Keten. Part 17.[1] Addition Reactions of Ketens with *N*-Phenyl Nitrones

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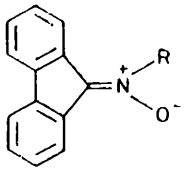
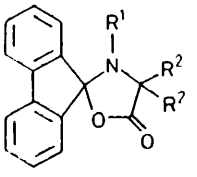
The *N*-phenyl nitrones (1a), (4b), and (15) react with ketens in two totally different ways. Triphenylnitrone (4b) forms oxindoles (6) whereas (1a) and (15) form oxazolidinones (2) and (17). The differences appear to be caused by steric interactions in (1a) and (15) which distort the nitrone function and prevent the *N*-phenyl group adopting the conformation necessary for the oxindole-forming pathway.

STUDIES of the reactions of dimethylketen [2] and diphenylketen [3] with a series of *N*-fluoren-9-ylidenealkylamine *N*-oxides (1; R = alkyl) have shown that one of the important reaction pathways leads to formation of adducts of structure (2). The adducts formed



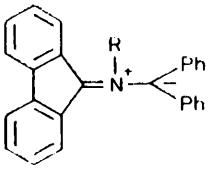
(1)

a; Ph
b; *p*-MeC_6H_4
c; *p*-$MeOC_6H_4$
d; *p*-FC_6H_4
e; *p*-$CF_3C_6H_4$



(2)

	R^1	R^2
a.	Ph	Ph
b:	Ph	Me
c:	Me	Me
d.	Pr^i	Me
e.	Me	Ph



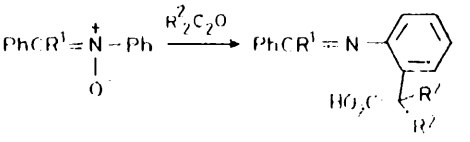
(3)

a; R = Ph

by diphenylketen (2; R^2 = Ph) are thermally unstable and readily lose carbon dioxide to form dark green ylides (3). Since this behaviour is closely similar to that reported by Staudinger [4] for the 1 : 1 adduct of diphenylketen with (1a), we assigned structure (2a) to *this adduct*.[3] However, other studies [5–8] of keten additions to *N*-phenyl nitrones [e.g. (4a)] have shown that in these cases the major pathway is formation of an oxindole (6) *via* an imino-acid (5), and no sign of oxazolidinones like (2) were found in the products of reaction of dimethylketen or keten [9] with diphenylnitrone and related diarylnitrones. Furthermore, Staudinger has also reported that diphenylketen reacts with triphenylnitrone (4b) to form initially a 1 : 1 adduct and thence a 2 . 1 (keten nitrone) adduct. Since Hassall and Lippman have shown [5] that the intermediate 1 : 1 adduct has the structure (5b) the oxindole structure (6b) seems highly likely for the 2 : 1 adduct. If these assignments are correct, then the two structurally similar nitrones (1a) and (4b) react in fundamentally different ways with diphenylketen.

As a preliminary to investigating the reasons for the difference in behaviour of the nitrones (1a) and (4b) we first sought to confirm the structures (2a) and (6b) assigned to the diphenylketen adducts and to examine the behaviour of the two nitrones with other ketens.

The reaction of triphenylnitrone (4b) with diphenylketen gave an insoluble solid which seemed to be the 1 : 2 adduct described by Staudinger.[4] It proved quite impossible to recrystallise this material which showed a single carbonyl absorption in the i.r. spectrum at 1 705 cm^{-1}, a rather low frequency for the ester and oxindole carbonyl functions. The compound dissolved slowly in boiling methanol forming a product, identified by its

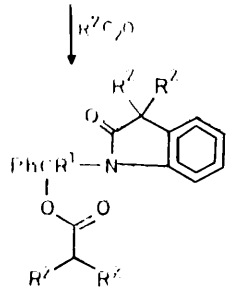


(4)

a, R^1 = H
b, R^1 = Ph

(5)

a, R^1 = H
b, R^1 = R^2 = Ph



(6)

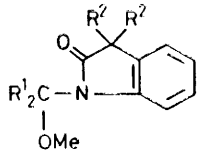
	R^1	R^2
a.	H	
b.	Ph	Ph
c.	Ph	Me
d.	H	H

spectroscopic properties as (7a), presumably arising by solvolysis of the benzhydryl ester in (6b). Acidic hydrolysis of the adduct gave benzophenone and a second compound, the properties of which were compatible with it being the expected 3,3-diphenyloxindole

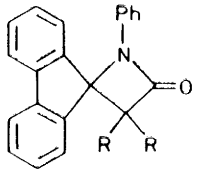
reported by Hassall [5] to be formed by acidic hydrolysis of the intermediate 1 : 1 adduct (5b) of triphenylnitrone and diphenylketen. Whilst these results do not comprise a complete proof of structure (6b) for the adduct, they are consistent with that assignment and show that the *N*-phenyl group in (4b) is involved in the addition reaction.

