Ketene. Part 21.[1] Reactions of Heterocumulenes with Nitrones

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Degradative and mass spectrometric evidence confirms the formation of the isoxazolidinones (**2**) from the reaction of cyano-t-butylketene with the *N*-alkyl nitrones (**1**), whilst the reaction with the *N*-phenyl nitrone (**1d**) gives the expected oxazolidinone (**3b**). Cyano-t-butylketene reacts with diphenyl nitrone to give the indolones (**10a**) and (**10b**). The reaction of phenyl isocyanate with diphenyl nitrone, and the *N*-alkyl nitrones (**1a**) and (**1d**) gives the normal 1,3-dipolar cycloadducts without rearrangement.

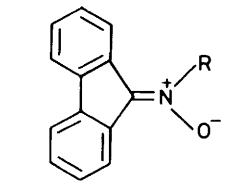
Ethoxycarbonyl-t-butylketene reacts with the *N*-phenyl nitrone (**1d**) to give an oxazolidinone, but reaction with the *N*-alkyl nitrones (**1**) gives only fluorenone azine. This ketene reacts with diphenyl nitrone to give the anil (**15**) and the dihydroindole (**16**).

Cycloaddition reactions of ketenes with nitrones[2–7] and nitrile oxides[8] usually occur with rearrangement involving cleavage of the N–O bond. The only recorded exceptions to this generalisation involve the addition of cyano-t-butylketene to nitrones of type (**1a**—**c**) which are reported[2] to give spiro-isoxazolidinones of structure (**2a**—**c**). A range of *N*-aryl derivatives of (**1**), however, gave adducts with cyano-t-butylketene having the spiro-oxazolidinone structure (**3**), a type of product observed for the reactions of several other ketenes with both *N*-alkyl and *N*-aryl derivatives of (**1**).[5–7] The structures (**2**) and (**3**) were assigned by Joullié and co-workers on the basis of spectroscopic evidence, and the distinction between the two types of adduct was based, in part, on the ^{13}C n.m.r. chemical shift of the spirocarbon atom [δ 83 in (**2**) and δ 102 in (**3**)] and the ^{1}H n.m.r. chemical shift of the t-butyl protons (δ 0.8 and 1.25, respectively). These assignments were supported by the isolation of both compounds (**2d**) and (**3a**) from the reaction of the oxaziridine (**4**) with cyano-t-butylketene,[9] the structures again being assigned on the basis of the spectroscopic evidence.

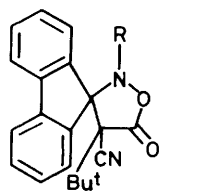
Notwithstanding the consistency of the spectroscopic evidence, the formation of adducts of type (**2**) from the reaction of a ketene with a nitrone is so exceptional that we have repeated and extended the work to seek further evidence, and our results entirely confirm the structures previously assigned.

The reaction of cyano-t-butylketene with the *N*-phenyl nitrone (**1d**) either in benzene at room temperature or in boiling toluene gave fluorenone and a 1:1 adduct, $C_{26}H_{22}N_2O_2$; no trace of the corresponding azetidinone, arising *via* deoxygenation of the nitrone,[6,7] could be detected. As in the case of related adducts,[5–7] reaction of the 1:1 adduct with methanol and sulphuric acid gave fluorenone, and reaction with hydroxylamine gave fluorenone oxime. These reactions have previously been taken as evidence for the existence of a fluorenone *O,N*-acetal unit in the adduct structures. However, later results show that this interpretation may not be so certain in this case.

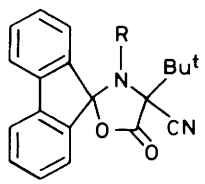
The spectroscopic properties of the adduct were consistent with the oxazolidinone structure (**3b**); in particular, there was a signal in the ^{13}C n.m.r. spectrum at δ 102.7, and the t-butyl proton resonance was at δ 1.24. There was no evidence for a cyano group in the i.r. spectrum, but a characteristic signal was observed at δ_C 118.2. The mass spectrum was more complicated than those which have previously been analysed for dimethyl ketene adducts,[5,7] but was also consistent with structure (**3b**). In particular, peaks at *m/z* 186 $(C_{12}H_{14}N_2)^+$, 158 $(C_9H_6N_2O)^+$, and 129 $(C_8H_5N_2)^+$ appear to correspond to fragments (**5**), (**6**), and (**7**), in which the PhNCCN fragment of (**3b**) is preserved. The last of these closely resembles the $R\overset{+}{N}{\equiv}CCH_3$ peak which is prominent in the mass spectra of the corresponding dimethyl ketene adducts.[5,7]



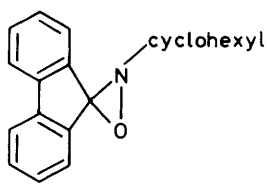
(**1**) **a**; R = Me
b; R = Et
c; R = CH_2Ph
d; R = Ph
e; R = Pr^i
f; R = *p*-$CH_3C_6H_4$



