# Preparation of α-Diazo-β-disulphones; a Novel Sulphinate Elimination in their Coupling Reactions

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Bisarylsulphonyldiazomethanes are most conveniently prepared by the addition of a bisarylsulphonylmethane in aqueous ethanol containing 1 equiv. of sodium hydroxide to 3 mol. equiv. of toluene-*p*-sulphonyl azide. The reverse order of addition, with equimolar amounts of reactants as suggested by Klages and Bott, is unsatisfactory, since under these conditions the first-formed diazodisulphone undergoes secondary reactions, a major product of which is the bisarylsulphonylformaldehyde hydrazone (XI). In anhydrous tetrahydrofuran, α-diazo-β-disulphones react with 2 mol. equiv. of the sodium salt of a β-disulphone to provide a vinylhydrazone and sodium arenesulphinate. The latter must arise exclusively from the carbanion since interaction of bisphenylsulphonyldiazomethane (V; Ar = Ph) and the carbanion from the 2,4-xylyl disulphone (II; Ar = 2,4-xylyl) yields exclusively sodium 2,4-xylene-sulphinate whilst a similar reaction between bis 2,4-xylylsulphonyldiazomethane and the carbanion from the phenyl disulphone (II; Ar = Ph) provides only sodium benzenesulphinate. In contrast, sulphinate elimination occurs from the diazo-compound when it is coupled with a carbanion containing carbonyl rather than sulphonyl groups. The mechanism of the reactions is discussed.

REQUIRING the hitherto unknown bismesitylsulphonyldi-azomethane (V; Ar = mesityl) we attempted to use the procedure described by Klages and Bott [1] for the preparation of a number of bisarylsulphonyldiazo-methanes (V). In this method toluene-*p*-sulphonyl azide (III; Ar′ = *p*-MeC₆H₄) is rapidly added to a stirred solution of a β-disulphone (I) in aqueous alcoholic sodium hydroxide. By analogy with other reactive methylene compounds,[2] reaction may be envisaged as coupling of the sulphonyl azide with the carbanion (II) to give an adduct

$$ArSO_2 \cdot CH_2 \cdot SO_2Ar \xrightarrow{\ \bar{O}H\ } (ArSO_2)_2\bar{C}H + H_2O$$
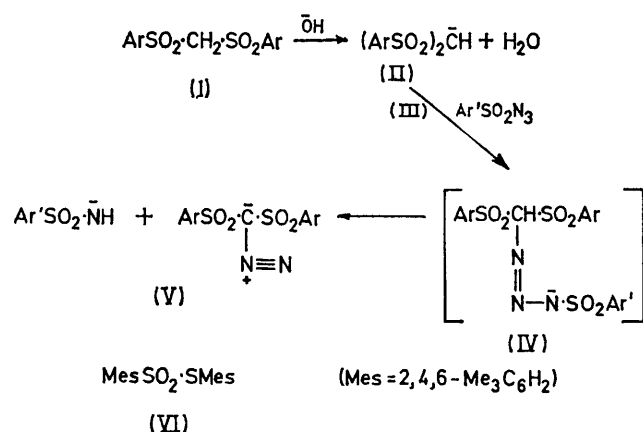
SCHEME 1

(IV) which then fragments into the diazo-disulphone (V) and the anion of toluene-*p*-sulphonamide. However, the mesityl disulphone (I; Ar = mesityl) did not dissolve in aqueous alcoholic sodium hydroxide, and when toluene-*p*-sulphonyl azide was added to the suspension little reaction appeared to take place. Similar results were obtained when the sodium hydroxide was replaced by lithium or potassium hydroxide. In an attempt to ensure carbanion formation the disulphone in tetra-hydrofuran was stirred with sodium hydride until hydrogen evolution was complete. The resultant in-

