Cycloaddition Reactions of Quinoneimine *N*-Oxides and of Fluorenoneimine *N*-Oxide: Exocyclic Nitrones conjugated with Electron-withdrawing Rings

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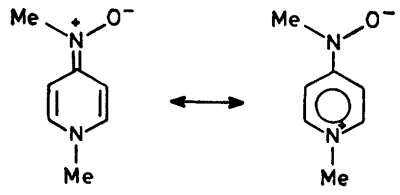
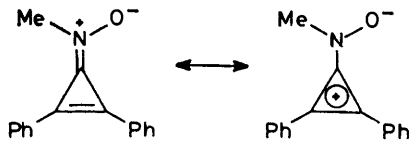
N-Phenyl-*p*-benzoquinoneimine *N*-oxide is generally unreactive in 1,3-dipolar cycloaddition reactions, but with acetylenedicarboxylate esters it gives indolones, formed from the initial adducts by a rearrangement which entails an alkoxycarbonyl migration. The analogous nitrone derived from anthraquinone gives unrearranged adducts with a variety of 1,3-dipolarophiles; monosubstituted alkynes and alkenes give 4-substituted-isoxazolines and -isoxazolidines. Fluorenoneimine *N*-oxide behaves similarly. We also describe some reactions of diphenylcyclopropenone which were performed in an attempt to prepare cyclopropenoneimine *N*-oxides.

THE nitrone group is capable of both electron donation (from the oxygen atom) and electron withdrawal (towards the nitrogen atom). It is therefore interesting to investigate the effect of conjugation with electron-withdrawing and electron-donating substituents on nitrone reactivity.

We have recently made unsuccessful attempts to prepare the nitrones (1) and (2), containing electron-donating substituents,[1] and while our work was in progress Houk reported an analogous nitrone (3) with a cycloheptatriene ring.[2]



(1)



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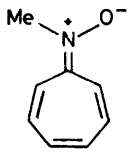
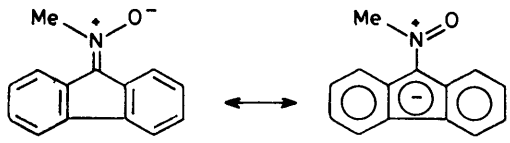


(3)

The preparation of nitrone (4) was reported by Taylor and his co-workers [3] in 1975. It provides an example of conjugation with an electron-withdrawing substituent, and we here describe some cycloaddition reactions of this compound. The quinoneimine oxide (5a) has been known for much longer [4,5] but its chemistry has been little studied. We have investigated its behaviour, and that of the anthraquinone analogue, in cycloaddition reactions, and have discovered an unusual and remarkable rearrangement.



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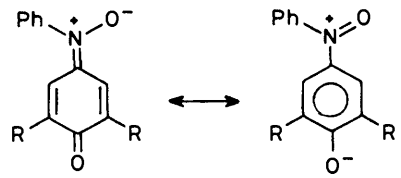


(5)

a; R = H
b; R = Me

RESULTS AND DISCUSSION

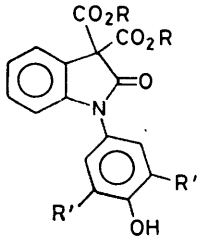
The quinoneimine oxide (5a), prepared by a two-stage oxidation of diphenylamine,[5] was very unreactive towards dipolarophiles. Acrylonitrile, methyl acrylate, maleic anhydride, phenyl isocyanate, and phenylpropiolic acid all failed to react, even after prolonged treatment. However, dimethyl acetylenedicarboxylate (DMAD) and the diethyl ester (DEAD) did react sluggishly to give 1 : 1 adducts. The structures of these adducts proved difficult to determine; in particular ^{1}H and ^{13}C n.m.r. spectroscopy indicated that the two alkyl groups from the ester were in equivalent environments in the adduct, and that the quinone ring became symmetrical about the 1,4-axis. The latter observation was confirmed by the behaviour of the dimethyl derivative (5b): the methyl groups are non-equivalent in this nitrone, but become equivalent in the adducts with DMAD and DEAD.

The structures were finally established by *X*-ray crystallography (for which we thank Professor T. J. King; details will be published separately). The adducts are the dihydroindolones (6)—(9), formed by a

1,2-shift of one of the alkoxycarbonyl groups. Such migrations are not unknown, but they are relatively uncommon (see *e.g.* ref. 6).

We have not established a mechanism for this reaction, but a reasonable possibility is indicated in the Scheme, in which the driving force for each step is either the aromatisation of one of the benzene rings or the opening of an anti-aromatic oxazine ring; one could envisage several possible variations on this mechanism.

