Elimination–Addition. Part XII.¹ Rates of Addition of Amines to Alkenyl, Allenyl, and Alkynyl *p*-Tolyl Sulphones

By S. T. McDowell and C. J. M. Stirling,* Queen's University, Belfast

Rates of addition of amines to a series of αβ-unsaturated amines have been determined for reactions in ethanol at temperatures between 5 and 45°.

Replacement of a β -hydrogen atom in ρ -tolyl vinyl sulphone by a methyl group reduces the reactivity of the double bond towards piperidine by a factor of 840. Similar replacement of an α -hydrogen atom reduces the reactivity by a factor of 6500. The operative factors are discussed and the steric contribution towards deactivation by a β-methyl group has been assessed.

Piperidine did not add to isobutenyl p-tolyl sulphone but catalysed its conversion into the methylallyl isomer. The same behaviour was found in reactions with sodium ethoxide, but no reaction occurred with sodium benzenesulphinate. Thiophenoxide gave the normal adduct.

Rates of addition of piperidine to prop-1-ynyl, prop-2-ynyl, and propadienyl p-tolyl sulphone have been determined. Reaction with the terminal acetylene is preceded by isomerisation to the allene. Such a pathway is excluded for the non-terminal acetylene by the absence of base catalysis, and this sulphone is less than one tenth as reactive as its isomers.

IN Parts X² and XI¹ reactions of amines with aryl vinyl sulphones were examined with respect to the effects on reactivity of the basicity and steric requirements of the amine, and to the electronic effects of substituents in the aromatic nucleus of the sulphone. We now report the reactivities towards amines of homologues (II-IV) of the simple vinyl sulphone (I) studied ² previously; we have also measured the reactivities of the series of acetylene-allene isomers (V--VII).

(I) $Ar \cdot SO_2 \cdot CH \cdot CH_2$	(V) Ar•SO2•CH2•C•CH
(II) Ar•SO ₂ •CH:CH•Me (trans)	(VI) Ar•SO2•CH:C:CH2
(III) Ar·SO ₂ ·C(Me):CH ₂	(VII) Ar•SO ₂ •C•C•Me
(IV) Ar•SO ₂ •CH•C(Me) ₂	$(Ar = p - Me \cdot C_{s}H_{4} \cdot)$

Previous work³ showed that alkyl groups situated β to the activating group retard nucleophilic additions to double bonds, but few kinetic data are available. Morton and Landfield⁴ showed that in additions of sulphite ion to acrylic esters, β -methylation raised the energy of activation by 6 kcal./mole and caused a twohundred-fold reduction in the PZ factor. Similarly, that pent-3-en-2-one is 5.6 times as reactive ⁵ towards hydroperoxide ion as 4-methylpent-3-en-2-one. α -Methylation is also reported ⁶ to depress the reactivity of $\alpha\beta$ -unsaturated esters towards amines.

RESULTS AND DISCUSSION

We examined first the series of olefinic sulphones (I)—(IV) in reactions with piperidine. The overall reaction is

$$Ar \cdot SO_2 \cdot C: C' + HN \longrightarrow Ar \cdot SO_2 \cdot C - C - N$$

Reaction rates were measured as described earlier² and determinations at least three temperatures for each sulphone allowed us to evaluate the reaction parameters (Table 1). Piperidine did not react with sulphone (IV) (see later).

