89. *Action of Grignard Solutions on* (a) *Naphthasultone,* (b) *Tolylene-3 : 4-sulphonylide, and* (c) NN′-*Diarylsulphonyl Derivatives of Dianthranilide.*

By Ahmed Mustafa and Ahmed Mohamed Gad.

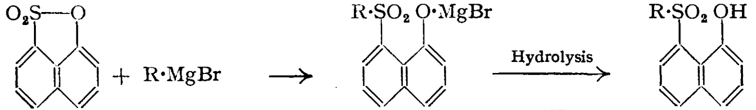
(*a*) 1-Hydroxy-8-phenylsulphonylnaphthalene (II) and 1-hydroxy-8-α-naphthylsulphonylnaphthalene (III) were obtained by the action of phenyl- and α-naphthyl-magnesium bromide respectively on naphthasultone (I).

(*b*) 2-Hydroxy-5-methyldiphenyl sulphone (V) was similarly obtained by the action of phenylmagnesium bromide on tolylene-3 : 4-sulphonylide (IV).

(*c*) The action of Grignard solutions on *NN*′-diarylsulphonyl derivatives of dianthranilide (VI*a*, VI*b*) leads to the formation of *N*-arylsulphonyl derivatives of *o*-aminotriarylcarbinols

(VII*a*—VII*c*), and 2-toluene-*p*-sulphonamidophenyldimethylcarbinol (VII*d*) is obtained by the action of methylmagnesium iodide on (VI*b*). The latter, when heated with aniline, gives *o*-toluenesulphonamidobenzanilide.

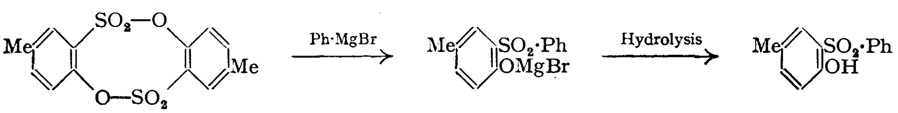
DURING the investigation of the action of diazomethane on *o*-hydroxydiaryl sulphones and the corresponding *peri*-compounds (Schönberg and Mustafa, *J.*, 1948, 605), 1-hydroxy-8-phenyl-(II) and -8-α-naphthyl-sulphonylnaphthalene (III) were synthesised. The synthesis was carried out by the action of phenyl- and α-naphthyl-magnesium bromide, respectively, on naphthasultone (I), followed by hydrolysis; (II) and (III) react with ethereal diazomethane to form the corresponding methoxy-derivatives (Schönberg and Mustafa, *loc. cit.*), dissolve in aqueous alkalis, and contain active hydrogen.



(I.)

(II, R = Ph; III, R = α-$C_{10}H_7$.)

2-Hydroxy-5-methyldiphenyl sulphone (V) was obtained, similarly, by the action of phenylmagnesium bromide on tolylene-3 : 4-sulphonylide (IV), followed by hydrolysis; (V) reacts with ethereal diazomethane to give 2-methoxy-5-methyldiphenylsulphone (Schönberg and Mustafa, *loc. cit.*).

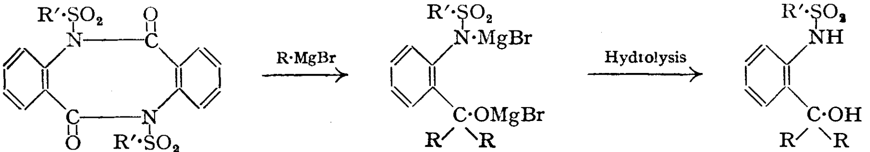


(IV.)

(V.)

The action of Grignard solutions on (I) and (IV) constitutes a new method for the preparation of *o*-hydroxydiaryl sulphones and the corresponding *peri*-compounds.

Very little is known about the action of Grignard solutions on *NN'*-diarylsulphonyl derivatives of dianthranilide. We have investigated the action of Grignard solutions on (VI*a*) and (VI*b*) and obtained the corresponding o-*arylsulphonamidotriarylcarbinols* (VII*a*—VII*c*). The action of methylmagnesium iodide on the dianthranilide (VI*b*) yields 2-toluene-*p*-sulphonamidophenyldimethylcarbinol (VII*d*). We believe that the reaction occurs according to the following scheme :



(VI*a*, R' = Ph;
VI*b*, R' = *p*-C_6H_4Me.)