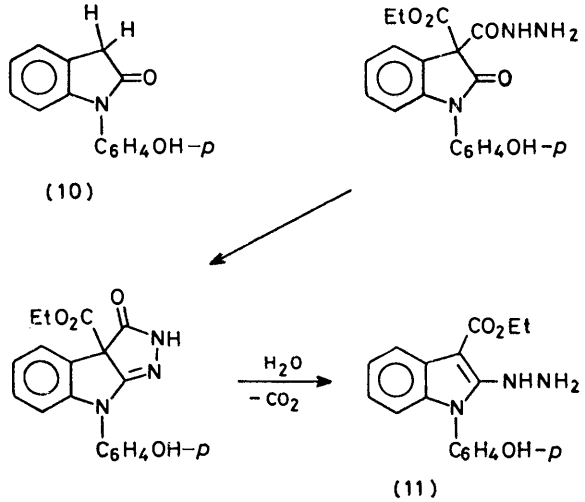
The dihydroindolone adducts (6)—(9) are relatively unreactive compounds. Vigorous hydrolysis of (6) or (7) under acidic or alkaline conditions is accompanied by decarboxylation to give the dihydroindolone (10) which could not be obtained analytically pure. The same compound is also formed by reduction of the adducts with sodium borohydride. Hydrazine reacted with adduct (7) to give the hydrazinoindole (11), perhaps by the route shown.



	R	R'
(6)	Me	H
(7)	Et	H
(8)	Me	Me
(9)	Et	Me

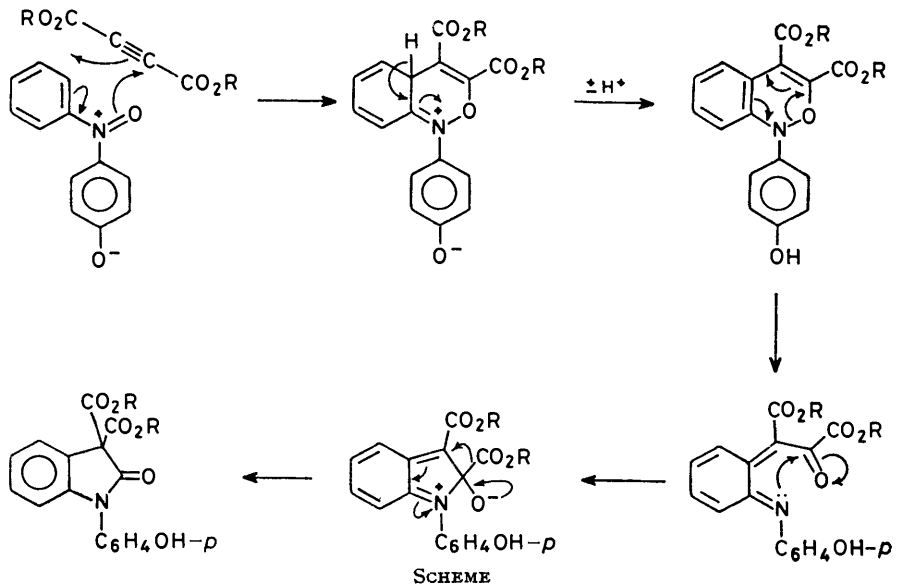
Compound (12), the anthraquinone analogue of nitrone (5a), was prepared by the reaction of diazoanthrone with nitrosobenzene. We were unable to obtain the yield of diazoanthrone reported in ref. 7, and found that an earlier (and simpler) synthesis, namely the reaction of toluene-*p*-sulphonyl azide with anthrone,[8] was preferable.

Nitrone (12) was more reactive towards dipolarophiles than was nitrone (5a); with DMAD it gave a simple cycloadduct (13) which did not rearrange, and cycloadducts were also formed with *N*-phenylmaleimide, acrylonitrile, and methyl acrylate. In the latter two reactions the adducts were 4-substituted isoxazolidines (14) (^{1}H n.m.r.). Phenyl isocyanate gave the expected oxadiazolidinone (15) together with a somewhat larger



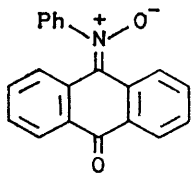
amount of a compound $C_{20}H_{15}N_3O_2$ (compare the starting nitrone $C_{20}H_{13}NO_2$) whose structure we have not yet been able to determine. Methyl propiolate gave a mixture of two compounds. One was anthraquinone, but the other could not be obtained free of anthraquinone as an impurity. I.r. and n.m.r. spectra indicated that it was the spiro-adduct (16), and microanalysis of the mixture was in accord with this. In particular, the i.r. spectrum closely resembled that of the DMAD adduct (13) save for the lack of a high-frequency ester band at 1 745 cm^{-1}, implying that the adduct (16) is the 4-substituted isoxazoline as shown. Nitrone (12) did not react with electron-donating dipolarophiles, such as dihydropyran.

The fluorene nitrone (4) behaved in much the same way



SCHEME

as the anthraquinone derivative (12), giving cycloadducts with DMAD, phenylpropiolic acid, *N*-phenylmaleimide, acrylonitrile, methyl acrylate, and phenyl isocyanate. With unsymmetrical dipolarophiles the regioselectivity was the same as with nitrone (12); thus acrylonitrile and methyl acrylate gave the 4-substituted isoxazolidines (17). This behaviour makes an interesting comparison with that of the troponeimine oxide (3); in that system the conjugation of the nitrone function with an electron-donating group shifts the regioselectivity towards the normally less-favoured 4-isomer.[2] In our compounds the same outcome follows from conjugation with electron-withdrawing substituents.