TABLE 1

Mean rate constants and activation parameters for additions of piperidine to unsaturated sulphones at 25°

	104k			
	(l. mole ⁻¹	ΔE^{\ddagger}	ΔS^{\ddagger}	ΔG_{25}°
Sulphone	sec1)	(kcal./mole)	(e.u.)	(kcal./mole)
(I)	5850 ± 20	6.6 ± 0.5	-41 ± 1	18.4 ± 0.8
(II)	7.00 ± 0.03	$7\cdot3\pm0\cdot1$	-52 ± 1	$22 \cdot 2 \pm 0 \cdot 4$
(III)	0.90 ± 0.03	10.1 ± 0.2	-47 ± 1	$23\cdot 6 \pm 0\cdot 6$

The effect of alkylation in decreasing the reactivity of the double bond is clear. At least three factors may be responsible: (i) an increase in non-bonded interaction between the nucleophile and the olefin, (ii) additional stabilisation of the olefin in the ground state by hyperconjugative interaction with the methyl group, and (iii) destabilisation, by electron accession from the methyl group, of the carbanionic centre developed in the transition state.

The steric factor (i) will affect the β -methyl homologue to a much greater extent than the α -methyl isomer, and this type of reaction is known² to be very sensitive to steric effects.

The olefin stabilisation (ground state) factor might be expected to affect both isomers to a comparable extent, but in fact it appears to be significant only in the β -methyl isomer (II). Thermochemical measurements ⁷ have been carried out on sulphones (I-III). The standard gas-phase heats of formation have been evaluated from the heats of combustion 8 and the groundstate heats of atomisation derived from them have been compared with calculated values derived from Mackle and O'Hare's ⁸ bond-energy scheme and its later

⁴ M. Morton and H. Landfield, J. Amer. Chem. Soc., 1952, 74, 3523.

^{*} Present address: Department of Chemistry, King's College, London W.C.2.

¹ Part XI, S. T. McDowell and C. J. M. Stirling, preceding

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³ C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p. 693.

⁵ C. A. Bunton and G. J. Minkoff, J. Chem. Soc., 1949, 665. ⁶ K. L. Mallik and M. N. Das, Z. phys. Chem. (Frankfurt),

^{1960, 25, 205.} H. Mackle, D. McNally, and W. V. Steele, unpublished work.

⁸ H. Mackle and P. A. G. O'Hare, Trans. Faraday Soc., 1961, 57. 1521.

revisions.9 The discrepancies between the observed and calculated values (ΔQ) show destabilisation energies of -4.0 and -4.5 kcal./mole for compounds (I) and (III), respectively, but of only -0.4 kcal./mole for the β -methyl analogue (II). It appears that the destabilisation of the double bond caused by its direct attachment to the sulphonyl group ¹⁰ is offset appreciably when a β -methyl but not an α -methyl group is also attached to it.

Destabilisation of the incipient carbanion, factor (iii), is much more serious in the α -methyl isomer (III) in which the methyl group is attached directly to the developing carbanionic centre.

The results in Table 1 show that the combination of factors more effectively retards addition to the α -methyl isomer and indicate that the carbanion-destabilising effect of an α -methyl group has a greater influence on rates of addition than the combination of the adverse steric and olefin stabilisation effects of a β -methyl group.

In the β -methyl homologue, the relative effects of olefin stabilisation and steric hindrance to addition are not easy to assess. We have compared the reactivities of piperidine and of di-n-butylamine towards the vinyl (I) and trans-propenyl (II) sulphones. We reasoned that the difference in reactivity between these amines towards the vinyl sulphone could largely be due to steric effects. The amines are both secondary, are of comparable basicity, and probably have comparable degrees of solvation in ethanol. If, therefore, the steric contribution to the low reactivity of the propenyl sulphone with piperidine is significant, an even greater differential in reactivity between the vinyl and propenyl sulphones towards di-n-butylamine should be manifested. This is found to be so; the value of $k_{\text{vinyl}}/k_{\text{propenyl}}$ for piperidine is 835 at 25° while that for di-n-butylamine is 3150 at 25° . We consider that this result indicates a considerable steric contribution to the reduced reactivity of the propenyl homologue.

