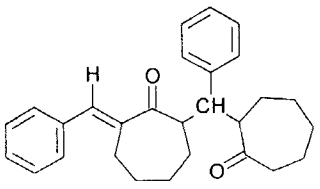
(R.T. = room temperature and TEBA = triethylbenzylammonium chloride)

and distillation under nitrogen, immediately prior to use. The stereoelectronic effect of the substituent groups altered the reaction rate but appeared to have little effect on the overall yield.

The condensation of cyclobutanone with benzaldehyde was reported by Neilsen *et al.*[13] Repetition of their procedure gave the desired 2,4-dibenzylidenecyclobutanone (**1**) contaminated with a dimer (≈5%). The mixture was very difficult to purify and, in view of the ease with which these compounds form dimers in basic media, the synthesis was modified to reduce the base concentration to 0.1 mole equivalents and the reaction time to 15 minutes. The precipitate of the crude derivative (**1**) was immediately removed from the basic mother liquor and was neutralised with dilute hydrochloric acid. This modification appeared to drastically reduce the amount of dimer without seriously depressing the overall yield and afforded 43% of the pure dibenzylidenecyclobutanone (**1**) compared with 47% of a crude product contaminated with the dimer. A similar method was used to prepare 2,4-(2-dithienylidene)-cyclobutanone (**18**) and with careful monitoring of the reaction by TLC, to ensure that the mono (2-thienylidene)cyclobutanone had reacted with a second mole of 2-thienylcarboxaldehyde before neutralisation, the reaction time was established as 1 hour. In contrast, the normal procedure for condensation, afforded excellent yields of the dithienylidene derivatives from cyclopentanone and cyclohexanone (**19**, **20**) (Chart 2). The physical data are summarized in Table I.

Application of the general method used to prepare the diarylidene derivatives of cyclopentanone and cyclohexanone to cycloheptanone and cyclooctanone only afforded complex mixtures of the starting materials and respective monoarylidene ketones. A series of experiments were designed to optimise the yield of 2,7-dibenzylidenecycloheptanone (**11**) (Table II).

The results show that more forcing conditions are required with the higher cycloalkanones, the optimum yields were realised using sodium hydroxide or sodium methoxide in boiling alcohol (experiments 3 and 7 respectively). Surprisingly the procedure[6] used to condense the very unreactive camphor molecule with benzaldehyde completely failed to afford the desired product (experiments 4 and 5). Previous workers[20] have used phase-transfer catalysis and the absence of a solvent to promote the yields in difficult aldol condensations but, in this instance, mainly the monobenzylidene derivative was isolated (experiments 8 and 9). The use of sodium amide in DMF has also been successfully exploited,[21] in the condensation of 2-methylbenzoxazole with benzaldehyde, but with cycloheptanone under these conditions the desired compound (**11**) was not isolated: at reflux temperature complete decomposition occurred (experiment 10) and at lower temperatures an intractable oil of a highly complex nature formed (experiment 11). The mass spectrum of the oil indicated a higher molecular mass impurity m/z 400 which may have corresponded to the 1,5-diketone (**21**) formed from a Michael addition reaction between two molecules of 2-benzylidenecycloheptanone.[14]



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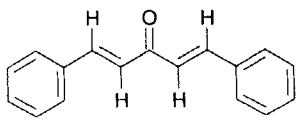


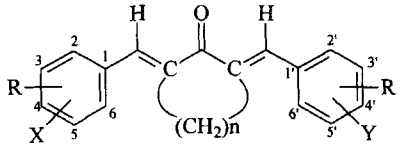
(22)

The observed difficulties encountered in the preparation of the diarylidene derivatives from the larger ring cycloalkanones (n = 4, 5) may be due to several factors. Shecter *et al.*[22] observed that the relative rate of enol formation in cycloalkanones drastically decreased with the increasing ring size, however as neither increasing the reaction time (experiment 2) or preforming the enolate (experiment 4) increased the yield, the ease of enolate formation did not appear to be the most significant factor. More likely candidates were the combined unfavourable equilibrium and solubility factors. The diarylidene derivatives of the 4-, 5- and 6-membered cycloalkanones all crystallised from the mother liquor and therefore were effectively removed from the equilibrium mixture, whereas, the derivatives of cycloheptanone and cyclooctanone were oils. The exceptions were the diarylidenes derived from 4-biphenylcarboxaldehyde which crystallised from the mother liquor in significantly higher yield. The formation of oils was probably due to the less effective conjugation in the diarylidene derivatives of larger alicyclic rings, resulting in contamination with the mono-arylidene derivative and increasing the possibility of forming mixtures of the *E* and *Z* isomers, as previously reported by Braude *et al.*[23]

The chlorosulfonation of 2,5-dibenzylidenecyclopentanone (**2**) (Chart 3, Table III) occurred using practically identical conditions to those previously observed with dibenzylideneacetone (**22**).[10] Reaction with chlorosulfonic acid (12 mole equivalents) for 1 week at room temperature afforded the 4,4′-bis-sulfonyl chloride (**23**) in good yield (73%). The position of sulfonation was confirmed by the PMR spectrum which clearly showed the expected AA′BB′ splitting pattern in the aromatic region (δ 8.0–7.4). When a smaller amount of chlorosulfonic acid (6 mole equivalents) was employed, the 4′-mono-sulfonyl chloride (**24**) was isolated in lower yield (43%). The sulfonyl chlorides (**23**, **24**) were characterised as the sulfonamides (**25–29**). Treatment of compound (**23**) with hydrazine hydrate afforded the sulfonohydrazide (**30**) which was characterised by conversion into the acetone hydrazone (**31**).

