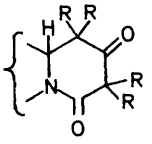
Keten. Part XIV.[1] Adducts of Diphenylketen with Aza-arenes

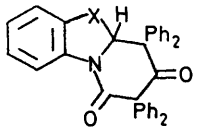
By **Giles A. Taylor**, Department of Chemistry, University of Sheffield, Sheffield S3 7HF

The cycloadducts of diphenylketen with quinoline, isoquinoline, 3-methylisoquinoline, phenanthridine, benzoxazole, 5-methylbenzoxazole, 6-methylbenzoxazole, and benzothiazole are assigned the oxazinone part-structure (3b). These adducts react with nucleophiles in two ways. Benzylamine attacks the oxazinone ring directly in some cases, whereas aniline only reacts after dissociation of the adduct to form free diphenylketen. Addition of diphenylketen to benzimidazoles gives two types of adduct. Oxazinones (5) are formed by benzimidazoles with electronegative substituents at position 1, whereas 1-methyl-, 1-benzyl-, and 1-phenyl-benzimidazoles form 1,2-disubstituted benzimidazoles (14). 1-Methylimidazole behaves similarly, giving the 1,2-disubstituted imidazole (15). The benzothiazole adduct (5c) is isomerised to the other type of adduct (14d) on heating in acetonitrile.

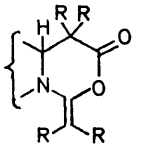
THE formation of adducts with aza-arenes was amongst the earliest of the reactions of ketens described by Staudinger.[2,3] Both dimethyl- and diphenyl-keten were reported to behave in this way, and the part-structures (1a and b) were assigned to the products. Whereas the dimethylketen adducts were stable compounds, the diphenylketen adducts were highly dissociated in solution, and the chemistry of these solutions was identical with that of diphenylketen. Only the quinoline adducts of diphenylketen and 2,2'-biphenylyleneketen were fully characterised. Much later, during studies related to penicillin, a number of diphenylketen adducts of thiazolines and benzothiazole were described [4] and the 2 : 1 (keten : imine) adducts were assigned the piperidinedione structure (1b). This work was subsequently extended by Kimbrough, who described the formation of adducts of diphenylketen with benzoxazole, benzimidazole, and a number of related heterocyclic species.[5]



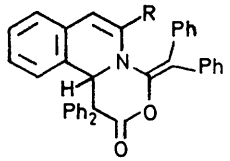
(1) a; R = Me
b; R = Ph



(2)

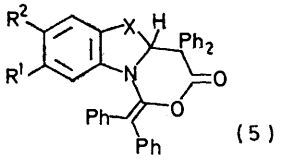


(3) a; R = Me
b; R = Ph



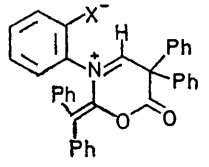
(4) a; R = H
b; R = Me

These were assigned structures similar to (1) [*e.g.* (2)] and i.r. spectra were claimed to support this conclusion. Shortly thereafter the cycloadducts of dimethylketen with benzopyridines were shown [6,7] to have the part-structure (3a), and the adduct of isoquinoline with diphenylketen was assigned [8] the structure (4a) by analogy with these results and studies on the diphenylketen adducts of *N*-methylbenzylideneamine. Finally, during the course of the work described below, Haddadin and Hassner proposed [9] the structure (5a) for Kimbrough's *N*-methylbenzimidazole–diphenylketen adduct, and structures (6a and b) for the adducts of benzoxazole and benzothiazole. The discrepancies between Kimbrough's i.r. data and the assigned structures [5] noted by Hassner had also been observed by us, and this paper describes work leading to new structural assignments for Kimbrough's adducts and a reappraisal of the evidence for the other adducts previously described.



(5)

	X	R^1	R^2
a;	NMe	H	H
b;	O	H	H
c;	S	H	H
d;	O	Me	H
e;	O	H	Me
f;	N·SO_2Me	H	H
g;	NAc	H	H
h;	N·COCHPh$_2$	H	H



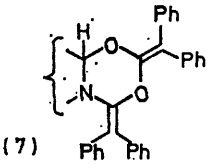
(6) a; X = O
b; X = S

Benzothiazole and Benzoxazole Adducts.—These were obtained by reaction of diphenylketen in benzene with the appropriate hetera-arene. Their i.r. spectra agreed with previous reports; in particular, both compounds had two very strong absorptions at *ca.* 1770 and 1650

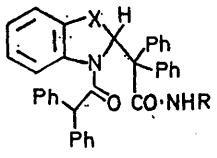
[1] Part XIII, R. N. Pratt, D. P. Stokes, and G. A. Taylor, *J.C.S. Perkin I*, 1975, 498.
[2] H. Staudinger, *Ber.*, 1906, **39**, 3062; *Annalen*, 1907, **356**, 51 (p. 105); *Ber.*, 1907, **40**, 1145.
[3] H. Staudinger, H. W. Klever, and P. Kober, *Annalen*, 1910, **374**, 1.
[4] H. T. Clark, J. R. Johnson, and R. Robinson, 'The Chemistry of Penicillin,' Princetown University Press, 1949, pp. 989—991.
[5] R. D. Kimbrough, *J. Org. Chem.*, 1964, **29**, 1242.
[6] J. C. Martin, V. A. Hoyle, and K. C. Brannock, *Tetrahedron Letters*, 1965, 3589; J. C. Martin, K. C. Brannock, R. D. Burpitt, P. G. Gott, and V. A. Hoyle, *J. Org. Chem.*, 1971, **36**, 2211.
[7] R. N. Pratt, G. A. Taylor, and S. A. Procter, *J. Chem. Soc.* (*C*), 1967, 1569.
[8] R. Huisgen, B. A. Davis, and M. Morikawa, *Angew. Chem.*, 1968, **80**, 802; *Angew. Chem. Internat. Edn.*, 1968, **7**, 826.
[9] M. J. Haddadin and A. Hassner, *J. Org. Chem.*, 1973, **38**, 2650.

cm^{-1} consistent with the presence of a vinyl ester group as in (5) or (6). The u.v. spectra were uninformative, but the n.m.r. spectra showed significant features. The ^1H spectrum (100 MHz) of the benzothiazole adduct showed a complex twenty-proton absorption below τ 3·1 and a group of four signals above τ 3·1 due to five protons. One of these, a singlet at τ 3·24, was assigned to the proton at C-2 of the benzothiazole unit of (5c), and this assignment was confirmed by synthesis of the adduct of 2-deuteriobenzothiazole, which showed a signal at this position in the ^1H n.m.r. spectrum diminished in proportion to the isotopic labelling. The other high-field signals consisted of a one-proton multiplet at τ 3·2, a two-proton multiplet at τ 3·5, and a one-proton multiplet at τ 4·05, which in the 220 MHz spectrum is resolved into a double doublet typical of an *o*- and *m*-coupled aromatic proton. These high-field signals clearly arise from overlapping of aromatic rings in (5) as is the case in the helicenes [10] and related compounds.[11] In order to discover which protons are responsible for these high-field signals, the benzothiazole–di-*p*-tolylketen adduct was prepared. The n.m.r. spectrum of the aromatic protons of this compound is quite different from that of the benzothiazole–diphenylketen adduct below τ 3·2 but virtually identical above that point, the signals being of identical appearance but shifted slightly downfield, the highest multiplet (a double doublet) appearing at τ 3·96. This leaves little doubt that the multiplets in this region are due to the protons at positions 4—7 of the benzothiazole unit in (5c). The n.m.r. spectrum of the benzoxazole–diphenylketen adduct is similar in form to those described above, but the shielded protons on the benzoxazole ring are less effectively screened, the highest field signal being a broadened doublet at τ 3·71. This reduced shielding may be due to the smaller size of the oxygen atom resulting in diminished overlap between the aromatic rings. By preparation of the diphenylketen adducts of 5- and 6-methylbenzoxazole (5d and e) and examination of their ^1H n.m.r. spectra it is possible to assign the high field absorption to H-4 of the benzazole skeleton in (5). The zwitterionic structure (6) proposed by Hassner [9] would not be expected to show such effective screening of one particular proton on account of free rotation or libration in the molecule. The observations that the diphenylketen adducts of benzoxazole and benzothiazole are recovered unchanged after treatment with benzoyl chloride and pyridine, and that the benzothiazole adduct is unchanged after 6 days in solution in neat methyl iodide are inconsistent with structures of type (6) which are expected to be highly nucleophilic at the X^- atom.

