# Keten. Part 15.[1] Reactions of Diphenylketen with some N-Alkyl Nitrones [2]

By **Anthony F. Gettins, David P. Stokes, Giles A. Taylor,*** and (in part) **Christopher B. Judge,** Department of Chemistry, University of Sheffield, Sheffield S3 7HF

N-(Fluoren-9-ylidene)alkylamine N-oxides (1) react with diphenylketen to give spiro-oxazolidinones (2) and spiro-azetidinones (13). The adduct (2d) dissociates thermally to give the ylide (9). The N-oxides (1) behave like normal nitrones in cycloaddition reactions with dipolarophiles.

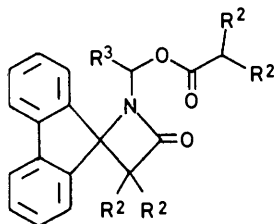PREVIOUS studies of the reactions of dimethylketen with a series of N-alkyl nitrones (1) have identified two types of
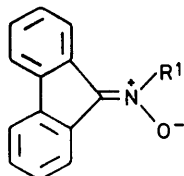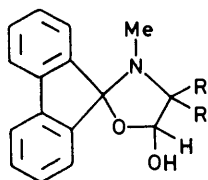

(1)

a; R = Me
b; R = Et
c; R = Pr^i
d; R = Ph
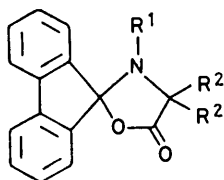
(2)

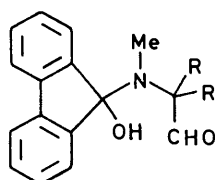|	R^1	R^2
a;	Me	Me
b;	Et	Me
c;	Pr^i	Me
d;	Me	Ph
e;	Ph	Ph
f;	Et	Ph
g;	Pr^i	Ph
h;	Ph	Me

(3)

R^2 = Me   R^3 = H, Me

(4)   (5)

a; R = Ph
b; R = Me

adduct (2a—c) and (3).[3] This paper reports the results of an investigation of the reactions of diphenylketen with the nitrones (1a—c) and some related studies.

The reaction of diphenylketen with the N-methyl nitrone (1a) in benzene gave an oily product from which two compounds were isolated. One, $C_{28}H_{21}NO_2$, a 1 : 1 adduct of nitrone and keten, was identified as the oxazolidinone (2d) by comparison of its i.r. and n.m.r. spectra with those of (2a), and the following degradative evidence. Reduction of this compound with lithium aluminium hydride gave a dihydro-compound whose i.r. spectrum (paraffin paste) showed the presence of a hydroxy-group but no carbonyl group. Chromatography on silica gel converted this compound into fluorenone in high yield, but we were unable to isolate any other material from the silica. The constitution (4a) is assigned to this material by analogy with the compound (4b) obtained by lithium aluminium hydride reduction of (2a).[3] However (4a) is much more stable than (4b), even surviving brief treatment with aqueous acid. The n.m.r. spectrum of (4a) in chloroform or dimethyl sulphoxide shows no sign of the hydroxy-aldehyde (5a) [unlike the case of (4b)] but the i.r. spectrum of a solution of (4a) in chloroform shows a weak absorption at 1 719 cm^{-1} indicating a low concentration of (5a). The unexpected stability of (4a) with respect to its tautomer is probably due to the large steric effect of the *gem*-diphenyl group.[4] Acid-catalysed methanolysis of the adduct was attempted in the hope of confirming the structural assignment (2d) by identification of the fragments. However, fluorenone, expected by analogy with a similar degradation of (2a),[3] was not obtained, the reaction proceeded very slowly, and the products were not identified, although in the light of other results 9,9-dimethoxyfluorene may well have been among them.

The reaction of the adduct with benzylamine gave a white solid, insoluble in most normal solvents. Recrystallisation was achieved from acetic acid, but a satisfactory sample for analysis was not obtained. The solubility in acidic or alkaline methanol, coupled with the n.m.r. spectrum of a solution in trifluoroacetic acid, suggested that the material was the amino-acid (6), and this was confirmed by synthesis of an authentic sample. Although the product of the benzylamine reaction and the synthesised compound appeared to be identical, the inability to obtain satisfactory analytical results from either led us to reduce both with lithium aluminium hydride to the corresponding amino-alcohol (7), which could be fully characterised.

The formation of (6) in this reaction suggests that nucleophilic attack on the highly hindered carbonyl

[1] Part 14, G. A. Taylor, *J.C.S. Perkin I*, 1975, 1001.

[2] Preliminary communication, A. F. Gettins and G. A. Taylor, *J.C.S. Chem. Comm.*, 1972, 1146.

[3] R. N. Pratt, D. P. Stokes, and G. A. Taylor, *J.C.S. Perkin I*, 1975, 498.

[4] B. Capon, *Quart. Rev.*, 1964, **18**, 45.

group of (2d) is not a step in the process, and we suggest the mechanism shown in Scheme 1. This implies that

$$Ph_2C—CO_2^-$$
$$\overset{|}{\underset{+}{}}$$
$$Me\overset{+}{N}H_2$$

(6)

$$Ph_2C·CH_2·OH$$
$$\overset{|}{}$$
$$Me\overset{|}{N}H$$

(7)