Triphenylnitrone also formed an adduct with two molecules of dimethylketen which, again, could not be recrystallised although an acceptable analysis could be obtained with the crude material. Methanolysis gave the methoxy-compound (7b), which could be hydrolysed to benzophenone and 3,3-dimethyloxindole. The degradative and spectroscopic evidence clearly show the adduct to have the structure (6c), so that in its reactions with diphenylketen and dimethylketen triphenylnitrone behaves exactly like diphenylnitrone.[6] An attempt to react triphenylnitrone with keten gave a dark oily product containing several components which have not so far been further examined. In this respect triphenylnitrone differs from diphenylnitrone which reacts with keten to give a moderate yield of the oxindole (6d).[9]

The *N*-phenylnitrone (1a) reacted with diphenylketen exactly as described by Staudinger to give the thermally labile 1 : 1 adduct as well as traces of the β-lactam (8a) presumably arising *via* deoxygenation of (1a) as previously observed for the corresponding *N*-alkyl nitrones.[3] The ^{1}H n.m.r. spectrum showed all proton signals to be in the aromatic region, suggesting that the *N*-phenyl



(7)

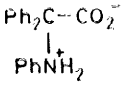


(8)

R^1	R^2
a; Ph	Ph
b; Ph	Me

a; R = Ph

b; R = Me



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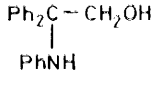
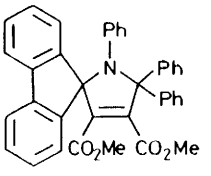


(10)

group had not participated directly in reaction. Reaction with hydroxylamine gave fluorenone oxime and the amino-acid (9) which was identified by conversion into its reduction product (10). Solutions of this adduct were very labile, rapidly turning dark green on warming, which prevented the measurement of the ^{13}C n.m.r. spectrum. This dark green colour was shown to be due to formation of the ylide (3a) by reaction with dimethyl butynedioate to give a compound identified by its spectroscopic properties as (11). This compound occluded solvent very tenaciously preventing a successful microanalysis, but the molecular formula was established by mass spectrometry. All these observations support the assignment of structure (2a) to the adduct of diphenylketen with (1a).



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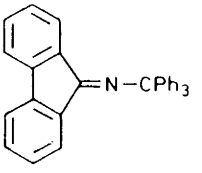

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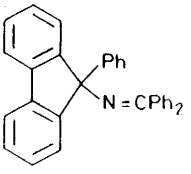


(13)

It was observed that the green ylide (3a) was less stable than the *N*-alkyl analogues.[3] Prolonged boiling of a solution of (2a) in dry benzene under nitrogen gave initially the dark green colour which faded slowly to yellow. Although it proved impossible to characterise the oily product, acidic hydrolysis led to the formation of fluorenone and benzophenone. The reaction may involve the N to C migration of the *N*-phenyl group of (3a) to give two imines (12) and (13), which could be the sources of the observed ketones. However, triphenylmethanol, an expected product of acidic hydrolysis of (12) was not detected.

The nitrone (1a) also reacted with dimethylketen to give a β-lactam (8b) and a 1 : 1 adduct. The spectroscopic properties of the adduct clearly indicate structure (2b), in particular the presence of 13 protons absorbing in the aromatic region show that, here too, the *N*-phenyl group has not been substituted during reaction. Chemical evidence for the structure (2b) was obtained by acidic methanolysis leading to the isolation of fluorenone, and reaction with hydroxylamine to form fluorenone oxime. In this case the expected amino-acid was not isolated. Additional evidence comes from the mass spectrum, the major features of which are rationalised in the Scheme. For all save the $(M - 15)^+$ peak, ion formulae were obtained by low-resolution, accurate-mass measurements and metastable peaks corresponding to most of the transition in the Scheme were observed. For the adduct (2b) the $(M - 176)^+$ peak was the base peak with very strong peaks at 133^+ and 118^+ which are wholly consistent with the assigned structure. It is noteworthy that the 133^+ ion is prominent in the mass spectrum of (2b), whereas in the mass spectrum of (2c) and other *N*-alkyl analogues no corresponding ion is observed.[2]

