# Ketene. Part 23.[1] Conformational Control of the Addition Reactions of Ketenes with *N*-Phenylnitrones

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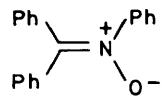
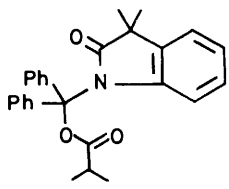
*X*-Ray analysis shows that the nitrone group in (**5a**) is not distorted, disproving a previous explanation for the formation of oxazolidinones rather than indolones in the reactions with ketenes. Nitrone (**5c**) reacts with dimethylketene and diphenylketene to form oxazolidinones (**6c,d**) whereas nitrones (**5d**) and (**5e**) under similar conditions form indolone derivatives (**9**). Oxazolidinone formation by the reaction of ketenes with nitrones (**5a—c**) results from restricted rotation about the *N*-phenyl bond preventing the [3,3]-migration (**3**) ⟶ (**4**), which precedes indolone formation.

The reactions of ketenes with *N*-phenyl nitrones are known to proceed by either of two mutually exclusive pathways giving either indolones or oxazolidinones as the major products. In the examples so far studied no one reaction gives both of these types of adduct, and the factors influencing the choice of reaction path have, hitherto, been unknown.

In a study of ketene additions to a set of constitutionally related *N*-phenyl nitrones we have shown that triphenylnitrone (**1**) reacts with diphenylketene and dimethylketene to give indolones of part-structure (**2**)[2] and this reaction pathway, with



(**1**)



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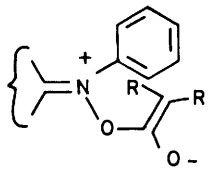
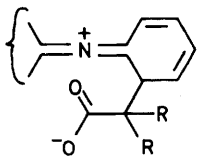
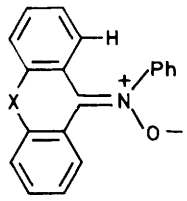


(**3**)



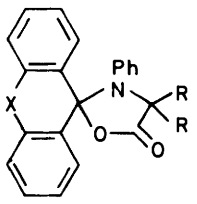
(**4**)

some minor variations[3,4] is shown by all the known reactions of *C,N*-diphenylnitrone with ketenes.[4–7] The characteristic step of this class of reactions is the Claisen-type rearrangement of the initially formed intermediate (**3**) to give substitution at the *ortho*-position of the *N*-phenyl group (**4**). The alternative reaction pathway leading to oxazolidinones is followed when the reaction involves the nitrones (**5a,b**) and gives products of structure (**6a,b**).[2,8] In a previous investigation[2] it was suggested that the differences in behaviour between (**1**) and (**5a**), which differ only in the presence of a bond linking the two geminal phenyl groups in (**1**), might be related to differences in the ground state polarisation of the nitrone group in these two compounds. However the discovery that (**5b**) reacts in the same way as (**5a**) disproved this hypothesis. Two other explanations were considered, either that steric interactions in (**5a**) and (**5b**) distort the nitrone group from planarity, or that the additional



(**5**)

**a**; X = bond
**b**; X = O
**c**; X = $CMe_2$
**d**; X = $CH_2CH_2$
**e**; X = CH=CH



(**6**)

**a**; X = bond
**b**; X = O
**c**; X = $CMe_2$, R = Me
**d**; X = $CMe_2$, R = Ph
**e**; X = bond, R = Ph

conjugation between the two aromatic rings in (**5a,b**) changes the frontier orbital energies in those sections of the molecules such that they compete with the frontier orbitals of the *N*-phenyl substituents for the migrating group.

In order to test the steric proposal, an *X*-ray crystallographic study of the two nitrones (**1**) and (**5a**) was undertaken. The *X*-ray structure of triphenylnitrone has been reported previously,[9] but it was thought worthwhile to repeat this. In the event, the *X*-ray structures of (**1**) and (**5a**) were readily determined using the direct methods SHELX program. The structures are shown in Figures 1 and 2 while relevant bond lengths and angles are contained in Table 1; bond lengths and angles of the aromatic residues in both molecules are unexceptional and have thus not been indicated. The results obtained in the present study of (**1**) agree closely with those obtained before.[9] The main difference in structural terms between the two nitrones (**1**) and (**5a**) is shown at the *N*-phenyl bond. The torsion angles O(1)–N(1)–C(14)–C(15) are 67.1° for triphenylnitrone (**1**) and 90.2° in the case of the fluorenylidene compound (**5a**). The reason for this difference resides in the planarity of the fluorene residue which causes all relief of steric compression about the nitrone functional group in (**5a**) to be concentrated in twisting about the *N*-phenyl bond. In the case of triphenylnitrone (**1**) this relief may be shared by twisting about the two phenyl–C(7) bonds, and the

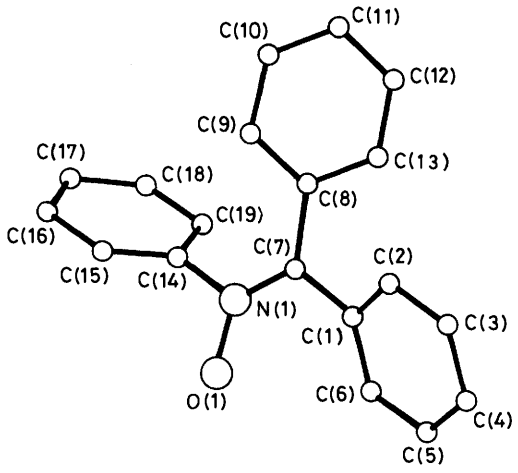



**Figure 1.** The molecular structure of triphenylnitrone (**1**)

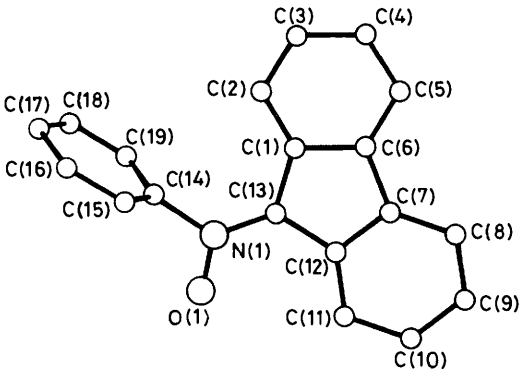



**Figure 2.** The molecular structure of compound (**5a**)

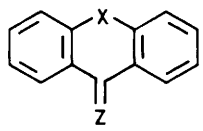
**Table 1.** Selected bond lengths (Å), bond angles (°) and torsion angles (°) for the two nitrones, triphenylnitrone (**1**) and *N*-fluoren-9-ylidenephenylamine *N*-oxide (**5a**), standard deviations in parentheses