Throughout the series, entropies of activation are very negative. This is, of course, expected for adduct formation from neutral species but the magnitudes of the values point to a highly ordered transition state and suggest, in conjunction with the high sensitivity of the system to the steric demands of the reagents and the relatively high value ¹ of ρ (+1.58) for the reactions with aryl vinyl sulphones, that bond formation in the transition state is well advanced. Very negative entropies of activation have also been found ¹¹ for additions of tertiary amines to tricyanovinyl chloride. The somewhat less negative entropy of activation found for the α -methyl compound (III) than for the β -analogue possibly reflects the smaller contribution of non-bonded interactions between substrate and nucleophile to the free energy of activation.

- ¹⁰ D. E. O'Connor and W. I. Lyness, J. Amer. Chem. Soc., 1964, 86, 3840.
- ¹¹ Z. Rappoport, P. Greenzaid, and A. Horowitz, J. Chem. Soc., 1964, 1334.
 ¹² K. Mackenzie in "Alkenes," ed. S. Patai, Interscience,
- New York, 1964.

The ßß-dimethyl homologue (IV) did not add piperidine; instead, the sole product was the isomer (VIII). The failure of this compound to undergo addition must

be accounted for in terms of the joint effect of olefin stabilisation by two methyl groups and of the sterically unfavoured reaction site. Further, addition has to compete with isomerisation of the $\alpha\beta$ - to the $\beta\gamma$ -unsaturated sulphone. The latter is not susceptible to nucleophilic addition. Equilibria of this type have been studied by O'Connor and Lyness 10 who showed that a sulphonyl group destabilises an αβ-double bond. In the case of the $\beta\beta$ -dimethylolefin, the *cis*-interaction ¹² between the sulphonyl group and a methyl group will also exacerbate the tendency towards isomerisation. Likewise, cyclohexenyl p-tolyl sulphone (IX) failed to add to piperidine. This compound combines the adverse characteristics of both α - and β -alkylation and our observations substantiate earlier work ¹³ on related αβ-dialkyl $\alpha\beta$ -unsaturated sulphones.

It was of interest to discover whether isomerisation was the predominant mode of reaction of the sulphone (IV) with a variety of types of necleophile. Arenesulphinate ions,¹⁴ thiophenoxide ions,¹⁵ and alkoxide ions ¹⁶ all add readily to $\alpha\beta$ -unsaturated sulphones so we examined their reactions with the $\beta\beta$ -dimethyl sulphone (IV). Benzenesulphinate ion in ethanol buffered with acetic acid 17 did not react with the sulphone even after long periods. This nucleophile is both weakly basic and weakly reactive and as additions of this nucleophile are reversible,18 failure to form an adduct is understandable. Ethoxide ion is strongly basic but only moderately nucleophilic towards this type of centre,¹⁹ and isomerisation to the $\beta\gamma$ -unsaturated sulphone is again the only observed reaction. Thiophenoxide, by contrast, is a powerful but feebly basic nucleophile and in this case the adduct (X) is formed in high yield as addition is favoured with respect to isomerisation. Our results with this sulphone do not accord with observations made by Backer, Strating, and Drenth ¹³ on the closely related compound (IV; Ar =CH₂Ph). They reported that both hydroxide and ethoxide ions added normally, albeit in low yield, to this sulphone but that no addition was observed with thiophenoxide or with piperidine. In the latter instance, they did not report whether isomerisation of the sulphone had occurred.

¹³ H. J. Backer, J. Strating, and J. Drenth, Rec. Trav. chim.,

 1951, 70, 377.
 ¹⁴ A. T. Kader and C. J. M. Stirling, J. Chem. Soc., 1962, 3686.
 ¹⁵ A. H. Ford-Moore, R. A. Peters, and R. W. Wakelin, J. Chem. Soc., 1949, 1754.

 ¹⁶ C. J. M. Stirling, *Chem. and Ind.*, 1960, 933.
 ¹⁷ C. J. M. Stirling, *J. Chem. Soc.*, 1964, 5856.
 ¹⁸ W. E. Truce and E. Wellisch, *J. Amer. Chem. Soc.*, 1952, 74, 5177.

