Intramolecular Reactions. Part 12.[1] Ring Size and Leaving Group Effects on Inter- and Intra-molecular Nucleophilic Substitution by Carbanions

By **Roger Bird, Gwerydd Griffiths, Gwynfor F. Griffiths,** and **Charles J. M. Stirling,*** School of Physical and Molecular Sciences, University College of North Wales, Bangor, Gwynedd LL57 2UW

In cyclisations of aryl ω-halogenoalkyl ketones to aryl cycloalkyl ketones with base, cyclopropanes are formed up to 23 000 times faster than cyclopentanes. Hydrogen–deuterium exchange experiments and very low bromide–chloride ratios (1.9) for three-membered ring formation are consistent with rate-determining deprotonation of the ketone. By contrast, in five-membered ring formation, hydrogen–deuterium exchange adjacent to the carbonyl group occurs much faster than cyclisation and the chloride–bromide ratio is ' normal ' at 99. In formation of arylsulphonylcyclopropanes from arylsulphonylpropyl arenesulphonates, the Hammett ρ value for the leaving group is +1.7, and for intermolecular substitution by bis-sulphonyl stabilised carbanions, +1.2. Attempts to obtain ρ_{LG} values for five-membered ring formation were frustrated by competing intermolecular reactions. The results are discussed against the background of previous work on ring formation by intramolecular nucleophilic substitution.

As part of our general study of reactivity in intramolecular nucleophilic substitution reactions and with particular reference to the diagnosis of the transition state structures for such processes, we now report on the formation of cycloalkyl ketones from ω-halogenoalkyl ketones, and of aryl cycloalkyl sulphones from arylsulphonates of ω-hydroxyalkyl sulphones.

We had shown previously [2,3] that for intramolecular nucleophilic substitutions in which the internal nucleophile is a conjugatively stabilised carbanion, *e.g.* [1a; G = $(CO_2R)_2$ or SO_2-*p*-tolyl], rates of formation of three-membered rings ($n = 1$) greatly exceed those of five-membered rings ($n = 3$) (Scheme). Further we had shown [4] that in cyclisation of carbanions from ω-halogenoalkyl sulphones, small ' element effects ' (chloride : bromide ratios) of *ca.* 2 are observed, but ' normal ' ones for four-membered ring formation ($k_{Br:Cl}$ 99) in cyclisation of ω-halogenoalkyl malonates. A critique of element effects suggests [1] these findings to be consistent with the general hypothesis [2] that closure to three-membered rings by conjugatively stabilised carbon or sulphur [1] nucleophiles proceeds with a large degree of ring formation in the transition state.

The purpose of this paper is to delineate further the transition states for carbocyclic ring formation by intramolecular nucleophilic substitution. Work has proceeded in two directions, (i) examination of the element effect, equivalent to bromide : chloride ratio, in cyclisation of ω-halogenoalkyl ketones as a function of ring size, and (ii) use of ' Hammett ' leaving groups in a variety of cyclisation systems.

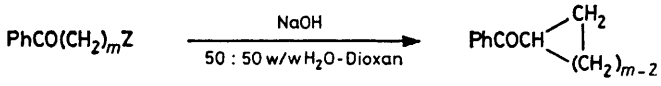
RESULTS AND DISCUSSION

Cyclisation of ω-Halogenoalkyl Ketones.—Rates of cyclisation of ω-halogenoalkyl aryl ketones (1b or c; $n = 1$ or 3) to cycloalkyl aryl ketones (2a; $n = 1$ or 3) in 50 : 50 dioxan–water have been measured with respect to the element effect. The compounds studied are in Table 1. Yields of cycloalkyl ketones are close to quantitative in all cases.

The rate constants show that formation of cyclopropanes in this system is very much faster than that of cyclopentanes, notwithstanding the very much larger degree of ring strain in the smaller ring. For the significance of the element effect (chloride : bromide ratio) to be evident, however, the mechanisms of cyclisation for each ring size must be known. For formation of the cyclopentyl ketone from 1-benzoyl-5-bromopentane, deuterium–hydrogen exchange in both starting material *and* product is observed when water is replaced in the reaction mixture by deuterium oxide. If the energy of activation for cyclisation of the derived carbanion is lower than that of the concerted deprotonation–cyclisation process, this result suggests that cyclisation of the carbanion is rate-determining. Formation of the cyclo-

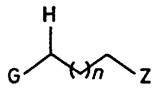
TABLE 1

Cyclisation of aryl ω-halogenoalkyl ketones



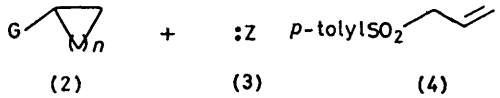
m (Ring size)	Z	Cycloalkyl ketone (%)	Other products (%)	10^5k/ l mol^{-1} s^{-1}	$k_{rel.}$
3	Cl	91	*	38 700	23 300
3	Br	98	*	80 700	48 600
5	Cl	90	~1 †	1.66	1
5	Br	91	~2 †	165	99

* Not detected. † Detected but not identified.