In agreement with previous work with dibenzylideneacetone (**22**),[10] monosulfonation of 2,5-dibenzylidenecyclopentanone (**2**) was possible because the carbonyl group was initially protonated (**32**) in the highly acidic medium (Scheme I). This caused a pronounced halochromic effect, as the positive charge was extensively delocalised throughout the substrate (**33**). The protonation promoted through-conjugation which resulted in substantial deactivation of the adjacent phenyl ring upon mono-sulfonation, hence by restricting the amount of chlorosulfonic acid the 4-sulfonyl chloride could be isolated.

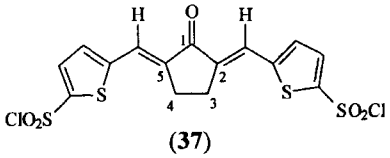
The chlorosulfonation of 2,5-di(4-methoxybenzylidene)cyclopentanone (**3**) and 2,5-di-(2-thienylidene)cyclopentanone (**19**) only afforded bis-sulfonyl chlorides (**34**, **37**) irrespective of the amount of chlorosulfonic acid used. The additional electron donation from the methoxyl group and the sulfur heteroatom respectively presumably increased the electron density in the substrate sufficiently to nullify the electron-withdrawing influence of the conjugated carbocation allowing further facile sulfonation. 2,5-Di(4-methoxybenzylidene)cyclopentanone-3,3′-bis-sulfonyl chloride (**34**) was characterised as the N,N-dimethylsulfonamide (**35**) and the morpholidate (**36**). The PMR spectrum of the aromatic region of the dimethylsulfonamide (**35**) contained an ABC splitting pattern suggesting 3-sulfonation due to the powerful $+M$ effect of the methoxyl group. The negative and positive ion FAB mass spectra of the morpholidate (**36**) clearly exhibited the anticipated molecular ion m/z 618, however the



Compound No.	n	R	X	Y
23	2	H	4-SO_2Cl	X
24	2	H	4-SO_2Cl	H
25	2	H	4-SO_2NMe_2	H
26	2	H	4-SO_2-*N*-(2,6-dimethylmorpholino)	H
27	2	H	4-SO_2-*N*-(3,4-dichloroanilino)	H
28	2	H	4-SO_2NMe_2	X
29	2	H	4-SO_2-*N*-(2,6-dimethylmorpholino)	X
30	2	H	4-SO_2NHNH_2	X
31	2	H	4-$SO_2NHN{=}CMe_2$	X
34	2	4-OCH_3	3-SO_2Cl	X
35	2	4-OCH_3	3-SO_2NMe_2	X
36	2	4-OCH_3	3-SO_2-*N*-morpholino	X
39	3	H	4-SO_2Cl	X
40	3	H	4-SO_2NMe_2	X
41	3	H	4-SO_2NEt_2	X
42	3	H	3-SO_2-*N*-morpholino	X
43	3	H	4-SO_2-*N*-(2,6-dimethylmorpholino)	X
44	3	H	4-SO_2-*N*-piperidino	X
45	4	H	4-SO_2Cl	X
46	4	H	4-SO_2NMe_2	X
47	4	H	4-SO_2-*N*-morpholino	X
48	4	H	4-SO_2-*N*-(2,6-dimethylmorpholino)	X
51	5	H	4-SO_2Cl	X
52	5	H	4-SO_2-*N*-morpholino	X
53	4	4-OCH_3	3-SO_2Cl	X
54	4	4-OCH_3	3-SO_2NEt_2	X

CHART 3 The sulfonyl derivatives of the diarylidene ketones.

negative ion trace also contained a significant peak at m/z 549 which correlated with a substrate containing one sulfonyl morpholidate group and one sulfonic acid group. Steric factors and the possibility of intramolecular hydrogen bonding possibly made the conversion of the sulfonic acid to the chloride less favourable in this substrate. The sulfonyl chloride (**37**) was characterised as the 2,6-dimethylmorpholidate (**38**); the PMR spectrum of compound (**38**) contained a complex aromatic region which suggested a mixture of isomers as the elemental analysis confirmed a molecular formula of $C_{27}H_{34}N_2O_7S_4$. The predominant resonance in the PMR spectrum consisted of a doublet of doublets (δ 7.4 and 7.6), with a coupling constant *J*, 4.0 Hz, indicative of the coupling between the H_3 and H_4 protons in the thiophene ring. The PMR spectral data therefore indicated that 2,5-di(2-thienylidene)cyclopentanone-5,5′-bis-sulfonyl chloride (**37**) appeared to be the major product isolated.