N-benzylfluorenylideneamine should be the other product of the reaction of (2d) with benzylamine, but we have been unable to confirm this. However, the reaction between (2d) and hydroxylamine in dry methanol gave both (6) (40%) and fluorenone oxime (80%) in yields

solution of (2d) in [^{2}H$_6$]benzene heated to 80 °C showed no change for a few hours, even though a dark green colour had developed, and the eventual appearance of new signals seemed linked with the fading of the colour. No e.s.r. signal was observed for the dark green solution, and an i.r. spectrum of the green oil obtained on evaporation showed absorptions attributable to (2d) and fluorenone, but gave no other information. Repeated scanning of the u.v. spectrum of a solution of (2d) in dimethoxy-ethane at 70 °C showed a slow decrease in the absorption due to (2d) and appearance of strong absorption at 258 nm and other minor peaks. After 6 h the absorption
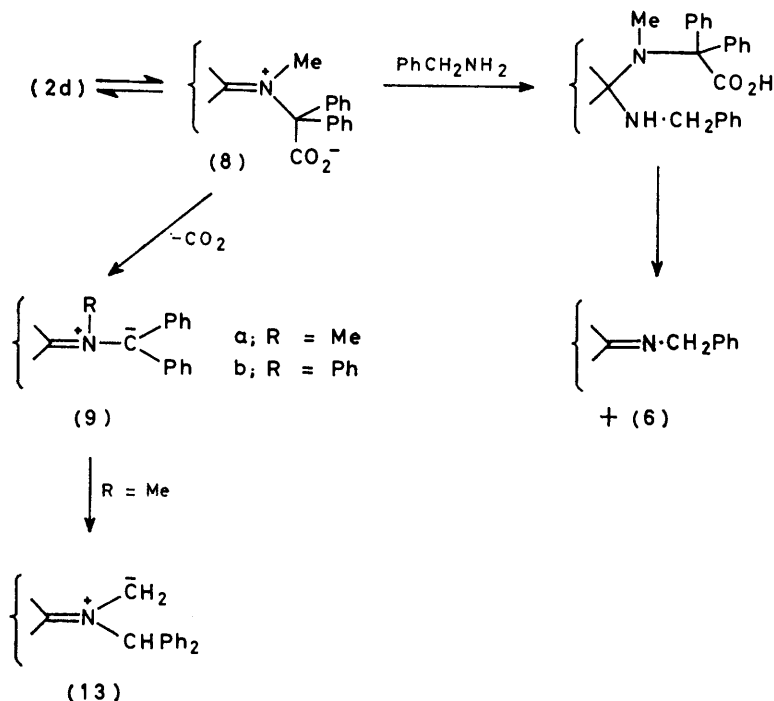
Scheme 1

which leave no doubt that both are products of the same reaction pathway. Under the conditions of this reaction, fluorenone and hydroxylamine do not react to any appreciable extent.

On heating a solution of (2d) in benzene a dark green colour developed, which faded slowly on cooling; also during the m.p. determination the solid turned green below the m.p. and melted to a green liquid, which at higher temperatures turned orange. Attempts to isolate the green material were unsuccessful. Evaporation of the green solution obtained by heating (2d) in benzene or light petroleum gave a green oil whose colour faded rapidly. The only compound isolated from this oil was unchanged (2d). After heating a solution of (2d) in benzene for 2 days the green colour had faded and the adduct (2d) could no longer be detected. Heating the adduct (2d) in propan-2-ol gave a similar green solution, but in this case the colour disappeared much more rapidly and benzophenone was isolated on work-up.

The appearance of the green colour was followed by spectroscopic methods. The n.m.r. spectrum of a

due to (2d) had disappeared. Three isosbestic points at 240, 267, and 289 nm were observed for this reaction. A similar study in the visible region of the spectrum using a solution of (2d) in xylene at 70 °C showed development of a broad absorption at 652 nm.

The absence of an e.s.r. absorption discounted the possibility of a stable radical being responsible for the colour, and we guessed that an ylide (9a) arising from (8) might be the cause. Trapping experiments confirmed this hypothesis. Heating (2d) with dimethyl but-2-ynedioate gave the expected adduct (10), which also formed by adding the acetylenic ester to the preformed green solution, whereupon the colour was rapidly discharged. An unexpected result was obtained when (2d) was heated with dimethyl fumarate which led to the adduct (11) rather than the expected (12). The product (11) was identified from the n.m.r. spectrum, which showed only two methyl signals and a one proton singlet at τ 5.54, and the mass spectrum, which showed a strong peak at m/e 167$^+$ (Ph$_2\overset{+}{C}$H) and a fragment at $(M - 167)^+$.

with a metastable peak corresponding to $M^+ \longrightarrow$ $(M - 167)^+$. It was not possible to assign the stereo-chemistry of (11) from the n.m.r. spectrum. A minor

(10)

(11)

(12)

(13)
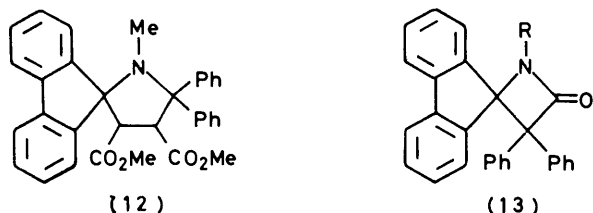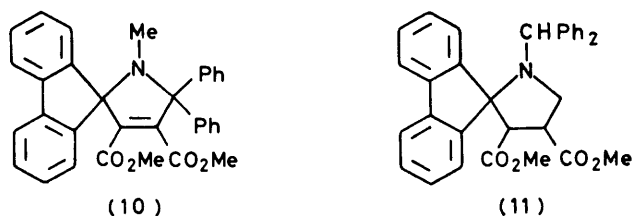
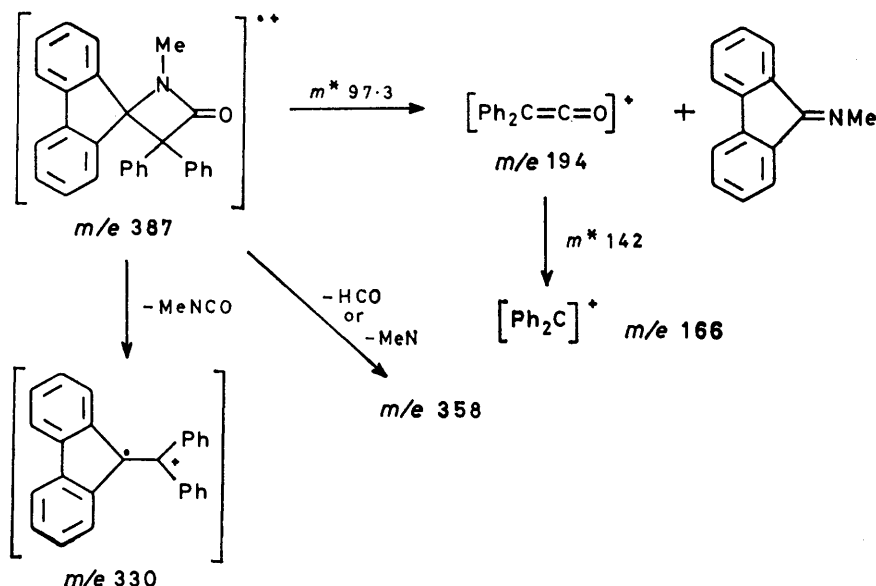a; R = Me
b; R = Et
c; R = Pr^i