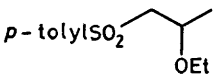
(1)

a; H = -
b; G = PhCO, Z = Cl
c; G = PhCO, Z = Br
d; G = MeCO, Z = Cl, $n = 1$
e; G = PhCO, Z = SAr, $n = 1$
f; G = PhCO, Z = $Et\overset{+}{S}$-Ar, $n = 1$
g; G = p-tolylSO$_2$, Z = $Et\overset{+}{S}$-p-tolyl, $n = 1$
h; G = p-tolylSO$_2$, Z = OSO$_2$C$_6$H$_4$-m-X, $n = 1$
i; G = PhSO$_2$, Z = OSO$_2$-p-tolyl, $n = 3$

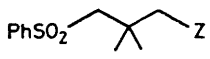


(2) (3) (4)

a; G = PhCO
b; G = PhSO$_2$, $n = 3$

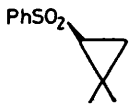


(5)



(6)

a; Z = OTs
b; Z = SPh
c; Z = $Et\overset{+}{S}$Ph



(7)

$MeSO_2CHRSO_2Ph$

(8)

a; R = H
b; R = Me

SCHEME

propyl ketone in the same deuteriated medium, however, produces hydrogen–deuterium exchange neither in starting material nor product. Failure of the *product* to incorporate the heavy isotope is not surprising in view of the results of De Boer [5] and others.[6] Failure of the starting material to incorporate the heavy isotope shows that if internal return, whose incidence is improbable in this medium with these substrates,[7] can be neglected, rate-determining cyclisation of an intermediate carbanion is not involved. Reprotonation of ketones is slow [8] by comparison with, for example, that of sulphones and nitriles. This can often make deprotonation of the substrate the rate-determining step in reactions, notably eliminations [9] in which loss of a leaving group follows a pre-equilibrium. This is evidently the case in the present instance, indicating that cyclisation is even faster than the comparison of overall rate constants for the two ring sizes implies.

In the cyclisation of 4-chlorobutyrophenone (1b; $n = 1$) to benzoylcyclopropane, the possibility exists that oxygen alkylation occurs yielding a dihydrofuran; such a species has been proposed as an intermediate in the solvolysis of γ-halogenoalkyl ketones [10] and has been obtained on pyrolysis of 3-benzoylpropyltrimethylammonium hydroxide [11] at 290 °C. We reject the possibility that a dihydrofuran can be intermediate in our reactions, however, as dihydrofuran is unstable with respect to cyclopropanal,[12] and rearranges only at high temperatures. Further, dihydrofurans have been recovered from strongly basic solutions at lower temperatures.[13]

The overwhelmingly great preference for three-membered ring *versus* five-membered ring formation was already known from the careful work of Bartsch [14] who showed that ketone (1d) on treatment with bases gave not more than 0.2% of cyclopentanone.

As loss of the leaving group in cyclopropyl ketone formation is not rate determining, no comparison of the transition states for formation of three- and five-membered rings can be made. Suffice it to say that in formation of the five-membered ring, the element effect is normal for this solvent system. It is not surprising that the element effect is close to unity in the formation of cyclopropanes; the sole difference between the chloride and the bromide is the effect of the leaving group on deprotonation, and these effects are closely similar.[15]

The very much more rapid formation of three- rather than five-membered rings in this system is consistent with ideas advanced previously.[2,16] It appears that for a carbon or sulphur nucleophile bearing an electron-acceptive conjugative group ($-R$, $-I$) a transition state of lower energy is achieved specifically for three- rather than five-membered ring formation because of the conjugative interaction between the group and the carbon–carbon bond orbitals of the three-membered ring.[17,18] Such a hypothesis requires that the extent of bond formation in the transition state should be large. The second part of this paper reports on our examination of this point.

Hammett Leaving Groups in Intra- and Inter-molecular Nucleophilic Substitution.—Use of the element effect to diagnose differential leaving group bond extension has been criticised elsewhere.[1] Use of a Hammett leaving group, susceptible to structural variation in terms of a linear free energy relationship, would be ideal. The most obvious type to meet such requirements would be to have an 'onium leaving group bearing on the hetero-atom an aryl group into which appropriate substituents can be inserted. We have tried to use a number of series.

Treatment of 3-benzoyl-1-bromopropane (1c; $n = 1$) with aromatic thiols in basic conditions gives the sulphides (1e) which gave, with triethyloxonium fluoro-

borate, the salts (1f; Ar = C_6H_4-*p*-H, -OMe, -Cl, -Me). Only the *p*-chloro and *p*-methyl compounds could be obtained crystalline. Treatment of the crystalline salts with potassium t-butoxide in t-butyl alcohol gave, in high yield, benzoylcyclopropane, together with the sulphide (3; Z = ArSEt). Deuterium exchange studies showed that deprotonation was much faster than elimination, hence reaction proceeded by a mechanism appropriate to the use of a Hammett leaving group. Our purpose, however, was frustrated in these promising instances by the failure to obtain the other starting materials in the series absolutely pure for kinetic work.

