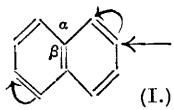
411. *The Bromination of β-Naphthylamine.*

By F. BELL.

FOLLOWING the general theory of Mills and Nixon (J., 1930, 2510), it appears probable that the naphthalene molecule adopts a configuration in which the angle α is considerably smaller than β (I) and consequently the normal distribution of valencies is as shown (cf. Robinson and Thompson, this vol., p. 2015). This agrees with the fact that naphthalene derivatives with electron-donating groups in position 2 undergo substitution first in position 1 and then in position 6. Simple substitution in position 3 has hitherto not been described (Bell, J., 1929, 2784; Fries and Schimmelschmidt, *Annalen*, 1930, **484**, 245; Kerkhof, *Rec. trav. chim.*, 1932, **51**, 739).



(I.)

The directive power of the *p*-toluenesulphonamido-group can be considerably increased by combination with pyridine (J., 1931, 2338). Consequently it appeared of interest to determine whether

under any conditions *p*-toluenesulphon-2-naphthalide undergoes substitution in position 3 rather than 6.

In chloroform solution *p*-toluenesulphon-2-naphthalide was readily brominated in positions 1 : 6, the reaction being comparable with nitration in acetic acid solution (Morgan and Micklethwait, J., 1912, **101**, 148). In pyridine solution, it furnished first the 1-*bromo*-derivative and then the 1 : 3-*dibromo*-derivative. Moreover, in pyridine solution 1 : 6-*dibromo*-p-*toluenesulphon*-2-*naphthalide* was easily converted into the 1 : 3 : 6-*tribromo*-derivative.

It is probable that this 3-substitution occurs under the general influence of the negative pole created by the pyridinium salt formation of the *p*-toluenesulphonamido-group rather than through tautomeric displacements. The part played by intermediate additive compounds, however, must not be omitted from consideration; otherwise it is difficult to account for the formation of 1 : 4 : 6-tribromo-β-naphthol from β-naphthol (Fries and Schimmelschmidt, *loc. cit.*). Moreover, 1 : 6-dibromo-2-methoxynaphthalene undergoes ready bromination to give apparently the 1 : 4 : 6-tribromo-derivative, whereas 3 : 4′-dibromo-4-methoxydiphenyl is resistant under the same conditions.

It was hoped to gain further information by studying the nitration of β-naphthol, but although it was easy to obtain the 1 : 6-dinitro-derivative, no higher products could be isolated in pure condition. Protection of the hydroxyl group by conversion into the *m*-nitrobenzenesulphonate resulted in the expected fall in orienting power, so that quite vigorous nitration gave only a mixture of 5- and 8-*mononitro*-derivatives (cf. the nitration of β-naphthylamine in sulphuric acid solution; Friedländer and Szymanski, *Ber.*, 1892, **25**, 2077).

EXPERIMENTAL.

Bromination of p-*Toluenesulphon-2-naphthalide.*—Br (5·5 g.) was added drop by drop to a solution of this compound (5 g.) in pyridine. After 12 hrs. the mixture was poured into dil. HCl, and the resultant gum rendered solid by rubbing with EtOH. On crystn. from AcOH it gave 1 : 3-*dibromo*-p-*toluenesulphon*-2-*naphthalide*, m. p. 163° (Found: C, 45·0; H, 3·2. $C_{17}H_{13}O_2NBr_2S$ requires C, 44·8; H, 2·9%), which was also obtained by bromination of 1-bromo-*p*-toluenesulphon-2-naphthalide in pyridine solution.

1-*Bromo*-p-*toluenesulphon*-2-*naphthalide*, prepared from 1-bromo-β-naphthylamine and *p*-toluenesulphonyl chloride in pyridine solution, crystallised from EtOH in stout needles, m. p. 100° (Found: C, 54·4; H, 3·8. $C_{17}H_{14}O_2NBrS$ requires C, 54·3; H, 3·7%).