isomeric product was also isolated which was not (12). Although the n.m.r. spectrum showed three methyl signals at the chemical shifts consistent with one methyl-amino- and two methoxy-groups the methoxy-signals were very close together and there were, in addition,

The formation of the adduct (10) supports the inter-mediate formation of the ylide (9a) in the decomposition of (2d), but the formation of (11) suggests that (9a) can undergo a tautomeric change to (13), which reacts more rapidly with dimethyl fumarate than (9a).

In his original work on the reaction of diphenyl-keten with nitrones, Staudinger recorded [5] the formation of a 1 : 1 adduct of diphenylketen with the nitrone (1d) which was unstable and turned green on boiling in benz-ene. He isolated an amorphous green solid from this decomposition which our results suggest was the ylide (9b), presumably arising from an adduct of constitution (2e).

A second product was isolated from the reaction of diphenylketen with (1a). Although it did not prove possible to characterise this compound completely, the molecular weight of 387 (mass spectrum), the n.m.r. spectrum, and the i.r. absorption at 1 750 cm^{-1} suggested the β-lactam structure (13a), which could reasonably arise by deoxygenation of the nitrone [6] and cyclo-addition of the resulting imine to more diphenylketen. Structure (13a) was confirmed by the synthesis of N-methylfluorenylideneamine and reaction of this compound with diphenylketen to give a product identical with that isolated from the reaction of diphenylketen and (1a). The mass spectrum of this compound is consistent with the assigned constitution, fragmentation occurring according to Scheme 2.

The reactions of the nitrones (1b and c) with diphenyl-keten gave the adducts (2f and g) which were fully

m^* 97·3 $\longrightarrow$ $\left[Ph_2C=C=O\right]^+$ m/e 194 $+$

$\left[Ph_2C\right]^+$ m/e 166

m^* 142

m/e 387

$-MeNCO$

$-HCO$ or $-MeN$

m/e 358

m/e 330

Scheme 2

three one-proton multiplets which cannot be reconciled with the constitution (12). This compound has not been further investigated. Heating (2d) with dimethyl maleate gave a complex mixture of products from which no characterisable material was isolated.

characterised. Products assigned the β-lactam struc-tures (13b and c) were also obtained but not fully charac-terised. In no case was there any sign of an adduct

[5] H. Staudinger and K. Miescher, Helv. Chim. Acta, 1919, 2, 554.

[6] R. N. Pratt and G. A. Taylor, J. Chem. Soc. (C), 1968, 1653; T. Koenig and T. Barklow, Tetrahedron, 1969, 25, 4875; R. N. Pratt, D. P. Stokes, G. A. Taylor, and S. A. Procter, J. Chem. Soc. (C), 1971, 1472.

similar to (3) in these reactions with diphenylketen. The proportions of the adducts (2) and the β-lactams (13) varied widely with changes in *N*-alkyl substituent [*N*-substituent, (2) : (13); Me, 1 : 1; Et, 1 : 2; Pr^i, 4.5 : 1]. The ratios of products were measured from the n.m.r. spectra of the crude reaction mixtures, and in the case of the *N*-methyl nitrone the ratio was shown to be independent of the initial proportions of keten and nitrone. The wide variation presumably reflects steric rather than electronic effects of the *N*-alkyl group on the competing pathways.

The chemistry of the adducts (2f and g) was not studied, but they were observed to decompose in boiling benzene to give dark green solution as for (2d). The *N*-isopropyl adduct (2 g) seemed more stable in this respect, appearance of the colour requiring a higher temperature or longer heating. On one occasion, some large, well formed crystals of (2f) turned green on exposure to sunlight.

The choice of the fluorenone-derived *N*-alkyl nitrones (1) was originally made for practical convenience [3] and we have tried to confirm that the fluorenylidene group does not make these compounds atypical of *N*-alkyl nitrones in general. Staudinger's adduct of diphenylketen and the *N*-phenyl nitrone (1d) appears to have the structure (2e), which is different in type from those observed for a series of adducts of *CN*-diaryl nitrones
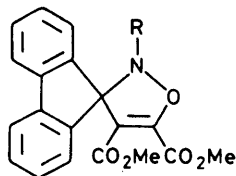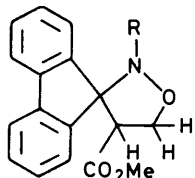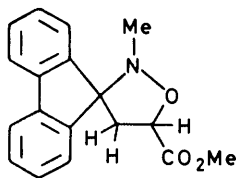

(14)

a; R = Me
b; R = Et
c; R = Pr^i
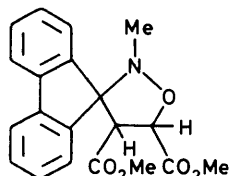
(15)

a; *trans*-isomer
b; *cis*-isomer

(16)

a; R = Me
b; R = Et

(17)

with dimethylketen,[7] and preliminary studies suggest that (1d) reacts with dimethylketen to give (2h).[8] We therefore looked at cycloaddition reactions of (1a) with a series of dipolarophiles to see if any abnormal behaviour occurred.