Although the spectroscopic evidence strongly supports structure (5) for the benzoxazole and benzothiazole adducts, chemical evidence was sought which would eliminate alternatives of part-structure (7) which are known to occur in a few cases.[12,13] The reaction of the benzothiazole–diphenylketen adduct with aniline in boiling benzene gave a high yield of diphenylacetanilide whilst prolonged treatment with aniline in benzene at room temperature procured no reaction. Benzylamine

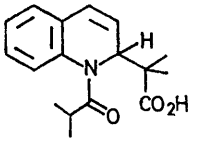


(7)

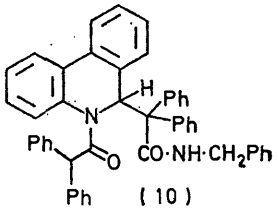


(8)

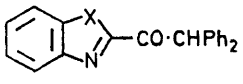
	X	R
a;	S	CH_2Ph
b;	O	CH_2Ph
c;	S	Ph
d;	S	H
e;	NAc	CH_2Ph



(9)

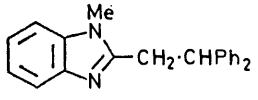


(10)



(11)

a; X = NMe
b; X = NCH_2Ph
c; X = S



(12)

reacted with this adduct both at room temperature and in boiling benzene to form a product assigned structure (8a) from spectroscopic data. This result eliminates adduct structures of type (7) from further consideration. The benzoxazole adduct also reacted with benzylamine to form (8b) but was unaffected by aniline at 80°. The formation of diphenylacetanilide by the reaction of aniline with (5c) could either arise by dissociation of the adduct to form diphenylketen, as is known to occur with the quinoline–diphenylketen adduct,[2] or *via* decomposition of an intermediate (8c) analogous to the thermal decomposition of the acid (9) to isobutyric anhydride and quinoline.[3] The thermal stability of (8a and b) favours the former explanation, which was proved by reaction of (5c) with benzophenone anil in boiling benzene to form pentaphenylazetidin-2-one, a reaction clearly indicating the intermediacy of diphenyl-

[10] R. H. Martin, N. Defay, H. P. Figeys, M. Flammang-Barbieux, J. P. Cosyn, M. Gelbcke, and J. J. Schurter, *Tetrahedron*, 1969, **25**, 4985.

[11] N. Kannen, T. Umemoto, T. Otsubo, and S. Misumi, *Tetrahedron Letters*, 1973, 4537; T. Otsubo, Z. Tozuka, S. Mizogami, Y. Sakata, and S. Misumi, *ibid.*, 1972, 2927, and other papers in this series; A. Maquestiau, Y. Van Haverbeke, R. Flammang, and M. Flammang-Barbieux, *ibid.*, 1973, 1335.

[12] J. C. Martin, R. D. Burpitt, P. G. Gott, M. Harris, and R. H. Meen, *J. Org. Chem.*, 1971, **36**, 2205.

[13] A. Hassner, A. S. Miller, and M. J. Haddadin, *Tetrahedron Letters*, 1972, 1353; A. Hassner, M. J. Haddadin, and A. B. Levy, *ibid.*, 1973, 1015.

keten. In contrast to this evidence for the dissociation of (5c) at 80°, comparison of the i.r. spectra of (5c) in a KBr disc and in chloroform solution showed no significant differences; in particular the spectrum of the solution showed no absorption at 2100 cm^{-1} characteristic of ketens. To show that benzothiazole was a product of the reactions and thereby establish the preservation of the benzothiazole skeleton in the adduct, the adduct was treated with ammonia in boiling benzene, resulting in the formation of some benzothiazole, some of the amide (8d), and presumably some diphenylacetamide which was not isolated. Benzothiazole was also detected by t.l.c. as a product of the reaction of (5c) with benzophenone anil, and pyrolysis of (5c) was shown to give benzothiazole. The benzoxazole adduct (5b) did not react with benzophenone anil, consistent with its failure to react with aniline. It therefore appears that the oxazinone ring in (5) is inert to direct attack by weak nucleophiles, which can only react after initial dissociation of the adduct. Despite the apparent stability of the benzoxazole adduct to dissociation, which is consistent with the close similarity of its i.r. spectra in KBr disc and in chloroform solution, Hassner has shown [9] that on pyrolysis benzoxazole is formed.

Attempts to isolate adducts from the reaction of diphenylketen with 2-methylbenzothiazole and 1-methylbenzotriazole were unsuccessful.

Benzopyridine Adducts.—The 2 : 1 adducts of diphenylketen with quinoline,[2] isoquinoline,[8] 3-methylisoquinoline, and phenanthridine were prepared. The i.r. spectra of the solids (in paraffin paste) all showed strong absorption at *ca.* 1760, 1630, and 1140 cm^{-1}, suggesting that these compounds have the same type of oxazinone structure (3b) established for the benzothiazole and benzoxazole adducts, and previously proposed by Huisgen for the isoquinoline adduct. The band at 1630 cm^{-1} appears to be due to the diphenylketen acetal unit, and there are several cases known, apart from those described in this paper, in which diphenylketen acetals absorb in the region 1630—1670 cm^{-1}.[8,13-15]

Of these four compounds, the quinoline adduct is known to be substantially dissociated in solution and the i.r. spectra of chloroform solutions show that this is also the case for the other three adducts. All these solution spectra show absorption at 2100 cm^{-1} due to free diphenylketen, and the spectra of the isoquinoline and 2-methylisoquinoline adducts also show a marked change in the carbonyl region compared with the spectra of the solids. The strong band at 1760 cm^{-1} disappears and is replaced by a strong peak at 1732 cm^{-1} and a weaker absorption at 1816 cm^{-1}. These changes are scarcely apparent in the case of the phenanthridine adduct. The n.m.r. spectra of deuteriochloroform solutions of the adducts also give limited information about the constitution of the adducts and the degree of dissociation. The only feature of the n.m.r. spectrum of the phenanthridine adduct, other than a very complex multiplet due to aromatic protons, is a broad singlet at τ 3·8 corresponding to *ca.* 0·75H. If this can be assigned to the angular proton in (3b) it suggests *ca.* 25% dissociation of the adduct. The n.m.r. spectrum of the isoquinoline adduct shows three signals clearly separated from the aromatic region. A singlet at τ 4·98 [8] and an AB quartet (τ 4·64 and 5·44) correspond to the signals expected for protons at positions 1, 3, and 4 of the isoquinoline residue in (4a). The integrals of these signals are consistent with *ca.* 70% dissociation of the adduct. Similarly the n.m.r. spectrum of the 3-methylisoquinoline adduct shows weak singlets at τ 4·99 and 5·51, a strong singlet at τ 7·31 due to free 3-methylisoquinoline, and a weaker singlet at τ 8·61 due to the methyl group in the adduct. The relative intensities of the two methyl signals suggest 75% dissociation and the shielding of the methyl group in the adduct is consistent with its environment in (4b). (The corresponding methyl resonance in the 3-methylisoquinoline–dimethylketen adduct occurs at τ 8·13.[7]) The n.m.r. spectrum of the quinoline adduct is uninformative. A few very weak signals are observed above τ 4·5 but their assignment is uncertain. If they do correspond to the protons at positions 2—4 of the quinoline residue then their intensity suggests *ca.* 90% dissociation.

Attempts to observe a direct reaction of the phenanthridine adduct led to slight success. Reaction with benzylamine at room temperature gave a low yield of (10) as well as much *N*-benzyldiphenylacetamide. The isoquinoline adduct under similar conditions gave only the latter compound, and both the isoquinoline and phenanthridine adducts react with benzophenone anil to give the azetidinone.

Attempts to isolate an adduct of acridine with diphenylketen failed.

Adducts of Benzimidazoles.—Kimbrough's work [5] included a description of the adducts of diphenylketen with *N*-methylbenzimidazole, *N*-methylimidazole, *N*-diphenylacetylbenzimidazole, and *N*-diphenylacetylimidazole. The i.r. data in this paper show that the last two adducts absorb significantly in the region 6—6·1 μm (1670—1640 cm^{-1}), whereas the first two do not. Hassner [9] noted the presence of a very weak absorption at 1600 cm^{-1} for the first two adducts.

Adducts of diphenylketen (2 : 1) were prepared with *N*-methylimidazole and benzimidazoles with the following *N*-substituents: methyl, benzyl, phenyl, acetyl, diphenylacetyl, and methylsulphonyl, and their i.r. and n.m.r. spectra were compared. The spectral differences clearly divide these adducts into two groups. The n.m.r. spectra of the first four adducts show a one-proton singlet at τ *ca.* 4·9 absent from the spectra of the last three. The i.r. spectra of the last three compounds show strong absorption at *ca.* 1650 cm^{-1} in addition to peaks due to the *N*-substituents, whereas the first four adducts show no corresponding band. All the adducts have a strong peak at *ca.* 1750 cm^{-1} and absorb

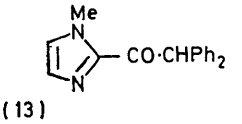
[14] K. Gulbins and K. Hamann, *Chem. Ber.*, 1961, **94**, 3287; J. Markert and E. Fahr, *Tetrahedron Letters*, 1970, 769.