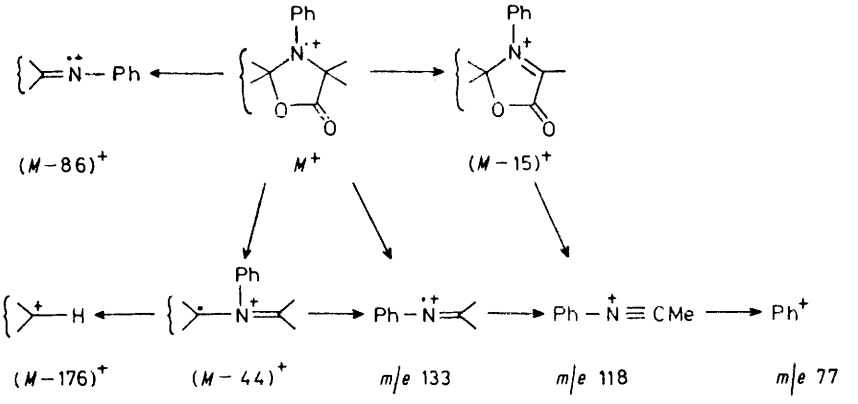
In an independent investigation Abou-Gharbia, Joullie, and Miura [10] have shown that a series of *N*-aryl nitrones (1b—e) react with cyclopentamethyleneketen, t-butylethoxycarbonylketen, and t-butylcyanoketen to

give oxazolidinones of general structure (2) but these workers did not observe azetidinone formation. An important part of their observations is the chemical shift of the ^{13}C n.m.r. absorption of the spiro-carbon atom in (2). The corresponding absorptions for the adducts (2b—e) are between δ_C 100.8 and 102.8 in good agreement with Joullie's results (δ_C 101.8—102.8).

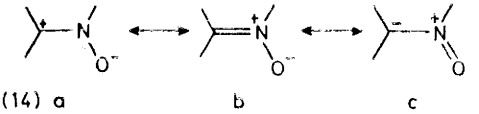
In an attempt to see how experimental conditions might control the ratio of adduct : β-lactam formation in the reaction we varied the solvent and temperature. The low solubility of the nitrone in solvents of low polarity limited the scope of the variation and only modest changes in the product ratio were observed. Joullie's work is reported to be performed in toluene so it is possible that the low polarity of the hydrocarbon solvent disfavours deoxygenation of the nitrone and subsequent β-lactam formation.

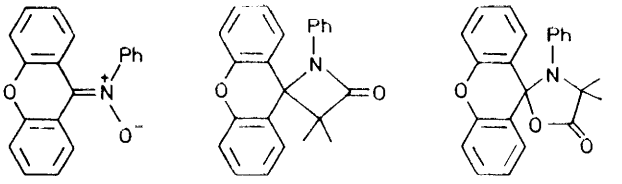
Attempts to obtain an adduct from (1a) and keten were unsuccessful. Keten reacted rapidly with (1a) in ethyl acetate and t.l.c. on alumina showed the formation of a new compound. This new compound was converted into fluorenone very rapidly on silica gel, Florisil, and Kieselguhr, and could not be eluted from alumina. Prolonged treatment of (1a) in ethyl acetate with an excess of keten gave a complex mixture of products which was not further examined.

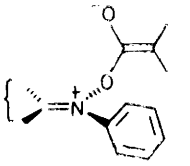
These results show that there is an important difference between the reactions of (1a) and (4b) with ketens, which could be due either to steric or electronic factors. The only significant steric difference between these two nitrones arises from the freedom of rotation of the *C*-phenyl groups in (4b) but substantial electronic differences might be expected arising from the differences in charge stabilisation by diphenyl and biphenylene substitution of the nitrone function. Three canonical structures (14) can be drawn for the nitrone function in which the electron distribution may be substantially affected by the substituent groups. *C,C*-Diphenyl substitution would stabilise both (14a) and (14c) whereas *C,C*-biphenylene substitution would destabilise (14a) as the cation would then be part of an antiaromatic system. In order to distinguish between the steric and electronic factors the nitrone (15) was synthesised. This compound is sterically similar to (1a) but is expected to have the opposite electronic effects on the charge distribution in the nitrone group. This compound reacted with dimethylketen to give a mixture of a β-lactam (16) and a 1 : 1 adduct to which we assign the structure (17). The ^1H n.m.r. spectrum of the 1 : 1 adduct shows that the *N*-phenyl group is intact, and the i.r. spectrum contains a single carbonyl absorption at 1 790 cm^{-1} like (2b). Acidic hydrolysis of the adduct gave xanthone and reaction with hydroxylamine gave xanthone oxime and 2-methyl-2-phenylaminopropanoic acid. The mass spectrum of the adduct was wholly consistent with the structure (17) and closely resembled the mass spectrum of (2b) shown in the scheme except for the absence of an $(M - 15)^+$ peak. In this case the 133^+ peak was the base peak, and, as in the previous case, metastable peaks were observed corresponding to most of the transformations in the Scheme.