[7] R. N. Pratt, D. P. Stokes, G. A. Taylor, and P. C. Brookes, *J. Chem. Soc.* (*C*), 1968, 2086.

The nitrones (1a—c) reacted smoothly with dimethyl but-2-ynedioate to give the expected adducts (14a—c), identified on the basis of spectroscopic data. Likewise (1a) reacted with dimethyl fumarate and dimethyl maleate to give (15a and b), respectively. The stereochemistry of these isomers could be assigned from the coupling constants (6 and 9 Hz, respectively) of the two protons of the isoxazoline ring. Chromatography of the reaction mixtures showed no sign of (15b) in the reaction (1a) with the fumarate ester and only a trace of (15a) in the maleate ester reaction product. Since dimethyl maleate is probably isomerised slowly into the furmarate under the reaction conditions, these results suggest that the cycloadditions are stereospecific and concerted. The addition of methyl acrylate to (1a) afforded two adducts, identified as (16a) and (17) on the basis of their n.m.r. spectra, (16a) having the lower field methoxy-resonance, owing to shielding by the aromatic system. A series of mixtures of identical concentrations of (1a) and methyl acrylate in a variety of solvents of widely differing polarity were allowed to react at 23 °C for three weeks and the product ratios were estimated from the n.m.r. spectra (methoxy-absorptions). For dioxan (dielectric constant 2.21), benzene (2.28), dimethylformamide (37.60), nitromethane (37.50), and acetonitrile (37.50), the product ratio (16) : (17) was 4 : 1 within experimental error. A similar result was obtained for diethyl ether (dielectric constant 4.53) for which a lower concentration had to be used on account of the low solubility of the nitrone. When methanol (33.03) was used as solvent the ratio (16) : (17) changed to 8 : 1, but this anomalous result may be due to methanol being the only hydrogen-bonding solvent employed. The uniformity of the other results is consistent with the competing pathways to (16) and (17) not involving stepwise mechanisms *via* zwitterionic intermediates which might have been expected to be differentially influenced by large changes in solvent polarity. All this evidence is consistent with the nitrones (1) undergoing normal concerted cycloadditions with dipolarophiles, and to this extent they may be regarded as typical *N*-alkyl nitrones.

EXPERIMENTAL

N.m.r. spectra were measured with a Varian A60 or HA 100 or a Perkin-Elmer RS12 spectrometer, i.r. spectra with a Unicam SP 100 or Perkin-Elmer 180 spectrometer, u.v. spectra with a Unicam SP 700C or Cary 14 spectrometer, and mass spectra with an A.E.I. MS9 or MS12 spectrometer. Diphenylketen was prepared by pyrolysis of benzoyl(diazo)phenylmethane.[9]

Reaction of Diphenylketen with the N-*Methyl Nitrone* (1a). —A solution of diphenylketen (from 1 g of diazoketone) in benzene (10 ml) was added to an ice-cooled solution of *N*-(fluoren-9-ylidene)methylamine *N*-oxide (1a) (0.6 g) in benzene (10 ml) and the mixture was stirred for 10 min. Evaporation under reduced pressure left an oil which, on addition of acetone, precipitated 3'-*methyl*-4',4'-*diphenyl*-

[8] R. S. Johnson and G. A. Taylor, unpublished results.
[9] G. Brooks, M. A. Shah, and G. A. Taylor, *J.C.S. Perkin I*, 1973, 1297.

fluorene-9-spiro-2'-oxazolidin-5'-one (2d) (0.4 g, 35%), m.p. 138° (decomp.) (from benzene and light petroleum; temp. <60 °C) (Found: C, 82.9; H, 5.0; N, 3.4. $C_{28}H_{21}NO_2$ requires C, 83.3; H, 5.2; N, 3.5%), $\lambda_{max.}$ (EtOH) 228, 236, 267, and 292s nm [sat. solution, OD (1 cm; 25 °C) 0.54, 0.51, 0.32, and 0.095], $\nu_{max.}$ (KBr) 1 779 cm^{-1}, τ (CDCl$_3$) 2.3—2.9 (18 H, m) and 7.91 (3 H, s), m/e 403 (1.7%), 359(81), 358(94), 344(29), 326(9), 282(100), 194(42), 165(52), 118(88), and 77(48), m^* 221.5 (359 $\longrightarrow$ 282) and 50.2 (118 $\longrightarrow$ 77).

Evaporation of the acetone solution left an oil which was dissolved in benzene (10 ml). Addition of light petroleum precipitated a gummy solid which was separated by fractional recrystallisation into (2d) and 1'-methyl-3',3'-diphenylfluorene-9-spiro-2'-azetidin-4'-one (13a) (0.05 g, 4%), m.p. 195°, $\nu_{max.}$ (paste) 1 740 cm^{-1}, identified by mixed m.p. comparison with an authentic sample. Preparative t.l.c. separated the residue in the mother liquors into (2d), (13a), and unchanged (1a) (17%).