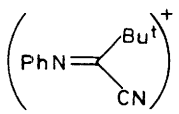
(**2**) **a**; R = Me
b; R = Et
c; R = CH_2Ph
d; R = cyclohexyl
e; R = Pr^i



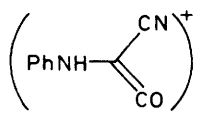
(**3**) **a**; R = cyclohexyl
b; R = Ph



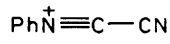
(**4**)



(**5**)

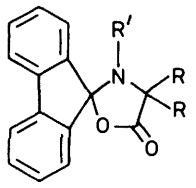


(**6**)

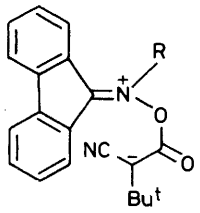


(**7**)

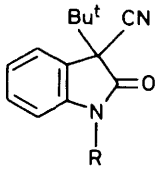
The reaction of cyano-t-butylketene with the *N*-alkyl nitrones (**1a**), (**1b**), and (**1e**) gave the 1:1 adducts (**2a**), (**2b**), and (**2e**). The spectroscopic properties of the adducts of (**1a**) and (**1b**) were identical with those previously reported,[2] and those of the adduct with (**1e**) were closely similar. The mass spectra of the adducts of (**1a**) and (**1e**) were totally different from those of (**3b**) and the dimethyl ketene adducts (**8a**) of nitrones of type (**1**).[5,7] The ion formula of the base peak in both cases corresponded to the parent nitrone with no strong peaks of higher *m/z* value. To check whether the adducts were decomposing thermally on the probe of the mass spectrometer, a sample of the adduct of (**1b**) was heated with dimethyl butynedioate in toluene for a prolonged period, but the adduct was recovered unchanged and no trace of the adduct of the nitrone with the alkyne could be detected.



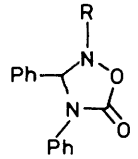
(8) a; R = Me
b; R = Ph



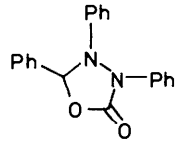
(9)



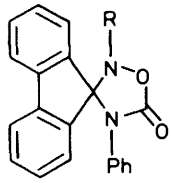
(10) a; R = CHPhOCOCH(CN)Bu^t
b; R = H



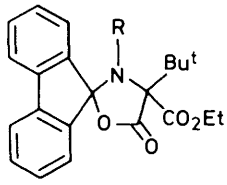
(11) a; R = Me
b; R = Ph



(12)



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



(14) a; R = p-$CH_3C_6H_4$
b; R = Ph

Alkaline hydrolysis of the adduct of (**1e**) at room temperature led to the formation of the parent nitrone (1e) in good yield, conclusively demonstrating the preservation of an N–O bond in the adduct and confirming the structure (**2e**) for this adduct, and, by analogy, structures (**2a**) and (**2b**) for the adducts of (**1a**) and (**1b**). Other attempts at chemical degradation gave confusing results. Acidic methanolysis of the adduct of compound (**1a**) gave fluorenone, and the reaction of this adduct with hydroxylamine gave fluorenone oxime, which at first seemed to indicate a structure like (**3**). These results can be explained in terms of the interception by the nucleophilic reagents of an equilibrium concentration of the stabilised zwitterion (**9**) or its protonated equivalent. An analogous, reversible dissociation of adducts of structure (**8b**) has been proposed[6] to account for their chemistry.

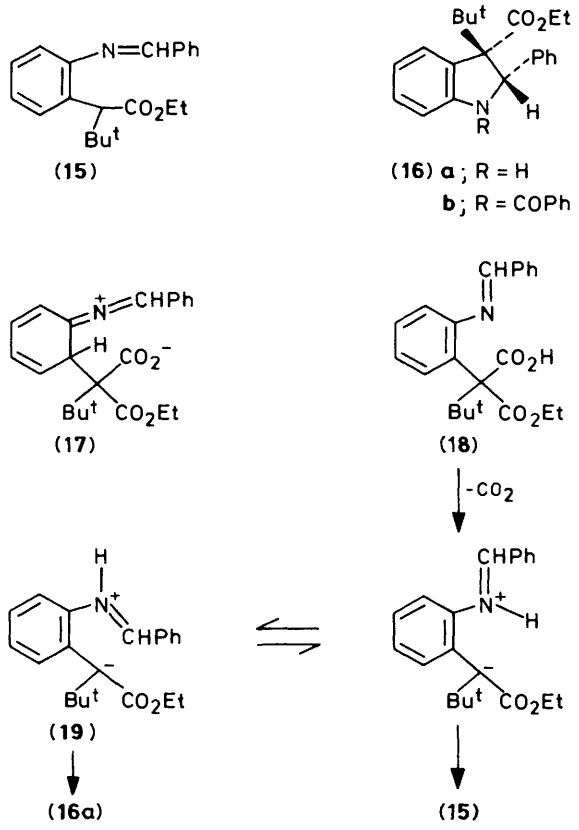
Because of the unusual behaviour of cyano-t-butylketene with this series of nitrones, the reaction with diphenyl nitrone was investigated. T.l.c. examination of the product of the reaction in boiling benzene showed the presence of two compounds which were isolated by preparative t.l.c. The slower moving component was identified by its spectroscopic properties as the indolone (**10a**), which on hydrolysis gave (**10b**), identical with the faster moving component in the original reaction mixture. In this case the reaction of the cyanoketene with the nitrone proceeds exactly in accord with previous examples.[3,7]

