## 1013. *The Formation and Thermal Rearrangement of Diphenylketen–Arenediazocyanide Adducts.**

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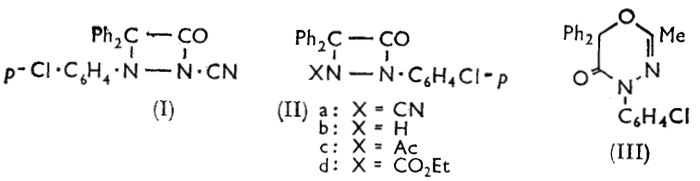
The structure of the diphenylketen–*p*-chlorobenzenediazocyanide adduct has been established. The formation of similar adducts from other arenediazocyanides has been investigated. Most of the adducts obtained undergo thermal rearrangement to derivatives of the previously unknown 1-*H*-imidazo[1,2-*a*]benzimidazole ring system.



Addition of diphenylketen to either *cis*- or *trans*-*p*-chlorobenzenediazocyanide is known to give an adduct to which the structure (I) was assigned [1] by analogy with an earlier formulation of the diphenylketen–ethyl benzeneazocarboxylate adduct.[2] The structure of the latter has recently been revised [3] and this suggested that the structure (I) should be amended to (IIa). The subsequent discovery of an unusual thermal rearrangement undergone by the diphenylketen–*p*-chlorobenzenediazocyanide adduct (see below) necessitated an unambiguous confirmation of its formulation.

The four-membered ring structure of the adduct was confirmed by the high-frequency carbonyl band at 1790 cm.$^{-1}$. The infrared spectrum also showed absorption bands characteristic of nitrile (2200 cm.$^{-1}$), *p*-disubstituted benzene (830 cm.$^{-1}$), and phenyl groups (700 cm.$^{-1}$). Treatment of the adduct with hydrochloric acid in ethanol gave a product (IIb) which still contained a strained carbonyl group (1740 cm.$^{-1}$), *p*-disubstituted benzene ring (830 cm.$^{-1}$), and phenyl groups (*ca.* 700 cm.$^{-1}$). In addition a band at




3200 cm.$^{-1}$ indicated the presence of an NH group, which was confirmed by the formation of an acetyl derivative (IIc) on treatment with acetic anhydride, acid treatment of which regenerated compound (IIb). In contrast the reaction of compound (IIb) with acetyl chloride gave an isomeric product the infrared spectrum (1680, 1650 cm.$^{-1}$) of which suggested [3] the dihydro-oxadiazinone structure (III). This was confirmed by an alternative synthesis of compound (III) from chlorodiphenylacetyl chloride and *N'*-acetyl-*N*-*p*-chlorophenylhydrazine. The oxadiazinone (III) was also obtained by isomerisation of compound (IIc) with iodine in refluxing xylene. When the oxadiazinone (III) was treated with hydrochloric acid in ethanol the products isolated were compound (IIb) and apparently unchanged compound (III). No products of the oxindole type could be isolated after these reactions, presumably as a result of the lower reactivity of the *p*-chlorophenyl group to electrophilic attack. Independent confirmation of the structure (IIa) was obtained by synthesis of the diazetidinone (IId) from chlorodiphenylacetyl chloride and ethyl *N'*-*p*-chlorophenylhydrazine-*N*-carboxylate. The product (IId) also gave the diazetidinone (IIb) on acid hydrolysis.