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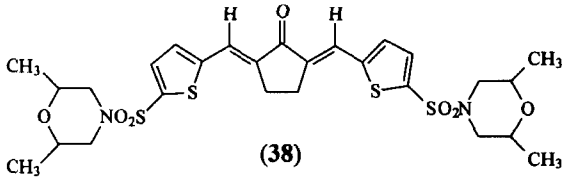


(38)

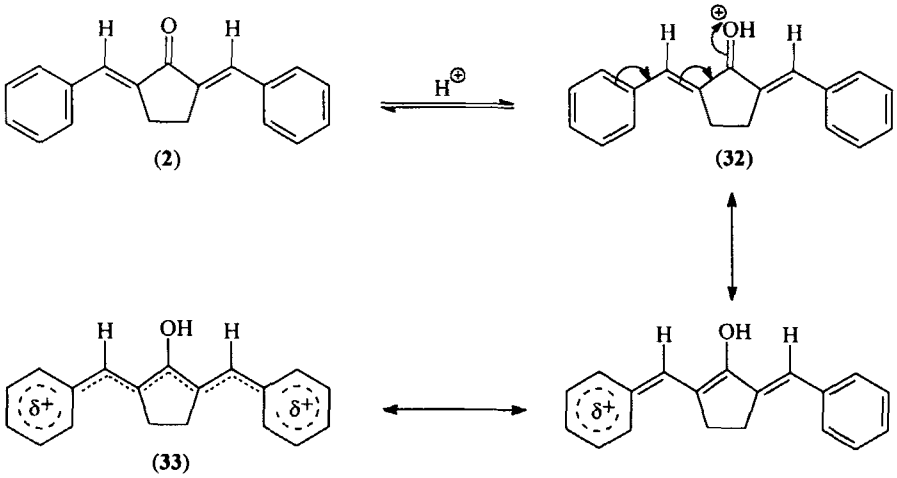
Previous preliminary work by Bartlett[24] at the University of Hertfordshire indicated that treatment of 2,6-dibenzylidenecyclohexanone with chlorosulfonic acid (12 mole equivalents) at 50°C gave a complex mixture of products. The PMR spectral inter-

TABLE III

Physical data of the sulfonyl derivatives

Compound No	Yield (%)	m.p. °C	Molecular formula	Microanalysis found (calc.) % C	H	N	MS(M+)
25	59	248-249	$C_{21}H_{21}NO_3S$	68.6 (68.7)	5.8 (5.7)	4.4 (3.8)	367
26	84	229-230	$C_{25}H_{27}NO_4S$	69.0 (68.6)	6.2 (6.2)	3.2 (3.2)	437
27	78	220-222	$C_{25}H_{19}Cl_2NO_3S$	62.0 (62.1)	4.0 (3.9)	3.0 (2.9)	487
28	63	280	$C_{23}H_{26}N_2O_5S_2$	58.1 (58.2)	5.3 (5.5)	6.1 (5.9)	474
29	49	260-263	$C_{31}H_{38}N_2O_7S_2$	60.0 (60.6)	6.3 (6.2)	5.0 (4.6)	614
30	30	183-186	----------	----------			------
31	38	230 (d)	$C_{25}H_{28}N_4O_5S_2$	56.6 (56.8)	5.1 (5.3)	10.4 (10.6)	529⌘
35	35	238-240	$C_{25}H_{30}N_2O_7S_2.½H_2O$	55.2 (55.2)	5.5 (5.7)	5.1 (5.2)	532†
36	27	254-257	$C_{29}H_{34}N_2O_9S_2$	56.1 (56.3)	5.6 (5.5)	4.5 (4.5)	534⌘
40	62	239-243	$C_{24}H_{28}N_2O_5S_2.H_2O$	56.5 (56.9)	5.6 (5.9)	5.3 (5.5)	488
41	69	197-199	$C_{28}H_{36}N_2O_5S_2.½H_2O$	60.5 (60.8)	6.5 (6.7)	5.3 (5.1)	544
42	70	226-229	$C_{28}H_{32}N_2O_7S_2.½H_2O$	58.2 (57.8)	5.9 (5.7)	4.5 (4.8)	572
43	75	230-233	$C_{32}H_{40}N_2O_7S_2.H_2O$	59.5 (59.4)	6.3 (6.5)	4.1 (4.3)	628
44	64	235-237	$C_{30}H_{36}N_2O_5S_2.½H_2O$	62.3 (62.4)	6.6 (6.4)	4.7 (4.9)	568
48	28	170-173	$C_{25}H_{30}N_2O_5S_2$	59.5 (59.8)	6.3 (6.0)	5.3 (5.5)	502
49	34	231-235	$C_{29}H_{34}N_2O_7S_2$	59.1 (59.4)	6.1 (5.8)	4.6 (4.8)	586
50	37	234-237	$C_{33}H_{42}N_2O_7S_2$	61.2 (61.7)	6.9 (6.6)	4.1 (4.4)	642
52	8	122-126	$C_{30}H_{36}N_2O_7S_2$	59.5 (60.0)	6.2 (6.0)	4.3 (4.7)	600
54	48	97-101	$C_{31}H_{42}N_2O_7S_2$	60.9 (60.2)	6.9 (6.8)	4.8 (4.5)	618

† highest mass observed ⌘ $(M+H)^+$ ion observed in the FAB positive ion mass spectrum