| Compound (**1**) | | Compound (**5a**) | |
|---|---|---|---|
| N(1)–O(1) | 1.306(4) | N(1)–O(1) | 1.287(4) |
| N(1)–C(14) | 1.450(6) | N(1)–C(14) | 1.455(5) |
| N(1)–C(7) | 1.311(5) | N(1)–C(13) | 1.311(5) |
| C(7)–C(8) | 1.483(6) | C(13)–C(1) | 1.464(5) |
| C(7)–C(1) | 1.469(6) | C(13)–C(12) | 1.457(5) |
| O(1)–N(1)–C(14) | 111.8(4) | O(1)–N(1)–C(14) | 114.4(3) |
| O(1)–N(1)–C(7) | 125.1(4) | O(1)–N(1)–C(13) | 123.3(3) |
| C(14)–N(1)–C(7) | 123.1(4) | C(14)–N(1)–C(13) | 122.4(3) |
| N(1)–C(7)–C(1) | 121.0(4) | N(1)–C(13)–C(1) | 128.2(4) |
| N(1)–C(7)–C(8) | 119.7(4) | N(1)–C(13)–C(12) | 123.8(3) |
| C(1)–C(7)–C(8) | 119.3(4) | C(1)–C(13)–C(12) | 108.0(3) |
| O(1)–N(1)–C(14)–C(15) | 67.1 | O(1)–N(1)–C(14)–C(15) | 90.2 |
| O(1)–N(1)–C(14)–C(19) | −109.8 | O(1)–N(1)–C(14)–C(19) | −86.3 |
| O(1)–N(1)–C(7)–C(8) | −178.1 | O(1)–N(1)–C(13)–C(1) | 177.0 |
| O(1)–N(1)–C(7)–C(1) | 1.6 | O(1)–N(1)–C(13)–C(12) | −1.0 |
| N(1)–C(7)–C(8)–C(9) | 58.8 | C(11)–C(12)–C(13)–N(1) | −5.2 |
| N(1)–C(7)–C(8)–C(13) | −123.5 | C(2)–C(1)–C(13)–N(1) | 1.0 |
| C(6)–C(1)–C(7)–N(1) | 32.7 | C(6)–C(1)–C(13)–N(1) | −177.0 |
| C(2)–C(1)–C(7)–N(1) | 149.7 | C(7)–C(12)–C(13)–N(1) | 177.1 |

molecule can adopt a propeller-like conformation. Amplification of this point may be obtained by reference to Table 1 which contains torsion angles for the relevant portions of the two molecules.

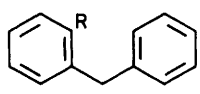
Following these results, a study of molecular models showed that if the rearrangement (**3**) ⟶ (**4**) occurred *via* a chair-shaped conformation[10] which would enable the interacting terminal atoms to achieve the closest approach prior to commencement of bonding, this would require a dihedral angle of *ca.* 45° between the planes of the *N*-phenyl and nitrone groups. In the case of the zwitterion (**3**) derived from (**5a**) such a conformation involves a very close approach between one of the *ortho* carbon atoms of the *N*-phenyl group and the nearby hydrogen atom on the large, planar, aromatic system [indicated in (**5**)]. In the corresponding reaction of (**1**), free rotation about C–Ph bonds will relieve this congestion.

The way in which the nitrone (**5c**) reacts with ketenes appeared to provide a test which would distinguish between the explanations based on frontier orbital energies and restriction of rotational freedom about the *N*-phenyl bond. The route chosen to synthesize (**5c**) was *via* the dimethylanthrone (**7a**). It has been reported[11] that treatment of the tertiary alcohol (**8a**) with 70% aqueous sulphuric acid at 100 °C gives the dimethyldihydroanthracene (**7b**) contaminated by the alkene (**8b**). However the reported method of purification of (**7b**) by vacuum distillation and thick layer chromatography appeared inconvenient for the preparation of (**7b**) in quantity. The same authors also reported that oxidation of (**7b**) with chromium trioxide gave (**7a**), but again separation from products of further oxidation was difficult. It seemed to us that under the conditions described for converting (**8a**) into (**7b**) and (**8b**) these products should be in equilibrium *via* the cation (**8c**) and that the major product (**7b**) should be thermodynamically preferred. We have confirmed that at 100 °C this reaction forms a small amount of (**8b**). However, when the reaction was conducted for a prolonged period at room temperature, (**7b**) was formed cleanly in very high yield, and none of the olefin (**8b**) could be detected in the crude product by $^1$H n.m.r. spectroscopy.




(**7**)

**a**; X = $CMe_2$ Z = O
**b**; X = $CMe_2$ Z = $H_2$
**c**; X = $CMe_2$ Z = $Br_2$
**d**; X = $CMe_2$ Z = $NNH_2$
**e**; X = $CH_2CH_2$ Z = O
**f**; X = $CH_2CH_2$ Z = $NNH_2$
**g**; X = $CH_2CH_2$ Z = NPh
**h**; X = CH=CH Z = O
**i**; X = CH=CH Z = $NNH_2$




(**8**)

**a**; R = $CMe_2OH$
**b**; R = $CMe=CH_2$
**c**; R = $\overset{+}{C}Me_2$

Oxidation of (**7b**) to (**7a**) was achieved *via* photochemical bromination. It was expected that the dibromo derivative (**7c**) would be isolated and could, subsequently, be hydrolysed to (**7a**). However, in the event this hydrolysis occurred spontaneously during the work-up of the reaction mixture from the bromination step giving cleanly, a good yield of the ketone (**7a**). This ketone was then converted into the corresponding

hydrazone (**7d**) employing Nagata and Itazaki's procedure,[12] and this was then oxidised by mercuric oxide to the diazo compound which was treated with nitrosobenzene to form the nitrone (**5c**).