soluble sodium salt was then treated with toluene-*p*-sulphonyl azide in aqueous ethanol. Reaction was extremely slow: after 4 days 12% of the sulphone remained, the diazo-compound (V; Ar = mesityl) was isolated in 19% yield, and the balance of the material was alkali-soluble. Attempts to use triethylamine as base, acetonitrile as solvent, and *p*-carboxybenzene-sulphonyl azide [3] (III; Ar′ = C₆H₄·CO₂H) in place of tosyl azide, did not effect any significant improvement. Since aqueous alcohol appeared to be a poor solvent for the reaction, but a carbanion was formed when the disulphone was treated with sodium hydride in tetra-hydrofuran, attempts were made to carry out the reaction in this solvent. There then resulted the diazo-disulphone (V; Ar = mesityl) (10%), the thiolsulphonate (VI) (40%), and a vinylhydrazone (XIV; Ar = mesityl, Y = Z = 2,4,6-Me₃C₆H₂·SO₂) (11%). The consumption of toluene-*p*-sulphonyl azide indicated that diazo-group transfer had indeed taken place although probably not quantitatively. The formation of the vinylhydrazone involves the reaction of diazo-disulphone with 2 mol. equiv. of carbanion, suggesting that the first formed diazo-compound has reacted with as yet unconsumed carbanion. This vinylhydrazone, however, contains only four arylsulphonyl groups rather than the six present in its progenitors. The suggestion is therefore that two arylsulphonyl groups have been lost as arene-sulphinate during the condensation. Evidence in support of this view is obtained by the isolation of the thiolsulphonate (VI). Had mesitylenesulphinate anion been eliminated during the reaction it might well have been converted into the observed thiolsulphonate during the acid work-up procedure. Indeed tests with authentic mesitylenesulphinic acid showed that the thiolsulphonate is in fact obtained under similar conditions. These products cannot have arisen from simple decomposition of the disulphone with sodium hydride since in a blank reaction to which no tosyl azide was added the disulphone was recovered in high yield.

[1] F. Klages and K. Bott, *Ber.*, 1964, **97**, 735.
[2] M. Regitz, 'Newer Methods of Preparative Organic Chemistry,' Academic Press, New York, 1971, vol. VI, p. 81.
[3] J. B. Hendrickson and W. A. Wolf, *J. Org. Chem.*, 1968, **33**, 3610.

The complexity of these results prompted us to re-investigate the Klages and Bott procedure using bis-2,4-xylylsulphonylmethane (I; Ar = 2,4-xylyl). We obtained the diazo-compound in 52% yield (V; Ar = 2,4-xylyl) rather than the 85% claimed. The solution from which this had separated was deep red and from it was isolated the hydrazone (XI; Ar = 2,4-xylyl) (26%). This result, in terms of diazo-compound formation, is only qualitatively different from that of Klages and Bott who, however, make no reference to the formation of a hydrazone. When bisphenylsulphonylmethane was used in place of the 2,4-xylyl compound a deep red solution was obtained and no diazo-compound was precipitated (Klages and Bott claim a yield of 70%). The hydrazone (XI; Ar = Ph) (24%) slowly separated. Since in both reactions tosyl azide is consumed and toluene-p-sulphonamide is formed it seems probable that the diazo-compound is indeed produced but undergoes further reaction either with carbanion or hydroxide ion.
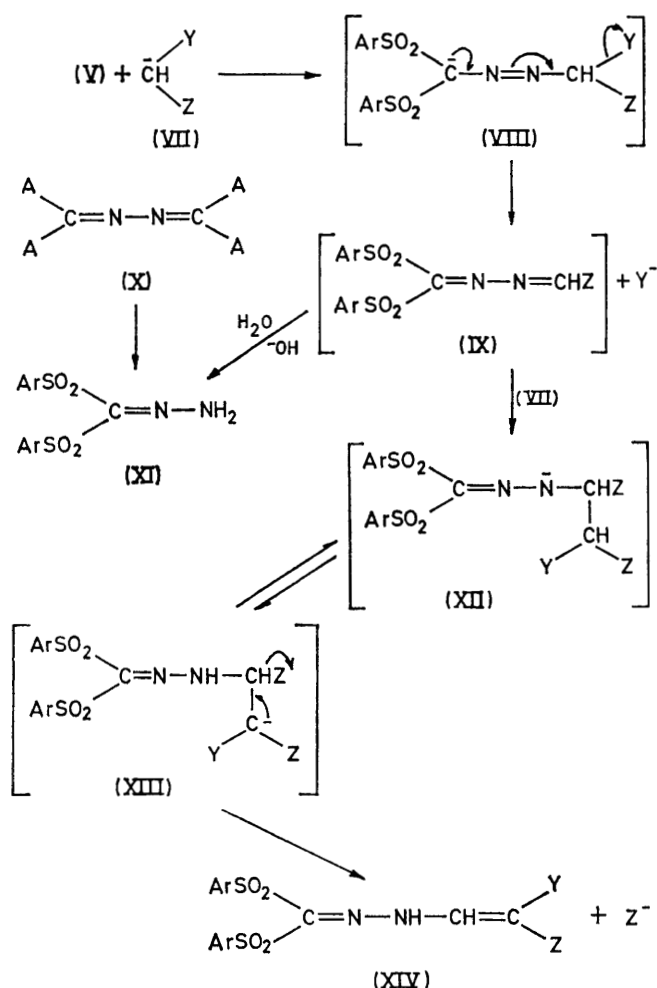
toluene-p-sulphonyl azide, the diazo-compound (V; Ar = 2,4-xylyl) was obtained in 82% yield. Bisphenylsulphonyldiazomethane (V; Ar = Ph) (54%) was similarly prepared and, although the reaction was very slow, the required bismesitylsulphonyldiazomethane (V; Ar = mesityl) was obtained in 45% yield. The use of an excess of tosyl azide clearly serves to reduce reaction between the first-formed diazo-disulphone and as yet unconsumed carbanion. The validity of this suggestion is further exemplified by restricting the tosyl azide to 1 mol. proportion, when the diazo-compound that is first precipitated is visibly consumed as reaction proceeds, so that after 1·5 and 4 h the yields are 21 and 14%, respectively. Further, as the yield of diazo-compound falls, the yield of hydrazone increases (9 and 30%).