In view of the remarkable differences in the behaviour of the nitrones (**1**) arising from apparently small differences in structure, attempts were made to see if similar effects occur in analogous reactions. Isocyanates are isoelectronic with ketenes but are reported to participate normally in 1,3-dipolar cycloadditions with nitrones. In the work describing the addition of phenyl isocyanate to *N*-methyl-*C*-phenyl nitrone and *C*,*N*-diphenyl nitrone,[10] the structure (**11a**) was established for the adduct of the *N*-methyl nitrone by the mass spectrum, whilst (**11b**) was assigned to the adduct of diphenyl nitrone by analogy, supported by a similar carbonyl absorption in the i.r. spectrum. The possibility that this adduct has the structure (**12**) arising by an oxygen migration similar to that found with ketenes cannot be excluded; comparison of the i.r. spectra of the adducts (**2**) and (**3**) suggest that the carbonyl absorptions of (**11b**) and (**12**) may not differ significantly. We have therefore prepared and examined the adducts of phenyl isocyanate with diphenyl nitrone, (**1a**) and (**1d**). Our evidence suggests that these are formed without rearrangement and have the expected structures (**11b**), (**13a**), and (**13b**), respectively.

The diphenyl nitrone–phenyl isocyanate adduct had spectroscopic properties which were not conclusive for either alternative structure. However, prolonged alkaline hydrolysis led to the formation of a low yield of *N*,*N*′-diphenylbenzamidine, which is conclusive for structure (**11b**). Similar attempts to degrade the adducts of (**1a**) and (**1d**) gave no characterisable material, and the mass spectra were unhelpful, but in these cases the ^{13}C n.m.r. resonances of the spiro-carbon atoms at δ 92 are clearly consistent with the structures of type (**13**) rather than the spiro-1,3,4-oxadiazolidinones akin to (**12**) in which this signal would be expected to be at δ 102 by analogy with (**3a**) and (**3b**)[2,9] and (**8**).[7] We therefore conclude that oxygen migration, such as that found in many ketene cycloadditions with nitrones, does not occur with isocyanates, which behave as typical 1,3-dipolarophiles. Nitrile oxides, which add to ketenes with rearrangement,[8a] also add to phenyl isocyanate to form normal 1,3-dipolar cycloadducts.[8b]

In addition to the study of the adducts of cyano-t-butylketene with nitrones, Joullié *et al.* described[2] the addition of ethoxycarbonyl-t-butylketene with the nitrone (**1f**) to give the oxazolidinone (**14a**), but did not mention any study of the reaction of this ketene with the corresponding *N*-alkyl nitrones. Since the electronic effect of the ethoxycarbonyl group might have been expected to be similar to that of the cyano group, possibly leading to adducts similar to (**2**), we have investigated the reaction of this ketene with the *N*-phenyl and *N*-alkyl nitrones (**1d**), (**1a**), and (**1e**). Attempts to prepare ethoxycarbonyl-t-butylketene from the monoethyl ester of t-butylmalonic acid following Newman's method[11] were rarely successful. The unsuccessful step involved the use of thionyl chloride for conversion of the half ester into its acyl chloride. The use of phosphorus pentachloride in ether[12] provided an alternative, consistently reliable method.

The ethoxycarbonylketene reacted with the *N*-phenyl nitrone (**1d**) in boiling benzene to give, in addition to traces of fluorenone azine, an adduct identified as (**14b**) by its spectroscopic properties. In particular, the ^{13}C n.m.r. spectrum showed a signal at δ 102.4 attributable to the spiro carbon atom adjacent to nitrogen and oxygen atoms, and the t-butyl ^1H resonance is at δ 1.3; both of these agree closely with the data reported for (**14a**).[2] The mass spectrum of this compound shows a very weak parent peak and no significant peak corresponding to the nitrone (**1d**). Two prominent peaks at *m*/*z* 176 $(C_{10}H_{10}NO_2)^+$ and 160 $(C_{11}H_{14}N)^+$ correspond to $PhN^+{\equiv}CCO_2Et$ and $PhN^+{\equiv}CCMe_3$, respectively, and the base peak at *m*/*z* 104 $(C_7H_6N)^+$ corresponds to $PhN^+{\equiv}CH$. The



strong peak at m/z 181 $(C_{13}H_9O)^+$ corresponds to protonated fluorenone. All the data are entirely consistent with the structure (**14b**).

