126. *Experiments with Diazomethane and its Derivatives. Part XIV. Action of Diazomethane on* (a) N-*Acyl Compounds and* (b) o-*Hydroxydiaryl Sulphones and the Corresponding* peri-*Compounds.*

By ALEXANDER SCHÖNBERG and AHMED MUSTAFA.

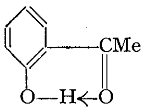
It was found that certain *N*-diacyl compounds are stable towards ethereal diazomethane but are converted into the corresponding monoacyl compounds by an ether–methyl alcoholic diazomethane solution.

o-Hydroxydiaryl sulphones (in contrast to many *o*-hydroxydiaryl ketones) can be converted into the corresponding methoxy-derivatives by the action of ethereal diazomethane.

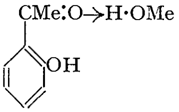
(*a*) SCHÖNBERG and MUSTAFA (*J.*, 1946, 746) found that diazomethane in a mixture of ether and an aliphatic alcohol forms an addition product (*e.g.*, I*a* or I*b*) which has powerful alkylating properties. For instance, with *n*-propyl alcohol the di-*n*-propyl ether of stilboestrol is produced, and in methyl alcohol benzophenone oxime can be methylated, whereas it is unaffected by *ethereal* diazomethane. We now show that diazomethane in ether–methyl alcohol quantitatively converts *N*-diacetyl-α- or -β-naphthylamine, -aniline, or -*p*-toluidine, or *N*-dibenzoyl-aniline or -α-naphthylamine into the corresponding monoacyl compounds. The *N*-diacyl compounds are stable to ether, to a mixture of ether and methyl alcohol, or to ethereal diazomethane under the experimental conditions used (24 hours in the cold): reaction takes place only with diazomethane in a mixture of ether and alcohol. It is believed that the reaction proceeds according to the following scheme, in which (II) is hypothetical.

$$\underset{(\text{I}a.)}{\mathrm{CH_3{\cdot}N{:}N{\cdot}OMe}} \leftrightarrows \underset{(\text{I}b.)}{\mathrm{CH_2{:}N{\cdot}NH{\cdot}OMe}} + \mathrm{NPhAc_2} \longrightarrow \mathrm{Ph{\cdot}NHAc} + \underset{(\text{II}.)}{\mathrm{CH_2{:}N{\cdot}NAc{\cdot}OMe}}$$

(*b*) It is known that many *o*-hydroxy-ketones (Schönberg and Mustafa, *loc. cit.*) do not react with ethereal diazomethane but are methylated by diazomethane in an ether–alcohol medium. This is due, not only to the formation of an alkylating agent (*e.g.*, I*a* and I*b*), but also to the fact that by the action of methyl alcohol the chelated ring systems are opened (*e.g.*, III and IV). We were interested to discover whether *o*-hydroxydiaryl sulphones as well as the corresponding *peri*-compounds are capable of reacting with diazomethane even in the absence of alcohol; this is indeed the case with (VI) and (VII; R = Ph or α-naphthyl). This fact may be interpreted in two ways: either there is no chelation at all in these compounds, or the ring formed by chelation is easily broken. Reference should be made to formula (V) (cf. Gilman "Organic Chemistry, An Advanced Treatise", 2nd edtn., p. 1870, New York, 1944).



(III.)



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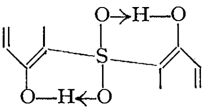
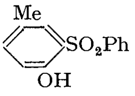
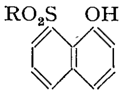


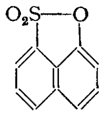
(V.)



(VI.)



(VII.)



(VIII.)

1-Hydroxy-8-phenylsulphonylnaphthalene (VII, R = Ph) and 1-hydroxy-8-α-naphthylsulphonylnaphthalene (VII, R = $C_{10}H_7$) were synthesised by the action of phenyl- and α-naphthyl-magnesium bromide respectively on naphthasultone (VIII), followed by hydrolysis. (This method will be described in detail later.) Phenyl 4-hydroxy-*m*-tolyl sulphone (VI) was obtained in a similar manner from tolylene-3 : 4-sulphonylide (Anschütz, *Annalen*, 1918, **415**, 76).

We found that naphthasultam (VIII, but with NH instead of O) is converted into the *N*-methyl derivative by the action of diazomethane in ether (for the *N*-methylation of saccharin and related substances, see Schönberg *et al.*, *Ber.*, 1933, **66**, 244).

EXPERIMENTAL.