The reaction of this nitrone with dimethylketene gave a 1:1 adduct in rather low yield, whose spectroscopic properties were clearly consistent with the structure (**6c**). The i.r. absorption at 1 780 $cm^{-1}$ compared well with those in the spectra of other oxazolidinones,[2,13,14] the presence of signals due to 13 aromatic protons in the $^1H$ n.m.r. spectrum showed that the *N*-phenyl group had not been modified, and in the mass spectrum the base peak at *m/z* 133 and a very strong peak at *m/z* 118 corresponded to $(PhNCMe_2)^+$ and $(PhNCMe)^+$. Analogous peaks are characteristically strong in the mass spectra of other oxazolidinones obtained from the reactions of ketenes with nitrones.[2,13] In addition to this adduct a low yield of dimethylanthrone was obtained, and also a trace of a compound for which the molecular formula $C_{30}H_{31}NO_4$ was established by high resolution mass spectrometry. It proved impossible to characterize this compound fully. However, its molecular formula corresponded to a combination of one molecule of the nitrone, two of the ketene, and one oxygen atom. The reaction of pyridine *N*-oxide with dimethylketene gave a product with an allied composition,[15] which appeared to be formed by capture of an α-lactone arising from the oxidation of the ketene by the *N*-oxide.

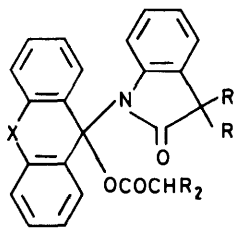
The nitrone (**5c**) reacted with diphenylketene in benzene to give a 1:1 adduct in high yield, and this compound also appeared to have an oxazolidinone structure (**6d**). Like the related adduct (**6e**) of (**5a**) and diphenylketene, this compound was unstable and solutions decomposed on warming to give a dark green colour which we assume to be an ylide such as is formed by loss of carbon dioxide from (**6e**).[2,14] It did not prove possible to purify this compound by recrystallisation, and analytical and spectroscopic data were obtained on crude material. The i.r. and $^1H$ n.m.r. spectra were consistent with structure (**6d**), and though the mass spectrum showed no parent peak at *m/z* 507, prominent peaks occurred at *m/z* 463 $(M^+ - CO_2)$, 386 $(M^+ - CO_2 - Ph)$, 257 $(Ph\overset{+}{N}CPh_2)$, and 180 $(Ph\overset{+}{N}CPh)$, compatible with fragmentation of structure (**6d**).

From these results we infer that electronic differences are probably not responsible for the difference in reaction pathway between (**1**) and (**5a—c**), leaving the explanation based on conformational restriction. To check this, we examined the behaviour of the two *N*-phenylnitrones (**5d**) and (**5e**). Although at first sight these may appear to differ substantially in the conjugation between the aromatic rings, the u.v. spectra of the corresponding ketones are very closely similar,[16] the lowest frequency absorptions being at $\lambda_{max.}$(EtOH) 350 (log ε 2.8) and 352 nm (3.55) respectively. These values of $\lambda_{max.}$ are intermediate between the corresponding values for fluorenone and benzophenone.[16] The major change in going from (**5c**) to (**5d**) is that introduction of another carbon atom into the bridge between the two aromatic rings produces a significant decrease in the dihedral angle between the planes of these two rings. The *N*-phenyl group is thereby moved away from the obstructing hydrogen atom and achieves greater freedom of rotation about the N–Ph bond. By contrast, the change from (**5a**) to (**5c**) produces a very small change in the dihedral angle between the planes of the aromatic rings and the conformational restraints in (**5a**) do not appear (from studies of molecular models) to be much reduced in (**5c**). The substitution of the unsaturated bridge in (**5e**) for the $CH_2CH_2$ group in (**5d**) makes a further small decrease in the dihedral angle.

The nitrones (**5d**) and (**5e**) were synthesized from the readily available ketones (**7e**) and (**7h**)[17] by routes similar to that used to prepare (**5c**). The reaction of nitrone (**5d**) with dimethylketene gave a mixture of two products, of which the major component was a substance which proved impossible to purify by recrystallisation. Nevertheless, it was possible to obtain it in a reasonable degree of purity by washing with ether. Analytical results were consistent with an adduct of two molecules of the ketene with one of the nitrone and the spectroscopic properties indicated the indolone structure (**9a**), with two carbonyl absorptions in the i.r. and $^{13}C$ n.m.r. spectra. The mass spectrum showed only rather weak peaks at high *m/z* values but significant peaks occur at $(M - 71)^+$ (loss of $Me_2CHCO$) and $(M - 87)^+$ (loss of $Me_2CHCO_2$), and a strong peak at *m/z* 161 corresponds to the molecular ion of 3,3-dimethylindol-2-one. Acidic hydrolysis of this compound confirmed the structural assignment by giving 3,3-dimethylindol-2-one and the ketone (**7e**), and presumably isobutyric acid, though this was not isolated.

The second product of the reaction was identified as the anil (**7g**) from analytical and spectroscopic data. Together the isolated yields of these two compounds account virtually quantitatively for the fate of the nitrone used. It was initially surprising that the anil (**7g**) did not react with the excess of dimethylketene to form an azetidinone, but inspection of models shows that approach to the π-orbitals of the C=N group is severely hindered either by the hydrogen atoms in the *peri*-positions or by the transannular methylene groups. Had the azetidinone been formed by a process commencing with attack on the apparently less hindered lone pair of the nitrogen atom, then there would have been very severe steric interaction between the substituents on the four-membered ring and the $CH_2CH_2$ bridge. Attempts to convert the ketone (**7e**) into the anil (**7g**) by conventional methods were unsuccessful. An attempted reaction between (**7e**) and aniline in the presence of zinc chloride failed as also did attempts to proceed by conversion of (**7e**) into the *gem*-dichloro derivative using either phosphorus pentachloride or oxalyl chloride.