Attempts to form an adduct of the ethoxycarbonylketene with the *N*-alkyl nitrones (**1a**) and (**1e**) were unsuccessful. The only significant product obtained after reaction in boiling benzene was fluorenone azine (14%) and in both cases much unchanged nitrone was recovered. The azine has been obtained previously as a product of the reaction of dimethyl ketene with *N*-alkyl nitrones (**1a**) and (**1b**)[5] but, as reported above for the reaction with (**1d**), only in very low yield. At present we have no mechanistic explanation for its formation, nor has the fate of the ketene in this reaction beeen discovered.

To extend the survey of reactions of ethoxycarbonyl-t-butylketene with nitrones, the reaction with diphenyl nitrone was examined. A reaction occurred in boiling benzene, but was incomplete after several hours. Prolonged reaction in boiling xylene led to the formation of two products which were separated by column chromatography and identified from the spectroscopic data as (**15**) and (**16a**). Both of these products can reasonably be derived from the zwitterion (**17**), arising from the normal reaction path of diphenyl nitrone with ketenes.[3] Subsequent aromatisation of (**17**) by proton migration to give (**18**) followed by synchronous proton transfer to nitrogen and decarboxylation would give a zwitterion (**19**) which might subsequently give either (**15**) or (**16a**) from different conformations about the CN bond. The relative configuration shown for the dihydroindole in (**16**) is assigned on the basis of nuclear Overhauser experiments. Irradiation of the t-butyl signal produces an enhancement (16%) of the one-proton singlet at δ 4.86, and of the aromatic one-proton signal at δ 7.55 (11%) which we assign to the hydrogen atoms at positions 2 and 4 of the indole skeleton respectively. Irradiation at δ 4.86 produces enhancement of the t-butyl signal (1%) and an aromatic absorption at δ 7.2, presumably due to the *ortho* protons of the adjacent phenyl group. These observations strongly suggest the relative configuration shown, which is also consistent with the rather low-frequency resonance of the methyl group of the ester function, presumably arising by shielding by the *cis*-phenyl substituent.

As part of the identification of (**16a**), the *N*-benzoyl derivative (**16b**) was prepared. The ^1H n.m.r. spectrum of this compound showed the characteristic broadening of signals arising from a slow rotation about the amide link.

Experimental

^1H N.m.r. spectra were measured with a Perkin-Elmer R34 220 MHz spectrometer, ^{13}C n.m.r. spectra with a JEOL PFT-100 spectrometer, and i.r. spectra with Perkin-Elmer 457 and 180 spectrometers. Mass spectra were measured with Kratos MS25 and MS80 spectrometers. M.p.s were measured with a Koffler apparatus. Ether refers to diethyl ether, and light petroleum to the fraction with b.p. 60—80 °C.

4′-Cyano-3′-phenyl-4′-t-butylfluorene-9-spiro-2′-oxazolidin-5′-one (**3b**).—A solution of the *N*-phenyl nitrone (**1d**) (0.3 g) and cyano-t-butylketene [from azidoquinone[13] (0.3 g)] in benzene (5 ml) was stirred at room temperature for 8 h. Preparative t.l.c. (dichloromethane and silica gel) separated fluorenone (0.07 g, 35%) and the *adduct* (**3b**) (0.26 g, 60%), m.p. 163—164 °C (from ethanol) (Found: C, 78.7; H, 5.2; N, 7.3. $C_{26}H_{22}N_2O_2$ requires C, 79.2; H, 5.6; N, 7.1%), $\nu_{max.}$(paste) 1 790 cm^{-1}; $\delta_H(CDCl_3)$ 1.24 (9 H, s), 6.9—7.5 (11 H, m), 7.7—7.8 (1 H, m), and 7.9—8.1 (1 H, m); $\delta_C(CDCl_3)$ 25.8, 41.7, 68.1, 102.7, 118.2, 120.2, 125.0, 127.4, 128.3, 128.6, 129.9, 130.8, 131.5, 139.7, 140.9, 141.3, and 166.6; m/z, M^+, 394.1681 (1.5%) ($C_{26}H_{22}N_2O_2$ requires *M*, 394.1680), 350 ($C_{25}H_{22}N_2$, 2), 338 ($C_{22}H_{14}N_2O_2$, 100), 293 ($C_{21}H_{13}N_2$, 79), 186 ($C_{12}H_{14}N_2$, 2), 181 ($C_{13}H_9O$, 38), 180 ($C_{13}H_8O$, 26), 158 ($C_9H_6N_2O$, 12), 129 ($C_8H_5N_2$, 18), 77 (C_6H_5, 28), and 57 (C_4H_9, 20).

