

The Dianion of Benzyl Phenyl Sulphone. A General Method for obtaining $\alpha\beta$ -Unsaturated Phenyl Sulphones from Aldehydes and Ketones

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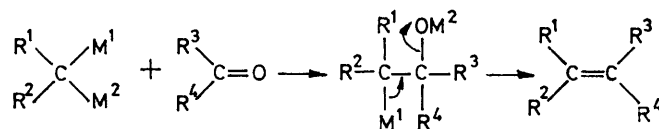
The reaction between $\alpha\alpha$ -dimetallo-derivatives of benzyl phenyl sulphone and carbonyl compounds has been shown to give $\alpha\beta$ -unsaturated phenyl sulphones (IV), in yields strongly dependent upon the nature of the metal. Good yields have been obtained from saturated aliphatic and aromatic aldehydes and ketones, including $\alpha\beta$ -unsaturated carbonyl compounds. The stereochemistry of the reaction has been studied. In the case of benzaldehyde and *p*-chlorobenzaldehyde only the *Z*-isomer was isolated: in the other cases a *ca.* 1:1 mixture of *Z*- and *E*-isomers was obtained.

gem-DIMETALLO-COMPOUNDS, $R^1R^2CM^1M^2$, are often useful synthetic intermediates. *gem*-Diboron¹ and -dialuminium² compounds can be prepared by dihydroboration and dihydroalumination of terminal acetylenes. Although these compounds are not particularly suitable as intermediates, owing to their relative stability, they can be converted into other *gem*-dimetallo-derivatives by transmetallation. In fact, highly active mixed lithium-boron³ and lithium-aluminium⁴ compounds can be obtained by treatment of *gem*-diboron and -dialuminium derivatives with *n*-butyl-lithium. The very reactive *gem*-dimagnesium⁵ and -dizinc⁶ derivatives have recently been obtained by halogen-metal replacement reactions.

gem-Di(alkali metal) compounds can also be obtained by metallation of compounds containing acidic hydrogen atoms.^{7,8} These organometallic species have been carboxylated to give malonic acid derivatives,³ and alkylated.^{7,8}

The majority of the *gem*-dimetallo-compounds (containing at least one carbon-metal bond capable of adding to a carbonyl group) react with aldehydes and ketones yielding olefins, probably by an addition-elimination sequence.^{3,5,6} This reaction constitutes a useful alternative to the Wittig reaction. Its course, however, is highly dependent upon the conditions (especially solvent and temperature) and upon the nature of the metal in

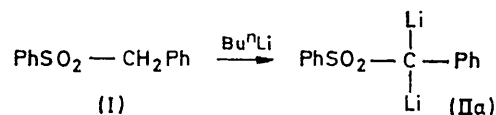
the organometallic species. Methylenebis(magnesium iodide)⁵ and *gem*-lithium-boron³ alkyls react rapidly in ethereal medium even below room temperature,



whereas methylenebis(zinc iodide)⁶ reacts more slowly and only with aldehydes.

In the present work we wished to establish whether the *gem*-dimetallo-compounds arising from dimetallation of active methylene compounds could be used for making olefins from carbonyl compounds.

Benzyl phenyl sulphone (I) is easily converted into the $\alpha\alpha$ -dilithio-derivative (IIa) by treatment with *n*-butyl-lithium in tetrahydrofuran-heptane at room temperature.⁷ The product (IIa) reacts with propionaldehyde at



room temperature in tetrahydrofuran (THF) to give the expected $\alpha\beta$ -unsaturated phenyl sulphone (IV; $R^3 = \text{H}$, $R^4 = \text{Et}$) in 8% yield, the main product being the hydroxy-phenyl sulphone (V; $R^3 = \text{H}$, $R^4 = \text{Et}$).

* H. Hashimoto, M. Hida, and S. Miyano, *J. Organometallic Chem.*, 1967, **10**, 518.