¹⁹ C. J. M. Stirling, J. Chem. Soc., 1964, 5863.

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Reactions with Acetylene-Allene Isomers.-Additions of amines to acetylenic and allenic sulphones have been reported.¹⁹⁻²² 1:1-Adducts are formed in high yields from each isomer (V—VII; Ar = Ph), and with secondary amines only trans-enamines, such as (XI), are formed. It was further shown by labelling experiments that the trans-enamine is produced either by isomerisation of the acetylenes (V) and (VII) to the allene (VI) before addition [the allene is known from both equilibrium studies ¹⁹ and thermochemistry 7 (Table 2) to be the most stable member of the series] or by isomerisation of the adducts initially formed. It was considered probable that the terminal actylene (V) isomerises to the allene before addition, as nucleophilic addition to an unactivated triple bond would not be expected to occur in the conditions used.



We have now measured the rates of formation of the adduct (XI) obtained from each of the three isomers (V-VII) and piperidine; an ultraviolet spectroscopic method was used. Results are in Table 2. Adduct

TABLE 2

Rates of addition of piperidine to acetylenic and allenic sulphones

Sulphone	$10^{3}k_{2}$ (l. mole ⁻¹ sec. ⁻¹) (mean)	$\Delta H_{\rm f}^{\circ}$ (gas) (kcal./mole)
(V)	387 + 1	-4.5 ± 0.9
(ÌIÍ)	388 + 10	-15.5 ± 1.1
(ÌII)	$36.9 \pm 0.3; \ 37.6 \ a \pm 0.3; \ 37.7 \ b \pm 0.3$	$-2\cdot 3 \pm 1\cdot 0$

^a In the presence of 1.75 mole of N-methylpyrrolidine per mole of acetylene. ^b In the presence of 7 moles of N-methylpyrrolidine per mole of acetylene.

formation from the terminal acetylene (V) and the allene (VI) occurs at the same rate within experimental error. We suggest that addition to the allene is rate-determining, while with the terminal acetylene a fast isomerisation to the allene precedes the slow addition step. The much slower rate with the non-terminal acetylene (VII) is consistent either with a rate-determining isomerisation to the allene or with direct addition to the acetylene. We favour the latter alternative in view of the very small effect on rate produced by the addition of substantial proportions of strong tertiary amine. If isomerisation to the allene were rate-determining, addition of extra base should accelerate formation of adduct. The slower rate of addition found with the non-terminal acetylene is again consistent with ground-state stabilisation and steric retardation. The low rate of addition to the propenyl sulphone (II) compared with the prop-1-ynyl sulphone is notable and is consistent with the

greater reactivity of acetylenes towards nucleophilic addition.²³ The much greater reactivity of the allene is accounted for by the formation of a mesomeric carbanion intermediate whose stabilisation is reflected in the lowering of the free energy of the transition state. This greater reactivity has been observed qualitatively before.19

EXPERIMENTAL

For general directions see Part X.²

Olefinic Sulphones

Propenyl p-tolyl sulphone had m. p. 99-100.5° (from methanol) (lit.,²⁴ m. p. 100°). The n.m.r. spectrum gave a coupling constant J = 15.6 c./sec. for the vinyl protons, confirming that this compound is the trans-isomer. Treatment of the sulphone with piperidine as described² previously gave the adduct (93%), m. p. 81° (lit.,¹⁴ m. p.

Isopropenyl p-tolyl sulphone had m. p. 56° (from benzenehexane) (lit.,²⁵ m. p. 56-57°).