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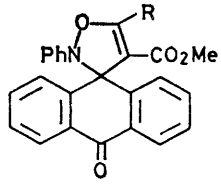
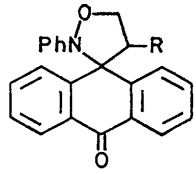
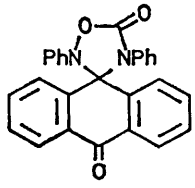


(13; R = CO_2Me)
(16; R = H)



(14)
a; R = CN
b; R = CO_2Me



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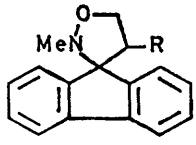

(17)
a; R = CN
b; R = CO_2Me

EXPERIMENTAL

Dimethyl 2,3-*Dihydro*-1-(4-*hydroxyphenyl*)-2-*oxo*-1H-*indole*-3,3-*dicarboxylate* (6).—*N*-Phenylbenzoquinoneimine *N*-oxide (prepared by the method of ref. 5 save that extraction with sodium hydroxide solution was used in the work-up in place of column chromatography) (1 g) was dissolved in chloroform (15 ml) and dimethyl acetylenedicarboxylate (1.13 g) was added. After 5 h heating under reflux the mixture was cooled and refrigerated overnight. The resulting precipitate was recrystallised from ethanol to give the *oxoindole* as white plates (0.9 g, 60%), m.p. 208—210 °C (Found: C, 62.9; H, 4.6; N, 4.2. $C_{18}H_{15}NO_6$ requires C, 63.3; H, 4.4; N, 4.1%); $\nu_{max.}$ (Nujol) 3 350, 1 765, 1 705, 1 610, 1 600, 1 205, and 750 cm^{-1}; δ_H ([$^2H_6$]-DMSO) 9.32 (s, 1 H), 7.6—6.6 (m, 8 H), and 3.80 (s, 6 H); δ_C ([$^2H_6$]acetone) 53.8 (q); *m/e* (%) 341 (100) (*M*), 340 (4), 297 (5) (*M* — CO_2), 282 (54) (*M* — MeOCO), 266 (5) (282 — O), 265 (6) (282 — OH), 254 (14) (282 — CO), 251 (10) (282 — MeO), 222 (16) (282 — MeOCHO), 211 (11), 210 (14), 196 (5), 195 (16), 194 (15), 167 (9), 166 (9), 159 (5), 139 (5), 113 (9), and 59 (8). Acetylation using acetic anhydride–acetic acid (1 : 3) gave *dimethyl* 1-(4-*acetoxyphenyl*)-2,3-*dihydro*-2-*oxo*-1H-*indole*-3,3-*dicarboxylate* (82%) as white plates from ethanol, m.p. 155—155.5 °C (Found: C, 62.4; H, 4.6; N, 3.7. $C_{20}H_{17}NO_7$ requires C, 62.7; H, 4.4; N, 3.7%); $\nu_{max.}$ (Nujol) 1 770, 1 740—1 720, 1 610, and 1 600 cm^{-1}; δ_H ($CDCl_3$) 7.7—6.8 (m, 8 H), 3.85 (s, 6 H), and 2.31 (s, 3 H). A similar reaction between the quinoneimine oxide and diethyl acetylenedicarboxylate gave *diethyl*-2,3-*dihydro*-1-(4-*hydroxyphenyl*)-2-*oxo*-1H-*indole*-3,3-*dicarboxylate* (7) as white plates from toluene (40%), m.p. 173.5—175 °C (Found: C, 65.2; H, 5.3; N, 4.1. $C_{20}H_{19}NO_6$ requires C, 65.0; H, 5.1; N, 3.8%); $\nu_{max.}$ (Nujol) 3 350, 1 760, 1 730, 1 705, 1 610, 1 600, and 760 cm^{-1}; δ_H ($CDCl_3$) 7.6—6.7 (m, 9 H), 4.30 (q, *J* 7 Hz, 4 H), and 1.30 (t, *J* 7 Hz, 6 H).