An identical product was obtained when the reaction was carried out in boiling toluene.[2]

3′-Cyano-1′-phenyl-3′-t-butylfluorene-9-spiro-2′-azetidin-4′-one.—This compound was prepared by the reaction of cyano-t-butylketene with fluorenone anil in benzene at room temperature for 1 h. Addition of light petroleum precipitated the *azetidinone* (61%), m.p. 193—195 °C (from methanol) (Found: C, 81.4; H, 5.9; N, 7.3. $C_{26}H_{22}N_2O$ requires C, 82.5; H, 5.8; N, 7.4%), $\nu_{max.}$(paste) 2 220 (v. weak) and 1 760 cm^{-1}; $\delta_H(CDCl_3)$ 1.15 (9 H, s) and 6.9—7.9 (13 H, m).

4′-Cyano-2′-methyl-4′-t-butylfluorene-9-spiro-3′-isoxazolidin-5′-one (**2a**).—A solution of the *N*-methyl nitrone (**1a**) (0.3 g) and cyano-t-butylketene [from azidoquinone[13] (0.4 g)] in benzene was stirred at room temperature for 12 h. Evaporation of the solvent left an oil which was separated by preparative t.l.c. (dichloromethane and silica gel) into unchanged nitrone (0.06 g) and the isoxazolidinone (**2a**) (0.25 g, 66%), m.p. 168—176 °C (decomp.) (lit.,[2] 178—180 °C) (Found: C, 75.6; H, 5.7; N, 8.4. Calc. for $C_{21}H_{20}N_2O_2$: C, 75.9; H, 6.0; N, 8.4%), $\nu_{max.}$(paste) 2 220 (v. weak) and 1 785 cm^{-1}; $\delta_H(CDCl_3)$ 0.75 (9 H, s), 2.34 (3 H, s), 7.2—7.6 (5 H, m), 7.70 (1 H, d, *J* 8 Hz), 7.78 (1 H, d, *J* 8 Hz), and 8.25 (1 H, d, *J* 8 Hz); $\delta_C(CDCl_3)$ 27.8 (q), 36.4 (s + q), 61.8 (s), 83.2 (s), 116.3 (s), 120.3 (d), 121.2 (d), 126.4, 127.1, 127.9, 128.4, 130.7, 131.0, 137.0 (s), 137.9 (s), 140.9 (s), 141.2 (s), and 166.3 (s); m/z, M^+, 332.1529 (7%) (Calc. for $C_{21}H_{20}N_2O_2$: *M*, 332.1536), 317 ($C_{20}H_{17}N_2O_2$, 2), 273 ($C_{19}H_{17}N_2$, 2), 209 ($C_{14}H_{11}NO$, 100), 193 ($C_{14}H_{11}N$, 12), and 180 ($C_{13}H_8O$, 12).

4′-Cyano-2′-ethyl-4′-t-butylfluorene-9-spiro-3′-isoxazolidin-5′-one (**2b**).—This compound was prepared from the *N*-ethyl

nitrone (**1b**) and cyano-t-butylketene by an identical procedure. Preparative t.l.c. [light petroleum–ether (2:1) and silica gel] separated the adduct (39%), m.p. 159—162 °C (from methanol) (lit.,[2] 161—162 °C), $\nu_{max.}$(paste) 2 225 (v. weak) and 1 780 cm^{-1}; $\delta_H(CDCl_3)$ 0.73 (9 H, s), 1.13 (3 H, t), 2.0—2.1 (2 H, m), 7.15—7.3 (1 H, m), 7.3—7.55 (4 H, m), 7.62 (1 H, d), 7.70 (1 H, d), and 8.26 (1 H, d).

4'-Cyano-2'-isopropyl-4-t-butylfluorene-9-spiro-3'-isoxazolidin-5'-one (**2e**).—This compound was prepared from the *N*-isopropyl nitrone (**1e**) and cyano-t-butylketene by an identical procedure. Preparative t.l.c. [light petroleum–ether (2:1) and silica gel] separated the *adduct* (75%), m.p. 168—169 °C (from methanol) (Found: C, 76.7; H, 6.7; N, 7.8. $C_{23}H_{24}N_2O_2$ requires C, 76.7; H, 6.7; N, 7.8%), $\nu_{max.}$(paste) 2 220 (v. weak) and 1 782 cm^{-1}, $\delta_H(CDCl_3)$ 0.15 (3 H, d, *J* 7 Hz), 0.68 (9 H, s), 1.21 (3 H, d, *J* 7 Hz), 3.07 (1 H, sept, *J* 7 Hz), 7.2—7.6 (5 H, m), 7.67 (1 H, d, *J* 8 Hz), 7.77 (1 H, d, *J* 8 Hz), and 8.30 (1 H, d, *J* 8 Hz); $\delta_C(CDCl_3)$ 20.3 (q), 22.3 (q), 27.7 (q), 36.7 (s), 54.7 (d), 62.3 (s), 82.4 (s), 116.4 (s), 120.2 (d), 121.2 (d), 126.8, 127.0, 127.7, 128.0, 130.6 (d), 137.5 (s), 140.6 (s), 140.9 (s), and 165.9 (s); *m/z* M^+, 360.1847 (12%) ($C_{23}H_{24}N_2O_2$ requires *M*, 360.1856), 345 ($C_{22}H_{21}N_2O_2$, 4), 259 ($C_{18}H_{15}N_2$, 8), 244 ($C_{18}H_{14}N$, 5), 237 ($C_{16}H_{15}NO$, 100), 230 ($C_{16}H_8NO$, 16), 221 ($C_{16}H_{15}N$, 6), 220 ($C_{16}H_{14}N$, 11), 207 ($C_{15}H_{13}N$, 8), 206 ($C_{15}H_{12}N$, 47), 203 ($C_{15}H_9N$, 7), 202 ($C_{15}H_8N$, 11), 195 ($C_{13}H_9NO$, 87), 178 ($C_{13}H_8N$, 14), and 165 ($C_{13}H_9$, 12).