(VII*a*, R = R' = Ph;
VII*b*, R = Ph, R' = *p*-C_6H_4Me;
VII*c*, R = R' = *p*-C_6H_4Me;
VII*d*, R = Me, R' = *p*-C_6H_4Me.)

Constitution of the Products obtained (VIIa—VIId).—These products are of analogous structure; 2-toluene-*p*-sulphonamidotriphenylcarbinol (VII*b*) is taken as an example. Its constitution is based on its identity with a synthetic specimen obtained by the action of toluene-*p*-sulphonyl chloride on *o*-aminotriphenylcarbinol. These products are almost colourless, soluble in aqueous alkali (cf. Gilman, " Organic Chemistry," 2nd edtn., 1944, Vol. 1, p. 901), contain an active hydrogen atom and give the expected molecular weights; both (VII*b*) and the synthetic substance, when heated with aniline, gave (probably) bis-(2-toluene-*p*-sulphonamidotriphenylmethyl) ether; (VII*b*) also reacts with ethereal diazomethane (details will be published later).

Action of Aniline on NN'-*Ditoluene*-p-*sulphonyldianthranilide* (VIb).—This reaction affords 2-toluene-*p*-sulphonamidobenzanilide. When aniline is replaced by tetralin, (VI*b*) is recovered unchanged. The anilide was also obtained by the action of aniline on 2-toluene-*p*-sulphonamidobenzoyl chloride in dry benzene.

EXPERIMENTAL.

1-*Hydroxy*-8-*phenylsulphonylnaphthalene* (II).—To an ethereal solution of phenylmagnesium bromide [from magnesium (0·9 g.), bromobenzene (9·4 g.), and dry ether (40 c.c.)], naphthasultone (I) (1·5 g.)

(Erdmann, *Annalen*, 1888, **247**, 306) and dry benzene (30 c.c.) were added. The mixture was refluxed for 3 hours and set aside overnight, then decomposed with cold dilute hydrochloric acid and extracted with ether. The ethereal solution was dried and evaporated, and the residue extracted several times with light petroleum (b. p. 30—50°); it then crystallised from benzene–light petroleum (b. p. 50—70°) in almost colourless crystals, m. p. 140° (Found : C, 67·4; H, 4·0; S, 11·0; active hydrogen, 0·32. $C_{16}H_{12}O_3S$ requires C, 67·6; H, 4·2; S, 11·3; active hydrogen, 0·35%). This *compound* dissolves in aqueous sodium hydroxide solution with a yellow colour and is regenerated on acidification; it is converted into its methyl ether when treated with ethereal diazomethane solution (Schönberg and Mustafa, *loc. cit.*). It is soluble in benzene and ethyl alcohol, difficultly soluble in light petroleum (b. p. 50—70°), and gives no colour when treated with concentrated sulphuric acid.

1-*Hydroxy*-8-α-*naphthylsulphonylnaphthalene* (III).—Similarly, naphthasultone (1 g.) was treated with α-naphthylmagnesium bromide [magnesium (1·2 g.), α-bromonaphthalene (10 g.), dry ether (40 c.c.)]. The *compound* was obtained in colourless crystals from benzene–light petroleum (b. p. 50—70°), m. p. 188° (brown melt) (Found : C, 71·5; H, 4·0; S, 9·7; active hydrogen, 0·26. $C_{20}H_{14}O_3S$ requires C, 71·8; H, 4·2; S, 9·6; active hydrogen, 0·29%). It was difficultly soluble in aqueous sodium hydroxide solution with a brilliant yellow colour, gave no colour with concentrated sulphuric acid, and was methylated like (II). It was soluble in benzene and xylene and difficultly soluble in light petroleum (b. p. 70—80°).