2,6-*Dimethyl*-N-*phenyl*-p-*benzoquinoneimine* N-*Oxide* (5b).—The imine [9] (3.5 g) in dichloromethane (10 ml) was oxidised by the dropwise addition of 3-chloroperoxybenzoic acid (3.5 g) in dichloromethane. After being stirred for 6 h at room temperature, the mixture was filtered, the filtrate washed with aqueous sodium hydroxide (0.2M, 50 ml) and water (2 × 25 ml), and then dried ($MgSO_4$). The solvent was removed under reduced pressure and the red residue was recrystallised from toluene to give the *imine* N-*oxide* (5b) as red needles (3.5 g, 97%), m.p. 192—192.5 °C (Found: C, 74.1; H, 5.9; N, 6.0. $C_{14}H_{13}NO_2$ requires C, 74.0; H, 5.7; N, 6.2%); $\nu_{max.}$ (Nujol) 1 600, 1 270, 780, and 700 cm^{-1}; δ_H ($CDCl_3$) 7.9 (m, 1 H), 7.5 (s, 5 H), 6.9 (m, 1 H), 2.15 (d, *J* 1 Hz, 3 H), and 1.95 (d, *J* 1 Hz, 3 H). In a manner similar to that described above, but with heating for only 2 h, were prepared *dimethyl* 2,3-*dihydro*-1-(4-*hydroxy*-3,5-*dimethylphenyl*)-2-*oxo*-1H-*indole*-3,3-*dicarboxylate* (8) (49%) as white plates from ethanol, m.p. 227—229 °C (Found: C, 64.8; H, 5.5; N, 3.85. $C_{20}H_{19}NO_6$ requires C, 65.0; H, 5.1; N, 3.8%); $\nu_{max.}$ (Nujol) 3 350, 1 765—1 745, 1 705, 1 610, and 765 cm^{-1}; δ_H ([$^2H_6$]DMSO) 8.7 (s, 1 H), 7.6—6.5 (m, 6 H),

3.78 (s, 6 H), and 2.25 (s, 6 H): and *diethyl*-2,3-*dihydro*-1-(4-*hydroxy*-3,5-*dimethylphenyl*)-2-*oxo*-1H-*indole*-3,3-*dicarboxylate* (9) (87%) as white plates from ethanol, m.p. 174—175 °C (Found: C, 66.4; H, 5.95; N, 3.6. $C_{22}H_{23}NO_6$ requires C, 66.5; H, 5.8; N, 3.5%); $\nu_{max.}$ (Nujol) 3 450, 1 755, 1 740, 1 705, 1 605, and 705 cm^{-1}; δ_H ($CDCl_3$) 7.5—6.6 (m, 6 H), 5.53 (s, 1 H), 4.25 (q, *J* 7 Hz, 4 H), 2.18 (s, 6 H), and 1.29 (t, *J* 7 Hz, 6 H).

1-(4-*Hydroxyphenyl*)-1H,3H-*indol*-2-*one* (10).—This compound was obtained from both adducts (6) and (7) under the following conditions: (*a*) hydrolysis using formic acid (98%) and methanesulphonic acid under reflux for 3 h; (*b*) hydrolysis with aqueous sodium hydroxide (30%) under reflux for 3 h; (*c*) reduction with sodium borohydride in ethanol under reflux for 3 h. It was also obtained from the acetate of adduct (6) with formic and methanesulphonic acids. In all these experiments 1-(4-*hydroxyphenyl*)-1H,3H-*indol*-2-*one* was obtained as white needles, subliming between 180 and 200 °C (1 mmHg) (Found: C, 74.0; H, 4.9; N, 6.2. $C_{14}H_{11}NO_2$ requires C, 74.6; H, 4.9; N, 6.2%); $\nu_{max.}$ (Nujol) 3 300—3 100, 1 690, 1 620, 1 600, 1 370, 820, and 750 cm^{-1}; δ_H ([$^2H_6$]DMSO) 7.4—6.7 (m, 9 H) and 3.70 (s, 2 H); *m/e* 225.

Ethyl 2-*Hydrazino*-1-(4-*hydroxyphenyl*)-1H-*indole*-3-*carboxylate* (11).—The adduct (7) (0.3 g) and hydrazine hydrate (50%, 0.2 g) in ethanol (2 ml) were refluxed for 2 h. The solvent was removed under reduced pressure and the oily residue was treated with ether (15 ml) and refrigerated overnight. The white precipitate which deposited was recrystallised from acetonitrile to give the *hydrazinoindole ester* as white needles (0.25 g, 89%), m.p. 125—127 °C (Found: C, 59.0; H, 6.1; N, 12.1. $C_{17}H_{17}N_3O_3 2H_2O$ requires C, 58.8; H, 6.1; N, 12.1%); $\nu_{max.}$ (Nujol) 3 400—2 400, 1 640, and 1 600 cm^{-1}; δ_H ([$^2H_6$DMSO) 7.5—6.5 (m, 8 H), 4.5—5.5 (NH and OH), 4.20 (q, 2 H), and 1.28 (t, 3 H).