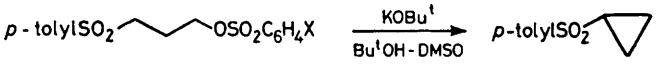
Change of the activating group G from benzoyl to *p*-tolylsulphonyl gave the crystalline sulphonium salt (1g). Treatment of the salt with potassium t-butoxide in t-butyl alcohol gave ethyl *p*-tolyl sulphide in high yield, together with 2-ethoxypropyl *p*-tolyl sulphone (5). This compound is the end-product of an initial 1,2-elimination to give *p*-tolylsulphonylpropene (4) which isomerises and undergoes addition of ethoxide ion.[19]

We attempted to block this 1,2-elimination by using the 2,2-dimethyl compound (6c). Treatment of the tosylate (6a) with benzenethiolate ion gave the cyclopropane (7) and attempts to obtain the sulphide (6b) in a pure state failed.

Our failure to find an ideal Hammett system in which the aromatic ring is connected directly to the leaving atom made us fall back on the sulphonate leaving group used satisfactorily by Cockerill[20] in studies of *E*2 reactions. Accordingly, the substrates (1h) were prepared by standard procedures. *meta*-Substituents were employed throughout to minimise the ambiguities arising from conjugative interaction with *para*-substituents.[21] These substrates in the standard base–solvent system, potassium t-butoxide in t-butyl alcohol–dimethyl sulphoxide, gave *p*-tolylsulphonylcyclopropanes in high yields, rates of reaction being obtained spectrophotometrically (Table 2). Treatment of the

TABLE 2

Cyclisation of 3-*p*-tolylsulphonylpropyl arenesulphonates



X	Yield of cyclopropane (%)	$10k$/ l mol^{-1} s^{-1} (25 °C)
H	90	3.33
m-Me	92	1.72
m-Cl	91	9.14
m-MeO	88	2.43
m-NO_2	90	40.7

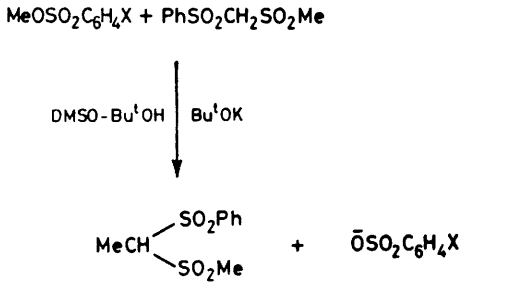
ρ 1.70; *r* 0.98; *s* 0.24

m-H and *m*-NO_2 compounds of the series under the standard reaction conditions, but using But OD, showed that the deuterium–hydrogen exchange at the methylene group adjacent to the sulphonyl group had occurred in the starting material much more rapidly than cyclisation. Deuteriation of the product was also very rapid. This establishes as before [3] that the rate-determining step is cyclisation following a rapidly established pre-equilibrium formation of the carbanion. The Hammett ρ value for cyclisation was +1.70, a value which undoubtedly comprises a small positive component attributable to the differential effects of the remote substituents on the pre-equilibrium.

The significance of this value ideally requires comparison with a corresponding value for a ' normal ' process. We have, therefore, made comparisons with two related systems to find out whether three-membered ring formation is exceptional in any respect so far as extension of the bond to the leaving group is concerned.

TABLE 3

Methylation of methylsulphonylmethyl phenyl sulphone



X	Yields of methylated sulphone (%)	10^2k/ l mol^{-1} s^{-1} (25 °C)	λ/nm
H	91	2.94	290
m-Me	92	2.52	290
m-Cl	94	11.4	305
m-MeO	91	5.45	290
m-NO_2	92	21.3	306

ρ +1.21; *r* 0.98; *s* 0.08

First, reaction of the sulphone (8a) with a series of methyl arenesulphonates, $MeOSO_2Ar$, bearing identical nuclear substituents and under identical conditions as for the compounds in Table 2 has been shown to give high yields (Table 3) of the methylated bis-sulphone (8b). Rates of reaction were obtained as before and ρ for this intermolecular system was +1.21.

The difference between these values is not large, but the Hammett leaving group is insensitive because of the large separation between the substituent and the bond undergoing cleavage. Additionally, there is evidence that for sulphonate leaving groups in methyl transfer reactions, bond cleavage to the leaving group [22] is on the low side (α values, 0.37—0.43). The difference unambiguously shows a greater degree of bond cleavage to the leaving group for the intramolecular process. The implication of this result is that bond formation is also further advanced, particularly when it is borne in mind that the nucleophilic atom and the electrophile are both closely similar in the comparison made. This conclusion accords with the suggestion [2] that the rapidity of certain three-membered ring closures is a consequence of

transition-state stabilisation by interaction of an electron-acceptive conjugative substituent and a cyclopropane ring which is substantially formed in the transition state.

Very recently Buncel and Chuaqui [23] have examined nucleophilic displacement at the methyl group of a series of aryl methyl sulphates and also find small values of ρ (1.34—0.74) varying with the reactivity of the nucleophile.

