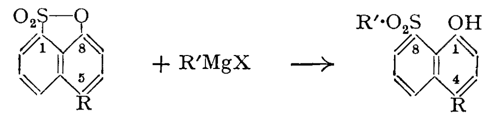
456. *Action of Grignard Solutions. Part III.* Action of Grignard Solutions on Naphthasultone and its Substituted Derivatives.*

By Ahmed Mustafa.

The action of Grignard solutions on naphthasultone (I; R = H) and its 5-methyl, 5-phenylsulphonyl, and 5-toluene-*p*-sulphonyl derivatives leads to a number of new *peri*-compounds, namely hydroxydiaryl sulphones (II). These react readily with ethereal diazomethane in the absence of methyl alcohol to form the corresponding methyl ethers.

In Part I (Mustafa and Gad, this vol., p. 384) it was shown that the action of Grignard solutions on tolylene-3 : 4-sulphonylide and naphthasultone (8-hydroxynaphthalene-1-sulphonic acid sultone) (I; R = H) provides a new method of preparing *o*-hydroxydiaryl sulphones and the corresponding *peri*-compounds. The reaction has been further investigated and a number of new *peri*-compounds has been synthesised.

8-Methylsulphonyl-, 8-ethylsulphonyl-, and 8-*tert*.-butylsulphonyl-1-naphthol were obtained by the action of the methyl-, ethyl-, and *tert*.-butyl-magnesium halide, respectively, on naphthasultone (I; R = H), followed by hydrolysis, and 8-ethylsulphonyl-4-methyl-, 8-phenylsulphonyl-4-methyl-, 8-methylsulphonyl-4-methyl-, and 8-1′-naphthylsulphonyl-4-methyl-1-naphthol by the action of the appropriate Grignard reagent on 5-methylnaphthasultone (I; R = Me). In an analogous way, use of 5-phenylsulphonyl- or 5-toluene-*p*-sulphonyl-naphthasultone as starting material led to the disulphonylnaphthols recorded in the table (overleaf).

(I.)  (II.)

The constitution of the products follows from the facts that they are colourless, react with ethereal diazomethane in the absence of methyl alcohol to form the corresponding methyl ethers (cf. Schonberg and Mustafa, *J.*, 1948, 605), dissolve in aqueous alkali, and contain active hydrogen.

The action of Grignard solutions on the sultones is an example of the breaking of the S–O linkage by this reagent. The application of the method for the synthesis of *o*-hydroxydiaryl sulphones and corresponding *peri*-compounds is under further investigation.

Experimental.

Action of Grignard Solutions on Naphthasultones.—The following exemplifies the procedure. Naphthasultone (I; R = H) (Erdmann, *Annalen*, 1888, **247**, 306) (3·5 g.) in dry benzene (50 c.c.) was added to a solution of *tert*.-butylmagnesium bromide [prepared from magnesium (1 g.), *tert*.-butyl bromide (14 g.), and dry ether (40 c.c.)], and the mixture was heated under reflux for 4 hours and then set aside overnight. The complex which separated was filtered off, decomposed with cold dilute hydrochloric acid, and extracted with ether. The ethereal solution was dried, the solvent evaporated, and the residue washed twice with cold light petroleum (b. p. 30—50°) and then with hot benzene (*ca.* 15 c.c.). The 8-tert.-*butylsulphonyl*-1-*naphthol* (3·5 g., *ca.* 75%) obtained was filtered off and crystallised (cf. the table).

The *naphthols* listed in the table were prepared similarly (for the compound in which R = $PhSO_2$ and R′ = Ph heating was for only 3 hours); except for methylmagnesium iodide, the Grignard reagents were bromides.

The naphthols dissolve in cold aqueous sodium hydroxide to give yellow solutions. In general they dissolve in hot alcohol, benzene, or acetone, but are sparingly soluble in light petroleum (b. p. 30—50°); the di- are less soluble than the mono-sulphonyl compounds.

Methylation.—This was effected by ethereal diazomethane (prepared from 8 g. of nitrosomethylurea) during 24 hours at 0°. The reaction mixture was evaporated, and an ethereal solution of the residue was treated with aqueous potassium hydroxide (to remove unchanged naphthol) and then with water, dried, and evaporated. The *ethers* prepared are recorded in the table. They are insoluble in aqueous alkali and give no colour in concentrated sulphuric acid. They are rather more soluble than the parent naphthols in organic solvents.

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* Part II, this vol., p. 1662.