Since coupling reactions of α-diazo-β-disulphones giving vinylhydrazones (XIV) with concomitant sulphinate elimination have not previously been reported, some typical examples were studied. Thus the rapid addition of bisphenylsulphonyldiazomethane (V; Ar = Ph) to 2 mol. equiv. of the sodium salt of bisphenylsulphonylmethane in tetrahydrofuran at 0° led to a rapid precipitation of sodium benzenesulphinate and the formation of the vinylhydrazone (XIV; Y = Z = PhSO$_2$, Ar = Ph). When the carbanion was restricted to 1 mol. equiv., not all the diazo-disulphone was consumed, less sodium sulphinate was formed, and only traces of the vinyl-hydrazone appeared to be present in the complex mixture. It therefore appears that two molecules of carb-anion react with each molecule of diazo-disulphone with the elimination of two arenesulphinate ions. The latter apparently arise from the carbanion since, for example, interaction of bisphenylsulphonyldiazomethane (V; Ar = Ph) and the carbanion from the 2,4-xylyl disulphone (II; Ar = 2,4-xylyl) yields exclusively sodium 2,4-xylenesulphinate whilst a similar reaction between bis-2,4-xylylsulphonyldiazomethane and the carbanion from the phenyl disulphone (II; Ar = Ph) provides only sodium benzenesulphinate. Loss of sulphinate from the diazo-compound is, however, possible when coupling takes place with a carbanion which does not contain sulphone groups. For example, sodium benzenesulphinate was obtained from the interaction of bisphenylsulphonyldiazomethane (V; Ar = Ph) and the carbanion from benzoylacetone (VII; Y = Bz, Z = Ac), presumably since sulphinate is the best available leaving group.

The structures of the vinylhydrazones (XIV) and (XIX) were established by analysis and by i.r., n.m.r., and high resolution mass spectrometry. For example (XIV; Ar = Ph, Y = Z = PhSO$_2$) showed i.r. bands attributable to N–H and vinyl groups and the n.m.r. spectrum showed two doublets (J 10 Hz) at τ −3·07 (1H, exchanged by D$_2$O) and 1·69 (1H, collapsed to singlet in D$_2$O) corresponding to the >C=CH–NH– group. High resolution mass spectrometry verified the molecular formula and showed the presence of four phenylsulphonyl groups.