The reaction of the nitrone (**5d**) with diphenylketene also gave a high yield of an adduct which could not be purified by conventional procedures, and was identified as the indolone derivative (**9b**) largely on the basis of acidic hydrolysis to ketone (**7e**), 3,3-diphenylindol-2-one, and diphenylethanoic acid. No anil (**7g**) was isolated in this case.




(**9**)

a; X = $CH_2CH_2$ R = Me
b; X = $CH_2CH_2$ R = Ph
c; X = CH=CH R = Me
d; X = CH=CH R = Ph

The nitrone (**5e**) reacted with both dimethylketene and diphenylketene to give high yields of the indolones (**9c,d**) respectively. In these cases no anil corresponding to (**7g**) was isolated. Neither of the indolones (**9c**) nor (**9d**) could be recrystallised and the spectroscopic characterisation was carried out on ether-washed crude materials for which acceptable analyses were obtained. Confirmation of the assigned structures was obtained by hydrolysis, which gave the ketone (**7h**), the appropriate 3,3-disubstituted indolone, and, in the case of (**9d**), diphenylethanoic acid.

In conclusion, these results appear to indicate that the marked differences in the products of reaction of ketenes with nitrones (**5a—c**) on the one hand and nitrones (**1d, e** and **5d, e**)

on the other arise from restricted rotation about the *N*-phenyl bond in the former group, which prevents the intermediate species in these cases adopting conformations favourable for the Claisen-like rearrangement (**3**) ⟶ (**4**) which is an essential stage in the formation of the indolones (**2**). The mechanistic details of the pathway by which the zwitterions (**3**) form the oxazolidinones (**6**) are still unknown.

## 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 Bruker AM250 spectrometer, and i.r. spectra with a Perkin-Elmer 457 spectrometer. Mass spectra were measured with Kratos MS25 and MS80 spectrometers. Diphenylketene was prepared by pyrolysis of benzoylphenyldiazomethane[18] and dimethylketene was prepared by pyrolysis of tetramethylcyclobutane-1,3-dione in a modified version of Johnson and Witzel's apparatus,[19] and used without further purification. Ether refers to diethyl ether.

2-(2-*Benzylphenyl*)*propan*-2-*ol* (**8a**).—This compound was prepared by the reaction of methylmagnesium iodide with methyl 2-benzylbenzoate in diethyl ether, m.p. 66—67 °C (from light petroleum b.p. 40—60 °C) (lit.,[11] 66—67 °C).

9,9-*Dimethyl*-9,10-*dihydroanthracene* (**7b**).—Aqueous sulphuric acid (100 ml; 70%) was cooled in ice and the alcohol (**8a**) (20 g) was added slowly with stirring. The mixture was stirred at room temperature overnight and then diluted with water and extracted with benzene. The organic layer was washed with aqueous sodium hydrogen carbonate, dried ($CaCl_2$), and evaporated to leave compound (**7b**) as an oil which crystallised on storage (18 g, 98%), m.p. 84—86 °C (from light petroleum, b.p. 40—60 °C) (previously described only as an oil[11]), $\delta_H(CDCl_3)$ 1.60 (6 H, s), 4.07 (2 H, s), 7.1—7.3 (6 H, m), and 7.5—7.6 (2 H, m); *m*/*z* 208 ($M^+$, 4%), 193 (100), and 178 (80).

10,10-*Dimethylanthrone* (**7a**).—A solution of the dihydroanthracene (**7b**) (10 g) in carbon tetrachloride (100 ml) was heated under reflux and irradiated by a tungsten–halogen lamp (100 W) whilst a solution of bromine (16 g) in carbon tetrachloride (160 ml) was added slowly; heating and irradiation were continued for 6 h. The reaction mixture was washed with water, dried ($MgSO_4$) and evaporated to give 10,10-dimethylanthrone (7.5 g, 70%), m.p. 102—103 °C (from light petroleum, b.p. 40—60 °C) (lit.,[11] 101—102 °C) (Found: C, 86.3; H, 6.3. Calc. for $C_{16}H_{14}O$: C, 86.4; H, 6.3%); $\nu_{max.}(CHCl_3)$ 1 660 and 1 605 cm$^{-1}$; $\delta_H(CDCl_3)$ 1.70 (6 H, s), 7.3—7.5 (2 H, m), 7.5—7.8 (4 H, m), and 8.3—8.5 (2 H, m); $\delta_C(CDCl_3)$ 32.9, 37.8, 126.6, 127.4, 129.9, 133.3, 150.4, and 183.6; *m*/*z* 222 ($M^+$, 48%), 208 (73), 207 (100), 179 (42), 178 (84), 177 (29), 176 (52), and 152 (35).

10,10-*Dimethylanthrone Hydrazone* (**7d**).—A mixture of 10,10-dimethylanthrone (4 g), triethylene glycol (100 ml), hydrazine hydrate (100% 40 ml), and hydrazine dihydrochloride (17.6 g) was boiled under reflux overnight and then cooled and diluted with water. Extraction of the mixture with ether and work-up of the ethereal solution gave the *hydrazone* (**7d**) as a gum (4 g, 95%), $\nu_{max.}(CHCl_3)$ 3 400, 1 620, and 1 600 cm$^{-1}$; $\delta_H(CDCl_3)$ 1.60 (6 H, s), 7.2—7.7 (8 H, m), 7.8 (1 H, m), and 8.1 (1 H, m); *m*/*z* 236 ($M^+$, 68%), 222 (20), 221 (100), 207 (33), and 206 (54). The *picrate* was obtained as yellow crystals, m.p. 193—197 °C (from ethanol) (Found: C, 56.4; H, 4.5; N, 15.2. $C_{16}H_{16}N_2 \cdot C_6H_3N_3O_7$ requires C, 56.7; H, 4.1; N, 15.1%).