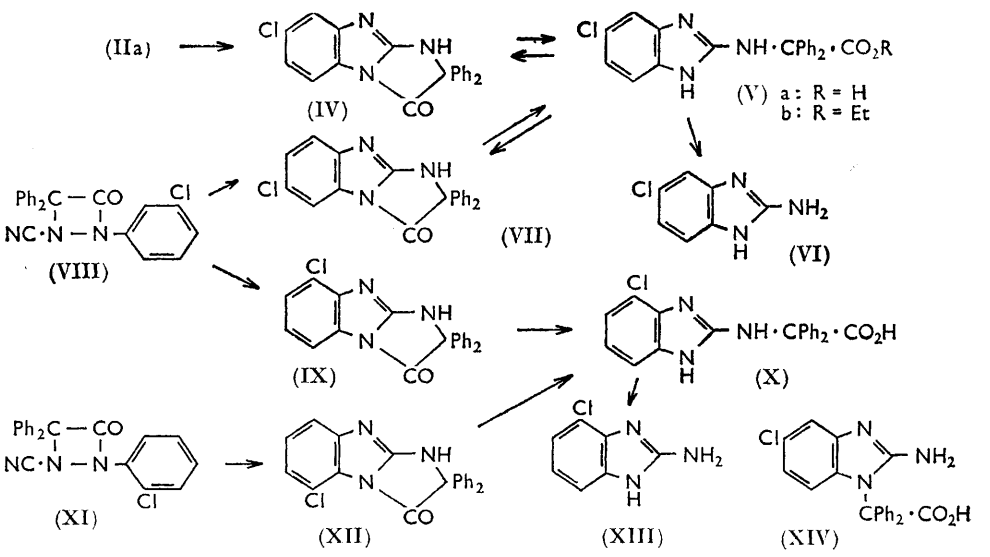
* For a preliminary communication see Bird, *Chem. and Ind.*, 1963, 1556.

[1] Cook and Jones, *J.*, 1941, 184.
[2] Ingold and Weaver, *J.*, 1925, **127**, 378.
[3] Bird, *J.*, 1963, 674.

The addition of diphenylketen to a variety of *cis*-arenediazocyanides was investigated subsequently. A rapid, exothermic reaction occurred with *m*- and *o*-chloro-, *p*-bromo-, *p*-nitro-, and 2,4- and 2,6-dichloro-benzenediazocyanides. In contrast no reaction was observed with benzene-, *p*-methoxybenzene-, or naphthalene-1-diazocyanide. These substituent effects indicate that diphenylketen fills the role of electron donor in these additions [4] in contrast to its usual electron-accepting character. The recently demonstrated [5] two-step mechanism for keten addition then predicts its observed orientation.

As mentioned above, most of these adducts readily undergo thermal rearrangement. This phenomenon was first observed for the diphenylketen–*p*-chlorobenzenediazocyanide adduct which suddenly solidified several degrees above its melting point (123°) and then remelted (~260°). The same transformation was more conveniently effected by briefly refluxing a xylene solution of compound (IIa). The product is probably the same as that reported [1] as having once been obtained from the reaction of diphenylketen with *p*-chlorobenzenediazocyanide. The following evidence shows that this isomerisation product has the structure (IV).

The infrared spectrum indicated the possible presence of an NH group (3100 cm.$^{-1}$), a carbonyl group (1760 cm.$^{-1}$), a C=N group (1660 cm.$^{-1}$), and a 1,2,4-trisubstituted benzene ring (835, 810 cm.$^{-1}$). The presence of the NH group was confirmed by the formation of an acetyl derivative and also by the nuclear magnetic resonance spectrum in deuteriochloroform at 60 Mc./sec., which had a typical NH resonance at 570 c./sec. relative to tetramethylsilane. Although a full analysis of the complicated aromatic proton resonances between 400 and 450 c./sec. was impossible, the spectrum appeared compatible with that expected for structure (IV).




The thermal rearrangement product (IV) was rapidly hydrolysed by dilute sodium hydroxide to an acid (Va). Reductive cleavage of this acid with iodine and phosphorus in acetic acid gave almost quantitative yields of diphenylacetic acid and 2-amino-5-chlorobenzimidazole [6] (VI) isolated as its acetic acid salt. While this degradation and the