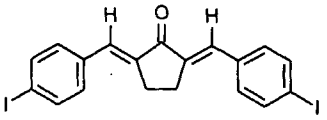


(2) (32) (33)

SCHEME I

pretation was inconclusive, but aromatisation of the alicyclic ring was proposed, based upon the absence of the resonance signals at δ 3.1 and 2.5 corresponding to the aliphatic protons. However, although the reaction of 2,6-dibenzylidenecyclohexanone (**5**) with chlorosulfonic acid was very susceptible to impurities in the starting materials and the reaction temperature Bartlett's results could not be reproduced. The authentic 4,4′-bis-sulfonyl chloride (**39**) was obtained in good yield (84%) by treating the purified compound (**5**) with fresh chlorosulfonic acid (12 mole equivalents) for 3 days at room temperature, followed by reaction with excess redistilled thionyl chloride for 30 minutes. The sulfonyl chloride (**39**) was characterised as the sulfonamides (**40**–**44**) which were difficult to purify and the microanalysis data suggested these were obtained as hydrates. The aromatisation of compound (**5**) was reported to be catalysed by hydrogen bromide,[25] however we found no evidence to suggest a similar rearrangement was operating with chlorosulfonic acid when rigorously purified 2,6-dibenzylidenecyclohexanone (**5**) was used. Although possibly the preliminary work by Bartlett[24] may indicate that the aromatisation of the 2,6-dibenzylidenecyclohexanone (**5**) is catalysed by the presence of impurities in the substrate.

2,6-Dibenzylidenecyclohexanone-4-sulfonyl chloride (**45**) could not be isolated irrespective of the concentration of chlorosulfonic acid used. This observation was in stark contrast to 2,5-dibenzylidenecyclopentanone (**2**) where both the mono and bis-sulfonyl chlorides (**23**, **24**) were readily prepared. The replacement of the essentially planar cyclopentanone ring with the flexible puckered cyclohexanone ring introduced additional constraints to the planarity of the molecule. The net effect was a reduction in the delocalisation of charge in the protonated form, which in turn diminished the deactivation of the adjacent phenyl ring. Consequently selective mono-sulfonation was not possible.

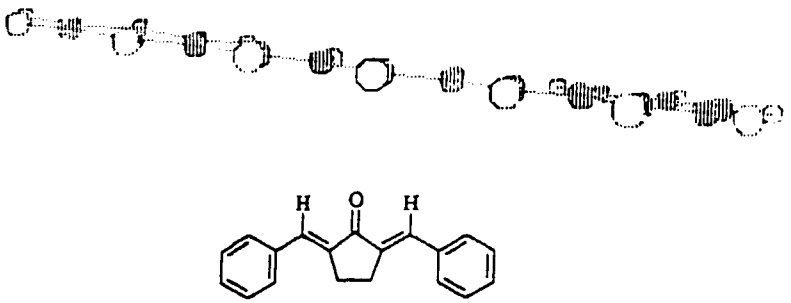


(**46**)

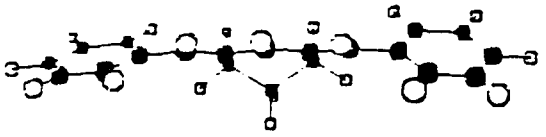
Further evidence was obtained from a study of the shape of the respective 2,5-dibenzylidenecyclopentanone (**2**) and 2,6-dibenzylidenecyclohexanone (**5**) molecules, using the experimental crystal structures available for 2,5-di(4′-iodobenzylidene)cyclopentanone (**46**)[26] and compound (**5**).[27]

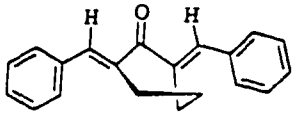
The lowest energy conformers were generated using the COSMIC force field in the COSMIC molecular modelling package.[28]

The lowest energy conformers (Figure 1) clearly showed the phenyl rings in 2,6-dibenzylidenecyclohexanone (**5**) were twisted, with respect to the rest of the molecule, reducing the efficiency of the π-orbital overlap between the phenyl rings and the alkenic double bonds. The effect was caused by the puckered 6-membered alicyclic ring which prevented flattening of the α,β-unsaturated carbonyl moiety in one plane. On the other hand, 2,5-Dibenzylidenecyclopentanone (**2**) was essentially coplanar throughout the whole molecule which allowed maximum delocalisation of the protonated species and therefore increased resistance to formation of the bis-sulfonyl chloride. The ultra-violet spectrum of 2,5-dibenzylidenecyclopentanone (**2**) showed bathochromic shifts, with respect to 2,6-dibenzylidenecyclohexanone (**5**), under neu-



(2)





(5)

FIGURE 1 The computer generated shapes of 2,5-dibenzylidenecyclopentanone (**2**) and 2,6-dibenzylidenecyclohexanone (**5**).

tral (λmax 347, 330 nm) and acidic conditions (λmax 484, 457 nm), which is in agreement with the result.

