106. *The Nature of Some Diazetidinone Rearrangements.*

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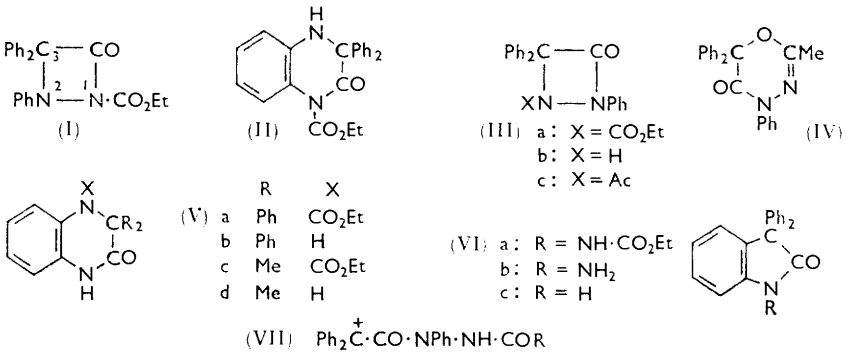
The acid-catalysed rearrangement of the diphenylketen–ethyl phenylazocarboxylate adduct has been re-examined and found to give mainly 1-ethoxycarbonylamino-3,3-diphenyloxindole. Similar transformations of related compounds are also reported.

Diphenylketen has been reported [1] to add to ethyl phenylazocarboxylate, giving the diazetidinone (I), which isomerises on treatment with hydrochloric acid in ethanol. The isomer was tentatively assigned the structure (II) since it was envisaged as arising by an *ortho*-semidine rearrangement. In addition, small amounts of another compound were isolated which was assigned the molecular formula $C_{20}H_{16}N_2O_2$ and was thought to be a " keto-triphenyloxadiazole." In the light of current views on the mechanism of the benzidine rearrangement additional experimental evidence for structure (II) seemed desirable.

To establish first the orientation of the original adduct, it was synthesised from chlorodiphenylacetyl chloride and ethyl *N'*-phenylhydrazine-*N*-carboxylate which showed it to have the alternative orientation (IIIa). The four-membered ring structure of this adduct was confirmed by the high-frequency carbonyl band at 1790 cm.$^{-1}$. Normally the product from the reaction of chlorodiphenylacetyl chloride with an acid hydrazide is formulated [2] as an oxadiazinone, *e.g.*, (IV); examination of their infrared spectra, which

[1] Ingold and Weaver, *J.*, 1925, **127**, 378.
[2] Van Alphen, *Rec. Trav. chim.*, 1929, **48**, 163.

exhibit a single carbonyl band at 1690 cm.$^{-1}$ and a band at 1640 cm.$^{-1}$ attributable to the –O–C=N-group, dispelled a suspicion that such products might be diazetidinones.



Treatment of the diazetidinone (IIIa) with hydrochloric acid in ethanol, and chromatography of the reaction mixture, gave the reported isomeric and minor products,[1] which were also obtained when the ethanol was replaced by methanol or dioxan. The reported stability of the isomer to hydrolysis was confirmed, as was its formation of a monoacetyl derivative. The lack of typical ketonic carbonyl reactions such as oxime formation, or reduction by sodium borohydride, suggested that both carbonyl groups were present in amide functions.

If the isomerisation product were derived by *ortho*-semidine rearrangement of the ester (IIIa) it would have the structure (Va). Unfortunately, although compound (Vb) was readily obtained from chlorodiphenylacetic acid and *o*-phenylenediamine, attempts to convert it into the ester (Va) by reaction with ethyl chloroformate were unsuccessful. However, the analogous ester (Vc) could be obtained from its parent (Vd) and ethyl chloroformate. A comparison of the spectral properties of this ester (Vc) with those of the isomerisation product indicated a marked dissimilarity. The ultraviolet spectrum of (Vc), $\lambda_{max.}$ 230 (ε 22,500) and 261 mμ (ε 6500), was completely different from that of the isomerisation product which showed shoulders only at 250 (ε 4900) and 278 mμ (ε 1300). Similar divergences were obvious in the infrared spectra; for example, the carbonyl bands for (Vc) were at 1710 and 1670 cm.$^{-1}$, but those in the isomerisation product were at 1740 and 1700 cm.$^{-1}$. Thus it was clear that the isomerisation product could not have the structure (Va). Additional structural features of the isomerisation product indicated by the infrared spectrum were an *ortho*-disubstituted benzene ring (765 cm.$^{-1}$) and a N–H group (3250 cm.$^{-1}$), the latter absent from the spectrum of the monoacetyl derivative. The evidence thus far led to tentative reformulation of the isomerisation product as (VIa), which was confirmed by subsequent transformations.