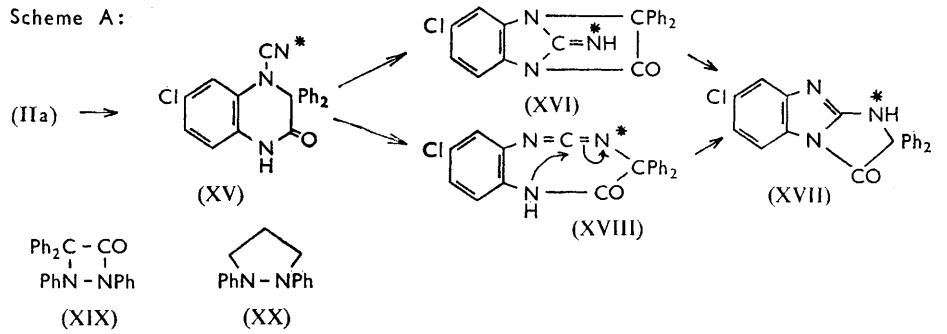
[4] Kresze and Trede, *Tetrahedron*, 1963, **19**, 133.
[5] Katz and Dessau, *J. Amer. Chem. Soc.*, 1963, **85**, 2172.
[6] Leonard, Curtin, and Beck, *J. Amer. Chem. Soc.*, 1947, **69**, 2459.

spectra established the nature of the two units present they did not differentiate between, for example, (Va) and (XIV) as possible expressions for the carboxylic acid. The reaction of the rearrangement product (IV) with hydrochloric acid in ethanol gave what was obviously the ethyl ester (Vb) of the aforementioned carboxylic acid. On being heated to its melting point this ethyl ester eliminated ethanol with generation of a mixture of the original rearrangement product (IV) and an isomeric compound (VII). The spectra ($\theta_{max.}$ 3100, 1760, 1670, 845, 815 cm.$^{-1}$) of the latter were similar to those of compound (IV) and on alkaline hydrolysis it gave the same carboxylic acid (Va). This precluded the occurrence of a sketetal rearrangement in the formation of compound (VII) from compound (IV). These transformations confirm the assignment of structure (Va) to the carboxylic acid.

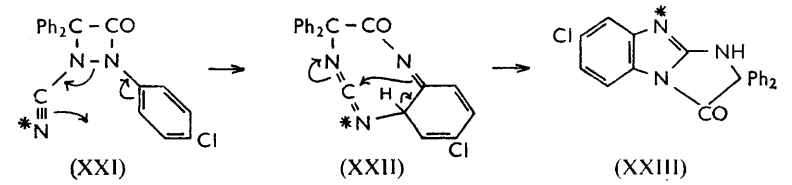
These structures were further supported by thermal rearrangement of the diphenylketen-*o*- and *m*-chlorobenzenediazocyanide adducts (XI and VIII). The adduct (XI) gave a single product (XII), which on alkaline hydrolysis gave the carboxylic acid (X). This, on reductive cleavage, yielded diphenylacetic acid and 2-amino-4-chlorobenzimidazole (XIII), the structure of which was confirmed by deamination with nitrous acid to the known 4-chlorobenzimidazolid-2-one.[7] As expected, thermal rearrangement of compound (VIII) produced the previously encountered compound (VII), together with a new isomer (IX), which gave the carboxylic acid (X) on alkaline hydrolysis.

Similar rearrangements were observed with the diphenylketen adducts of *p*-bromo- and *p*-nitro-benzenediazocyanide, although the isomerisation of the latter appeared somewhat slower. Both of the resulting products had the expected infrared spectra To examine the effect of blocking both *ortho*-positions of the aryl ring the thermal behaviour of the 2,6-dichlorobenzenediazocyanide adduct was examined. Although this compound appeared slowly to form a solid material on being heated above its melting point, no characterisable product could be isolated. In contrast, the isomeric 2,4-dichlorobenzenediazocyanide adduct was readily rearranged to the expected product.

Scheme A:




Scheme B:




Two mechanisms appear worthy of consideration for the thermal rearrangement of compound (IIa) to compound (IV). The first of these, scheme A, entails an *ortho*-semidine

[7] Clark and Pessolano, *J. Amer. Chem. Soc.*, 1958, **80**, 1657.