2,7-Dibenzylidenecycloheptanone (**11**) and 2,8-dibenzylidenecyclooctanone (**14**) afforded the expected 4′,4-bis-sulfonyl chlorides (**45**, **51**) by reaction with chlorosulfonic acid (10 mole equivalents). The sulfonyl chlorides (**45**, **51**) were characterised with difficulty as the sulfonamides (**47**, **48**, **52**). The reactivity of the diarylidenecycloalkanones with respect to sulfonation increased slightly with increasing size of the alicyclic ring. This probably can be ascribed to the decreasing resonance stabilization of the molecule resultant from protonation. The more reactive diarylidenecycloheptanones and cyclooctanones did not yield the mono-chlorosulfonyl derivatives; this result is in accord with stereoelectronic predictions.

Reaction of 2,7-di(4′-methoxybenzylidene)cycloheptanone (**12**) with chlorosulfonic acid (10 mole equivalents) and excess thionyl chloride afforded the 3,3′-bis-sulfonyl chloride (**53**) which was characterised as the N,N-diethylsulfonamide derivative (**54**). The mass spectrum of the crude sulfonamide showed the desired molecular ion m/z 618 but the early scans contained a volatile component m/z 271 which corresponded to the sulfonated methoxybenzaldehyde, suggesting the chlorosulfonic acid catalysed a retro-aldol reaction of the substrate (**12**).

2,4-Dibenzylidenecyclobutanone (**1**) with chlorosulfonic acid (12 mole equiva-

lents) producted a tan solid in moderate yield (52%), which contained chlorine and sulfur (fusion test) and exhibited additional bands in the IR spectrum corresponding to the sulfonyl group (ν_{max} 1370 and 1160 cm^{-1}). Condensation with dimethylamine afforded a mixture of products (TLC, 4 spots and baseline material); the mass spectrum showed a molecular ion (M^+, 460) and a fragmentation pattern corresponding to the loss of the dimethylamino and sulfonyl groups (m/z 352, 244), indicative of a bis-sulfonamide. However, although an AA'BB' pattern (δ 7.3 and 6.9) could be distinguished in the PMR spectrum, the aromatic region was generally poorly resolved and the resonance (δ 3.9) corresponding to the cyclobutanone protons was low compared to the overall aromatic proton resonance. Experiments using smaller amounts of chlorosulfonic acid and chlorosulfonic acid/thionyl chloride mixtures gave similar results and the problems may be associated with the sensitivity of the cyclobutanone ring to ring-opening reactions.

EXPERIMENTAL

Melting points were determined with a Gallenkamp electric apparatus and are uncorrected. IR spectra were measured as potassium chloride discs with a Unicam SP 3-100 spectrophotometer. NMR spectra were recorded with a Brucker AC250 spectrometer using tetramethylsilane as internal standard and unless stated otherwise deuterochloroform as solvent. The * denotes a signal which exchanged with D_2O. EI mass spectra were measured with a VG Micromass 16F spectrometer operating at 70 eV. TLC was carried out using Camlab silica gel plates sensitised to UV 256 nm and eluants of either a) cyclohexane/ethyl acetate 1:1 b) cyclohexane/ethyl acetate 2:1 or c) ethyl acetate/cyclohexane 2:1. The computer molecular modelling was carried out using the COSMIC molecular modelling package run on a VAX computer.

2,4-Dibenzylidenecyclobutanone (**1**)

A solution of cyclobutanone (2.0 g, 0.029 mole) and redistilled benzaldehyde (6.15 g, 0.058 mole) in ethanol (25 ml) was added dropwise to a stirred 75% aqueous ethanol solution (100 ml) containing sodium hydroxide (0.1 g, 0.0025 mole). After 15 minutes the mother liquor was decanted off and the precipitate was neutralised by the addition of a dilute acetic acid ethanolic solution. The crude product (**1**) was filtered off and recrystallised from aqueous acetone to give the dibenzylidene ketone (**1**) (3.1 g, 43%). TLC showed one spot R_F 0.61[b], IR: ν_{max} 1670 (C=O), 1590 (C=C) cm^{-1}. ^1H NMR: (acetone-d6) δ 7.8–7.4 (m, 10H, ArH), 7.2 (t, 2H, CH; *J*, 2.5 Hz), 4.0 (t, 2H, CH_2; *J*, 2.5 Hz).

2,4-Di(2-thienylidene)cyclobutanone (**18**)

Cyclobutanone and thiophen-2-carboxaldehyde were similarly converted into compound (**18**) except that a longer reaction time was required (1 hour). TLC showed 1 major spot R_F 0.51[b]. IR: ν_{max} 1710 (C=O), 1610 (C=C), 710 ($CH_{deform.}$) cm^{-1}. MS: 258 (M^+), 257 (M—H), 230/229 (M—CO)/(M—H—CO). ^1H NMR: δ 7.6–7.0 (m, 8H, thiophenH and alkenylH), 3.6 (t, 2H, CH_2). ^{13}C NMR: δ 188.7 (C-1), 143.3 (C-2,4), 139.0 (thiophenC-2), 133.2, 129.8, 128.2, 120.2 (thiophenC-3,4,5 and alkenylC), 34.9 (C-3).

General Method for the Preparation of Diarylidene Derivatives of Cyclopentanone and cyclohexanone (**2–10, 19, 20**)

A mixture of the aromatic aldehyde (0.050 mole) and cyclopentanone or cyclohexanone (0.025 mole) was added to 50% aqueous ethanol (50 ml) containing sodium hydroxide (0.012 mole). The mixture was refluxed on a steam bath for 4 hours, left in a freezer overnight and the resultant yellow precipitate was filtered off. The crude diarylidene derivative was washed with water, until the washings were neutral to litmus, and purified by recrystallisation from boiling ethanol.