2-*Hydroxy*-5-*methyldiphenyl Sulphone* (V).—By an exactly analogous procedure to that used for (II), the sulphone (V) was obtained by the action of phenylmagnesium bromide on tolylene-3 : 4-sulphonylide (IV) (Anschütz, *Annalen*, 1918, **415**, 76); it formed colourless crystals from benzene–light petroleum (b. p. 50—70°), m. p. 137—138° (Heppenstall and Smiles, *J.*, 1938, 899, gave m. p. 139°); it dissolves readily in benzene, xylene, and hot ethyl alcohol and is difficultly soluble in light petroleum (b. p. 70—80°) (Found : C, 62·7; H, 4·6; S, 12·7. Calc. for $C_{13}H_{12}O_3S$: C, 62·9; H, 4·8; S, 12·9%). It was *O*-methylated by ethereal diazomethane.

Action of Phenylmagnesium Bromide on NN′-*Diphenylsulphonyldianthranilide* (VI*a*).—To an ethereal solution of phenylmagnesium bromide [magnesium (0·9 g.), bromobenzene (9·4 g.) and dry ether (25 c.c.)] dry benzene (50 c.c.) and (VI*a*) (1·5 g.) (Heller, *Ber.*, 1916, **49**, 547) were added. The mixture was refluxed with stirring for 3 hours, the ether being allowed to evaporate slowly. The substance dissolved completely, and the reaction mixture was left overnight and then decomposed with cold water followed by aqueous ammonium chloride solution. The organic matter was extracted with ether, and the residue remaining after evaporation of the ether was washed with light petroleum (b. p. 30—50°) and crystallised from benzene–light petroleum (b. p. 50—70°), forming colourless crystals, m. p. 188° (decomp.; yellow melt) [Found : C, 72·2; H, 4·9; N, 3·3; S, 7·6; active hydrogen, 0·23; *M* (micro-Rast), 402. $C_{25}H_{21}O_3NS$ requires C, 72·3; H, 5·1; N, 3·4; S, 7·7; active hydrogen, 0·24%; *M*, 415]. o-*Phenylsulphonamidotriphenylcarbinol* (VII*a*) is soluble in hot benzene and xylene and difficultly soluble in cold benzene and ethyl alcohol; it gives a reddish-brown colour with concentrated sulphuric acid.

Action of Grignard Solutions on NN′-*Ditoluene*-p-*sulphonyldianthranilide* (VI*b*).—(*a*) *Phenylmagnesium bromide*. The dianthranilide (Anschütz, *loc. cit.*) (1·5 g.) was treated with phenylmagnesium bromide as detailed above. 2-*Toluene*-p-*sulphonamidotriphenylcarbinol* (VII*b*) was obtained in colourless crystals from benzene–light petroleum (b. p. 30—50°), m. p. 196° (yellow melt) [Found : C, 72·5; H, 5·4; N, 3·2; S, 7·3; active hydrogen, 0·21; *M* (micro-Rast), 418. $C_{26}H_{23}O_3NS$ requires C, 72·7; H, 5·4; N, 3·3; S, 7·5; active hydrogen, 0·23%; *M*, 429]; it gives a reddish-brown colour with concentrated sulphuric acid, and its solubility properties are similar to those of (VII*a*).

For comparison (VII*b*) was synthesised as follows. *o*-Aminotriphenylcarbinol (1 g.) (Baeyer and Villiger, *Ber.*, 1904, **37**, 3193), dissolved in the minimum of dry pyridine, was treated with toluene-*p*-sulphonyl chloride. The mixture was heated on a water-bath for 4 hours, kept overnight, and then poured on ice. The oil which separated solidified on cooling and rubbing; it was filtered off, washed several times with light petroleum (b. p. 50—70°), and crystallised from benzene–light petroleum (b. p. 30—50°), forming colourless crystals, m. p. 195°, identical with (VII*b*) (m. p. and mixed m. p. and colour reaction with sulphuric acid) (Found : C, 72·4; H, 5·2; N, 3·3; S, 7·6%).

(*b*) p-*Tolylmagnesium bromide*. 2-*Toluene*-p-*sulphonamidophenyldi*-p-*tolylcarbinol* (VII*c*) was obtained similarly, in colourless crystals, m. p. 140° (yellow melt), from ethyl alcohol [Found : C, 73·5; H, 5·7; N, 3·1; S, 6·8; *M* (micro-Rast), 430. $C_{28}H_{27}O_3NS$ requires C, 73·5; H, 5·9; N, 3·1; S, 7·0%; *M*, 457]. It gives an yellow-orange colour with sulphuric acid.