[15] G. Brooks, M. A. Shah, and G. A. Taylor, *J.C.S. Perkin I*, 1973, 1297.

weakly at *ca.* 1600 cm^{-1}. The n.m.r. spectrum of the *N*-diphenylacetylbenzimidazole adduct is uninformative, being a complex band of unresolved signals at τ 2—4 with two weak, broadened signals at τ 4·7 and 5·5 which may be due to the methine proton of the *N*-substituent associated with slow rotation about the CO–N bond. The n.m.r. spectrum of the *N*-acetylbenzimidazole adduct is better resolved and shows two absorptions at high field due to the methyl group in the alternative conformations of the amide function, but with no other signals above τ 3·5. The *N*-mesyl adduct, however, shows a set of signals between τ 3·3 and 4·0 resembling the high-field signals of the benzothiazole adduct (5c). The spectroscopic evidence in this case clearly points to structure (5f) and somewhat less conclusively to the *N*-acetyl and *N*-diphenylacetyl adducts having the structures (5g and h), respectively. It is conceivable that in the latter cases the absence from the n.m.r. spectra of the high-field aromatic signals is caused by the conformational requirements of the *N*-substituent resulting in the oxazinone ring conformation being changed, reducing the screening of H-4 of the benzimidazole residue. The i.r. spectra of chloroform solutions of these adducts show no absorption at 2100 cm^{-1} so that dissociation into diphenylketen is insignificant in the cold. However in boiling benzene all three react with benzophenone anil to form the pentaphenylazetidinone. At room temperature, the *N*-acetyl adduct reacts with benzylamine to form both the amide (8e) and *N*-benzyldiphenylacetamide.

Examination of the *N*-methylbenzimidazole adduct elucidated the structure of the other group of adducts. The *N*-methylbenzimidazole adduct did not react with aniline at 80° or with hot acidified methanol. However the adduct was degraded to a compound, $C_{22}H_{18}N_2O$, by reaction with benzylamine, 2-aminoethanol, potassium hydroxide in aqueous tetrahydrofuran, sodium methoxide in methanol, or water in acidified acetic acid. The reaction with benzylamine also gave *N*-benzyldiphenylacetamide. Reaction with 2-aminoethanol had preparative advantages since the desired product was readily separated from the *N*-(2-hydroxyethyl)diphenylacetamide by chromatography. The compound $C_{22}H_{18}N_2O$ was identified as the ketone (11a) by its spectroscopic properties and Wolff–Kishner reduction to (12) under conditions recommended [16] for highly hindered ketones. An earlier attempt to reduce (11a) by the Wolff–Kishner method, involving use of a short reaction time with hydrazine, led to isolation of *N*-methylbenzimidazole, which is the principal product of reaction of (11a) with potassium hydroxide in boiling diethylene glycol. Similar treatment of the adducts of *N*-benzylbenzimidazole and *N*-methylimidazole with either benzylamine or 2-aminoethanol gave the corresponding ketones (11b) and (13). The assignment of a 2-substituted imidazole structure to the latter product rather than the isomeric 4- or 5-substituted constitution is based on the presence of n.m.r. signals at τ 2·93 and 3·15, assigned respectively to H-5 and H-4 of the imidazole system.[17]

These results point unambiguously to the structures (14a—c) for the *N*-methyl-, *N*-benzyl-, and *N*-phenylbenzimidazole adducts and (15) for the *N*-methylimidazole adduct. The one-proton singlets in the n.m.r. spectrum at τ 4·9 can be assigned to the methine proton of the diphenylacetyl group, and the absence of



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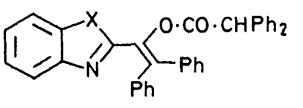
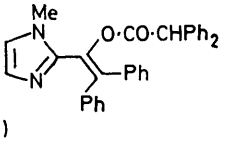
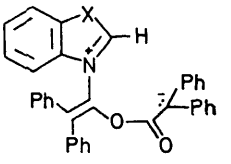


(14)

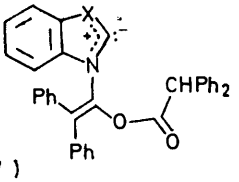
X
a; NMe
b; NCH_2Ph
c; NPh
d; S
e; O



(15)



(16) a; X = NMe



(17)

strong absorption in the i.r. at 1650 cm^{-1} is consistent with the absence of a diphenylketen acetal group. We believe that the two types of adduct [(5) and (14)] formed by benzimidazoles arise from a common initial reaction pathway diverging at a late stage. Experiments show that (11a) is not converted into (14a) by treatment with diphenylketen, nor is (11a) detectable in the product of reaction of an excess of *N*-methylbenzimidazole with a deficiency of diphenylketen. It is noticeable that electron-withdrawing substituents at position 1 of benzimidazole favour formation of adduct (5) whilst alkyl and phenyl groups favour (14). If the common pathway involves formation of the intermediate zwitterion (16),[8] then ring closure would lead to (5). However for (16a) the positive charge in the heterocyclic ring would be greatly delocalised and we suggest that in such a case the rate of cyclisation would be decreased and instead proton transfer occurs to form (17) followed by intramolecular migration of the *N*-substituent to position 2. Should (16a) ring-close to

[16] W. Nagata and H. Itazaki, *Chem. and Ind.*, 1964, 1194.

[17] G. S. Reddy, R. T. Hobgood, and J. H. Goldstein, *J. Amer. Chem. Soc.*, 1962, **84**, 336; A. Mannschreck, W. Seitz, and H. A. Staab, *Ber. Bunsengesellschaft Phys. Chem.*, 1963, **67**, 470; G. S. Reddy, L. Mandell, J. H. Goldstein, *J. Chem. Soc.*, 1963, 1414.

form (5a) then the charge delocalisation in (16a) would facilitate ring opening of (5a) to re-form (16a). Formation of adducts (5) and (14) would therefore be simply another example of kinetic *versus* thermodynamic control. Since charge stabilisation in (16) appeared to be the crucial factor attempts were made to achieve this for the addition reactions of benzoxazole and benzothiazole by use of acetonitrile as solvent. The reaction of diphenylketen with benzothiazole in acetonitrile at room temperature gave traces of a second compound whose i.r. spectrum resembled that expected for (14d), and (5c) was isomerised to (14d) by heating in acetonitrile at 160° for 24 h. Compound (14d) was degraded to (11c) by reaction with benzylamine or 2-aminoethanol. No such isomerisation was achieved for the benzoxazole adduct under similar conditions, but in view of Hassner's report [9] of the pyrolytic dissociation of (5b), it is possible that more vigorous conditions might lead to conversion of (5b) into (14e).

The reactions of *N*-methylimidazole, *N*-benzylbenzimidazole, and *N*-phenylbenzimidazole with diphenylketen led to formation of significant quantities of the β-lactone dimer of diphenylketen.[5,18] It seems probable that reduction of the rate of conversion of (16) into either (5) or (14) by electronic or steric effects may result in dimer formation competing successfully. Dimer formation was not observed during the other addition reactions.

The mass spectra of the adducts (5b—e), (14a—d), and (15) were examined by using a low energy electron beam to show the more important fragmentations, and the two groups showed characteristic differences consistent with the assigned structures.

For the adducts (5) the parent peaks were very weak, and small peaks at $(M - 194)^+$ (loss of diphenylketen) and $(M - 222)^+$ (loss of Ph_2C_2O and CO) were the only other significant peaks above *m/e* 194 which was the base peak in most cases. Relatively intense peaks at *m/e* 166 and 165 were common to these spectra, the *m/e* 167 peak being much weaker. A single metastable peak at *m/e* 142 (194 ⟶ 166) was common to all four spectra, and no others were observed.