Compound (**4**): TLC showed 1 spot R_F 0.63[b]. IR: ν_{max} 1685 (C=O), 1605 (ArC=C), 760 ($CH_{deform.}$). MS: 420, 418, 416 (M^+), 339, 337 (M—Br). ^1H NMR: δ 7.9 (s, 2H, CH), 7.7–7.2 (m, 8H, ArH), 3.0 (s, 4H, CH_2).

Compound (**9**): TLC showed 1 spot R_F 0.75[b]. IR: ν_{max} 1660 (C=O), 1605 (C=C) cm^{-1}. ^1H NMR: δ 7.65 (s, 2H, alkenylH), 7.3–6.6 (m, 6H, ArH), 3.8 (s, 12H, OCH_3), 2.5–1.6 (m, 6H, CH_2).

General Method for the Formation of Diarylidene Derivatives of Cycloheptanone and Cyclooctanone

A mixture of the aromatic aldehyde (0.050 mole) and cycloheptanone or cyclooctanone (0.025 mole) was added to ethanol (50 ml) containing sodium hydroxide (0.012 mole). The mixture was refluxed on a steam bath for 4 hours and left in a freezer overnight. If the crude diarylidene derivative precipitated from the mother liquor this solid was collected by filtration, however with most arylaldehydes an oil formed which was poured onto water and extracted with ether. Washing and concentration of the ether fraction gave the crude derivative which was recrystallised from boiling ethanol.

Compound (**13**): TLC showed 1 spot R_F 0.78[b]. IR: ν_{max} 1660 (C=O), 1605 (C=C) cm^{-1}. MS: 440 (M^+), 439 (M—H), 412 (M—CO), 384 (M—COC_2H_4). ^1H NMR δ 7.8–7.2 (m, 20H, ArH and alkenylH), 2.9–1.9 (m, 8H, CH_2).

Compound (**17**): TLC showed 1 spot R_F 0.66[b]. IR: ν_{max} 1670 (C=O), 1590 (C=C), 1510 and 1340 (NO_2) cm^{-1}. MS 392 (M^+), 391 (M—H), 376/375 (M—O/M—H—O), 346 (M—NO_2). ^1H NMR: δ 8.3–7.5 (m, 8H, ArH; AA'BB'), 7.05 (s, 2H, alkenylH), 2.8–1.6 (m, 10H, CH_2).

2,5-Dibenzylidenecyclopentanone-4,4'-bis-sulfonyl Chloride (**23**)

2,5-Dibenzylidenecyclopentanone (**2**) (3.5 g, 0.013 mole) was added to chlorosulfonic acid (18.6 g, 0.16 mole) at 0°C with occasional stirring. The resulting deep-red solution was left at room temperature for one week and poured onto crushed ice producing a fine precipitate which was filtered off, washed (water/ethanol) and dried over phosphorus pentoxide to give (**23**) (4.3 g, 73%), m.p. 183–188°C, TLC showed two spots R_F 0.81 and 0.91. The sodium fusion test was positive for Cl, N, S, IR: ν_{max} 1700 (C=O), 1610 (C=C), 1370 and 1180 (SO_2) 830 (CH) cm^{-1}.

2,5-Dibenzylidenecyclopentanone-4-sulfonyl Chloride (**24**)

2,5-Dibenzylidenecyclopentanone (**2**) (5.0 g, 0.019 mole) was added to chlorosulfonic acid (12.8 g, 0.11 mole) at 0°C with occasional stirring. The resulting red solution was left at room temperature for a week and poured onto crushed ice (60 g). The buff precipitate was collected by filtration, washed aqueous acetone and dried over phosphorus pentoxide, to give compound (**24**) (3.2 g, 47%). m.p. 195–197°C. TLC showed 1 spot R_F 0.70[b]. IR: ν_{max} 1700 (C=O), 1600 (C=C), 1370 and 1180 (SO_2) cm^{-1}. MS: 360, 358 (M^+), 359, 357 (M—H), 323 (M—Cl), 259, 258 (M—SO_2Cl and M—H—SO_2Cl).

2,5-Dibenzylidenecyclopentanone-4,4'-bis-sulfonyl Hydrazide (**30**)

The sulfonyl chloride (2.0 g, 0.0044 moles) was reacted with 98% hydrazine hydrate (1.32 g, 0.026 moles) in methanol (30 ml). The mixture was initially kept at 0°C and left at room temperature for 3 hours. The mixture was poured onto crushed ice (100 ml), the precipitate was collected, washed with water (3 × 50 ml) and dried to give the hydrazide (**30**) (0.59 g, 30%). TLC showed 1 spot R_F 0.51[c]. IR: ν_{max} 3200 (NH), 1700 (C=O), 1620 (C=C), 1380 and 1170 (SO_2).