⁷ E. M. Kaiser, L. E. Solter, R. A. Schwarz, R. D. Beard, and C. R. Hauser, *J. Amer. Chem. Soc.*, 1971, **93**, 4237.

⁸ W. E. Truce and L. W. Christensen, *Chem. Comm.*, 1971, 588; G. A. Gornowicz and R. West, *J. Amer. Chem. Soc.*, 1971, **93**, 1714.

¹ H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, 1961, **83**, 3834; P. Binger and R. Koester, *Angew. Chem.*, 1962, **74**, 652.

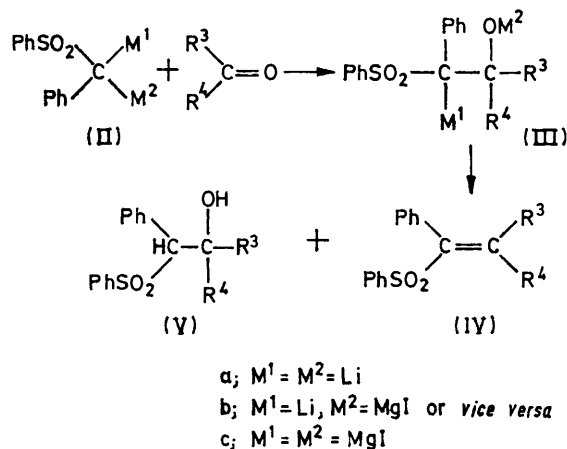
² G. Wilke and H. Müller, *Annalen*, 1960, **629**, 222.

³ G. Cainelli, G. Dal Bello, and G. Zubiani, *Tetrahedron Letters*, 1966, 4315.

⁴ G. Zweifel and R. B. Steele, *Tetrahedron Letters*, 1966, 6021.

⁵ F. Bertini, P. Grasselli, G. Zubiani, and G. Cainelli, *Tetrahedron*, 1970, **26**, 1281.

The low yield of olefin and the predominant formation of the hydroxy-compound can be explained if the intermediate dianionic adduct (IIIa) is in this case relatively



stable and does not tend to undergo olefin-forming elimination.*

The stability of the species (IIIa) to elimination is probably attributable to the poor leaving-group character of OLi. We therefore attempted to exchange the lithium for magnesium¹⁰ in α -dilithiobenzyl phenyl sulphone (IIa) to obtain an adduct (III) containing an OMgX group, which is known to possess remarkable leaving-group properties.^{5,11}

The *gem*-dimetallo-derivative (II) obtained from α -dilithiobenzyl phenyl sulphone (IIa) by means of lithium-magnesium exchange with 2 mol. equiv. of magnesium iodide, when treated with aldehydes or ketones, gave good yields of $\alpha\beta$ -unsaturated phenyl

Conversion of carbonyl compounds into $\alpha\beta$ -unsaturated phenyl sulphones

Carbonyl compound	R ³	R ⁴	Yield (%) ^a
Benzaldehyde	H	Ph	75 ^{b,c}
<i>p</i> -Chlorobenzaldehyde	H	<i>p</i> -ClC ₆ H ₄	72 ^{b,c}
Propanal	H	Et	78 ^{c,d}
Butanal	H	Pr ⁿ	70 ^{c,d}
Octanal	H	C ₇ H ₁₅	55 ^{c,d}
Butan-2-one	Me	Et	50 ^{c,d}
Octan-2-one	Me	C ₆ H ₁₃	50 ^{c,d}
Benzophenone	Ph	Ph	82 ^c
Cholest-4-en-3-one	Cholest-4-en-3-ylidene		65 ^{c,d}

^a Of pure isolated compound. ^b Only the *Z*-isomer was isolated (n.m.r. and t.l.c.). ^c Remaining material was chiefly unchanged starting material. ^d Mixture of isomers (n.m.r. and t.l.c.).

sulphones (IV) after chromatography on silica gel. Results with typical carbonyl compounds are shown in the Table.