The mass spectra of the other five compounds [(14) and (15)] had a common pattern, with $(M - 194)^+$ being the base peak in all cases, and metastable peaks corresponding to $M^+ \longrightarrow (M - 194)^+$ occurring in most cases. The *m/e* 167 peak (Ph_2CH^+) was always stronger than *m/e* 166 or 165 and in three cases metastable peaks corresponding to $(M - 194)^+ \longrightarrow 167^+$ were observed. There was no evidence from metastable peaks for $M^+ \longrightarrow$ *m/e* 167 despite the presence of a diphenylacetyl group in (14) and (15). Another weak peak at $(M - 211)^+$, shown to arise from $(M - 194)^+$ in two cases, presumably corresponds to loss of OH from the enol of the cation of (11) and appears in the mass spectra of the ketones (11a—c). Two other weak peaks at $(M - 222)^+$ and $(M - 223)^+$ arising from loss of 28 and 29 mass units (CO and COH) from $(M - 194)^+$ are also common to all spectra in this group.

EXPERIMENTAL

N.m.r. spectra were measured with a Varian HA100 or HR220 spectrometer. I.r. spectra were measured on a Unicam SP 100, a Perkin-Elmer PE 180, or a Perkin-Elmer 137 spectrometer. U.v. spectra were measured with a Cary 14 spectrometer. Mass spectra were measured on an A.E.I. MS 12 instrument (20 eV electron beam). Diphenylketen was prepared by pyrolysis of benzoylphenyldiazomethane.[15]

Preparation of the Diphenylketen Adducts.—Approximately stoicheiometric quantities of diphenylketen and the aza-arene were mixed in benzene (5—10 ml per g of keten) and the mixture was left at room temperature for several days. Evaporation of the solution left a gummy product, which usually crystallised on rubbing with petroleum, ethyl acetate, or ethanol.

1-*Diphenylmethylene*-4,4a-*dihydro*-4,4-*diphenyl*[1,3]*oxazino*[4,3-b]*benzoxazol*-3-*one* (5b), from benzoxazole and diphenylketen (59%), had m.p. 202—203° (from ethyl acetate and ethanol) (lit.,[5] 209—210°), $\nu_{max.}$ (KBr) 1770 and 1668 cm^{-1}, $\nu_{max.}$ ($CHCl_3$) 1776 and 1657 cm^{-1}, $\lambda_{max.}$ (EtOH) 266, 270sh, 272, 279, and 341 nm (log ε 4·19, 4·20, 4·21, 4·19, and 3·09), τ ($CDCl_3$; 220 MHz) 2·5—2·9 (16H, m), 2·9—3·2 (6H, m), 3·25 (1H, s), 3·39 (1H, t, *J* 7·5 Hz), and 3·71 (1H, d, *J* 7·5 Hz), *m/e* 507 (2·4%), 313 (0·7), 285 (0·7), 195 (19), 194 (100), 167 (4), 166 (27), 165 (19), 120 (1), 119 (9), and 91 (4), *m** 142 (194 ⟶ 166).

A mixture of diphenylketen (from 2 g of the diazoketone) and benzoxazole (0·6 g) in acetonitrile (10 ml), set aside at room temperature for several days, deposited crude (5b) (1·2 g, 52%). No other adduct was detected in the mixture by t.l.c.

This adduct was recovered unchanged after (i) treatment with benzoyl chloride and pyridine, (ii) boiling with aniline in benzene, (iii) boiling with benzophenone anil in benzene.

1-*Diphenylmethylene*-4,4a-*dihydro*-4,4-*diphenyl*[1,3]*oxazino*[4,3-b]*benzothiazol*-3-*one* (5c), from benzothiazole and diphenylketen, had m.p. 163—164° (decomp.) [from benzene and light petroleum (b.p. 60—80°)] (lit.,[5] 163—164°) (Found: C, 79·9; H, 5·2; N, 2·4. $C_{35}H_{25}NO_2S$ requires C, 80·3; H, 4·8; N, 2·7%), $\nu_{max.}$ (KBr) 1762 and 1631 cm^{-1}, $\nu_{max.}$ ($CHCl_3$) 1770 and 1636 cm^{-1}, $\lambda_{max.}$ (EtOH) 264sh and 341 nm (log ε 4·07 and 3·75), τ ($CDCl_3$; 220 MHz) 2·3—3·1 (20H, m), 3·24 (1H, s), 3·15—3·35 (1H, m), 3·4—3·65 (2H, m), and 4·05 (1H, dd, *J* 7 and 2 Hz), *m/e* 523 (0%), 329 (0·4), 301 (0·8), 300 (0·8), 224 (1), 195 (13), 194 (67), 167 (15), 166 (71), 165 (100), 164 (8), 152 (1·6), 151 (3), 139 (2·5), and 135 (12), *m** 142 (194 ⟶ 166).

The adduct (5c) (0·8 g crude; 54%) crystallised from a mixture of diphenylketen (from 1·25 g of diazoketone) and benzothiazole (0·3 ml) in acetonitrile (10 ml) left at room temperature for several days. Evaporation of the mother liquor left a gum, which on shaking with ethanol (3 ml) deposited a small amount of solid identified as (14d) by i.r. and t.l.c. comparison.

The adduct (5c) was recovered unchanged after treatment with (i) benzoyl chloride in pyridine, (ii) aniline in benzene at room temperature for several weeks, (iii) neat methyl iodide at room temperature for 6 days. Boiling the adduct (5c) with aniline in benzene gave diphenylacetanilide in nearly quantitative yield as the only isolated product.

On pyrolysis of the adduct, a small amount of distillate, b.p. 240—250°, was obtained, identified as benzothiazole by a mixed m.p. determination on the picrate.

[18] R. Anet, *Chem. and Ind.*, 1961, 1313.

1-*Di*-p-*tolylmethylene*-4,4a-*dihydro*-4,4-*di*-p-*tolyl*[1,3]*oxazino*[4,3-b]*benzothiazol*-3-*one*, from benzothiazole and di-*p*-tolylketen [19] (28%; based on *pp'*-dimethylbenzil hydrazone), m.p. 188° (decomp.) (from benzene) (Found: C, 80·4; H, 5·9; N, 2·3. $C_{39}H_{33}NO_2S$ requires C, 80·7; H, 5·7; N, 2·4%), $\nu_{max.}$ (KBr) 1759 and 1626 cm^{-1}, $\lambda_{max.}$ (EtOH) 274 nm (log ε 4·24), τ [$CDCl_3$ (supersaturated solution); 220 MHz] 2·6—3·2 (16H, m), 3·2—3·35 (1H, m), 3·23 (1H, s), 3·4—3·55 (2H, m), 3·96 (1H, dd, *J* 7 and 2 Hz), 7·67 (3H, s), 7·71 (3H, s), 7·81 (3H, s), and 7·83 (3H, s).

1-*Diphenylmethylene*-4,4a-*dihydro*-8-*methyl*-4,4-*diphenyl*-[1,3]*oxazino*[4,3-b]*benzoxazol*-3-*one* (5d), from 5-methylbenzoxazole and diphenylketen, had m.p. 187—188° (decomp.) (from ethyl acetate and ethanol) (Found: C, 82·7; H, 5·4; N, 2·3. $C_{36}H_{27}NO_3$ requires C, 82·9; H, 5·2; N, 2·7%), $\nu_{max.}$ (KBr) 1777 and 1647 cm^{-1}, $\lambda_{max.}$ (EtOH) 281, 286, and 345 nm (log ε 4·08, 4·08, and 3·42), τ ($CDCl_3$) 2·5—2·9 (16H, m), 2·9—3·2 (4H, m), 3·31 (1H, d, *J* 7·5 Hz), 3·34 (1H, s), 3·89 (1H, s), and 7·95 (3H, s), *m/e* 521 (2·4%), 327 (1·4), 299 (1), 195 (19), 194 (100), 167 (10), 166 (52), 165 (65), 164 (2·4), 134 (2), 133 (20), 132 (9), 106 (3), 105 (2), 104 (2), and 78 (6), *m** 142 (194 ⟶ 166).

1-*Diphenylmethylene*-4,4a-*dihydro*-7-*methyl*-4,4-*diphenyl*-[1,3]*oxazino*[4,3-b]*benzoxazol*-3-*one* (5e), from 6-methylbenzoxazole and diphenylketen, had m.p. 196° (decomp.) (from ethyl acetate and ethanol) (Found: C, 82·7; H, 5·5; N, 2·4. $C_{36}H_{27}NO_3$ requires C, 82·9; H, 5·2; N, 2·7%), $\nu_{max.}$ (KBr) 1777 and 1658 cm^{-1}, $\lambda_{max.}$ (EtOH) 268, 274, 277, 283, and 343 nm (log ε 4·20, 4·20, 4·18, 4·17, and 2·98), τ ($CDCl_3$) 2·5—2·9 (16H, m), 2·9—3·2 (4H, m), 3·31 (1H, s), 3·37br (1H), 3·56br (1H, d, *J* 8 Hz), 3·81 (1H, d, *J* 8 Hz), and 7·81 (3H, s), *m/e* 521 (2%), 327 (0·5), 299 (1·4), 195 (19), 194 (100), 167 (9), 166 (50), 165 (64), 164 (5), 152 (2), 151 (5), 134 (2), 133 (21), 132 (10), 106 (3), 105 (3), and 104 (4), *m** 142 (194 ⟶ 166).