Addition of Piperidine to Isopropenyl p-Tolyl Sulphone.-Isopropenyl p-tolyl sulphone (0.491 g., 0.0025 mole) and piperidine (2.13 g., 0.025 mole) were refluxed in ethanol (50 ml.) for 3 days. The solution was poured into excess of dilute hydrochloric acid and extracted with ether to remove non-basic material. The aqueous layer was neutralised with saturated aqueous sodium hydrogen carbonate and extracted with ether. The ether extract was dried and the solvent removed. The residue, on distillation, gave 1-piperidino-2-p-tolylsulphonylpropane (0.62 g., 88%), b. p. 162-163°/0.2 mm. (Found: C, 64.3; H, 8.0. C15H23NO2S requires C, 64.0; H, 8.2%).

Addition of Di-n-butylamine to trans-Propenyl p-Tolyl Sulphone .--- The sulphone (500 mg.) and di-n-butylamine (3.3 g., 10 mol.) were kept in ethanol (10 ml.) for 6 days. The solution was evaporated and addition of light petroleum to the residue precipitated recovered sulphone (75 mg.), m. p. and mixed m. p. 97-98°. Re-evaporation of the filtrates gave the crude adduct (90%) which on distillation had b. p. 149°/0·1 mm. (bath 165-170°), n_D²⁶ 1·5109 (Found: C, 65.8; H, 9.3. C₁₈H₃₁NO₂S requires C, 66.5; H, 9.55%). The somewhat low percentages of carbon and hydrogen are attributed to the co-distillation of the small amount of residual propenyl sulphone not removed by precipitation. Treatment of the product with acid and subsequent basification as in the preceding experiment gave a much reduced yield of material (b. p. 150°/0·1 mm.; n_p²¹ 1·5124). 2-Hydroxy-2-methyl-1-toluene-p-sulphonylpropane.—Methyl

p-tolyl sulphone (30 g.) in benzene (30 ml.) was added to ethylmagnesium bromide [from ethyl bromide (38 g.) and magnesium (7.1 g.)] in ether during 15 min. The mixture was stirred for 10 min., diluted with benzene (75 ml.), heated rapidly to boiling, and then cooled to 2°. Acetone (15.6 g.) in benzene (40 ml.) was added with stirring during 30 min. The mixture was stirred at 20° for 3 hr. N-Hydrochloric acid (187 ml.) was added, the aqueous layer was saturated with sodium chloride, and extraction with

²⁰ R. C. Pink, R. Spratt, and C. J. M. Stirling, J. Chem. Soc., 1965, 5714.

²¹ C. H. McMullen and C. J. M. Stirling, J. Chem. Soc. (B), 1966, 1217. ²² W. E. Truce and D. G. Brady, Abs. American Chemical

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²³ R. A. Raphael, "Acetylenic Compounds in Organic Synthesis," Butterworths, London, 1955.

²⁴ J. Weinstock, R. G. Pearson, and F. G. Bordwell, J. Amer. Chem. Soc., 1956, 78, 3468, 3473.

²⁵ S. Chodroff and W. F. Whitmore, J. Amer. Chem. Soc., 1950, 72, 1073.

benzene gave a yellow oil. Distillation gave the hydroxysulphone (92%), b. p. 152°/1 mm., m. p. 49° (Found: C, 57.5; H, 7.4. $C_{11}H_{16}O_3S$ requires C, 57.9; H, 7.1%). Attempts to convert the sulphone into the chloride with either calcium chloride in concentrated hydrochloric acid, or with hydrogen chloride in acetonitrile, failed.

2-Chloro-2-methyl-1-p-tolylthiopropane.-Toluene-p-

sulphenyl chloride was prepared from toluene-*p*-thiol (20 g.) and chlorine (30 g.) in carbon tetrachloride according to Kurzer and Powell's ²⁶ directions. Isobutene was bubbled through the solution for 1 hr. with stirring. After 16 hr., evaporation of the mixture and distillation of the residue gave the *chloro-sulphide* (25.5 g., 74%), b. p. 92°/0.01 mm. (Found: C, 61.55; H, 7.2. $C_{11}H_{15}CIS$ requires C, 61.55; H, 7.0%).