rearrangement of compound (IIa) to compound (XV). The intermediate (XV) could then undergo intramolecular cyclisation to compound (XVI) followed by an N-to-N migration, for which there are analogies,[8] yielding compound (XVII). Alternatively the intermediate (XV) might rearrange to the carbodi-imide (XVIII) which by intramolecular cyclisation would also give compound (XVII). However, it seems doubtful whether the proposed *ortho*-semidine rearrangement is likely to occur. Attempts to effect rearrangements of this kind with compounds such as (IId) have been unsuccessful and compound (XIX) has long been known [9,1] to undergo thermal decomposition to diphenylketen, phenyl isocyanate, azobenzene, and benzophenone phenylimine. Further, failure to effect the benzidine rearrangement of the five-membered ring compound (XX) has been recorded.[10]

What appears to be a more attractive mechanism is shown in scheme B. This entails a novel Cope-type rearrangement [11] of compound (XXI) via a carbodi-imide intermediate (XXII), followed by transannular cyclisation to compound (XXIII). An examination of Catalin molecular models indicates that no appreciable change of atomic positions would be involved in a rearrangement by this route. This mechanism would also account for the apparently slower rate of rearrangement of the *p*-nitrobenzenediazocyanide adduct.

In principle, differentiation between schemes A and B should be possible by using suitably labelled precursors since, for example, these routes predict different locations for the nitrile-nitrogen in the rearrangement product. It is hoped to report appropriate experiments later.

## Experimental

Infrared spectra were recorded for Nujol mulls on a Perkin-Elmer model 137E spectrophotometer. The (nuclear magnetic resonance) n.m.r. spectrum was recorded for a deuteriochloroform solution on a Varian A.60 instrument with tetramethylsilane as the internal reference. Chromatography was in benzene on silica gel. Where compounds were obtained by alternative routes their identity was established by mixed m. p.s and infrared spectra.

*Acid Treatment of the Diazetidinone* (IIa).—The diazetidinone [1] (IIa) (0·5 g.) was heated in ethanol (10 ml.) on the steam-bath for 1 hr. with concentrated hydrochloric acid (5 ml.). The product was isolated by addition of water and extraction with chloroform. Crystallisation from aqueous acetic acid gave 1-p-*chlorophenyl*-3,3-*diphenyldiazetidin*-4-*one* (IIb) (0·25 g.) m. p. 173—174° (Found: C, 71·9; H, 4·6; Cl, 10·8; N, 8·5. $C_{20}H_{15}ClN_2O$ requires C, 71·8; H, 4·5; Cl, 10·6; N, 8·4%). This was converted by refluxing in acetic anhydride into its *acetyl derivative* (IIc), m. p. 130—131° (from ethanol) (Found: C, 69·8; H, 4·7; Cl, 9·6; N, 7·5. $C_{22}H_{17}ClN_2O_2$ requires C, 70·1; H, 4·5; Cl, 9·4; N, 7·4%).

*Formation of the Oxadiazinone* (III).—(*a*) *N'*-Acetyl-*p*-chlorophenylhydrazine [12] (1·85 g.) (conveniently prepared by acetylation of *p*-chlorophenylhydrazine) and chlorodiphenylacetyl chloride [13] (2·65 g.) in toluene (20 ml.) were heated under reflux overnight. The toluene was evaporated *in vacuo* and the residue crystallised from ethanol, to give 4-p-*chlorophenyl*-5,6-*dihydro*-6,6-*diphenyl*-2-*methyl*-5H-1,3,4-*oxadiazin*-5-*one* (III), m. p. 148—149° (Found: C, 70·3; H, 4·6; Cl, 9·9; N, 7·5. $C_{22}H_{17}ClN_2O_2$ requires C, 70·1; H, 4·5; Cl, 9·4; N, 7·4%).

(*b*) The diazetidinone (IIb) and acetyl chloride were heated under reflux for 1 hr. and the acetyl chloride subsequently evaporated *in vacuo*. Crystallisation of the residue from ethanol gave compound (III).

(*c*) The diazetidinone (IIc) (0·2 g.) and a crystal of iodine in xylene (10 ml.) were heated under reflux for 1 hr. The xylene was evaporated *in vacuo* and the residue crystallised from ethanol to give compound (III) (0·14 g.).

