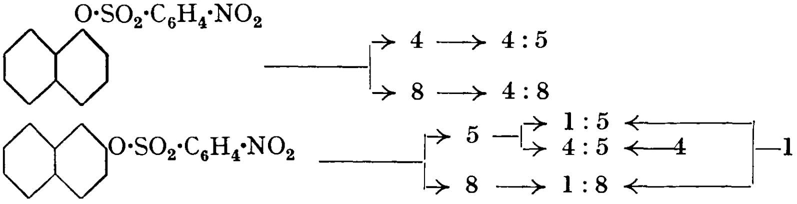
79. *The Nitration of α- and β-Naphthols.*

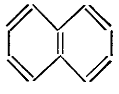
By F. Bell.

NITRATION of α- and β-naphthyl *m*-nitrobenzenesulphonates is shown to proceed according to the schemes :

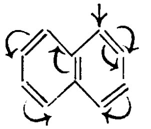


The direction of mononitration of the α-compound is in large part determined by the concentration of the acid employed, high concentration favouring formation of the 8-derivative. By severing the nitro-*m*-nitrobenzenesulphonates with piperidine, the corresponding nitronaphthols were obtained. 8-*Nitro-α-naphthol* was easily isolated in spite of previously reported failures to prepare it by diazotisation of 8-nitro-α-naphthylamine (*e.g.*, Meldola and Streatfeild, J., 1893, **63**, 1056). In the β-series, 1 : 5- and 4 : 5-*dinitro-β-naphthols* are described for the first time, and it is obvious that the method could be extended to the production of compounds such as 2 : 5- and 2 : 8-dinitro-α-naphthols.

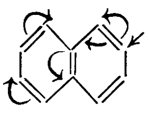
If naphthalene normally reacts in the symmetrical form (I) (Thompson, *J. Soc. Chem. Ind.*, 1933, **52**, 61), electronic displacements originating at the α-atom should lead to 2 : 4 : 5 : 7-substitution (II), and at the β-atom to 1 : 6 : 8-substitution (III). The results obtained on nitration of α- and β-naphthols and their methyl and ethyl ethers (Table I) are in agreement with this view. On the other hand, if the effects are not of sufficient magnitude to be transmitted from one nucleus to the other, the molecule might be expected to show the presence of two mutually reacting ethenoid systems.



(I.)



(II.)



(III.)

TABLE I.

	Nitro-compounds produced.				Nitro-compounds produced.		
1-Substituent.	First.	Second.	Third.	2-Substituent.	First.	Second.	Third.
OH	4	2 : 4	2 : 4 : 5 2 : 4 : 7	OH	1	1 : 6	
OMe OEt	2 4	2 : 4 4 : 5	2 : 4 : 5	OMe OEt	1 6 8	1 : 6 1 : 8	1 : 6 : 8

EXPERIMENTAL.

The author is indebted to Mr. R. Cohen, B.Sc., for the substances indicated by an asterisk.

Nitration of α-Naphthyl m-*Nitrobenzenesulphonate*.—(a) 7 G. were added to a mixture of fuming HNO_3 (7 c.c.) and AcOH (14 c.c.), and the whole gently warmed until solution occurred. On cooling, there separated crystals (3·5 g.) which, after recrystn. from AcOH, had m. p. 135°, alone or mixed with an authentic specimen of 4-*nitro*-1-*naphthyl* m-*nitrobenzenesulphonate* (Found: C, 51·5; H, 2·8. $C_{16}H_{10}O_7N_2S$ requires C, 51·3; H, 2·7%). No pure compound could be isolated from the mother-liquor.

(b) 10 G. were added to a mixture of fuming HNO_3 (15 c.c.) and AcOH (15 c.c.). After standing for 1 hr., the cryst. crop was filtered off and recryst. from AcOH. It gave needle crystals (1·7 g.), m. p. 166°, of 8-*nitro*-1-*naphthyl* m-*nitrobenzenesulphonate* (Found: C, 51·2; H, 2·8%), oriented by conversion into the 4 : 8-dinitro-compound (below). The sulphonate was severed by piperidine to 8-*nitro-α-naphthol*, which separated from $CHCl_3$ as a yellow cryst. powder, m. p. 130° (Found: C, 63·2; H, 3·8. $C_{10}H_7O_3N$ requires C, 63·5; H, 3·7%). This naphthol dissolves in NaOH aq. with a deep orange colour.

Nitration of 4-Nitro-1-naphthyl m-*Nitrobenzenesulphonate*.—2 G. were added slowly to fuming HNO_3 (6 c.c.), and the solution poured into H_2O. The resultant gum was boiled with C_6H_6 and the product (1·0 g., m. p. 170°) recrystallised from AcOH. It gave 4 : 5-*dinitro*-1-*naphthyl* m-*nitrobenzenesulphonate* as small needles, m. p. 174° (Found: C, 45·7; H, 2·2. $C_{16}H_9O_9N_3S$ requires C, 45·8; H, 2·2%). This compound was very readily severed to 4 : 5-dinitro-α-naphthol, which crystallised from aq. EtOH in needles, m. p. 198° (decomp.). A synthetic specimen * from 4 : 5-dinitrobromonaphthalene also had this m. p. (Friedländer, *Ber.*, 1899, **32**, 3528, gives 230°; Ullmann and Consonno, *Ber.*, 1902, **35**, 2802, give 208°). The identity was further confirmed by ethylation with Et_2SO_4 in xylene solution. 4 : 5-Dinitro-α-ethoxynaphthalene was obtained in plates, m. p. 186°, which showed no depression in m. p. on admixture with a specimen from 1-bromo-4 : 5-dinitronaphthalene.