Isobutenyl p-Tolyl Sulphone.—The preceding sulphide (7 g.) was oxidised with a 4-molar excess of hydrogen peroxide (30%) in acetic acid at 100°. The resulting sulphone (b. p. 144—146°/0·01 mm.) in benzene (60 ml.) was refluxed with triethylamine (10 ml.) for 16 hr. The mixture was washed with water, dried, and evaporated. The residual yellow oil was chromatographed in benzene on silica gel yielding the sulphone (3 g., 44%), m. p. 55—63° raised to 66—67° (from di-isopropyl ether) (Found: C, 63·0; H, 6·9. $C_{11}H_{14}O_2S$ requires C, 62·8; H, 6·7%); n.m.r. τ values 2·27(d), 2·73(d), 3·89(q), 7·54(s), 7·83(d), 8·1(d), ratio: 2:2:1:3:3:3.

Reactions of Isobutenyl p-Tolyl Sulphone.—(a) With piperidine. The sulphone (210 mg., 0.001 mole) and piperidine (850 mg., 0.01 mole) were refluxed in ethanol (20 ml.) for 48 hr. Removal of the solvent and distillation of the residue gave 2-methyl-3-toluene-p-sulphonylpropene (200 mg., 95%), m. p. 67—69° (from hexane) (Found: C, 63.3; H, 6.9. $C_{11}H_{14}O_2S$ requires C, 62.8; H, 6.7%). The n.m.r. spectrum showed bands at $\tau 2.41(d)$, 2.68(d), 4.59(q), 5.29(s), 6.22(s), 7.54(s), 8.12(d); integrals in the ratio: 2:2:1:1:2:3:3.

(b) With ethanolic sodium ethoxide. A solution of sodium ethoxide was prepared from sodium (23 mg.) and ethanol (15 ml.). To the solution was added the sulphone (210 mg.) in ethanol (10 ml.), and the mixture was stirred for 3 hr. at 20°. Addition of dilute acid and extraction with dichloromethane gave the isomeric olefin (195 mg., 93%), m. p. 55-57°, raised to 67-69° alone or mixed with the specimen obtained from the piperidine reaction above.

(c) With thiophenol. (i) Thiophenol (220 mg., 0.002 mole) was added to a solution of sodium ethoxide [from sodium (23 mg.) and ethanol (15 ml.)] followed by the sulphone (210 mg., 0.001 mole). The mixture was refluxed under nitrogen for 6 hr., poured into water, and extracted with dichloromethane. Evaporation of the extracts and treatment of the residue with light petroleum gave 2-methyl-2-phenylthio-1-toluene-p-sulphonylpropane (100 mg., 41%), m. p. 103—107°, raised to 110—112° [from light petroleum (b. p. 60—80°)] (Found: C, 63.85; H, 6.2. $C_{17}H_{20}O_2S_2$ requires C, 63.7; H, 6.3%). The n.m.r. spectrum showed bands at τ values 2.19—2.75(m), 6.63(s), 7.56(s), and 8.44(s) in the ratio 9:2:3:6.

(ii) The experiment was repeated except that the residue from evaporation of the dichloromethane extracts was taken up in acetic acid (5 ml.) and kept with 30% hydrogen peroxide (2 ml.) for 1 hr. at 90° . The solution was poured

²⁶ F. Kurzer and J. R. Powell, Org. Synth., 1955, **35**, 99.

²⁷ F. G. Bordwell and R. J. Kern, J. Amer. Chem. Soc., 1955, 77, 1141.

into water and extracted with dichloromethane. The extracts were washed with saturated aqueous sodium hydrogen carbonate and evaporation yielded 2-benzene-sulphonyl-2-methyl-1-toluene-p-sulphonylpropane (350 mg., 99%), m. p. 168—175° raised to 180—181° (from ethanol) (Found: C, 57.5; H, 5.8. $C_{17}H_{20}O_4S_2$ requires C, 57.9; H, 5.7%). The n.m.r. spectrum showed bands at τ values 2.09-2.75(m), 6.47(s), 7.54(s), and 8.38(s) in the ratio 9:2:3:6.

