

### 544. Some 1- and 2-Halogenobenzimidazoles.

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Evidence has been obtained that the compound formulated previously as 2-iodobenzimidazole is actually an *N*-iodo-compound. The preparation of 2-chlorobenzimidazoles by the interaction of phosphoryl chloride and benzimidazolin-2-ones has been systematically studied, and improved yields have been obtained without the use of sealed tubes. The structure of an intermediate isolated from one of these reactions is considered.

ALTHOUGH benzimidazolin-2-one (I) is potentially tautomeric, very little of the hydroxy-form (II) is present in equilibrium under normal conditions.<sup>1</sup> The known dialkyl and diacyl derivatives are "fixed" forms derived from structure (I). With the exception of 2-ethoxybenzimidazole,<sup>2</sup> compounds derived from the hydroxy-form (II) appear not to have been prepared. Two apparent exceptions, the compounds formulated as 2-acetoxy-<sup>3</sup> and 2-acetoxy-1-acetyl-benzimidazole,<sup>4</sup> have been shown<sup>5</sup> to be 1-acetyl- and 1,3-diacetyl-benzimidazolin-2-one, respectively. As a possible route to compounds derived from the hydroxy-structure might involve nucleophilic displacement of a 2-halogen substituent, the preparation of 2-halogenobenzimidazoles has been studied.



The compound described as 2-iodobenzimidazole<sup>6</sup> was first examined in view of its alleged ready preparation from benzimidazole, but doubts have been expressed concerning its structure.<sup>7</sup> These were confirmed when we observed that the infrared spectrum of this compound contained no strong bands in the 3000—3300  $\text{cm}^{-1}$  region (absence of NH) and that a very similar product could be obtained by iodination of 2-methylbenzimidazole. Further, the supposed 2-iodobenzimidazole was found to react with aniline, giving *p*-iodoaniline and benzimidazole. This evidence strongly suggests that the compound is actually 1-iodobenzimidazole and is thus of no value for the present purpose.

<sup>1</sup> Efros and Eltsov, *Zhur. obshchei Khim.*, 1957, **27**, 684.

<sup>2</sup> Sandmeyer, *Ber.*, 1886, **19**, 2650.

<sup>3</sup> Heller, Buchwaldt, Fuchs, Kleinicke, and Kloss, *J. prakt. Chem.*, 1925, **111**, 1.

<sup>4</sup> Montanari and Risaliti, *Gazzetta*, 1953, **83**, 278.

<sup>5</sup> Harrison and Smith, *J.*, 1961, 4827.

<sup>6</sup> Pauly and Gundermann, *Ber.*, 1908, **41**, 3099.

<sup>7</sup> de la Mare and Ridd, "Aromatic Substitution," Butterworths Scientific Publns., London, 1959, p. 203.

Two methods have been described for the preparation of 2-chlorobenzimidazole. Manuelli and Recchi<sup>8</sup> heated benzimidazolin-2-one with phosphorus pentachloride and a little phosphoryl chloride; their directions are vague, and attempts to repeat this preparation gave only dark products of indefinite melting point and with infrared spectra very different from that of the material described below as 2-chlorobenzimidazole. Efros, Porai-Koshits, and Farbenstein<sup>9</sup> used phosphoryl chloride in a sealed tube at 160—170°. The melting point of the product is quoted as 212—215°, agreeing with that given by Manuelli and Recchi<sup>8</sup> (215°) and more recently by Bednyagina and Postovskii<sup>10</sup> (210—212°). By following these directions we obtained, in a yield lower than recorded by the Russian workers, a product which softened at 180°, bubbled, and resolidified. In spite of these discrepancies, we believe that our product is in fact 2-chlorobenzimidazole, and detailed evidence for this is given below. As the sealed-tube method is not convenient for larger-scale preparations, we investigated the reaction between benzimidazolin-2-one and an excess of phosphoryl chloride at the b. p. for times between 1 and 12 hr. The yield of 2-chlorobenzimidazole increased during the first 3 hr. to a maximum of ~40% and then fell slowly, probably owing to the formation of polymers. Raising the reaction temperature, *e.g.*, by addition of nitrobenzene, had little effect on the yield, nor was the addition of dimethylaniline<sup>11</sup> or diethylaniline beneficial in this case—in fact working-up of the reaction mixture was made more difficult. Addition of a little pyridine to the phosphoryl chloride unexpectedly led to a negligible yield of 2-chlorobenzimidazole. The presence of small amounts of water is desirable in some reactions with phosphoryl chloride,<sup>12</sup> but in the present reaction the exclusion of water was found to be essential for even moderate yields. The use of "pyrophosphoryl chloride"<sup>13</sup> was also less satisfactory than the use of normal phosphoryl chloride. However, when dry hydrogen chloride was passed through the refluxing solution of benzimidazolin-2-one in phosphoryl chloride, the yield reached 80—90% after 3 hr. and little polymer was formed.