SCHEME







This result indicates that steric factors are responsible for the difference between the reactions of (1a) and (4b). We have previously suggested[6] that in the nitrone–keten reaction leading to (6) the initially formed zwitterion (18) requires the conformation shown for the sigmatropic rearrangement leading to (5), which we assumed had a preferred chair-shaped transition state.[11] In the case of triphenylnitrone (4b) such a conformation can be achieved without difficulty, but with the large and rigid fluorenylidene or xanthylidene groups present steric interaction may prevent the *N*-phenyl group adopting the necessary conformation for a [3,3] migration. Alternatively the steric interaction may distort the planarity of the nitrone group and thereby raise the energy of the π-orbitals to such an extent that the reaction path leading to (2) becomes preferred. Increasing distortion of the nitrone function in the series (1; R = Me, Et, and Pr^i) might also explain the progressive change in the product spectrum observed for the reactions of these nitrones with dimethylketen.[2]

EXPERIMENTAL

^{1}H N.m.r. spectra were measured with a Perkin-Elmer R34 220 MHz spectrometer, ^{13}C n.m.r. spectra with a JEOL PFT-100 spectrometer, and i.r. spectra with a Perkin-Elmer 457 spectrometer. Mass spectra were measured by P.C.M.U. Aldermaston with a Kratos (AEI) MS50 mass spectrometer and DS-50SM data system. Diphenylketen was prepared by pyrolysis of benzoylphenyldiazomethane[12] and dimethylketen was prepared by pyrolysis of tetramethylcyclobutane-1,3-dione in a modified version of Johnson and Witzel's apparatus,[13] and used without further purification.

3,3-*Diphenyl*-2-*oxoindol*-1-*yl*(*diphenyl*)*methyl Diphenylacetate* (6b).—A mixture of triphenylnitrone (0.4 g), diphenylketen (from 0.55 g of diazoketone), and benzene (9 ml) was stirred at room temperature under nitrogen for 8 h. The precipitate was collected and washed with benzene and light petroleum to give the *adduct* (6b) (0.6 g) as a pale yellow solid, m.p. 176—178 °C (lit.,[4] 166—168 °C) which could not be recrystallised (Found: C, 86.7; H, 6.0; N, 2.7. $C_{47}H_{35}NO_3$ requires C, 85.3; H, 5.3; N, 2.1%), $\nu_{max.}$ (paste) 1 705 cm^{-1}; δ_H ($CDCl_3$) 6.32 (1 H, d, *J* 8 Hz), 6.69 (2 H, d, *J* 8 Hz), 6.8—7.05 (2 H, m), and 7.1—7.5 (30 H, m).

1-(*Methoxydiphenylmethyl*)-3,3-*diphenyloxindole* (7a).—A suspension of the adduct (6b) (0.3 g) in methanol (20 ml) was boiled under reflux for 5 h by which time the solid had dissolved. Cooling the solution deposited the *oxindole* (0.23 g, 100%), m.p. 171—172 °C (from methanol) (Found: N, 2.8. $C_{34}H_{27}NO_2$ requires N, 2.9%), $\nu_{max.}$ (paste) 1 720 cm^{-1}; δ_H ($CDCl_3$) 3.44 (3 H, s), 6.10 (1 H, d, *J* 8 Hz), 6.65 (2 H, d, *J* 8 Hz), 6.8—7.0 (2 H, m), and 7.0—7.4 (19 H, m).

Hydrolysis of the Adduct (6b).—A mixture of the adduct (6b) (0.11 g), water (15 ml), and concentrated sulphuric acid (a few drops) was boiled under reflux overnight. Extraction of the mixture with ether and work-up of the ethereal solution gave a solid (0.1 g) which t.l.c. showed to contain three components. Preparative t.l.c. (silica gel–dichloromethane) separated benzophenone (0.04 g), identified by i.r. comparison and a mixed m.p. determination on the dinitrophenylhydrazone, and a solid compound (0.03 g) identified as 3,3-diphenyloxindole by its m.p. 229—230 °C (lit.,[14] 230—231 °C) and i.r. spectrum, $\nu_{max.}$ (paste) 1 720 and 3 220 cm^{-1}.

3,3-*Dimethyl*-2-*oxoindol*-1-*yl*(*diphenyl*)*methyl Isobutyrate* (6c).—Dimethylketen (from 10 g of dimer) was passed into a solution of triphenylnitrone (1 g) in dry ethyl acetate (60 ml). After standing overnight the mixture was evaporated leaving an oil which solidified on rubbing with a little light petroleum. Washing the solid with light petroleum left the *adduct* (6c) (0.8 g, 53%) as a solid which could not be recrystallised, m.p. 101—102 °C (Found: C, 78.2; H, 6.7; N, 3.6. $C_{27}H_{27}NO_3$ requires C, 78.5; H, 6.5; N, 3.4%), $\nu_{max.}$ (paste) 1 750 cm^{-1}; δ_H ($CDCl_3$) 1.13 (6 H, d, *J* 7 Hz), 1.38 (6 H, s), 2.67 (1 H, septet, *J* 7 Hz), 6.32 (1 H, d, *J* 8 Hz), 6.85—7.05 (2 H, m), and 7.1—7.5 (11 H, m).

