Electrophilic Substitution in Anthranils

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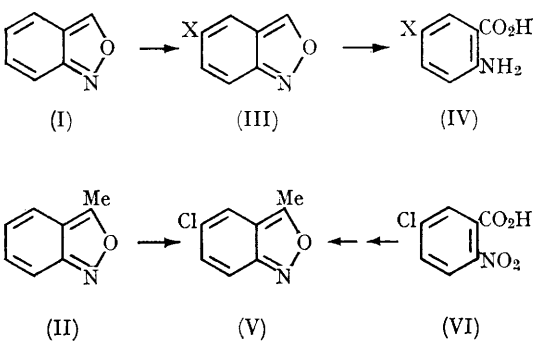
WE report the structures of Bamberger's "x-chloroanthranil,"[1] "x-bromoanthranil,"[1] and "x-chloro-3-methylanthranil,"[2] and report on the nitration of anthranil (I) and of 3-methylanthranil (II). The "x-position" of the halogeno-compounds is in every case the 5-position (*c.f.* III). When the 3-position

[1] E. Bamberger and J. Lublin, *Ber.*, 1909, **42**, 1676.
[2] E. Bamberger and F. Elger, *Ber.*, 1903, **36**, 1611.

of the anthranils is unsubstituted, alkaline degradation leads to the corresponding anthranilic acid: thus, "x-chloro-anthranil," on heating for ½ hr. with alcoholic sodium hydroxide (10%), followed by careful neutralisation of the alkali, gave 5-chloroanthranilic acid (IV; X = Cl) (75%), requiring the halogen to be in the 5-position in the anthranil. Similarly, "x-bromoanthranil" gave 5-bromoanthranilic acid (IV; X = Br) (85%). When the 3-position is occupied by a methyl group, alkaline degradation is no longer useful, and "x-chloro-3-methylanthranil" was established as the 5-chloro-compound (V) by synthesis from 5-chloro-2-nitrobenzoic acid (VI). Nitration of anthranil (H_2SO_4–KNO_3, 10°) gave two products, 5-nitroanthranil (32%, m.p. 120—121°, from petroleum) and 7-nitroanthranil (5%, m.p. 144—145°, from petroleum), as shown by their degradation by alkali to 5-nitro- and 3-nitro-anthranilic acids [(65%) and (90%)], respectively. 3-Methylanthranil, on the other hand, gave 3-methyl-5-nitroanthranil [80%, m.p. 145—146°, from benzene–petroleum (1 : 1)] as the sole nitration product isolated. The identity of the last product was established by comparison with a sample prepared by standard methods from 2-acetamido-5-nitroacetophenone.



(I) (III) (IV)

(II) (V) (VI)

(*Received, August 11th*, 1965; *Com.* 503.)