The preparation of 2-chloro-5-methylbenzimidazole in 80% yield by reaction of 5-methylbenzimidazolin-2-one with phosphoryl chloride in a sealed tube at 160° has been described.<sup>10</sup> We find that the use of boiling phosphoryl chloride with passage of hydrogen chloride is a satisfactory alternative in this case also. It is noteworthy that in the absence of hydrogen chloride the maximum yield of 2-chloro-compound (40%) was obtained after only 5 minutes.

5-Nitrobenzimidazolin-2-one has been converted into 2-chloro-5-nitrobenzimidazole by Kym and Ratner<sup>14</sup> (phosphoryl chloride, sealed tube) and by James and Turner<sup>15</sup> (phosphoryl chloride, reflux); in neither case is a yield stated. Kym and Ratner mention that the reaction temperature must not be taken too high, and in a sealed-tube reaction with deliberate overheating we obtained only the polymer described below. Reaction at the b. p. is again satisfactory, but the period of heating must be longer than that given by James and Turner and passage of hydrogen chloride is desirable. By this method 70% conversion can be achieved in small-scale experiments in 6 hr. (it is somewhat less on a larger scale). Separation of the product from unchanged starting material is the main difficulty in this case and, whilst chromatography on alumina can be used on a small scale, fractional precipitation was more convenient in the larger preparations though it led to somewhat reduced yields. Ultraviolet spectroscopy was used to determine the approximate amount of 2-chloro-5-nitrobenzimidazole in the crude products before separation.

<sup>8</sup> Manuelli and Recchi, *Atti R. Accad. Lincei, Rend.*, 1900, **9**, 269.

<sup>9</sup> Efros, Porai-Koshits, and Farbenstein, *Zhur. obshchei Khim.*, 1953, **23**, 1691.

<sup>10</sup> Bednyagina and Postovskii, *Zhur. obshchei Khim.*, 1960, **30**, 1431.

<sup>11</sup> Baddiley and Topham, *J.*, 1944, 678.

<sup>12</sup> Stephenson, Walker, Warburton, and Webb, *J.*, 1962, 1282.

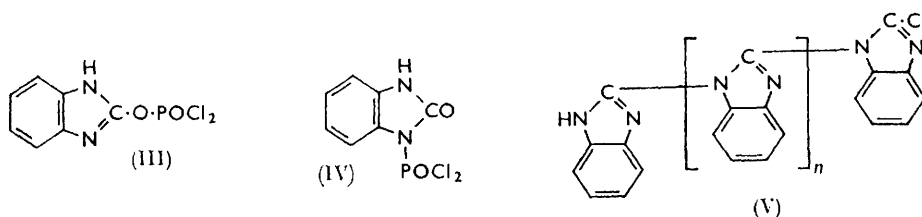
<sup>13</sup> Elion and Hitchings, *J. Amer. Chem. Soc.*, 1956, **78**, 3508.

<sup>14</sup> Kym and Ratner, *Ber.*, 1912, **45**, 3238.

<sup>15</sup> James and Turner, *J.*, 1950, 1515.