1-(*Methoxydiphenylmethyl*)-3,3-*dimethyloxindole* (7b).—A mixture of the adduct (6c) (0.4 g) and methanol was boiled under reflux for 6 h by which time the solid had all dissolved. Cooling deposited the *oxindole* (7b) (0.25 g, 72%), m.p. 160—161 °C (from methanol) (Found: C, 80.5; H, 6.6; N, 3.7. $C_{24}H_{23}NO_2$ requires C, 80.7; H, 6.4; N, 3.9%), $\nu_{max.}$ (paste) 1 730 cm^{-1}; δ_H ($CDCl_3$) 1.44 (6 H, s), 3.33 (3 H, s), 6.60 (1 H, d, *J* 7 Hz), 6.9—7.1 (2 H, m), 7.1—7.4 (7 H, m), and 7.49 (4 H, d, *J* 8 Hz).

Hydrolysis of the Oxindole (7b). A mixture of the methanolysis product (7b) (0.2 g) of the adduct (6c), water, (20 ml), and concentrated sulphuric acid (a few drops) was boiled under reflux overnight. Extraction of the mixture with ether and work-up of the ethereal solution gave an oil (0.18 g) which was separated by preparative t.l.c. into 3,3-dimethyloxindole (0.08 g, 89%), identified by i.r. comparison and mixed m.p. determination with an authentic sample, and benzophenone (0.04 g, 39%) identified by i.r. comparison with an authentic sample and mixed m.p. determination on the dinitrophenylhydrazone.

Reaction of Diphenylketen with the N-*Phenyl Nitrone* (1a).—A solution of the *N*-phenyl nitrone (1a) (0.32 g) and diphenylketen (from 0.3 diazoketone) in benzene (10 ml) was stirred at room temperature for 1 h. Dilution with ether and washing of the precipitate with ether left 3′,4′,4′-*triphenylfluorene*-9-*spiro*-2′-*oxazolidin*-5′-*one* (2a) (0.42 g, 76%) as an amorphous solid, m.p. 156—158 °C (decomp.) [lit.,[4] 157—158° (decomp.)] A sample was prepared for analysis by dissolution in chloroform and reprecipitation with ether (Found: C, 83.9; H, 5.0; N, 3.2. $C_{33}H_{23}NO_2$ requires C, 85.2; H, 4.9; N, 3.0%), $\nu_{max.}$ (paste) 1 795 cm^{-1}; δ_H ($CDCl_3$) 6.32 (2 H, d, *J* 8 Hz), 6.60 (1 H, m), 6.7—6.8 (2 H, m), 7.1—7.5 (12 H, m), and 7.6—7.9 (6 H, m).

T.l.c. analysis of the mother liquor from the reaction showed the presence of traces of a compound indistinguishable chromatographically from the β-lactam (8a).

1′,3′,3′-*Triphenylfluorene*-9-*spiro*-2′-*azetidin*-4′-*one* (8a).—This compound was prepared by the reaction of diphenylketen with fluorenone anil in benzene at room temperature, m.p. 292—293 °C (from methanol) (Found: C, 87.7; H, 5.0; N, 3.2. $C_{33}H_{23}NO$ requires C, 88.2; H, 5.1; N, 3.1%), $\nu_{max.}$ (paste) 1 740 cm^{-1}; δ_H ($CDCl_3$) 6.52 (2 H, d, *J* 8 Hz), 6.8—7.0 (3 H, m), 7.0—7.2 (10 H, m), 7.2—7.4 (6 H, m), and 7.80 (2 H, d, *J* 8 Hz).

Reaction of the Adduct (2a) *with Dimethyl Butynedioate*.—A solution of the adduct (2a) (0.2 g) in benzene (5 ml) and dimethyl butynedioate (0.6 g) was boiled for 2 h. Evaporation of the solvent left a dark oil which solidified slowly on shaking with light petroleum to give *dimethyl* 2′,5′-*dihydro*-1′,5′,5′-*triphenylfluorene*-9-*spiro*-2′-*pyrrole*-3′,4′-*dicarboxylate* (11) (0.18 g, 74%), m.p. 239—240 °C

(from acetone and light petroleum) (mass spectrum, M^+ 563.209 4. Calc. for $C_{38}H_{29}NO_4$: 563.209 6), $\nu_{max.}$ (paste) 1 735 cm^{-1}; δ_H ($CDCl_3$) 3.37 (3 H, s), 3.73 (3 H, s), 6.3—6.4 (4 H, m), 6.4—6.6 (1 H, m), 6.6—6.8 (2 H, m), 6.9—7.5 (12 H, m), and 7.7—7.9 (4 H, m).