1-*Diphenylmethylene*-4,4a-*dihydro*-4,4-*diphenyl*[1,3]*oxazino*[3,4-a]*quinolin*-3-*one*, precipitated from a mixture of stoicheiometric proportions of diphenylketen and quinoline in ether or benzene by addition of light petroleum (b.p. 60—80°) and cooling to 0°, had m.p. (crude; several preparations) 132—135, 128—135, or 117—120° (decomp.) (lit.,[2] 121—122°), $\nu_{max.}$ (paste) 1758, 1637, and 1145 cm^{-1}, τ ($CDCl_3$) (>4·5) 4·61 (d, *J* 7 Hz), 5·00 (s), and 5·42 (d, *J* 7 Hz) (relative intensity 1 : 1 : 1).

4-*Diphenylmethylene*-1,11b-*dihydro*-1,1-*diphenyl*[1,3]*oxazino*[4,3-a]*isoquinolin*-2-*one* (4a), precipitated from a mixture of diphenylketen (from 3·6 g of diazo-ketone) and isoquinoline (1 ml) in benzene (20 ml) by addition of light petroleum (25 ml; b.p. 40—60°) and cooling to 0° (yield 2·5 g crude, 59%), had m.p. 143—144° (decomp.) (lit.,[8] 146—148°), $\nu_{max.}$ (paste) 1765, 1633, and 1135 cm^{-1}, $\nu_{max.}$ ($CHCl_3$) 2100, 1816, 1732, and 1628 cm^{-1}, τ ($CDCl_3$) (>4·5) 4·64 (d, *J* 8 Hz), 4·98 (s), and 5·44 (d, *J* 8 Hz) (relative intensity 1 : 1 : 1).

Treatment of the adduct with benzylamine in benzene at room temperature for several days gave *N*-benzyldiphenylacetamide as the sole isolated product.

4-*Diphenylmethylene*-1,11b-*dihydro*-6-*methyl*-1,1-*diphenyl*-[1,3]*oxazino*[4,3-a]*isoquinolin*-2-*one* (4b), precipitated from a mixture of diphenylketen (from 1·6 g of diazo-ketone), 3-methylisoquinoline (0·6 g), and benzene (10 ml) by addition of light petroleum (b.p. 60—80°) (yield 1·2 g crude, 62%), had m.p. 130—133° (decomp.) (Found: C, 86·3; H, 5·8; N, 2·5. $C_{38}H_{29}NO_2$ requires C, 85·8; H, 5·5; N, 2·6%), $\nu_{max.}$ (paste) 1760, 1642, 1633, and 1140 cm^{-1}, $\nu_{max.}$ ($CHCl_3$) 2100, 1816, 1731, and 1631 cm^{-1}, τ ($CDCl_3$) (>4·5) 4·99 (s), 5·51br (s), 7·31 (s), and 8·61 (s) (relative intensity 1 : 1 : 9 : 3).

1-*Diphenylmethylene*-4,4a-*dihydro*-4,4-*diphenyl*[1,3]*oxazino*[3,4-f]*phenanthridin*-3-*one*, precipitated from a mixture of diphenylketen (from 2 g of diazo-ketone) and phenanthridine (0·9 g) in benzene (10 ml), had m.p. 160—163° (decomp.) (Found: C, 86·5; H, 5·3; N, 2·4. $C_{41}H_{29}NO_2$ requires C, 86·7; H, 5·1; N, 2·5%), $\nu_{max.}$ (paste) 1758, 1632, 1140, and 1125 cm^{-1}, $\nu_{max.}$ ($CHCl_3$) 2100, 1754, and 1648 cm^{-1}, τ ($CDCl_3$) 2·9—3·9 (m) and 3·80 (*ca.* 0·75H, s).

The phenanthridine adduct reacted with aniline in benzene at 40° to give diphenylacetanilide as the only isolated product.

1-(1-*Methylbenzimidazol*-2-*yl*)-2,2-*diphenylvinyl diphenylacetate* (14a), from 1-methylbenzimidazole and diphenylketen (55%), had m.p. 211—212° [from benzene and light petroleum (b.p. 60—80°)] (lit.,[5] 206—208°) (Found: C, 82·6; H, 5·5; N, 5·1. $C_{36}H_{28}N_2O_6$ requires C, 83·1; H, 5·4; N, 5·4%), $\nu_{max.}$ (KBr) 1751 and 1115 cm^{-1}, $\lambda_{max.}$ (EtOH) 261 and 305 nm (log ε 4·08 and 4·25), τ ($CDCl_3$) 2·1—2·3 (1H, m), 2·6—3·2 (23H, m), 4·93 (1H, s), and 6·80 (3H, s), *m/e* 520 (5%), 328 (4), 327 (25), 326 (100), 325 (25), 309 (11), 298 (2·5), 297 (6), 207 (0·7), 194 (6), 168 (4·5), 167 (27), 166 (4), 165 (5), and 152 (0·5), *m** 293 (326 ⟶ 309), 272 (326 ⟶ 298), 204 (520 ⟶ 326), 163 (167 ⟶ 165), 142 (194 ⟶ 166), 138 (167 ⟶ 152), and 86 (326 ⟶ 167).

2,2-*Diphenyl*-1-(1-*phenylbenzimidazol*-2-*yl*)*vinyl diphenylacetate* (14c) was obtained from a mixture of 1-phenylbenzimidazole (3 g) and diphenylketen (from 6·9 g of diazo-ketone) in benzene (50 ml), set aside at room temperature for 7 days. Evaporation of the solution left an oil which crystallised. Recrystallisation from ethyl acetate and petroleum gave diphenylketen dimer (2·3 g). Evaporation of the mother liquor and cooling gave the adduct (14c) (1·7 g crude, 18%), m.p. 209—210° (from benzene) (Found: C, 84·6; H, 5·7; N, 4·7. $C_{41}H_{30}N_2O_2$ requires C, 84·5; H, 5·2; N, 4·8%), $\nu_{max.}$ (KBr) 1743 and 1115 cm^{-1}, $\lambda_{max.}$ (EtOH) 235sh and 316 nm (log ε 3·70 and 4·24), τ ($CDCl_3$) 2·1—2·3 (1H, m), 2·4—3·4 (26H, m), 3·5—3·7 (2H, m), and 4·85 (1H, s), *m/e* 582 (3%), 390 (5), 389 (34), 388 (100), 387 (29), 371 (1·8), 360 (3·5), 359 (6), 276 (2), 275 (1), 243 (1), 222 (2), 221 (13), 195 (2), 194 (11), 193 (1), 168 (3), 167 (16), 166 (10), and 165 (13), *m** 386 (388 ⟶ 387), 332 (388 ⟶ 359), and 259 (582 ⟶ 388).

1-(1-*Benzylbenzimidazol*-2-*yl*)-2,2-*diphenylvinyl diphenylacetate* (14b), from 1-benzylbenzimidazole and diphenylketen (70%), had m.p. 126—132° (decomp.) (from ethyl acetate and ethanol) (Found: C, 81·7; H, 6·2; N, 4·5. $C_{42}H_{32}N_2O_2,C_2H_5OH$ requires C, 82·3; H, 5·9; N, 4·4%), $\nu_{max.}$ (KBr) 1750 and 1115 cm^{-1}, $\lambda_{max.}$ (EtOH) 259 and 303 nm (log ε 4·07 and 4·20), τ ($CDCl_3$) 2·22 (1H, d, *J* 8 Hz), 2·7—3·2 (25H, m), 3·2—3·5 (3H, m), 4·95 (1H, s), 4·98 (2H, s), and signals due to ethanol of crystallisation, *m/e* 596 (5%), 404 (6), 403 (36), 402 (100), 401 (14), 385 (3), 374 (0·7), 373 (1·5), 312 (2), 311 (12), 283 (2), 236 (2), 235 (10), 195 (3), 194 (21), 168 (4), 167 (28), 166 (16), 165 (22), and 91 (6), *m** 400 (402 ⟶ 401), 369 (402 ⟶ 385), 271 (596 ⟶ 402), 241 (402 ⟶ 311), 164 (166 ⟶ 165), 142 (194 ⟶ 166), and 69 (402 ⟶ 167).

The crude product of this reaction is contaminated by the β-lactone dimer of diphenylketen.