Nitration of 8-Nitro-1-naphthyl m-*Nitrobenzenesulphonate*.—2 G. were added to fuming

HNO_3 (6 c.c.), and the resultant solution diluted with AcOH and filtered from the cryst. ppt. (1·2 g.). This recrystallised from AcOH to give pure 4 : 8-*dinitro*-1-*naphthyl* m-*nitrobenzenesulphonate* as prisms, m. p. 165° (Found : C, 45·8; H, 2·2%). Scission with piperidine gave 4 : 8-dinitro-α-naphthol, which crystallised from EtOH in small needles, m. p. 230° (decomp.) alone or mixed with an authentic specimen * from 1-chloro-4 : 8-dinitronaphthalene.

Nitration of β-*Naphthyl* m-*Nitrobenzenesulphonate.*—100 G., nitrated by the method previously described (J., 1932, 2734), gave 33 g. (29%) of the 5- and 20 g. (18%) of the 8-nitro-isomeride. The yield of mixed nitro-compounds is high but the separation difficult.

Nitration of 5-*Nitro*-2-*naphthyl* m-*Nitrobenzenesulphonate.*—10 G. were added slowly to fuming HNO_3 (20 c.c.). The resultant solution was poured into H_2O and the ppt. filtered off and dried. It was extracted with hot C_6H_6 and the residue crystallised from AcOH. Pure 4 : 5-*dinitro*-2-*naphthyl* m-*nitrobenzenesulphonate*, m. p. 212°, was obtained (Found : C, 45·7; H, 2·2. $C_{16}H_9O_9N_3S$ requires C, 45·8; H, 2·2%). The C_6H_6 filtrate was evaporated and the residue crystallised from AcOH; 1 : 5-*dinitro*-2-*naphthyl* m-*nitrobenzenesulphonate*, m. p. 153°, was obtained (Found : C, 46·1; H, 2·4%), together with a small amount of the 4 : 5-isomeride. The total yields were : 4 : 5, 3·2 g. (29%) and 1 : 5, 2·7 g. (24%). On piperidine scission, the former gave 4 : 5-*dinitro*-β-*naphthol*, small orange-red needles, m. p. *ca.* 230°, from aq. EtOH (Found : C, 51·7; H, 2·9. $C_{10}H_6O_5N_2$ requires C, 51·3; H, 2·6%), and the latter gave 1 : 5-*dinitro*-β-*naphthol*, yellow needles, m. p. 187° (decomp.), from EtOH (Found : C, 51·4; H, 2·7%).

Nitration of 8-*Nitro*-2-*naphthyl* m-*Nitrobenzenesulphonate.*—15 G. were introduced into fuming HNO_3 (30 c.c.), and after 1 hr. the solution was diluted with an equal vol. of AcOH. This pptd. the major part of the 1 : 8-dinitro-2-naphthyl *m*-nitrobenzenesulphonate. The filtrate when poured into H_2O gave gummy material from which by crystn. from AcOH only the 1 : 8-compound could be obtained. 1 : 8-*Dinitro*-2-*naphthyl* m-*nitrobenzenesulphonate* crystallised from AcOH in small needles, m. p. 201° (total yield, 4·3 g.; 26%) (Found : C, 45·7; H, 2·2%). Fission with piperidine gave in poor yield 1 : 8-dinitro-β-naphthol, golden scales, m. p. 195°, from EtOH. This naphthol was readily ethylated by the xylene–K_2CO_3 method, and the resulting 1 : 8-dinitro-β-naphthyl ethyl ether, m. p. 215°, dissolved in fuming HNO_3 to give a good yield of 1 : 6 : 8-trinitro-β-naphthyl ethyl ether, m. p. 188°.

Nitration of 4-*Nitro*-2-*naphthyl* m-*Nitrobenzenesulphonate.*—This compound dissolved readily in fuming HNO_3, and on dilution with AcOH, 4 : 5-dinitro-2-naphthyl *m*-nitrobenzenesulphonate (above) crystallised in 54% yield. The mother-liquor was not further examined. 4-*Nitro*-2-*naphthyl* m-*nitrobenzenesulphonate*, obtained by interaction of 4-nitro-β-naphthol * (Morgan and Evans, J., 1919, **115**, 1127) and *m*-nitrobenzenesulphonyl chloride in C_5H_5N, formed small rosettes, m. p. 149°, from AcOH (Found : C, 51·6; H, 2·8%).

Nitration of 1-*Nitro*-2-*naphthyl* m-*Nitrobenzenesulphonate.*—1 G. was dissolved in fuming HNO_3 (4 c.c.) and the solution poured into H_2O. The resultant ppt. was readily separated into a mixture of 1 : 8-dinitro- and 1 : 5-dinitro-isomerides (above), the former preponderating. 1-*Nitro*-2-*naphthyl* m-*nitrobenzenesulphonate*, obtained by interaction of 1-nitro-β-naphthol (from α-nitroso-β-naphthol by application of the method of Hodgson and Kilner, J., 1924, **125**, 809) and *m*-nitrobenzenesulphonyl chloride in C_5H_5N, formed prisms, m. p. 176°, from AcOH (Found : C, 51·7; H, 2·8%).

Onufrowicz (*Ber.*, 1890, **23**, 3360) describes the preparation of 5 : 8-dinitro-2-naphthyl ethyl ether, m. p. 215°, by the nitration of β-naphthol sulphide. On repetition of this experiment only 1 : 8-dinitro-2-naphthyl ethyl ether, m. p. 215°, was obtained.

BATTERSEA POLYTECHNIC, S.W. 11.

[*Received, January* 30*th*, 1933.]