Reaction of the Adduct (2a) *with Hydroxylamine.*—Hydroxyammonium chloride (5 g) was boiled with triethylamine (7 ml) in dry methanol (30 ml) for ½ h and the mixture was evaporated to dryness. Extraction of the residue with chloroform and evaporation of the extract left crude hydroxylamine as a waxy solid which was added to dry methanol (30 ml) and the adduct (2a) (0.42 g). After heating the mixture at 60 °C for 18 h the methanol was evaporated and the residue washed with water. Extraction with methanol and work-up of the methanol solution gave fluorenone oxime (0.15 g, 85%), identified by i.r. comparison and mixed m.p. determination with an authentic sample. The residue (0.08 g) was reduced by lithium aluminium hydride in ether to give the amino-alcohol (10) identified by i.r. comparison with an authentic sample.

2-*Phenylamino*-2,2-*diphenylethanol* (10).—A mixture of diphenylacetic acid (5 g), phosphorus trichloride (0.1 g), and carbon tetrachloride (30 ml) was boiled under reflux and a solution of bromine (1.5 ml) in carbon tetrachloride (20 ml) was added slowly. The mixture was heated for 2 h and evaporated leaving an oil which solidified on shaking with light petroleum. The crude bromodiphenylacetic acid was dissolved in benzene (45 ml), aniline (21 g) was added, and the mixture was stirred at room temperature overnight. The precipitate of crude amino-acid was collected, washed with ether, dried, and added (5 g) slowly to a stirred suspension of lithium aluminium hydride (5 g) in ether (30 ml). The reaction mixture was boiled under reflux for 36 h and then the excess of reagent was decomposed by addition of ethyl acetate followed by water. The ethereal solution was collected, dried (K_2CO_3), and evaporated leaving the *amino-alcohol* (10) as an oil (2.1 g), b.p. 146—156 °C/0.04 mmHg (bulb-to-tube distillation) (Found: C, 82.6; H, 6.6; N, 4.8. $C_{20}H_{19}NO$ requires C, 83.0; H, 6.6; N, 4.8%), $\nu_{max.}$ (film) 3 550 and 3 420 cm^{-1}; δ_H ($CDCl_3$) 1.7br (1 H), 4.25 (2 H, s), 4.9br (1 H), 6.35 (2 H, d, *J* 8 Hz), 6.57 (1 H, t, *J* 7 Hz), 6.92 (2 H, t, *J* 7 Hz), 7.1—7.4 (6 H, m), and 7.46 (4 H, d, *J* 8 Hz).

Pyrolysis of Compound (2a).—A solution of the adduct (2a) in dry benzene was boiled under reflux under nitrogen. A dark green colour developed almost immediately and after 7 h the solution had become yellow. Evaporation of the solvent left a yellow oil which was dissolved in a mixture of acetic acid, water, and a little concentrated sulphuric acid. After boiling for 4 h the mixture was extracted with ether. Work-up and evaporation of the ethereal extract left a residue which t.l.c. analysis showed to contain fluorenone and benzophenone, but not triphenylmethanol.

Reaction of Dimethylketen with the N-*Phenyl Nitrone* (1a).—Dimethylketen (from 10 g of dimer) was passed into a solution of the *N*-phenyl nitrone (1a) (2 g) in ethyl acetate (200 ml). After 1 h at room temperature the mixture was evaporated to dryness and the residue separated by preparative t.l.c. (silica gel–dichloromethane) giving unchanged nitrone (0.1 g) and two other products: 4′,4′-*dimethyl*-3′-*phenylfluorene*-9-*spiro*-2′-*oxazolidin*-5′-*one* (2b) (0.5 g, 21%), m.p. 117—118 °C (from methanol) (Found: C, 80.8; H, 5.5; N, 4.3. $C_{23}H_{19}NO_2$ requires C, 80.9; H, 5.6; N, 4.1%), $\nu_{max.}$ (paste) 1 790 cm^{-1}; δ_H ($CDCl_3$), 2.02 (6 H, s), 6.47 (2 H, d, *J* 8 Hz), 6.63 (1 H, t, *J* 7 Hz), 6.92 (2 H, t, *J* 7 Hz), 7.2—7.5 (6 H, m), and 7.64 (2 H, d, *J* 8 Hz); δ_C ($CDCl_3$) 26.0 (q), 60.2 (s), 100.8 (s), 116.9 (d), 119.2 (d), 120.8 (d), 123.7 (d), 128.7 (d), 130.9 (d), 139.4 (s), 139.8 (s), 142.0 (s), and 176.8 (s); *m/e* 341 (M^+, 13%), 326 (5%), 297 ($C_{22}H_{19}N$, 34%), 294 ($C_{22}H_{16}N$, 16%), 255 ($C_{19}H_{13}N$, 18%), 254 ($C_{19}H_{12}N$, 17%), 166 ($C_{13}H_{10}$, 28%), 165 ($C_{13}H_9$, 100%), 164 ($C_{13}H_8$, 12%), 133 ($C_9H_{11}N$ 45%), 118 (C_8H_8N, 76%), and 77 (C_6H_5, 28%), *m** 311.7 (341→326), 190.8 (341→255), 104.8 (133→118), 91.7 (297→165), 51.9→(341→133), 50.2 (118→77), 46.9 (297→118), and 42.8 (326→118); and the β-lactam (8b) (0.15 g, 7%) identified by i.r., n.m.r., and t.l.c. comparison with an authentic sample.