N-(10,10-*Dimethyl*-9,10-*dihydroanthracen*-9-*ylidene*)*phenylamine* N-*Oxide* (**5c**).—A suspension of the hydrazone (**7d**) (2 g), anhydrous sodium sulphate (1 g), Celite (7 g), and yellow mercuric oxide (6 g) in dry ether (15 ml) was stirred vigorously whilst a saturated solution of potassium hydroxide in ethanol (1 ml) was added. After 3 h the purple solution was filtered and a solution of nitrosobenzene (4 g) in dry ether (100 ml) was added. The resulting gas evolution was accompanied by warming of the mixture. After a further 6 h the precipitated *nitrone* (**5c**) was collected (2 g, 71%), m.p. 173—174 °C (from ethanol) (Found: C, 84.1; H, 6.2; N, 4.8. $C_{22}H_{19}NO$ requires C, 84.3; H, 6.1; N, 4.5%); $\nu_{max.}$(paste) 1 235 cm$^{-1}$; $\delta_H(CDCl_3)$ 1.72 (6 H, s), 6.7—6.9 (2 H, m), 7.1 (1 H, m), 7.2—7.6 (9 H, m), and 9.0—9.1 (1 H, m); *m*/*z* 313 ($M^+$, 54%), 298 (56), 297 (75), 282 (58), 280 (29), 267 (45), 207 (83), 178 (64), 133 (52), and 91 (100).

*Reaction of the* N-*Phenylnitrone* (**5c**) *with Dimethylketene.*—An excess of dimethylketene (from 16 g of the dimer) was passed into a solution of the nitrone (**5c**) (2 g) in dry ethyl acetate (100 ml) at room temperature and the mixture was set aside overnight. Evaporation of the solvent left a brown solid from which column chromatography [silica gel, light petroleum (b.p. 40—60 °C)–ether] separated the following compounds: 4′,4′,10,10-*tetramethyl*-3′-*phenyl*-9,10-*dihydroanthracene*-9-*spiro*-2′-*oxazolidin*-5′-*one* (**6c**) (0.6 g, 24%), m.p. 195—200 °C (decomp.) (from ethanol) (Found: C, 80.9; H, 6.5; N, 3.5. $C_{26}H_{25}NO_2$ requires C, 81.5; H, 6.5; N, 3.7%); $\nu_{max.}(CHCl_3)$ 1 780 cm$^{-1}$; $\delta_H(CDCl_3)$ 1.68 (3 H, s), 1.80 (3 H, s), 2.06 (6 H, s), 6.4—6.5 (2 H, m), 6.6—6.7 (1 H, m), 6.9—7.1 (2 H, m), 7.15—7.3 (2 H, m), 7.35—7.5 (4 H, m), and 7.65—7.8 (2 H, m); *m*/*z* 383 ($M^+$, 11%), 336 (12), 324 (16), 322 (9), 321 (9), 300 (9), 297 (11), 207 (51), 178 (36), 133 (100), and 118 (94); and 10,10-dimethylanthrone (**7a**) (150 mg) identified by spectroscopic comparison with an authentic sample. Additionally a trace of another compound (Found $M^+$, 469.2249. $C_{30}H_{31}NO_4$ requires 469.2253) was isolated in too small an amount for identification, *m*/*z* 469 (80%), 383 (86), and 338 (100).

*Reaction of the* N-*Phenylnitrone* (**5c**) *with Diphenylketene.*—Nitrone (**5c**) (1.5 g) was added to a solution of diphenylketene (from 2.5 g of diazoketone) in benzene (25 ml) and the mixture was stirred at room temperature for 1 h. The solvent was evaporated at low temperature under reduced pressure, and dry ether was added to the residue. The precipitate was collected and washed with ether and light petroleum (b.p. 40—60 °C) leaving crude 10,10-*dimethyl*-3′,4′,4′-*triphenyl*-9,10-*dihydroanthracene*-9-*spiro*-2′-*oxazolidin*-5′-*one* (**6d**) (1.94 g, 80%) m.p. 199—210 °C (decomp.) (Found: C, 85.4; H, 6.0; N, 2.7. $C_{36}H_{29}NO_2$ requires C, 85.2; H, 5.7; N, 2.8%); $\nu_{max.}(CHCl_3)$ 1 775 cm$^{-1}$; $\delta_H(CDCl_3)$ 1.38 (3 H, s), 1.65 (3 H, s), 6.2—6.4 (2 H, m), 6.7—6.9 (2 H, m), and 7.1—7.7 (19 H, m); *m*/*z* 507 ($M^+$, 0%), 463 (23), 462 (31), 447 (37), 386 (5), 370 (20), 355 (7), 339 (5), 297 (68), 282 (47), 267 (43), 257 (82), 224 (25), 194 (21), 180 (69), 165 (78), and 77 (100).

10,11-*Dihydro*-5H-*dibenzo*[a,d]*cyclohepten*-5-*one Hydrazone* (**7f**).—A mixture of 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-one[17] (11 g), triethylene glycol (60 ml), hydrazine hydrate (100%, 100 ml), and hydrazine dihydrochloride (12 g) was boiled under reflux overnight. The mixture was cooled, diluted with water, and extracted with ether. Work-up of the ether extract gave the *hydrazone* (**7f**) (11 g, 94%), m.p. 78—80 °C (from aqueous ethanol) (Found: C, 81.3; H, 6.5; N, 12.7. $C_{15}H_{14}N_2$ requires C, 81.1; H, 6.3; N, 12.6%); $\delta_H(CDCl_3)$ 3.05 (4 H, s), 5.17 (2 H, s), and 6.9—7.9 (8 H, m).