Reaction of Diphenylketen with the N-*Ethyl Nitrone* (1b).— Under conditions similar to those described above, N-(fluoren-9-ylidene)ethylamine N-oxide (1b) (0.6 g) reacted with diphenylketen (from 1 g of diazoketone) to give *3'-ethyl-4',4'-diphenylfluorene-9-spiro-2'-oxazolidin-5'-one* (2f) (0.3 g, 25%), m.p. 150° (decomp.) (from benzene and light petroleum) (Found: C, 83.3; H, 5.8; N, 3.4. $C_{29}H_{23}NO_2$ requires C, 83.5; H, 5.5; N, 3.4%), $\lambda_{max.}$ (EtOH) 222, 228, 237, 267, and 276s nm (log ε 4.53, 4.56, 4.54, 4.10, and 4.05), $\nu_{max.}$ (KBr) 1 778 cm^{-1}, τ (CDCl$_3$) 2.3—2.9 (18 H, m), 7.43 (2 H, q, J 7 Hz), and 9.51 (3 H, t, J 7 Hz), m/e 417 (5.5%), 373(55), 372(50), 358(20), 344(90), 340(11), 296(40), 194(16), 165(100), 132(35), and 104(50), and 1'-ethyl-3',3'-diphenylfluorene-9-spiro-2'-azetidine-4'-one (13b) (0.03 g), m.p. 239—242° (sublimes) (from benzene and light petroleum), identified by spectroscopic data [$\nu_{max.}$ (paste) 1 750 cm^{-1}, τ (CDCl$_3$) 2.5—3.5 (18 H, m), 6.92 (2 H, q, J 6 Hz), and 9.20 (3 H, t, J 6 Hz)].

Reaction of Diphenylketen with the N-*Isopropyl Nitrone* (1c).—Under similar conditions N-(fluoren-9-ylideneisopropylamine N-oxide (1c) (0.6 g) reacted with diphenylketen (from 1 g of diazoketone) to give *3'-isopropyl-4',4'-diphenylfluorene-9-spiro-2'-oxazolidin-5'-one* (2) (0.9 g, 73%), m.p. 212° (decomp.) (from benzene and light petroleum) (Found: C, 82.6; H, 5.9; N, 3.1. $C_{30}H_{25}NO_2$ requires C, 83.5; H, 5.8; N, 3.2%), $\lambda_{max.}$ (EtOH) 223, 230, 237, 273, 282, and 304s nm (log ε 4.61, 4.66, 4.66, 4.13, 4.10, and 3.28), $\nu_{max.}$ (KBr) 1 779 cm^{-1}, τ (CDCl$_3$) 2.1—2.8 (18 H, m), 6.38 (1 H, septet, J 5 Hz), and 9.59 (6 H, d, J 5 Hz), m/e 431(11%), 416(36), 387(9), 386(1), 372(5), 354(14), 344(64), 310(1), 208(100), 194(3), 181(7), 165(21), 146(14), and 104(39), m^* 401.5 (431 $\longrightarrow$ 416), 305.8 (387 $\longrightarrow$ 344), 104 (416 $\longrightarrow$ 208), 74 (146 $\longrightarrow$ 104), and 60.2 (354 $\longrightarrow$ 146), and a white acetone-insoluble solid (60 mg) which t.l.c. showed to contain (2g) and another compound, $\nu_{max.}$ (paste) 1 780 cm^{-1}, τ (CDCl$_3$) 8.92 (d), tentatively assigned structure (13c).

Lithium Aluminium Hydride Reduction of the Adduct (2d).—The adduct (2d) (0.5 g) was added to a slurry of lithium aluminium hydride (0.5 g) in ether (30 ml) and the mixture was stirred overnight. Water was added dropwise to destroy the excess of hydride and the ethereal solution was decanted. The inorganic residue was washed several times with ether and benzene and finally dissolved in hydrochloric acid and further extracted with ether. The combined ether and benzene solutions were dried (K$_2$CO$_3$) and evaporated to leave 3'-*methyl-4',4'-*

diphenyl-5'-hydroxyfluorene-9-spiro-2'-oxazolidine (4) (0.23 g, 46%) as a gelatinous solid, m.p. 177° (decomp.) (Found: C, 82.8; H, 5.7; N, 3.6. $C_{28}H_{23}NO_2$ requires C, 83.0; H, 5.7; N, 3.5%), $\lambda_{max.}$ (EtOH) 222s, 230, 238, 257, 268, 279s, 303s, and 315s nm (log ε 4.47, 4.53, 4.53, 4.10, 4.12, 4.07, 3.41, and 3.22), $\nu_{max.}$ (C$_4$Cl$_6$ paste) 3 515 cm^{-1}, (CHCl$_3$) 1 719w cm^{-1}, τ [(CD$_3$)$_2$SO] 2.2—2.9 (16 H, m), 2.9—3.2 (2 H, m), 3.50 (1 H, d, J 7.5 Hz), 3.85 (1 H, d, J 4.5 Hz), and 8.19 (3 H, s), τ [(CD$_3$)$_2$SO–D$_2$O] 3.06 (1 H, t, J 7.5 Hz), 3.50 (1 H, d, J 7.5 Hz), and 3.85 (1 H, s), m/e 405(2%), 359(15), 358(20), 344(8), 195(100), 193(18), 181(45), 165(18), 152(73), 118(88), and 104(10).

Reaction of the Adduct (2d) *with Benzylamine.*—A mixture of the adduct (2d) (1 g), benzylamine (2 g), and dry methanol (10 ml) was heated at 60 °C for 2 h. On cooling a gelatinous precipitate separated. The mixture was evaporated to dryness and the residue was washed with water and extracted with chloroform, to leave the insoluble 2-methylamino-2,2-diphenylacetic acid (0.42 g, 70%), m.p. 210° (decomp.) (from acetic acid) [lit.,[10] 211° (decomp.)], (Found: N, 5.9. Calc. for $C_{15}H_{15}NO_2$: N, 5.8%), τ (CF$_3$·CO$_2$H) 2.40 (10 H, s) and 7.28 (3 H, m), identified by i.r. comparison with an authentic sample.