Performing the reaction at a different temperature or in different solvents made only slight differences to the ratio (2b) : (8b) : ethyl acetate at 0 °C (3.8 : 1), ether at 22 °C (5.5 : 1), and acetonitrile at 22 °C (2.6 : 1).

3′,3′-*Dimethyl*-1′-*phenylfluorene*-9-*spiro*-2′-*azetidin*-4′-*one* (8b).—This compound was prepared by the reaction of dimethylketen with fluorenone anil in ethyl acetate at room temperature, m.p. 185—186 °C (from methanol) (Found: C, 84.6; H, 6.0; N, 4.4. $C_{23}H_{19}NO$ requires C, 84.9; H, 5.8; N, 4.3%); $\nu_{max.}$ (paste) 1 760 cm^{-1}; δ_H ($CDCl_3$) 1.26 (6 H, s), 6.8—7.0 (3 H, m), 7.0—7.15 (2 H, m), 7.15—7.3 (2 H, m), 7.3—7.5 (4 H, m), and 7.78 (2 H, d, *J* 7 Hz).

Methanolysis of the Adduct (2b). A solution of the adduct (2b) (0.1 g) in methanol (5 ml) and concentrated sulphuric acid (3 drops) was boiled under reflux for 8 h and then evaporated. Ether extraction of the residue and work-up of the ethereal solution gave fluorenone (0.055 g, 100%) identified by i.r. and mixed m.p. comparison with an authentic sample.

Reaction of the Adduct (2b) *with Hydroxylamine.*—This reaction under conditions identical with those described above for (2a) gave fluorenone oxime (79%) identified by i.r. comparison with an authentic sample.

N-*Xanthen*-9-*ylideneaniline* N-*Oxide* (15).—A mixture of xanthone (10 g), hydrazine hydrate (160 ml; 98—100%), hydrazine dihydrochloride (44.4 g), and triethylene glycol (200 ml) was boiled under reflux for 24 h. The mixture was cooled, filtered free from xanthone azine (1.2 g), and diluted with water to precipitate xanthone hydrazone (5.1 g, 48%), m.p. 128—129 °C (from ethanol) (lit.,[15] 128—130 °C).

A mixture of xanthone hydrazone (4.5 g), yellow mercuric oxide (8 g), and anhydrous sodium sulphate (11.2 g) was ground in a mortar and added to dry ether (50 ml). Addition of saturated ethanolic potassium hydroxide (1 ml) initiated a reaction and the mixture was stirred at 10 °C for 40 min. The ethereal solution was filtered and evaporated at room temperature under reduced pressure. The residue (3.8 g) was dissolved in benzene and a solution of nitrosobenzene (1.9 g) in benzene (20 ml) was added. After the mixture had been stirred at room temperature for 15 h the precipitated *nitrone* (15) was collected (2.1 g, 34%), m.p. 161—163° (from ethanol) (Found: C, 79.4; H, 4.7; N, 4.6. $C_{19}H_{13}NO_2$ requires C, 79.4; H, 4.5; N, 4.9%), $\nu_{max.}$ (paste) 1 210, 1 228, 1 260, and 1 450 cm^{-1}.