[8] Chapman, *J.*, 1929, 2133; 1930, 2462; 1932, 1771.
[9] Skraup and Binder, *Ber.*, 1929, **62**, *B*, 1127.
[10] Wittig, Joos, and Rathfelder, *Annalen*, 1957, **610**, 180.
[11] Rhoads, "Molecular Rearrangements" ed. de Mayo, Interscience Publ., Inc., New York, 1963, Vol. I, p. 655.
[12] Pechmann and Vanino, *Ber.*, 1894, **27**, 224.
[13] McKenzie and Boyle, *J.*, 1921, **119**, 1131.

*Ethyl* 2-p-*Chlorophenyl*-4,4-*diphenyl*-3-*oxodiazetidine*-1-*carboxylate* (IId).—Ethyl *N'*-*p*-chlorophenylhydrazine-*N*-carboxylate [14] (2·7 g.) and chlorodiphenylacetyl chloride [13] (3·33 g.) in benzene (50 ml.) were heated under reflux for 40 hr. The cooled solution was chromatographed; the product (IId) (3 g.), eluted with benzene, had m. p. 132—133° (from benzene–light petroleum) (Found: C, 67·9; H, 4·9; Cl, 8·7; N, 7·1. $C_{23}H_{19}ClN_2O_3$ requires C, 67·9; H, 4·7; Cl, 8·7; N, 6·9%).

*Acid Treatment of the Diazetidinones* (IIc) *and* (IId).—This was carried out as for the preceding diazetidinone (IIa) except that heating was extended to 2 hr. The yield of 1-*p*-chlorophenyl-3,3-diphenyldiazetidin-4-one (IIb) was about the same in each case.

*Acid Treatment of the Oxadiazinone* (III).—The oxadiazinone (III) (2 g.) was heated under reflux for 2 hr. with ethanol (60 ml.) and concentrated hydrochloric acid (30 ml.). The crude products were isolated by addition of water and extraction with chloroform, and then chromatographed. Elution with benzene gave successively the diazetidinone (IIb) (0·1 g.) and the oxadiazinone (III) (0·3 g.) as the only crystalline products.

*Diphenylketen–Arenediazocyanide Adducts.*—The arenediazocyanides [15–17] were prepared immediately before use by the method of Le Fèvre and Vine,[15] which gives the *cis*-isomers. The crude arenediazocyanides were dissolved in ether and dried ($Na_2SO_4$) before use. No attempt was made to characterise the previously unreported *m*-chloro- and 2,6-dichloro-benzenediazocyanides. The adducts were prepared by slowly adding the calculated amount of diphenylketen [18] to the filtered ethereal solution, which was usually rapidly decolourised, and the reaction mixture set aside overnight. Except in one or two cases, where the product crystallised, the ethereal solution was evaporated in the cold and triturated with methanol, to give the solid adduct. In this way were prepared the following 1-*aryl*-2-*cyano*-3,3-*diphenyldiazetidin*-4-*ones*: m-*chlorophenyl*- (80%), m. p. 105—108°, 260—280° (from ether–methanol) (Found: C, 70·3; H, 4·1; Cl, 9·5; N, 11·4. $C_{21}H_{14}ClN_3O$ requires C, 70·1; H, 3·9; Cl, 9·9; N, 11·7%); o-*chlorophenyl*- (87%) m. p. 123°, 286—288° (from ether) (Found: C, 70·2; H, 3·9; Cl, 9·8; N, 11·5%); p-*bromophenyl*- (92%), m. p. 126—127°, 230—240° (from ether) (Found: C, 62·2; H, 3·4; Br, 19·7; N, 10·3. $C_{21}H_{14}BrN_3O$ requires C, 62·4; H, 3·5; Br, 19·8; N, 10·4%); p-*nitrophenyl*- (70%), m. p. 143—146°, 240—260° (from methanol) (Found: C, 68·1; H, 4·0; N, 15·3. $C_{21}H_{14}N_4O_3$ requires C, 68·1; H, 3·8; N, 15·2%); 2,4-*dichlorophenyl*- (38%), m. p. 104—106°, 265—270° (from ether–methanol) (Found: C, 64·3; H, 3·3; Cl, 17·5; N, 11·2. $C_{21}H_{13}Cl_2N_3O$ requires C, 64·0; H, 3·3; Cl, 18·0; N, 10·7%); 2,6-*dichlorophenyl*- (55%), m. p. 140—142°, then slowly partially solidified and gave a clear melt at *ca.* 280—300° (from ether) (Found: C, 63·9; H, 3·4; Cl, 17·8; N, 10·6%).