Dimethyl 10-*Oxo*-2′-*phenylanthracene*-9(10H)-*spiro*-3′-(2′H)-*isoxazoline*-4′,5′-*dicarboxylate* (13).—A mixture of the anthraquinone nitrone (12) [7,8] (0.3 g) and dimethyl acetylenedicarboxylate (0.15 g) in chloroform (5 ml) was stirred at room temperature for 1 day. The solvent was removed under reduced pressure to leave a yellow oil, to which was added light petroleum (40—60 °C) (5 ml). The mixture was cooled in an ice-bath for 4 h, giving a yellow precipitate of the *spiro-adduct* which was recrystallised from ethanol to give a yellow powder (0.22 g, 75%), m.p. 138—140 °C (Found: C, 70.4; H, 4.4; N, 3.6. $C_{26}H_{19}NO_6$ requires C, 70.7; H, 4.3; N, 3.2%); $\nu_{max.}$ (Nujol) 1 745, 1 715, 1 675, 1 650, 1 600, and 1 320 cm^{-1}; δ_H ($CDCl_3$) 8.5—6.5 (m, 13 H), 4.05 (s, 3 H), and 3.35 (s, 3 H); δ_H ($CDCl_3$) 74.5 (s), 53.6 (q), and 51.7 (q). A similar reaction of nitrone (12) (0.2 g) with methyl propiolate (0.2 g) gave a white solid from which 9,10-anthraquinone could be sublimed, leaving a mixture of 9,10-anthraquinone and *methyl* 10-*oxo*-2′-*phenylanthracene*-9(10H)-*spiro*-3′(2′H)-*isoxazoline*-4′-*carboxylate* (16) [Found: C, 76.2; H, 4.6; N, 3.0. $C_{24}H_{17}NO_4$ (70%) + $C_{14}H_8O_2$ (30%) requires C, 76.3; H, 4.4; N, 3.0%]; $\nu_{max.}$ (Nujol) 1 720, 1 665, 1 630, 1 600, 1 320, 1 140, 1 125, and 1 100 cm^{-1}; δ_H ($CDCl_3$) 8.5—6.4 (m) and 3.4 (s) (areas, 5.9 : 1).

4′-*Cyano*-2′-*phenylanthracene*-9-*spiro*-3′-*isoxazolidin*-10-*one* (14a).—Anthraquinone nitrone (12) (0.5 g) in acrylonitrile (5 ml) was refluxed for 2 h. The reaction mixture was cooled and a polymeric residue was filtered off. The filtrate was concentrated under reduced pressure, and the resulting oil was treated with light petroleum (40—60 °C) (10 ml) to give a yellow precipitate. Crystallisation from ethanol gave the *spiro-isoxazolidine* (0.45 g, 80%) as pale yellow needles, m.p. 203.5—204.5 °C (decomp.) (Found: C, 78.7; H, 4.7; N, 8.0. $C_{23}H_{16}N_2O_2$ requires C, 78.4; H, 4.5; N, 8.0%); $\nu_{max.}$ (Nujol) 2 240, 1 665, 1 655, 1 600, 1 585, and 1 320 cm^{-1}; δ_H ($CDCl_3$) 8.5—6.4 (m, 13 H), 4.74 (t, *J* 4 Hz, 1 H), 4.56 (t, *J* 4 Hz, 1 H), and 4.02 (t, *J* 4 Hz, 1 H).

Methyl 10-*Oxo*-2′-*phenylanthracene*-9(10H)-*spiro*-3′-*isoxazolidine*-4′-*carboxylate* (14b).—This was prepared in a manner similar to that for nitrile (14a) using methyl acrylate to give the *spiro-isoxazolidine* (60%) as white needles from ethanol–light petroleum (40—60 °C), m.p. 136—137 °C (Found: C, 74.5; H, 5.2; N, 3.8. $C_{24}H_{19}NO_4$ requires C, 74.8; H, 4.9; N, 3.8%); $\nu_{max.}$ (Nujol) 1 725, 1 665, 1 605, 1 325, and 1 305 cm^{-1}; δ_H ($CDCl_3$) 8.5—6.4 (m, 13 H), 4.78 (t, *J* 4 Hz, 1 H), 4.53 (t, *J* 4 Hz, 1 H), 3.94 (t, *J* 4 Hz, 1 H), and 3.00 (s, 3 H).

2′,5′-*Diphenylanthracene*-9-*spiro*-3′-*perhydropyrrolo*-[3,4-d]*isoxazole*-4′,6′,9-*trione*.—This was prepared in a manner similar to that for nitrile (14a) using *N*-phenylmaleimide to give the *spiro-pyrroloisoxazole* (85%) as a white powder from toluene, m.p. 247—247.5 °C (decomp.) (Found: C, 76.3; H, 4.5; N, 5.75. $C_{30}H_{20}N_2O_4$ requires C, 76.3; H, 4.2; N, 5.9%); $\nu_{max.}$ (Nujol) 1 725, 1 670, 1 600, and 1 320 cm^{-1}; δ_H ($CDCl_3$) 8.5—6.6 (m, 18 H), 5.40 (d, *J* 8 Hz, 1 H), and 4.05 (d, *J* 8 Hz, 1 H).