(d) With sodium benzenesulphinate. The sulphone (210 mg., 0.001 mole), sodium benzenesulphinate (606 mg., 0.003 mole), and acetic acid (72 mg., 0.0012 mole) were refluxed in ethanol (30 ml.) for 34 hr. The mixture was poured into water and extracted with dichloromethane. Evaporation of the extracts gave recovered sulphone (210 mg.), m. p. $55-63^{\circ}$. The m. p. on admixture with an authentic specimen was $60-65^{\circ}$ and infrared spectra of the recovered and authentic materials were identical. Thinlayer chromatography of the material on silica gel with dichloromethane as eluent revealed no addition or isomerised products.

Attempted Additions of Piperidine to 1-Toluene-p-sulphonylcyclohexene.—The sulphone 27 (236 mg., 0.001 mole) and piperidine (170 mg., 0.002 mole) were kept in benzene (15 ml.) at 20° for 7 days. Solvent was removed and the residue (218 mg.) had m. p. 77—82° alone or mixed with an authentic specimen of the sulphone. Similar results were obtained when ethanol was used as the solvent and the mixture was refluxed for 5 days.

Kinetics.—The procedures described previously were used. Results are summarised in Table 3.

TABLE 3

Additions of piperidine to olefinic sulphones

		1 1		T
		Initial	Initial	10 ⁴ k
Sulphone	Temp.	[amine]	[sulphone]	(l. mole ⁻¹ sec. ⁻¹)
I	5°	0.01	0.01	2310
I	5	0.01	0.012	2500
I	15	0.012	0.01	3500
I	15	0.0075	0.01	3300
I	25	0.012	0.01	5850
II	5	0.02	0.02	2.73
II	5	0.08	0.05	2.98
II	15	0.12	0.02	4.69
11	15	0.1	0.05	4.69
II	25	0.12	0.02	6.97
II	25	0.1	0.02	7.03
II	35	0.0787	0.0194	11.5
11	35	0.0582	0.0194	10.7
11	25 a	0.1	0.02	0.0375
II	25 ª	0.12	0.05	0.030
III	25	0.072	0.025	0.877
111	25	0.1	0.025	0.925
III	35	0.1	0.025	1.655
III	35	0.075	0.025	1.62
III	45	0.075	0.025	$2 \cdot 62$
III	45	0.1	0.025	2.78

^a Results for reactions with di-n-butylamine.

Acetylenic and Allenic Sulphones

Prop-2-ynyl p-Tolyl Sulphone.—Prop-2-ynyl p-tolyl sulphide ²⁸ was heated with a four-molar excess of 30% hydrogen peroxide in acetic acid at 95° for 1 hr. The mixture was diluted with cold water and the sulphone (99%) precipitated. It had m. p. 99— $100 \cdot 5^{\circ}$ (from ethanol-di-isopropyl ether) (Found: C, $61 \cdot 7$; H, $5 \cdot 3$. $C_{10}H_{10}O_2S$ requires C, $61 \cdot 8$; H, $5 \cdot 2\%$).

²⁸ K. Sato and O. Mujamoto, Nippon Kagaku Zasshi, 1956, 77, 1409.

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Prop-1-ynyl p-Tolyl Sulphone.—Prop-2-ynyl p-tolyl sulphide (29.7 g.) in dry tetrahydrofuran (300 ml.) was stirred for 17 hr. with finely powdered potassium hydroxide (45 g.). The solution was diluted with light petroleum (1 l.) and decanted. The decantate was washed with water, dried, and evaporated. Distillation of the residue gave prop-1-ynyl p-tolyl sulphide (25 g., 84%), b. p. 137—142°/16 mm., (lit.,²⁹ b. p. 83—84°/4 mm.). Oxidation of the sulphide as before gave the sulphone (89%), m. p. 96—97° (from hexane) (lit.,²⁹ m. p. 98—99°).