N-(10,11-*Dihydro*-5H-*dibenzo*[a,d]*cyclohepten*-5-*ylidene*)-*phenylamine* N-*Oxide* (**5d**).—The hydrazone (**7f**) (5 g) was

oxidised with yellow mercuric oxide (10 g) anhydrous sodium sulphate (2 g), and Celite (5 g) in dry ether (150 ml) with ethanolic potassium hydroxide as described above for (**5c**). The resulting purple solution was filtered and evaporated under reduced pressure to *ca.* half its volume. Nitrosobenzene (2.5 g) was added and the mixture was stirred overnight and then evaporated to dryness. The residue was extracted with chloroform and the chloroform solution was washed with dilute acetic acid and aqueous sodium hydrogen carbonate and dried ($CaCl_2$). Evaporation of the solvent left the *nitrone* (**5d**) (4.4 g, 65%), m.p. 142—145 °C (from ether) (Found: C, 84.0; H, 5.9; N, 4.4. $C_{21}H_{17}NO$ requires C, 84.3; H, 5.7; N, 4.7%); $\nu_{max.}$(paste) 1 250 $cm^{-1}$; $\delta_H(CDCl_3)$ 3.0 (2 H, m), 3.5 (2 H, m), 6.7—6.9 (2 H, m), 7.0—7.4 (10 H, m), and 8.3 (1 H, m); *m/z* 299 ($M^+$, 51%), 298 (22), 283 (100), and 282 (68).

*Reaction of the* N-*Phenylnitrone* (**5d**) *with Dimethylketene.*—An excess of dimethylketene was passed into a solution of the nitrone (**5d**) (1.4 g) in ethyl acetate (100 ml) and the mixture was set aside for 12 h. Evaporation of the solvent left a viscous oil from which the addition of benzene–light petroleum (b.p. 60—80 °C) (7:3) precipitated the crude adduct. This was washed with ether to leave 5-(3,3-*dimethyl*-2-*oxo*-2,3-*dihydroindol*-1-*yl*)-10,11-*dihydrodibenzo*[a,d]*cyclohepten*-1-*yl* 2-*methylpropanoate* (**9a**) (1.7 g, 83%), m.p. 169—172 °C (Found: C, 79.0; H, 6.4; N, 3.3. $C_{29}H_{29}NO_3$ requires C, 79.3; H, 6.6; N, 3.2%); $\nu_{max.}$(paste) 1 755 and 1 690 $cm^{-1}$; $\delta_H(CDCl_3)$ 1.21 (6 H, d, *J* 7 Hz), 1.36 (6 H, s), 2.83 (1 H, sept, *J* 7 Hz), 2.91 (2 H, d, *J* 10 Hz), 3.45 (2 H, d, *J* 10 Hz), 6.5—6.6 (1 H, m), 6.8—7.3 (9 H, m), and 7.5—7.8 (2 H, br); $\delta_C(CDCl_3)$ 19.2 (Me), 25.3 (Me), 31.6 ($CH_2$), 35.4 (CH), 43.9 (C), 91.9, 113.2, 122.4, 122.7, 124.0, 125.3, 126.5, 126.9, 127.8, 128.5, 130.1, 131.4, 136.4, 139.2, 141.0, 173.5, and 181.1; (Found $M^+$, 439.2154. $C_{29}H_{29}NO_3$ requires 439.2148); *m/z* 368 ($C_{25}H_{22}NO_2$, 0.4%), 352 ($C_{25}H_{22}NO$, 1.2), 324 ($C_{24}H_{22}N$, 1.7), 231 ($C_{18}H_{15}$, 1), 209 ($C_{15}H_{13}O$, 1), 191 ($C_{15}H_{11}$, 100), and 161 ($C_{10}H_{11}NO$).

The benzene and light petroleum solution and the ether washings were combined and evaporated. From the residue column chromatography (silica gel and dichloromethane) separated 5-*phenylimino*-10,11-*dihydro*-5H-*dibenzo*[a,d]*cycloheptene* (**7g**) as yellow crystals (0.2 g, 15%), m.p. 132—134 °C (from ethanol) (Found $M^+$, 283.1354, N, 4.9%. $C_{21}H_{17}N$ requires N, 4.9%, *M*, 283.1361); $\nu_{max.}(CHCl_3)$ 1 620 and 1 595 $cm^{-1}$; $\delta_H(CDCl_3)$ 3.23 (4 H, br s), 6.6—7.4 (12 H, m), and 8.0 (1 H, m).

*Hydrolysis of the Adduct* (**9a**).—A solution of compound (**9a**) (0.5 g) in acetic acid (7 ml), and water (4 ml), and hydrochloric acid (10M; 4 ml) was boiled under reflux for 0.5 h. After cooling and dilution with water, the mixture was extracted with chloroform and the chloroform extract was washed with sodium bicarbonate solution and dried ($CaCl_2$). Evaporation of the solvent left a residue which was separated by preparative t.l.c. (silica gel and dichloromethane) into dibenzocycloheptenone (**7e**), (220 mg, 93%) and 3,3-dimethylindol-2(3*H*)one (170 mg, 93%) identified by i.r. and t.l.c. comparison and, in the latter case, by mixed m.p. determination.

*Reaction of the* N-*Phenylnitrone* (**5d**) *with Diphenylketene.*—The nitrone (**5d**) (1 g) was added to a solution of diphenylketene (from 2.5 g diazoketone) in benzene (20 ml) and the mixture was stirred at room temperature for 4 h. The precipitate was collected and washed with ether to leave 5-(2-*oxo*-3,3-*diphenyl*-2,3-*dihydroindol*-1-*yl*)-10,11-*dihydro*-5H-*dibenzo*[a,d]*cyclohepten*-1-*yl diphenylethanoate* (**9b**) (1.6 g). A further quantity (0.4 g, total 87%) was precipitated by the addition of ether to the benzene solution, m.p. 162—164 °C (Found: C, 85.6; H, 5.6; N, 1.8. $C_{49}H_{37}NO_3$ requires C, 85.6; H, 5.4; N, 2.0%); $\nu_{max.}$(paste) 1 765 and 1 745 $cm^{-1}$; $\delta_H(CDCl_3)$ 2.5 (2 H, br), 2.8 (2 H, br), 5.35 (1 H, s), and 6.5—7.5 (m); $\delta_C(CDCl_3)$ 31.4 ($CH_2$), 58.3 (CH), 62.4 (C), 113.9 (CH), 168.8 (CO), 177.0 (CO), and numerous signals between δ 122.8 and 142.2.