* Hauser *et al.* have reported the formation of $\alpha\beta$ -diphenylcinnamitrile in 47% yield by refluxing benzophenone with dilithio(phenyl)acetonitrile for 48 h.⁹

† The assignment of the 2-(*p*-chlorophenyl)-1-phenylvinyl phenyl sulphone as the *Z*-isomer is based on the observation that in n.m.r. spectrum the vinyl proton signal occurs at δ 7.9, as observed for the vinyl proton of (*Z*)-1,2-diphenylvinyl phenyl sulphone.¹²

The reaction seems to have a wide applicability. Saturated aliphatic and aromatic aldehydes and ketones, including $\alpha\beta$ -unsaturated carbonyl compounds, can be employed. Products were identified either by direct comparison with authentic materials or by spectroscopic data and elemental analysis.

A possible mechanism for the reaction involves an addition-elimination sequence between the carbonyl compound and the bis(magnesium halide) (IIc). An alternative sequence involves attack of the monolithium mono(magnesium halide) (IIb) on the carbonyl compound, followed by lithium-magnesium exchange in the intermediate adduct (IIIb). It has been shown that treatment of the adduct (IIIa) with 2 mol. equiv. of magnesium iodide gives the $\alpha\beta$ -unsaturated phenyl sulphone (IV) in moderate yield. Whatever the structure of the organometallic species involved, it is well established that 2 mol. equiv. of magnesium iodide are required; the use of 1 mol. equiv. reduces the yield of $\alpha\beta$ -unsaturated phenyl sulphone (IV) by half.

No simple pattern of stereoselective double-bond formation is evident. Reactions with benzaldehyde and *p*-chlorobenzaldehyde give (*Z*)-1,2-diphenylvinyl phenyl sulphone¹² and (*Z*)-2-(*p*-chlorophenyl)-1-phenylvinyl phenyl sulphone,[†] whereas reactions with other carbonyl compounds give *ca.* 1 : 1 mixtures of *Z*- and *E*-isomers. The stereochemistry of the isomers was assigned by analogy with literature data and by consideration of their n.m.r. spectra.

EXPERIMENTAL

I.r. spectra were determined with a Hilger and Watts H 9007 Infracord spectrophotometer. N.m.r. spectra were recorded with a Varian A60 instrument, with tetramethylsilane as internal standard. Mass spectra were measured on a Hitachi-Perkin-Elmer RMU6D (single focus) spectrometer at 70 eV. T.l.c. was performed on silica gel HF₂₅₄ (Merck) and column chromatography on silica gel 0.05—0.20 mm (Merck), with hexane-ether as solvent.

Tetrahydrofuran was obtained dry and oxygen-free by distillation over sodium and lithium aluminium hydride under argon. *n*-Butyl-lithium was purchased from Schuchardt (München) as a 2.5M-solution in *n*-heptane.

General Procedure for Synthesis of $\alpha\beta$ -Unsaturated Phenyl Sulphones.—(a) *With 2 mol. equiv. of magnesium iodide.* A dry vessel was flushed with argon and charged with benzyl phenyl sulphone (1.62 g, 7 mmol) and dry THF (20 ml). The mixture, under argon, was stirred vigorously, and *n*-butyl-lithium in heptane (2.5M; 6 ml, 15 mmol) was added. The mixture was stirred for 1 h at room temperature, then a solution of magnesium iodide (4.17 g, 15 mmol) in dry ether (40 ml) and dry benzene (20 ml) was

⁹ E. M. Kaiser, R. L. Vaulx, and C. R. Hauser, *J. Org. Chem.*, 1967, **32**, 3640.

¹⁰ Cf. R. M. Salinger and R. E. Dessy, *Tetrahedron, Letters* 1963, 729.

¹¹ G. Cainelli, G. Cardillo, M. Contento, G. Trapani, and A. Umani-Ronchi, *J.C.S. Perkin I*, 1973, 400.