The view has frequently been expressed that the conversion of the group  $\text{NH}\cdot\text{CO}$  in a heterocyclic ring into  $\text{N}=\text{CCl}$  proceeds through a very small amount of the tautomeric hydroxy-form present in equilibrium. This has been elaborated by Albert,<sup>16</sup> with particular reference to such replacements in  $\pi$ -deficient heteroaromatic systems, as involving the formation of a phosphorus ester as intermediate which is then split by the action of hydrogen chloride produced in the first stage of the reaction. Our observations of the effect of passing hydrogen chloride through the reaction mixture might be regarded as supporting this view, but isolation of the intermediate seemed desirable. If benzimidazolin-2-one is boiled with phosphoryl chloride, complete dissolution requires  $\sim 15$  min. and is accompanied by evolution of hydrogen chloride. Rapid cooling at this stage leads to the separation of a white solid which can be washed with ether and dried *in vacuo*. It is too unstable for purification, but the analytical results are close to those expected for the formula  $\text{C}_7\text{H}_5\text{Cl}_2\text{N}_2\text{O}_2\text{P}$ . Two possible structures may be suggested, one of them (III) being of the type discussed by Albert, and the other (IV) resulting from attack by phosphoryl chloride on one of the two nitrogen atoms. Structure (III) was initially favoured since protonation of benzimidazolin-2-one is known to occur at the oxygen atom,<sup>1</sup> and attack by phosphoryl chloride is probably electrophilic; formation of this intermediate does not necessitate the hydroxy-form. The intermediate has infrared bands at 1260—1280s ( $\text{P}=\text{O}$  stretching), 3280 ( $\text{NH}$ ), and 1760  $\text{vs. cm}^{-1}$ . If the last band is regarded as an Amide I band, the spectrum seems to support structure (IV). The alternative (III) is not eliminated, however, since, as recently discussed by Katritzky and Jones,<sup>17</sup> a band in the 1700—1800  $\text{cm}^{-1}$  region in the spectrum of amide derivatives is not necessarily an indication of the presence of a  $\text{C}=\text{O}$  group. In discussing the structure of a compound derived from phosphorus pentachloride and imidazolin-2-one, Najer, Giudicelli, and Sette<sup>18</sup> associated a strong band at 750  $\text{cm}^{-1}$  with the presence of an  $\text{N}-\text{P}$  linkage. Unfortunately, most simple benzimidazoles and benzimidazolin-2-ones absorb strongly in the 730—750  $\text{cm}^{-1}$  region, hence the presence of a band at 746  $\text{cm}^{-1}$  in the spectrum of the intermediate isolated in the present work does not provide any certain structural evidence. Also, the ease of hydrolysis of the intermediate does not permit a clear distinction between the structures (III) and (IV): the stability of the  $\text{C}\cdot\text{O}\cdot\text{P}=\text{O}$  system may be considerably reduced by the incorporation of the carbon atom in an aromatic system.

Although the product which we describe above as 2-chlorobenzimidazole differs in melting point from that described in the literature, we have no doubt as to its formulation. It is soluble in dilute aqueous sodium hydroxide ( $\text{NH}$  present) and with boiling aniline it gave 2-anilinobenzimidazole. Acetyl chloride in pyridine converted it into a monoacetyl



derivative, and with methyl sulphate in aqueous sodium hydroxide it gave a monomethyl derivative. The latter appears to be identical with the 2-chloro-1-methylbenzimidazole prepared by Bednyagina and Postovskii<sup>10</sup> using methyl iodide. Although relatively inert to strongly basic reagents, *e.g.*, sodium hydroxide or alkoxides, the chlorine is easily displaced by glacial acetic acid or acetic anhydride at the b. p.: the products are, respectively, benzimidazolin-2-one and 1,3-diacetylbenzimidazolin-2-one.

<sup>16</sup> Albert, "Heterocyclic Chemistry," Athlone Press, London, 1959, p. 80.

<sup>17</sup> Katritzky and Jones, *Chem. and Ind.*, 1961, 722.

<sup>18</sup> Najer, Giudicelli, and Sette, *Bull. Soc. chim. France*, 1961, 2114.

Ultraviolet spectra of aqueous solutions of the 2-chlorobenzimidazoles and benzimidazolin-2-ones are recorded in the Table. The solutions were prepared by using buffer solutions whose pH's ensured that the neutral molecule was present in the maximum concentration. Where necessary, approximate  $pK_a$  values were determined potentiometrically to enable this selection to be made.

	pH	$\nu_{max}$ . (log $\epsilon$ in parentheses)
Benzimidazolin-2-one .....	7	222 * (3.84); 276.5 (3.83)
5-Methylbenzimidazolin-2-one ...	7	224 * (3.84); 282.5 (3.85)
5-Nitrobenzimidazolin-2-one .....	6	220.5 (4.20); 248.5 (4.07); 330—343 (3.93)
2-Chlorobenzimidazole .....	6	241.5 (3.78); 266 * (3.71); 272.5 (3.86); 279.5 (3.85)
2-Chloro-5-methylbenzimidazole	6	244 (3.78); 278 (3.85); 284.5 (3.84)
2-Chloro-5-nitrobenzimidazole ...	5	235 (4.32); 308—312 (4.00)

\* Infection.