The formation of such vinylhydrazones may be

SCHEME 2

With this in mind we reversed the order of addition of the reagents. When 1 mol. equiv. of the 2,4-xylyl carbanion (II; Ar = 2,4-xylyl) was added to 3 mol. equiv. of
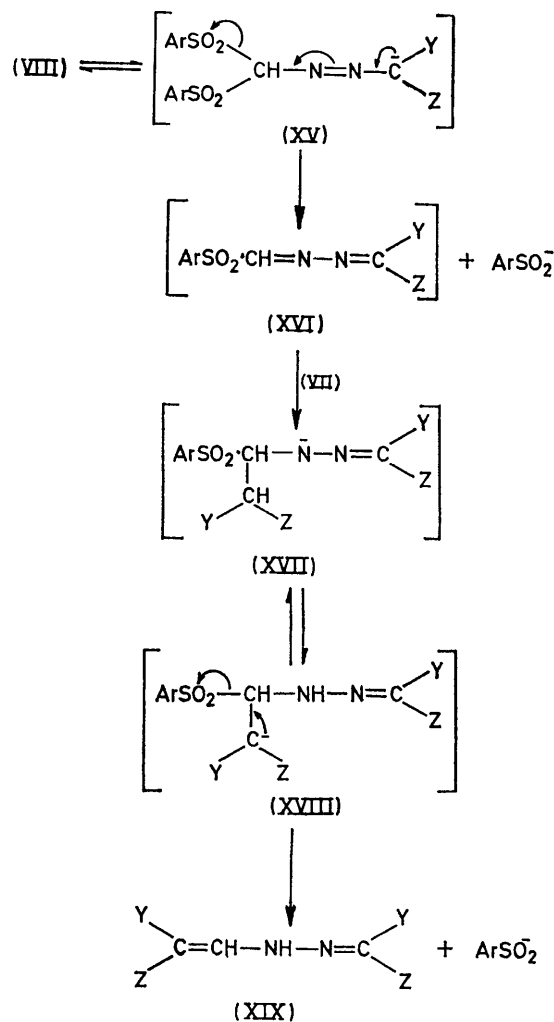
rationalised by assuming coupling of the diazo-disulphone with the carbanion [(V) ⟶ (VIII)]. Coupling reactions of diazo-disulphones with triphenylphosphine and with phenylmagnesium bromide have been described [4]

SCHEME 3

but we believe this to be the first example of such a reaction in which the nucleophile possesses a hydrogen atom at the carbanionic centre. Loss of arenesulphinate ion from the adduct (VIII) would then lead to the azine (IX). Diekmann [4] attempted to prepare a compound of this type by the action of sodium benzenesulphinate on carbonyl bromide azine (X; A = Br). It seems likely that the expected azine (X; A = $PhSO_2$) was formed but suffered hydrolysis to the hydrazone (XI; Ar = Ph). According to Diekmann such a hydrolysis is a consequence of the ease with which this azine undergoes nucleophilic attack. Such a process would serve to explain the formation of hydrazones [(IX) ⟶ (XI)] in our reactions where aqueous ethanol is used as solvent.

In those of our experiments carried out under anhydrous conditions nucleophilic attack on the azine (XI) by a second molecule of carbanion gives the adduct (XII), the tautomer of which (XIII) may then lose a sulphinate ion [Z in (XIII)] to give the observed vinylhydrazone (XIV).

When the carbanion contains carbonyl rather than sulphonyl groups the initial adduct (VIII) apparently tautomerises to (XV) in order to permit the departure of a sulphinate ion [(XV) ⟶ (XVI)]. Beyond this point elimination of the remaining sulphonyl group from the azine (XVI) consequent on attack by a second molecule of carbanion presumably follows a pattern [(XVI) ⟶ (XVII) ⟶ (XVIII) ⟶ (XIX)] to give the tetracarbonyl hydrazone (XIX) by a mechanism analogous to that previously outlined for the formation of the tetrasulphonyl hydrazone (XIV).

EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer 257 instrument, [1]H n.m.r. spectra on Perkin-Elmer R10, Perkin-Elmer–Hitachi R20A, and Varian HA100 instruments, and mass spectra on an A.E.I. MS902 spectrometer. Further mass spectral data for compounds marked with an asterisk are available in Supplementary Publication No. SUP 20598 (7 pp., 1 microfiche).*