The chloroform extract was evaporated to leave a yellow oil. T.l.c. showed the presence of several components but not that of fluorenone.

Reaction of the Adduct (2d) *with Hydroxylamine.*—Hydroxyammonium chloride (5 g) was boiled with triethylamine (7 ml) in dry methanol (30 ml) for 20 min and the solution was then evaporated to dryness under reduced pressure. The residue was extracted with chloroform and the extract evaporated to leave crude hydroxylamine as a waxy solid. This was dissolved in dry methanol (30 ml), the adduct (2d) (0.4 g) was added, and the mixture was heated at 60 °C for 12 h. Evaporation of the mixture and extraction of the residue with water and then methanol left an insoluble, white solid identified as the amino-acid (6) by i.r. comparison with an authentic sample. Evaporation of the methanolic extract and extraction of the residue with chloroform gave a further yield of compound (6). Neutralisation of the aqueous washings precipitated still more of compound (6) (total 0.1 g, 41%). Evaporation of the chloroform solution gave fluorenone oxime (0.17 g, 85%), identified by i.r. comparison and mixed m.p. determination.

2-*Methylamino-2,2-diphenylethanol* (7).—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 then heated for 2 h, and evaporated to dryness. The residual oil solidified on shaking with light petroleum. Extraction of the solid with benzene dissolved the crude 2-bromo-2,2-diphenylacetic acid and to this solution was added methylamine (7 g) in dry benzene (20 ml). After stirring the mixture for 3 h the precipitate of crude amino-acid (6) was collected and added slowly to lithium aluminium hydride (6 g) in ether (30 ml). After boiling this mixture under reflux overnight, the excess of hydride was decomposed by cautious addition of water and the ethereal solution was decanted from the residue. The residue was extracted with ethanol and the combined organic solutions were dried (K$_2$CO$_3$) and evaporated to give the *amino-alcohol* (7) (2.3 g, 43%), m.p. 109° (from benzene and light petroleum) (Found: C, 79.5; H, 7.3; N, 6.4.

[10] H. Biltz and K. Seydel, *Annalen*, 1912, **391**, 215.

$C_{15}H_{17}NO$ requires C, 79.4; H, 7.5; N, 6.2%), $\lambda_{max.}$ (EtOH) 252, 259, and 264s nm (log ε 2.71, 2.77, and 2.65), τ (CDCl₃) 2.75 (10 H, s), 5.86 (2 H, s), 7.74br (2 H, removed by D₂O), and 7.88 (3 H, s).

An identical product was obtained by reduction with lithium aluminium hydride of the chloroform-insoluble product of the reaction of (2d) with benzylamine.

Dimethyl 2',5'-Dihydro-1'-methyl-5',5'-diphenylfluorene-9-spiro-2'-pyrrole-3',4'-dicarboxylate (10).—A solution of (2d) (0.4 g) in benzene (10 ml) containing dimethyl but-2-ynedioate (1.5 g) was boiled under reflux for 2 h. Evaporation left an oil which crystallised slowly after shaking with a little light petroleum giving *compound* (10) (0.45 g, 90%), m.p. 195—196° (from acetone and light petroleum) (Found: C, 78.9; H, 5.6; N, 3.0. $C_{33}H_{27}NO_4$ requires C, 79.0; H, 5.4; N, 2.8%), $\lambda_{max.}$ (EtOH) 224, 233, 262, 271s, and 313 nm (log ε 4.58, 4.50, 4.32, 4.24, and 3.45), $\nu_{max.}$ (KBr) 1 740, 1 724, and 1 652 cm⁻¹, τ (CDCl₃) 2.2—2.9 (18 H, m), 6.42 (3 H, s), 6.68 (3 H, s), and 8.30 (3 H, s), *m/e* 501 (26%), 470(6), 442(35), 424(100), 411(8), 398(3), 392(30), 383(30), 380(21), 365(59), 348(56), 334(33), 321(22), 306(7), 291(8), 276(3), 265(9), and 118(12), *m** 389.9 (501 ⟶ 442), 362.4 (424 ⟶ 392), 358.8 (501 ⟶ 424), 350.6 (380 ⟶ 365), 340.6 (424 ⟶ 380), 331.9 (442 ⟶ 383), 318.7 (380 ⟶ 348), 314.2 (424 ⟶ 365), 305.6 (365 ⟶ 344), 285.6 (424 ⟶ 348), and 271.4 (411 ⟶ 334).

A solution of (2d) in benzene was boiled under reflux for 1 h. The dark green solution was cooled in ice and dimethyl but-2-ynedioate was added. After a few minutes the green colour had disappeared and t.l.c. showed the presence of (10) and no other product.