A preliminary investigation of the effect of heating the 2-chlorobenzimidazoles at a temperature a little above their softening (decomposition) points has been made. The products, which are similar to those encountered in some of the preparations, contain very little chlorine and appear to be condensation polymers. Although we have at present no supporting evidence, (V) may be suggested as a possible structure.

#### EXPERIMENTAL

Infrared spectra were determined for potassium bromide discs by using a Unicam S.P. 100 instrument.

**1-Iodobenzimidazole.**—This was prepared as a yellow powder, m. p. 172—181° (decomp.), in 88% yield by the method of Pauly and Gundermann.<sup>6</sup> As no solvent could be found for recrystallisation, it was purified by dissolution in *N*-hydrochloric acid, filtration, and reprecipitation by 10% aqueous sodium hydroxide. The white precipitate was collected, washed with water, and dried *in vacuo*. Although the m. p. recorded by Pauly and Gundermann is 187°, we found it to depend on the rate of heating, and usually obtained a value of 173—176° (decomp.).

**1-Iodo-2-methylbenzimidazole.**—A solution of 2-methylbenzimidazole (1.12 g.) in water (400 ml.) and 10% aqueous sodium hydroxide (5 ml.) was stirred at room temperature for 1 hr. whilst a solution of iodine (2.15 g.) in 10% aqueous potassium iodide (160 ml.) was added. Collection of the solid, washing with water (2 × 50 ml.), and drying *in vacuo* gave a yellow powder (2.05 g.). Purification as described above gave 1-iodo-2-methylbenzimidazole, m. p. 153—156° (decomp.) (Found: I, 49.3.  $C_8H_7IN_2$  requires I, 49.2%). The properties of this compound, particularly its tendency to lose iodine when heated in solvents and failure to dissolve in dilute aqueous sodium hydroxide solution, are very similar to those of 1-iodobenzimidazole.

**Reaction of 1-Iodobenzimidazole with Aniline.**—1-Iodobenzimidazole (1.31 g.) was stirred at room temperature for 4 hr. with redistilled aniline (0.5 ml.) in ethanol (15 ml.). A small amount of solid was removed by filtration and the filtrate evaporated under reduced pressure. The dark residue was steam-distilled, the distillate being extracted with ether. After washing, drying ( $Na_2SO_4$ ), and evaporation, the extract gave *p*-iodoaniline (0.34 g.), m. p. 62—65°, identified by conversion into *p*-iodoacetanilide, m. p. 183—186° (lit.,<sup>19</sup> 184°). The aqueous residue from the steam-distillation was filtered hot and, on concentration, the filtrate gave benzimidazole (0.37 g.), m. p. and mixed m. p. 169—172°. The aqueous filtrate was shown to contain iodide ions; this suggests that the formation of *p*-iodoaniline and benzimidazole is not the only reaction.

**Substituted Benzimidazolin-2-ones.**—These were prepared by recorded methods from the corresponding *o*-diamine and urea (5-methyl) or by nitration of benzimidazolin-2-one<sup>15</sup> (5-nitro). In view of the high and somewhat uncertain m. p. of these compounds, they were characterised as their diacetyl derivatives. These were prepared by boiling the benzimidazolin-2-one (1 g.) with acetic anhydride (20 ml.) for 3 hr. Recrystallisation of the products from

<sup>19</sup> Beringer, Drexler, Gindler, and Lumpkin, *J. Amer. Chem. Soc.*, 1953, **75**, 2705.

ethanol afforded 1,3-diacetyl-5-methylbenzimidazolin-2-one, m. p. 174—175° (Found: C, 62.3; H, 5.5; N, 11.8.  $C_{12}H_{12}N_2O_3$  requires C, 62.1; H, 5.2; N, 12.1%), and 1,3-diacetyl-5-nitrobenzimidazolin-2-one, m. p. 127—128° (lit.,<sup>20</sup> 131—132°) (Found: C, 50.15; H, 3.1; N, 16.1. Calc. for  $C_{11}H_9N_3O_5$ : C, 50.2; H, 3.4; N, 15.9%).