A further crucial comparison is that with five-membered rings, for which the element effect was found to be normal (99) in formation of cycloalkyl ketones (Table 1). We have examined the cyclisation of 5-phenylsulphonylpentyl toluene-*p*-sulphonate (1i) under the conditions used for the intermolecular and three-membered ring series. G.l.c. analysis of a mixture of products showed that, at most, only *ca.* 25% of phenylsulphonylcyclopentane (2b) was obtained. This result emphasises again [4] the comparatively low tendency for a five-membered ring to be formed in competition with 1,2-elimination. In ethanolic sodium ethoxide, the sole product (92%) was 5-ethoxypentyl phenyl sulphone, the result of *inter*-molecular nucleophilic displacement.

Conclusions.—In reactions of carbanions as nucleophiles in intramolecular nucleophilic displacement reactions, cyclopropanes are much more readily formed than cyclopentanes. For enolates, cyclisation is so rapid that the rate-determining step is deprotonation of the ketone. For sulphonyl stabilised carbanions, formation of cyclopropanes excludes the competing 1,2-elimination which dominates in the competition with formation of sulphonylcyclopentanes.

The substantial preference for three-membered ring formation is consistent with interaction between the forming cyclopropane ring and the electron-acceptive conjugative group in the transition state. The quantitative significance of such interactions is however obscure.[24] We entirely endorse the statement,[25] ' It is clear that (in such systems) rate predictions based on classical explanations are of limited value.'

EXPERIMENTAL

General.—Unless otherwise stated, extracts were of dichloromethane and were dried over $MgSO_4$. Light petroleum had b.p. 40—60 °C. Dioxan was refluxed over sodium and distilled.

1-Benzoyl-3-chloropropane (1b; $n = 1$) had b.p. 152 °C at 13 mmHg, n_D^{20} 1.5488 (lit.,[9] b.p. 106—107 °C at 1.1 mmHg, n_D^{20} 1.5488). 1-Benzoyl-5-chloropentane (1b; $n = 3$) had b.p. 176 °C at 13 mmHg, m.p. 29—30 °C (lit.,[26] m.p. 29—30 °C). 1-Benzoyl-3-bromopropane (1c; $n = 1$) had m.p. 38 °C (from pentane) (lit.,[27] m.p. 38—38.5 °C). Benzoylcyclopropane (2a) had b.p. 120 °C at 13 mmHg, n_D^{20} 1.5530 (lit.,[28] b.p. 102 °C at 7 mmHg, n_D^{25} 1.5514).

1-*Benzoyl-5-bromopentane* (1c; n = 3).—1-Benzoyl-5-chloropentane (8 g) was heated under reflux with anhydrous lithium bromide (40 g) in a mixture of dry butanone (50 ml) and t-butyl alcohol (10 ml) for 12 h. After removal of solvent, water and dichloromethane were added and the organic extracts on evaporation gave the *bromo-ketone* (82%), m.p. 36—37 °C (from light petroleum) (Found: C, 56.8; H, 5.8; Br, 31.6. $C_{12}H_{15}BrO$ requires C, 56.5; H, 5.9; Br, 31.4%).

TABLE 4

3-*p*-Tolylsulphonylpropyl arenesulphonates (1h)

X	M.p. (°C)	Solvent for recrystallisation	Yield [a] (%)	Found (%) C	Found (%) H	Formula	Required (%) C	Required (%) H
H	70	EtOH	68	54.3	5.2	$C_{16}H_{18}O_5S_2$	54.2	5.1
m-Me	51	Et_2O	95	55.3	5.5	$C_{17}H_{20}O_5S_2$	55.4	5.4
m-Cl	65	$Pr^i{}_2O$	50	49.2	4.3	$C_{16}H_{17}ClO_5S_2$	49.5	4.4
m-MeO	75	$Pr^i{}_2O$	67	53.5	5.1	$C_{17}H_{20}O_6S_2$	53.1	5.2
m-NO_2	128	$Pr^i{}_2O$	58	48.1	4.2 [b]	$C_{16}H_{17}NO_7S$	48.1	4.3 [c]

[a] From crude sulphide-sulphonate. [b] N, 3.5%. [c] N, 3.5%.

The bromo-ketone (0.20 g) was kept with 50 : 50 w/w dioxan–water (50 ml) containing sodium hydroxide (0.035 g, 2 mol) for 36 h at 60 °C. Addition to saturated brine and extraction gave benzoylcyclopentane (150 mg, 91%). G.l.c. of the residue before distillation showed two peaks in the ratio 50 : 1. The minor (longer retention time) peak was not identified. Other analyses of products from ketones (1b and c) were carried out similarly.

The bromo-ketone showed no hydrogen–deuterium exchange (^1H n.m.r.) when kept with 50 : 50 w/w dioxan–deuterium oxide at 25 °C for 12 h, but when sodium deuterioxide (50 mol%) was added and the solution was kept at 25 °C for 3 h, the recovered material was starting material and benzoylcyclopentane in approximately equal amounts (g.l.c.; Apiezon; 210 °C). The ^1H n.m.r. spectrum showed no triplet signal at τ 6.95 ($COCH_2$) and no multiplet at τ 6.2 (methine proton of the cyclopentyl ring).