Dimethyl 1'-Diphenylmethylfluorene-9-spiro-2'-pyrrolidine-3',4'-dicarboxylate (11).—A mixture of the adduct (2d) (1 g), dimethyl fumarate (1 g), and benzene (20 ml) was boiled under reflux for 4 h, after which the initial green colour had disappeared. The mixture was evaporated to a small volume and light petroleum (10 ml) was added to precipitate dimethyl fumarate (0.7 g). The filtrate slowly deposited the *pyrrolidine* (11) as a powder (0.4 g, 32%), m.p. 142° (from benzene and light petroleum) (Found: C, 78.7; H, 6.0; N, 3.1. $C_{33}H_{29}NO_4$ requires C, 78.6; H, 5.8; N, 2.8%), $\lambda_{max.}$ (EtOH) 263, 270s, 288s, 300s, and 313 nm (log ε 4.14, 4.09, 3.73, 3.56, and 3.41), $\nu_{max.}$ (KBr) 1 736 cm⁻¹, τ (CDCl₃) 2.3—3.5 (18 H, m), 5.54 (1 H, s), 5.95 (2 H, m), 6.25 (3 H, s,) 6.50 (2 H, m), and 7.06 (3 H, s), *m/e* 503 (35%), 472(1), 444(3), 426(38), 394(2), 344(6), 336(24), 304(11), 276(6), 192(18), 167(100), 165(21), 152(12), and 91(13), *m** 391.9 (503 ⟶ 444), 364.4 (426 ⟶ 394), 360.8 (503 ⟶ 426), 275 (336 ⟶ 304), 250.6 (304 ⟶ 276), 235.3 (503 ⟶ 344), 224.4 (503 ⟶ 336), 183.7 (503 ⟶ 304), and 141.7 (192 ⟶ 165).

From the mother liquors was obtained a second compound (0.1 g) (Found: *m/e*, 503.2070. Calc. for $C_{33}H_{29}NO_4$: M, 503.2093), $\nu_{max.}$ (paste) 1 740 cm⁻¹, τ (CDCl₃) 2.2—3.1 (15 H, m), 3.23 (1 H, t, *J* 7 Hz), 3.53 (1 H, d, *J* 8 Hz), 3.68 (1 H, d, *J* 7 Hz), 5.65 (1 H, dd, *J* 2 and 11 Hz), 6.36 (3 H, s), 6.41 (3 H, s), 6.43—6.82 (2 H, m), 7.54 (1 H, dd, *J* 2 and 17 Hz), and 7.98 (3 H, s).

1'-Methyl-3',3'-diphenylfluorene-9-spiro-2'-azetidin-4'-one (13a).—A mixture of fluorenone (6 g), dry methylamine (13 g), and benzene (260 ml) was cooled to 4 °C under nitrogen and a solution of titanium tetrachloride (4 ml) in dry benzene (35 ml) was added slowly with vigorous stirring at such a rate that the initial bright red colour did not persist. The mixture was then stirred at room temperature for 3

days. The solution was separated from the precipitate by centrifugation and evaporated to leave a yellow oil shown by t.l.c. to contain fluorenone and one other major component, τ (CDCl₃) 6.16 (s). A solution of diphenylketen (from 1 g of diazoketone) in benzene (10 ml) was added to a solution of this yellow oil (2 g) in dry benzene (10 ml) and the mixture was set aside for 10 min. Addition of light petroleum precipitated the *azetidinone* (13a) (2.6 g), m.p. 203° (from benzene and light petroleum) (Found: C, 86.6; H, 5.6; N, 3.6. $C_{28}H_{21}NO$ requires C, 86.9; H, 5.4; N, 3.6%), $\lambda_{max.}$ (EtOH) 239, 247, 265s, 272, 280, and 289 nm (log ε 4.47, 4.54, 3.91, 3.98, 4.03, and 3.93), $\nu_{max.}$ (KBr) 1 742 cm⁻¹, τ (CDCl₃) 2.5—3.4 (18 H, m) and 7.48 (3 H, s), *m/e* 387 (23%), 358 (0.3), 330(2), 194(100), 193(8), 166(88), and 165(95), *m** 142 (194 ⟶ 166) and 97.3 (387 ⟶ 194).

Dimethyl 2',3'-Dihydro-2'-methylfluorene-9-spiro-3'-isoxazole-4',5'-dicarboxylate (14a).—A solution of the N-methyl nitrone (1a) (0.5 g) and dimethyl but-2-ynedioate (2 ml) in benzene (100 ml) was boiled under reflux for 2 h and then evaporated. The residual oil solidified giving the *adduct* (14a) as pale yellow needles (0.55 g, 65%), m.p. 121° (from light petroleum) (Found: C, 68.3; H, 5.2; N, 4.1. $C_{20}H_{17}NO_5$ requires C, 68.4; H, 4.8; N, 4.0%), $\lambda_{max.}$ (EtOH) 211, 220, 227, 235, and 274 nm (log ε 4.60, 4.41, 4.45, 4.42, and 4.17), $\nu_{max.}$ (KBr) 1 749, 1 707, and 1 630 cm⁻¹, τ (CDCl₃) 2.3—2.9 (8 H, m), 6.09 (3 H, s), 6.71 (3 H, s), and 7.56 (3 H, s).

Dimethyl 2'-ethyl-2',3'-dihydrofluorene-9-spiro-3'-isoxazole-4',5'-dicarboxylate (14b), prepared similarly from (1b) and dimethyl but-2-ynedioate (36%), had m.p. 109—111° (from benzene and light petroleum) (Found: C, 69.2; H, 5.3; N, 3.8. $C_{21}H_{19}NO_5$ requires C, 69.0; H, 5.2; N, 3.8%), $\nu_{max.}$ (KBr) 1 763, 1 720, and 1 640 cm⁻¹, τ (CDCl₃) 2.3—2.9 (8 H, m), 6.09 (3 H, s), 6.72 (3 H, s), 7.41 (2 H, q, *J* 7 Hz), and 9.07 (3 H, t, *J* 7 Hz).