*Reaction of Benzimidazolin-2-one with Phosphoryl Chloride.—General method.* Benzimidazolin-2-one (2 g.) was boiled under reflux with freshly distilled phosphoryl chloride (20 ml.), a clear solution being formed after *ca.* 15 min. In some experiments a stream of dry hydrogen chloride was then passed through the refluxing liquid. After a certain period of heating, an excess of phosphoryl chloride was removed at *ca.* 40 mm. and the residue treated with ice-water (40 ml.). The cold acid solution was filtered, and the insoluble material (*A*) washed with dilute hydrochloric acid, then with water, and dried at 80°. The filtrate and washings were combined and made just alkaline (litmus) by addition of dilute ammonia solution. After being cooled well, the crude 2-chlorobenzimidazole was collected, washed with water, and dried. The total recovery, *i.e.*, crude 2-chlorobenzimidazole + *A*, was 1.7—2.1 g. The yields of 2-chlorobenzimidazole isolated from experiments (*a*) without hydrogen chloride, and (*b*) with passage of hydrogen chloride after the first 15 min., are as follows:

Time (hr.) .....	0.25	1	2	3	6	12
Yield (g.) .....	(a) 0.86	0.94	0.96	0.96	0.72	0.57
	(b) 0.86	1.18	1.51	1.84	2.01	

Increasing the proportion of phosphoryl chloride had no appreciable effect on the yield; decreasing it only increased the time required for formation of the initial clear solution. If the passage of hydrogen chloride was started before a clear solution had been obtained, the latter process was considerably retarded.

The solid *A* in all of the experiments in which hydrogen chloride was passed, and in those of shorter duration in its absence, was mainly benzimidazolin-2-one. In experiments of 3 or more hours' duration without hydrogen chloride, a fluffy solid separated during later stages of the reaction. This was shown (infrared spectrum) to be the polymer of 2-chlorobenzimidazole discussed below. In these experiments, ethanol was used to separate the solid *A* into the polymer and benzimidazolin-2-one.

*2-Chlorobenzimidazole.*—Benzimidazolin-2-one (15 g.) was boiled under reflux for 3.5 hr. with phosphoryl chloride (150 ml.), hydrogen chloride being passed during the last 3 hr. only. Working up as described above gave benzimidazolin-2-one (0.5 g.) and 2-chlorobenzimidazole (15.6 g.) which formed white needles (from aqueous ethanol), m. p. 180° (softens, bubbles, then resolidifies) [Found: C, 55.1; H, 3.4; Cl, 23.2; N, 18.4. *M* (Rast), 150. Calc. for  $C_7H_5ClN_2$ : C, 55.1; H, 3.3; Cl, 23.2; N, 18.4%; *M*, 152.6],  $v_{max}$ . 3065s, 2980s, 2890s, 2820s, 2720s, 2650s, 1629w, 1597w, 1518w, 1479m, 1439s, 1367s, 1351s, 1300m, 1270s, 1232s, 1210m, 1159m, 1015m, 980s, 965m, 933w, 849w, 800s, 759s, 744s, 667w  $cm^{-1}$ .

*Reaction of 5-Methylbenzimidazolin-2-one with Phosphoryl Chloride.*—In a similar series of experiments to those described above, it was found that the time for complete dissolution in this case was considerably less (*i.e.*, 5 min.) and no polymer was isolated. In experiments in which hydrogen chloride was passed, the yield of 2-chloro-compound (crude) had reached 80% after only 1 hr. and increased later only a little. Without hydrogen chloride, a 43% yield of 2-chloro-compound was obtained after only 5 min., but this was not increased with longer reaction times up to 8 hr.