¹² Y. Shirota, J. Nagai, and N. T. Okura, *Tetrahedron*, 1967, **23**, 639.

added during 15 min.* After 10 min the carbonyl compound (7 mmol) was added. The mixture was stirred for 2 h under reflux, poured into water (100 ml), and extracted with ether. The extracts were washed with water, dried (Na_2SO_4), and evaporated, and the product was purified by chromatography on silica gel. In most cases only $\alpha\beta$ -unsaturated phenyl sulphone and starting material were isolated.

(Z)-2-(p-Chlorophenyl)-1-phenylvinyl phenyl sulphone (72%) had m.p. 227° (from EtOH), δ [(CD₃)₂SO] 7.9 (p-ClC₆H₄·CH, s) and 7—7.7 (aromatic), *m/e* 354 (*M*⁺), 229 (*M*⁺ - C₆H₅SO), and 213 (*M*⁺ - C₆H₅SO₂) (Found: C, 67.4; H, 4.4; Cl, 10.1. C₂₀H₁₅ClO₂S requires C, 67.8; H, 4.2; Cl, 9.9%). 2-Ethyl-1-phenylvinyl phenyl sulphone, obtained in 78% yield as a ca. 1:1 mixture of isomers, had m.p. 87—90° (from hexane-benzene), δ (CDCl₃) 1.1 (CH₃·CH₂), 2.1 (CH₃·CH₂), 6.8 [EtCH (*E*-isomer)],¹⁴ and 7.05 [EtCH (*Z*-isomer)],¹⁴ *m/e* 272 (*M*⁺), 147 (*M*⁺ - C₆H₅SO), and 131 (*M*⁺ - C₆H₅SO₂) (Found: C, 70.2; H, 5.8. C₁₆H₁₆O₂S requires C, 70.6; H, 5.9%). 1-Phenyl-2-propylvinyl phenyl sulphone, obtained in 70% yield as a ca. 1:1 mixture, had m.p. 72—74° (from hexane-benzene), δ (CDCl₃) 0.85 (CH₃·CH₂), 1.4 (CH₃·CH₂), 2 (CH₂·CH₂), 6.8 [C₃H₇·CH (*E*-isomer)],¹⁴ and 7.05 [C₃H₇·CH (*Z*-isomer)],¹⁴ *m/e* 286 (*M*⁺), 161 (*M*⁺ - C₆H₅SO), and 145 (*M*⁺ - C₆H₅SO₂) (Found: C, 71.2; H, 6.4. C₁₇H₁₈O₂S requires C, 71.3; H, 6.3%). 2-Heptyl-1-phenylvinyl phenyl sulphone, obtained in 55% yield as a ca. 1:1 mixture of isomers, had m.p. 53—55° (from hexane), δ (CDCl₃) 0.8 (CH₃·[CH₂]₆), 6.75 [C₇H₁₅·CH (*E*-isomer)],¹⁴ and 7 [C₇H₁₅·CH (*Z*-isomer)],¹⁴ *m/e* 342 (*M*⁺), 217 (*M*⁺ - C₆H₅SO), and 201 (*M*⁺ - C₆H₅SO₂) (Found: C, 74.2; H, 7.9; S, 8.8. C₂₁H₂₆O₂S requires C, 73.7; H, 7.6; S, 9.3%). 2-Ethyl-2-methyl-1-phenylvinyl phenyl sulphone, obtained in 50% yield as a ca. 1:1 mixture of isomers, had m.p. 59—61° (from hexane-benzene), δ (CDCl₃) 1.2 (CH₃·CH₂, t), 1.65 (CH₃·C=, s), 2.9 (CH₃·CH₂, q), and 6.9—7.7 (aromatic), *m/e* 286 (*M*⁺), 161 (*M*⁺ - C₆H₅SO), and 145 (*M*⁺ - C₆H₅SO₂) (Found: C, 71.4; H, 6.5; S, 11.2. C₁₇H₁₈O₂S requires C, 71.3; H, 6.3; S, 11.2%). 2-Hexyl-2-methyl-1-phenylvinyl phenyl sulphone, obtained in 50% yield as a ca. 1:1 mixture of isomers, had m.p. 75—77° (from hexane), δ (CDCl₃) 1.65 (CH₃·C=) and 6.9—7.8 (aromatic), *m/e* 342 (*M*⁺), 217 (*M*⁺ - C₆H₅SO), and 201 (*M*⁺ - C₆H₅SO₂) (Found: C, 73.9; H, 7.6; S, 9.1.