*Hydrolysis of the Adduct* (**9b**).—A solution of the adduct (**9b**) (1 g) in ethanoic acid (5 ml), water (9 ml), and hydrochloric acid (10M, 9 ml) was boiled under reflux for 1 h. The reaction mixture was cooled and extracted with chloroform, and the chloroform solution was washed with water. The chloroform solution was washed with dilute aqueous sodium carbonate and acidification of the aqueous extract precipitated diphenylethanoic acid (240 mg, 78%), identified by i.r. comparison and mixed m.p. determination. The residual chloroform solution was dried and evaporated leaving a residue which was separated by preparative t.l.c. (silica gel and dichloromethane) into the dibenzocycloheptenone (**7e**) (260 mg, 86%) (identified by i.r. and t.l.c. comparison) and 3,3-diphenylindol-2(3*H*)one (380 mg, 92%) (identified by i.r. and mixed m.p. comparison).

5H-*Dibenzo*[a,d]*cyclohepten*-5-*one Hydrazone* (**7i**).—This compound was prepared from the ketone (**7h**)[17] by a method similar to that described above for (**7f**) and obtained as a crude gum (94%) which could not be induced to crystallise but was shown by t.l.c. to be homogeneous. Neither the hydrochloride nor the picrate could be obtained crystalline, and the crude material was used in subsequent preparations.

*Dibenzo*[a,d]*cyclohepten*-5-*ylidene*(*phenyl*)*amine* N-*Oxide* (**5e**).—The crude hydrazone (**7i**) (12 g) was oxidised with yellow mercuric oxide (13 g), anhydrous sodium sulphate (2 g), and Celite (5 g) in dry ether with ethanolic potassium hydroxide as described above for (**5c**). The ethereal solution was concentrated, nitrosobenzene (6 g) was added, and the mixture was shielded from light and stirred overnight at room temperature. The precipitated product was collected to give *nitrone* (**5e**) (7 g, 43%), m.p. 162—163 °C [from benzene and light petroleum (b.p. 60—80 °C)] (Found: C, 84.6; H, 5.1; N, 4.9. $C_{21}H_{15}NO$ requires C, 84.8; H, 5.1; N, 4.7%); $\nu_{max.}$(paste) 1 250 $cm^{-1}$; $\delta_H(CDCl_3)$ 6.8—7.6 (14 H, m) and 8.14 (1 H, d, *J* 8 Hz); *m/z* 297 ($M^+$, 63%), 281 (63), 268 (66), 206 (63), 188 (74), and 178 (100). This compound is somewhat light sensitive and darkens slowly on exposure to daylight.

*Reaction of the* N-*Phenylnitrone* (**5e**) *with Dimethylketene.*—An excess of dimethylketene was passed into a solution of the nitrone (**5e**) (2 g) in ethyl acetate (120 ml) at room temperature and the mixture was set aside overnight. Evaporation of the solvent left a viscous residue which was shaken with dry ether to precipitate 5-(3,3-*dimethyl*-2,3-*dihydro*-2-*oxoindol*-1-*yl*)*dibenzo*[a,d]*cyclohepten*-1-*yl* 2-*methylpropanoate* (**9c**) (2.8 g, 95%), m.p. 168—169 °C (Found: C, 79.9; H, 6.4; N, 3.1. $C_{29}H_{27}NO_3$ requires C, 79.6; H, 6.2; N, 3.2%); $\nu_{max.}$(paste) 1 755 and 1 740 $cm^{-1}$; $\delta_H(CDCl_3)$ 1.13, 1.23, 1.30 (total 12 H), 2.90 (1 H, sept, *J* 8 Hz), 5.86 (1 H, d, *J* 7 Hz), 6.7—8.0 (14 H); *m/z* 437 ($M^+$), 367 (6%), 350 (16), 322 (11), 277 (25), 231 (25), 207 (100), 191 (48), 178 (81), and 161 (98).

*Hydrolysis of the Adduct* (**9c**).—The hydrolysis was effected under conditions similar to those described above for (**9a**); separation of the products by preparative t.l.c. gave the ketone (**7h**) (51%) and 3,3-dimethylindol-2-one (43%) (identified by i.r. and mixed m.p. comparisons).

*Reactions of the* N-*Phenylnitrone* (**5e**) *with Diphenylketene.*—The nitrone (**5e**) (2 g) was added to a solution of diphenylketene (from 4 g of diazoketone) in benzene (25 ml) and the mixture was stirred for 8 h. Evaporation of *ca.* half the benzene and

**Table 2.** *N*-Fluoren-9-ylidenephenylamine *N*-oxide (**5a**), refined atomic co-ordinates with standard deviations in parentheses

| | *x/a* | *y/b* | *z/c* |
|---|---|---|---|
| C(1) | 10 059(7) | 1 466(1) | 3 605(3) |
| C(2) | 11 946(7) | 1 804(1) | 4 303(4) |
| C(3) | 14 039(8) | 1 533(2) | 5 044(4) |
| C(4) | 14 256(8) | 963(2) | 5 112(4) |
| C(5) | 12 399(8) | 620(2) | 4 440(4) |
| C(6) | 10 303(7) | 866(1) | 3 690(3) |
| C(7) | 8 100(8) | 609(2) | 2 876(4) |
| C(8) | 7 466(9) | 39(2) | 2 658(4) |
| C(9) | 5 200(10) | −90(2) | 1 852(5) |
| C(10) | 3 621(9) | 335(2) | 1 285(4) |
| C(11) | 4 277(8) | 912(2) | 1 494(4) |
| C(12) | 6 503(8) | 1 038(1) | 2 286(4) |
| C(13) | 7 697(7) | 1 586(2) | 2 718(4) |
| C(14) | 7 935(7) | 2 617(1) | 2 795(4) |
| C(15) | 7 147(8) | 2 864(2) | 3 776(4) |
| C(16) | 8 169(9) | 3 386(2) | 4 176(4) |
| C(17) | 9 975(9) | 3 651(2) | 3 590(4) |
| C(18) | 10 721(9) | 3 397(2) | 2 611(4) |
| C(19) | 9 739(8) | 2 872(2) | 2 194(4) |
| N(1) | 6 763(6) | 2 082(1) | 2 314(3) |
| O(1) | 4 731(6) | 2 140(1) | 1 483(3) |