1-(1-*Methylimidazol*-2-*yl*)-2,2-*diphenylvinyl diphenylacetate*

[19] H. Gilman and C. E. Adams, *Rec. Trav. chim.*, 1929, **48**, 465.

(15) was obtained by chromatography of the crude reaction product of diphenylketen (from 25 g of diazo-ketone) and 1-methylimidazole (5 g) in benzene (200 ml) on silica gel. Dichloromethane eluted diphenylketen dimer (8·4 g), and subsequently ether eluted the adduct (15) (8·7 g, 32%), m.p. 158—159° [from ethyl acetate and light petroleum (b.p. 60—80°)] (lit.,[5] 157—158°), $\nu_{max.}$ (KBr) 1747, 1652vw, and 1120 cm^{-1}, $\lambda_{max.}$ (EtOH) 230 and 289 nm (log ε 4·38 and 4·07), τ ($CDCl_3$) 2·4—3·3 (21H, m), 3·43br (1H, s), 4·98 (1H, s), and 6·96 (3H, s), *m/e* 470 (3%), 277 (24), 276 (100), 275 (38), 259 (1), 248 (1·5), 247 (5), 224 (2), 195 (2), 194 (14), 168 (4), 167 (18), 166 (11), 165 (12), 152 (2), 151 (7), and 109 (4), *m** 274 (276 ⟶ 275).

1-(*Benzothiazol-2-yl*)-2,2-*diphenylvinyl diphenylacetate* (14d), was obtained by heating a mixture of the benzothiazole–diphenylketen adduct (5c) (11 g) and acetonitrile (35 ml) in a sealed tube at 160—165° for 24 h. On cooling the solution deposited the adduct (14d) (5·75 g, 52%), m.p. 171—172° [from benzene and light petroleum (b.p. 60—80°)] (Found: C, 79·8; H, 5·2; N, 2·4. $C_{35}H_{25}NO_2S$ requires C, 80·3; H, 4·8; N, 2·7%), $\nu_{max.}$ (KBr) 1760 and 1125 cm^{-1}, $\lambda_{max.}$ (EtOH) 318 nm (log ε 4·27), τ ($CDCl_3$; 220 MHz) 2·1—3·2 (24H, m) and 4·78 (1H, s), *m/e* 523 (0·5%), 332 (2), 331 (9), 330 (25), 329 (100), 328 (16), 312 (1), 301 (2), 300 (2), 194 (4), 169 (1), 168 (11), 167 (60), 166 (2), and 165 (2), *m** 327 (329 ⟶ 328), 207 (523 ⟶ 329), 142 (194 ⟶ 166), and 85 (329 ⟶ 167).

1-*Diphenylmethylene*-4a,5-*dihydro*-5-*methylsulphonyl*-4,4-*diphenyl*[1,3]*oxazino*[3,4-a]*benzimidazol*-3(4H)-*one* (5f), obtained from 1-methylsulphonylbenzimidazole and diphenylketen as a solvate with ethyl acetate (70%), had m.p. 130—135° (decomp.) [from ethyl acetate and light petroleum (b.p. 60—80°)] (Found: C, 71·0; H, 5·2; N, 4·1. $C_{36}H_{28}NO_4S,C_4H_8O_2$ requires C, 71·4; H, 5·3; N, 4·2%), $\nu_{max.}$ (KBr) 1758, 1657, 1165, and 1130 cm^{-1}, $\nu_{max.}$ ($CHCl_3$) 1764 and 1640 cm^{-1}, τ ($CDCl_3$) 2·4—2·63 (2H, m), 2·63—3·1 (19H, m), 3·12 (1H, s), 3·3—3·6 (2H, m), 3·75—3·9 (1H, m), and 7·45 (3H, s), with signals due to ethyl acetate.

1-*Diphenylmethylene*-4a,5-*dihydro*-4,4-*diphenyl*-5-*diphenylacetyl*[1,3]*oxazino*[3,4-a]*benzimidazol*-3(4H)-*one* (5h),[5] obtained from the reaction of benzimidazole with an excess of diphenylketen in boiling benzene by precipitation of the product with light petroleum (b.p. 40—60°), showed $\nu_{max.}$ (paste) 1768, 1686, and 1662 cm^{-1}, $\nu_{max.}$ ($CHCl_3$) 1764 and 1670 cm^{-1}.

5-*Acetyl*-1-*diphenylmethylene*-4a,5-*dihydro*-4,4-*diphenyl*-[1,3]*oxazino*[3,4-a]*benzimidazol*-3(4H)-*one* (5g), from 1-acetylbenzimidazole and diphenylketen (73% crude), had m.p. 135—138° (decomp.) (Found: C, 81·4; H, 5·6; N, 5·0. $C_{37}H_{28}N_2O_3$ requires C, 81·0; H, 5·1; N, 5·1%), $\nu_{max.}$ (paste) 1756, 1678, 1644, and 1135 cm^{-1}, $\nu_{max.}$ ($CHCl_3$) 1763 and 1668 cm^{-1}, τ ($CDCl_3$) 2·2—3·5 (25H, m), 8·25 and 8·73 (singlets, total 3H).

Reaction of the Phenanthridine–Diphenylketen Adduct with Benzophenone Anil.—A mixture of the phenanthridine–diphenylketen adduct (0·18 g), benzophenone anil (0·15 g), and benzene (3 ml) was heated under reflux for 2 h. T.l.c. (SiO_2; CH_2Cl_2) showed no trace of the adduct, and spots corresponding to phenanthridine and 1,3,3,4,4-pentaphenylazetidin-2-one. The mixture slowly deposited the azetidinone (0·15 g, 52%), identified by mixed m.p. and i.r. comparison with an authentic sample.

A similar reaction was observed under identical conditions for the diphenylketen adducts of isoquinoline (4a), benzothiazole (5c), 1-methylsulphonylbenzimidazole (5f), 1-acetylbenzimidazole (5 g), and 1-diphenylacetylbenzimidazole (5h).

Reaction of the Phenanthridine–Diphenylketen Adduct with Benzylamine.—A suspension of the finely powdered phenanthridine–diphenylketen adduct (0·3 g) in benzene (3 ml) and benzylamine (1 ml) was left at room temperature, with occasional shaking, for several weeks. The mixture was diluted with chloroform, washed with dilute hydrochloric acid and water, and dried ($MgSO_4$). Evaporation left an oil (0·5 g) which solidified on trituration with methanol. Boiling light petroleum (b.p. 80—100°) extracted *N*-benzyldiphenylacetamide (*ca.* 0·3 g), identified by mixed m.p. and i.r. comparison with an authentic sample. The petroleum-insoluble residue, recrystallised from benzene and light petroleum (b.p. 60—80°), gave N-*benzyl*-2-(5-*diphenylacetyl*-5,6-*dihydrophenanthridin*-6-*yl*)*diphenylacetamide* (10) (0·093 g, 26%), m.p. 211—212° (Found: C, 85·7; H, 5·8; N, 3·8. $C_{48}H_{38}N_2O_2$ requires C, 85·4; H, 5·6; N, 4·1%), $\nu_{max.}$ (paste) 3386, 1664, and 1641 cm^{-1}, $\lambda_{max.}$ (EtOH) 251 and 278 nm (log ε 4·16 and 4·01), τ ($CDCl_3$) 2·04 (1H, s), 2·2—3·6 (33H, m), 3·78br (1H), 4·68 (1H, s), and 5·7br (2H).

2-(1-*Acetyl*-3-*diphenylacetyl*-1,2-*dihydrobenzimidazol*-2-*yl*)-N-*benzyldiphenylacetamide* (8e) and *N*-benzyldiphenylacetamide were the products of reaction of the 1-acetylbenzimidazole–diphenylketen adduct (0·5 g) with benzylamine under conditions identical with those described above. Boiling light petroleum (b.p. 80—100°) extracted the *N*-benzyldiphenylacetamide from the crude mixture of products leaving a residue of (8e) (0·16 g, 26%), m.p. 205—206° (from ethyl acetate and ethanol) (Found: C, 80·3; H, 5·8; N, 6·5. $C_{44}H_{37}N_3O_3$ requires C, 80·6; H, 5·7; N, 6·4%), $\nu_{max.}$ (KBr) 3416, 1689, and 1670 cm^{-1}.