α-*Diazo*-β-*disulphones.*—(a) *Klages and Bott procedure.* When toluene-*p*-sulphonyl azide in ethanol was added to bisphenylsulphonylmethane in 60% aqueous ethanol containing 1 equiv. of sodium hydroxide under conditions where Klages and Bott report the precipitation of bisphenylsulphonyldiazomethane (70%), no solid separated until the deep red solution had been stored for several days. The material deposited proved to be bisphenylsulphonylformaldehyde hydrazone (XI; Ar = Ph) (24%), m.p. *ca.* 200° (from acetic acid) (lit.,[4] *ca.* 200°) (Found: C, 48·4; H, 3·8; N, 8·3; S, 20·4. Calc. for $C_{13}H_{12}N_2O_4S_2$: C, 48·4; H, 3·7; N, 8·6; S, 19·8%), ν_{max} 3380 and 3280 (NH$_2$), 3210m, 1622m, 1450s, 1330s (SO$_2$), 1152s (SO$_2$), 750m, 720s, and 680s cm⁻¹, τ [(CD$_3$)$_2$SO] −0·3 [2H, ABq, *J* 14 Hz (at 31°; at 60° collapses to broad s), NH$_2$] and 1·9—2·6 (10H, m, 2 × Ph). It was identical (i.r. spectra) with that obtained by the reduction of bisphenylsulphonyldiazomethane with hydrogen sulphide under the general conditions described [5] for the reduction of diazo-ketones. Under similar conditions bis-2,4-xylylsulphonylmethane gave the corresponding diazo-compound (52%), m.p. 133—136° (decomp) (from ethanol) [lit.,[1] 85% yield, m.p. 135—136° (decomp)]. The deep red solution from which this had separated deposited (during several days) *bis*-2,4-*xylylsulphonylformaldehyde hydrazone* (26%), m.p. 210—213° (decomp) (from toluene) (Found: C, 53·9; H, 5·1; N, 7·2; S, 16·8. $C_{17}H_{20}N_2O_4S_2$ requires C, 53·7; H, 5·3; N, 7·4; S, 16·9%), ν_{max} 3382s and 3280m (NH$_2$), 3205w, 1620m, 1603m, 1575s, 1310s (SO$_2$), 1155m, 1125s (SO$_2$), 1050 m, 818m, 805s, 728s, 710s, 702s, and 680s cm⁻¹, τ [(CD$_3$)$_2$SO] 0·27br (2H, s, NH$_2$), 2·18 (2H, d, *J* 8 Hz, aromatic), 2·78 (4H, m, aromatic), 7·56 (6H, s, 2 × *o*-Me), and 7·64 (6H, s, 2 × *p*-Me).

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* For details of Supplementary Publications, see Notice to Authors No. 7 in *J. Chem. Soc.* (A), 1970, Issue No. 20.

[4] J. Diekmann, *J. Org. Chem.*, 1965, **30**, 2272.
[5] F. Weygand and H. J. Bestmann, 'Newer Methods of Preparative Organic Chemistry,' Academic Press, New York, 1964, vol. p. 451.

Bismesitylsulphonylmethane did not dissolve in the aqueous alcoholic alkali, and when toluene-p-sulphonyl azide was added to the stirred suspension *ca.* 70% of the disulphone was still present after 4 h. The sodium salt obtained by the interaction of the disulphone (5·0 g, 0·013 mol) and sodium hydride (1 equiv.) in tetrahydrofuran (100 ml) was suspended in 60% aqueous ethanol (50 ml) and to it was added toluene-p-sulphonyl azide (2·6 g, 0·013 mol). There was no immediate colour change but on stirring the mixture slowly became pale yellow. After 4 days the suspended material (1·9 g) (A) was separated from the pale yellow solution (B). The solid (A) was extracted with ether until coloured material was no longer removed. The residue was bismesitylsulphonylmethane (0·8 g, 16%), m.p. and mixed m.p. 175—180°. Evaporation of the ethereal solution provided nearly pure (m.p. 140—145°) *bismesitylsulphonyldiazomethane* (1·0 g, 19·0%), m.p. 145—147° (decomp) (from methanol) (Found: C, 55·6; H, 5·3; N, 7·7; S, 15·6. $C_{19}H_{22}N_2O_4S_2$ requires C, 56·1; H, 5·4; N, 6·9; S, 15·8%), $\nu_{max.}$ 2982m, 2960m, 2110s (diazo), 1600s, 1460s, 1332s (SO_2), 1240s, 1145s (SO_2), 1050m, 960m, 865m, 720m, and 682m cm^{-1}, τ (CDCl$_3$) 3·05 (4H, s, aromatic), 7·45 (12H, s, 4 × o-CH$_3$), and 7·75 (6H, s, 2 × p-CH$_3$). The solution (B) was freed from ethanol by distillation under reduced pressure and, after extraction with ether to remove toluene-p-sulphonyl azide, was acidified and extracted with chloroform. Concentration of the extract provided a sticky solid (1·0 g), a solution of which in ether (*ca.* 50 ml), on treatment with light petroleum (b.p. 30—40°), precipitated toluene-p-sulphonamide (0·5 g, 23%), m.p. 134—138°.