Methanolysis of the Adducts (**3b**) *and* (**2a**).—A solution of the adduct (**3b**) (0.1 g) in methanol (5 ml) and concentrated sulphuric acid (3 drops) was boiled for 8 h and then evaporated. Extraction of the residue with ether followed by normal work-up gave fluorenone (98%), identified by comparison of i.r. spectra and mixed m.p.

Under identical conditions the adduct (**2a**) was also converted into fluorenone (92%)

Reaction of the Adducts (**3b**) *and* (**2a**) *with Hydroxylamine.*—A solution of the adduct (*ca.* 0.1 g) in dry methanol (8 ml) and hydroxylamine [from the hydrochloride[6] (1 g)] was boiled for 30 min and then evaporated to dryness. Extraction of the residue with chloroform and evaporation of the chloroform gave fluorenone oxime [yield 85% from (**3b**), and 62% from (**2a**)].

Hydrolysis of the Adduct (**2e**).—Aqueous sodium hydroxide (15 ml; 2M) was added to a solution of the adduct (**2e**) (0.1 g) in ethanol (8 ml) and the mixture was stirred at room temperature for 72 h. The mixture was extracted with chloroform and the chloroform extract was washed with water, dried ($MgSO_4$), and evaporated to leave a brown oil. Preparative t.l.c. (dichloromethane and silica gel) separated the *N*-isopropyl nitrone (**1e**) (0.04 g, 61%), identified by comparison of the i.r. spectra and mixed m.p. with those of an authentic sample.

Reaction of Diphenyl Nitrone with Cyano-t-butylketene.—A mixture of *N*-phenylbenzylideneamine *N*-oxide (diphenyl nitrone) (0.9 g), cyano-t-butylketene [from azidoquinone[13] (1.3 g)], and benzene (5 ml) was boiled under reflux for 3 h. Evaporation of the solvent left a semi-solid residue from which preparative t.l.c. (dichloromethane and silica gel) separated 3-*cyano*-1-(α-2-*cyano*-3,3-*dimethylbutanoyloxybenzyl*)-3-*t-butylindol*-2(3H)-*one* (**10a**) (0.65 g, 32%) as an oil solidifying on being rubbed with light petroleum, m.p. 155—157 °C (Found: C, 72.9; H, 6.7; N, 9.3. $C_{27}H_{29}N_3O_3$ requires C, 73.1; H, 6.6; N, 9.5%), $\nu_{max.}$(paste) 2 240 (weak), 1 765, and 1 745 cm^{-1}; $\delta_H(CDCl_3)$ 1.10 (9 H, s), 1.20 (9 H, s), 3.45 (1 H, s), 6.7—7.5 (9 H, m), and 7.98 (1 H, s).

A faster moving component of the product mixture was chromatographically identical with compound (**10b**) obtained by hydrolysis of (**10a**).

Hydrolysis of the Indolone (**10a**).—A mixture of the adduct (**10a**) (0.11 g), water (5 ml), acetic acid (3 ml), and concentrated sulphuric acid (3 drops) was boiled and stirred for 20 h during which time all the solid dissolved. Extraction of the reaction mixture with ether and separation by preparative t.l.c. (dichloromethane and silica gel) of the ether soluble material gave 3-*cyano*-3-*t-butylindol*-2(3H)-*one* (**10b**) (0.05 g, 94%), m.p. 132—133 °C (from methanol) (Found: C, 72.0; H, 6.4; N, 12.9. $C_{13}H_{14}N_2O$ requires C, 72.9; H, 6.5; N, 13.1%), $\nu_{max.}$(paste) 3 220 and 1 720 cm^{-1}; $\delta_H(CDCl_3)$ 1.20 (9 H, s), 6.9—7.5 (4 H, m), and 8.93 (1 H, broad).

2,3,4-*Triphenyl*-1,2,4-*oxadiazolidin*-5-*one* (**11b**).—This was prepared by the reaction of phenyl isocyanate with diphenyl nitrone in dichloromethane at room temperature, m.p. 165 °C (decomp.) (from acetone) [lit.,[9] 167 °C (decomp.)], $\nu_{max.}$(KBr) 1 758 cm^{-1}; $\delta_C(CDCl_3)$ 86.5, 117.3, 121.0, 125.6, 127.1, 129.2, 129.4, 130.3, 135.7, 135.8, and 149.5.