N-*Benzyl*-2-(3-*diphenylacetyl*-2,3-*dihydrobenzoxazol*-2-*yl*)-*diphenylacetamide* (8b) was obtained by boiling a mixture of the benzoxazole–diphenylketen adduct (5b) (2 g), benzylamine (8 ml), and benzene (20 ml) under reflux for 3 h. Normal work-up gave a gum (2·9 g) which solidified on shaking with a little methanol to form the amide (8b) (1·8 g, 74%), m.p. 132° (from methanol) (Found: C, 81·7; H, 5·7; N, 4·4. $C_{42}H_{34}N_2O_3$ requires C, 82·1; H, 5·5; N, 4·6%), $\nu_{max.}$ (paste) 3290, 1678, and 1656 cm^{-1}, $\lambda_{max.}$ (EtOH) 253 and 290 nm (log ε 3·85 and 3·71), τ ($CDCl_3$) 2·12 (1H, s), 2·4—3·2 (26H, m), 3·2—3·7 (4H, m), 4·08br (1H, s), and 5·64 (2H, d, *J* 6 Hz).

N-*Benzyl*-2-(3-*diphenylacetyl*-2,3-*dihydrobenzothiazol*-2-*yl*)-*diphenylacetamide* (8a) was obtained (83%) from the reaction of the benzothiazole–diphenylketen adduct (5c) with benzylamine under conditions identical with those described above; m.p. 145—146° [from benzene and light petroleum (b.p. 60—80°)] (Found: C, 80·3; H, 5·8; N, 3·9. $C_{42}H_{34}N_2O_2S$ requires C, 80·0; H, 5·4; N, 4·4%), $\nu_{max.}$ (paste) 3412 and 1674 cm^{-1}, $\lambda_{max.}$ (EtOH) 261 and 298sh nm (log ε 3·80 and 3·22), τ ($CDCl_3$) 2·34 (1H, s), 2·5—3·6 (30H, m), 4·16br (1H), and 5·66 (2H, d, *J* 6 Hz).

An identical product was obtained from prolonged treatment of (5c) with benzylamine in benzene at room temperature.

Reaction of the Benzothiazole–Diphenylketen Adduct with Ammonia.—Ammonia gas was passed into a solution of the adduct (5c) (3 g) in boiling benzene for 7 h. Cooling the mixture precipitated 2-(3-*diphenylacetyl*-2,3-*dihydrobenzothiazol*-3-*yl*)*diphenylacetamide* (8d) (0·35 g, 11%), m.p. 203—204° (from benzene) (Found: C, 77·8; H, 5·6; N, 5·2. $C_{35}H_{28}N_2O_2S$ requires C, 77·8; H, 5·2; N, 5·2%), $\nu_{max.}$ (paste) 3445, 3425, 1678, and 1644 cm^{-1}, $\lambda_{max.}$ (EtOH)

261 and 298sh nm (log ε 3·76 and 3·28), τ ($CDCl_3$) 2·41 (1H, s), 2·45—3·2 (20H, m), 3·46 (5H, s), and 4·27br (2H). Extraction of the benzene solution with dilute hydrochloric acid gave benzothiazole, identified as its picrate by mixed m.p.

2-Diphenylacetyl-1-methylbenzimidazole (11a).—A mixture of the adduct (14a) (7 g), 2-aminoethanol (3 ml), and benzene (40 ml) was boiled under reflux for 5 h, and the benzene was evaporated off under reduced pressure. Chromatography of the residue on silica gel (elution with dichloromethane) gave the *ketone* (11a) (3·3 g, 75%), m.p. 129—130° (from methanol) (Found: C, 80·9; H, 5·5; N, 8·7. $C_{22}H_{18}N_2O$ requires C, 81·0; H, 5·5; N, 8·6%), $\nu_{max.}$ (KBr) 1684 cm^{-1}, $\lambda_{max.}$ (EtOH) 239, 243, and 311 nm (log ε 4·02, 4·00, and 4·26), τ ($CDCl_3$) 2·05—2·3 (1H, m), 2·4—3·0 (13H, m), 3·06 (1H, s), and 6·00 (3H, s), *m/e* 326 (100%), 325 (22), 309 (2), 298 (6·5), 297 (13), 209 (3), 207 (6·5), 194 (3), 168 (9), 167 (56), 166 (7), 165 (5), 160 (3), 159 (33), and 152 (3), *m** 324 (326 → 325), 293 (326 → 309), 272 (326 → 298), 163 (167 → 165), and 138 (167 → 152).

Treatment of the adduct with sodium methoxide in boiling methanol, benzylamine in boiling benzene, potassium hydroxide in aqueous tetrahydrofuran, or concentrated hydrochloric acid in glacial acetic acid at 100°, all resulted in formation of (11a). Chromatography of the reaction mixture with benzylamine (SiO_2; CH_2Cl_2 followed by Et_2O) gave (11a) and *N*-benzyldiphenylacetamide, identified by i.r. comparison with an authentic specimen.

Under identical conditions, reaction of the adducts (14b and d) and (15) gave the following products.

1-Benzyl-2-diphenylacetylbenzimidazole (11b), from (14b) and benzylamine or 2-aminoethanol (78%), had m.p. 120° (from ethanol) (Found: C, 83·3; H, 5·6; N, 7·0. $C_{28}H_{22}N_2O$ requires C, 83·6; H, 5·5; N, 7·0%), $\nu_{max.}$ (KBr) 1688 cm^{-1}, $\lambda_{max.}$ (EtOH) 239, 242sh, and 309 nm (log ε 4·00, 3·97, and 4·25), τ ($CDCl_3$) 2·04—2·20 (1H, m), 2·4—3·3 (19H, m), and 4·23 (2H, s), *m/e* 402 (100%), 401 (9), 385 (6), 374 (3), 312 (6), 311 (24), 284 (3), 283 (8), 236 (6), 235 (33), 207 (5), 206 (4), 194 (3), 193 (2), 168 (4), 167 (28), 105 (5), and 91 (6), *m** 400 (402 → 401), 369 (402 → 385), and 241 (402 → 311).

2-Diphenylacetylbenzothiazole (11c), from (14d) and 2-aminoethanol in boiling benzene (53%), had m.p. 144° (from ethyl acetate and methanol) (Found: C, 76·8; H, 4·8; N, 4·3. $C_{21}H_{15}NOS$ requires C, 76·6; H, 4·6; N, 4·3%), $\nu_{max.}$ (KBr) 1700 and 1684 cm^{-1}, $\lambda_{max.}$ (EtOH) 248, 252, and 303 nm (log ε 3·79, 3·77, and 4·13), τ ($CDCl_3$) 1·75—2·0 (1H, m), 2·05—2·3 (1H, m), 2·4—3 (12H, m), and 3·25 (1H, s), *m/e* 329 (100%), 328 (13), 312 (3), 301 (6), 300 (5), 194 (4), 168 (25), 167 (100), 166 (10), 165 (5), 162 (6), 152 (6), and 134 (2), *m** 327 (329 → 328), 296 (329 → 312), 163 (167 → 165), and 138 (167 → 152).

2-Diphenylacetyl-1-methylimidazole (13) was obtained from (15) and 2-aminoethanol in boiling ethanol. Evaporation of the reaction mixture and chromatography of the residue (SiO_2; Et_2O) gave the ketone (13) (72%), m.p. 85—86° [from benzene and light petroleum (b.p. 60—80°)] (Found: C, 78·2; H, 6·1; N, 10·1. $C_{18}H_{16}N_2O$ requires C, 78·2; H, 5·8; N, 10·1%), $\nu_{max.}$ (KBr) 1670 and 1664 cm^{-1}, $\lambda_{max.}$ (EtOH) 286 nm (log ε 4·22), τ ($CDCl_3$) 2·45—2·90 (10H, m), 2·93 (1H, d, *J* 0·9 Hz), 3·15br (1H, s), 3·29 (1H, s), and 6·15 (3H, s), *m/e* 276 (100%), 275 (57), 269 (2), 248 (6), 247 (17), 238 (2), 195 (3), 194 (7), 169 (3), 168 (26), 167 (100), 166 (10), 165 (7), 159 (2), 157 (4), 152 (6), and 109 (26).

Further elution of the column with 10% ethanol in ether gave *N*-2-hydroxyethyldiphenylacetamide, m.p. 124—125° (from benzene) (lit.,[20] 122—123°), $\nu_{max.}$ (KBr) 1649 cm^{-1}.