The acetone hydrazone (**31**) was obtained by dissolving the hydrazide (**30**) (0.5 g, 0.001 moles) in acetone (15 ml). The solution was left for 2 hours and then added to ice-water (10 ml). The resultant crystals (0.2 g, 38%) were collected. TLC showed 1 spot R_F 0.55[c]. IR: ν_{max} 3300 (NH), 1705 (C=O), 1620 (C=C), 1380 and 1180 (SO_2) cm^{-1}. ^1H NMR: δ 10.2* (s, 2H, NH), 8.0–7.5 (m, 10H, ArH and alkenylH), 3.2 (s, 4H, CH_2), 1.8 (s, 12H, CH_3).

2,5-Di(4-methoxybenzylidene)cyclopentanone-3,3'-bis-sulfonyl Chloride (**34**)

2,5-Di(4-methoxybenzylidene)cyclopentanone (**3**) (5.0 g, 0.016 mole) was gradually added to chlorosulfonic acid (18.6 g, 0.16 mole) at 0°C. After a week, an excess of thionyl chloride (20 ml) was added and once the evolution of sulfur dioxide and hydrogen chloride had ceased, the solution was poured onto ice-water (50 ml). The crude sulfonyl chloride (**34**) (7.2 g, 87%), m.p. 170°C (d), was collected by filtration and dried over calcium chloride. The Beilstein test was positive. The sodium fusion test was positive for Cl and S. IR: ν_{max} 1680 (C=O), 1620 (C=C), 1370 and 1180 (SO_2) cm^{-1}.

2,5-Di(2-thienylidene)cyclopentanone-5,5'-bis-sulfonyl Chloride (**37**)

2,5-(2-thienylidene)cyclopentanone (**19**) (5.0 g, 0.018 mole) was added portionwise to chlorosulfonic acid (21.0 g, 0.18 mole) with cooling and rapid stirring. The resultant purple solution was left to stand for 1 week, at room temperature and poured onto crushed ice (100 ml) affording a brown precipitate. The crude product was filtered off with suction, washed (water) and dried over phosphorus pentoxide to give the bis-sulfonyl chloride (**37**) (5.4 g, 64%), m.p. 165°C (d) TLC showed 2 spots R_F 0.81 and 0.58 with some baseline material.[c]

2,6-Dibenzylidenecyclohexanone-4,4'-bis-sulfonyl Chloride (**39**)

Purified 2,6-dibenzylidenecyclohexanone (**5**) (10.0 g, 0.037 mole), which had been recrystallised 3 times from ethanol, was slowly added to fresh chorosulfonic acid (51.3 g, 0.44 mole) at 0°C with mechanical stirring. An intensely red coloured solution formed which was left to stand for 5 days at room temperature. An excess of freshly distilled thionyl chloride (20 ml) and dry DMF (2 drops) was added and the solution was stirred until the endothermic evolution of hydrogen chloride was complete (45 minutes). The mixture was slowly poured onto crushed ice (150 ml). The product was filtered off under reduced pressure and the solid was washed with water until the washings were neutral to litmus, and dried in a vacuum desiccator over a mixture of calcium chloride and phosphorus pentoxide, to give compound (**39**) (14.6 g, 84%) m.p. 121–126°C. The Beilstein test was positive and the sodium fusion test was positive for Cl and S. TLC showed 1 major spot R_F 0.93 with some baseline material[c]. IR: ν_{max} 3400 (OH), 1660 (C=O), 1600 (C=C), 1380 and 1170 (SO_2). ^{1}H NMR: (DMSO-d_6) δ 8.0–7.0 (m, 10H, alkenyl**H** + Ar**H**; AA'BB'), 2.9–1.0 (m, 6H, CH_2).

2,7-Dibenzylidenecycloheptanone-4,4'-bis-sulfonyl chloride (**45**)

2,7-Dibenzylidenecycloheptanone (**II**) (2.0 g, 0.0069 mole) was added portionwise to chlorosulfonic acid (9.7 g, 0.083 mole) at 0°C. The resulting deep-red solution was left to stand at room temperature for 3 days, treated with excess thionyl chloride (30 ml), for 1 hour, and poured onto crushed ice (100 ml). The precipitate was collected by vacuum filtration, well washed with water and dried over phosphorus pentoxide in a vacuum desiccator to give (**45**) (2.7 g, 81%), m.p. 143°C (d). TLC showed 1 spot RF 0.89 with some baseline material, IR: ν_{max} 1660 (C=O), 1610 and 1580 (C=C), 1360 and 1160 (SO_2) cm^{-1}.

2,8-Dibenzylidenecyclooctanone-4,4'-bis-sulfonyl Chloride (**51**)

2,8-Dibenzylidenecyclooctanone (**14**) (2.0 g, 0.0066 mole) was similarly treated with chlorosulfonic acid (9.2 g, 0.079 mole) and excess thionyl chloride (20 ml) to give the sulfonyl chloride (**51**) (2.8 g, 85%) m.p. 84–86°C (d). TLC showed 1 major spot 0.80 and some baseline material[c]. IR: ν_{max} 1655 (C=O), 1580 (C=C), 1360 and 1160 (SO_2) cm^{-1}.