*2-Chloro-5-methylbenzimidazole.*—Preparation on a 10-g. scale was carried out as described for 2-chlorobenzimidazole. The preliminary heating was for 0.25 hr., hydrogen chloride then being passed for a further 1.75 hr. This gave 2-chloro-5-methylbenzimidazole (7.9 g., 70%) which, after crystallisation from aqueous ethanol, formed needles, m. p. 176—178° (softens, bubbles, then resolidifies) (lit.,<sup>10</sup> 176—180°) (Found: C, 57.6; H, 4.2; Cl, 21.6; N, 17.0. Calc. for  $C_8H_7ClN_2$ : C, 57.7; H, 4.2; Cl, 21.3; N, 16.8%),  $v_{max}$ . 3080s, 3005s, 2915s, 2815s, 2735s, 2645s, 1636w, 1595w, 1561w, 1527w, 1471s, 1455s, 1442s, 1430s, 1380w, 1362w, 1341m, 1298m, 1280s, 1232s, 1144w, 1134w, 987s, 942w, 861w, 851w, 831w, 805s, 797s, 767w, 751w, 664w  $cm^{-1}$ .

*Reaction of 5-Nitrobenzimidazolin-2-one with Phosphoryl Chloride.*—Experiments were performed by the general method as far as the addition of water to the residue after removal of phosphoryl chloride. At this stage a substantial amount of yellow solid separated; this was

<sup>20</sup> Clark and Pessolano, *J. Amer. Chem. Soc.*, 1958, **80**, 1657.

not removed, but dilute ammonia solution was added to adjust the solution to pH ~6. After cooling, the solid (*X*) was collected, washed with water, and dried. Material *X* is a mixture of 5-nitrobenzimidazolin-2-one, 2-chloro-5-nitrobenzimidazole, and in some cases a third compound. The method of separation used in the other cases described above depends on the fact that the 2-chloro-compounds are readily soluble in acid solution whereas the benzimidazolin-2-ones are not. The presence of the nitro-group, however, reduces the solubility of the 2-chloro-compound so that the initial solid which separates is a mixture. Hence an alternative method of separation was necessary. First, a method was devised by means of which the yield of 2-chloro-compound could be determined without isolation. For this, the solid (*X*) was first freed from a small quantity of polymer of low molecular weight by warming it with concentrated hydrochloric acid (80 ml./g.), filtration from the small amount of insoluble material, and addition of concentrated ammonia solution to the filtrate until it was only slightly acid. After cooling, the yellow solid (*Y*) was collected, washed with water, dried, and weighed. The composition of material *Y* was easily determined by ultraviolet spectroscopy, the spectra of 2-chloro-5-nitrobenzimidazole and 5-nitrobenzimidazolin-2-one being quite different. Originally Dewar and Urch's method<sup>21</sup> was used, but it was later found possible to obtain results of sufficient accuracy by determining the positions of the main maxima and minima and comparison with mixtures of known composition. From these results the weight of 2-chloro-compound present in the whole of material *Y* and hence the weight present in the original reaction product could be calculated. The yields of 2-chloro-compound obtained from 5-nitrobenzimidazolin-2-one (1 g.) (*a*) without hydrogen chloride and (*b*) with passage of hydrogen chloride after the first 1.5 hr., are as follows:

Time (hr.) .....	2	3	6	8	9	10
Yield (g.) .....	(a) 0.10	0.48	0.62	0.47	—	0.26
	(b) 0.44	0.52	0.75	—	0.70	

Thus it appears that the effect of passing hydrogen chloride is much less in this case and that, under the optimum conditions, the yield does not exceed 70%. Isolation of the pure 2-chloro-compound from the crude product can be achieved by chromatography on alumina. For this, the crude product (*X*) was treated with ethanol (25 ml.), and the solution was filtered and then diluted with benzene (75 ml.) before introducing it on to the column. Elution with benzene-ethanol (3:1) gave first the required 2-chloro-compound, followed on change to benzene-ethanol (1:1) by the benzimidazolin-2-one. Some polymeric material remained on the column. This method was not convenient, however, for large-scale preparations and was replaced by the fractional-precipitation method described below.