Reduction of the Ketone (11a).—(*a*) A mixture of (11a) (1 g), sodium borohydride (1 g), and isopropyl alcohol (30 ml) was boiled under reflux for 1 h. Aqueous acetic acid was added dropwise to decompose residual sodium borohydride, and the mixture was evaporated to dryness under reduced pressure. Extraction of the residue with chloroform and water and work-up of the chloroform solution gave *2-(1-hydroxy-2,2-diphenylethyl)-2-methylbenzimidazole* (0·6 g, 59%), m.p. 224—225° (from ethanol) (Found: C, 80·5; H, 6·3; N, 8·4. $C_{22}H_{20}N_2O$ requires C, 80·5; H, 6·1; N, 8·5%), $\nu_{max.}$ (paste) *ca.* 3000 cm^{-1}, $\lambda_{max.}$ (EtOH) 257, 270, 277, and 284 nm (log ε 3·88, 3·83, 3·91, and 3·90), τ ($CDCl_3$) 2·4—3·2 (14H, m), 4·40 (1H, d, *J* 10 Hz), 5·27 (1H, d, *J* 10 Hz), *ca.* 5·3br (1H, removed by treatment with D_2O), and 6·80 (3H, s).

(*b*) [16] A mixture of the ketone (11a) (0·2 g), diethylene glycol (5 ml), hydrazine hydrate (100%; 2·2 ml), and hydrazine dihydrochloride (0·5 g) was heated at 140° (xylene vapour jacket) for 18 h. The mixture was cooled and potassium hydroxide (2·5 g) in diethylene glycol (8 ml) was added. The mixture was distilled under nitrogen until the temperature reached 240° and was then maintained at this temperature for 1 h. After addition of water, the mixture was extracted several times with benzene, and the benzene extracts were washed with water, dried ($MgSO_4$), and evaporated. Preparative t.l.c. of the residual oil (0·18 g) separated 2-(2,2-diphenylethyl)-1-methylbenzimidazole (12) (0·06 g, 31%), identified by i.r. comparison and mixed m.p. with an authentic specimen.

Reaction of the Ketone (11a) *with Potassium Hydroxide*.—A mixture of the ketone (11a) (0·1 g), diethylene glycol (2·5 ml), and potassium hydroxide (2 pellets) was boiled under reflux for 1·5 h. The mixture was cooled, diluted with water, and extracted with benzene. Evaporation of the extract left an oil, which was mixed with saturated ethanolic picric acid. The yellow precipitate was identified as 1-methylbenzimidazole picrate by mixed m.p. with an authentic sample.

2-(2,2-Diphenylethyl)benzimidazole. A mixture of *o*-phenylenediamine (2 g), 3,3-diphenylpropionic acid (4·4 g), and xylene (15 ml) was boiled overnight. Evaporation left a residue which was dissolved in chloroform and extracted with dilute sodium hydroxide solution. The chloroform solution was washed with water, dried ($MgSO_4$), and evaporated giving the *benzimidazole* as needles (3·6 g, 65%), m.p. 196—197° (from aqueous methanol) (Found: C, 84·5; H, 6·3; N, 9·5. $C_{21}H_{18}N_2$ requires C, 84·6; H, 6·0; N, 9·4%), τ ($CDCl_3$) 2·5—3·2 (14H, m), 5·38 (1H, t, *J* 8 Hz), 6·36 (2H, d, *J* 8 Hz), and 6·2—6·6br (1H, removed by treatment with D_2O).

2-(2,2-Diphenylethyl)-1-methylbenzimidazole (12).—Methylation of 2-(2,2-diphenylethyl)benzimidazole with sodium hydride (50% oil dispersion) and methyl iodide in 1,2-dimethoxyethane at room temperature gave (12) as *needles* (67%), m.p. 127° [from benzene and light petroleum (b.p. 60—80°)] (Found: C, 84·5; H, 6·7; N, 9·0. $C_{22}H_{20}N_2$ requires C, 84·6; H, 6·4; N, 9·0%), τ ($CDCl_3$) 2·2—2·4 (1H, m), 2·6—3·2 (13H, m), 5·23 (1H, t, *J* 8 Hz), 6·47 (2H,

[20] V. G. Gokhale, N. L. Phalnikar, and B. V. Bhide, *J. Univ. Bombay*, 1948, **16**, No. 5, 32 (*Chem. Abs.*, 1949, **43**, 1144e).

d, J 8 Hz), and 6·85 (3H, s). The picrate precipitated from ethanol; m.p. 211°.

1-*Phenylbenzimidazole*.—A solution of *N*-phenyl-*o*-phenylenediamine (10 g) in formic acid (40 ml) was boiled for 5 h. Distillation gave 1-phenylbenzimidazole (10·4 g, 99%) as an oil, b.p. 220—224° at 22 mmHg, 211—213° at 17 mmHg, which failed to crystallise (lit.,[21,22] m.p. 97—98°). The picrate [21] was obtained as yellow needles, m.p. 157—158° (from aqueous ethanol) (Found: C, 54·3; H, 3·5; N, 16·6. Calc. for $C_{13}H_{10}N_2,C_6H_3N_3O_7$: C, 53·9; H, 3·1; N, 16·6%), and likewise the *picrolonate* as a hydrate, m.p. 185—188° (decomp.) (from aqueous ethanol) (Found: C, 57·7; H, 4·2; N, 17·7. $C_{13}H_{10}N_2,C_{10}H_8N_4O_5,H_2O$ requires C, 57·9; H, 4·2; N, 17·6%).

1-*Methylsulphonylbenzimidazole*.— Methanesulphonyl chloride (15 ml) was added dropwise to an ice-cooled mixture of benzimidazole (20 g), pyridine (20 ml), and chloroform (100 ml) and the mixture was set aside for 2 h. After addition of water the chloroform solution was washed with dilute hydrochloric acid and water and dried ($MgSO_4$). Evaporation left 1-*methylsulphonylbenzimidazole* (22 g crude, 66%), m.p. 151—152° [from benzene and light petroleum (b.p. 60—80°)] (Found: C, 49·2; H, 4·1; N, 14·4. $C_8H_8N_2O_2S$ requires C, 49·0; H, 4·1; N, 14·3%), $\lambda_{max.}$ (EtOH) 241, 266, 274, and 282 nm (log ε 3·93, 3·25, 3·37, and 3·35), τ ($CDCl_3$) 1·77 (1H, s), 2·05—2·30 (2H, m), 2·45—2·8 (2H, m), and 6·72 (3H, s).

2-*Deuteriobenzothiazole*.—A mixture of [$^2H_2$]formic acid (0·8 ml, 1 g) and 2-aminobenzenethiol (3·5 ml) was heated at 100° in a sealed tube overnight. The mixture was cooled and dissolved in concentrated hydrochloric acid (5 ml) and an excess of saturated ammonium nitrate solution was added. The precipitate of benzothiazolium nitrate was collected, washed with a little saturated ammonium nitrate solution, and shaken with dilute sodium hydroxide solution. Repeated extraction with ether followed by normal work-up gave 2-deuteriobenzothiazole (1·2 g, 41%), b.p. 230—238°.

2-(2-*Benzoylphenyl*)*benzimidazole*.—A mixture of *o*-phenylenediamine (10 g), *o*-benzoylbenzoic acid (21 g), and xylene (100 ml) was boiled under reflux with a water-trap for 8 h. Evaporation, and recrystallisation of the residue from glacial acetic acid and water (with animal charcoal) gave the *benzimidazole* as golden plates (15·5 g, 56%), m.p. 184—185° (Found: C, 79·6; H, 4·9; N, 9·4. $C_{20}H_{14}N_2O$ requires C, 80·5; H, 4·7; N, 9·4%), $\nu_{max.}$ (KBr) 1696 cm^{-1}, $\lambda_{max.}$ (EtOH) 298 and 331 nm (log ε 3·53 and 3·32), τ ($CDCl_3$) 2·1—2·3 (1H, m), 2·3—2·9 (9H, m), 2·9—3·3 (3H, m), and 5·06br (1H).

Alkylation with sodium hydride and methyl iodide in 1,2-dimethoxyethane gave 2-(2-*benzoylphenyl*)-1-*methylbenzimidazole* (70%), m.p. 158—159° [from benzene and light petroleum (b.p. 60—80°)] (Found: C, 80·9; H, 5·4; N, 9·1. $C_{21}H_{16}N_2O$ requires C, 80·8; H, 5·1; N, 9·0%), $\nu_{max.}$ (KBr) 1714 cm^{-1}, $\lambda_{max.}$ (EtOH) 250 and 355 nm (log ε 4·02 and 3·17), τ ($CDCl_3$) 2·0—2·2 (1H, m), 2·2—3·6 (12H, m), and 7·03 (3H, s).

Alkylation with sodium hydride and benzyl chloride in dimethoxyethane gave 2-(2-*benzoylphenyl*)-1-*benzylbenzimidazole* (32%), m.p. 178° (from acetic acid and water) (Found: C, 83·7; H, 5·4; N, 7·2. $C_{27}H_{20}N_2O$ requires C, 83·5; H, 5·2; N, 7·2%).

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