		Naphthols (II).										Methyl ethers of (II).								
			Solvent for	Colour in	Found, %.				Required, %.				Solvent for	Found, %.				Required, %.		
R.	R′.	M. p.*	crystn.	H_2SO_4.	C.	H.	S.	Formula.	C.	H.	S.	M. p.*	crystn.	C.	H.	S.	Formula.	C.	H.	S.
H	Me	150°	A	yellow	59·3	4·5	14·1	$C_{11}H_{10}O_3S$	59·4	4·5	14·4	138—139°	A	61·0	5·1	12·9	$C_{12}H_{12}O_3S$	61·0	5·1	13·5
H	Et	210	B	,,	60·8	5·0	13·3	$C_{12}H_{12}O_3S$	61·0	5·1	13·5	146	A	62·2	5·5	12·5	$C_{13}H_{14}O_3S$	62·4	5·6	12·8
H	Bu^t	240 (pale brown)	B	none	63·5	5·9	12·0	$C_{14}H_{16}O_3S$ [a]	63·5	6·1	12·1	205—206 (pale yellow)	B or C	64·5	6·3	11·3	$C_{15}H_{18}O_3S$	64·7	6·5	11·5
Me	Me	155	C	yellow	60·7	4·9	13·4	$C_{12}H_{12}O_3S$	61·0	5·1	13·5	125	G	62·2	5·4	12·4	$C_{13}H_{14}O_3S$	62·4	5·6	12·8
Me	Et	158	D	,,	62·3	5·6	12·6	$C_{13}H_{14}O_3S$	62·4	5·6	12·8	126	G	63·3	6·0	11·9	$C_{14}H_{16}O_3S$	63·6	6·1	12·1
Me	Ph	170	D	,,	68·1	4·5	10·6	$C_{17}H_{14}O_3S$ [b]	68·4	4·7	10·7	147	A	68·9	5·0	10·1	$C_{18}H_{16}O_3S$	69·2	5·1	10·3
Me	1-$C_{10}H_7$	180	E	,,	72·0	4·5	8·9	$C_{21}H_{16}O_3S$	72·4	3·6	9·2	133	F	72·8	4·9	8·7	$C_{22}H_{18}O_3S$	72·9	4·9	8·8
$PhSO_2$	Bu^t	148—149	F	none	59·3	4·7	15·6	$C_{20}H_{20}O_5S_2$	59·4	4·9	15·8	—	—	—	—	—	—	—	—	—
$PhSO_2$	Ph	282 (brown)	B	,,	62·2	3·7	14·9	$C_{22}H_{16}O_5S_2$ [c]	62·3	3·9	15·1	—	—	—	—	—	—	—	—	—
$PhSO_2$	*p*-tolyl	237—238	B	pale brown	62·95	4·0	14·5	$C_{23}H_{18}O_5S_2$	63·0	4·1	14·6	—	—	—	—	—	—	—	—	—
$PhSO_2$	1-$C_{10}H_7$	218 (pale yellow)	B	none	65·9	3·7	13·4	$C_{26}H_{18}O_5S_2$ [d]	65·8	3·8	13·5	148	B	66·2	4·0	12·9	$C_{27}H_{20}O_5S_2$ [g]	66·4	4·1	13·1
Tos †	Me	146	B	—	57·2	4·3	16·8	$C_{18}H_{16}O_5S_2$	57·4	4·3	17·0	96	B	58·4	4·4	16·3	$C_{19}H_{18}O_5S_2$ [h]	58·5	4·6	16·4
Tos	Ph	260	B	none	62·9	3·9	14·3	$C_{23}H_{18}O_5S_2$	63·0	4·1	14·6	205	A	63·5	4·4	14·0	$C_{23}H_{18}O_5S_2$	63·8	4·4	14·2
Tos	Tos	247—248	—	—	63·7	4·2	14·1	$C_{24}H_{20}O_5S_2$ [e]	63·8	4·4	14·2	232—233	C	64·2	4·5	13·4	$C_{25}H_{22}O_5S_2$ [j]	64·4	4·7	13·7

* Colours are those of the melts. † Toluene-*p*-sulphonyl.

Solvents: A, methyl alcohol; B, benzene; C, ethyl alcohol; D, benzene–light petroleum (b. p. 30—50°); E, benzene–ethyl alcohol; F, light petroleum (b. p. 30–50°) (slow evaporation); G, light petroleum, (b. p. 100—110°).

[a] Active H: found, 0·37; required, 0·38%. [b] Active H: found, 0·32; required, 0·33%. [c] Found: active H, 0·23%; *M*, 417. Required: active H, 0·24%; *M*, 424. [d] *M*: found, 465; required, 474. [e] *M*: found, 446; required 452. OMe: found, 11·0; required 11·2%. [g] OMe: found, 6·3; required, 6·4%. [h] OMe: found, 7·6; required, 7·9%. [j] OMe: found, 6·5; required, 6·7%.