* Magnesium iodide was made from magnesium and iodine in anhydrous ether.¹³ Benzene was added to prevent the crystallisation of magnesium iodide.

C₂₁H₂₆O₂S requires C, 73.7; H, 7.6; S, 9.3%). 1,2,2-Triphenylvinyl phenyl sulphone, obtained in 82% yield, had m.p. 163—164° (from EtOH), *m/e* 396 (*M*⁺), 271 (*M*⁺ - C₆H₅SO), and 255 (*M*⁺ - C₆H₅SO₂) (Found: C, 78.9; H, 5.1; S, 8.0. C₂₆H₂₀O₂S requires C, 78.8; H, 5.0; S, 8.1%). 3-(α -Phenylsulphonylbenzyl)cholest-4-ene, obtained in 65% yield as a ca. 1:1 mixture of isomers, had m.p. 168—169° (from EtOAc), δ (CDCl₃) 5.35 (CH=C) and 7.1—7.7 (aromatic), *m/e* 598 (*M*⁺) and 457 (*M*⁺ - C₆H₅SO₂) (Found: C, 80.4; H, 9.2; S, 5.1. C₄₀H₅₄O₂S requires C, 80.3; H, 9.1; S, 5.3%).

(b) *With 1 mol. equiv. of magnesium iodide.* The procedure described in (a) was used except that the quantity of magnesium iodide was halved. 1,2,2-Triphenylvinyl phenyl sulphone was isolated in 40% yield.

(c) *Reaction between $\alpha\alpha$ -dilithiobenzyl phenyl sulphone and propionaldehyde.* To a solution of the sulphone (IIa) [prepared from benzyl phenyl sulphone (0.81 g, 3.5 mmol) in dry THF (20 ml) and n-butyl-lithium in heptane (2.5 ml; 2.8 ml, 7 mmol)] was added propionaldehyde (0.205 g, 3.5 mmol) in dry THF (20 ml). The mixture was stirred for 2 h at room temperature and then worked up. Chromatography on silica gel gave 2-ethyl-1-phenylvinyl phenyl sulphone (0.083 g, 8%) and 1-phenyl-1-phenylsulphonylbutan-2-ol (0.66 g, 60%), m.p. 120—121° (from EtOH), δ (CDCl₃) 3.2 (d, OH), 4 (d, PhSO₂·CH), and 4.7 (m, EtCH), *m/e* 290 (*M*⁺) (Found: C, 66.1; H, 6.3; S, 10.8. C₁₆H₁₈O₃S requires C, 66.2; H, 6.2; S, 11.0%).

(d) *Treatment of the adduct (IIIa; R³ = R⁴ = Ph) with magnesium iodide.* To a solution of $\alpha\alpha$ -dilithiobenzyl phenyl sulphone (IIa) [from benzyl phenyl sulphone (0.81 g, 3.5 mmol) in dry THF (16 ml) and n-butyl-lithium in heptane (2.5 ml; 2.8 ml, 7 mmol)] was added benzophenone (0.63 g, 3.5 mmol) in dry THF (10 ml). After 20 min magnesium iodide (1.95 g, 7 mmol) in dry ether (20 ml) and dry benzene (10 ml) was added. The mixture was stirred for 2 h under reflux, poured into water (60 ml), and extracted with ether. The extracts were washed with water, dried (Na_2SO_4), and evaporated. Chromatography on silica gel gave 1,2,2-triphenylvinyl phenyl sulphone (35%).

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