2,7-Di(4-methoxybenzylidene)cycloheptanone-3,3'-bis-sulfonyl Chloride (**53**)

2,7-Di(4-methoxybenzylidene)cycloheptanone (**12**) (2.0 g, 0.0057 mole) was slowly added to chlorosulfonic acid (6.6 g, 0.057 mole) at 0°C. The resultant red solution was left at room temperature for 4 days, treated with excess thionyl chloride (30 ml) for 1 hour and poured onto crushed ice (100 ml). The crude sulfonyl chloride (**53**) (1.8 g, 58%), m.p. 94°C (d), was isolated by vacuum filtration, washed well with cold water and dried over phosphorus pentoxide. TLC showed 1 major spot R_F 0.76[c]. IR: ν_{max} 1670 (C=O), 1595 (C=C), 1360 and 1160 (SO_2) cm^{-1}. MS: 548, 546, 544 (M^+), 547, 545, 543 (M—H), 520, 518, 516 (M—CO), 509, 511 (M—Cl), 473 (M—HCl_2), 445, 447 (M—SO_2Cl), 410 (M—SO_2Cl_2), 381 (M—S_2O_4Cl), 346 (M—SO_2Cl_2).

General Method for the Synthesis of Sulfonamides

The appropriate amine [2.1 mole equivalents; with the bis-sulfonyl chlorides a larger amount of amine (4.2 mole equivalents) was used] was added dropwise to a solution of the sulfonyl chloride (1 g) in ethanol or acetone (20 ml) at 0°C. The suspension was either stirred for 3 hours or left to stand overnight, at room temperature and then poured onto crushed ice (50 ml). The resulting precipitate was filtered off and well washed with water, until any traces of the amine hydrochloride salt were removed, and the filtrate gave no precipitate with silver nitrate solution. The crude sulfonamide was purified by recrystallisation from ethanol, unless otherwise stated, and was dried either in a vacuum desiccator over phosphorus pentoxide or in a low temperature oven (40°C).

Compound (**25**): TLC showed 1 spot R_F 0.62[a]. IR: ν_{max} 1710 (C=O), 1590 (C=C), 1370 and 1190 (SO_2). MS: 367 (M^+), 366 (M—H), 323 (M—NMe_2), 259/258 (M—SO_2NMe_2 and M—H—SO_2NMe_2). ^{1}H NMR: δ 7.9–7.2 (m, 11H, Ar**H** and alkenyl**H**), 3.2 (s, 4H, CH_2), 2.7 (s, 6H, CH_3).

Compound (**29**): TLC showed 1 spot R_F 0.74[c] IR: ν_{max} 1700 (C=O), 1610 (C=C), 1370 and 1180 (SO_2), 810 (CH). MS: 614 (M^+), 436 (M—$SO_2NC_6H_{12}O$), 114 ($NC_6H_{12}O$). ^{1}H NMR: δ 8.0–7.4 (m, 10H, Ar**H** and alkenyl**H**), 3.2 (s, 4H, cyclopentane**H**), 3.7–1.8 (m, 12H, morpholino**H**), 1.2 (s, 12 CH_3).

Compound (**38**): TLC showed 2 spots R_F 0.58 and 0.41[a]. IR: ν_{max} 1680 (C=O), 1610 (C=C), 1370 and 1180 (SO_2) cm^{-1}. MS: 626 (M^+), 447 (M—H—$SO_2NC_6H_{12}O$), 114 ($NC_6H_{12}O$), ^{1}H NMR: δ 7.8 (s, 2H, alkenyl**H**), 7.6–7.2 (m, 4H, thiophen**H**), 4.0–3.6 (m, 4H, OCH_2), 3.0 (s, 4H, cyclopentane**H**), 2.3–1.9 (m, 4H, $NCH)_2$), 1.1 (d, 12H, CH_3).

Compound (**40**): TLC showed 1 spot R_F 0.68[c]. IR: ν_{max} 3400 (OH), 1660 (C=O), 1610 (C=C), 1340 and 1150 (SO_2) cm^{-1}. ^1H NMR: δ 7.8–7.5 (m, 10H, alkenyl**H** and Ar**H**; AA'BB'), 2.9 7 1.8 (m, 6H, cyclohexane**H**), 2.7 (s, 12H, CH_3). ^{13}C NMR: δ 189.5 (C-1), 140.2 (ArC-4), 138.1, 135.5, 135.2 (ArC-1, C-2,6 and alkenylC), 130.5 (ArC-2,6), 128.5 (ArC-3,5), 37.9 (CH_3), 28.4 (C-3,5), 22.7 (C-4).

Compound (**47**): TLC showed 1 spot R_F 0.67[c]. IR: ν_{max} 1670 (C=O), 1610 and 1595 (C=C), 1380 and 1165 (SO_2) cm^{-1}. ^1H NMR: δ 7.8–7.2 (m, 8H, Ar**H**; AA'BB'), 7.4 (s, 2H, alkenyl**H**), 3.8–3.0 (m, 16H, morpholino**H**), 2.7–2.0 (m, 8H, cycloheptane**H**). ^{13}C NMR: δ 198.2 (C-1), 143.3 (C-2,7), 141.1 (ArC-4), 135.0 (ArC-1), 134.0 (alkenylC), 130.2 and 127.2 (ArC-2,3,5,6), 67.6 (CH_2O), 46.2 (CH_2N), 29.2 (C-3,6), 28.3 (C-4,5).

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