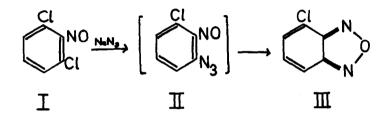
## A NEW BENZOFURAZAN SYNTHESIS

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We have discovered a new and convenient synthesis of benzofurazans (benzo-1,2,5-oxadiazoles) in the spontaneous (at  $100^{\circ}$ ) loss of nitrogen and ring closure of <u>o</u>-nitrosophenyl azides. Thus, 1,3-dichloro-2-nitrosobenzene (I), m.p. 170 - 171 ° (Lit.<sup>2</sup> m.p. 175.5 - 176°) (conveniently prepared by the peracetic acid oxidation of 2,6-dichloroaniline<sup>2</sup>), on heating with sodium azide at  $100^{\circ}$  in dimethyl sulphoxide, gave 4-chlorobenzofurazan (III), m.p. 83 - 84° (Lit.<sup>3</sup> m.p. 83 - 84°) in 93% yield. 1,3-Dichloro-2-nitrobenzene was recovered unchanged after a similar treatment with azide; thus it appears that, at least in the crowded environment between two chlorine atoms, the nitroso-group is a more powerful activating group to nucleophilic halogen displacement than the nitro-group.

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Eenzofurazans have previously been prepared<sup>4, 5</sup> by the cyclo-dehydration of <u>o</u>-quinone dioximes or by the oxidation of <u>o</u>-nitrosoaniline derivatives (neither of which starting materials are readily available) or by the indirect method of deoxygenation of the benzofuroxans. The presently described route is analogous to the well known preparation of benzofuroxans from <u>o</u>-nitrophenyl azides<sup>6</sup>.

Further examples of the new synthesis are provided by the conversion of 1,3-dibromo-5-methyl-2-nitrosobenzene, m.p. 136 - 137° (Lit.  $^2$  m.p. 136.5 - 138°), into 4-bromo-6-methylbenzofurazan, m.p. 81 - 81.5°, and 1,3,5-trichloro-2nitrosobenzene, m.p. 142 - 143° (Lit.  $^2$  m.p. 145 - 146°), into 4,6-dichlorobenzofurazan,  $^7$  m.p. 52 - 53°, in yields of 92% and 90% respectively.

The foregoing nitroso-compounds were also prepared by the peracetic oxidation of the corresponding anilines<sup>2</sup>, but it was found that this method is general only for 2,6-disubstituted anilines and that other anilines gave azoxy-compounds; e.g. 4-methyl-2nitroaniline yielded 4,4'-dimethyl-2,2'-dinitroazoxybenzene, m.p. 24' - 242<sup>°</sup>.

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- <sup>2</sup> R.P. Bayer and R.R. Holmes, <u>J.Amer.Chem.Soc.</u>, <u>82</u>, 3454, (1960).
- <sup>3</sup> D.Dal Monte and E.Sandri, <u>Ann.Chim.(Italy)</u>, 53, 1701, (1963).
- <sup>4</sup> L.C.Behr, in "The Chemistry of Heterocyclic Compounds", (A.Weissberger, Ed.), Interscience, New York, 1962, 17, 263.
- <sup>5</sup> J.H.Boyer, in "Heterocyclic Compounds", (R.C.Elderfield, Ed.), Wiley, New York, 1961, 7, 462.
- <sup>6</sup> E.Noelting and A.Kohn, <u>Chem.Ztg.</u>, 18, 1905 (1894): T.Zincke and P.Schwarz, Annalen, 307, (1899).
- 7 Satisfactory analytical results were obtained for all new compounds prepared.