2′,4′-*Diphenylanthracene*-9-*spiro*-3′-1′,2′,4′-*oxadiazolidine*-5′,10-*dione* (15).—This was prepared in a manner similar to that for nitrile (14a) using phenyl isocyanate and heating for 1 h to give the *spiro-oxadiazolidinone* (0.12 g, 30%) as white needles from ethanol–toluene, m.p. 218—220 °C (Found: C, 77.7; H, 4.5; N, 6.7. $C_{27}H_{18}N_2O_3$ requires C, 77.5; H, 4.3; N, 6.7%); $\nu_{max.}$ (Nujol) 1 770, 1 670, 1 600, 1 585, 1 320, and 1 220 cm^{-1}. The filtrate obtained after the addition of light petroleum was concentrated under reduced pressure, treated with a little ethanol, and cooled in ice to give a pale yellow precipitate which was crystallised from toluene to give long white needles (0.2 g) of a compound which analysed as $C_{20}H_{15}N_3O_2$ (Found: C, 73.3; H, 4.55; N, 13.1. $C_{20}H_{15}N_3O_2$ requires C, 73.0; H, 4.6; N, 12.8%), but whose structure remains uncertain: $\nu_{max.}$ (Nujol) 3 320—3 150, 1 650, 1 600, 1 550, 1 315, and 1 230 cm^{-1}; δ_H ($CDCl_3$) 8.30 (s) and 7.5—6.8 (m) (area ratio *ca.* 1 : 9).

N-*Fluorenylidenemethylamine* N-*Oxide* (4).—*N*-Phenylfluoreneimine [10] (1.25 g) was dissolved in methanol (50 ml) and cooled to 5 °C in an ice-bath. *N*-Methylhydroxylamine-*O*-sulphonic acid (0.7 g) was added slowly. The reaction mixture was stirred at 10 °C for 1 h and then extracted with dichloromethane (3 × 30 ml). The extracts were dried ($MgSO_4$) and concentrated under reduced pressure to give an oil, which was recrystallised from ethanol to give the nitrone as yellow needles (0.9 g, 90%), m.p. 145—146 °C (lit.,[3] 145—146 °C) (Found: C, 80.2; H, 5.3; N, 6.5. Calc. for $C_{14}H_{11}NO$: C, 80.4; H, 5.3; N, 6.7%).

Dimethyl 2′-*Methylfluorene*-9-*spiro*-3′(2′H)-*isoxazole*-4′,5′-*dicarboxylate*.—The fluorene nitrone (4) (0.3 g) was dissolved in chloroform (5 ml) and dimethyl acetylenedicarboxylate (0.5 g) was added. The reaction mixture was stirred at room temperature for 17 h and then concentrated under reduced pressure. The oily residue was treated with ethanol (0.5 ml) and light petroleum (40—60 °C), (5 ml) and refrigerated overnight. A white precipitate of the *spiro-isoxazoline* formed and was recrystallised from ethanol to give white needles (0.4 g, 80%), m.p. 124—125 °C (Found: C, 68.3; H, 5.0; N, 3.9. $C_{20}H_{17}NO_5$ requires C

68.4; H, 4.8; N, 4.0%); $\nu_{max.}$ (Nujol) 1 725, 1 700—1 670, and 1 600 cm^{-1}; δ_H ($CDCl_3$) 7.8—7.2 (m, 8 H), 3.95 (s, 3 H), 3.33 (s, 3 H), and 2.48 (s, 3 H).

2'-Methyl-5'-phenylfluorene-9-spiro-3'-(2'H)-isoxazole-4'-carboxylic Acid.—The fluorene nitrone (4) (0.3 g) was dissolved in xylene (10 ml) and phenylpropiolic acid (0.25 g) was added. The mixture was refluxed for 1 h. Subsequent treatment as above gave the *spiro-isoxazoline* (0.12 g, 24%) as white plates from ethanol, m.p. 195—197 °C (Found: C, 77.7; H, 4.8; N, 3.8. $C_{23}H_{17}NO_3$ requires C, 77.7; H, 4.8; N, 3.9%); $\nu_{max.}$ (Nujol) 3 600—2 400; 1 665, 1 620, and 1 600 cm^{-1}; δ_H ($CDCl_3$) 7.8—7.1 (m, 13 H) and 2.36 (s, 3 H).

2'-Methyl-5'-phenylfluorene-9-spiro-3'-perhydropyrrolo-[3,4-d]isoxazole-4',6'-dione.—This was prepared in a similar manner, using *N*-phenylmaleimide and with heating for 4 h. The *spiro-pyrroloisoxazole* was obtained from toluene as a white powder (67%), m.p. 178—179 °C (Found: C, 75.7; H, 5.0; N, 7.0. $C_{24}H_{18}N_2O_3$ requires C, 75.4; H, 4.7; N, 7.3%); $\nu_{max.}$ (Nujol) 1 720—1 680 cm^{-1}; δ_H ($CDCl_3$) 7.8—7.0 (m, 13 H), 5.25 (d, *J* 8 Hz, 1 H), 3.90 (d, *J* 8 Hz, 1 H), and 2.20 (s, 3 H).

4'-Cyano-2'-methylfluorene-9-spiro-3'-isoxazolidine (17a).—This was prepared in a similar manner, using acrylonitrile as solvent and dipolarophile, and with heating for 1 h. The *spiro-isoxazolidine* was recrystallised from ethanol as white needles (50%), m.p. 145—146 °C (Found: C, 77.7; H, 5.5; N, 10.5. $C_{17}H_{14}N_2O$ requires C, 77.9; H, 5.3; N, 10.7%); $\nu_{max.}$ (Nujol) 2 250, 1 620, and 1 300 cm^{-1}; δ_H ($CDCl_3$) 7.8—7.3 (m, 8 H), 4.56, 4.36, 3.94 (ABX: J_{AB} 8, J_{AX} 10, J_{BX} 6 Hz), and 2.15 (s, 3 H).