(*c*) *Methylmagnesium iodide*. The dianthranilide (VI*b*) (1 g.) was treated with methylmagnesium iodide [from magnesium (0·6 g.), methyl iodide (3·6 g.), and dry ether (50 c.c.)] as described for (VII*b*). The oily residue was washed several times with light petroleum (b. p. 70—80°) and formed colourless crystals, m. p. 112° [Found : C, 62·8; H, 5·9; N, 4·4; S, 10·2; *M* (micro-Rast), 295. $C_{16}H_{19}O_3NS$ requires C, 62·9; H, 6·2; N, 4·6; S, 10·5%; *M*, 305]. 2-*Toluene*-p-*sulphonamidophenyldimethylcarbinol* (VII*d*) dissolves in cold aqueous sodium hydroxide and is recovered unchanged on acidification with dilute hydrochloric acid; it gives a yellow colour with sulphuric acid and is easily soluble in benzene and ethyl alcohol.

The carbinol (VII*b*) (1 g.) was refluxed with freshly distilled aniline (20 c.c.) for 3 hours. The mixture was then steam-distilled and the oily residue extracted with ether; the ethereal extract was dried (Na_2SO_4), evaporated, and the solid crystalline residue was recrystallised from benzene–light petroleum (b. p. 30—50°), forming colourless crystals, m. p. 212° (yellow melt). *Bis*-(2-*toluene*-p-*sulphonamidotriphenylmethyl*) *ether* is soluble in hot benzene and xylene, difficultly soluble in cold ethyl alcohol, benzene, and light petroleum (b. p. 30—50°); it gives a yellowish-brown colour with sulphuric acid [Found : C, 73·9; H, 4·9; N, 3·2; S, 7·5; *M* (micro-Rast), 795. $C_{52}H_{44}O_5N_2S_2$ requires C, 74·3; H, 5·2; N, 3·3; S, 7·6%; *M*, 840]. This ether was also obtained when the synthetic (VII*b*) was treated similarly (m. p. and mixed m. p.) (Found : C, 74·0; H, 5·1; N, 3·2; S, 7·4%).

Action of Aniline on NN′-*Ditoluene*-p-*sulphonyldianthranilide* (VI*b*).—The substance (Anschütz, *loc. cit.*) under exactly the same conditions afforded an oily residue, which after being washed several times with light petroleum (b. p. 30—50°) and crystallised from benzene–light petroleum (b. p. 30—50°) formed colourless crystals, m. p. 140° [Found : C, 65·5; H, 4·8; N, 7·4; S, 8·4; *M* (micro-Rast), 360. $C_{20}H_{18}O_3N_2S$ requires C, 65·6; H, 4·9; N, 7·7; S, 8·8%; *M*, 366]. *2-Toluene-*p*-sulphonamidobenzanilide* is easily soluble in benzene and hot ethyl alcohol and difficultly soluble in light petroleum (b. p. 50—70°); it gives no colour when treated with concentrated sulphuric acid and reacts with ethereal diazomethane solution (details will be published later). The same substance was synthesised by interaction of a solution of 2-toluene-*p*-sulphonamidobenzoyl chloride (2 g.) (Anschütz, *loc. cit.*) in dry benzene (40 c.c.) and freshly distilled aniline (5 c.c.). The reaction mixture was refluxed for 4 hours, cooled, and filtered from the separated aniline hydrochloride. The benzene solution was washed with dilute hydrochloric acid, followed by aqueous sodium carbonate solution and then with water; it was dried (Na_2SO_4) and evaporated. The oily residue was washed several times with light petroleum (b. p. 50—70°) and the resulting solid crystallised from benzene–light petroleum (b. p. 30—50°) in colourless crystals identical (m. p. and mixed m. p.) with the foregoing (Found : C, 65·5; H, 4·9; N, 7·6; S, 8·5%).

FOUAD I UNIVERSITY, FACULTY OF SCIENCE,
ABBASSIA, CAIRO, EGYPT.

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