*Thermal Rearrangement of the Diphenylketen–Arenediazocyanide Adducts.*—The adduct in xylene was usually heated under reflux for about 5 min., except in the case of the *p*-nitrophenyl compound (2 hr.). The rearrangement product separated either before or after cooling. In this way were prepared the following substituted 2,3-*dihydro*-3-*oxo*-2,2-*diphenyl*-1H-*imidazo*-[1,2-a]*benzimidazoles*: 7-*chloro*- (78%), m. p. 268—270° (from xylene) (Found: C, 70·0; H, 4·2; Cl, 10·0; N, 11·9%; *M*, 370. $C_{21}H_{14}ClN_3O$ requires C, 70·1; H, 3·9; Cl, 9·9; N, 11·7%; *M*, 359·8), which with acetic anhydride gave the *acetyl derivative*, m. p. 218—220° (Found: C, 69·0; H, 4·1; N, 10·1. $C_{23}H_{16}ClN_3O_2$ requires C, 68·7; H, 4·0; N, 10·5%); 5-*chloro*- (80%), m. p. 296—298° (from nitromethane) (Found: C, 70·1; H, 4·1; Cl, 9·8; N, 11·4%); 7-*bromo*- (55%), m. p. 272—276° (from xylene) (Found: C, 62·3; H, 3·5; Br, 20·0; N, 10·3. $C_{21}H_{14}BrN_3O$ requires C, 62·4; H, 3·5; Br, 19·8; N, 10·4%); 7-*nitro*- (52%), m. p. 280—283° (from xylene) (Found: C, 68·6; H, 4·0; N, 15·0. $C_{21}H_{14}N_4O_3$ requires C, 68·1; H, 3·8; N, 15·2%); 5,7-*dichloro*- (80%), m. p. 285—287° (from xylene) (Found: C, 64·3; H, 3·4; Cl, 17·7; N, 10·5. $C_{21}H_{13}Cl_2N_3O$ requires C, 64·0; H, 3·3; Cl, 18·0; N, 10·7%).

Thermal rearrangement of the diphenylketen–*m*-chlorobenzenediazocyanide adduct (VIII) (2 g.) gave a mixture of compounds (VII) and (IX) which were chromatographed. Elution with benzene–ethyl acetate (24 : 1) gave, first, the 8-*chloro-compound* (IX) (0·43 g.), m. p. 335—337° (from xylene) (Found: C, 68·9; H, 4·0; Cl, 9·4; N, 12·0%), then mixed fractions (~0·25 g.),

[14] Pieroni and Giannini, *Gazzetta*, 1924, **54**, 170.
[15] Le Fèvre and Vine, *J.*, 1938, 431.
[16] Stephenson and Waters, *J.*, 1939, 1796.
[17] Hantzsch and Danziger, *Ber.*, 1897, **30**, 2529.
[18] Smith and Hoehn, *Org. Synth.*, Coll. Vol. III, p. 356.

and finally the 6-*chloro*-isomer (VII) (0·84 g.), m. p. 291—293° (from xylene) (Found: C, 70·6; H, 4·2; Cl, 9·8; N, 11·8%; *M*, 350).

*Alkaline Hydrolysis of Compound* (IV).—The rearrangement product (IV) (1 g.), with ethanol (20 ml.), and 2N-sodium hydroxide (5 ml.) were heated under reflux for 1 hr. The solution was cooled, diluted with water (100 ml.), and acidified with dilute hydrochloric acid. A portion of the white precipitate (0·8 g.) recrystallised from aqueous acetic acid, to give α-(5-*chloro*-2-*benzimidazolylamino*)-αα-*diphenylacetic acid* (Va), m. p. 180—182° (Found: C, 66·5; H, 4·4; N, 11·4. $C_{21}H_{16}ClN_3O_2$ requires C, 66·8; H, 4·3; N, 11·1%).