Methyl 2'-Methylfluorene-9-spiro-3'-isoxazolidine-4'-carboxylate (17b).—This was prepared in a similar manner, using methyl acrylate as solvent and dipolarophile, and with heating for 5.5 h. The *spiro-isoxazolidine* was obtained after several recrystallisations from ethanol as white needles (41%), m.p. 96—98 °C (Found: C, 73.4; H, 5.75; N, 4.8. $C_{18}H_{17}NO_3$ requires C, 73.2; H, 5.8; N, 4.7%); $\nu_{max.}$ (Nujol) 1 705 cm^{-1}; δ_H ($CDCl_3$) 7.8—7.2 (m, 8 H), 4.9—3.9 (m, 3 H), 3.10 (s, 3 H), and 2.10 (s, 3 H).

2'-Methyl-4'-phenylfluorene-9-spiro-3'-1',2',4'-oxadiazolidin-5'-one.—This was prepared in a similar manner using phenyl isocyanate as solvent and dipolarophile and with heating for 6 h. The *spiro-oxadiazolidinone* was obtained from ethanol as white needles (64%), m.p. 139—141 °C (Found: C, 76.8; H, 5.05; N, 8.7. $C_{21}H_{16}N_2O_2$ requires C, 76.8; H, 4.9; N, 8.5%); $\nu_{max.}$ (Nujol) 1 780—1 750 cm^{-1}; δ_H ($CDCl_3$) 7.8—7.2 (m, 8 H), 7.0 (m, 5 H), and 2.49 (s, 3 H); δ_C ($CDCl_3$) 155.0 (s), 140.0 (s), 138.0 (s), 134.0 (s) 131.0 (d), 128.6 (d), 128.0 (d), 126.4 (d), 126.0 (d), 124.1 (d), 120.0 (d), 92.0 (s), and 38.0 (q).

Some Reactions of Diphenylcyclopropenone.—*2-Methyl-4,5-diphenyl-3-isoxazolone.* Sodium metal (1 g) was dissolved in methanol (10 ml) and to this was added a solution of *N*-methylhydroxylammonium chloride (3.7 g) in methanol (11 ml); the precipitate of sodium chloride was filtered off. The resulting solution (5 ml) was added to a stirred solution of diphenylcyclopropenone [11] (1 g) in methanol (5 ml). The temperature rose and the solution changed from yellow to colourless. The solution was stirred overnight and the solvent was then removed under reduced pressure. The oily residue was dissolved in light petroleum (40—60 °C) and absolute ethanol, and the precipitate which formed was recrystallised from cyclohexane to give the *isoxazolone* as white plates (0.5 g, 42%), m.p. 107—109 °C (Found: C, 76.0; H, 5.3; N, 5.7. $C_{16}H_{13}NO_2$ requires C, 76.4; H, 5.3; N, 5.7%); $\nu_{max.}$ (Nujol) 1 670, 770, and 695 cm^{-1}; δ_H ($CDCl_3$) 7.5 (s, 10 H), and 3.80 (s, 3 H). [The isomeric 5-isoxazolone has been reported [12] to have m.p. 92 °C or 102—104 °C, and would be expected [13] to have $\nu_{C=O} > 1\ 700$ cm^{-1}.]

N-Methyl-2,3-diphenylcyclopropeneiminiosulphate. A solution of diphenylcyclopropenone (1 g) in methanol (10 ml) was added to a solution of *N*-methylhydroxylamine-*O*-sulphonic acid (0.5 g) in methanol (15 ml). The white precipitate which formed was washed with hot toluene and filtered to give the *zwitterionic product* as a white powder (0.8 g, 53%). Attempts to recrystallise the compound from methanol or ethanol led to decomposition to diphenylcyclopropenone. The crude product had m.p. 243—245 °C (decomp.) (Found: C, 59.7; H, 4.45; N, 4.5; S, 10.25. $C_{16}H_{13}NO_4S$ requires C, 60.9; H, 4.1; N, 4.4; S, 10.2%); $\nu_{max.}$ (Nujol) 1 910, 1 280, and 1 055 cm^{-1}.

N-Benzyl-2,3-diphenylacrylamide. Benzylamine (0.5 g) was added to diphenylcyclopropenone (1 g) in methanol (10 ml). The mixture was stirred at room temperature overnight. The solvent was removed under reduced pressure and the oily residue was dissolved in light petroleum (40—60 °C) (5 ml) with a few drops of ethanol. The solution was cooled in ice and a pale yellow precipitate formed. Recrystallisation from cyclohexane gave the *acrylamide* as white needles (1 g, 67%), m.p. 129—131 °C (Found: C, 84.1; H, 6.1; N, 4.6. $C_{22}H_{19}NO$ requires C, 84.3; H, 6.1; N, 4.5%); $\nu_{max.}$ (Nujol) 3 330, 1 660, and 1 615 cm^{-1}; δ_H ($CDCl_3$) 7.88 (s, 1 H), 7.4—6.9 (m, 15 H), 5.8 (br, 1 H), and 4.49 (d, *J* 6 Hz, 2 H). [The singlet at δ 7.88 suggests that the compound is the *E*-isomer (phenyl groups mutually *cis*) with the vinyl hydrogen strongly deshielded by the adjacent carbonyl group.]