**2-Chloro-5-nitrobenzimidazole.**—5-Nitrobenzimidazolin-2-one (8 g.) was boiled under reflux with phosphoryl chloride (160 ml.) for 1.5 hr. A rapid stream of hydrogen chloride was then passed through the boiling solution for 4.5 hr. The crude product (*X*) was isolated as above and weighed 8.4 g. Ultraviolet spectroscopy showed it to contain 60% of the required compound. The whole of material *X* was stirred with concentrated hydrochloric acid (150 ml.) and warmed gently. The small amount of insoluble material was filtered off and washed with a little concentrated hydrochloric acid. The combined filtrate and washings were treated with concentrated ammonia solution until the first yellow precipitate was formed. After strong cooling, the bright yellow solid was collected, washed with water, and dried; it was mainly 5-nitrobenzimidazolin-2-one (1.5 g.). More ammonia solution was added to the filtrate until it was only just acid. After cooling, the pale yellow solid was filtered off, washed repeatedly with water, dried, and after one recrystallisation from aqueous ethanol afforded 2-chloro-5-nitrobenzimidazole of 95% purity (4.3 g.). Repetition of the fractional precipitation gave material of 99% purity (3.5 g.). Final traces of 5-nitrobenzimidazolin-2-one were removed from a small sample by chromatography, followed by recrystallisation from aqueous ethanol. The pure material had m. p. 222—223° (softens, bubbles, then resolidifies) (lit., 222—223°, 220°<sup>25</sup>) (Found: C, 42.7; H, 2.4; Cl, 17.6; N, 21.0. Calc. for C<sub>7</sub>H<sub>4</sub>ClN<sub>3</sub>O<sub>2</sub>: C, 42.6; H, 2.0; Cl, 17.9; N, 21.3%),  $\nu_{\max}$  3120s, 3055s, 2955s, 2815s, 2695s, 2630s, 2480m, 1769w, 1632m, 1603m, 1534s, 1495s, 1476s, 1439s, 1422s, 1386s, 1372s, 1349s, 1318s, 1281w, 1250m, 1233w, 1211m, 1183w, 1130w, 1067m, 989s, 948w, 883s, 839m, 817s, 751m, 732s, 693w,

<sup>21</sup> Dewar and Urch, *J.*, 1957, 345.

668w  $\text{cm}^{-1}$ . Although the overall conversion of starting material into the 2-chloro-compound of 99% purity was only ~40%, the first fractions from the precipitations can be recycled.

*Polymers from 2-Chlorobenzimidazoles.*—In view of the behaviour of the 2-chlorobenzimidazoles on melting, and the isolation of insoluble and high-melting solids from some of the preparations, the nature of the changes was investigated more fully.

The 2-chlorobenzimidazole was heated in an oil-bath at 5–10° above its m. p. for 1 hr. Hydrogen chloride was evolved from the molten material and a solid was gradually re-formed. The process was repeated until the weight of the residue became constant. For 2-chlorobenzimidazole itself, 1.2 g. gave a residue of 0.93 g. of buff-coloured solid, which contained a negligible amount of chlorine and did not melt below 360°. The loss in weight is very close to that expected if 1 mol. of hydrogen chloride is lost from 1 mol. of chloro-compound, *i.e.*, a polymer and not a simple dimer, trimer, etc., is formed. Similar polymers were made from the 5-methyl and the 5-nitro-compound. The infrared spectra showed very little similarity to those of the monomers, but since definite assignments of bands could not be made the details are not given.

In some reactions of 5-nitrobenzimidazolin-2-one with phosphoryl chloride, the polymer isolated had m. p. ~330° and had a different infrared spectrum from that of the polymer described above. In particular, several peaks were much stronger than in the normal polymer. We tentatively suggest that this is a polymer of considerably lower molecular weight, the stronger peaks being due to vibrational modes which are being eliminated as the polymerisation proceeds. Prolonged heating (340°) of the low-molecular-weight polymer gave a product in which these peaks were very weak indeed. Our low-molecular-weight polymer is probably essentially the same as the "high molecular weight condensation product" mentioned by Kym and Ratner.<sup>14</sup>

*Intermediates in the Reaction of Benzimidazolin-2-ones with Phosphoryl Chloride.*—Benzimidazolin-2-one (2 g.) was boiled under reflux for 30 min. with phosphoryl chloride (20 ml.), the clear solution cooled in ice and the white solid filtered off. After rapid washing with sodium-dried ether, it was dried *in vacuo* over potassium hydroxide. The m. p. was indefinite and attempted recrystallisation from dry solvents only caused decomposition. Analysis of the crude material gave the following results (3 different samples): [Found: (a) C, 33.4; H, 1.9; Cl, 27.8; (b) C, 31.0; H, 2.6; Cl, 32.7; N, 10.5; P, 12.0; (c) Cl, 27.6; P, 12.5.  $\text{C}_7\text{H}_5\text{Cl}_2\text{N}_2\text{O}_2\text{P}$  requires C, 33.5; H, 2.0; Cl, 28.3; N, 11.1; P, 12.3%]. In view of the instability of the compound we regard these as reasonable support for the suggested formula. The compound fumes in air and is converted into benzimidazolin-2-one by treatment with ice-water, ethanol, or sodium acetate solution.