Action of Ethereal Diazomethane in the Presence or in the Absence of Methyl Alcohol on N-*Diacetylamines and on Acet-α-naphthalide.*—(i) The ethereal diazomethane solution was prepared by reaction between aqueous potassium hydroxide and a suspension of nitrosomethylurea (8 g.), followed by distillation of the ether and diazomethane (*Org. Synth.*, **15**, 3). The ethereal distillate containing the diazomethane was divided into two equal portions of 55 c.c. In each portion *N*-diacetyl-α-naphthylamine (0·1 g.) was dissolved, and to one solution methyl alcohol (5 c.c.) was added; both were then kept in an ice-chest overnight. The solution containing methyl alcohol afforded acet-α-naphthalide (m. p. and mixed m. p.) in quantitative yield, whereas the other afforded the diacetyl derivative (m. p. and mixed m. p.).

(ii) Precisely similar experiments with acet-α-naphthalide led to its recovery unchanged in each case.

(iii) A solution of *N*-diacetyl-α-naphthylamine in ether–methyl alcohol of the above composition was unchanged after 24 hours in an ice-chest.

(iv) By the procedure described for *N*-diacetyl-α-naphthylamine [(i) above], the other five diacyl compounds mentioned on p. 605 were quantitatively transformed into monoacyl derivatives (identified by m. p. and mixed m. p.).

Action of Ethereal Diazomethane Solution on N-*Diacetyl-α-naphthylamine in the Presence of* n-*Propyl Alcohol.*—The experiment (first paragraph) was repeated but with *n*-propyl alcohol (5 c.c.) in place of methyl alcohol. Acet-α-naphthalide (m. p. and mixed m. p.) was obtained in quantitative yield.

Action of Ethereal Diazomethane on o-*Hydroxydiaryl Sulphones and the Corresponding* peri-*Compounds.*—(i) Phenyl 4-hydroxy-*m*-tolyl sulphone (VI) was allowed to react with ethereal diazomethane, prepared as above, for 24 hours at 0°. The reaction product was evaporated to dryness, and an ethereal solution of the residue was treated with aqueous potassium hydroxide (to remove unchanged VI) and then with water, dried (Na_2SO_4), and the ether evaporated at room temperature. Phenyl 4-methoxy-*m*-tolyl sulphone crystallised from benzene–light petroleum (b. p. 50—70°) as colourless crystals, m. p. 139°, insoluble in aqueous sodium hydroxide (Found: C, 63·7; H, 5·5; S, 12·2. Calc. for $C_{14}H_{14}O_3S$: C, 64·1; H, 5·3; S, 12·2%). Heppenstall and Smiles (*J.*, 1938, 899) gave m. p. 137—138°.

(ii) 1-*Methoxy*-8-*phenylsulphonylnaphthalene* was obtained from 1-hydroxy-8-phenylsulphonylnaphthalene (VII, R = Ph) by the above method in colourless crystals, m. p. 165°, from benzene–light petroleum (b. p. 50—70°); they were insoluble in aqueous sodium hydroxide and gave no colour reaction with sulphuric acid (Found: C, 68·3; H, 4·6; S, 10·7. $C_{17}H_{14}O_3S$ requires C, 68·5; H, 4·7; S, 10·7%).

(iii) 1-*Methoxy*-8-α-*naphthylsulphonylnaphthalene* was obtained similarly from 1-hydroxy-8-α-naphthylsulphonylnaphthalene (VII, R = $C_{10}H_7$) as colourless crystals, m. p. 220°, from benzene–light petroleum (b. p. 50—70°); they were insoluble in hot aqueous sodium hydroxide (Found: C, 72·2; H, 4·6; S, 8·9; OMe, 8·5. $C_{21}H_{16}O_3S$ requires C, 72·4; H, 4·6; S, 9·2; OMe, 8·9%).

Action of Ethereal Diazomethane on 1 : 8-*Naphthasultam.*—*N*-Methylnaphthasultam was similarly obtained by the action of ethereal diazomethane on naphthasultam (Dannerth, *J. Amer. Chem. Soc.*, 1907, **29**, 1319) as colourless crystals, m. p. 125—126°, from benzene–light petroleum (b. p. 50—70°). It was soluble in hot ethyl alcohol with a greenish-violet fluorescence and gave a violet fluorescence with sulphuric acid after some time (Found: C, 60·4; H, 4·4; N, 6·0; S, 14·3. Calc. for $C_{11}H_9O_2NS$: C, 60·2; H, 4·1; N, 6·4; S, 14·6%). Dannerth (*loc. cit.*) gave m. p. 125°.

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