Propadienyl p-Tolyl Sulphone.—Prop-2-ynyl p-tolyl sulphone (15 g.) was dissolved in dichloromethane (140 ml.) which had previously been washed with aqueous sodium hydrogen carbonate and dried (CaCl₂). The solution was poured on to a column of activated alumina and elution with further dichloromethane (500 ml.) gave the allene (9.8 g., 65%), m. p. 85—87° (Found: C, $61\cdot8$; H, $5\cdot0$. C₁₀H₁₀O₂S requires C, $61\cdot8$; H, $5\cdot2\%$). The n.m.r. spectrum showed bands at $\tau 2\cdot2(d)$, $2\cdot64(d)$, $3\cdot75(t)$, $4\cdot57(d)$, and $7\cdot53(s)$ with integrals in the ratio 2:2:1:2:3. The infrared spectrum showed the strong doublet at 1960 and 1920 cm.⁻¹ characteristic of allenes.

2-Piperidino-1-toluene-p-sulphonylpropene.—Prop-1-ynyl p-tolyl sulphone (388 mg.) was treated with piperidine (425 mg., 2.5 mol.) in ether (30 ml.). After 12 hr., evaporation of the solvent and excess of amine gave the adduct (550 mg., 98%), m. p. 116—123°, raised to 127—128° (from di-isopropyl ether), λ_{max} 35,250 cm.⁻¹ ϵ 19,700 (Found: C, 64·2; H, 7·65. C₂₅H₂₁NO₂S requires C, 64·5; H, 7·6%). The n.m.r. spectrum showed bands with the following τ values: 2·22(d), 2·76(d), 4·75(s), 6·76(d), 7·61(s), 7·85(s), 8·42 (broad) with integrals in the ratio 2:2:1:4:3:3:6.

Kinetics.—Reactions were followed by measurement of absorption of reaction mixtures at 35,250 cm.⁻¹, the absorption maximum of the adduct obtained from each of the three isomeric sulphones with piperidine. Corrections for the absorption of the acetylenes at this frequency were made; they were not required for the allene. The optical densities of reaction mixtures were plotted automatically against a continuous time scale on a Unicam SP 700C instrument previously calibrated over the range of concentrations used in the rate determinations. Reaction mixtures were prepared by rapid mixing of equal volumes of standard solutions of amine and of sulphone in ethanol which had been kept in the thermostat at 25° . The mixture was then used to fill a silica cell (5 mm. path-length) in the thermostatted cell-block of the instrument. Approximately 20-fold excesses of amine over sulphone were used and pseudo-unimolecular rate constants were obtained from plots of log [sulphone] against time. A typical series of results is shown in Table 4.

TABLE 4

Rate of reaction of prop-2-ynyl p-tolyl sulphone with piperidine in ethanol at 25°

Initial [sulphone] = 1.226×10^{-4} M; Initial [amine] = 2.4×10^{3} M

	•		_	•	
t (min.)	2	3	5	8	
O.D. (at 35,250 cm. ⁻¹)	0.028	0.076	0.16	0.299	
10 ⁵ [adduct]	0.12	0.43	1.3	$2 \cdot 7$	
<i>t</i> (min.)	12	18	22	30	
O.D. (at 35,250 cm. ⁻¹)	0.472	0.691	0.800	0.965	
10 ⁵ [adduct]	4.45	6.7	7.8	9.45	
$k = 9.28 \times 10^{-4} \text{ sec.}^{-1}$.					

Results are in Table 2. Stability of the adducts under the conditions of the rate measurements was confirmed by the constancy of the infinity readings given by solutions kept in the spectrometer.

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²⁹ L. Maioli, G. Modena, and P. E. Todesco, Boll. sci. Fac. Chim. ind. Bologna, 1960, **18**, 66.