*Alkaline Hydrolysis of Compounds* (IX) *and* (XII).—These hydrolyses, effected as described for compound (IV), gave α-(4-*chloro*-2-*benzimidazolylamino*)-αα-*diphenylacetic acid* (X), m. p. 154—157° (from aqueous acetic acid) (Found: C, 63·3; H, 4·7; Cl, 8·2; N, 9·8. $C_{21}H_{16}ClN_3O_2$, $C_2H_4O_2$ requires C, 63·1; H, 4·6; Cl, 8·1; N, 9·6%).

*Reductive Cleavage of the Acid* (Va).—Red phosphorus (1 g.) and iodine (0·6 g.) were stirred together in acetic acid (20 ml.) for 30 min. A few drops of water were added, then the acid (Va) (2 g.), and the mixture was finally stirred and heated under reflux for 14 hr. The reaction mixture was cooled, filtered, and diluted with water; diphenylacetic acid (1 g.) crystallised. Neutralisation of the filtrate by solid sodium hydrogen carbonate gave a precipitate (0·95 g.) of the acetic acid salt, m. p. 224—226° (from nitromethane), of 2-amino-5-chlorobenzimidazole (VI) [6] identical with an authentic specimen (Found: C, 47·3; H, 4·5; Cl, 15·3; N, 18·5. Calc. for $C_9H_{10}ClN_3O_2$: C, 47·5; H, 4·4; Cl, 15·6; N, 18·5%).

*Reductive Cleavage of the Acid* (X).—Reduction of this acid (2 g.) was carried out as described for compound (Va). On cooling of the reaction mixture a product crystallised. The mixture was consequently filtered hot and the residue extracted several times with hot acetic acid. The combined filtrates were cooled, the white crystals [presumably the hydriodide of compound (XIII)] were filtered off and dissolved in a small volume of water, and sodium hydrogen carbonate was added. The precipitate (0·6 g.) crystallised from ethanol–benzene, to give 2-*amino*-4-*chlorobenzimidazole* (XIII), m. p. 197—199° (Found: C, 50·3; H, 3·6; Cl, 21·1; N, 25·0. $C_7H_6ClN_3$ requires C, 50·1; H, 3·6; Cl, 21·2; N, 25·1%). Dilution of the acetic acid filtrate gave diphenylacetic acid (0·8 g.).

*De-amination of Compound* (XIII).—The benzimidazole (XIII) (0·1 g.) in acetic acid (5 ml.) and 2N-sulphuric acid (5 ml.) was treated with sodium nitrite (0·1 g.) in a few drops of water. The solution was warmed briefly to complete the reaction, then cooled, and the resulting 4-chlorobenzimidazolid-2-one [7] (60 mg.) filtered off. It was identical with an authentic sample.

*Acid Treatment of Compound* (IV).—The compound (IV) (1 g.) in ethanol (40 ml.) was heated under reflux for 4 hr. with concentrated hydrochloric acid (20 ml.), dissolution then being complete. The crude product was isolated by addition of water and chloroform-extraction. The gum obtained was crystallised successively from a small volume of ethanol and from aqueous ethanol, to give ethyl α-(5-*chloro*-2-*benzimidazolylamino*)-αα-*diphenylacetate* (Vb) (0·4 g.), m. p. 210—215° with gas evolution, then 247—255° (Found: C, 68·0; H, 4·8; Cl, 9·2; N, 10·4. $C_{25}H_{26}ClN_3O_3$ requires C, 68·1; H, 5·0; Cl, 8·7; N, 10·4%).

*Action of Heat on Compound* (Vb).—The ester (Vb) (1·8 g.) was carefully heated to 220° after melting and resolidifying at *ca.* 210—215°. The product was dissolved in benzene and chromatographed. Elution with benzene–ethyl acetate (24 : 1) gave, first, compound (IV) (0·36 g.), then mixed fractions, and finally compound (VII) (0·29 g.).

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