Dimethyl 2',3'-dihydro-2'-isopropylfluorene-9-spiro-3'-isoxazole-4',5'-dicarboxylate (14c), prepared similarly from (1c) and dimethyl but-2-ynedioate, (81%), had m.p. 145° (from light petroleum)(Found: C, 69.5; H, 5.8; N, 3.7. $C_{22}H_{21}NO_5$ requires C, 69.7; H, 5.5; N, 3.7%), $\lambda_{max.}$ (EtOH) 212, 227, 234, and 274 nm (log ε 4.57, 4.36, 4.34, and 4.06), $\nu_{max.}$ (KBr) 1 753, 1 724, and 1 649 cm⁻¹, τ (CDCl₃) 2.2—2.8 (8 H, m), 6.10 (3 H, s), 6.59 (1 H, sept, *J* 7 Hz), 6.75 (3 H, s), and 9.27 (6 H, d, *J* 7 Hz).

trans-*Dimethyl 2'-Methylfluorene-9-spiro-3'-isoxazolidine-4',5'-dicarboxylate* (15a).—A mixture of the N-methyl nitrone (1a) (1 g), dimethyl fumarate (3 g), and xylene (10 ml) was boiled under reflux for 3 days. On cooling, dimethyl fumarate crystallised out. The filtrate was evaporated and the residue extracted with chloroform. Preparative t.l.c. separated the *adduct* (15a) (0.3 g, 18%), m.p. 100° (from light petroleum) (Found: *m/e*, 353.1 260. $C_{20}H_{19}NO_5$ requires M, 353.1261), $\lambda_{max.}$ (EtOH) 225, 232, 270, 283s, 296s, and 307 nm (log ε 4.38, 4.29, 4.14, 4.03, 3.53, and 3.15), $\nu_{max.}$ (KBr) 1 733 cm⁻¹, τ (CDCl₃) 2.2—2.8 (8 H, m), 4.58 (1 H, d, *J* 6 Hz), 5.50 (1 H, d, *J* 6 Hz), 6.07 (3 H, s), 6.88 (3 H, s), and 7.86 (3 H, s).

T.l.c. of the crude reaction mixture showed no trace of (15b).

cis-*Dimethyl 2'-Methylfluorene-9-spiro-3'-isoxazolidine-4',5'-dicarboxylate* (15b).—A mixture of the N-methyl nitrone (1a) (1 g), dimethyl maleate (2 g), and xylene (10 ml) was boiled for 2 days and then evaporated. The residual oil solidified slowly, and the solid was extracted with light petroleum (b.p. 40—60 °C) to remove the excess of dimethyl

maleate, leaving the *adduct* (15b) (0.7 g, 42%), m.p. 144° (from benzene and light petroleum) (Found: C, 67.9; H, 5.4; N, 4.0. $C_{20}H_{19}NO_5$ requires C, 68.0; H, 5.4; N, 4.0%), $\lambda_{max.}$ (EtOH) 225, 232, 270, 282s, 294s, and 305 nm (log ε 4.33 4.25, 4.06, 3.96, 3.45, and 3.01), $\nu_{max.}$ (KBr) 1 747 and 1 758 cm^{-1}, τ (CDCl$_3$) 2.1—2.8 (8 H, m), 4.88 (1 H, d, J 9 Hz), 5.62 (1 H, d, J 9 Hz), 6.12 (3 H, s), 6.93 (3 H, s), and 7.81 (3 H, s).

T.l.c. of the crude reaction mixture showed a trace of (15a) under u.v. light.

Reaction of the N-*Methyl Nitrone* (18) *with Methyl Acrylate.* —A mixture of the *N*-methyl nitrone (1a) (1 g), methyl acrylate (5 ml), and benzene (10 ml) was boiled for 2 h and then evaporated. The oily residue solidified on rubbing with light petroleum, and the solid was separated by preparative t.l.c. (silica; chloroform) into two components. The faster moving component was *methyl 2'-methylfluorene-9-spiro-3'-oxazolidine-5'-carboxylate* (17) (0.23 g, 16%), m.p. 117—119° (Found: *m/e*, 295.1198. $C_{18}H_{17}NO_3$ requires *M*, 295.1208), $\lambda_{max.}$ (EtOH) 224, 232, 261s, 270, 282s, 295, and 307 nm (log ε 4.35, 4.25, 4.14, 4.15, 4.04, 3.59, and 3.38), $\nu_{max.}$ (KBr)

1 747 cm^{-1}, τ (CDCl$_3$) 2.2—2.8 (8 H, m), 5.09 (1 H, t, J 7 Hz), 6.15 (3 H, s), 6.98br (2 H, d, J *ca.* 9 Hz), and 7.87 (3 H, s).

The slower moving component was *methyl 2'-methylfluorene-9-spiro-3'-oxazolidine-4'-carboxylate* (16a) (0.9 g, 64%), m.p. 99—100° (Found: *m/e* 295.1209, $C_{18}H_{17}NO_3$ requires *M*, 295.1209), $\lambda_{max.}$ (EtOH) 224, 232, 261, 270, 295s, and 307 nm (log ε 4.35, 4.25, 4.14, 4.15, 3.59, and 3.38), $\nu_{max.}$ (KBr) 1 747 cm^{-1}, τ (CDCl$_3$) 2.1—2.8 (8 H, m), 5.30 (1 H, dd, J 6 and 8 Hz), 5.61 (1 H, dd, J 8 and 9 H), 5.95 (1 H, dd, J 6 and 9 Hz), 6.95 (3 H, s), and 7.94 (3 H, s).

Reaction of the N-*Ethyl Nitrone* (1b) *with Methyl Acrylate.* —This reaction under conditions similar to those described above, gave *methyl 2'-ethylfluorene-9-spiro-3'-oxazolidine-5'-carboxylate* (16b) (38%), m.p. 106—108° (from light petroleum), τ (CDCl$_3$) 2.2—2.9 (8 H, m), 5.31 (1 H, dd, J 6 and 8 Hz), 5.60 (1 H, dd, J 8 and 9 Hz), 5.92 (1 H, dd, J 6 and 9 Hz), 6.93 (3 H, s), 7.5—8.2 (2 H, m), and 9.11 (3 H, t, J 7 Hz).