**Table 3.** Triphenylnitrone (**1**), refined atomic co-ordinates with standard deviations in parentheses

| | *x/a* | *y/b* | *z/c* |
|---|---|---|---|
| N(1) | 2 266(2) | 2 528(5) | 2 060(2) |
| O(1) | 2 953(2) | 2 327(5) | 1 832(2) |
| C(1) | 2 619(3) | 2 604(6) | 3 345(3) |
| C(2) | 2 405(3) | 2 017(7) | 4 020(3) |
| C(3) | 2 900(3) | 1 999(7) | 4 606(3) |
| C(4) | 3 614(3) | 2 571(8) | 4 525(4) |
| C(5) | 3 828(3) | 3 148(8) | 3 858(4) |
| C(6) | 3 344(3) | 3 165(7) | 3 271(3) |
| C(7) | 2 062(2) | 2 647(6) | 2 750(3) |
| C(8) | 1 257(2) | 2 831(6) | 2 936(2) |
| C(9) | 718(3) | 1 774(6) | 2 737(3) |
| C(10) | −20(3) | 1 970(7) | 2 946(3) |
| C(11) | −227(3) | 3 204(8) | 3 357(3) |
| C(12) | 303(3) | 4 260(7) | 3 558(3) |
| C(13) | 1 042(3) | 4 064(6) | 3 353(3) |
| C(14) | 1 744(2) | 2 652(8) | 1 452(2) |
| C(15) | 1 620(3) | 1 395(7) | 1 021(3) |
| C(16) | 1 146(3) | 1 510(8) | 419(3) |
| C(17) | 803(3) | 2 874(9) | 263(3) |
| C(18) | 935(3) | 4 113(8) | 692(3) |
| C(19) | 1 409(3) | 4 021(7) | 1 293(3) |

addition of ether precipitated a solid, which was washed with ether to leave 5-(3,3-*diphenyl*-2,3-*dihydro*-2-*oxoindol*-1-*yl*)*dibenzo*[a,d]*cyclohepten*-1-*yl diphenylethanoate* (**9d**) (3.8 g, 82%), m.p. 153—154 °C (Found: C, 85.8; H, 5.3; N, 2.0. $C_{49}H_{35}NO_3$ requires C, 85.8; H, 5.1; N, 2.0%); $\nu_{max.}$(paste) 1 755 and 1 740 $cm^{-1}$; $\delta_H(CDCl_3)$ 5.50 (1 H, s), 5.77 (1 H, d, *J* 8 Hz), 5.95 (1 H, m), 6.33 (1 H, m), and 6.7—7.7; *m/z* 285 (44%), 256 (44), 196 (82), and 167 (100).

*Hydrolysis of the Adduct* (**9d**).—The hydrolysis was effected under conditions similar to those described above for (**9b**) and gave diphenylethanoic acid (74%), the ketone (**7h**) (83%), and 3,3-diphenylindol-2-one (53%) (all identified by i.r. and mixed m.p. comparisons).

*X-Ray Crystallography.—Crystal data for compound* (**5a**). $C_{19}H_{13}NO$, $M$ = 271.32. Monoclinic, $a$ = 5.205(4), $b$ = 23.492(7), $c$ = 11.232(6) Å, $\beta$ = 100.38(1)° $V$ = 1 350.69 Å$^3$, $D_c$ = 1.35, space group $P2_{1/c}$, $Z$ = 4, Cu-$K_\alpha$ radiation $\lambda$ = 1.5418 Å.

*X*-Ray data were collected using an Enraf-Nonius CAD-4 diffractometer. Reflections were scanned for $\theta \leqslant 60°$ and of 2 747 reflections recorded 1 185 $I > 3\sigma(I)$ and were used in the structure refinement. The structure was readily solved using the direct methods SHELX program and then refined with the CRYSTALS package. After several cycles of isotropic and then anisotropic refinement all the hydrogen atoms were located in a difference map. Hydrogen atoms were included in their calculated positions but not refined in the final cycles of refinement, $R$ converged at 5.22%. Refined atomic co-ordinates are contained in Table 2, while Table 1 lists selected bond lengths, bond angles, and relevant torsion angles.

*Crystal data for compound* (**1**).[9] $C_{19}H_{15}NO$, $M$ = 273.33. Orthorhombic, $a$ = 17.831(1), $b$ = 8.840(1), $c$ = 18.177(2) Å, $V$ = 2 865.17 Å$^3$, $D_c$ = 1.27, space group *Pbca*, $Z$ = 8, Cu-$K_\alpha$ radiation $\lambda$ = 1.5418 Å. 1 795 reflections scanned.

*X*-Ray data were collected as described for compound (**5a**), and the structure was solved and refined in a similar manner to a final $R$ value of 4.84% for 944 reflections. Final atomic co-ordinates are listed in Table 3. Full lists of bond lengths and angles together with refined anisotropic thermal parameters for compounds (**1**) and (**5a**) have been treated as a Supplementary publication [SUP No. 56282 (5 pp.)].* The structure factors are available on request from the editorial office.

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* For details of the Supplementary publications scheme, see Instructions for Authors, *J. Chem. Soc., Perkin Trans. 1*, 1985, Issue 1.

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