Reaction of 1-Benzoyl-3-bromopropane with Sodium Deuterioxide in Dioxan–Water.—Treatment of the ketone as in the preceding experiment gave a mixture of the cyclopropyl ketone and unreacted starting material in which ^1H n.m.r. showed no exchange of protons adjacent to the carbonyl group in either compound.

Kinetics.—Reactions were followed by quenching portions of pre-thermostatted mixtures of halogeno-ketone and sodium hydroxide in 50 : 50 w/w H_2O–dioxan with acetate buffer (pH 4.6) and subsequently determining halide ion potentiometrically in a darkened vessel.

3-p-*Tolylsulphonyl Arenesulphonates.*—3-*p*-Tolylthiopropan-1-ol [29] was treated with benzenesulphonyl chloride in pyridine at 0 °C to give the *ester* (47%), m.p. 47 °C (from toluene–light petroleum) (Found: C, 59.7; H, 5.7. $C_{16}H_{18}S_2O_3$ requires C, 59.6; H, 5.6%). The ester was oxidised with 30% aqueous hydrogen peroxide–ammonium molybdate in methanol giving the *sulphone-sulphonate* (68%), m.p. 70 °C raised to 74 °C (from ethanol). Details of other sulphone esters prepared similarly are in Table 4.

Cyclisation of Sulphone Sulphonate Esters.—3-*p*-Tolyl-

sulphonylpropyl benzenesulphonate (1h; X = H) (1 g) in t-butyl alcohol (37 ml) and dimethyl sulphoxide (6 ml) was treated with a 0.5M-solution of potassium t-butoxide in t-butyl alcohol (17 ml). After 24 h at 40 °C, the mixture was neutralised (HCl) and poured into saturated brine. Extraction gave a residue which on dry column chromatography (Woelm dry column grade SiO_2; activity III) using 70 : 30 ether–light petroleum gave cyclopropyl *p*-tolyl sulphone (0.50 g, 90%), m.p. 66 °C (from methanol) (lit.,[29] m.p. 65—66 °C). Other esters were treated similarly. Yields are in Table 2.

Kinetics.—Reactions were followed spectrophotometrically at 30 °C using the Guggenheim treatment of absorbance–time data to deal with unstable infinity values. Data were processed *via* a multi-channel analyser connected to a teletype with punched tape output.

was separated by p.l.c. to give the sulphide (205 mg, 87%), b.p. 83 °C at 0.1 mmHg, n_D^{17} 1.5540 (lit.,[31] n_D^{20} 1.555) and the ketone (190 mg, 85%), b.p. 127 °C at 15 mmHg, n_D^{20} 1.5530. The reaction was repeated using sodium deuteroxide in deuterium oxide. After removal of covalent products (Et_2O), ^1H n.m.r. spectra of the reaction mixture showed the absence of signals at τ 6.6 (CH_2 adjacent to CO).

The rate of cyclisation in aqueous sodium hydroxide at 25 °C was followed by u.v. spectroscopy at 250 nm. An isosbestic point was present at 242 nm. The mean rate constant, 2.26 l mol^{-1} s^{-1}, was obtained from five runs with variation of both [base] and [substrate].

3-Benzoylpropyl-(4-chlorophenyl)ethylsulphonium tetrafluoroborate (1f; Ar = p-ClC_6H_4). 4-Chlorobenzenethiol (51 mmol) in ethanolic 0.92M-sodium ethoxide (55 ml) was added dropwise to 1-benzoyl-3-bromopropane (51 mmol) in

TABLE 5

Methyl arenesulphonates, $MeOSO_2C_6H_4X$

X	Yield (%)	B.p. (°C)	*p*/mmHg	n_D^{20}	Found (%) C	Found (%) H	Formula	Required (%) C	Required (%) H
H	79	83	0.1	1.5174 (lit.,[a] 1.5151)					
m-Me	69	95	0.1	1.5187	51.7	5.5	$C_8H_{10}O_3S$	51.6	5.4
m-MeO	37	116	0.1	1.5304	47.0	5.0	$C_8H_{10}O_4S$	47.5	5.0
m-Cl	70	101	0.1	1.5342	40.6	3.4	$C_7H_7ClO_3S$	40.7	3.4
m-NO_2	81	89 [b]			38.4	3.3 [c]	$C_7H_7NO_5S$	38.7	3.2 [d]

[a] R. E. Robertson, *Can. J. Chem.*, 1953, **31**, 589. [b] M.p. [c] N, 6.4%. [d] N, 6.5%.

Methyl Arenesulphonates.—Methanolic 0.66M-sodium methoxide (150 ml) was added over 2 h with stirring to the sulphonyl chloride (0.1 mol) in tetrahydrofuran (100 ml) at 25 °C. The neutral solution was poured into saturated brine and extraction gave the ester. Details are in Table 5.