Reanalysis of the minor product from the acid treatment of the product (IIIa) showed it to have the revised formula $C_{20}H_{16}N_2O$, corresponding to the loss of the ethoxycarbonyl group. It was not produced when compound (VIa) was subjected to the isomerisation conditions, and the infrared spectrum supported its formulation as (IIIb), since it indicated a N–H group (3200 cm.$^{-1}$) and a strained amide carbonyl group (1735 cm.$^{-1}$). Although attempts to reconvert it into the ester (IIIa) were unsuccessful, it was acetylated by acetic anhydride. The product (IIIc) had the expected infrared spectrum, with carbonyl bands at 1790 and 1705 cm.$^{-1}$.

Acid treatment of the acetyl derivative (IIIc) gave three products, two of which were recognised as the diazetidinone (IIIb) and the known [2] oxadiazinone (IV). An identical mixture was obtained by acid treatment of the oxadiazinone (IV) under the same conditions, which provided a more accessible source of the third compound. The latter was found to have the formula $C_{20}H_{16}N_2O$. Its formulation as (VIb) followed from the infrared spectrum

which indicated the presence of an *ortho*-disubstituted benzene ring (755 cm.$^{-1}$), a carbonyl group (1690 cm.$^{-1}$), and an amino-group (3600 and 3400 cm.$^{-1}$), the last confirmed by formation of a benzylidene derivative. As expected, this amine (VIb) was converted into its derivative (VIa) by reaction with ethyl chloroformate. A final proof of the structure (VIb) was supplied by conversion into the known [3] 3,3-diphenyloxindole (VIc) on treatment with nitrous acid.

The rearrangements of these diazetidinones are readily rationalised if the initial step is the protonation of N-2 or the 2-acyl group. Subsequent fission of the 2,3-bond would lead to formation of the carbonium ion (VII) which may then attack the *N*-phenyl group, N-2, or the 2-acyl group, with formation of the observed products. The same carbonium ion intermediate can also arise by protonation of the oxadiazinone.

Experimental

Infrared spectra were recorded for Nujol mulls on a Perkin-Elmer model 137E spectrophotometer. Ultraviolet spectra were measured for ethanol solutions on a Unicam S.P. 700 instrument. Solutions for chromatography were prepared in benzene and chromatographed on silica gel. Where compounds were obtained by alternative routes their identity was established by mixed melting points and infrared spectra.

Ethyl 3-*Oxo*-2,4,4-*triphenyldiazetidine*-1-*carboxylate* (IIIa).—Ethyl *N'*-phenylhydrazine-*N*-carboxylate [1] (1·8 g.) and chlorodiphenylacetyl chloride [4] (2·65 g.) in toluene (30 ml.) were heated under reflux overnight. The toluene was evaporated *in vacuo* and the residue chromatographed. Elution with benzene, followed by crystallisation from benzene–light petroleum, gave the product (2·6 g.), m. p. 129—130°, identical with the adduct [1] from diphenylketen and ethyl phenylazocarboxylate and having $\lambda_{max.}$ 262 mμ (ε 12,400).

Rearrangement of the Diazetidinone (IIIa).—The compound (IIIa) (5 g.) was dissolved in warm ethanol (40 ml.), and concentrated hydrochloric acid (20 ml.) was added. The solution was heated on the steam-bath for 2 hr., a small amount of oil slowly separating. The product was isolated by addition of an excess of water and extraction by chloroform and was chromatographed. Elution with benzene gave 2,4,4-*triphenyldiazetidin*-3-*one* (IIIb) (0·3 g.), m. p. 180—182° (from ethanol) (Found: C, 79·8; H, 5·1; N, 9·2. $C_{20}H_{16}N_2O$ requires C, 80·0; H, 5·4; N, 9·3%), $\lambda_{max.}$ 250 mμ (ε 14,500). This was converted by refluxing in acetic anhydride (15 min.) into its *acetyl derivative*, m. p. 169—170° (from ethanol) (Found: C, 76·8; H, 5·4; N, 8·3. $C_{22}H_{18}N_2O_2$ requires C, 77·2; H, 5·3; N, 8·2%), $\lambda_{max.}$ 261 mμ (ε 12,100). Elution with benzene–ethyl acetate (19 : 1) gave 1-*ethoxycarbonylamino*-3,3-*diphenyloxindole* (VIa) (3·5 g.), m. p. 166—167° (from acetic acid) (Found: C, 74·1; H, 5·2; N, 7·6. $C_{23}H_{20}N_2O_3$ requires C, 74·2; H, 5·4; N, 7·5%), $\lambda_{max.}$ 250 mμ (ε 4900) and 278 mμ (ε 1330).