1 : 3-Dibromo-*p*-toluenesulphon-2-naphthalide did not react with Br in pyridine and reacted only slowly with Br in boiling $CHCl_3$. The only isolable product was 1 : 3 : 6-tribromo-2-naphthylamine, m. p. 143° (orientation; *Annalen*, 1930, **484**, 250, footnote).

1 : 3-*Dibromo*-β-*naphthylamine*, obtained by solution of the above *p*-toluene-

sulphonyl derivative in H_2SO_4, crystallised from EtOH in needles, m. p. 119° (large depression on admixture with the 1 : 6-isomeride) (Found: C, 40·0; H, 2·4. $C_{10}H_7NBr_2$ requires C, 39·9; H, 2·3%). With Ac_2O this base gave 1 : 3-*dibromoaceto*-2-*naphthalide*, which crystallised from AcOH in needles, m. p. 201° (Found: C, 42·2; H, 2·7. $C_{12}H_9ONBr_2$ requires C, 42·0; H, 2·6%).

1 : 6-*Dibromo*-p-*toluenesulphon*-2-*naphthalide*, m. p. 145° (Found: C, 45·1; H, 2·9%), from 1 : 6-dibromo-β-naphthylamine and *p*-toluenesulphonyl chloride, was obtained also by bromination of 1-bromo-*p*-toluenesulphon-2-naphthalide in $CHCl_3$ solution. With Br (1 mol.) in pyridine, it readily gave 1 : 3 : 6-*tribromo*-p-*toluenesulphon*-2-*naphthalide*, which crystallised from AcOH in needles, m. p. 184° (Found: C, 39·2; H, 2·3. $C_{17}H_{12}O_2NBr_3S$ requires C, 38·7; H, 2·2%). This compound was converted into 1 : 3 : 6-tribromo-2-naphthylamine by solution in cold conc. H_2SO_4.

Bromination of 1 : 6-*Dibromo*-2-*methoxynaphthalene*.—A solution of this compound (6 g.) and Br (2 c.c.) in $CHCl_3$ (20 c.c.) was boiled under reflux for 2 hrs. The crop obtained on cooling, after recrystn. from $CHCl_3$, had m. p. 147° alone or mixed with authentic 1 : 4 : 6-tribromo-2-methoxynaphthalene (Franzen and Stauble, *J. pr. Chem.*, 1921, **103**, 352; orientation, Fries and Schimmelschmidt, *loc. cit.*).

Nitration of β-Naphthol.—100 G. were added slowly to a cold well-stirred mixture of HNO_3 (150 c.c.) and AcOH (1 l.). The clear solution so obtained soon began to deposit crystals, which were filtered off after 24 hrs. (yield, 80 g.; m. p. *ca.* 175°). No pure compound could be isolated from the mother-liquor; the crop on recrystn. from AcOH gave pure 1 : 6-dinitro-β-naphthol. More vigorous nitration of this compound led to no isolable products.

Nitration of β-Naphthyl m-*Nitrobenzenesulphonate*.—8 G. were added slowly to a mixture of fuming nitric acid (12 c.c.) and AcOH (12 c.c.). After 1 hr. the solution was filtered from a cryst. deposit, and the mother-liquor poured into H_2O. The gummy ppt., after repeated crystn. from AcOH, gave pure 8-*nitro*-2-*naphthyl* m-*nitrobenzenesulphonate*, m. p. 144—146° (Found: C, 51·2; H, 2·7. $C_{16}H_{10}O_7N_2S$ requires C, 51·3; H, 2·7%). The crop recrystallised from AcOH to give needle crystals of 5-*nitro*-2-*naphthyl* m-*nitrobenzenesulphonate*, m. p. 166° (Found: C, 51·3; H, 2·8%). Both sulphonates were hydrolysed by warm piperidine and the products gave no depression in m. p. on admixture with authentic 8-nitro- and 5-nitro-β-naphthol, respectively.

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