Methylation of Methylsulphonyl(phenylsulphonyl)methane.—The sulphone (8a)[30] (4.27 mmol) and potassium t-butoxide (8.15 mmol) in a mixture of t-butyl alcohol (8.15 ml) and dimethyl sulphoxide (5 ml) was added to the methyl arenesulphonate (8.5 mmol) in t-butyl alcohol (20 ml) at 40 °C. After 12 h, the mixture was poured into saturated brine. Extraction gave a mixture of the product and excess of ester, which were separated by p.l.c. on silica. The lower R_F band gave the methylated *bis-sulphone* (91%), m.p. 103 °C (from methanol) (Found: C, 43.5; H, 4.9. $C_9H_{12}O_4S$ requires C, 43.5; H, 4.8%). Other yields are in Table 3.

Kinetics.—Reactions were followed spectroscopically at the wavelengths given in Table 3, decrease in absorbance corresponding to the decreasing concentration of bis-sulphonyl carbanion. The space above the solutions in the cells was flushed with oxygen-free nitrogen before thermostatting.

3-Benzoylpropyl(ethyl)arylsulphonium Salts.—*3-Benzoylpropyl(ethyl)-*p*-tolylsulphonium tetrafluoroborate* (1f; Ar = p-*tolyl*). 3-Benzoylpropyl *p*-tolyl sulphide[1] (22 mmol) was treated at 0 °C under N_2 in dry CH_2Cl_2 (50 ml) with triethyloxonium fluoroborate (33 mmol). After 12 h, addition of dry ether precipitated the *salt* (58%), m.p. 80—82 °C (decomp.) (from chloroform–ether) (Found: C, 59.3; H, 5.9; S, 8.3. $C_{19}H_{23}BF_4OS$ requires C, 59.1; H, 6.0; S, 8.3%).

Treatment of the salt (0.60 g) in water (40 ml) with aqueous 1M-sodium hydroxide (2 ml) at 25 °C for 48 h, gave, on extraction and distillation (b.p. 100 °C at 13 mmHg) an equimolecular mixture (0.43 g, 94%) of ethyl *p*-tolyl sulphide and benzoylcyclopropane (^1H n.m.r.). The mixture ethanol (60 ml) under nitrogen. The solution was heated under reflux for 2 h when addition of acidified (HCl) saturated brine and extraction gave the *oxo-sulphide* (66%), m.p. 51 °C (Found: C, 66.4; H, 5.1. $C_{16}H_{15}ClOS$ requires C, 66.1; H, 5.2%). Ethylation of the sulphide as before gave the sulphonium salt (72%), m.p. 66—68 °C (decomp.) (from acetone–ether) (Found: C, 53.1; H, 5.0. $C_{18}H_{20}BClF_4OS$ requires C, 53.2; H, 4.9%).

The salt in ethanolic 0.36M-sodium ethoxide gave, as for the preceding salt, *p*-chloroethyl phenyl sulphide (85%) and benzoylcyclopropane (85%).

3-Benzoylpropyl(ethyl)-4-methoxyphenylsulphonium tetrafluoroborate (1f; Ar = p-$MeOC_6H_4$). 4-Methoxybenzenethiol[32] reacted as before with 1-benzoyl-3-bromopropane to give the oxo-sulphide (75%), b.p. 187 °C at 0.05 mmHg, n_D^{21} 1.5975, which was methylated directly with triethyloxonium fluoroborate to give an oily sulphonium salt, which on treatment with saturated ethanolic picric acid gave the *sulphonium picrate* (38%), m.p. 98 °C (from ethanol) (Found: C, 55.5; H, 4.7; N, 7.9. $C_{25}H_{25}O_9N_3S$ requires C, 55.2; H, 4.6; N, 7.7%).

*Ethyl-(3-*p*-tolylsulphonylpropyl)-*p*-tolylsulphonium benzenesulphonate.* 3-Bromopropyl *p*-tolyl sulphone[4] (10 g) in ethanol (300 ml) under nitrogen was treated with toluene-*p*-thiol (5 g) and ethanolic 0.12M-sodium ethoxide (345 ml). After 1 h at 80 °C, the usual work-up gave the *sulphone-sulphide* (87%), m.p. 48 °C (from light petroleum) (Found: C, 63.4; H, 6.3. $C_{17}H_{20}O_2S_2$ requires C, 63.7; H, 6.3%). The sulphide (2.2 g) was treated with triethyloxonium fluoroborate (2.6 g) in dry dichloromethane. After 4 h, dry ether was added to the solution at 0 °C and the precipitated oil in dry chloroform (12 ml) was shaken with potassium benzenesulphonate (6.8 g) for 12 h. Extraction with chloroform and evaporation gave the *salt* (60%), m.p. 115 °C (decomp.) (from methanol) (Found: C, 59.0; H, 5.9; S, 18.9. $C_{25}H_{31}O_5S_3$ requires C, 59.3; H, 5.9; S, 19.0%).