Attempted preparations of similar intermediates from the other benzimidazolin-2-ones were unsuccessful, solubilities being apparently less favourable.

*2-Chloro-1-methylbenzimidazole.*—2-Chlorobenzimidazole (5 g.) was dissolved in a mixture of water (50 ml.) and 5*N*-sodium hydroxide (15 ml.) and to the cooled solution was added dimethyl sulphate (5.5 ml.). Precipitation soon commenced and the mixture was stirred for 1 hr. and then left for 1 hr. The white solid was collected, washed with water ( $5 \times 100$  ml.), and dried at 70°, giving 2-chloro-1-methylbenzimidazole (4.5 g.). After recrystallisation from light petroleum (b. p. 60–80°) this formed leaflets, m. p. 114–116° (lit.,<sup>10</sup> 108–109°) (Found: C, 57.9; H, 3.9; Cl, 21.25; N, 17.0. Calc. for  $\text{C}_8\text{H}_7\text{ClN}_2$ : C, 57.7; H, 4.2; Cl, 21.3; N, 16.8%). An identical product was obtained by reaction of 1-methylbenzimidazolin-2-one with phosphoryl chloride.

*1-Acetyl-2-chlorobenzimidazole.*—To a solution of 2-chlorobenzimidazole (3 g.) in dry pyridine (20 ml.), cooled in ice-water, acetyl chloride (redistilled) (6 ml.) was added in small portions, with shaking, during 30 min. The mixture was left at room temperature with occasional agitation for a further 30 min. The resulting paste was poured into cold water (250 ml.) and stirred. After 1 hr. the yellow solid was collected, washed with water ( $2 \times 100$  ml.), and dried *in vacuo*, giving 1-acetyl-2-chlorobenzimidazole (2.68 g.), m. p. 82–85°, raised on recrystallisation from light petroleum (b. p. 60–80°) to 86–88° (Found: C, 56.0; H, 3.3; Cl, 18.3; N, 14.4.  $\text{C}_9\text{H}_7\text{ClN}_2\text{O}$  requires C, 55.6; H, 3.6; Cl, 18.2; N, 14.4%).

*2-Anilinobenzimidazole.*—2-Chlorobenzimidazole (0.98 g.) was boiled under reflux with redistilled aniline (10 ml.) for 1.5 hr. The excess of aniline was then removed in steam and to the residue were added a little concentrated hydrochloric acid and sufficient water to form a practically clear solution. This was filtered and the filtrate (*ca.* 120 ml.) was basified with

concentrated ammonia solution. The solid was collected, washed with water, and recrystallised from aqueous ethanol, giving 2-anilinobenzimidazole (0.71 g.), m. p. 188—192° (lit.,<sup>22</sup> 188°).

*Reaction of 2-Chlorobenzimidazole with Acetic Acid.*—2-Chlorobenzimidazole (0.34 g.) was boiled under reflux with glacial acetic acid (10 ml.) for 3 hr. A clear solution was formed after a few minutes. At the end of the reaction, the acetic acid was removed, the last traces under reduced pressure, and the residual white solid (0.29 g.) was washed with ether and dried. Recrystallisation from ethanol gave benzimidazolin-2-one, m. p. and mixed m. p. 314—316°.

*Reaction of 2-Chlorobenzimidazole with Acetic Anhydride.*—2-Chlorobenzimidazole (0.37 g.) was boiled with acetic anhydride (3 ml.) for 20 min. On cooling, a solid (0.32 g.) separated, and this was collected and washed with ether (2 × 5 ml.). It had m. p. 149—150°, not depressed on admixture with 1,3-diacetylbenzimidazolin-2-one.<sup>5</sup>

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<sup>22</sup> Deck and Dains, *J. Amer. Chem. Soc.*, 1933, **55**, 4986.

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