Reaction of the N-*Phenyl Nitrone* (15) *with Dimethylketen.*—Dimethylketen (from 12 g dimer) was passed into a solution of the nitrone (15) (1 g) in dry ethyl acetate (70 ml) at room temperature and the mixture left to stand overnight. Evaporation of the solvent and preparative t.l.c. (silica gel–dichloromethane) separated two compounds: the β-lactam (16) (0.06 g, 5%), m.p. 170—177 °C, identified

by i.r. and n.m.r. comparison with an authentic sample, and *3′-phenyl-4′,4′-dimethylxanthene-9-spiro-2′-oxazolidin-5-one* (17) (0.8 g, 64%), m.p. 188—189 °C (from light petroleum) (Found: C, 77.2; H, 5.4; N, 3.7. $C_{23}H_{19}NO_3$ requires C, 77.3; H, 5.3; N, 3.9%), $\nu_{max.}$ (paste) 1 790 cm^{-1}; δ_H ($CDCl_3$) 2.03 (6 H, s), 6.49 (2 H, d, *J* 8 Hz), 6.70 (1 H, t, *J* 8 Hz), 6.98 (2 H, t, *J* 8 Hz), 7.11 (2 H, t, *J* 8 Hz), 7.2—7.35 (3 H, m), and 7.35—7.5 (3 H, m); *m/e* 357 (M^+, 6%), 313 ($C_{22}H_{19}NO$, 2%), 310 ($C_{22}H_{16}NO$,6%), 271 ($C_{19}H_{13}NO$ 7%), 270 ($C_{19}H_{12}NO$, 9%), 236 ($C_{16}H_{14}NO$, 3%), 196 ($C_{13}H_8O_2$, 5%), 181 ($C_{13}H_9O$, 4%), 180 ($C_{13}H_8O$, 3%), 165 ($C_{13}H_9$, 2%), 152 ($C_{12}H_8$, 2%), 133 ($C_9H_{11}N$, 100%), 118 (C_8H_8N, 67%), and 77 (C_6H_5, 22%); *m** 284, 128.5 (180→152), 104.8 (313→181, 133→118), 91.8 (357→181), 50.2 (118→77), 49.6 (357→133), and 44.5 (313→118, 133→77).

3′,3′-Dimethyl-1′-phenylxanthene-9-spiro-2′-azetidin-4′-one (16).—A mixture of xanthone (9.8 g) and oxalyl chloride (20 g) was boiled under reflux for 5 h and then evaporated to dryness. The residue was boiled with an excess of aniline and benzene (40 ml) for 5 h. Evaporation of the mixture and washing of the residue with cold methanol left xanthone anil as a yellow residue (3.9 g, 29%), m.p. 133—134 °C (from methanol) (lit.,[16] 134—135 °C). A solution of the anil (1 g) in ethyl acetate (40 ml) was treated with an excess of dimethylketen at room temperature. Evaporation of the mixture left an oil which solidified on rubbing with light petroleum to give the β-*lactam* (16) (0.85 g), m.p. 176—178 °C (from methanol) (Found: C, 81.0; H, 5.6; N, 3.9. $C_{23}H_{19}NO_2$ requires C, 80.9; H, 5.6; N, 4.1%), $\nu_{max.}$ (paste) 1 755 cm^{-1}; δ_H ($CDCl_3$) 0.82 (6 H, s) and 6.9—7.5 (13 H, m).

Reaction of the Adduct (17) *with Hydroxylamine.*—This reaction under conditions identical with those described above for (2a) gave xanthone oxime (82%), identified by i.r. comparison and mixed m.p. determination with an authentic sample, and 2-methyl-2-phenylaminopropanoic acid, identified by i.r. comparison with an authentic sample.

Hydrolysis of the Adduct (17).—A mixture of the adduct (17) (0.12 g), acetic acid (10 ml), water (8 ml), and concentrated sulphuric acid (3 ml) was boiled under reflux for 14 h during which the adduct dissolved completely. Cooling precipitated xanthone (0.07 g, 100%) identified by t.l.c., i.r., and mixed m.p. comparison with an authentic sample.

3′,4′,4′-Trimethylfluorene-9-spiro-2′-oxazolidin-5′-one (2c).[2]—δ_C ($CDCl_3$) 25.4 (q), 27.6 (q), 58.9 (s), 102.2 (s), 120.0 (d), 124.6 (d), 128.1 (d), 130.6 (d), 140.3 (s), 142.0 (s), and 178.4 (s).

3′-Isopropyl-4′,4′-dimethylfluorene-9-spiro-2′-oxazolidin-5′-one (2d).[2]—δ_C ($CDCl_3$) 24.0 (q), 28.3 (q), 45.8 (d), 60.0 (s), 101.5 (s), 120.1 (d) 124.8 (d), 128.0 (d), 130.4 (d), 139.7 (s), 144.5 (s), and 178.5 (s).

3′-Methyl-4′,4′-diphenylfluorene-9-spiro-2′-oxazolidin-5′-one (2e).[3]—δ_C ($CDCl_3$) 30.6 (q), 73.0 (s), 102.8 (s), 120.1 (d), 125.2 (d), 128.2 (d), 128.7 (d), 130.6 (d), 140.4 (s), 140.6 (s), 142.0 (s), and 174.1 (s).

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