The salt, in ethanolic 0.152M-sodium ethoxide (20 ml), was kept at 25 °C for 48 h. The mixture was neutralised (HCl), reduced in volume to 5 ml, poured into water, and extracted. Distillation gave first ethyl *p*-tolyl sulphide (91%), b.p. 80 °C at 0.04 mmHg, n_D^{17} 1.5538, then 2-ethoxypropyl *p*-tolyl sulphone (91%), b.p. 136 °C at 0.05 mmHg, m.p. 75—76 °C (from methanol), alone or mixed with an authentic specimen.[19] G.l.c. of the crude product before distillation showed no cyclopropyl *p*-tolyl sulphone.

Attempted Preparation of 2,2-Dimethyl-1-phenylthio-3-phenylsulphonylpropane (6b).—2,2-Dimethylpropane-1,3-diol (50 g) was added slowly to toluene-*p*-sulphonyl chloride in dry pyridine at 5 °C. After 90 h, extraction as usual gave the *bis-ester* (170 g, 86%), m.p. 122 °C (from toluene) (Found: C, 55.1; H, 5.8. $C_{19}H_{24}O_6S_2$ requires C, 55.3; H, 5.8%).

The bis-ester (50 g) in ethanol (720 ml) was heated under reflux with benzenethiol (13.4 g) and sodium ethoxide (8.9 g) for one week. The usual work-up gave the *sulphide-toluene*-p-*sulphonate* (57%), m.p. 69 °C (from toluene) (Found: C, 62.0; H, 6.4. $C_{18}H_{22}O_3S_2$ requires C, 62.0; H, 6.3%).

The preceding compound (3 g) was treated with aqueous 30% hydrogen peroxide (22.5 ml) and ammonium molybdate (1 g) in 10% w/v water–methanol (200 ml) for 24 h at 20 °C. The usual work-up gave the *sulphone-ester* (6a) (95%), m.p. 56 °C (from methanol) (Found: C, 56.9; H, 5.9. $C_{18}H_{22}O_5S_2$ requires C, 56.5; H, 5.8%).

The sulphone-ester (1 g) in ethanol (10 ml) was heated under reflux with benzenethiol (0.29 g) in ethanolic M-sodium ethoxide (3 ml) under nitrogen for 5 days. The usual work-up and p.l.c. of the crude residue gave 1-phenylsulphonyl-2,2-dimethylcyclopropane (7) (61%), identical with an authentic specimen.[33]

5-Phenylsulphonylpentyl Toluene-p-*sulphonate*.—5-Chloropentyl acetate [34] (5 g) was added to sodium benzenethiolate (1.1 mol) in ethanol and the mixture was kept at 80 °C under nitrogen for 2 h. Usual work-up gave the sulphide-acetate (100%), b.p. 135 °C at 0.4 mmHg, n_D^{20} 1.5373 (Found: C, 65.2; H, 7.3. $C_{13}H_{18}O_2S$ requires C, 65.5; H, 7.5%). Oxidation of the sulphide (3.58 g) with hydrogen peroxide and ammonium molybdate as before gave the oily *sulphone* (4.00 g) ($\nu_{SO_2\ str.}$ 1 300 and 1 150 cm^{-1}) (Found: C, 57.8; H, 6.1. $C_{13}H_{18}O_4S$ requires C, 57.8; H, 6.6%) which (2.7 g) was hydrolysed with methanolic sodium hydroxide (0.11 mol) to give, after p.l.c. of the crude product, the alcohol (1 g) ($\nu_{OH\ str.}$ 3 500 cm^{-1}) (Found: C, 58.4; H, 6.8. $C_{11}H_{16}O_3S$ requires C, 57.9; H, 7.0%). Tosylation of the alcohol with toluene-*p*-sulphonyl chloride in pyridine at −5 °C gave the *sulphonate ester* (67%), m.p. 71 °C (from methanol) (Found: C, 55.0; H, 5.9. $C_{18}H_{22}O_5S_2$ requires C, 56.5; H, 5.8%), τ 2.0—2.8 (9 H, m), 6.00 (2 H, t), 6.92 (2 H, t), 7.55 (3 H, s), and 8.4 (6 H, m). The microanalysis for carbon was consistently low even after exhaustive recrystallisation and variation of conditions in the microanalytical procedure. T.l.c. showed homogeneous material. The ester (0.2 g) with potassium t-butoxide (5 ml of 0.2M-solution in t-butyl alcohol) and dimethyl sulphoxide (1 ml) was kept for 6 h at 50 °C. Neutralisation and extraction gave a residue (0.16 g) which on g.l.c. (SE 30 at 220 °C) showed four compounds to be present. One peak (25.8% of total eluate integration) was identical in retention time with authentic phenylsulphonylcyclopentane [35] but the i.r. spectrum of this sulphone showed strong absorption at 900 cm^{-1} which was entirely absent from the spectrum of the product mixture.

When the sulphonate was treated with ethanolic 0.1M-sodium ethoxide under the same conditions, the product (92%; one peak only on g.l.c.) was 1-ethoxy-5-phenylsulphonylpentane, τ ($CDCl_3$) 2.0—2.8 (5 H, m), 6.2—6.8 (6 H, m), 8.5br (6 H, s), and 8.8 (3 H, t) (Found: C, 61.2; H, 7.5. $C_{13}H_{20}O_3S$ requires C, 60.9; H, 7.8%).