(b) *Inverse addition.* (i) To toluene-p-sulphonyl azide (19·7 g, 0·10 mol) in ethanol (30 ml) at −5 to 0°, bisphenylsulphonylmethane (10·0 g, 0·034 mol) in 60% aqueous ethanol (70 ml) containing sodium hydroxide (1·4 g, 0·035 mol) was added with stirring. The yellow solid that had separated after the mixture had been stirred for 30 min at the same temperature was removed and washed with water. The dried product was stirred with ice-cold ether (20 ml); the mixture was filtered to provide bisphenylsulphonyldiazomethane (6·0 g, 54%), m.p. 95—98° (decomp) [m.p. 99—100° (decomp.) (from methanol); lit.,[1] 99° (decomp.)].

(ii) When in similar experiments less toluene-p-sulphonyl azide (6·7 g, 0·034 mol) was used, and the carbanion solution was added, in 1·5 and 4·0 h the yields of diazo-disulphone were 21 and 14%, respectively. The alkaline solutions from which the crude diazo-disulphones had been removed slowly deposited bisphenylsulphonylformaldehyde hydrazone (9 and 30%, respectively), identical (mixed m.p. and spectra) with that already described. In addition toluene-p-sulphonamide (26 and 32%, respectively) was isolated as described in (a).

(iii) When bis-2,4-xylylsulphonylmethane was added to toluene-p-sulphonyl azide as in (i), bis-2,4-xylylsulphonyldiazomethane (82%), identical with that already described, was obtained.

(iv) When a suspension of the sodium salt prepared from bismesitylsulphonylmethane and sodium hydride as already described was stirred with 3 equiv. of toluene-p-sulphonyl azide, bismesitylsulphonyldiazomethane (45%), m.p. 143—146° (decomp.), was obtained.

(c) *In tetrahydrofuran.* To a stirred suspension of sodium hydride (0·62 g, 0·026 mol) in dry tetrahydrofuran (THF) (120 ml), maintained under nitrogen, bismesitylsulphonylmethane (10·0 g, 0·026 mol) was added. When evolution of hydrogen had ceased (*ca.* 30 min) the suspension was cooled

in ice and toluene-p-sulphonyl azide (8% solution) in THF was added. An immediate yellow colour developed and the reaction was monitored by t.l.c. The sulphonyl azide (3·81 g, 0·0193 mol) was consumed over about 3 h, beyond which point no further reaction took place even when more sodium hydride was added. The red suspension was filtered to give a red solution (A) and a sticky solid. The latter was extracted with boiling water until only tarry material remained and the resulting solution was acidified with hydrochloric acid. The precipitated material largely redissolved on heating and, after removal of a trace of tar, the cool solution slowly deposited not the expected toluene-p-sulphonamide but *S*-mesityl mesitylenethiosulphonate (0·8 g, 40%), m.p. 136—139° (from methanol), identical (mixed m.p., i.r., and n.m.r. spectra) with that obtained by boiling mesitylenesulphinic acid with dilute sulphuric acid.[6] The sticky material obtained by concentrating the red solution (A) was triturated with ethanol to give a product which was shown by t.l.c. to consist essentially of two components. Extraction with ether (200 ml) removed bismesitylsulphonyldiazomethane (1·1 g, 10%), identical with that already described. The ether-insoluble material after recrystallisation from acetic acid and then from benzene–ethanol provided *bismesitylsulphonylformaldehyde ββ-bismesitylsulphonylvinylhydrazone** (0·8 g, 11%), m.p. 243—246° (from acetic acid) (Found: C, 58·5; H, 5·8; N, 3·9; S, 16·6. $C_{39}H_{46}N_2O_8S_4$ requires C, 58·9; H, 5·8; N, 3·5; S, 16·0%), $\nu_{max.}$ 3140w,br (NH), 1710m, 1615s (vinyl), 1602s, 1537s, 1360s, 1310s, 1260m, 1152s, 1132s, 1050m, 1035m, 958m, 920m, 860m, 768s, 708m, 680s, and 663s cm^{-1}, τ(CDCl$_3$) −3·30 (1H, d, J 10 Hz, disappears on shaking with D$_2$O, NH), 2·14 (1H, d, J 10 Hz, collapses to a singlet on D$_2$O, C=CH−NH), 2·99 (2H, s, aromatic), 3·05 (2H, s, aromatic), 3·16 (4H, s, aromatic), 7·37 (6H, s, 2 × Me), 7·47 (6H, s, 2 × Me), and 7·7 (24H, m, 8 × Me), m/e 798 (M^+).