Hydrolysis of Compound (**11b**).—A mixture of (**11b**) (2 g), methanol (15 ml), and potassium hydroxide (1 g) was stirred at room temperature for 2 days. The mixture was evaporated, water was added, and the mixture was extracted with dichloromethane. The dichloromethane solution was washed with water, dried ($MgSO_4$), and evaporated leaving an oil (2 g) which partly crystallised on standing. The crystalline material was collected and washed with ice-cold methanol, m.p. 140—145 °C, identified as *N,N'*-diphenylbenzamidine (lit.,[14] m.p. 144—145 °C) by comparison of i.r. spectra and determination of mixed m.p.

2'-Methyl-4'-phenylfluorene-9-spiro-3'-[1,2,4]*oxadiazolidin-5'-one* (**13a**).—This was prepared by the reaction of phenyl isocyanate with the *N*-methyl nitrone (**1a**) in dichloromethane at room temperature for 2 days. Evaporation of the mixture left an oil which crystallised on standing to give the *adduct* (**13a**) (64%), m.p. 140 °C (from methanol) (Found: C, 77.1; H, 5.1; N, 8.4. $C_{21}H_{16}N_2O_2$ requires C, 76.8; H, 4.9; N, 8.5%), $\nu_{max.}$(KBr) 1 764 and 1 773 cm^{-1}; $\delta_H(CDCl_3)$ 2.46 (3 H, s), 6.8—7.1 (5 H, m), 7.25—7.4 (2 H, m), 7.4—7.5 (2 H, m), and 7.55—7.75 (3 H, m); $\delta_C(CDCl_3)$ 38.1, 92.0, 120.7, 124.2, 126.1, 126.4, 128.4, 128.7, 131.2, 135.0, 138.8, and 140.3. The compound turned blue slowly on exposure to light.

2',4'-Diphenylfluorene-9-spiro-3'-[1,2,4]*oxadiazolidin-5'-one* (**13b**).—This was prepared by an identical procedure; *product* (**13b**) (72%), m.p. 186—187 °C (decomp.) (from ethyl acetate–methanol) (Found: C, 80.2; H, 4.7; N, 6.8. $C_{26}H_{18}N_2O_2$ requires C, 80.0; H, 4.6; N, 7.2%), $\nu_{max.}$(KBr) 1 776 cm^{-1}; $\delta_C(CDCl_3)$ 92.7, 118.2, 120.5, 125.0, 125.3, 126.1, 127.0, 128.3, 128.5, 128.8, 131.1, 140.0, 140.5, and 144.1; *m/z* 390 (M^+, 0.5%), 345 ($C_{25}H_{17}N_2$, 3), and 255 ($C_{19}H_{13}N$, 64).

Copper(I)-catalysed Reaction of Methylmagnesium Iodide with Diethyl Isopropylidenemalonate.—The reaction of methylmagnesium iodide with diethyl isopropylidenemalonate in the presence of copper(I) cyanide gave diethyl t-butylmalonate[15] when ether was used as the solvent. Use of tetrahydrofuran as solvent with an otherwise identical procedure gave a mixture of diethyl t-butylmalonate and a second compound of closely similar b.p. in the ratio of 3:1 by weight. A sample of the second compound was separated by h.p.l.c. and identified as diethyl 1-methylvinylmalonate from the n.m.r. data: $\delta_H(CDCl_3)$ 1.18 (6 H, t, *J* 7 Hz), 1.75 (3 H, s), 6.12 (1 H, s), 6.41 (4 H, q, *J* 7 Hz), 7.95 (1 H, s), and 8.15 (1 H, s).

Ethoxycarbonyl-t-butylketene.—Diethyl t-butylmalonate[15] was hydrolysed to the half-ester following Newman's procedure.[11] The carboxylic acid was converted into the acyl chloride by reaction with phosphorus pentachloride in boiling ether[12] for 2 h. Distillation gave the acyl chloride in almost quantitative yield. Subsequent dehydrochlorination by triethylamine[11] gave the ketene.

Reaction of the N-*Phenyl Nitrone* (**1d**) *with Ethoxycarbonyl-t-butylketene.*—A mixture of the *N*-phenyl nitrone (**1d**) (1 g), ethoxycarbonyl-t-butylketene (1 g), and benzene (15 ml) was boiled under reflux under nitrogen for 4 h. Evaporation of the solvent left a residue from which preparative t.l.c. (silica gel and CH_2Cl_2) separated *4′-ethoxycarbonyl-3′-phenyl-4′-t-butylfluorene-9-spiro-2′-oxazolidin-5′-one* (**14b**) as an oil which solidified on being rubbed with methanol (0.52 g, 32%), m.p. 140—141 °C (from methanol) (Found: C, 76.1; H, 6.0; N, 3.0. $C_{28}H_{27}NO_4$ requires C, 76.2; H, 6.1; N, 3.2%), $\nu_{max.}$(paste) 1 710 and 1 790 cm^{-1}; $\delta_H(CDCl_3)$ 1.29 (9 H, s), 1.40 (3 H, t, *J* 7 Hz), 4.44 (2 H, q, *J* 7 Hz), 6.6—6.75 (2 H, m), 6.8—7.0 (3 H, m), 7.1—7.4 (6 H, m), and 7.7—7.9 (2 H, m); $\delta_C(CDCl_3)$ 13.9, 26.7, 39.8, 62.0, 75.0, 102.2, 119.8, 125.0, 125.2, 126.8, 127.4, 127.7, 128.0, 130.2, 130.7, 132.4, 139.8, 140.5, 142.6, 143.4, 170.4, and 170.5.