Phenylsulphonylcyclopentane (92%), m.p. and mixed m.p. 62 °C, was recovered from the product of the reaction of the toluene-*p*-sulphonate with $KOBu^t$ in Bu^tOH–DMSO.

We thank the S.R.C. for studentships (to R. B. and G. F. G.) and equipment.

[1/1415 *Received*, 9*th September*, 1981]

REFERENCES

[1] Part 11, R. Bird and C. J. M. Stirling, *J. Chem. Soc., Perkin Trans. 2*, 1973, 1221.
[2] A. C. Knipe and C. J. M. Stirling, *J. Chem. Soc. B*, 1968, 67.
[3] R. Bird and C. J. M. Stirling, *J. Chem. Soc. B*, 1968, 111.
[4] A. C. Knipe and C. J. M. Stirling, *J. Chem. Soc. B*, 1967, 808.
[5] W. T. van Wijnen, H. Steinberg, and T. J. De Boer, *Recl. Trav. Chim. Pays-Bas*, 1968, **87**, 844; *Tetrahedron*, 1972, **28**, 5423.
[6] H. Rappe and W. H. Sachs, *Tetrahedron*, 1968, **24**, 6287.
[7] P. J. Thomas and C. J. M. Stirling, *J. Chem. Soc., Perkin Trans. 2*, 1977, 1909.
[8] R. P. Bell, 'The Proton in Chemistry,' Chapman and Hall, London, 1973, 2nd edn., ch. 10.
[9] D. R. Marshall, P. J. Thomas, and C. J. M. Stirling, *J. Chem. Soc., Perkin Trans. 2*, 1977, 1914.
[10] D. J. Pasto and M. P. Serve, *J. Am. Chem. Soc.*, 1965, **87**, 1515; S. Oae, *ibid.*, 1956, **78**, 4030.
[11] H. W. Bersch, R. Meyer, A. v. Mletzko, and K. H. Fischer, *Arch. Pharm.*, 1958, **291**, 82.
[12] C. L. Wilson, *J. Am. Chem. Soc.*, 1947, **69**, 3002.
[13] C. L. Wilson, *J. Chem. Soc.*, 1945, 52.
[14] R. A. Bartsch and D. M. Cook, *J. Org. Chem.*, 1970, **35**, 1714.
[15] J. Hine, 'Structural Effects on Equilibria in Organic Chemistry,' Wiley, New York, 1975, p. 91.
[16] C. J. M. Stirling, *J. Chem. Educ.*, 1973, **50**, 844.
[17] W. G. Dauben and G. H. Berezin, *J. Am. Chem. Soc.*, 1967, **89**, 3449.
[18] R. Hoffmann and R. B. Davidson, *J. Am. Chem. Soc.*, 1971, **93**, 5699; D. Bischof, R. Gleiter, A. de Meijere, and L.-U. Meyer, *Helv. Chim. Acta*, 1974, **57**, 1519; P. Bruckmann and M. Klessinger, *Chem. Ber.*, 1974, **107**, 1108.
[19] A. T. Kader and C. J. M. Stirling, *J. Chem. Soc.*, 1962, 3686.
[20] J. Banger, A. F. Cockerill, and G. L. O. Davies, *J. Chem. Soc. B*, 1971, 498.
[21] H. van Bekkum, P. E. Verkade, and B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, 1959, **78**, 815.
[22] W. J. Albery and M. M. Kreevoy, *Adv. Phys. Org. Chem.*, 1978, **16**, 87.
[23] E. Buncel and C. Chuaqui, *J. Org. Chem.*, 1980, **45**, 2825.
[24] A. Greenberg and J. F. Liebman, 'Strained Organic Molecules,' Academic Press, New York, 1978, Section 5E2.
[25] D. F. De Tar and W. Brooks, *J. Org. Chem.*, 1978, **43**, 2245.
[26] J. W. Wilt and J. W. Hill, *J. Org. Chem.*, 1961, **26**, 3523.
[27] G. Baddeley and R. Williamson, *J. Chem. Soc.*, 1956, 4647.
[28] R. P. Mariella and R. R. Raube, *J. Am. Chem. Soc.*, 1952, **74**, 521.
[29] W. E. Truce and L. B. Lindy, *J. Org. Chem.*, 1961, **26**, 1463.
[30] H. Bohme and P. Heller, *Chem. Ber.*, 1953, **86**, 785.
[31] Beilstein's 'Handbuch der Organischen Chemie,' Springer, Berlin, 1966, 3rd suppl., vol. 6, p. 1395.
[32] C. M. Suter and H. L. Hansen, *J. Am. Chem. Soc.*, 1932, **54**, 4100.
[33] B. Issari and C. J. M. Stirling, unpublished work.
[34] R. Chretien, *Ann. Chim.* (*Paris*), 1957, **2**, 682.
[35] W. E. Truce, K. R. Hollister, L. B. Lindy, and J. E. Parr, *J. Org. Chem.*, 1968, **33**, 43.