The same products were obtained when the ethanol was replaced by an equal volume of methanol or dioxan.

1,2,3,4-*Tetrahydro*-3,3-*diphenylquinoxaline*-2-*one* (Vb).—Chlorodiphenylacetic acid [5] (2·2 g.) and *o*-phenylenediamine (3 g.) were heated together on the steam-bath for 30 min. The solid formed was dissolved in hot ethanol (charcoal) and allowed to cool. The product (1·2 g.), recrystallised from ethanol, had m. p. 211—212° (Found: C, 80·3; H, 5·3; N, 9·0. $C_{20}H_{16}N_2O$ requires C, 80·0; H, 5·4; N, 9·3%).

Ethyl 1,2,3,4-*tetrahydro*-2,2-*dimethyl*-3-*oxoquinoxaline*-1-*carboxylate* (Vc).—1,2,3,4-Tetrahydro-3,3-dimethylquinoxalin-2-one [6] (1·0 g.) was treated in pyridine (10 ml.) with ethyl chloroformate (2 ml.) and left overnight. An excess of water was then added and the product (0·4 g.) was isolated by chloroform-extraction. It had m. p. 158—159° (from aqueous ethanol) (Found: C, 62·8; H, 6·8; N, 11·2. $C_{13}H_{16}O_3N_2$ requires C, 62·9; H, 6·5; N, 11·3%), $\lambda_{max.}$ 230 mμ (ε 22,500), 261 mμ (ε 6500).

Acid Treatment of 1-*Acetyl*-2,4,4-*triphenyldiazetidin*-3-*one* (IIIc).—The diazetidinone (IIIc) (0·9 g.) was heated in ethanol (20 ml.) on the steam-bath for 2 hr. with concentrated hydrochloric acid (10 ml.). The product isolated by addition of an excess of water and chloroform-extraction

[3] Wegmann and Dahn, *Helv. Chim. Acta*, 1946, **29**, 415.
[4] McKenzie and Boyle, *J.*, 1921, **119**, 1131.
[5] Wasserman and Wharton, *J. Amer. Chem. Soc.*, 1960, **82**, 3457.
[6] Hinsberg, *Annalen*, 1888, **248**, 79.

was chromatographed. Elution with benzene gave, first, 2,4,4-triphenyldiazetidin-3-one (0·06 g.) and then 5,6-dihydro-2-methyl-4,6,6-triphenyl-5*H*-1,3,4-oxadiazin-5-one (IV) (0·21 g.), identified by comparison with an authentic specimen.[2] Benzene–ethyl acetate (19 : 1) eluted 1-*amino*-3,3-*diphenyloxindole* (VIb) (0·16 g.), m. p. 151—152° (from aqueous ethanol) (Found: C, 79·7; H, 5·6; N, 9·4. $C_{20}H_{16}N_2O$ requires C, 80·0; H, 5·4; N, 9·3%). A *benzylidene derivative* was prepared by refluxing this amine (0·3 g.) in ethanol (15 ml.) for 3 hr. with benzaldehyde (0·15 ml.). Evaporation to small volume and cooling gave the product which, recrystallised from ethyl acetate–methanol, had m. p. 183—185° (Found: C, 83·4; H, 5·3; N, 7·3. $C_{27}H_{20}N_2O$ requires C, 83·5; H, 5·2; N, 7·2%).

Acid Treatment of the Oxadiazinone (IV).—This was carried out as for the preceding acid treatment of (IIIc) and gave the same products in approximately the same amounts.

Deamination of 1-*Amino*-3,3-*diphenyloxindole* (VIb).—The compound (1·0 g.) was dissolved in acetic acid (20 ml.), and a concentrated aqueous solution of sodium nitrite (1·0 g.) was slowly added. The solution was set aside for 10 min. and then heated on the steam-bath for a further 10 min. Addition of water caused the separation of crystals which were filtered off and recrystallised from ethanol, to give 3,3-diphenyloxindole (0·6 g.), m. p. 228—232°, identical with an authentic sample.[3]

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