In addition, fluorenone azine (0.03 g, 4.6%) and unchanged nitrone (0.2 g) were isolated.

Reaction of Ethoxycarbonyl-t-butylketene with the N-*Alkyl Nitrones* (**1a**) *and* (**1e**).—The ketene and the nitrone were heated together in boiling benzene for several hours. Evaporation of the benzene and separation of the crude reaction mixture by preparative t.l.c. gave fluorenone azine (14 and 15% respectively) and unchanged nitrone (40 and 72%) as the only significant products.

Reaction of Ethoxycarbonyl-t-butylketene with Diphenyl-Nitrone.—A mixture of the ketene (2 g) and nitrone (2 g) in xylene (35 ml) was boiled under reflux for 12 h, when the mixture no longer absorbed in the i.r. at 2 100 cm^{-1}. Evaporation of the xylene left an oil, from which the following compounds were separated by chromatography (silica gel and light petroleum–ether, 9:1).

1-*Benzylideneamino*-2-(2,2-*dimethyl*-1-*ethoxycarbonylpropyl*)*benzene* (**15**) (0.25 g, 8%), m.p. 58 °C (from light petroleum) (Found: C, 78.0; H, 7.9; N, 4.2. $C_{21}H_{25}NO_2$ requires C, 78.0; H, 7.8; N, 4.3%), $\nu_{max.}$(paste) 1 728 and 1 632 cm^{-1}; $\delta_H(CDCl_3)$ 1.00 (9 H, s), 1.21 (3 H, t, *J* 8 Hz), 3.95—4.3 (2 H, m), 4.46 (1 H, s), 7.0 (1 H, dd, *J* 7, 2 Hz), 7.15—7.35 (2 H, m), 7.45—7.55 (3 H, m), 7.80 (1 H, dd, *J* 7, 2 Hz), 7.9—8.05 (2 H, m), and 8.40 (1 H, s); $\delta_C(CDCl_3)$ 14.2 (q), 28.1 (q), 35.7 (s), 52.9 (d), 60.0 (t), 117.7 (d), 125.3 (d), 127.8, 128.7, 128.9, 131.0, 131.2, 136.5, 151.0, 159.8 (s), and 173.6 (s).

2,3-*Dihydro*-3-*ethoxycarbonyl*-2-*phenyl*-3-*t-butylindole* (**16a**) (0.9 g, 28%), m.p. 91 °C (from light petroleum) (Found: C, 77.8; H, 7.7; N, 4.5. $C_{21}H_{25}NO_2$ requires C, 78.0; H, 7.8; N, 4.3%), $\nu_{max.}$(paste) 3 370, 1 714, and 1 610 cm^{-1}; $\delta_H(CDCl_3)$ 0.80 (3 H, t, *J* 8 Hz), 1.10 (9 H, s), 3.35—3.53 (1 H, m), 3.53—3.70 (1 H, m), 3.9 (1 H, broad, removed by D_2O treatment), 4.86 (1 H, s), 6.57 (1 H, d, *J* 8 Hz), 6.81 (1 H, t, *J* 8 Hz), 7.1—7.3 (6 H, m), and 7.55 (1 H, d, *J* 8 Hz); $\delta_C(CDCl_3)$ 13.5 (q), 26.6 (q), 38.6 (s), 59.9 (t), 67.2 (d), 69.9 (s), 108.4 (d), 118.0 (d), 126.6, 127.5, 127.9, 128.2, 128.3, 129.2, 144.1 (s), 151.2 (s), and 171.5 (s).

Treatment of (**16a**) with benzoyl chloride and pyridine gave the N-*benzoyl derivative*, m.p. 163 °C (from benzene–light petroleum) (Found: C, 78.5; H, 6.8; N, 3.1. $C_{28}H_{29}NO_3$ requires C, 78.7; H, 6.8; N, 3.3%), $\nu_{max.}$(paste) 1 722 and 1 646 cm^{-1}.

Acknowledgements

We thank the British Council (M. H.) and the S.E.R.C. (A. R. E.) for support, and Dr. B. E. Mann and the S.E.R.C. high-field n.m.r. service for the nuclear Overhauser effect experiments.

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Received 22nd September 1983; *Paper* 3/1672