Coupling Reactions of α-Diazo-β-disulphones.—(a) *With β-disulphones.* (i) To an ice-cold stirred suspension, prepared as already described, of sodium diphenylsulphonylmethanide (0·02 mol) in THF (70 ml) under nitrogen was added bisphenylsulphonyldiazomethane (3·22 g, 0·01 mol) in THF (70 ml) all at once. An immediate red colour developed and after stirring at 0° for 1 h the suspension was filtered. The residue, after washing with THF, proved to be sodium benzenesulphinate (1·6 g, 49%), δ (D$_2$O) 0·85(m) p.p.m. downfield from benzene; *S*-benzylthiouronium benzenesulphinate, m.p. 153—155° [from ethanol–light petroleum (b.p. 60—80°)], mixed m.p. 152—155° (lit.,[7] 154—155°) (Found: C, 54·5; H, 5·2; N, 8·9; S, 20·5. Calc. for $C_{14}H_{16}N_2O_2S_2$: C, 54·5; H, 5·2; N, 9·0; S, 20·8%). The THF solution from which the sodium benzenesulphinate had been separated was concentrated to provide a sticky solid (6·0 g) from which unchanged diazo-compound (0·4 g) was extracted with ether. The residue was most conveniently acidified by dissolution in hot acetic acid (*ca.* 15 ml), the excess of which was then removed under reduced pressure. The resulting mixture was purified by stirring with ethanol (30 ml) which, as t.l.c. indicated, took into solution numerous minor components. The insoluble material (3·0 g) proved to be essentially *bisphenylsulphonylformaldehyde ββ-bisphenylsulphonylvinylhydrazone** (2·5 g, 40%), m.p. 230—233° (from benzene) (Found: C, 51·7; H, 3·6; N, 4·5; S, 19·9%; M^+, 630·0278. $C_{27}H_{22}N_2O_8S_4$

[6] G. Leandri and A. Tundo, *Ann. Chim. (Italy)*, 1954, **44**, 255 (*Chem. Abs.*, 1955, **49**, 15,782e).
[7] F. Kurzer and J. K. Powell, *J. Chem. Soc.*, 1952, 3728.

requires C, 51·4; H, 3·5; N, 4·4; S, 20·3%; M, 630·0257), $\nu_{max.}$ 3180m (NH), 1612s, 1530s, 1450s, 1325s (SO$_2$), 1145s (SO$_2$), 1080s, 965s, 935m, 750m, 720s, and 680s cm^{-1}, τ (CDCl$_3$) $-3·07$ (1H, d, J 10 Hz, disappears on deuteriation, NH), 1·69 (1H, d, J 10 Hz, collapses to a singlet on deuteriation, CH=C), and 1·7—2·7 (20H, complex m, aromatic).

When in a similar experiment the carbanion was restricted to 1 mol. equiv. more diazo-disulphone (*ca.* 20%) was recovered. Significantly less sodium benzenesulphinate (36%) was isolated and only traces of the hydrazone (XIV; Ar = Ph, Y = Z = PhSO$_2$) were present.

(ii) When the bisphenylsulphonylmethane in experiment (i) was replaced by an equivalent quantity of bis-2,4-xylylsulphonylmethane, reaction appeared to proceed more slowly but after 12 h only a trace of diazo-compound remained and there were isolated sodium 2,4-xylenesulphinate (1·6 g, 40%), δ (D$_2$O) 1·2—0·42 p.p.m. (3H, aromatic) downfield from benzene and 4·1 (3H, s, *o*-Me) and 4·3 (3H, s, *p*-Me) upfield from benzene {S-*benzylthiouronium sulphinate*, m.p. 145—152° [from ethanol–light petroleum (b.p. 60—80°)] (Found: C, 57·2; H, 6·0; N, 8·6; S, 18·6. C$_{16}$H$_{20}$N$_2$O$_2$S$_2$ requires C, 57·2; H, 5·9; N, 8·4; S, 19·0%)}, and *bisphenylsulphonylformaldehyde* $\beta\beta$-*bis-2,4-xylylsulphonylvinylhydrazone,* m.p. 200—201° (from ethanol–benzene) (Found: C, 54·1; H, 4·6; N, 4·0; S, 18·4. C$_{31}$H$_{30}$N$_2$O$_4$S$_8$ requires C, 54·2; H, 4·4; N, 4·1; S, 18·6%), $\nu_{max.}$ 3160m (NH), 1610s, 1512s, 1460m, 1350s, 1318s, 1305s, 1152s, 1140s, 1082m, 1075m, 1050m, 960m, 816m, 780m, 750m, 720s, and 660s cm^{-1}, τ (CDCl$_3$) $-3·30$ (1H, d, J 10 Hz, disappears on deuteriation, NH), 1·61 (1H, d, J 10 Hz, collapses to a singlet on deuteriation, C=CH—NH), 1·9, 2·35, and 3·0 (16H, m, aromatic protons), 7·58 (6H, s, 2 × *o*-Me), and 7·66 (6H, s, 2 × *p*-Me).