N-p-Nitrophenyl-2,3-diphenylcyclopropeneiminium toluene-p-sulphonate. Toluene-*p*-sulphonic acid (1 g) was added to diphenylcyclopropenone (1 g) and *p*-nitroaniline (1 g). The mixture was refluxed for 3 h, during which time a pale yellow precipitate formed. Recrystallisation from methanol gave the *iminium tosylate* as pale yellow needles (2.2 g, 92%), m.p. 242—244 °C (Found: C, 67.4; H, 4.7; N, 5.7; S, 6.3. $C_{28}H_{22}N_2O_5S$ requires C, 67.5; H, 4.4; N, 5.6; S, 6.4%); $\nu_{max.}$ (Nujol) 1 880 (br), 1 620, 1 600, and 1 340 cm^{-1}; δ_H ([$^2H_6$]DMSO) 8.1—7.5 (m, 15 H), 7.17 (d, *J* 9 Hz, 2 H), 6.63 (d, *J* 9 Hz, 2 H), and 2.30 (s, 3 H). Neutralisation of the salt, using either triethylamine or sodium carbonate, gave *N-p*-nitrophenylcyclopropeneimine, m.p. 162—164 °C (lit.,[14] 163—163.5 °C); addition of toluene-*p*-sulphonic acid to this did not re-form the salt but led to decomposition.

NN',2,3-Tetraphenylacrylamidine. Aniline (1 g) and toluene-*p*-sulphonic acid (0.2 g) were added to a solution of diphenylcyclopropenone (1 g) in dry benzene (25 ml). The mixture was refluxed for 4 h, turning deep red. The solvent was removed under reduced pressure and the oily residue dissolved in absolute ethanol (20 ml) and light petroleum (40—60 °C) (5 ml). The solution was cooled in ice and a brown precipitate formed. Several recrystallisations from ethanol gave the *acrylamidine* as yellow needles (0.7 g, 50%), m.p. 161—163 °C (Found: C, 86.7; H, 6.0; N, 7.45. $C_{27}H_{22}N_2$ requires C, 86.6; H, 5.85; N, 7.5%); $\nu_{max.}$ (Nujol) 3 300, 1 615, and 1 595 cm^{-1}; δ_H ($CDCl_3$) 7.65 (br, 1 H), 7.3—6.5 (m, 20 H), and 6.20 (s, 1 H).

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REFERENCES

[1] N. Grzeskowiak, M.Sc. dissertation, University of East Anglia, 1977; J. A. Damavandy, Ph.D. thesis, University of East Anglia, 1978. [Some of this work is described in the reactions of diphenylcyclopropenone at the end of this paper.]
[2] D. Mukherjee, L. N. Domelsmith, and K. N. Houk, *J. Amer. Chem. Soc.*, 1978, **100**, 1954.
[3] R. N. Pratt, D. P. Stockes, and G. A. Taylor, *J.C.S. Perkin I*, 1975, 498.
[4] H. Wieland and K. Roth, *Ber.*, 1920, **53**, 210; H. J. Teuber and G. Staiger, *Chem. Ber.*, 1954, **87**. 1251.
[5] C. J. Pedersen, *J. Amer. Chem. Soc.*, 1957, **79**, 5014.
[6] J. N. Marx, J. C. Argyle, and L. R. Norman, *J. Amer. Chem. Soc.*, 1974, **96**, 2121; R. M. Acheson, *Accounts Chem. Res.*, 1971, **4**, 177; R. M. Acheson and R. F. Flowerday, *J.C.S. Perkin I*, 1974, 2339.
[7] J. C. Fleming and H. Shechter, *J. Org. Chem.*, 1969, **34**, 3962.
[8] M. Regitz, *Chem. Ber.*, 1964, **97**, 2742.
[9] W. Ried and H. Niedhardt, *Chem. Ber.*, 1961, **94**, 373.
[10] G. Reddelien, *Ber.*, 1910, **43**, 2476.
[11] R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Posner, *J. Amer. Chem. Soc.*, 1965, **87**, 1320.
[12] E. P. Kohler and A. H. Blatt, *J. Amer. Chem. Soc.*, 1928, **50**, 504; F. De Sarlo, L. Fabrini, and G. Renzi, *Tetrahedron*, 1966, **22**, 2989.
[13] A. J. Boulton and A. R. Katritzky, *Tetrahedron*, 1961, **12**, 41.
[14] T. Eicher and G. Frenzel, *Z. Naturforsch.*, 1965, **20B**, 274.