(iii) When as in (ii) bis-2,4-xylylsulphonyldiazomethane (3·8 g, 10 mmol) was added to the carbanion from bisphenylsulphonylmethane (5·92 g, 20 mmol), reaction proceeded slowly and after 15 h there had separated sodium benzenesulphinate (1·5 g, 46%), identical with that already described. The solution from which the sulphinate had separated was concentrated under reduced pressure to provide a sticky solid from which unchanged diazo-compound (1·5 g) was extracted with ether. The residue, after acidification with acetic acid, was chromatographed on silica (45 × 4 cm); elution with toluene–chloroform (4 : 1) gave further diazo-compound (0·5 g); subsequent elution with toluene–chloroform (1 : 1) gave as the only identifiable

product bisphenylsulphonylmethane (1·1 g), m.p. 113—117°, mixed m.p. 115—118°.

(b) *With benzoylacetone.* To sodium hydride (0·24 g, 10 mmol) in THF (60 ml) was added benzoylacetone (3·24 g, 20 mmol) under nitrogen at 0°. When hydrogen evolution was complete bisphenylsulphonyldiazomethane (3·22 g, 10 mmol) in THF (60 ml) was added all at once. After 12 h at 0°, the precipitated sodium benzenesulphinate (1·8 g, 100%) was separated and characterised as before. The filtrate was freed from solvent under reduced pressure and the residue stirred with ether (20 ml); the ether-insoluble material was agitated with chloroform (*ca.* 40 ml) and the small amount of insoluble impurity was removed. Evaporation of the chloroform solution gave a residue which on trituration with ethanol provided 1-*phenylbutane*-1,2,3-*trione*-2-(β-*acetyl*-β-*benzoylvinylhydrazone*)* (1·5 g, 82%), m.p. 137—140° (from ethanol) (Found: C, 69·3; H, 5·2; N, 7·6%; M^+, 362·1242. C$_{21}$H$_{18}$N$_2$O$_4$ requires C, 69·6; H, 5·0; N, 7·7%; M, 362·1266), $\nu_{max.}$ 3160br (NH), 1690s (MeCO), 1640s (PhCO), 1595s, 1458s, 1449s, 1400s, 1360s, 1350s, 1270s, 1248s, 1112s, 965s, 879s, 803s, 798s, and 730s cm^{-1}, τ (CDCl$_3$) $-3·52$ (1H, d, J 10 Hz, disappears with D$_2$O, C=CH—NH), 2·28 (d, J 10 Hz), becomes s with D$_2$O, C=CH—NH), 2·4 (10H, m, 2 × Ph), 7·54 (3H, s, Me), and 7·64 (3H, s, Me).

When the diazo-compound was treated with 1 equiv. of carbanion in the absence of free diketone a similar result was obtained but the hydrazone was only isolated after acidification with acetic acid as in (a)(i). Again, when the reaction was repeated with sufficient sodium hydride (0·48 g) to convert the whole of the diketone into carbanion there was a quantitative yield of sodium benzenesulphinate, but the organic products of the reaction appeared complex and no identifiable compound was isolated.

β-*Disulphones.*—These were prepared by condensation of benzenethiols with methylene chloride in alkaline solution followed by oxidation of the disulphides.[1] *Bismesitylthiomethane* had m.p. 60—61° (from methanol–benzene) (Found: C, 71·7; H, 8·3; S, 20·0. C$_{19}$H$_{24}$S$_2$ requires C, 71·2; H, 7·6; S, 20·3%), and *bismesitylsulphonylmethane* had m.p. 178—180° (from benzene–ethanol) (Found: C, 59·9; H, 6·4; S, 16·6. C$_{19}$H$_{24}$S$_2$O$_4$ requires C, 60·0; H, 6·3; S, 16·8%), $\nu_{max.}$ 1315s and 1150s (SO$_2$) cm^{-1}, τ (CDCl$_3$), 3·02 (4H, s, aromatic), 5·3 (2H, s, CH$_2$), 7·4 (12H, s, 4 × Me), and 7·7 (6H, s, 2 × Me).